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NEW SWISS CHEMICAL SOCIETY

Im Rahmen der ILMAC 96

Herbstversammlung NSCG

21. November 1996

Assemblée d'automne NSSC

21 novembre 1996

1st Swiss Cost Chemistry Symposium

20th november 1996

Programm und Kurzfassungen
aller Vorträge und Posters

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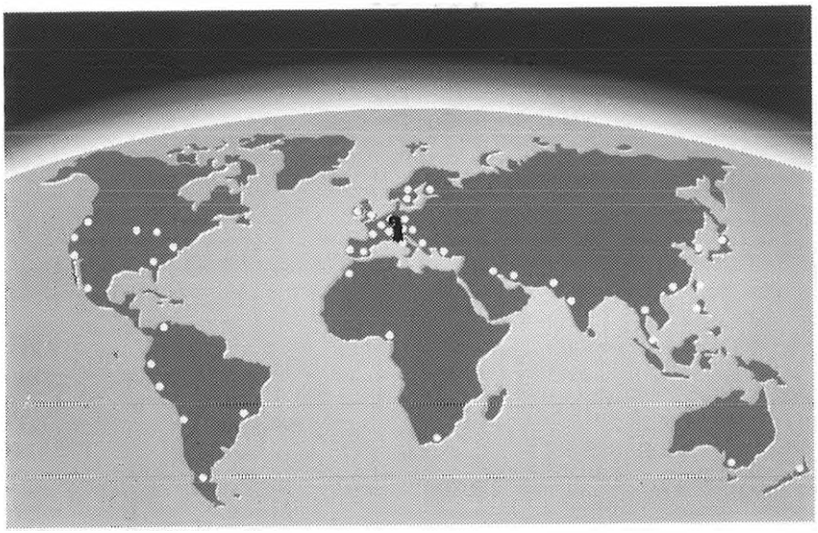

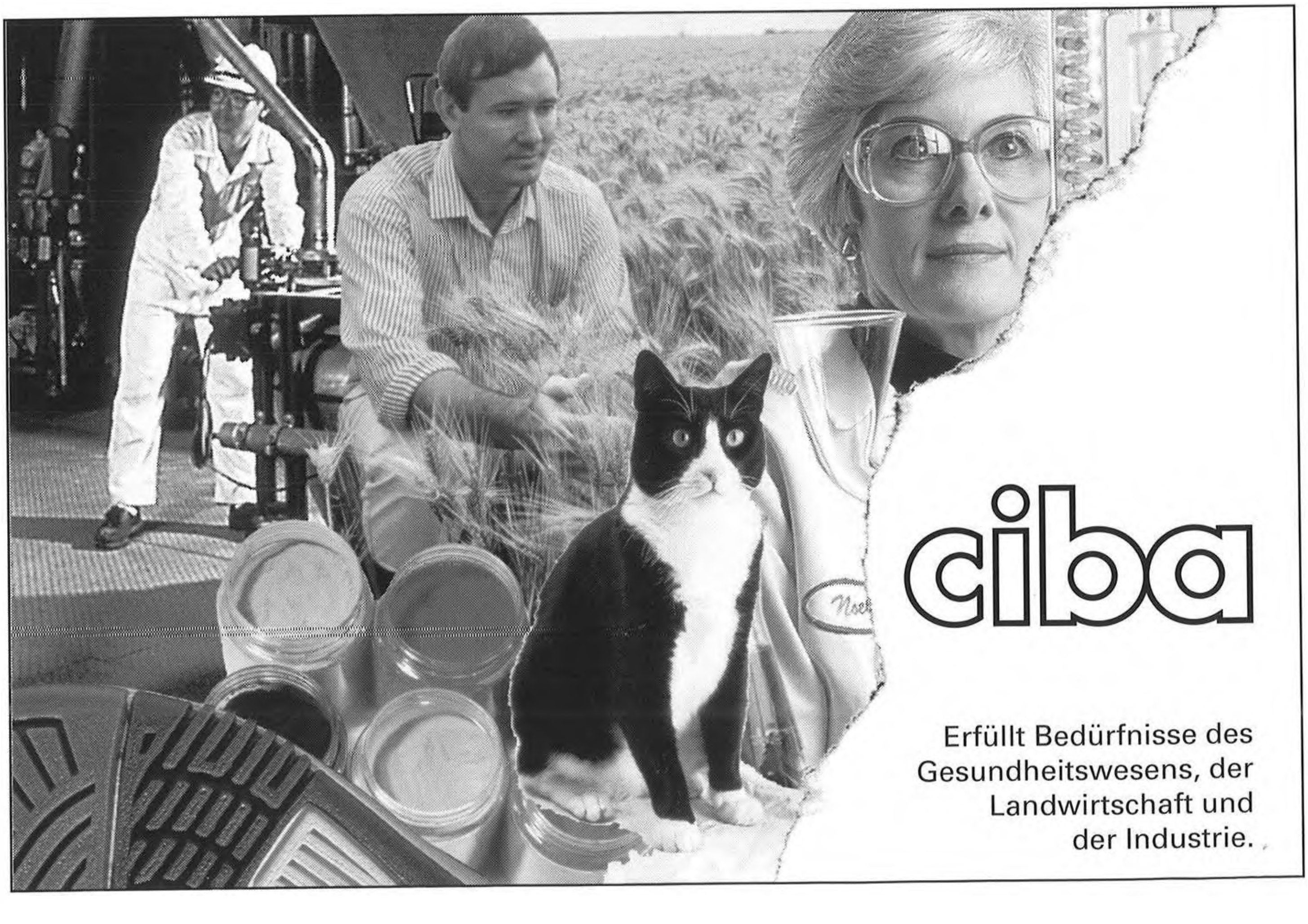

INHALT
SOMMAIRE
CONTENTS

EDITORIAL

NSCG/NSSC

COST

LEITARTIKEL
LEADING ARTICLES

EI – INFO – IS

PREISAUSSCHREIBUNGEN

INFORMATION

CHIMIA-REPORT

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Kongressveranstaltungen im Rahmen der ILMAC 96

EDITORIAL

An der diesjährigen ILMAC (19.–22. November 1996 in Basel) wird der traditionelle ILMAC-Kongress zum tragenden Element der Messe aufgewertet. Zu den Themengruppen gehören:
- Analytische Technologie (µTAS: Miniaturized Total Analysis Systems and Quality Assurance in the Analytical Laboratory)
- Biotechnologie (Bioproducts and Bioprocesses)
- Chemische Forschung (Protein Structures – Drug Design)

Weitere Kongressaktivitäten umfassen:
- Vorträge von Ausstellern
- eine Experimentalvorlesung für junge Wissenschafter
- die Herbstversammlung der Neuen Schweizerischen Chemischen Gesellschaft (NSCG)
- das 1st Swiss COST Chemistry Symposium

Die beiden letztgenannten Veranstaltungen sind im vorliegenden CHIMIA-Heft ausführlich dokumentiert:

Herbstversammlung 1996 der Neuen Schweizerischen Chemischen Gesellschaft (NSCG)
Donnerstag, 21. November 1996
Die folgenden Sektionen der NSCG sind vertreten (Vorträge, Posters):
- Sektion Analytische Chemie
- Sektion Medizinische Chemie
- Sektion Chemische Forschung
    - Anorganische Chemie und Koordinationschemie
    - Computerunterstützte Chemie
    - Organische Chemie
    - Physikalische Chemie

Die Kurzfassungen (Abstracts) sämtlicher Vorträge und Posters (gesamthaft *ca.* 250) sind bereits im vorliegenden CHIMIA-Heft abgedruckt. Darunter befinden sich auch solche der diesjährigen Preisträger (*Paracelsus*-, *Werner*-, *Sandmeyer*-Preis sowie Dr. *Max-Lüthy*-Auszeichnung).

1st Swiss COST Chemistry Symposium
Mittwoch, 20. November 1996
COST (ein französisches Akronym für 'Coopération Européenne dans le domaine de la recherche Scientifique et Technique') vereinigt auf Forschungsgebieten 25 europäische Länder. Die Aktivitäten der COST CHEMISTRY umfasst 86 Projekte verschiedenster Zusammenarbeiten von 391 europäischen Forschungsgruppen. Das Ziel des Symposiums ist es, die Fortschritte der 38 Schweizer Forschungsgruppen vorzustellen. Die 7 Vorträge von prominenten Referenten Europas und die über 50 Posters aus Schweizer Forschungsgruppen sind alle als Kurzfassungen (Abstracts) im vorliegenden CHIMIA-Heft aufgeführt.

Auf Wiedersehen an der ILMAC 96!

C. Ganter

Camille Ganter
Redaktor/Editor CHIMIA

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Neue Schweizerische Chemische Gesellschaft
Nouvelle Société Suisse de Chimie
New Swiss Chemical Society

Herbstversammlung 1996
Assemblée d'automne 1996

Donnerstag, 21. November 1996
Jeudi 21 novembre 1996

Basel/Bâle

Kongresszentrum Messe Basel
Centre de Congrès de la Foire de Bâle

Messeplatz 21, 2. Stock/2ème étage

CHIMIA *50* (1996) Nr. 7/8 (Juli/August)

09.45 **Eröffnung / Cérémonie d'ouverture**
Kongresssaal Montréal /Salle de congrès Montréal
Prof. ***A. von Zelewsky***
Präsident der NSCG / Président de la NSSC

Vorträge der *Werner*-Preisträger 1996
Conférences des lauréats du prix *Werner* 1996
PD Dr. ***Stefan Bienz***
Organisch-Chemisches Institut, Universität Zürich
Dr. ***Rafael Brüschweiler***
Laboratorium für Physikalische Chemie, ETH-Zürich

16.45 **Vortrag des *Paracelsus*-Preisträgers 1996**
Conférence du lauréat du prix *Paracelse*
Prof. ***Jack Lewis***
The Lord Lewis of Newnham
University of Cambridge, Cambridge, GB

Informationen:

Keine Anmeldung erforderlich, der Eintritt ist frei.

Studierende, die Mitglied der NSCG sind, erhalten folgende Reisekosten zurückerstattet: Bahnbillett nach Basel, 2. Kl. $^1/_2$ Tax (Anreise aus dem Ausland: Rückerstattung der Reisekosten ab Schweizer Grenze). Das Bahnbillett ist dem Rückerstattungsantrag beizulegen. Der Rückerstattungsantrag ist unter Angabe der Arbeits- und Privatadresse, des Bank- oder PC-Kontos sowie womöglich Beilage eines Einzahlungsscheines beim Sekretariat für Weiterbildung und Symposien der NSCG, Frau *B. Köchli*, Institut für organische Chemie, Universität Bern, Freiestrasse 3, CH–3012 Bern, einzureichen.

Lunch: Es hat Verpflegungsmöglichkeiten an der ILMAC oder in nahegelegenen Restaurants. Studierende, Doktoranden und Postdoktoranden können Eintrittskarten für die ILMAC beim Tagungssekretariat beziehen.

Informations:

L'inscription n'est pas nécessaire et l'entrée est gratuite.

Les étudiants membres de la NSSC peuvent demander le remboursement des frais de voyage sur la base du billet de train Bâle et retour, 2e classe, $^1/_2$prix (pour les membres qui viennent de l'étranger, seule les frais de voyage sur territoire suisse sont remboursés). Le billet doit être joint à la demande de remboursement. Veuillez indiquer l'adresse du lieu de travail et privée, le compte bancaire ou postal et joindre, si possible, un bulletin de versement. La demande est à adresser au Secrétariat de formation continue et des congrès de la NSSC, Mme *B. Köchli*, Institut de chimie organique, Université de Berne, Freiestrasse 3, CH–3012 Berne.

Lunch: On trouve des restaurants à l'ILMAC ou dans les alentours du centre de congrès. Les étudiants, doctorants et postdoctorants peuvent demander un billet d'entrée pour l' ILMAC auprès du secrétariat local de la NSSC.

Programm der Herbstversammlung 1996
Programme de l'assemblée d'automne 1996

09.45–10.50 *Kongresssaal / Salle de congrès: Montréal*
Eröffnung / Cérémonie d'ouverture
Prof. ***A. von Zelewsky***

Verleihung der Preise / Remise des prix
- ***Werner*-Preis 1996 / Prix *Werner* 1996**
- ***Sandmeyer*-Preis 1996 / Prix *Sandmeyer* 1996**
- **Dr. *Max-Lüthy*-Auszeichnung / Distinction Dr. *Max Lüthy***

Vorträge der *Werner*-Preisträger 1996
Conférences des lauréats du prix *Werner* 1996
- PD Dr. ***Stefan Bienz***
  Organisch-Chemisches Institut, Universität Zürich
  Stereoselektive Reaktionen ausgehend von chiralen Silicium-Verbindungen
- Dr. ***Rafael Brüschweiler***
  Laboratorium für Physikalische Chemie, ETH-Zürich
  Dynamik von Biomolekülen und NMR-Relaxation

16.45 **Verleihung des *Paracelsus*-Preises und Vortrag des *Paracelsus*-Preisträgers 1996**
Remise du prix *Paracelse* et conférence du lauréat du prix *Paracelse*
Prof. ***Jack Lewis***
The Lord Lewis of Newnham
University of Cambridge, Cambridge, GB
From Metal–Metal Interaction to Metal–Metal Bonds

Analytische Chemie / Chimie analytique
Mitgliederversammlung / Assemblée des membres
Kongresssaal / Salle de congrès: Rio
Traktanden s. Seite 395 / Ordre du jour v. page 395
Vorträge: *Kongresssaal: Rio* / Conférences: *Salle de congrès: Rio*
Postersession: *Foyer 2. Stock* / Session de posters: *Foyer 2ème étage*
Programm s. Seite 299 / Programme v. page 299
Abstracts s. Seite 304 / Abstracts v. page 304

Medizinische Chemie / Chimie thérapeutique:
Mitgliederversammlung / Assemblée des membres
Kongresssaal: Singapur / Salle de congrès: Singapur
Traktanden s. Seite 395 / Ordre de jour v. page 395
Vorträge: *Kongresssaal: Singapur* / Conférences: *Salle de congrès: Singapur*
Postersession: *Foyer 2. Stock* / Session de posters: *Foyer 2ème étage*
Programm s. Seite 299 / Programme v. page 299
Abstracts s. Seite 310 / Abstracts v. page 310

Chemische Forschung / Recherche chimique
Mitgliederversammlung / Assemblée des membres
Kongresssaal: Montréal / Salle de congrès: Montréal
Traktanden s. Seite 395 / Ordre du jour v. page 395

- **Anorganische Chemie und Koordinationschemie / Chimie minérale et de coordination**

Vorträge: *Kongresssaal: Montréal* / Conférences: *Salle de congrès: Montréal*
Postersession: *Foyer 2. Stock* / Session de posters: *Foyer 2ème étage*
Programm s. Seite 300 / Programme v. page 300
Abstracts s. Seite 313 / Abstracts v. page 313

- **Computerunterstützte Chemie / Chimie computationnelle**
  Vorträge: *Kongresssaal: Samarkand* / Conférences*: Salle de congrès: Samarkand*
  Postersession: *Foyer 2. Stock / Session de posters: Foyer 2ème étage*
  Programm s. Seite 300 / Programme v. page 300
  Abstracts s. Seite 337 / Abstracts v. page 337

- **Organische Chemie / Chimie organique**
  Vorträge: *Kongresssäle: Montréal, Singapur, Osaka*
  Conférences*: Salles de congrès: Montréal, Singapur, Osaka*
  Postersession: Foyer 2. Stock / Session de posters: *Foyer 2ème étage*
  Programm s. Seite 301 / Programme v. page 301
  Abstracts s. Seite 340 / Abstracts v. page 340

- **Physikalische Chemie / Chimie physique**
  Vorträge: *Kongresssäle: Samarkand, Rio*
  Conférences: *Salles de congrès: Samarkand, Rio*
  Postersession: *Foyer 2. Stock / Session de posters: Foyer 2ème étage*
  Programm s. Seite 303 / Programme v. page 303
  Abstracts s. Seite 357 / Abstracts v. page 357

Analytische Chemie
Chimie analytique

11.00–11.15 **Mitgliederversammlung**
Assemblée des membres
Kongresssaal: Rio / Salle de congrès: Rio

Vorträge: *Kongresssaal: Rio*
Conférences: *Salle de congrès: Rio*
Abstracts: 1–5, s. Seite 304 / v. page 304
Chairman: *M. Oehme*

11.20–11.40 ***M. Oehme****, H. Karlsson, L. Müller*
Institut für organische Chemie, Basel
Enantioselective Separations by HRGC – Problems and Solutions
Abstract 1

11.40–12.00 ***R. Falter***[a]), *H. Hintelmann*[b]), *G. Ilgen*[a])
[a]) *BITÖK, Bayreuther Institut für Terrestrische Ökosystemforschung, Universität Bayreuth*
[b]) *Environmental Science Centre, Trent University, Peterborough*
Methylquecksilberbestimmung: Die Fallen der Wasserdampf-Destillationstechnik, oder wie man sich Methylquecksilber während der Probenaufarbeitung selbst herstellt
Abstract 2

12.10–12.30 ***D. Zeisel****, T. Roth, B. Dutoit, R. Zenobi*
Laboratorium für Organische Chemie, ETH-Zürich
Scanning Near-field Spectroscopy as a New Tool for Micro- and Nanoanalysis
Abstract 3

12.30–12.50 ***J.-L. Wolfender***[a]), *S. Rodriguez*[a]), *W. Hiller*[b]), *K. Hostettmann*[a])
[a]) *Institut de Pharmacognosie et Phytochimie, Université de Lausanne*
[b]) *Varian GmbH, Darmstadt*
LC/UV, LC/MS and LC/NMR for the Rapid Identification of Natural Products in the Chemical Screening of Crude Plant Extracts
Abstract 4

12.50–13.10 ***B. Schlageter***[a]), *S. Pörting*[b]), *M.C. Moreno-Bondi*[c]), *S.E. Braslavsky*[b]), *E. Oliveros*[a]), *A.M. Braun*[a])
[a]) *Lehrstuhl für Umweltmesstechnik, Engler-Bunte-Institut, Universität Karlsruhe*
[b]) *MPI für Strahlenchemie, Mühlheim an der Ruhr*
[c]) *Department of Analytical Chemistry, Universidad Complutense de Madrid*
A Highly Sensitive Photoacoustic Sensor for CO_2 Measurements in Aqueous Systems
Abstact 5

14.00–15.00 **Postersession / Session de posters**
Foyer 2. Stock / Foyer 2ème étage
Abstracts: 6–26, s. Seite 305 / v. page 305

16.45 **Verleihung des *Paracelsus*-Preises**
Remise du prix *Paracelse*
Vortrag des *Paracelsus*-Preisträgers
Conférence du lauréat du prix *Paracelse*
Kongresssaal / Salle de congrès: Montréal

Medizinische Chemie
Chimie thérapeutique

11.00–11.10 **Mitgliederversammlung**
Assemblée des membres
Kongresssaal: Singapur
Salle de congrès: Singapur

Vorträge: *Kongresssaal: Singapur*
Conférences: *Salle de congrès: Singapur*
Abstracts: 27–34, s. Seite 310 /v. page 310
Chairman: *R. Giger*

11.10–11.30 ***R. Waelchli****, C. Beerli, H. Meigel, L. Revesz*
Sandoz Pharma Ltd., Preclinical Research, Basel
First Total Synthesis of Lysylpyridinoline and Hydroxylysylpyridinoline
Abstract 27

11.30–12.00 ***H.-G. Capraro, G. Bold****, A. Fässler, M. Lang, R. Cozens, J. Lazdins, J. Mestan, B. Poncioni, J.L. Rösel, D. Stover, T. Klimkait, K. Woods-Cook*
Ciba-Geigy AG, Pharma Forschung, Medizinische Chemie, Basel
Synthese und Entwicklung von HIV-Protease Hemmern bei *Ciba-Geigy*
Abstract 28

12.00–12.20 **H. Mühle**, *J. Nozulak, H. Kalkman, P. Floersheim, D. Hoyer, E. Küsters, P. Schöffter*
Sandoz Pharma Ltd., Preclinical Research, Basel
SDZ SER-082: A 5-HT$_{2C/2B}$ Receptor Antagonist with Low 5-HT$_{2A}$ Receptor Affinity
Abstract 29

12.30–14.00 **Postersession /Session de posters**
Foyer 2. Stock /Foyer 2ème étage
Abstracts: 35–38, s. Seite 312 / v. page 312

Chairman: *W. Froestl*
14.40–15.00 **A. Marx**, *B. Giese*
Institut für Organische Chemie, Universität Basel
Synthesis of 4'-Acylated Nucleotides and Their Action on Enzymes
Abstract 30

15.00–15.20 **G. Camenisch**a), *H. van de Waterbeemd*a), *G. Folkers*b)
a) *F. Hoffmann-La Roche Ltd., Pharma Research New Technologies, Basel*
b) *Department of Pharmacy, ETH-Zürich*
Estimation of Membrane Permeation from Physicochemical Drug Properties
Abstract 31

15.20–15.40 **C. Papageorgiou**
Sandoz Pharma Ltd., Basel
Conformational Control in the Cyclosporin Series
Abstract 32

15.40–15.55 **P.W. Manley**, *K. Bray, P. Floersheim, L. Mazzoni, T. Müller*
Sandoz Pharma Ltd., Preclinical Research, Basel
PDE 4 Inhibitors: Design, Synthesis and Antiinflammatory Activity of 4-(3-cyclopentylidinemethyl-4-methoxyphenyl)pyridine
Abstract 33

15.55–16.30 **S.J. Veenstra,** *W. Schilling, S. Ofner, K. Hauser, A. Vassout*
Ciba-Geigy AG, Basel
Approaches towards the Design and Synthesis of Non-peptidic Substance-P Antagonists
Abstract 34

16.45 **Verleihung des *Paracelsus*-Preises**
Remise du prix *Paracelse*
Vortrag des *Paracelsus*-Preisträgers
Conférence du lauréat du prix *Paracelse*
Kongresssaal: Montréal
Salle de congrès: Montréal

Chemische Forschung
Recherche chimique

11.00–11.15 **Mitgliederversammlung**
Assemblée des membres
Kongresssaal: Montréal
Salle de congrès: Montréal

Anorganische Chemie / Chimie inorganique

Minisymposium: *Kongresssaal: Montréal*
Salle de Congrès: Montréal
11.30–13.00 **'Some New Directions Main Group-metal Chemistry'**

11.30–12.00 ***Hansjörg Grützmacher***
Laboratorium für Anorganische Chemie, Universität Zürich
How Useful Is the Concept of Homologous Elements?

12.00–12.30 ***Michael F. Lappert***
School of Chemistry and Molecular Sciences, University of Sussex
Recent Results on Thermally Stable Open Shell Organic Compounds of Si, Ge, Sn and Pb

12.30–13.00 ***Walther Siebert***
Anorganisch-chemisches Institut, Universität Heidelberg
Tetraborylethenes and Diboraheterocycles

14.00–16.00 **Postersession / Session de posters:**
Foyer 2. Stock /Foyer 2ème étage
Abstracts: 39–135, s. Seite 313 / v. page 313

16.45 **Verleihung des *Paracelsus* Preises**
Remise du prix *Paracelse*
Vortrag des *Paracelsus* Preisträgers
Conférence du lauréat du prix *Paracelse*
Kongresssaal: Montréal
Salle de congrès: Montréal

Computerunterstützte Chemie / Chimie computationnelle

11.30–13.00 **Postersession / Session de posters**
Foyer 2. Stock / Foyer 2ème étage
Abstracts: 141–147, s. Seite 339 / v. page 339

Vorträge: *Kongresssaal: Samarkand*
Conférences: *Salle de congrès: Samarkand*
Abstracts: 136–140, s. Seite 337 / v. page 337
Chairman: *J. Weber*

14.00–14.20 ***M.J. Mayor-López***a), *J. Weber*a), *K. Hegetschweiler*b)
a) *Département de Chimie Physique, Université de Genève*
b) *Anorganische Chemie, Universität des Saarlandes*
Theoretical Study of the Structure and Reactivity of the $[Mo_3S_7]^{4+}$ Cluster and Its Derivatives
Abstract 136

14.20–14.40 ***F.P. Rotzinger***
Institut de chimie physique, EPF-Lausanne
The Structure of Transition States and Intermedi-

ates Formed in the Water-Exchange of the Hexa Aqua Ions of Scandium(III) through Zinc(II)
Abstract 137

14.50–15.10 ***J. Breidung***, *W. Thiel*
Organisch-chemisches Institut, Universität Zürich
Quantum-chemical Calculations of Harmonic and Anharmonic Force Fields of Small Reactive Molecules
Abstract 138

15.10–15.30 *E. Deiss, C.A. Daul,* ***J.-L. Barras***
Institut für anorganische Chemie, Universität Freiburg
Modeling of Lithium Thin-Film Electrochemical Cells
Abstract 139

15.30–15.50 ***B. Knopp***, *A.A. Gusev, U.W. Suter*
Institut für Polymere, ETH-Zürich
Calculation of Water Sorption in Polymers
Abstract 140

16.45 **Verleihung des *Paracelsus*-Preises**
Remise du prix *Paracelse*
Vortrag des *Paracelsus*-Preisträgers
Conférence du lauréat du prix *Paracelse*
Kongresssaal: Montréal
Salle de congrès: Montréal

Organische Chemie / Chimie organique

Vorträge: *Kongresssäle: Montréal, Singapur, Osaka*
Conférences: *Salles de congrès: Montréal, Singapur, Osaka*
Abstracts: 148–170, s. Seite 340 / v. page 340

11.30–12.30 **Postersession / Session de posters**
Foyer 2. Stock / Foyer 2ème étage
Abstracts: 171–212, s. Seite 346 /v. page 346

Vorträge: *Kongresssaal: Montréal*
Conférences: *Salle de congrès: Montréal*
Chairman: *B. Giese*

13.20–13.40 ***R. Prétôt***, *A. Pfaltz*
Max-Planck-Institut für Kohlenforschung, Mühlheim
Regio- and Enantiocontrol in Palladium-Catalyzed Allylic Substitutions
Abstract 148

13.40–14.00 *R.M. Stoop*[a]), *F. Spindler*[b]), ***A. Mezzetti***[a])
[a]) *Laboratorium für Anorganische Chemie, ETH-Zürich*
[b]) *Ciba, Central Research Services, Basel*
New P-Chiral Diphosphines in Enantioselective Catalysis
Abstract 149

14.00–14.20 ***D. Beruben***, *E.P. Kündig*
Département de Chimie Organique, Université de Genève
Radical Cyclization Reactions with Chiral Cyclohexadienes Derived from Sequential Additions to Tricarbonyl Chromium Arene Complexes
Abstract 150

14.20–14.40 ***S. El Houar***, *H.-J. Hansen*
Organisch-chemisches Institut, Universität Zürich
Synthesis of New Photo- and Thermochromic Systems Based on Cyclic Double Bond Shifts in Heptalenes
Abstract 151

14.50–15.10 ***J. Lacour***, *C. Ginglinger, A. Londez*
Département de Chimie Organique, Université de Genève
Synthesis and Applications of Enantiopure Hexacoordinated Phosphate Anions
Abstract 152

15.10–15.30 *A. Solladié-Cavallo,* ***D. Roche***, *T. Isarno, R. Andriamiadanarivo*
Laboratoire de Stéréochimie Organométallique, CNRS, ECPM/ULP, Strasbourg
Stereoselective Catalytic *Michael* Addition of a Chiral Iminoglycinate
Abstract 153

15.30–15.50 ***C. Boss***, *R. Keese*
Departement für Chemie und Biochemie, Universität Bern
Synthese, Struktur und Reaktivität von Cycloalkadiinen
Abstract 154

15.50–16.10 ***A. Stojanovic***, *L. Giraud, P. Renaud*
Institut de Chimie Organique, Université de Freiburg
Stereoselective Reactions of 1-Amido Substituted Radicals
Abstract 155

Vorträge: *Kongresssaal: Singapur*
Conférances: *Salle de congrès: Singapur*
Chairman: *C. Leumann*

12.30–12.50 ***P. Neuenschwander***, *C. Maurer*[a]), *F. Redha*[b]), *G.K. Uhlschmid*[b]), *U.W. Suter*
Institut für Polymere, Makromolekulare Chemie, ETH-Zürich
[a]) *Klinik für Viszerale und Transplantationschirurgie, Universität Bern*
[b]) *Forschungsabteilung des Departements für Chirurgie, Universitätsspital Zürich*
Degrabloc, a Novel Radioopaque Polymer for Chemoembolization
Abstract 156

12.50–13.10 ***M. Kurz***, *K. Schütz, M. Göbel*
Département de Chimie Organique, Université de Genève
Matrizengesteuerte, nichtenzymatische Polyme-

risation von RNA
Abstract 157

13.10–13.30 ***U. Diederichsen***
Institut für Organische Chemie und Biochemie, TU München
Paarung unnatürlicher Nucleobasen: Untersuchung von Alanyl-PNA-Paarungskomplexen
Abstracs 158

13.30–13.50 ***J. Marfurt**, C. Leumann*
Departement für Chemie und Biochemie, Universität Bern
Triplex-Bildungseigenschaften von Oligonukleotiden enthaltend die Nukleoside 7-(2'-Deoxy-α/β-D-ribofuranosyl)-hypoxanthin
Abstract 159

13.50–14.10 ***B. Rohwedder**, P. Dumy, P. Garrouste, C. Lehmann, M. Mathieu, C. Peggion, S. Peluso, A. Razaname, G. Tuchscherer, T. Wöhr, M. Mutter*
Institute de Chimie Organique, Université de Lausanne
Proteins as Templates for the Design of Functional Mimetics and Drugs
Abstract 160

14.10–14.30 ***J. Hunziker**, H.M.J. Herath*
Departement für Chemie und Biochemie, Universität Bern
Design and Synthesis of an Amide-linked 4'-Homo-DNA
Abstract 161

Vorträge: *Kongresssaal: Osaka*
Conférences: *Salle de congrès: Osaka*
Chairman: *W.-D. Woggon*

13.00–13.20 ***C. Strässler**, H. Heimgartner*
Organisch-chemisches Institut, Universität Zürich
Heterospirocyclische 3-Amino-2*H*-azirine als Synthone für α,α-hetercyclische α-Aminosäuren
Abstract 162

13.20–13.40 ***S.W. Ainge**, P. Vogel*
Section de Chimie de l'Université de Lausanne
The Total Synthesis of Sporeamicin *via* the Optically Pure *Diels-Alder* Adducts of 2,4-Dimethylfuran and 1-(*R*)- and 1'-(*S*)-Cyanovinyl Camphanates
Abstract 163

13.40–14.00 ***L. Kellenberger**, D. Holmes, B. Martinoni, D. Arigoni*
Laboratorium für Organische Chemie, ETH-Zürich
Zur Biosynthese von Bottromycin: Stereochemischer Verlauf der C-Methylierungsschritte
Abstract 164

14.00–14.20 ***H.-A. Wagenknecht**, W.-D. Woggon*
Institut für Organische Chemie, Universität Basel
The First Active-Site Analogue of Chloroperoxidase – Synthesis and Catalytic Reactions
Abstract 165

14.20–14.40 ***W. Ganci**, E.J. Meier, G. Przibille, U. Ringeisen, P. Rüedi*
Organisch-chemisches Institut, Universität Zürich
Stereochemie der Inhibition von δ-Chymotrypsin mit optisch aktiven bicyclischen Organophosphaten
Abstract 166

14.50–15.10 ***R. Bänteli**, H. C. Kolb, R. Oehrlein*
Ciba, Central Research Laboratories, Basel
Synthesis of Sialyl *Lewis* x Mimics with Modifications of the Galactose Unit
Abstract 167

15.10–15.30 ***A.J.F. Edmunds**[a]), W. Trueb[a]), N. Le-Van[a]), W. Oppolzer[b]), P. Cowley[b])*
[a]) *Sandoz Agro AG, Basel*
[b]) *Département de Chimie Organique, Université de Genève*
Herboxidiene: Relative and Absolute Configuration and Synthesis of an Aromatic Hybrid
Abstract 168

15.30–15.50 ***W. Mühlecker**[a]), K.-H. Ongania[a]), S. Hörtensteiner[b]), P. Matile[b]), B. Kräutler[a])*
[a]) *Institut für Organische Chemie, Universität Innsbruck*
[b]) *Institut für Pflanzenbiologie, Universität Zürich*
A Fluorescing Chlorophyll Catabolite from Higher Plants
Abstract 169

15.50–16.10 ***C. Terreaux**[a]), M. Maillard[a]), H. Stoeckli-Evans[b]), M.P. Gupta[c]), K. Hostettmann[a])*
[a]) *Institut de Pharmacognosie et Phytochimie, Université de Lausanne*
[b]) *Institut de Chimie, Université de Neuchâtel*
[c]) *CIFLORPAN, Faculdad de Farmacia, Universidad de Panama*
Antifungal Benzoic Acid Derivatives from *Piper dilatatum* L.C. Rich. (Piperaceae)
Abstract 170

16.45 **Verleihung des *Paracelsus*-Preises**
Remise du prix *Paracelse*
Vortrag des *Paracelsus*-Preisträgers
Conférence du laureat du prix *Paracelse*
Kongresssaal: Montréal
Salle de congrès: Montréal

CHIMIA 50 (1996) Nr. 7/8 (Juli/August)

Physikalische Chemie / Chimie Physique

Vorträge: *Kongresssäle: Samarkand, Rio*
Conférences: *Salles de congrès: Samarkand, Rio*
Abstracts: 213–225, s. Seite 357 / v. page 357

Postersession: ganztags
Session de posters: pendant toute la journée
Foyer 2. Stock / Foyer 2ème étage
Abstracts: 226–247, s. Seite 360 / v. page 360

Vorträge: *Kongresssaal: Samarkand*
Conférences: *Salle de congrès: Samarkand*
Chairman: *A. Hauser*

11.30–11.50 ***M. Bauer***, *S. Pawlik, M. Aeschlimann*
Laboratorium für Technische Chemie, ETH-Zürich
Femtosecond Lifetime Investigations of Hot Electrons Trapped by Adsorbates on a Metal Surface
Abstract 213

11.50–12.10 ***C. Högemann***, *E. Vauthey*
Institut für physikalische Chemie, Universität Freiburg
Picosecond Transient Grating Spectroscopy
Abstract 214

12.10–12.30 ***M. Pirotta***, *M.H.V. Werts, A. Renn, U.P. Wild*
Laboratorium für Physikalische Chemie, ETH-Zürich
Photophysical Properties and Stark Effect of Single Perylene Molecules
Abstract 215

12.40–13.00 ***K. Bergmann***, *J.R. Huber*
Physikalisch-chemisches Institut, Universität Zürich
Photoinduced Bimolecular Reactions in Clusters
Abstract 216

13.00–13.20 ***C. Wickleder***, *T. Bürgi, T. Droz, S. Leutwyler*
Departement für Chemie und Biochemie, Universität Bern
Accurate *van der Waals* and Hydrogen Bond Energies between 1-Naphthol and Several Solvent Partners
Abstract 217

13.20–13.40 ***T. Riedener***, *H.U. Güdel*
Departement für Chemie und Biochemie, Universität Bern
Dynamics of NIR-to-VIS Upconversion in $RbGd_2Br_7$:1%Er^{3+}
Abstract 218

Vorträge: *Kongresssaal: Rio*
Conférences: *Salle de congrès: Rio*
Chairman: *S. Leutwyler*

13.30–13.50 ***P. Bonhôte***, *J. Moser, N. Vlachopoulos, L. Walder, M. Grätzel*
Laboratoire de Photonique et Interfaces, EPF-Lausanne
Long-lived Photoinduced Charge Separation in Heterosupramolecular Systems. Redox-Type Photochromism
Abstract 219

13.50–14.10 ***M. Schweissguth***, *R. Deschenaux*
Institut de Chimie, Université de Neuchâtel
Electron Transfer-induced Mesomorphism in the Ferrocene-Ferrocenium Redox System
Abstract 220

14.10–14.30 ***N. Gfeller***, *F. Binder, G. Calzaferri*
Departement für Chemie und Biochemie, Universität Bern
Dye Molecules in Zeolites as Artificial Antenna
Abstract 221

14.30–14.50 ***M.E. von Arx***[a]), *A. Hauser*[a]), *H. Riesen*[b]), *R. Pellaux*[c]), *S. Decurtins*[c])
[a]) *Departement für Chemie und Biochemie, Universität Bern*
[b]) *Research School of Chemistry, Australian National University Canberra*
[c]) *Anorganisch-chemisches Institut, Universität Zürich*
Resonant and Phonon-assisted Energy Transfer within the R_1-Line of $[Cr(ox)_3]^{3-}$ in Three-dimensional Oxalato-networks
Abstract 222

15.00–15.20 ***K. Wüthrich***, *M. Billeter, P. Güntert, P. Luginbühl, R. Riek, G. Wider*
Institut für Molekularbiologie und Biophysik, ETH-Zürich
NMR Studies and MD Simulations of the Hydration of Proteins and Nucleic Acids in Aqueous Solutions
Abstract 223

15.20–15.40 ***F. Atamny***[a]), *A. Baiker*[a]), *R. Schlögl*[b])
[a]) *Laboratorium für Technische Chemie, ETH-Zürich*
[b]) *Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin*
Chemical Reactivity of Nonperiodic Surface Structures in Graphite
Abstract 224

15.40–16.00 ***L. Jing***
Eidg. Amt. für Messwesen, Wabern
Russbildung bei dieselmotorischer Verbrennung
Abstract 225

16.45 **Verleihung des *Paracelsus*-Preises**
Remise du prix *Paracelse*
Vortrag des *Paracelsus*-Preisträgers
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Kongesssaal: Montréal
Salle de congrès: Montréal

Analytische Chemie

1

Enantioselective separations by HRGC - Problems and solutions

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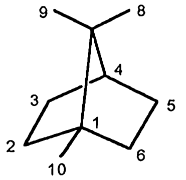
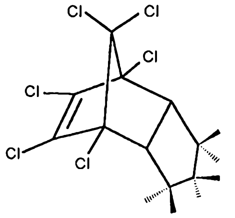
Enantioselective separations have gained a high interest. According to column suppliers more of 30-40% of all request deal with chiral separations. Modified cyclodextrins are widely applied in HRGC. However, the influence of different factors on the reproducibility of the separation and thermal stability of the stationary phase has not been studied in detail leading to many problems and disappointments. When derivatives are synthesized with bulky groups such as t-butyl silylated cyclodextrin, byproducts and mixtures influence both the thermal stability, the enantiomer elution order and the shelf life of the stationary phase. The importance of a proper purification and characterization of the chiral stationary phase for the achieved separation will be shown. Furthermore, the surface properties and the deactivation of the silica capillary surface have a big influence on the thermal stability and the amount of the chiral compound which can be added to the stationary phase. Polychlorinated chlordanes (A) and bornanes (B) were used as model compounds. They have the following carbon skeletons:



A



B

Nearly all polychlorobornanes are chiral. They are ideal test substances since even very small differences in the composition of the stationary phase lead to changes in the observed enantioselectivity and/or enantiomer elution order. Therefore, a test of chiral HRGC columns is suggested based on 4 critical congeners. Furthermore, proposal are made how to improve chiral separations by HRGC.

2

Analytische Chemie

Methylquecksilberbestimmung: Die Fallen der Wasserdampf-Destillationstechnik, oder wie man sich Methylquecksilber während der Probenaufarbeitung selbst herstellt

R. Falter[a], H.Hintelmann[b], G. Ilgen[a]

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Die Methylquecksilberspeciation bleibt nicht nur im Umweltbereich, sondern auch aufgrund der aktuellen Quecksilberamalgamproblematik von allgemeinem Interesse. Viele Studien sollen durchgeführt werden, doch sind die analytischen Messmethoden auch zuverlässig? Zur Methylquecksilberbestimmung wird immer häufiger die Wasserdampf-Destillationstechnik zur Vortrennung aus der Matrix verwendet. Durch eine neu entwickelte HPLC-ICP-MS- sowie mit einer schon bewährten GC-ICP-MS-Methode wurden Versuche mit stabilen angereicherten Quecksilberisotopen durchgeführt ($^{200}Hg^{2+}$, $^{202}Hg^{2+}$ und $CH_3{}^{199}Hg^{+}$), um die Destillationtechnik zu überprüfen. Die Isotope wurden in systematischen Experimenten verschiedenen Probenmatrices, insbesondere zertifizierten Referenzmaterialien zudotiert. Sowohl in Boden- und Sedimentproben als auch in Speichelproben und sterilen Bakteriennährlösungen wurde eine Methylquecksilberproduktion während der Probenaufarbeitung durch die häufig verwendete Technik festgestellt. In Urin- und Fischgewebeproben wurde keine Produktion beobachtet. Offensichtlich sind in einigen Matrices methylierende Komponenten vorhanden; in anderen Matrices fehlen diese, oder sie enthalten Inhibitoren.

Analytische Chemie

3

Scanning near-field spectroscopy as a new tool for micro- and nanoanalysis

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New methods of micro- and nanoanalysis for the investigation of clusters, domains and aggregates of molecules require both high spatial resolution and high sensitivity. At the same time the sampling should be performed at ambient conditions and nondestructively for the sample investigated. These requirements are met by scanning near-field optical microscopy (SNOM), a method that circumvents the fundamental diffraction limit of current optical imaging methods by scanning a nanometer sized fiber tip in close proximity (roughly a few nanometers) over the surface under investigation. The emitted, reflected or scattered light from the surface is collected and imaged onto a sensitive photodetector. The image is built up in a sequential manner point by point. The special advantage of this technique in comparison to other scanning probe microscopies, such as STM or AFM, is the addition of a spectral dimension, which enables chemical imaging of surface adsorbates.

The exceedingly low optical transmission coefficients (typically 10^{-5} to 10^{-6}) of commonly used pulled silica fiber tips has so far prevented many investigations in surface analysis and spectroscopy, which often require high photon fluxes. We are using chemically etched tips that are characterized by much shorter taper regions ranging from 150 to 800 µm and larger cone angles between 6° and 35°. These tips have a 100-1000 times higher power transmission compared to conventional tips used for SNOM. The lateral optical resolution obtained with these tips is 80 nm in transmission and fluorescence. SNOM combined with spectral analysis of the emitted light is used for the characterization of immobilized biomolecules onto self assembled monolayers with respect to domain growth and their orientation. More specific chemical information about surface adsorbates can be obtained by analyzing Raman spectra. Results from CVD deposited diamond films will be discussed.

Coupling pulsed laser light into the fiber tips leads to a strong heating of the very end of the tip due to absorption and back reflection. This local heat source can be used for laser-induced desorption from organic crystals and polymer surfaces. A ballistic heat transfer from the fiber tip to the surface seems to be the most likely mechanism for the desorption observed.

Analytical chemistry

4

LC/UV, LC/MS and LC/NMR for the rapid identification of natural products in the chemical screening of crude plant extracts

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Efficient detection and rapid characterisation of plant constituents play an important role as analytical supports in the work of a phytochemist. Indeed, the identification of already known compounds at the earliest stage of separation is a strategic element for a selective isolation procedure. Hyphenated techniques such as high pressure liquid chromatography (HPLC) coupled to UV photodiode array detection (LC/DAD-UV) and mass spectrometry (LC/MS) are powerful tools for the chemical screening of crude plant extracts and have been fully integrated into the isolation process [1]. The combined use of these techniques gives a rapid idea about the extract composition, allowing an on-line identification of common constituents and leading to a targeted isolation of compounds with original spectroscopic features.

LC/UV and LC/MS are routinely used in our laboratory in association with biological screening for a rapid survey of plant extract composition. However, these coupled techniques do not allow a full identification, except for some well-known natural products. Thus, complementary on-line spectroscopic information is needed. For this purpose, the use of the recently developed technique of LC/NMR has been evaluated. First trials performed on the crude extracts of *Swertia calycina* and *Gentiana ottonis* (Gentianaceae) showed that well resolved ^{1}H-NMR spectra could be obtained on-line for the major compounds. In the stop-flow mode, proton-proton correlation (COSY), as well as indirect proton-carbon correlation (HMBC, HMQC) were performed. Around 20 µg per peak (MW ca 400) were needed for on-line measurements on a 500 MHz instrument. Combination with UV and MS data permits a complete structure evaluation of simple molecules. Other investigations are in progress to evaluate the potential and the limits of this new tool for the direct identification of compounds in crude plant extracts.

[1] Rodriguez, S., Wolfender, J.-L., Hakizamungu, E. and Hostettmann, K. (1995) *Planta Med.* **61**, 362.

5

A highly sensitive photoacoustic sensor for CO_2-measurements in aqueous systems

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Laser Induced Photoacoustic Spectroscopy (LIPAS) [1,2] has been confirmed as an analytical tool, suitable for investigations on inorganic and organic species in solutions, microheterogeneous as well as heterogeneous systems, achieving detection limits which may be some orders of magnitude lower than those obtained with conventional spectrophotometric means.

In the present work, photoacoustic spectroscopy is used for the quantitative analysis of CO_2 in water. In contrast to the conventional method of optical sensing using reflection-spectroscopy, changes in absorption of membranes coated by indicator-dye mixture are quantified by LIPAS.

The pH sensitive membrane is immersed in a buffer solution the pH of which is depending on the different amounts of introduced CO_2. The pH changes produce a modification of the energy of the excited state of the pH sensitive dye and, as a consequence, of its absorption spectrum. Consequently, the radiationless desactivation processes detected by the piezoelectric ceramic are also pH-dependent.

The results of photoacoustic measurements in heterogeneous systems show for different pH values a linear response in function of the excitation energy. The titration curve of the indicator bromothymol blue used has a sensitivity range from pH 6 to 9. Optimized parameters, like the decision of indicator-dye, the concentration of indicator-dye on the membrane, or the position of the membrane in the detector cell and the buffer concentration lead to a highly sensitive method for CO_2 measurements in a low detection limit in order of ppm (< 10 ppm). In this concentration range a systematic error of ± 2 % is found.

[1] Braslavsky S. E., Heibel G., Chem. Rev. 92, 1381-1410 (1992).
[2] MacKenzie H. A., Christion G. B., Hodgson P., Blanc D., Sensors and Actuators B, 11, 213-220 (1993).

Analytische Chemie

6

Fast, automated & economical pesticide residue extraction of solid matrices with an Accelerated Solvent Extractor

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Accelerated Solvent Extraction (ASE) is a new automated procedure for extracting organic compounds from a variety of solid and semi-solid samples.

A commonly used organic solvent is pumped into an extraction cell containing the sample. The solvent is then brought to an elevated temperature (100°C) and pressure (105bar) to maintain the solvent in a liquid state during the extraction. Minutes later the extract is flushed from the sample cell into a standard collection vial and is ready for cleanup and analysis.

The extraction step traditionally requires rather large amounts of solvents. ASE needs less solvent (20-25ml per 10g sample) and significantly shorter time (<15min) than most of the conventional extraction techniques like Soxhlet, high-speed blending or sonication. Moreover, the dual carousels for sample cells and collection vials allow unattended preparation of up to 24 samples, which is very convenient for method validation in agreement with GLP or EN 45'001 conditions.

Solvents recommended for Soxhlet extraction methods generally have been found to be the solvents of choice used with ASE. With ASE the development of new methods is rapid when compared to SFE. With SFE the selection of matrix/analyte-specific parameters such as temperature, pressure, volume of fluid and amount of modifier is usually quite difficult.

The aim of our investigation was to establish a validated multiresidue method (MRM) for the quantitative determination of about 35 organophosphorous (OPs), 45 chlorinated pesticides (OCs) and 6 polychlorinated biphenyls (PCBs) in foods or medicinal plants with the ASE technique.

Our poster presentation describes the ASE method followed by an automated gel permeation chromatography (GPC) clean-up and direct gas chromatography (GC) with phosphorous flame photometric detection (FPD-P) for OPs and electron capture detection (ECD) after an optional silica gel clean-up-step for OCs and PCBs.

7

Analytische Chemie

Uniform Topology-Based Structure Descriptor Combined with Substructure Coding for the Estimation of Partition Coefficients of Organic Compounds

Ernö Pretsch, Martin Junghans
Laboratorium für organische Chemie, ETH, Universitätstr. 16, 8092 Zürich

Various structure descriptors of uniform length, based on path-counting of a node-colored molecular graph or on interatomic distances in 3D structures, as well as substructure coding have been investigated in view to predicting partition coefficients, K_{ow}. The dimension of the structure vectors generated in a first step are reduced by PCA or PLS.

A set of 245 molecules (from CH_3NH_2, to $C_{18}H_{12}$) with experimental log K_{ow} values has been used for model building. The best linear model was found to be capable of predicting log K_{ow} with RMS and maximal errors of 0.161 and 0.83, respectively. Surprisingly, only minor improvements were achieved by considering 3D information. A back-propagation artificial neural network optimized for the above problem with 19 input and 20 hidden nodes and 1 output node was somewhat less powerful.

Cross validation using 123 randomly selected molecules as training set and the remaining 122 molecules as test set showed a prediction capability with an RMS error of 0.326 and a maximal error of 1.12 in log K_{ow} for the best linear model.

8

Analytische Chemie

Local Modeling for Estimating Partition Coefficients of Organic Compounds

Ernö Pretsch, Martin Junghans
Laboratorium für organische Chemie, ETH, Universitätstr. 16, 8092 Zürich

A structure vector based on a combination of interatomic distances in 3D structures and substructure coding is calculated. Subsequent PLS analysis is applied to generate structure descriptors. These are then clustered with a KNN algorithm of weighted average-linkage. For each cluster, distinct structure descriptors are generated by individual PLS analyses and used to build local linear models. From a library containing 245 molecules, 219 (89 %) pertained to 17 clusters with 3 to 64 members and the linear models were able to reproduce the partition coefficients, log K_{ow}, with RMS errors between 0.016 and 0.420 and maximal errors between 0.04 and 0.75. The overall RMS error for the 219 estimations was 0.134. Compared with the corresponding global models based on structure descriptors and on parameters from AM1 calculations [1], the local models reduced the RMS error by a factor of 1.2 and 2.2, respectively.

For cross validation, a randomly selected training set of 123 molecules was used to build 15 linear models derived from its clusters. The test set with the remaining 122 molecules gave an RMS error of 0.325 and a maximal error of 1.33 for the 53 % of predictable log K_{ow} values.

[1] Nicholas Bodor and Ming-Ju Huang, J. Pharm. Sci. 81 (1992) 272-281

9

Analytical Chemistry

Spectro-Potentiometric Investigation of Dynamic Processes in Ion-Selective Membranes

Titus Zwickl, Bernhard Schneider, Beat Federer, and Ernö Pretsch,
Department of Organic Chemistry, ETH, CH-8092 Zürich

Cation interference in neutral carrier H^+-selective electrodes induces a long-term potential drift, the origin of which is investigated by using a new spectro-potentiometric imaging technique. High-resolution images allow to optically monitor time-dependent concentration profiles in polymer membranes that contain an indicator dye as chromoionophore, and to evaluate diffusion coefficients of different components. The time dependence of the EMF response is interpreted on the basis of these results.

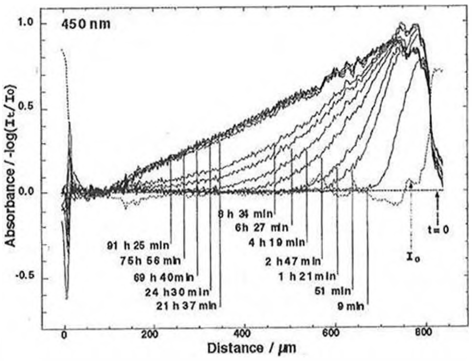

Figure: Time-dependent absorption profiles of the chromoionophore, ETH 2439, in an H^+-selective membrane observed in a spectro-potentiometric experiment at 450 nm

Analytical Chemistry

10

Biosensors for Process Control

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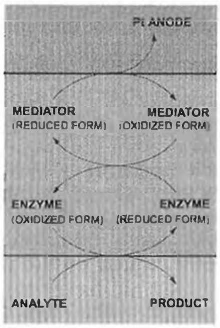
Selective analyses of chemical compounds in (bio)reactor media, food or process water are required in order to optimise and control a process. Biosensors enable simultaneous and continuous real-time as well as reagentfree batch analyses. Therefore, biosensors need to be integrated in modern control systems to ensure an effective monitoring of relevant compounds.



TURNOVER OF THE BIOSENSOR COMPONENTS DURING THE ANALYTE OXIDATION

In recent years, our group developed a new concept of a biosensor. In this biosensor, the host-guest interaction is based on an enzymatic recognition process. The enzymatic turnover of analyte generates an anodic or cathodic current, which is correlated with the analyte concentration in the specimen (see figure). The enzyme is suspended in an organic conducting salt (TTF-TCNQ)/ silicon-oil paste without the use of any membrane. The concept of this mediated amperometric enzymatic biosensor was evaluated in detail for an oxidative and a reductive reaction (hypoxanthine and hydrogen peroxide as analytes, respectively). The selectivity of these sensors is determined by the enzyme and the low applied potential. Therefore, even ascorbate is discriminated. The concept can be applied to various analytes such as glucose, lactate, sulfite, pyruvate, oxalate, amino acids, glutathione, purine derivatives and polyamines.

This year, the rotating disk electrode as pure scientific set-up was supplemented by a flow through system. In view of specific applications, further important parameters as e.g. repeatability, reproducibility, calibration procedure and throughput can now be evaluated.

Analytische Chemie

11

$Pb(OH)^+$ - selective Ionophores

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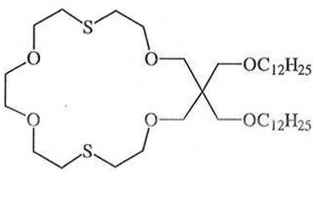
Department of Pharmacy, ETH-Technopark, CH-8005 Zürich

Based upon the structure of a lipophilized 19-crown-6-compound, two novel ionophores (DTK 1 and DTK 2) being selective for $Pb(OH)^+$ - ions were developed by introduction of sulfur donor sites at distinct positions of the molecule.

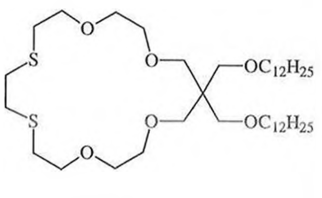
In potentiometric measurements with plasticized PVC-membranes containing lipophilized anionic sites, these ionophores showed enhanced selectivity over other heavy metal ions like Cu^{2+}, Cd^{2+} and Tl^+, while discriminating alkaline ions by at least 3 and earth alkaline ions by about 5 decades of concentration. Only Ag^+ and Hg^{2+} were preferred over $Pb(OH)^+$. An almost ideal Nernstian slope for $Pb(OH)^+$ - ions was achieved at a reversible response.

Potential stability was obtained within less than 15 minutes after changing the analyte solutions in almost all cases.

Structures:



DTK 1



DTK 2

According to their selectivity profiles, these novel ionophores are suitable for applications in environmental analysis.

12

Analytische Chemie

Stimulated Emission Pumping of OH and NH in Flames by Using Two-Color Resonant Four-Wave Mixing

P. P. Radi, B. Mischler, H.-M. Frey, P. Beaud, A. Tzannis and T. Gerber
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Nonlinear spectroscopic techniques continue to be developed and applied as sensitive and selective probes in combustion environments. A particularly interesting technique that has received much attention recently is degenerate four-wave mixing (DFWM). The method offers the combined advantages of a coherent signal, permitting efficient rejection of interfering radiation present in many combustion environments and the sensitivity necessary to detect trace species in flames. The use of separate two input frequencies, as in the experiments reported here, provides a further advantage because signal is obtained only when both frequencies interact with two distinct molecular transitions simultaneously. Two-color resonant four-wave mixing (RFWM) has been used for double resonance spectroscopy of stable molecules in sample cells and in free jet expansions. The aim of this work is to examine the analytical potential of this technique for the determination of trace elements, like radicals, in a combustion environment. Experimental results obtained for OH and NH in CH_4/air and NH_3/O_2 flames are presented.

The high sensitivity of the method is investigated by stimulated emission pumping (SEP) experiments on OH. Two-color RFWM is performed in the wavelength region of the ($A^2\Sigma^+$-$X^2\Pi$) electronic system. If the frequencies of the PUMP and DUMP lasers are tuned to distinct rotational transitions in the (0-0) vibrational band, signal-to-noise ratios of 500:1 are observed. This band exhibits an Einstein coefficient of $A_{00}=1.4 \times 10^6$ s^{-1}. Even though a squared dependency on the Einstein coefficients is given for the signal expression of the method, SEP experiments can be performed that involve the very weak rotational transitions in the (0-1) band of OH ($A_{01}/A_{00}=0.0037\pm0.0008$).

Analytische Chemie **13**

Rapid Analysis of Complexing Agents in Waste Water with HPLC

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Recently we developed a new method for the analysis of complexing agents in surface and ground water with HPLC/DAD[1]. While for river water it is necessary to enrich the analytes by solid phase extraction, waste water samples can be analysed without any concentration step as the concentration range in waste water from 50 to 1000 µg/L. High salt concentrations in the g/L range and high organic content at ppm level cause loss of signal in the chromatogram.

Elimination of the organic matrix was successful by precleaning the sample over a C18 solid phase cartridge. It was then possible to analyse communal waste water for NTA, EDTA and DTPA without any disturbances.

A second problem was the high salt content of industrial waste water. The high amount of chloride was the reason for a large negativ peak just before the signal of EDTA. A waste water sample spiked with EDTA showed no signal of EDTA in the chromatogram. When the chloride concentration was sufficiently lowered by precipitation with silver nitrate the EDTA peak reappeared. Spiking experiments with a simulated waste water sample (3 g/L of chloride) gave the following recoveries: NTA and EDTA: 93 to 106 %, DTPA: 60 to 80 %.

Total analysis time including the precleaning procedure is about 25 minutes per sample. Following procedure was successful for the analysis of industrial waste water:

1. Adjusting pH with sulfuric acid to about 2.5
2. Addition of 160 µL of Fe-(III)-solution to 2 mL of sample
3. Precipitation of chloride with 100 µL of 1.7 M $AgNO_3$
4. Cleanup over C18 reversed phase (500 mg RP C18 from Baker)

[1] R. Geschke and M. Zehringer: A New Method for the Determination of Complexing Agents in River Water using HPLC, Fres. Anal.Chem., in press.

Analytical Chemistry **14**

Heptakis (6-*O*-thexyldimethylsilyl)-2,3-di-*O*-alkyl-*β*-Cyclodextrins as Chiral Stationary Phases in Gas Chromatography.

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Heptakis (6-*O*-*tert.*-butyldimethylsilyl)-2,3-di-*O*-methyl-*β*-cyclodextrin is a chiral stationary phase introduced by *Mosandl and al.* [1] for the resolution of many racemic mixtures.

For the synthesis of this product, *tert.*-butyl-dimethylsilyl chlorid (TBDMSCl) was used as starting material. It presents the double disadvantage to be expensive and difficult to handle (solid and moisty sensitive).

Here, we report the preparation of other chiral stationary phases, the heptakis (6-*O*-thexyldimethylsilyl)-2,3-di-*O*-alkyl-*β*-cyclodextrins from the thexyl-dimethylsilyl chloride (TDSCl). This starting material is easy to manipulate, inexpensive and gives TDS-ethers which are about 2 to 3 times more stable to acidic hydrolysis than the corresponding TBDMS-ethers.

We also report the chiral analysis and an interesting comparative study of the new chiral phases and the known one heptakis (6-*O*-*tert.*-butyldimethylsilyl)-2,3-di-*O*-methyl-*β*-cyclodextrin.

[1] A. Dietrich, B. Maas, V. Karl, P. Kreis, D. Lehmann, B. Weber, A. Mosandl, *HRC.* **15** (1992) 176

Analytische Chemie **15**

Experiences in Analysing Hydrocarbons in Surface and Groundwater with Gaschromatography

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The official method for the determination of hydrocarbons in waste water is based on the analysis of the extract solutions (CCl_4) with infrared spectroscopy [1,2]. Though there are well known matrix effects (discrimination or overestimation of the hydrocarbon content by other compounds) this method is widely used for waste water, surface water, groundwater and soil. When additional information is needed about the composition of the hydrocarbon mixture, the origin of a spill or the comparison of hydrocarbon samples the common IR-method will not give any satisfactory answers. In search for a rapid alternative method for this purpose we developed a gaschromatographic method with flame ionisation detection based on ASTM methods [3].

The samples are analysed by a single step extraction with hexane. Therefore 2 mL of hexane are added to 100 mL of sample and stirred for 30 minutes.

2 µL of the extract are injected split/splitless on a 25 m x 0.32 mm i.D. capillary column (HT5 Aluminum Clad from SGE). Quantitation is based on the sum of all FID-peak areas. The system is calibrated from 0.05 to 100 mg/L with a hydrocarbon mixture (reference gas oil 4-8873 from Supelco).

Recoveries of water samples spiked with a gasoil extra light in the range from 0.05 to 100 mg/L were between 86 and 117 %.

The FID-fingerprint gives information about composition and origin of the hydrocarbon mixture. Over the last five years we were able to quantify and locate the sources of several oil spills in ground and surface water. Compared with the IR-method the GC-method is non toxic (no CCl_4 used), sensitive, fast (1.5 hours per analysis).

[1] Eidgen. Richtlinien zur Untersuchung von Oberflächengewässern: 48 „Gesamte Kohlenwasserstoffe", Eidgen. Departement des Innern
[2] Deutsche Einheitsverfahren zur Wasser-, Abwasser- und Schlammuntersuchung DIN 38409, H 18: Bestimmung von Kohlenwasserstoffen
[3] Standard Test Method for Boiling Range Distribution of Petroleum Fractions by Gaschromatography (1988), Annual Book of ASTM Standards

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Analytische Chemie **16**

Enantioselective Gas Chromatographic Analysis of D/L-Proline

Stefan Sollberger[1], Hans P. Stauffer[1], Therese Lüthi[2], Veronika R. Meyer[2]

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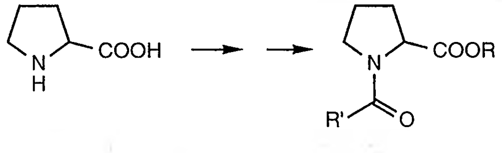
For the trace analysis of amino acids, especially if D and L isomers need to be separated, GC is preferred over HPLC due to its high peak capacity and unsurpassed theoretical plate number. The analysis can be performed well on Chirasil-Val, a chiral stationary phase which is able to separate all the common amino acids into their enantiomers. Problems arise with proline: the separation factor (i.e. the resolution) is low, probably due to the ring structure of the molecule. The resulting peak overlap affects the quantitation of the enantiomers.

In a systematic study we tried to find a derivative which gives adequate, preferably baseline D/L resolution. In this case "resolution" includes separation factor, tailing, and behavior during the gas chromatographic temperature program with regard to the other amino acids which can be present in a mixture of biological origin. The secondary amine function needs to be converted into a perfluorinated amide whereas the carboxylic acid is esterificated.



R = methyl, isopropyl, tert. butyl

R' = trifluoromethyl, heptafluorobutyryl

17

Analytische Chemie

Small Permanent Magnet Ion Cyclotron Resonance Mass Spectrometer

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During the last decade ion cyclotron resonance (ICR) mass spectrometers employing superconductive magnets have found widespread use in mass spectrometry due to their ultra high resolution, high sensitivity, long trapping times and the ease of consecutive mass spectrometry. Fields of application range from ion molecule reaction studies to electrospray ionization mass spectrometry, where the ICR technique has specific advantages.

At the sacrifice of ultra high resolution ion storage as well as resonance experiments and detection are also possible with much lower magnetic fields as they are produced with relatively small and inexpensive permanent magnets. Recently ICR instruments have been built using permanent magnets. Permanent magnets are attractive since they can be used in a stand-alone detector and, apart from the magnetization procedure, do not require cryogenics, electric current and cooling water.

The design of magnetic fields for ICR has not received much attention due to the fact that mostly magnets are used which originally were designed for NMR which demands very high homogeneity, and therefore rarely is the limiting factor for resolution in ICR experiments. However, the homogeneous region of NMR magnets is usually quite small and often is exceeded when larger (e.g. elongated) ICR trap cells are constructed.

A detailed description of the permanent magnet ICR instrument built in our laboratory and preliminary results, including ion/molecule reactions, will be presented.

18

Analytische Chemie

Reactions with HCN in an Ion Trap Mass Spectrometer

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Ion-molecule reactions involving hydrogen cyanide are of considerable interest, since in many astrochemical environments the existence of hydrogen cyanide has been detected. In such an atmosphere the presence of a large number of organonitrogen molecules produced by ion-molecule reactions is suggested. To explore those ion-molecule reaction pathways a series of experiments were carried out on the purpose built quadrupole, quistor, quadrupole tandem mass spectrometer.

The quadrupole, quistor, quadrupole tandem mass spectrometer allows very well to explore ion-molecule reactions for both positive and negative ions. After formation in an external source, one ion species is selected by the first quadrupole and injected into the quistor for reaction with one or more neutral counterparts. The storage time and the reactant gas pressure in the quistor can be varied over a great range.

A series of experiments involving hydrogen cyanide were performed on the quadrupole, quistor, quadrupole instrument. In particular the reactivity and reaction channels will be presented.

Analytische Chemie 19

Construction and Applications of a Quistor Time-of-Flight Mass Spectrometer

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The matrix-assisted laser desorption/ionization (MALDI) is a powerful method for creating ions of large biomolecules. The combination of this technique with a quadrupole ion store (QUISTOR) makes it possible to obtain more structural information of the sample molecules. One commonly used way is the fragmentation by resonant excitation. Sequence analyzing of peptides and proteins is an application of this method. An other approach of achieving structural data by specific gas-phase reactions within the quistor will be shown.

An instrument built in our lab is used for the measurement of gas-phase reactions of large ions with neutral gases. In this set-up MALDI is implemented on a quistor which serves as a reaction chamber. Mass measurement of the reaction products is performed by a time-of-flight analyzer. In a typical experiment the ions created by MALDI are trapped and stored in the quistor where they can react with a neutral gas. After a reaction time of 0.1 to 10 s the ions are extracted into the flight tube for the simultaneous detection of all the reaction products.

Details of the instrument and spectra of measured gas-phase reactions of bimolecular ions with small organic molecules will be presented.

Analytische Chemie 20

The Matrix Suppression Effect and Ionization Mechanisms in MALDI

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At appropriate matrix : analyte mixing ratios, small to moderate sized analyte ions (1000-20000 Da) can fully suppress positive matrix ions in MALDI mass spectra. This is true for all matrix species, including radical cations and adducts with protons or alkali metal ions. Full matrix suppression is also observed regardless of the preferred analyte ion form, be it protonated or an alkali adduct. These facts lead us to propose a mechanism for prompt, primary (not secondary gas-phase) MALDI ionization in which excited matrix is the key species. At least two such excited molecules are believed necessary for free ion generation. This model is found to be consistent with the available data, as well as making several predictions which are confirmed by new observations. The model also predicts that the matrix suppression effect will not be observable with heavy analytes because their large excluded volume precludes desorption at the necessary mixing ratios.

CHIMIA 50 (1996) Nr. 7/8 (Juli/August)

Analytische Chemie **21**

The Gas Phase Basicity of Matrix Ions Produced with MALDI

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Gas phase reactions have been found to play an important role in MALDI. The depletion of matrix velocity distributions in the presence of analyte indicated that ionization in the gas phase may sometimes be dominant [1]. Fragmentation of several analytes has been studied by Spengler et al. [2] who report that the rate constants for unimolecular decay of analytes are much larger in desorption from a sinapic acid matrix than from a DHB matrix. In the case of gas phase ionization by proton transfer this might be related to the gas phase basicity of the matrix ions. To gain more insight into the energetics of possible gas phase reactions we are studying the gas phase basicity (GB) of high abundance species produced from matrices in laser desorption.

Experiments were conducted on a Fourier Transform Mass Spectrometer. One ionic species from the matrix is isolated by ejecting others from the cell. A volatile base with a known gas phase basidity is admitted after which proton transfer may be observed from the isolated matrix ion MH^+ to neutral base B:

$$MH^+ + B \rightarrow M + BH^+ .$$

From the (non)observance of the reactions with several bases, the GB of M can be bracketed between two values. Apart from the GB of the intact matrix molecules, the GB of important matrix fragments were studied also, since these have a high abundance in TOF spectra and must therefore be present in the high density gas plume after laser desorption.

The results of this study will make it possible to compare different matrices and will yield an estimate for the excess energy which could be deposited within the analytes for gas phase chemical ionization processes (e.g. protonation) in MALDI.

1 Bökelmann V., Spengler B. and Kaufmann R., Eur. Mass Spectrom. 1995, 1, 81
2 Spengler B., Kirsch D. und Kaufmann R., J. Chem. Phys. 1992, 96, 9678

Analytical Chemistry **23**

Analyses of Coenzyme B_{12} Derivatives and Complexes with Non-Covalent Bondings using ESI-MS

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The vitamin B_{12} is one of the rare organometallic compounds in nature. The active parts are its coenzymes which are needed for more than ten biologically important rearrangements. One of them is the (2R)-methylmalonyl-CoA-succinyl-CoA rearrangement which takes also place in the human body. The chemical transformation of (2R)-methylmalonyl-CoA nto succinyl-CoA is catalysed in the cell by the methylmalonyl-CoA-mutase which depends on the coenzyme B_{12}.

For a better comprehension of this rearrangement several new derivatives of the coenzyme B_{12} had been prepared. Different chemical nteractions as hydrogen bondings, hydrophobic and electrostatic nteractions had been studied. Therefore new concepts and models for he imitation of the natural coenzyme-substrate system had been worked out based on molecular recognition. Analytical evidence for a oenzyme-substrate complex could be a proof for special molecular nteractions.

Up to day coenzyme B_{12} derivatives were usually analysed with FAB or LSIMS but these spectra had a relatively low quality. The substrate-oenzyme B_{12} complexes were never before analysed with mass pectrometric methods.

Electrospray data of coenzyme B_{12} derivatives and complexes with non-ovalent bondings are presented.

22

Analytische Chemie

Use of Low Resolution Mass Spectra for Predicting Molecular Formulae

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Most of today's structure generators require the input of a unique molecular formula.[1] Programs are available that help to reduce the number of possible formulae based on various pieces of information.[2] Here, we show that low resolution mass spectra can be applied as an additional source of information. The basis of the method consists in generating a constrained list of all possible element combinations from a given formula and comparing the corresponding masses with the spectrum. Signals that cannot be explained by possible element combinations contradict the formula. The capabilities and limits of the procedure have been evaluated by investigating a large number of database entries.

References

(1) Gray, N.A.B. *Computer-Assisted Structure Elucidation*; Wiley: New York, 1986.
(2) Fürst, A.; Clerc, J.T.; Pretsch, E. *Chemom. Intell. Lab. Syst.* **1989**, *5*, 329-334.

Analytische Chemie **24**

Graphite/Liquid Mixtures for Molecular Analysis by Laser Desorption/Ionisation Mass Spectrometry.

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The purpose of the present study was to investigate graphite/liquid-matrix mixtures for the laser desorption/ionisation of a broad range of molecular analytes. The work demonstrates that a simple preparative procedure can be used as a general protocol for the UV-laser desorption/ionisation mass spectrometry of low molecular weight proteins, carbohydrates and polymers (see Figure 1). We have investigated the roles of both the graphite and the liquid matrix in the desorption/ionisation process.

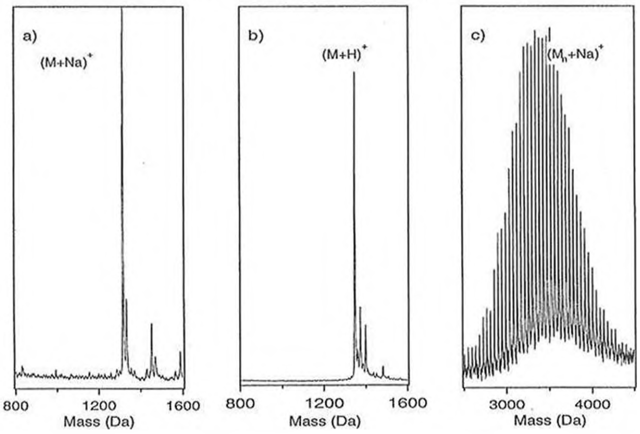

Figure 1. Laser desorption/ionisation mass spectra of a) γ-cyclodextrin, b) substance P and c) PEG 3000, obtained using graphite particulates in combination with a glycerol liquid matrix.

25

Analytische Chemie

Mass Spectrometry in surface analysis with a 100nm spatial Resolution

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Spatially resolved surface analysis is necessary in many fields such as in semiconductor industry, materials science and biology. We report here the design of an instrument capable of desorbing molecules from surfaces at ambient conditions on a 100nm scale, with subsequent analysis in a conventional mass spectrometer.

The basic aparatus consists of a scanning near-field microscope (SNOM). The end of an optical fiber is chemically etched and the resulting tip is metallized with a thin layer of aluminum. The tip is dithered at some nanometers (5-10nm) distance from the surface with a shear-force regulation mechanism.

A nanosecond laser pulse is coupled into the optical fiber and desorbs the material under the tip by a ballistic heat transfer mechanism.

The use of wide cone angle tips allows to couple high-power laser pulses (≈100µJ) with a relatively small elongation of the tip.

Analytische Chemie **26**

Screening Analysis of Rhine Water with GC/MS

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Since 1993 we are controlling the Rhine at the Rhein-Überwachungs-Station (RÜS) [1] at Weil. The water phase is analysed permanently for over 200 substances. Two screening analysis for organic compounds are performed workdaily. The headspace screening monitors a wide range of volatile chlorinated and non chlorinated solvents. The GC/MS-analysis of a loaded C18-cartridge screens for the middle volatile to the non volatile GC-analysable substances. The analytes are online adsorbed onto a solid phase cartridge (Lichrolute EN from E. Merck, Darmstadt) out of a automatically filtered (0.45 µm) sample stream of Rhine water [2]. In the laboratory the cartridge is dried with nitrogen, then eluted with 5 mL of ethyle acetate. The solvent is evaporated under nitrogen and the residue is resolved in 50 uL of isooctane. Analysis is performed on a benchtop GC/MS-system (TRIO 1000 from Fisons). 5 uL are injected on a 60 m x 0.32 mm i.D. column (DB-5 ms) with retention gap. Detection is performed in full scan mode between 45 and 450 m/z. The separation takes 75 minutes. The final reconstructed ion chromatogram (RIC) is analysed with special search routines. Every peak higher than ten fold of the internal standard n-chlorodecane is detected, integrated and identified with library searches. Three levels of identity grade are defined:
unknown: when no comparable spectra is got from any library. characterised: when good library spectra are obtained but reference substance is not available. Identified: when retention time and spectra are confirmed with a reference substance.
Since 1993 no substances of high acute toxicity could be detected higher than 0.5 µg/L. But we were successfull in the identification of a dozen substances of not well known toxicity: We identified steroids (e.g. sitosterol, cholesterol), vitamins (tocopherol, tocopherol acetate). Some of the substances originate from waste water treatment plants.

[1] Common project of the BUWAL and the Umweltministerium Stuttgart
[2] N.A. Corfù, I. Gallert, M. Zehringer, Chimia 49 (1995), 250, Abstract 4

27

Medizinische Chemie

FIRST TOTAL SYNTHESIS OF LYSYLPYRIDINOLINE AND HYDROXYLYSYLPYRIDINOLINE

Rudolf Waelchli, Christian Beerli, Harald Meigel and Laszlo Revesz
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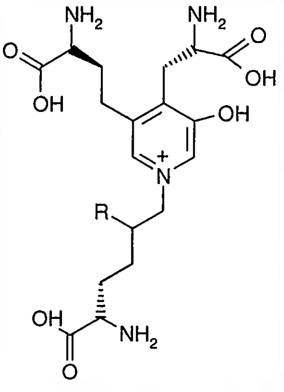
The collagen crosslinks lysylpyridinoline (DP) 1 and hydroxylysylpyridinoline (HP) 2 are two markers for bone resorption, especially DP which only occurs in bone and dentine. Suitable markers for bone resorption are important tools in the early diagnosis and drug therapy monitoring in patients with metabolic bone disease. So far these two collagen crosslinks were isolated from urine, using several cleaning steps and in low yields [1]. To overcome this pitfall we initiated the chemical synthesis of DP and HP. In addition we could couple BSA and KLH of defined sites to DP thus creating optimal tools to establish a diagnostic kit based on an immunological approach.



R= H; 1
R=OH; 2

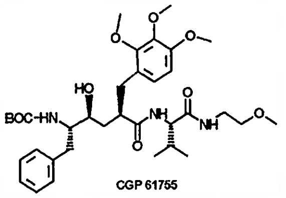
[1]: S.P. Robins, A. Duncan, M.J. Seibel; *J. Rheumatol.* 1989, 16, 964.

Medizinische Chemie **28**

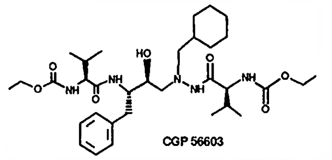
Synthese und Entwicklung von HIV-Protease Hemmern bei Ciba-Geigy

H.-G. Capraro, G. Bold, A. Fässler, M. Lang, R. Cozens, J. Lazdins, J. Mestan, B. Poncioni, J.L. Rösel, D. Stover, T. Klimkait und K. Woods-Cook
Ciba-Geigy AG, Basel

Die HIV-Protease gehört zu der Klasse der Aspartyl-Proteasen und ist ein Schlüsselenzym im Vermehrungsprozess der HI-Viren. Sie schneidet die viralen Poly-Proteine in strukturelle und funktionelle Untereinheiten und ist so u.a. für die Bildung der Virus-Struktur verantwortlich. Eine Hemmung der HIV-Protease lässt unreife, nicht-infektiöse Viruspartikel entstehen. Klinische Studien haben gezeigt, dass in der Tat mit der Verabreichung von HIV-Protease-Hemmern der Virustiter in HIV-infizierten Patienten drastisch gesenkt werden kann. Man hofft, dass dadurch der Ausbruch von AIDS verzögert und im besten Falle verhindert wird.



CGP 61755



CGP 56603

Mit CGP 61755 wurde bei Ciba ein synthetisch leicht zugänglicher Protease-Hemmer identifiziert. Dieser weist hohe antivirale Wirksamkeit, hohe Selektivität bzgl. anderen menschlichen Aspartyl-Proteasen und gute orale Bioverfügbarkeit in mehreren Tierspezies auf. Neben CGP 61755, einem Peptidomimetikum vom Phe-c-Phe-Typ, wurde bei Ciba mit den Azapeptiden noch eine weitere Substanzklasse bearbeitet (Bsp.: CGP 56603). Auch diese weisen Eigenschaften auf, die sie zu äusserst interessanten Entwicklungskandidaten machen.

CHIMIA *50* (1996) Nr. 7/8 (Juli/August)

Medizinische Chemie

29

SDZ SER-082: A 5-$HT_{2C/2B}$ Receptor Antagonist with Low 5-HT_{2A} Receptor Affinity

Herbert Mühle, Joachim Nozulak, Hans Kalkman, Philipp Floersheim, Daniel Hoyer, Ernst Küsters and Philippe Schöffter
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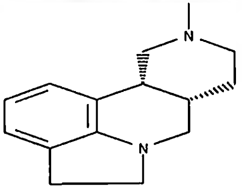
The indolo[1,7-bc][2,6]naphthyridine SDZ SER-082 binds with high affinity to the 5-HT_{2C} receptor (pK_D 7.8), exerting weak affinity towards the 5-HT_{2A} receptor site (pK_D 6.2). The compound behaves as a 5-HT_{2C} receptor antagonist on the 5-HT-induced accumulation of inositol phosphates in pig choroid plexus cells (pK_B 7.13) and acts as a 5-HT_{2B} receptor antagonist at the rat stomach fundus with a pK_B value of 7.34. SDZ SER-082 was found to be a potential development candidate in several CNS indications. The chemical key step in the initial laboratory synthesis was the photocyclization of an indolyl tetrahydropyridino-carbamic acid ethyl ester to afford a mixture of *cis-/trans*-naphthyridines. This process turned out to be inefficient for a scale-up. Three alternative synthetic routes A,B,C are discussed:
The "Imino-*Diels-Alder*" reaction applying indoline / formaldehyde / cyclopentadiene and the intramolecular *Heck* cyclization of 7-bromo tetrahydropyridyl-carbonyl-indoline were surpassed in their synthetic efficiency by the *Friedel-Crafts* cyclization of the indolinyl-piperidone, followed by reduction to give rise to a racemic *cis*-naphthyridine in high overall yield . It was subjected to racemic resolution by applying on a kg scale repetitive chromatography on chiral stationary phase.



SDZ SER-082

Organische Chemie / Medizinische Chemie

30

Synthesis of 4'-Acylated Nucleotides and their Action on Enzymes

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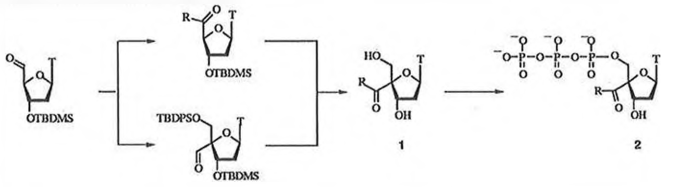
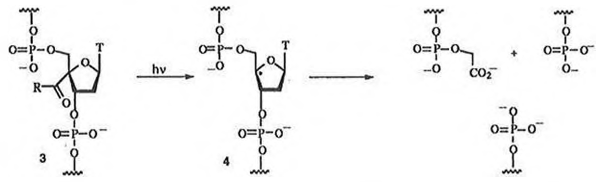
4'-Deoxyribonucleotide radicals are important intermediates in radical-induced DNA strand scission. Recently, we have shown that 4'-acylated nucleotides are precursors for the generation of 4'-DNA radicals. We have worked out two different synthetic strategies towards 4'-acylated thymidines **1** which will be discussed.



The 4'-acylated thymidines **1** were converted into the corresponding triphosphates **2** which have been tested on their action on several procaryotic and eucaryotic DNA polymerases and viral reverse transcriptases. It turned out that only human immunodeficiency virus (HIV) reverse transcriptase is able to incorporate 4'-acylated nucleotides **2**. Irradiation of the enzymatically synthesized 4'-acylated DNA **3** generates the 4'-oligonucleotide radical **4** which leads to selective DNA strand cleavage.



Our finding that among the enzymes we tested only HIV reverse transcriptase is able to incorporate photolabile 4'-acylated thymidines is giving rise to new anti-viral therapeutic strategies.

31

Medizinische Chemie

Estimation of Membrane Permeation from Physicochemical Drug Properties

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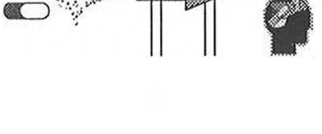
One important aspect of oral bioavailability is sufficient gastro-intestinal absorption. The majority of drugs is crossing biological membranes by passive diffusion. In addition active transport and P-glycoprotein-mediated efflux systems are important for the understanding of membrane transport processes. Permeability of a compound by passive diffusion through biological membranes, such as the gastro-intestinal and blood-brain barrier and cell cultures such as Caco-2 cells, depends mainly on lipophilicity, molecular size and hydrogen bonding potential of the solute [1].

Relationships between these physicochemical properties and their influence on membrane transport have been studied [2]. Both graphical and equation-based approaches and their potential use in the estimation of human oral absorption and brain uptake of drug candidates will be presented.

[1] Camenisch, G., Folkers, G., Van de Waterbeemd, H., *Pharm.Acta Helv.* (1996) in press.
[2] Van de Waterbeemd, H., Camenisch, G., Folkers, G., Raevsky, O.A., *Quant.Struct.Act.Relat.* (1996) in preparation.



32

Medicinal Chemistry

Conformational Control in the Cyclosporin Series

Chris Papageorgiou

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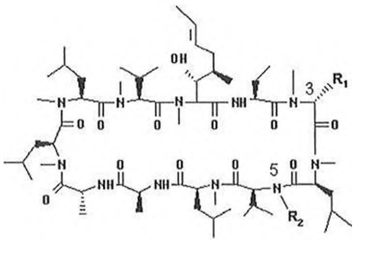
Cyclosporin A (CsA, **1**) is a cyclic undecapeptide which, in solution, exists as a mixture of various, slowly interconverting conformers. Among these, only those having all the -N(Me)-CO- bonds trans are biologically active. An effective conformational stabilization of CsA has been achieved through the regiospecific alkylation of either the C-3(**2**) or the N-5(**3**)position of **1**. The biological activity of these unique conformers, their structure and their comparison with the bioactive conformation of CsA will be discussed.



R_1=R_2=H CsA **1**

R_1= CH_2OH R_2=H **2**

R_1=H R_2=alkyl **3**

CHIMIA *50* (1996) Nr. 7/8 (Juli/August)

33

PDE 4 Inhibitors: Design, synthesis and anti-inflammatory activity of 4-(3-cyclopentylidinemethyl-4-methoxyphenyl)pyridine.

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A prominent feature of asthma is an intense infiltration of eosinophils, macrophages and lymphocytes into the airways. Of these the eosinophil is probably the main protagonist in inflicting injury to the bronchial mucosa. This damage leads to bronchial obstruction, hyperreactivity and to the symptoms of asthma. Inhibiting the infiltration of eosinophils and their subsequent activation results in a decreased secretion of proinflammatory mediators and is an attractive approach towards asthma therapy.

An increase in intracellular levels of the second messenger, adenosine 3′,5′-cyclic monophosphate (cAMP), inhibits the activation of many cell types, including eosinophils, where responses such as chemotaxis, oxidative burst and cytotoxic protein release are suppressed. Intracellular cAMP is regulated by the action of adenylyl cyclase and phosphodiesterase (PDE) enzymes, which respectively catalyse its formation and hydrolytic degradation. Of the seven known groups of PDE isoenzymes, the cAMP-specific Type 4 family is particularly important in regulating cAMP levels and of the four sub-types within this family, PDE 4A, PDE 4B and PDE 4D are expressed in high levels within human eosinophils. Consequently, selective inhibition of PDE 4 enzymes is considered a promising approach towards asthma therapy.

Whereas the non-selective PDE inhibitor, theophylline, is well known in asthma, selective PDE 4 inhibitors are only now entering clinical trials. The antidepressant agent, (±)-rolipram, is a selective PDE 4 inhibitor, which displays anti-inflammatory activity in animal models of asthma. This communication will describe the synthesis and SAR of a novel series of arylpyridines derived from the rolipram structure and illustrate the therapeutic potential of such compounds as locally active anti-asthma drugs. Thus, 4-(3-cyclopentylidinemethyl-4-methoxyphenyl)pyridine inhibits human recombinant PDE 4D and the oxidative burst of human eosinophils with respective pIC_{50} values of 7.0 and 8.1, and inhibits pulmonary eosinophilia in antigen-sensitized rats at 1 mg/kg following intratracheal administration.

34

Medizinische Chemie

Approaches towards the Design and Synthesis of non-peptidic Substance-P Antagonists

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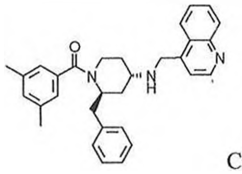
Substance-P (SP), binds selectively to the NK-1 receptor and plays a role in numerous peripheral and central physiological responses. SP is likely to be involved in a variety of diseases such as asthma, inflammation, inflammatory bowel disease, pain, migraine, emesis, psychosis and anxiety. Through selective screening we found a series of SP-antagonists with affinities to the NK-1 receptor in the micromolar range. By comparison of these weak SP-antagonists with substance-P itself we assumed the Phe^7-Phe^8 dipeptide unit of SP to be of importance for binding to the NK-1 receptor. Based upon this Phe-Phe hypothesis we describe the design, synthesis and SAR of potent, orally and centrally active, and selective antagonists at the NK1-receptor (e.g. CGP 49823).



CGP 49823

35

Medizinische Chemie

A Solid-Phase Synthetic Approach to Template-Stabilized Protein Loop Mimetics

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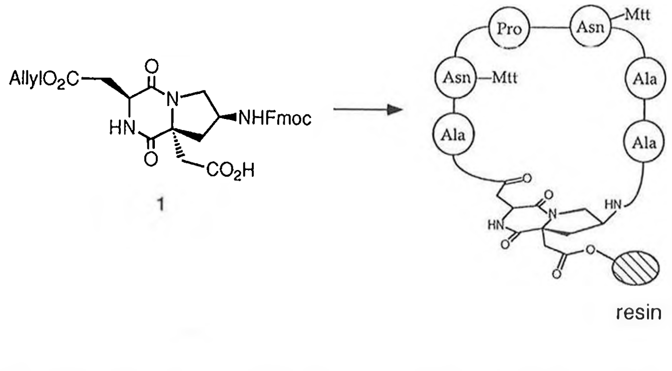
Small surface loops on proteins are of general interest in the design of peptide based vaccines and inhibitors. Poor results obtained with linear peptides often can be explained by bad mimicry of constrained protein epitopes by small, flexible peptides. It has been shown, for example, that the stabilization of turn conformations in small peptides may improve their antigenicity. This approach has been applied to the $(NPNA)_n$-repeat motif of the malaria parasite *Plasmodium falciparum* with the aim of stabilizing turn conformations within the NPNA-unit.



The diketopiperazine-based template **1** has been developed for the solid-phase assembly of cyclic loop mimetics. The template-bound loops can also be combined into multi-loop arrays, following the Multiple Antigen Peptide (MAP) strategy of Tam. By varying the two amino acid building blocks of **1** the synthetic approach can easily be modified to produce a variety of related templates.

36

Medizinische Chemie

Biodegradation of Novel Block-polyesterurethanes Based on Low-molecular-weight Poly[3-(*R*)-hydroxybutyric acid]

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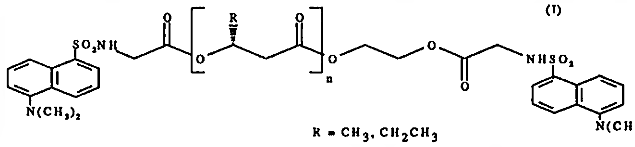
Low-molecular-weight hydroxy-terminated PHB polymers (M_n = 2'300) have been used in our group as crystallizable segment in the synthesis of bioresorbable block-polyesterurethanes or -polyesters (DegraPol®). The random hydrolytic cleavage of the amorphous part of these polymers might result, *in vivo*, in the production of small crystalline particles of low molecular weight PHB which could then undergo phagocytosis and biodegradation inside phagosomes. To test this possibility, a fluorescent labeled PHB (I) segment was synthesized, precipitated in the form of crystalline particles (1-10 µm diameter) and used for an *in vitro* investigation of its interaction with macrophage cell line.



By mean of fluorescence microscopy it was possible to identify PHB fluorescent particles inside macrophages after 4 hours of incubation. The decrease of the amount of fluorescent material inside cells was observed by fluorescence microscopy and quantified by mean of FACS analysis and Laser Cytometry.

This results suggest an active intracellular biodegradation of the polymeric material by macrophages, as supported by the identification of possible water-soluble degradation products in cell supernatants (Fluorescence Spectroscopy and HPLC analysis).

CHIMIA 50 (1996) Nr. 7/8 (Juli/August)

Medizinische Chemie

37

Hydrolytical cleavage of TAR RNA, the *trans*-activation responsive region of HIV, by a bis(guanidinium) catalyst attached to arginine

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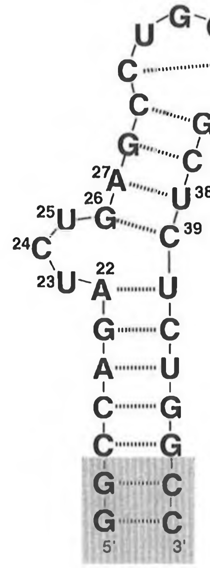
The synthesis of the bis(guanidinium) catalyst **2** will be presented as well as its ability to bind and to cleave the truncated TAR-sequence **1**.



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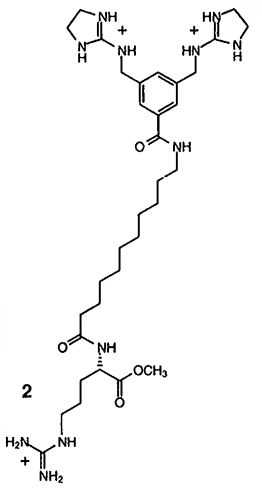

2

Medizinische Chemie

38

Crystallographic and Mutagenesis Studies Reveal a Neutralizing Epitope on the Human Interferon γ Receptor α-Chain

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The extracellular portion of the interferon γ receptor α-chain (IFNγR) is an interesting target for studies of protein-protein recognition, since both the natural ligand and several surrogate ligands in the form of neutralizing anti-receptor monoclonal antibodies (mAb) are available for investigation. The crystal structure of the IFNγ-IFNγR complex was reported recently (Walter et al., *Nature*, **1995**, *376*, 230). This revealed in atomic detail which residues on the receptor are buried upon complex formation with the cytokine IFNγ. We set out to study how the structural epitope bound by the neutralizing mAb A6 is related to the ligand binding site on the receptor surface.

A panel of homolog-scanning receptor mutants has been produced in *E. coli*, and their ability to bind to A6 has been assayed using a surface plasmon resonance biosensor (BIAcore). This revealed a loop on the receptor surface which contains residues that are essential for high affinity binding to A6. At the same time, a complex of the antigen-binding fragment (Fab) of A6 and a single domain of the receptor has been crystallized, and its structure determined to ≈3.0Å resolution. The crystal structure reveals how the receptor loop makes contact with the Fab. The complex is noteworthy for the large number of aromatic residues buried at the interface. The receptor loop bound by A6 is also important in binding the ligand IFNγ, thus nicely explaining the neutralizing activity of the antibody. Interestingly, this loop adopts quite different conformations in the two complexes, indicating an induced-fit mechanism of binding.

Anorganische-Koordinations Chemie

39

Mathematische Aufbereitung multivariater spektroskopischer Daten zur Verbesserung der kinetischen Multikomponentenanalyse

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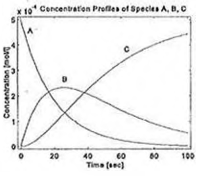
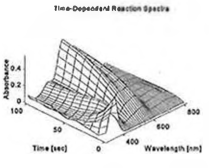
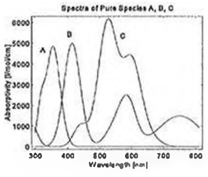
Kinetische spektroskopische Daten sind im allgemeinen unterbestimmt, und es ist notwendig, zur Ermittlung kinetischer Parameter und Spektren der Species zumindest die vorhandene Information möglichst effektiv zu nutzen.







Zwei Ansätze können den Weg dorthin erleichtern:

- Daten- und Fehlerreduktion der Rohdaten
- Einbindung bekannter Spektren einzelner Species

Anhand simulierter kinetischer multivariater spektrophotometrischer Daten wird eine Methode vorgestellt, die zu einer signifikanten Verbesserung in der Reproduzierbarkeit der eingesetzten Modell-Parameter führt. Das Verfahren beruht auf einer Vorbehandlung der Rohdaten durch eine Kombination von **Principal Component Analysis**(1) und **Wavelets-Transformation**(2).

Ein weiteres Verfahren nutzt die potentielle Kenntnis von Spektren einzelner Species. Durch die Einführung einer **Erweiterten Eigenvektor-Basis** bei Berechnungen mit simulierten und experimentellen Daten zeigt sich, dass dieses Wissen insbesondere dann sinnvoll eingesetzt werden kann, wenn die Daten eine hohe zeitliche und/oder spektrale Überlappung aufweisen.

(1) E. R. Malinowski, *Factor Analysis in Chemistry*, Wiley N.Y. 1991
(2) W. H. Press et al., *Numerical Recipes in C*, second edition, N.Y. 1992

Anorganische Chemie

40

Periodische Knotenflächen und Hierarchische Strukturprinzipien.

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Die dreidimensionalen Raumgruppen sind charakterisiert durch relativ wenige grundlegende topologische Formen [1,2], die über periodische Knotenflähchen (PNS) auf einfachste Art repräsentiert werden. Die PNS sind die Nullstellen kurzer Fourierreihen [3] mit nur einem oder wenigen, für die betrachtete Raumgruppe charakteristischen Reflexen. Wir haben mit dem Hilfsmittel der PNS isosymmetrische Strukturfamilien untersucht und die strukturellen Veränderungen als Funktion der Komplexität verfolgt. Man findet dabei hierarchische Ordnungsprinzipien, die im Sinne (fraktaler) Wiederholungsmuster gedeutet werden können.

In einigen bisher untersuchten Fällen fällt auf, dass sich die Strukturen einer kompletten Strukturtypenserie, die zu einer Raumgruppe bekannt sind, durch ebenfalls nur wenige ursprungsnahe, charakteristische Reflexe eindeutig unterscheiden. Im Gegensatz zu den prinzipiellen (einfachsten) PNS einer RG zeigen die PNS solcher schon strukturspezifischer Reflexgruppen klare Hinweise auf die charakteristischen Baugruppen der einzelnen Strukturtypen. Wir versuchen durch diese Untersuchungen u.a. zu klären, inwieweit aus der Kenntnis bekannter Strukturen Hinweise auf eine generelle Strukturbestimmungmethodik gewonnen werden können, die sich nur auf ab-initio Verfahren stützen sondern unter Ausnutzung der Fülle bekannter Strukturen arbeitet.

[1] L.Faelth, S.Andersson, Z.Kristallogr. **160**,313(1982)
[2] H.G.v.Schnering, R.Nesper, Angew.Chem.Int.Ed.Engl. **26**,1059(1987)
[3] H.G.v.Schnering, R.Nesper, Z.Phys. **B83**,407(1991)

CHIMIA 50 (1996) Nr. 7/8 (Juli/August)

Anorganische/Koordinations Chemie

41

Pulse Thermal Analysis-A Novel Method for Investigating Gas-Solid Reactions

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In order to increase the applicability and sensitivity of the conventional thermoanalytical measurements and to allow a more detailed interpretation of the investigated phenomena, a novel thermoanalytical method "Pulse Thermal Analysis" PTA has been developed.

In conventional thermal analysis (TA) the information is mostly extracted from the total transformation of reactant to intermediate phase(s) or product. Modifications applied, such as quasi-isothermal thermogravimetry, constant - rate TA, modulated- or alternating DSC, increasing on one side the potential of TA, do not allow, however, controlling exactly the course of the reaction at a specific temperature or extent of reaction.

PTA is based on injecting of a small quantity of the gaseous reactant into the inert carrier gas stream and monitoring of the changes of mass, enthalpy and gas composition (mass spectrometry) resulting from the very small progresses of reaction. The main advantage of PTA compared to conventional techniques is that the progress of the reaction (depending on the pulse volume) can be investigated at any temperature and conversion degree. This aspect of PTA gives unique opportunities for investigating the initial period of gas-solid reactions, particularly important in catalytic reactions occurring at the surface and generally leading to very small changes of the solid phase composition.

The potential of the method is illustrated by investigations of redox reactions of solids: reduction of supported and unsupported oxides such as PdO, CuO, NiO by hydrogen, carbon monoxide and methane and oxidation of respective metals formed, oxidation of CO or CH_4 over solid catalysts, isotopic exchange between oxygen and carbon dioxide and PdO labelled by ^{18}O. A series of examples illustrating the application of PTA also for quantitative calibration of mass spectrometric curves in coupled TA-MS system is presented.

Anorganische/Koordinations Chemie

43

Interrelation between Thermoanalytical and Mass Spectrometric Curves in Combined TA-MS System

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The convective and diffusional mass transfer occurring in combined thermoanylyzer-quadrupole mass spectrometer systems can cause significant deviation between measured thermoanalytical (TA) and mass spectrometric (MS) curves. As a test reaction for investigating the interrelation between these signals, the decomposition of $CaCO_3$ has been used. A model has been developed based on the separate consideration of three different zones in the system: the plug flow, mixed flow and dead zone. The model allows to quantify deviations such as time lag and shape of curves between measured TA and MS curves for particular experimental conditions such as carrier gas flow rate or diffusivity of evolved gas.

The applied model provides a criterion for finding the minimal carrier gas flow rate at which the diffusional effects do not cause significant deviation between thermogravimetric (DTG) and MS curves. The criterion relates the total residence time of the gas in the experimental system τ_{tot} to the characteristic time t_u of the gravimetrically recorded decomposition process. Generally it can be stated that the higher diffusivity of the evolving species in the carrier gas, the higher is the minimal required gas flow rate necessary to fulfil the global criterion of the residence time. Thus the choice of the carrier gas strongly influences its minimal required flow rate and thereby the intensity of MS signals.

Anorganische Chemie / Koordinationschemie

42

$^{55}Mn,^{13}CO$ and $^{55}Mn,^{31}P$ Coupling Constants of Organomanganese Complexes: Comparison Between Liquid and Solid-State NMR Methods

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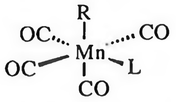
In solution, the J-multiplet structure of the NMR signal of a spin-1/2 nucleus S coupled to a quadrupolar nucleus Q is often partially or completely collapsed owing to the fast spin relaxation of Q. The coupling constant J(Q,S) can, however, be indirectly evaluated via a lineshape analysis. In this study scalar coupling constants based on the experimental data set of our previous work [1] and recalculated with the corrected version of the lineshape fitting programme QUADR [2] will be presented.

From the MAS solid-state NMR spectrum J(Q,S) can be determined directly, if the quadrupole coupling constant $\chi(Q)$ is not appreciably larger than the Q Zeeman frequency ν_Q [3]. While $^1J(^{55}Mn,^{31}P)$ values of several complexes were readily obtained, the ^{13}C MAS spectra could be interpreted only for selected molecules, such as $Mn(CO)_5Cl$ and $Mn(CO)_5I$, and the $^1J(Mn,C)$ values agree well with the solution data.



R : Alkyl or Halogen
L : Phosphine or Carbonyl

1. Torocheshnikov, V., Rentsch, D. and von Philipsborn, W., *Magn. Reson. Chem.* 1994, 32, 348.
2. Rentsch, D., Torocheshnikov, V. and von Philipsborn, W., *Magn. Reson. Chem.* 1996, submitted.
3. Olivieri, A.C., *J. Magn. Reson.* 1989, 81, 201.

44

Chimie minérale et de coordination

^{13}C AND ^{15}N NMR MECHANISTIC STUDY OF CYANIDE EXCHANGE ON OXOTETRACYANOMETALATE COMPLEXES OF W(IV), Mo(IV), Re(V), Tc(V), AND Os(VI).

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[2]Department of Chemistry, University of the Orange Free State, Bloemfontein 9300, South Africa.

The substitution and protonation behaviour of the dioxotetracyanometalate complexes of Re(V), Tc(V), W(IV) and Mo(IV) have been extensively investigated the past decade and have recently been reviewed. We have in the course of these investigations selected these oxygen/cyano containing complexes for a systematic study with regard to ligand, water and proton exchange studies. We correlated the oxygen exchange kinetics[1,2] of these complexes with the proton exchange studies to describe the dynamic behaviour of the coordination polyhedron upon protonation, as a function of pH, over a ten order of magnitude range.

Now we report the cyanide exchange on these complexes as well as data for the Os(VI) complex, which is further correlated with the above mentioned dynamics of these cyano systems. In fact, the cyanide exchange rates for the range of dioxotetracyanometalate complexes of W(IV), Mo(IV), Re(V), Tc(V), and Os(VI) shows a trend of M(IV)>M(V)>M(VI), which is in direct agreement with the acid/base behavior of these oxidation states and furthermore, in excellent agreement with the bond length of the oxidation states and with a dissociative activation for the cyanide exchange on these dioxo complexes. However the exchange on the protonated $[MO(H_2O)(CN)_4]^{m-}$ and $[MO(OH)(CN)_4]^{n-}$, as well as the substituted complexes, $[MO(X)(CN)_4]^{n-}$, compared to the dioxo complexes described above, shows a different cyano exchange pattern.

1 Roodt, A.; Leipoldt, J.G.; Helm, L.; Abou-Hamdan, A.; Merbach, A. *Inorg. Chem.* **1995**, *34*, 560.
2 Roodt, A.; Leipoldt, J.G.; Helm, L.; Merbach, A., *Inorg. Chem.* **1994**, *33*, 140.

CHIMIA 50 (1996) Nr. 7/8 (Juli/August)

Anorganische-Koordinations Chemie

45

Cooperative effects during spin-crossover in $[Fe(ptz)_6](BF_4)_2$ (ptz = 1-propyltetrazole) crystals

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Universität Bern
Freiestrasse 3, 3012 Bern

The investigated Fe(II) compound is a spin-crossover system which undergoes an entropy driven thermal spin transition from the low-spin ground state ($^1A_1$) at cryogenic temperatures, to the high-spin state ($^5T_2$) above the temperature of 100 K. The volume of the crystal changes by 26 $Å^3$ per molecular unit during the spin-crossover. This substantial volume change induces cooperative effects of elastic origin, which in turn affect the thermal spin transition and the high-spin ⇆ low-spin relaxation.

In order to understand the cooperativity we investigated the equilibrium and the kinetics of the spin-crossover compound $[Fe(ptz)_6](BF_4)_2$ as a function of pressure and temperature. A hydrostatic He-gas pressure up to 1000 bar was applied to a single crystal of the title compound. The low-spin state, which is of smaller volume, is stabilised by the external pressure. The effect of external pressure can be related to the cooperativity.

Spin-crossover systems are potential data storage materials, and understanding the cooperativity is therefore also of practical interest.

Chimie minérale et de coordination

46

High-Pressure Kinetic Studies of cation-binding to Na^+/K^+-ATPase

P. Bugnon[a], E. Schick[b], M. Doludda[b], E. Grell[b], A. E. Merbach[a]
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[b] Max-Planck-Institut für Biophysik, Kennedyallee 70, D-60596 Frankfurt a.M., Germany

Developments in the field of membrane biochemistry have allowed the investigation of alkali ion binding to proteins that are involved in relevant biochemical processes. Because of the large fluorescence intensity changes observed on the labelled FITC-(Na^+/K^+-ATPase) upon cation binding[1], the kinetics of these reactions can be studied with the use of the stopped-flow technique. As kinetic studies performed at variable pressure provide information about volume changes occurring during a reaction, experiments were performed with a high-pressure stopped-flow fluorometer recently conceived and constructed in our laboratory[2].

The binding of cation K^+ to the FITC-enzyme has been studied in detail. The dependence of the observed rate constant as a function of the total KCl concentration exhibits sigmoidal behaviour. Kinetic studies have been performed up to 100 MPa which allowed the determination of activation volumes of the reaction steps involved. This has in turn led to the build up of a complete volume profile. The results provide clear evidence for the differentiation between fast cation binding steps and a subsequent, slow rearrangement process, characterised by large positive volumes of activation, attributed to a conformational transition of the enzyme leading to the occluded state $E2(K^+)_2$.

1 M. Doludda, E. Lewitzki, H. Ruf, E. Grell, *The Sodium Pump*, E. Bamberg and W. Schoner eds, Steinkopff, Darmstadt, 1994, 629-632.
2. P. Bugnon, G. Laurenczy, Y. Ducommun, P.-Y. Sauvageat, A.E. Merbach, R. Ith, R. Tschanz, M. Doludda, R. Bergbauer, E. Grell *Anal. Chem.* accepted for publication (August issue)

Chimie minérale et de coordination

47

Kinetic Studies of Host-Guest Interactions Under High Pressure

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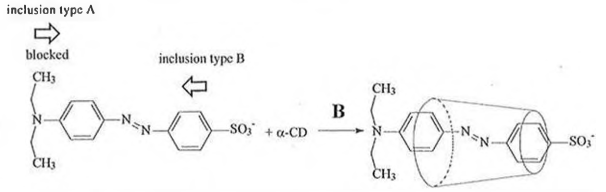
Over the last decade there has been increasing interest in the study of the physical and chemical properties of host-guest systems. The classical guest molecule is cyclodextrin which is well known to have a remarkable receptor capacity[1]. In order to determine the driving force for the inclusion reaction of guest molecules into the cavity of cyclodextrins, we have investigate the dynamic aspect of the interaction between a number of Azo dyes and α-cyclodextrin (α-CD) in aqueous solution. The dyes were selected so as to limit the inclusion into the α-CD cavity from one direction only, as shown below with Ethylorange as the dye. H^1-NMR experiments were initially performed so as to provide evidence for the inclusion of the dyes in the α-CD cavity. Using the stopped-flow technique, we have been able to measure the inclusion reaction at variable temperature and pressure. This has in turn led to the build up of a complete volume profile. The measurements obtained have confirmed the existence of two successive steps in the inclusion reaction[2,3]. A mechanism is proposed where the first step involves the inclusion of the dye into the α-CD cavity followed by a slower second step which may be assigned to a conformational rearrangement of the dye within the cavity.



1 Clarke, A. J.; Coates, J. H.; Lincoln, S. F. *Advances in Carbohydrate Chemistry and Biochemistry,* Academic Press: San Diego, **1988**, Vol 46, 205.
2 Hersey, A.; Robinson, B. H. *J. Chem. Soc. Faraday Trans. I* **1984**, 80, 2039.
3 Seiyama, A.; Yoshida, N.; Fujimoto, M. *Chem. Let.* **1985**, 1013.

Anorganische Chemie / Koordinationschemie

48

Anthracene Bipyridyl Complexes as a Potential Photosensitive Switch

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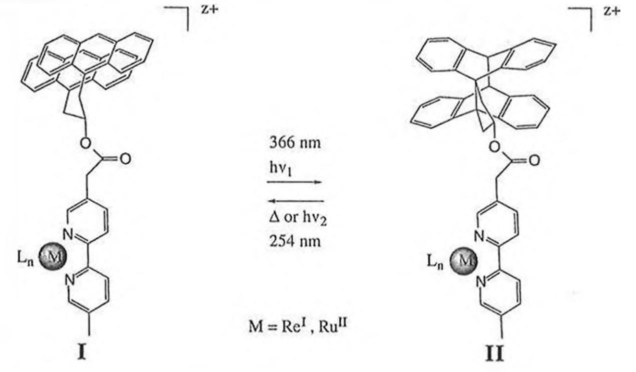
Anthracene derivatives are of photochemical interest because they are able to undergo 4π+4π - cycloaddition with a second anthracene moiety. In the case of bridged anthracenes an intramolecular cyclisation can take place. [1]
From the molecule shown below, we synthesized the rhenium complexes of **I** and **II** and the ruthenium complex of **II**. These represent a possible molecular switch.[2]



In case **I**, there are two anthracene systems able to quench the excited state of the transition metal diimine fragment. In case **II** however, the π system has been severely disrupted, preventing the quenching process. Therefore the typical excited state emission should be observed. Synthetic details and the photophysical properties of these complexes will be discussed.

[1] H.D. Becker, K.A. Amin, *J. Org. Chem.* **1989**, *54*, 3182.
[2] V. Balzani, F. Scandola, *Supramolecular Photochemistry*, Horwood, Chichester **1991**.

Anorganische Chemie **49**

Lokalisierungsmuster im interstitiellen Raum – Eine neue Eigenschaft der Elektronenlokalisierungsfunktion ELF

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Die Strukturbestimmung chemischer Ensembles hat in den letzten 50 Jahren eine ungeheure Entwicklung gezeigt und die Struktur einer Verbindung stellt wohl das wichtigste Modell dar, um Eigenschaften und Reaktivitäten zu verstehen und zu klassifizieren. Die Beugungsmethoden bilden nach überwältigendem Siegeslauf heute festen Bestandteil vieler Struktur-Eigenschaftsbestimmungen. Trotzdem hat auch die Röntgenstrukturbestimmung in bestimmten Fällen mit nicht-trivialen Problemen zu kämpfen, z.B. dann, wenn Überstrukturen oder nicht-kommensurable Strukturen bzw. Zwillingsbildung oder Fehlordnung die sachkundige Anwendung spezieller Verfahren verlangen oder wenn sehr schwache neben starken Streuzentren bestimmt werden müssen. Halbleiterverbindungen wie die Zintlphasen können in der Regel mit einfachen Bindungskonzepten verstanden werden. In einigen Fällen treten jedoch neue ungewöhnliche Anordnungen auf, bei denen nicht a priori klar ist, ob sie tatsächlich existieren oder ob fehlerhafte Strukturbestimmungen ihre Existenz vortäuschen. Andererseits ist das bloße Vorhandensein einer geometrischen Lücke kein sicheres Indiz für ein übersehenes Atom oder Atomgruppe. Der "freie Raum" kann auch von Elektronen beansprucht werden, z.B. durch freie Elektronenpaare, die an Atome gebunden sind, oder relativ freie Elektronen wie in Elektriden, intermetallischen Verbindungen und Metallen.

Wir beschreiben hier die Verwendung der Elektronenlokalisierungsfunktion ELF als eine neue, außerordentlich wirkungsvolle Sonde, die auch bei Problemen der Strukturbestimmung effektiv genutzt werden kann. In der vorliegenden Arbeit soll dargelegt werden, daß man im interstitiellen Raum, also dort, wo eine direkte Zuordnung zu einzelnen Atomen wenig sinnvoll ist, mit Hilfe der ELF Muster erkennen kann, die im vorher genannten Sinne als Lokalisierung von wenig gebundenen Elektronen und unter gewissen Umständen auch als Hilfsmittel zur Bestimmung von Atompositionen verwandt werden können.

Anorganische Chemie - Koordinationschemie **50**

Electrical Conductive Ceramic Composites

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The development of electrical conductive ceramics (ECCs) with an electrical conductivity in the range of metals and with mechanical properties matching the requirements for technical applications is not straightforward: inherent ECCs like transition metal carbides and borides, e.g., TiC, TiB_2, are too brittle or poorly sinterable, resp., and typical engineering ceramics, e.g., Al_2O_3, ZrO_2, Si_3N_4, SiC, are insulators. Promising approaches to ECC materials are:

i) combining insulating engineering ceramics with an electrical conductive part;
ii) doping SiC or SiC-B_4C composites with electron donor or acceptor dopants;
iii) adding reactive additives to poorly sinterable ECCs, e.g., TiB_2;
iv) combining brittle ECCs with ductil metals as binder phase.

We have paid particular attention to processes according to approaches i) and iii). In binary systems consisting of an electrical conductive and an insulating component, electrical conductivity arises when the volume fraction of the conducting phase exceeds the percolation threshold and hence a threedimensional network of conducting phase is formed which allows electrons to percolate through the composite material.

Besides common pressureless sintering, we studied reaction sintering (self-propagating high-temperature synthesis). In order to achieve homogenous dispersed composite phases and high densities, we used highly reactive submicron powders. To control and limit the heat evolution during reaction sintering processes causing formation of porosity and exaggerate grain growth, blends of reactive powders were diluted in various amounts of pre-reacted powders of the final composite phases.

Furthermore, both the densification processes and the resulting ceramic materials were characterized by different methods such as thermal analysis, dilatometry, optical and electron microscopy, X-ray powder diffractometry, and electron microprobe analysis. By established procedures the mechanical behaviour and the electrical properties of the prepared specimens were investigated and are discussed with respect to microstructure, phase distribution, phase composition with special consideration of the nature and properties of the interfaces.

For financial support we are grateful to the *Commission for Technology and Innovation* (CTI project No 2945.1).

Chimie Inorganic **51**

Study of Spin-Spin Interaction in Polyelectrolyte and Surface Systems using the Spin Labeling Method.

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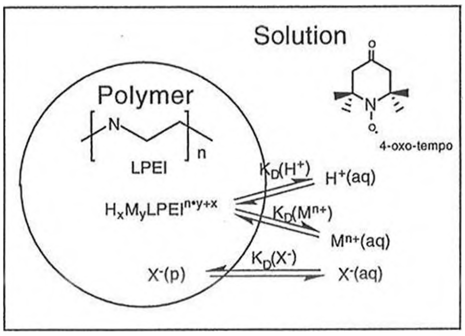
We've analyzed the complexation of the polyelectrolyte, linear polyethylenimin, with transition metal ions, Ni^{2+} and Cu^{2+}, using the spin probe - spin label method [1]. In acid solution we observe line broadening by Heisenberg exchange interaction between the free transition metal ion and the spin label. In basic solution the metal ions are bound to the polyamine and consequently the interaction with the spin label is weaker. This clearly indicates the micro heterogeneous character of these solutions. The method yields also information on the distribution of the metals ions.



Similar measurements with different spin labels, partially carrying a charge, to show the distribution of the metal ions between solution and SiO_2 are in progress.

[1] Spin Labeling , Vol. 1 and 2, Berliner L.J., Academic Press Inc.,1976

Anorganische Chemie - Koordinationschemie **52**

Ba_2ErCl_7 - a New and Efficient Upconversion Material

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The interest in materials showing resonant near infrared (NIR) to visible upconversion (UC) is mainly directed toward a development of compact solid state lasers emitting in the green to near UV range, being pumped by NIR laser diodes. Most of the UC lasers implemented so far are based on rare earth doped oxides or fluorides. Recently, progress was achieved in the case of ternary chlorides and bromides (e.g. $Cs_3Er_2Cl_9$ [1]), showing lower phonon energies (less efficient multiphonon relaxation) and therefore enhanced UC efficiencies. Such compounds should thus bring laser action within easier reach. However, the use of most known rare earth containing chlorides and bromides in laser experiments is complicated by their sensitivity to moisture. A systematic search for stable and efficient UC materials yielded Ba_2ErCl_7 and $Ba_2Y_{1-x}Er_xCl_7$ showing both bright UC luminescence and reasonable stability in air [2].

Luminescence spectra of Ba_2ErCl_7 (300 K) at 803 nm excitation showed that the emission in the yellowish-green (550 nm) is nearly one to three orders of magnitude more intense than measured for other known Er^{3+}-containing materials ($Cs_3Er_2Cl_9$, BaY_2F_8:Er, $LiYF_4$:Er etc.). In addition to this greenish emission, an intense multiplet at 385 nm was observed. Upon excitation at 980 nm, the emitted light consisted of many lines distributed over the whole visible range. Particularly, the contributions of the turquoise (490 nm) and blue (450 nm) emissions are more intense than observed for other materials.

Single crystals were obtained by Czochralski pulling under N_2 atmosphere. A structure determination [3] showed Er^{3+} ions surrounded by 7 Cl^- forming monocapped trigonal prisms, having C_1 point symmetry and being isolated by an Er-Er distance of 648 pm.

Summing up, Ba_2ErCl_7 and solid solutions of $Ba_2Y_{1-x}Er_xCl_7$ represent new and most efficient UC materials exhibiting only a moderate sensitivity to moisture when compared to konwn UC materials.

[1] M. P. Hehlen, K. Krämer, H. U. Güdel, R. A. McFarlane, R. N. Schwartz, *Phys. Rev. B.* **1994**, *49*, 12475.
[2] Ph. Egger, P. Rogin, T. Riedener, H. U. Güdel, M. S. Wickleder, J. Hulliger, *Adv. Mater.* **1996** (in press).
[3] M. S. Wickleder, Ph. Egger, T. Riedener, N. Furer, H. U. Güdel, J. Hulliger, *Chem. Mater.* (submitted).

Anorganische Chemie

53

Templatextraktionen an MCM-41, einem mesoporösen Molekularsieb und ihr Einfluss auf die Struktur

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Eidgenössische Technische Hochschule, 8092 Zürich

MCM-41 ist ein zeolithähnliches Molekularsieb mit Poren von 25-30 Å Durchmesser. Da diese Poren viel grösser sind als die üblichen Zeolithporen (5.5 bis 7.5 Å), eignet sich MCM-41 zur Umsetzung grosser Moleküle.

Bedingt durch die Synthese enthält getrocknetes MCM-41 noch 40-50 % Gewichtsprozente organisches Templat. Dieses wird üblicherweise durch Kalzinieren bei 540°C entfent.

Bis 2/3 des Templats können aber auch duch Extraktionen in ethanolischen Lösungen entfernt werden. Die verbleibende Menge an Templat muss durch Kalzinierung entfernt werden. Am effizientesten sind Extraktionsmittel, die 0.1 molare Säuren oder Salze enthalten. Man findet kaum Unterschiede in der entfernten Templatmenge zwischen Schwefel- bzw. Essigsäure oder Ammonium- resp. Natriumnitrat als Extraktionshilfsmittel. Die Kationen kompensieren einerseits als Ersatz für das kationische Templat die negativen Gerüstladungen, andererseits wird in saurem Medium ein Teil der Silanolgruppen an der Oberfläche vorkondensiert.

Die Silanolgruppen können sowohl mit ^{28}Si-MAS-NMR, als auch mit ^{1}H-MAS-NMR der dehydratisierten Proben gemessen werden. Ca. 45% der Siliziumatome tragen eine Hydroxylgruppe. Dies hängt mit der grossen Oberfläche (um 1000 m^2/g) von MCM-41 zusammen.

Es hat sich gezeigt, dass durch die Säurebehandlung die Aktivität der Katalysatoren für die Acetylierung von 2-Methoxynaphthalin nicht verändert wird. Die Katalysatoren wurden nach der Reaktion mittels Stickstoffadsorption untersucht: Die extrahierten Proben behalten ihre Porenstruktur und somit auch das Porenvolumen, während die Poren der Vergleichsproben, die durch Ionenaustausch erhalten wurden, fast zusammengebrochen waren.

Durch eine Extraktion in saurer, ethanolischer Lösung kann somit ein Teil des Templats mild entfernt, ein Grossteil der anderen Kationen entfernt und gleichzeitig das Gerüst durch Kondensation eines Teils der Silanolgruppen stabilisiert werden. Die so erhaltenen Katalysatoren sind thermisch deutlich stabiler als die durch Kalzinierung und Ionentausch erhaltenen Materialien.

Anorganische Chemie

55

Structures and Dynamics of Transition Metal Hydrides. A Theoretical Study of Isomers of [Fe(PR$_3$)$_4$H$_3$]$^+$ (R=H, Me).

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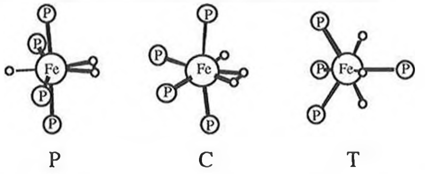
For [Fe(PR$_3$)$_4$H$_3$]$^+$, different isomers are experimentally known, which include nonclassical dihydrogen complexes, having the H and the H$_2$ ligands in cis or trans-position, respectively, (C and P type structures), as well as a classical trihydride complex (T-type structure).



The corresponding isomers of the title compounds have been subjected to a computational study, which was based on Density Functional Theory. It turns out that for this particular molecules PH$_3$ is not a satisfying model for the PMe$_3$ ligand. Although the optimized structures are similar for the isomers of [Fe(PH$_3$)$_4$H$_3$]$^+$, **1**, and [Fe(PMe$_3$)$_4$H$_3$]$^+$, **2**, significant differences for the stability of the various structures are obtained. For **1**, one finds in terms of stability C ≈ P << T, whereas for **2**, one has T < C < P. A rational is provided for these trends. The results are discussed in connection with the experimental findings for [Fe(PMe$_3$)$_4$H$_3$]$^+$. Further, we comment on possible mechanisms for isomerisation reactions as well as H exchange.

Anorganische Chemie

54

Structure and Electronic Description of a Novel Zintl–Phase:K$_6$Bi$_2$Sn$_{23}$

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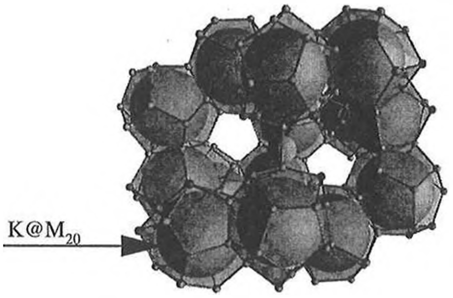
K$_6$Bi$_2$Sn$_{23}$ crystallizes in a recently discovered Clathrate–structure[1,2] in the space group P4$_3$32 (cubic, a=16.277Å, V=4312 Å^3) containing pentagonal dodecahedra of Sn and Bi as building blocks. The M$_{20}$–unit (M=Sn,Bi) consists of 4 three bonded (3b) and 16 four bonded (4b) atoms leading to a distortion of the dodecahedra. Each building block has an exo–bond and shares three faces with surrounding dodecahedra generating a chiral structure. Structure refinement leads to full occupancy of all 4b–positions with Sn and mixed occupancy of the 3b–positions with Sn/Bi. Thus the structure can be described using the Zintl–Klemm–concept: (K$^+$)$_6$(4b–Sn)$_{19}$(3b–Sn$^-$)$_4$(3b–Bi$^-$)$_2$. Here the structural and electronic properties (ELF[3], Partial Electron Density[4]) are discussed.



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[1] Kröner R., Doctoral Dissertation, University of Stuttgart, **1989**
[2] Zhao J.T., Corbett J.D., Inorg.Chem. *33*, 5721, **1994**
[3] Becke A.D., Edgecombe K.E., J.Chem.Phys. *92*, 5397, **1990**
[4] Fässler T.F., Häussermann U., Nesper R., Chem.Eur.J. 9, *1*, **1995**

56

Coordination Chemistry

Comparison of Mononuclear [ML$_3$]$^{n+}$ Complexes and Dinuclear Triple Helices [M$_2$L$_3$]$^{2n+}$

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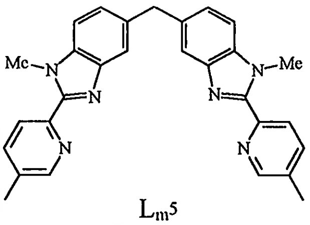
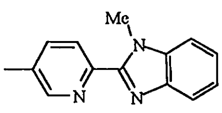
[b] University of Lausanne, BCH, CH-1015 Lausanne.

In order to understand the intrinsic properties of dinuclear triple helical complexes, we have attempted a systematic comparison of some of the properties of these complexes with those of their mononuclear analogues.



L$_m$5



ℓ$_m$5

The racemization process of the triple helix (-)$_{589}$-[Co$_2$(L$_m$^{5})$_3$]$^{4+}$ was found to be very slow ($k_{(298)}$=1.4(2)×10^{-5} s^{-1}). A ^{1}H-NMR study of *fac* ↔ *mer* exchange process in the mononuclear analogue [Co(ℓ$_m$^{5})$_3$]$^{2+}$ at variable temperature and pressure, showed the exchange to take place within the normal kinetic region for octahedral Co(II) complexes ($k_{f\to m(298)}$ = 8.0(6) s^{-1}), excluding a possible kinetic stabilization of the triple helix due to a particular ligand field.

Magnetic measurements on the triple helix [Fe$_2$(L$_m$^{5})$_3$]$^{4+}$ indicate a stabilization of the low-spin form compared to the mononuclear [Fe(ℓ$_m$^{5})$_3$]$^{2+}$ (ΔT_c = 113 K). It is thought that a destabilisation of the trigonal prismatic transition state is responsible for this particular behaviour.

57

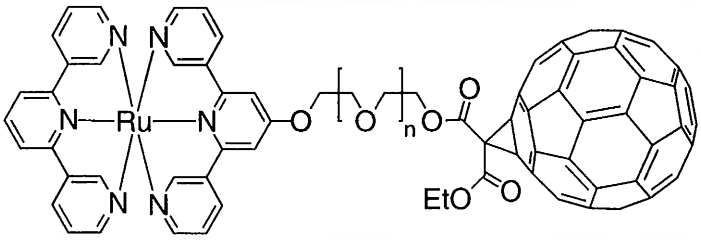
Anorganische Chemie

Cluster functionalised ligands

Dominique Armspach, Marco Cattalini, Edwin C. Constable, Catherine E. Housecroft, Jean-François Nierengarten and Alain Schneider.

Institut für Anorganische Chemie, Spitalstrasse 51, CH-4056 Basel and Laboratorium für Organische Chemie, ETH-Zentrum, Universitätstrasse 16 CH-8092 Zürich

A variety of oligopyridine ligands incorporating pendant cluster functionality will be presented. Clusters of ineterst include fullerenes, carboranes and platinum group metal carbonyl clusters.



58

Anorganische Chemie

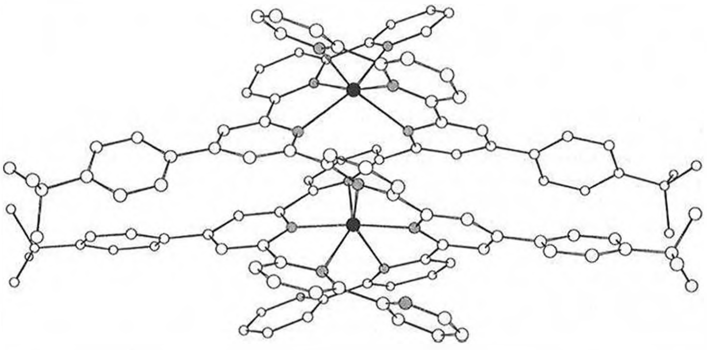
New developments in helication

Edwin C. Constable, Torsten Kulke, Markus Neuburger, Diane R. Smith, Louise Whall and Margareta Zehnder

Institut für Anorganische Chemie, Spitalstrasse 51, CH-4056 Basel

New oligopyridine-based systems for the designed construction of multiple-helical structures will be presented. In particular, approaches to linked multiple helicates will be demondtrated together with studies on the coordination behaviour of the higher (n > 6) oligopyridines will be presented. Control of chirality in helicate formation will also be addressed.

The figure below shows a directional helicate formed with a septipyridine.



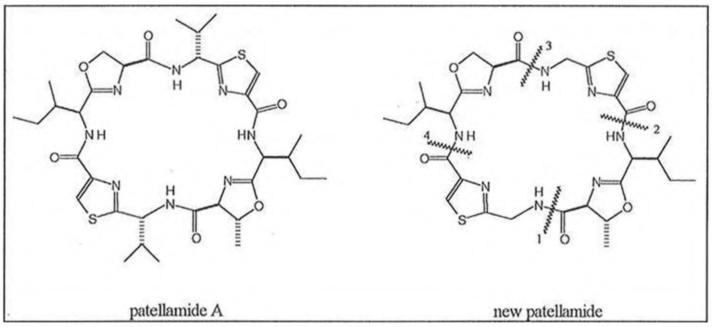
59

Anorganische Chemie

Transition Metal Complexes of Cyclic Octapeptides

Peter Comba, Anne Ramlow, Uli Kazmaier

Anorganisch-Chemisches Institut der Universität,
Im Neuenheimer Feld 270, 69120 Heidelberg, Germany



patellamide A

new patellamide

Patellamides are cyclic octapeptides which are found in marine animals, such as the ascidiacea, and can accumulate certain metal ions. We report the synthesis and analysis of a slightly simplified patellamide (see picture) and its transition metal complexes. The solution structures of patellamides coordinated to transition metal ions are to be determined using molecular mechanics calculations, with the help of spectroscopic characteristics (NMR, EPR). A comparison with known (crystal) structures of naturally occuring patellamides and their transition metal complexes should help to explain conformational changes due to altered amino acid sequences.

60

Anorganische Chemie

Modelling of tetracoordinated complexes

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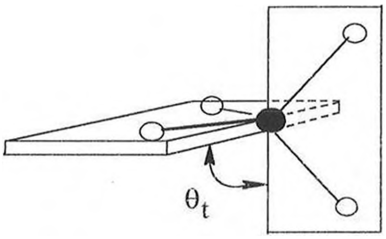

Due to partly unoccupied d-orbitals most tetracoordinated complexes of transition metal ions adopt a square planar or distorted square planar geometry. In the past this electronic effect has been accounted for by using either a valence angle or an out of plane function. We model this effect with a tetrahedral twist potential energy function. This method offers serveral advantages. The application of constraints in a full matrix Newton-Raphson minimizer may be used to compute an energy surface around the tetrahedral twist. Metal-donor distances depend on the tetrahedral twist θ_t. Therefore, force constants and strain free distances are adjusted based on the calculated twist.

CHIMIA 50 (1996) Nr. 7/8 (Juli/August)

Anorganische Chemie

61

Pulse Radiolysis of Peroxynitrite

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To understand the redox behaviour of peroxynitrite, we studied one-electron transfer reactions by pulse radiolysis. Under our experimental conditions (N_2O sat., pH > 11) radiolysis produces mainly $^{\bullet}OH$ and $O^{\bullet -}$. The kinetics are studied by UV/VIS spectroscopy in the time range of 1 µs up to 400 µs.

Irradiated solutions of 0.1 - 0.7 mM peroxynitrite show no simple kinetic behaviour. Several processes can be distinguished at wavelengths between 255 and 520 nm: For 287 nm $< \lambda <$ 330 nm a very rapid decay of peroxynitrite was detected. After 2 µs the absorption remains stable. Between 370 nm and 520 nm a rapid build up of a strongly absorbing species "X" with a lifetime of $\tau \approx 30$ µs and $\lambda_{max} \approx$ 430 nm was observed.

We could not detect $O_2^{\bullet -}$ as a product, nor did addition of nitrite affect the shape of the traces, except for an absorption offset which is due to the formation of $NO_2^{\bullet}$. This suggests that $ONOO^{\bullet}$ is produced in the reaction chain and that neither $O_2^{\bullet -}$ nor $NO_2^{\bullet}$ are precursors of "X". As the production of "X" is about as fast as the decay of peroxynitrite, "X" could be the direct product of the reaction $^{\bullet}OH + ONOO^-$.

The formation of $ONOO^{\bullet}$ would be analogous to that of $HOO^{\bullet}$ from HOO^- even though it usually prefers addition reactions to electron transfer reactions. In that case one would have expected as products either $NO_2^{\bullet}$ and HO_2^- or NO_2^- and $HO_2^{\bullet}$. Our finding stresses the peroxide character of peroxynitrite.

Anorganische Chemie

62

Peroxynitrite Reactions

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Nitrogen monoxide is the source of biogenerated peroxynitrite. Its important role in NO metabolism led to an investigation of the fundamental chemistry of this anion and its conjugate acid.

The synthesis of the starting material was carried out with solid KO_2 and NO gas. After dissolution in 0.01 M KOH, H_2O_2 from residual KO_2 was destroyed with MnO_2. Samples were analyzed for peroxynitrite and nitrite with UV spectrometry. Kinetic experiments were carried out with the stopped-flow technique.

Peroxynitrite is unstable in aqueous solution. Most of it isomerizes to nitrate in a pH dependent reaction:

$$ONOO^- + H^+ \rightleftharpoons ONOOH \longrightarrow H^+ + NO_3^-$$

The pK_a of peroxynitrite, which is about 7, is derived from the decay kinetics and somewhat controversial. We found that the experimental pK_a depends on the type and the concentration of the buffer. Lewis acid buffer components like boric acid accelerate the reaction, which leads to a higher pK_a. The same effect occurs with high concentrations of proton donating particles like $H_2PO_4^-$. The Lewis acids probably promote the isomerization by direct interaction. The proton donors might transfer the H^+ directly instead via dissociation at pH values around 7, where free protons and hydroxyl ions are balanced at low concentrations.

The isomerization reaction is usually described as a first-order process, because the protonation equilibrium is fast compared to the decomposition of the acid. Surprisingly, we found that it is clearly inhibited at concentrations above 200 µM and pH values around the pK_a. Below 100 µM, it approaches the expected behavior. Because of the concentration dependence of this effect, it must be a bimolecular reaction. We are investigating if this a reaction between peroxynitrous acid and peroxynitrite or nitrite, which is an inevitable contaminant.

Despite its simple structure, the chemistry of peroxynitrite turns out to be complex, especially at physiological pH values, and is worth further studies.

Anorganische-Koordinations Chemie

63

Highly Active Sol-Gel Derived Catalysts for the Synthesis of *N,N*-Dimethylformamide from Supercritical Carbon Dioxide

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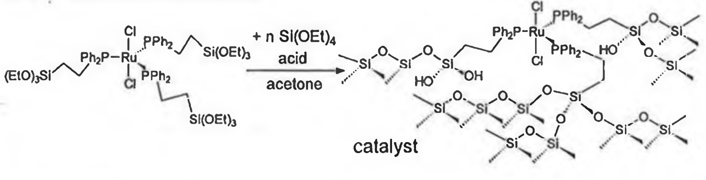
Laboratorium für Technische Chemie, ETH-Zentrum, 8092 Zürich

An advantageous heterogeneous catalytic route for the synthesis of DMF from CO_2, H_2 and dimethylamine under supercritical conditions, employing silica matrix stabilized transition metal complexes as catalysts, is reported.

$$CO_2 + H_2 + Me_2NH \rightarrow Me_2NC(O)H + H_2O$$

Group(VIII)-metal complexes of the type MCl_2X_2 (M = Pt, Pd), $MClX_3$ (M = Rh, Ir) and $RuCl_2X/Y_3$ with the silylether phosphine ligands X = $Ph_2P(CH_2)_2Si(OEt)_3$ and Y = $Me_2P(CH_2)_2Si(OEt)_3$ were co-polymerized with $Si(OEt)_4$ under sol-gel conditions to hybrid materials, in which the metal complexes are stabilized. Undestructed incorporation was confirmed by ^{31}P CP/MAS NMR. ^{29}Si solid state NMR techniques provided quantification of the silylspecies, condensed in different degrees. A typical gel consists of 55% Q^4 $\{Si(OSi)_4\}$, 30% Q^3 $\{(HO)Si(OSi)_3\}$, 2.7% Q^2 $\{(HO)_2Si(OSi)_2\}$, 6.4% T^3 $\{RSi(OSi)_3\}$, 4.8% T^2 $\{R(HO)Si(OSi)\}$ and 1.8% T^1 $\{R(HO)_2SiOSi\}$ species, indicating that a great proportion of the gel is uncondensed, giving rise to highly disordered structures.



These hybrid materials proved to be highly active for the heterogeneous catalytic hydrogenation of $scCO_2$ in the presence of dimethylamine, affording DMF in high yields and 100% selectivity. The ruthenium containing catalysts exhibited the highest activities, reaching turnover frequencies (TOF) up to 1800 h^{-1}, which is more than 600 times higher than the highest TOF reported so far for the heterogeneous catalytic synthesis of DMF.

Inorganic and Coordination Chemistry

64

High Resolution Optical Spectroscopy of [Re(CO)4(thpy)] (thpy⁻ = 2-(2-thienyl)pyridine)

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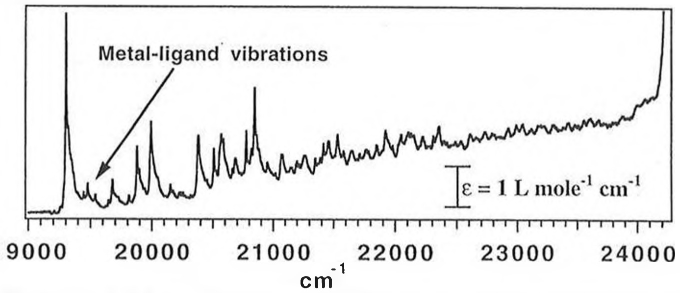
Freiestrasse 3, 3000 Bern 9

The new cyclometalated $5d^6$ complex [Re(CO)4(thpy)] was synthesised. Its single crystal absorption spectrum and the luminescence line narrowed spectrum of a PMMA glass reveal a lot of fine structure at cryogenic temperatures. The sidebands are mostly due to ligand vibrations. The first excited state is assigned to a ^{3}LC state (LC = ligand centered π-π^*).

The occurence of metal-ligand vibrational side bands in the absorption and luminescence spectra and the short luminescence lifetime of 258 ± 5 µsec at 20 K indicate that the higher lying ^{1}MLCT state is mixed into the ^{3}LC state by spin-orbit coupling.



Single crystal absorption spectrum of the lowest-energy excitation at 10 K

Anorganische-Koordinations Chemie **65**

Design of a Ten Electron-Donor Ligand Which Forces Pyramidalization of Coordinatively Unsaturated Two Legged Piano Stool Complexes

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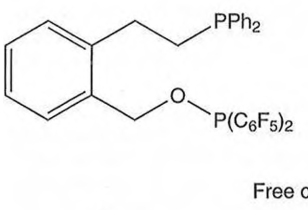
University of Berne, Freiestrasse 3, CH-3012 Berne, Switzerland

Recently, organometallic compounds with a d^6 electron count have been used as Lewis acid catalysts in C-C bond forming reactions.$^{1-3}$ Three legged piano stool complexes can be chiral at the metal and in many cases can be resolved.^{2} But, we have shown, theoretically that 16e$^-$ piano stool complexes are **not** configurationally stable. Therefore, we designed a 10e$^-$ donor ligand **1** which enforces pyramidalization of a coordinatively unsaturated two legged piano stool complex **2**.

With this new ligand, we want to focus on the role of the chirality at the metal and the *electronic asymmetry* in enantioselective catalysis.



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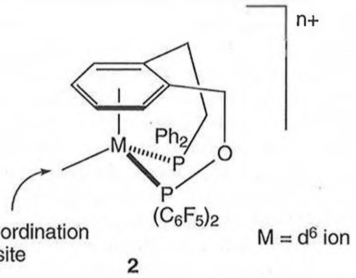

Free coordination site

M = d^6 ion

2

1) Kündig, E.P.; Bourdin, B.; Bernardinelli, G. *Angew. Chem. Int. Ed. Engl.* **1994**, *33*,, 1856.
2) Faller, J.W.; Mazzieri, M.R.; Nguyen, J.T.; Parr, J.; Tokunaga, M. *Appl. Chem.* **1994**, *66*, 1463.
3) Wang, Y.; Gladysz, J.A. *J. Org. Chem.* **1995**, *60*, 903.

66

Chimie minérale et de coordination

Metal-assisted electrophilic transformations of the meso-octaalkylporphyrinogen skeleton

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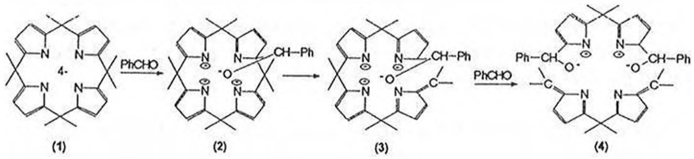
The metal-assisted transformation of macrocyclic structures is a rare event, expecially in the porphyrinogen-porphyrin series, where modifications or transformations of the skeleton are usually involved multistep time-consuming strategies.

However oxophilic metals like Titanium and Zirconium bonded to meso-octaalkylporphyrinogen, can be used to derivatise and transform the porphyrinogen ligand in reactions with electrophiles (PhCHO, PhN$_2^+$X$^-$ etc) and also to shed light on the metal-assisted reactivity of the porphyrinogen skeleton.

In the following scheme we illustrate the porphyrinogen modifications and transformations assisted by IV group metals:



Modified and transformed porphyrinogens (**2**, **3** and **4**) have been isolated as metal complexes and structurally characterized.

The reaction mechanism of the reaction with PhCHO along with other electrophilic induced transformations of the porphyrinogen skeleton will be presented.

Chimie minérale et de coordination **67**

Shaping the cavity of calix[4]arene using transition metals and binding alkali cations inside the cavity: the relevance of the alkali cation interactions

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So far the complexation of alkali cations by calixarenes has been almost always achieved through the functionalisation of the *lower rim*. Here we report the synthesis and the structural characterisation of some new calix[4]arenes niobium complexes capable of binding alkali cations inside the cavity (the *upper rim* of the calixarene). This work has achieved two major goals:

1. to control the *electronic properties and the shape of the cavity* of the transition metal calix[4]arene complexes through the coordination of an appropriate guest inside the cavity;

2. to build species able to act as *alkali cations carriers* in an hydrophobic environment.

The starting material, [CalNbCl]$_2$, is ready prepared by reacting *p-tert*-butylcalix[4]arene (CalH$_4$) with NbCl$_5$ in toluene. Subsequent addition of two equivalents of sodium phenoxide in either a coordinating (THF) or non-coordinating (benzene) solvent gives respectively CalNb(OPh)$_2$Na(THF)$_2$ and CalNb(OPh)$_2$Na, compounds soluble in hydrocarbons. The X-ray analysis revealed the presence of significant cation-arene interactions between the sodium inside the cavity and one of the aromatic rings of the *upper rim* (η^6 coordination). The compound CalNb(OPh)$_2$Na can be regarded as a new and interesting example of *bare* alkali cation interacting with a π basic cavity.

Chimie minérale et de coordination **68**

CARBONYL SITE EXCHANGE IN THE CLUSTER [Ir$_3$Ru(CO)$_{12}$]$^-$

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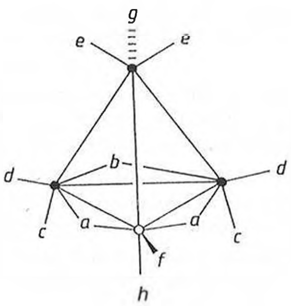
Institut de Chimie Minérale et Analytique, Université de Lausanne
BCH Dorigny, 1015 Lausanne

The intramolecular processes responsible for carbonyl site exchanges in Ir$_4$(CO)$_{12}$ and in mixed tetranuclear M$_x$M'$_{4-x}$ (CO)$_{12}$ (M,M'= Ir, Rh, Co) derivatives have been examined in the last few years.

In the present study the intramolecular rearrangements in PPN$^+$[Ir$_3$Ru(CO)$_{12}$]$^-$ (PPN$^+$= bis(triphenylphosphoranylidene) ammonium) (**1**) have been investigated using 1D and 2D ^{13}C NMR. In solution, cluster **1** exists as a single isomer with 3 edge-bridging CO's defining the basal plane containing the Ru atom (*Scheme*).

●= Ir; O= Ru; a,b,c,d,e,f,g,h= CO



Scheme

The exchange matrix derived from an EXSY spectrum at 150 K was used to simulate succesfully the variable temperature ^{13}C NMR spectra (143 K to 208 K). The intramolecular processes causing complete averaging of the CO ligands are the changes of basal face retaining the basal position of the Ru atom. One change of basal face takes place *via* an unbridged intermediate, and dominates at lower temperatures. A second change of face becomes operative on raising the temperature. Its postulated mechanism involves one μ_2-μ_3-μ_2 change in coordination mode of one CO ligand. This complex is the most fluxional species encountered in Ir clusters. The presence of a d^8 atom in the metallic cage does not introduce any restrictions in the site exchanges of the ligands.

Anorganische / Koordinations Chemie **69**

Methane Combustion over Catalysts Prepared by Oxidation of Ternary $Pd_{15}X_{10}Zr_{75}$ (X = Co, Cr, Cu, Mn and Ni) Amorphous Alloys

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Laboratorium für Technische Chemie, ETH Zentrum, CH-8092 Zürich

Catalysts for the combustion of methane have been prepared by controlled oxidation of various ternary amorphous alloys with the composition $X_{10}Pd_{15}Zr_{75}$ (X = Co, Cr, Cu, Mn and Ni). Their behavior was compared with the behavior of a $Pd_{25}Zr_{75}$ amorphous alloy. The chemical and morphological changes occurring during activation were investigated by TA, XRD and BET surface area measurements. The component X had a strong influence on these changes. The thermoanalytical studies revealed drastic differences in the crystallization and oxidation behavior of the alloys. The BET surface areas of the precursor alloys was < 0.1 m^2/g and increased, depending on the component X, to 1.1 - 34.1 m^2/g upon oxidation (activation) of the samples. XRD indicated the presence of PdO and poorly crystalline monoclinic and tetragonal ZrO_2 in all activated samples.

Kinetic studies were carried out in a fixed-bed microreactor at temperatures of 400-1000 K and atmospheric pressure using a reactant mixture with a ratio $CH_4 : O_2 = 1 : 4$. The activity of the activated alloys depended strongly on the component X and decreased in the order *Pd > Ni > Cu > Co > Mn > Cr*. The activity and stability of catalysts derived from $Pd_{25}Zr_{75}$ and $Ni_{10}Pd_{15}Zr_{75}$ were comparable, indicating that the more expensive palladium can be substituted by a certain amount of nickel. Good thermal stability was observed only with these catalysts, whereas the other materials showed strong deactivation at higher temperatures. Comparison with catalytic activities reported in the literature implied that the overall catalytic activity cannot be considered as the sum of the specific activities of palladium oxide and the oxide of the ternary metal component. The importance of the ternary metal (X) seems therefore mainly to reside in its influence on the structural and morphological properties of the final catalyst and less in its intrinsic catalytic activity.

Reduction of the catalysts by hydrogen with subsequent reoxidation of the reduced components by the reaction atmosphere in most cases led to more active catalysts. The reduction results in metallic palladium which is rapidly oxidized in the reacting gas atmosphere, even at room temperature. Thus, enhanced conversion cannot be attributed to metallic palladium.

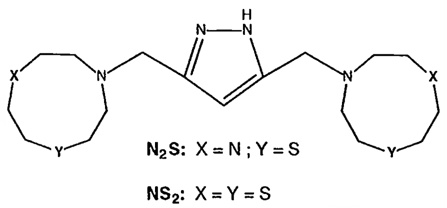
Koordinationschemie **70**

Binuclear Metal Complexes of Bis-Macrocycles with a Pyrazole Bridging Unit

H. Weller and Thomas A. Kaden

Institute of Inorganic Chemistry, Spitalstr. 51, 4056 Basel, Switzerland

Two pyrazole bridged binucleating ligands N_2S and NS_2 were prepared by alkylation of the corresponding macrocycles with 3,5-bis-(chloromethyl)-pyrazole.



N_2S: X = N ; Y = S

NS_2: X = Y = S

The equilibria in solution were studied for N_2S and Cu^{2+} using potentiometric titrations, which were evaluated with the program TITFIT. Besides mononuclear species, binuclear complexes were also identified and their stability was determined. In addition a series of binuclear complexes of N_2S and NS_2 with copper(II) and nickel(II) have been synthesized and characterized (elemental analysis, FAB-MS, IR, X-ray).

The binuclear copper(II) complexes exhibit a pentacoordinate geometry. In contrast the binuclear nickel(II) complexes prefer hexacoordination, which is achieved by binding additional solvent molecules. In all complexes the pyrazole group is deprotonated and bridges the two metal centres.

In case of the copper(II) complexes various exogenous bridging molecules can also be incorporated (for N_2S: pyrazolide, sulfate, azide and for NS_2: chloride, bromide).

Inorganic Chemistry **71**

Linear Poly(ethylenimin) as a model compound for the complexation of Heavy Metals to polyelectrolytes in water. An electrochemical approach.

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Linear Poly(ethylenimin) (LPEI) is a polymeric amine ligand, which interacts with a broad band of metal ions such as Cd, Cu, Ni and other. The metal affinity of the polymer is strongly pH dependent, due to the competition between protonation and complexation. We have investigated the electrochemical behavior of Cd^{2+} in a LPEI solution at different pH, different Cd^{2+} to Nitrogen ratios and with polymers of different chain length. Normal pulse polarography (NPP) and Chronoamperometry (CA) gave an electrochemical response characteristic for surface-aktiv compounds. The results are discussed within the context of the coordination chemistry of Cd^{2+} in these solutions.

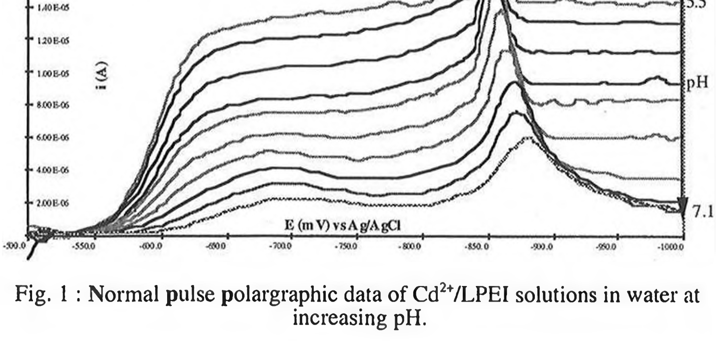

Fig. 1 : Normal pulse polargraphic data of Cd^{2+}/LPEI solutions in water at increasing pH.

Anorganische-Koordinations Chemie **72**

Stability and Structure of the Cu^{2+} Complexes of the Antiviral 9-[2-(Phosphonomethoxy)ethyl]adenine (PMEA) and of Its 1-, 3-, and 7-Deaza Analogues in Aqueous Solution

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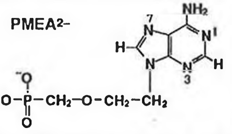
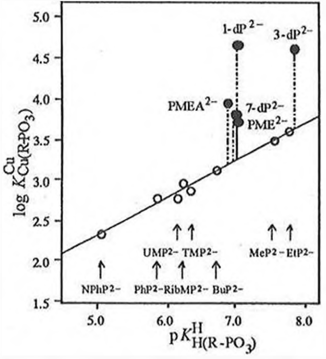
[a] Inst. of Inorg. Chem., University, Spitalstr. 51, CH-4056 Basel, Switzerland
[b] Inst. of Org. Chem. & Biochem., Acad. of Sci., CZ-16610 Prague, Czech Rep.

The biological action of PMEA occurs in metal ion-dependent enzymic systems and therefore we are studying the metal ion-binding properties of $PMEA^{2-}$ [1], as well as of its above mentioned deaza derivatives, abbreviated as 1-dP^{2-}, 3-dP^{2-}, and 7-dP^{2-}. Determination of the stability constants of the various Cu^{2+} complexes via potentiometric pH titrations ($I = 0.1$ M, $NaNO_3$; 25°C) reveals that all of them are more stable than is expected on the basis of the basicity of their -PO_3^{2-} group. This is clearly seen from the data depicted in the Figure. The straight reference line is constructed from the equilibrium data of simple phosphate monoester and phosphonate ligands (R-PO_3^{2-}) [2]. All the data points for the Cu^{2+} complexes of the four PMEAs are significantly above the reference line; however, this is also true for the complex with $PME^{2-} = CH_3CH_2\text{-O-}CH_2\text{-PO}_3^{2-}$. This means that 5-membered chelates form involving the ether O and the PO_3^{2-} group; yet, the stabilities of the Cu^{2+} complexes of the PMEAs are even larger. Consequently, in these cases the nucleobase residue must *in addition* be involved in metal ion binding. For example, for Cu(3-dP) this must take place via N-7 and for Cu(7-dP) via N-3; hence, isomeric equilibria occur and the formation degree of the various species needs to be evaluated.





Supported by the Swiss Nat. Sci. Found., the Swiss Fed. Office for Educ. & Sci. (COST D1), and the Government of the Czech Rep. (COST D1).

[1] H. Sigel, *Coord. Chem. Rev. 144*, 287-319 (1995).
[2] H. Sigel, D. Chen, N. A. Corfù, F. Gregáň, A. Holý & M. Strašák, *Helv. Chim. Acta 75*, 2634-2656 (1992).

CHIMIA *50* (1996) Nr. 7/8 (Juli/August)

73

Chimie minérale et de coordination

Conformations of chelate rings in metal complexes containing bis-(benzimidazol-2-yl) ligands.

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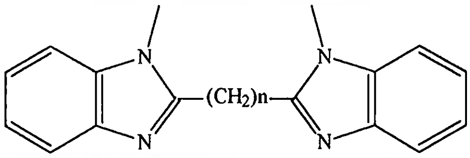
Département de chimie minérale, analytique et appliqué
30 Quai Ernest-Ansermet,
1211 Genève 4.

The conformations of the chelate rings formed upon the reaction of a metal (Cu^{2+}, Co^{2+} and Mn^{2+}) with bis-(benzimidazol-2-yl) ligands shown below:



n = 1 to 3, and R = H, ethyl, 3,5-dimethoxybenzyl

Complexes of the type [M(ligand)Cl_2] were formed when 1 equivalent of ligand was reacted with 1 equivalent of metal chloride salt. Reaction of 2 equivalents of ligand with 1 equivalent of metal perchlorate salt gave generally [M(ligand)$_2$(ClO_4)$_2$] complexes.

The crystal structures of some of these complexes was determined by x-ray diffraction. For n = 2, complexes of the type [M(ligand)Cl_2] (where M = Mn^{2+}, Cu^{2+}) were found to have a tetrahedral coordination geometry about the metal centre. For n = 3, the crystal structure of a [Co(ligand)$_2$](ClO_4)$_2$ complex also showed the cobalt atom to be in a tetrahedral environment. This preference for a tetrahedral arrangement of atoms about the metal centre is explained in terms of the chelate ring coordination.

74

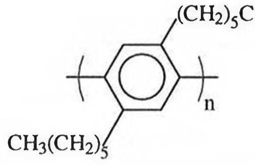
Sektion Anorganische-Koordinations Chemie

Poly(*p*-phenylene)s with flexible side chains on gold and copper surfaces

S. Brunner[1], U.B. Steiner[1], W. Caseri[1], U.W. Suter[1],
G. Hähner[2], N. Spencer[2], M. Rehahn[3]

[1] Institut für Polymere, ETH-Zentrum, 8092 Zürich,
[2] Laboratorium für Oberflächentechnologie, ETH-Zentrum, 8092 Zürich
[3] Polymer-Institut, Universität Karlsruhe, D-76128 Karlsruhe

Low and high molecular weight compounds can coordinate to metal surfaces can upon immersion of metal slides into solutions of organic substances. For example, coordination of olefines and nitriles on copper is evident from IR spectroscopy at grazing incidence reflection [1,2]. Poly(*p*-phenylene)s with various flexible side chains (an example is given below) adsorb from dichloromethane, benzene or toluene on gold and copper. The thickness of the formed layers depends on the nature of the side chains and the substrate. It varies from 1 nm to several 10 nm, determined by ellipsometry. The layers above ca. 3 nm probably consist of organometallic complexes rather than of organic multilayers. In some cases, there is evidence from IR spectroscopy and NEXAFS (near edge X-ray absorption fine structure spectroscopy) that aromaticity is strongly withdrawn, while new signals are detected in spectral regions in which also C=C bonds appear. The results might indicate that η^2- or η^4-coordination of arene moieties may occur on copper surfaces.



[1] U.B. Steiner, W.R. Caseri, U.W. Suter *Langmuir* **8**, 2771 (1992)
[2] U.B. Steiner, W.R. Caseri, U.W. Suter *Langmuir* **9**, 877 (1993)

75

Anorganische Chemie

Loop-directed mutagenesis of the type I blue copper protein amicyanin from *Thiobacillus versutus*

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The type I blue-copper protein amicyanin functions in the methylamine dehydrogenase redox chain of *Thiobacillus versutus*. The copper at the active centre of this protein is coordinated by cysteine and two histidines. The copper is ~0.3 Å out of the plane made by these three residues in the direction of an axial methionine ligand.[1]

Site directed mutagenesis has been extensively used to replace and remove the aminoacid residues responsible for copper ligation.[2] A novel approach that has recently been used is to replace the ligand containing loop of amicyanin with the corresponding sequence from plastocyanin.[3] The variant produced has features distinct from those of wild type amicyanin. All of the spectroscopic studies point towards a shorter bond to the axial methionine in the mutant.

Results aimed at introducing the ligand containing loop of azurin into amicyanin will be presented.

The amino-acid sequences of the C-terminal ligand containing loop of (a) amicyanin (*T. versutus)*, (b) poplar plastocyanin and (c) azurin (*P. aeruginosa):*

(a)	Cys	Thr	-	Pro	-	His	Pro	-	-	Phe	Met
(b)	Cys	Ser	-	Pro	-	His	Gln	Gly	Ala	Gly	Met
(c)	Cys	Thr	Phe	Pro	Gly	His	Pro	-	Ala	Leu	Met

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[1] A. Romero, H. Nar, R. Huber, A. Messerschmidt, A. Kalverda, G.W. Canters, R. Durley, F.S. Mathews, *J.Mol.Biol.*, **1994**, 236, 1196-1211

[2] G.W. Canters, G. Gilardi, *FEBS*, **1993**, 325, 39-48

[3] C. Dennison, E. Vijgenboom, W.R. Hagen, G.W. Canters, *J.Am.Chem.Soc.*, in press

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76

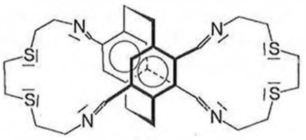
Anorganische Chemie

Dicopper(I) compounds of preorganized double helical bis-dithiadiimine ligands

Peter Comba and Andreas Fath

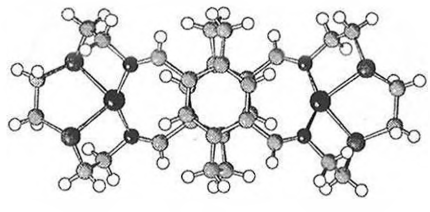
Anorganisch-Chemisches Institut der Universität Heidelberg,
69120 Heidelberg, Germany

A double helical ligand with a (N_2S_2)$_2$ donor set and a paracyclophane anchor group (L_1) was prepared by a new 2+1 Schiff base condenzation reaction. Upon coordination to copper(I) dinuclear double helical complexes are formed ($Cu_2L_1{}^{2+}$).



L_1

Structural, spectroscopic and electrochemical data of $Cu_2L_1{}^{2+}$ will be discussed in comparison to data of similar double helical compounds without the paracyclophane anchor group.



$[Cu_2L_1]^{2+}$

Anorganische Chemie / Koordinationschemie **77**

Chiral Supramolecular Chromium(II) and Copper(II) Oxalate-Bridged Networks with Supressed Jahn-Teller Effect A Structural and Magnetic Study

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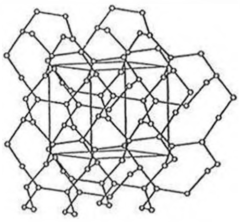
In the search for new molecular-based magnets the oxalate ion $(C_2O_4)^{2-}$ is an attractive building block because its bis-chelating coordinating ability enables it to form an exchange pathway between two metal ions. Several compounds have been reported in which oxalate ions are used to create homo- and heterometallic arrays that are infinite in two (2D) or three (3D) dimensions. Thus, long-range magnetic ordering behavior may occur and consequently, from this molecular class of compounds emerge materials with distinct magnetic properties.

Recently, we reported on extended, chiral 3D framework structures consisting of tris-bipyridyl metal complexes which function as chiral templates for the collective linking of metal ion centers through bis-chelating oxalate bridges.[1] Perceiving that the published structural results of the homometallic 3D compounds for the divalent 3d metals have been confined so far to manganese(II) and iron(II), we attempted to prepare and investigate the analogous compounds with chromium(II) and copper(II).

Both, the high-spin d^4 chromium (II) and d^9 copper (II) systems have in common that their electronic ground states are described by an orbitally degenerate electronic ground state, ^5E_g and ^2E_g (O_h symmetry), thus the ions are subject to the Jahn-Teller effect. Accordingly, a detailed structural analysis will be presented.



[1] S. Decurtins, H.W. Schmalle, R. Pellaux, P. Schneuwly, A. Hauser, *Inorg. Chem.* **1996**, 35, 1451.

Anorganische-Koordinations Chemie **78**

Reversible μ-peroxo and bis-μ-oxo complex formation and interconversion

B. Jung[a)], S. Kaderli[a)], A. Llobet[b)], S. Mahapatra[b)], Y.-M. Neuhold[a)], W. B. Tolman[b)], A. D. Zuberbühler[a)]
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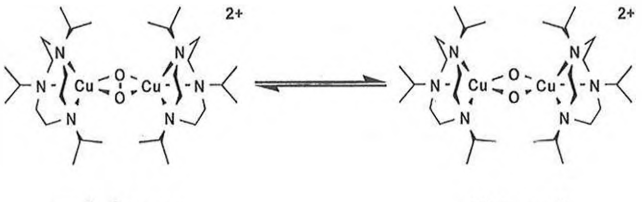
[b)]Department of Chemistry, University of Minnesota, Minneapolis, MN 55455, USA

In a copper complex with substituted 1,4,7-triazacyclononane (TACN), rapid interconversion of binuclear μ-peroxo $[M_2(\mu\text{-}\eta^2{:}\eta^2\text{-}O_2)]^{2+}$ and bis μ-oxo $[M_2(\mu\text{-}O)_2]^{2+}$ species with concomitant O-O bond splitting/formation has been observed for the first time. This may be a key step both in dioxygen evolution during photosynthesis and in dioxygen reduction by various enzymes such as cytochrome-C oxidase or tyrosinase(1).



μ-η^2:η^2 peroxo bis(μ-oxo)

The rapid equilibrium between μ-peroxo and bis-μ-oxo complexes is influenced by the nature of the TACN substituents, solvent and temperature. Low-temperature diode array spectrophotometry was used to study pseudo-reversible adduct formation starting from copper(I) and O_2 and subsequent oxidative degradation. Detailed kinetic analysis shows that initial rate limiting formation of a steady-state superoxo species is followed by a much faster binding of the second copper.

(1) J. A. Halfen, S. Mahapatra, E. C. Wilkinson, S. Kaderli, V. G. Young, L. Que, A. D. Zuberbühler, W. B. Tolman, *Science*, 271 (1996) 1397.

79

Anorganische Chemie

Copper (I) Complexes of Macrocyclic Tetraphosphine and Dithiadiphosphine Ligands

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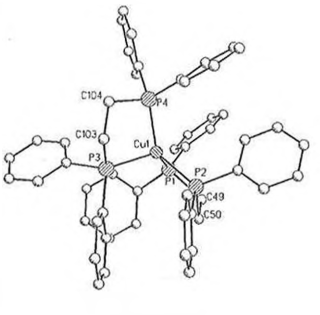
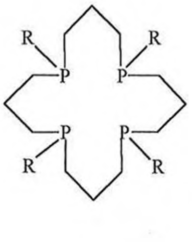
69120 Heidelberg, Germany

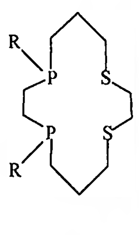
Chelating phosphine ligands stabilize copper(I). Thermodynamic, electrochemical and spectroscopic data of copper(I) compounds with chelating phosphines are correlated to their experimentally determined structural parameters (eg. structure 1).



structure 1



L₁



L₂

The copper(I) compounds of 14- and 16-membered macrocyclic ligands with P_4 and P_2S_2 donor sets (L_1 and L_2) are compared to the corresponding compounds with open-chained ligands. The differences are related to changes in the coordination geometries and donor sets.

Koordinationschemie **80**

Reactivity of Macrocyclic Ni^{II} and Cu^{II} Complexes with Thioether and Ether Side Chains

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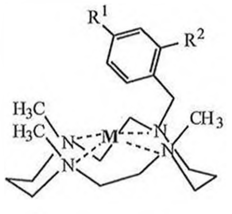
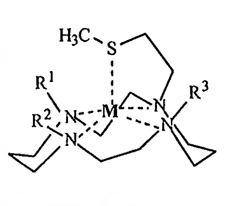
To investigate the role played by cofactor F430 in the production of methane, we prepared a series of macrocyclic Ni^{II} and Cu^{II} complexes and studied their structure and reactivity.
Compounds **1-4** have either a thioether or an ether group in the side chain, which does not bind to M^{2+} (CN=4), whereas compounds **5-7** have a variable number of thiomethyl side chains, one of which coordinates to M^{2+} (CN=5).





1: R^1=SCH$_3$ R^2=H
2: R^1=H R^2=SCH$_3$
3: R^1=OCH$_3$ R^2=H
4: R^1=H R^2=OCH$_3$

5: R^1=R^2=R^3=CH$_3$
6: R^1=(CH$_2$)$_2$-SCH$_3$ R^2=R^3=CH$_3$
7: R^1=R^2=R^3=(CH$_2$)$_2$-SCH$_3$

Cyclic voltammetry shows the reversible Ni^{II}/Ni^{I} pair (-0.7V *vs.* SCE), the cleavage of the thiomethyl group (-2.0V to -2.4V *vs.* SCE) and the formation of the corresponding thiol (+0.7V *vs.* SCE for GCE and 0V *vs.* SCE for HMDE); no similar behaviour could be observed for compounds **3** and **4** since, under similar conditions, no breaking of the O-CH$_3$ bond takes place.
All complexes were reduced with Na/Hg in DMF and the production of methane was monitored by GC: only complex **2** liberates small amounts of methane.

Anorganische Chemie

81

Electrochemical Li^+ Insertion Properties of Lithium Nickel Manganese Oxides Correlated to the Manganese Content and Electrode Porosity

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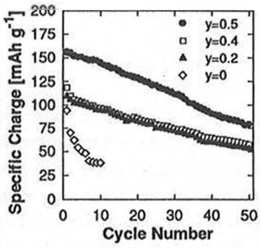
[b]Laboratorium für Anorganische Chemie, ETH-Zentrum, CH-8092 Zürich

As a prospective electroactive material for positive electrodes of rechargeable lithium-ion transfer batteries, a lithium nickel manganese mixed oxide with the orthorhombic α-$NaFeO_2$ structure has been prepared via a new solution technique. A nickel manganese oxide hydroxide precursor was prepared in an oxidative coprecipitation process prior to calcination with LiOH in oxygen. Test electrodes with various porosities containing the oxide and graphite or carbon black as electronically conducting additives were developed and characterized. Then, the electrochemical behavior of the $LiNi_{1-y}Mn_yO_{2+0.5y}$ oxides was investigated for different Mn contents, y.

Porosities of under 20 % were measured for the rather compact oxide/graphite electrodes, with median pore diameters typically between 0.1 and 0.01 µm. In the case of the oxide/carbon black electrodes, larger median pore diameters and porosities of over 40 % were obtained, leading to better wetting properties of the electrode as reflected in the higher specific charge obtained for this electrode. However, a higher cycling stability was achieved with the oxide/graphite electrodes which reflects their better mechanical stability. Therefore, for the comparison of various oxides, the oxide/graphite electrodes were used. Both, the specific charge and the cycling stability of the pure lithium nickel oxide was low but was significantly enhanced by increasing the manganese content, y, in $LiNi_{1-y}Mn_yO_{2+0.5y}$. About 160 mAh g^{-1} were obtained for oxides with a Ni:Mn ratio of about 1:1 using voltammetric measurements at 50 µV s^{-1} in the potential range between 2.5 V and 4.3 V *vs.* Li/Li^+. The specific charge decreased with increasing cycle number as illustrated in the figure.



We thank the Swiss Federal Office of Energy for financial support.

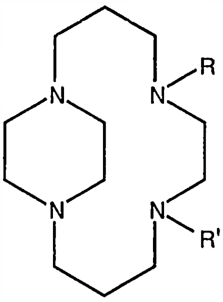
Koordinationschemie

82

Coordination Chemistry of Reinforced Macrocycles

Ralph Kowallick and Thomas A. Kaden
Institute of Inorganic Chemistry, Spitalstr. 51, CH-4056 Basel, Switzerland

The Cu^{2+} and Ni^{2+} complexes of tetraazamacrocycles reinforced by a piperazine ring (**1-3**) have been prepared and their structural properties studied.



1 R = H, R' = CH_3
2 R = R' = CH_3
3 R = R' = C_2H_5

The VIS spectrum of the Ni^{2+} complex with **1** in H_2O is typical for a D_{4h} chromophore. The X-ray study of the Cu^{2+} complexes shows a slightly tetrahedrally distorted square planar geometry around the metal ion for **1** and a square pyramidal coordination arrangement with four N-atoms and a water molecule for **3**. The main difference is that R and R' are *trans* for **1**, but *cis* for **3**.

Interesting is the observation that the complexes with Cu^{2+}, but not those with Ni^{2+}, can additionally bind a N_3^- ion to give pentacoordinate species. This contrast with the observation that in the case of 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane the Ni^{2+} complex is binding N_3^- better than the Cu^{2+} complex.

Anorganische-Koordinationschemie

83

Heterogeneous Coupling of Phenylethyne Catalysed by a Hydroxycarbonate Derived from Cu-Mg-Al-Hydrotalcite

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Substituted 1,4-diphenylbuta-1,3-diynes are an important class of liquid crystals for infrared and long wavelength applications. In this work, a novel route for a heterogeneous coupling of phenylethyne by a Cu-Mg-Al hydrotalcite-derived catalyst, oxygen and sodium hydroxide affords yields > 80 % of 1,4-diphenylbuta-1,3-diyne. These high yields and the simple way of catalyst preparation lead to a reaction system which is able to compete with conventional homogeneous systems.

A Cu-Mg-Al hydrotalcite-derived catalyst with molar ratios Cu:Mg:Al = 1:1:1 was prepared by precipitation of the corresponding nitrates and was calcined under vacuum at 673 K. The calcined catalyst was X-ray amorphous and contained 36 wt% copper. The specific surface area amounted to 72 m^2 g^{-1}, the specific pore volume to 0.52 cm^3 g^{-1}.

The phenylethyne coupling was carried out in an autoclave at 302 – 333 K using an initial oxygen pressure of 1 – 4 MPa. The reaction mixture comprised 2 g phenylethyne, 50 mg calcined catalyst, and 25 ml 0.05 – 0.4 mol l^{-1} dry sodium hydroxide in n-butanol.

Conversion of phenylethyne was found to increase with temperature, concentration of sodium hydroxide and oxygen pressure. The apparent activation energy amounted to 90 kJ mol^{-1}. In the first step of the reaction, phenylethyne is deprotonated by a base. As the intrinsic basicity of the hydrotalcite did not suffice for this alkyne deprotonation, sodium hydroxide was used as a co-catalyst to abstract the hydrogen atom in a preceding equilibrium. In the following reaction steps, phenylethynilide is oxidized to the corresponding radical by copper(II) and couples with a second radical to form 1,4-diphenylbuta-1,3-diyne. The copper(I) formed in this reaction is reoxidized with oxygen closing the catalytic cycle.

The selectivity to 1,4-diphenylbuta-1,3-diyne decreased with increasing temperature or sodium hydroxide concentration due to the higher instability of phenylethyne under these conditions. This instability caused homogeneous and heterogeneous side reactions like the formation of butyl phenylacetate. In contrast, the selectivity was only marginally affected by the oxygen pressure.

Chimie Minérale et de Coordination

84

Complex Formation Kinetics of Nickel(II) with 2,2'-Bipyridine

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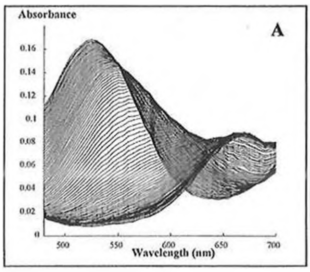
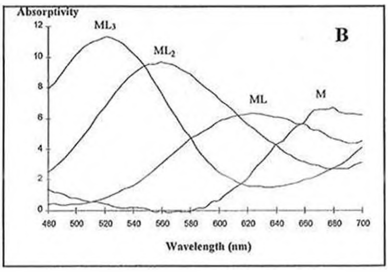
Bâtiment de Chimie (BCH), Ch-1015 Lausanne, Switzerland

Previous studies of Ni(II) reacting with bidentate ligands, such as 2,2'-bipyridine (bpy), have focused on either the formation of only the ML species, under pseudo first order conditions,[1] or the acid hydrolysis of the ML_3 complex.[2,3] We now report the first multi-wavelength kinetic measurements for the step wise addition of bpy to the Ni(II) centre, forming the ML_3 complex. The measurements have been performed in dimethylformamide (DMF) and under stoichiometric conditions (see Figure A). Using global analysis fitting software three distinct rates can be fitted to the measurements.

The calculated spectra of the ML_n species (see Figure B) are in excellent agreement with those previously determined from spectrophotometric titrations of Ni(II) reacting with bpy in DMF.[4] Work is continuing to extend this study to include high pressure kinetic measurements.





1. Bennetto, H. P.; Caldin, E. F. *J. Chem. Soc. (A)*, **1971**, 2191.
2. Kemp, T. J.; Moore, P.; Quick, G. R. *J. Chem. Soc. Dalton Trans.*, **1979**, 1377.
3. Wannowius, K. J.; Krimm, K.; Elias, H. *Inorg. Chim. Acta,* **1987**, 127, L43.
4. Ishiguro, S.; Ozutsumi, K.; Nagy, L.; Ohtaki, H. *J. Chem. Soc. Dalton Trans.*, **1989**, 655.

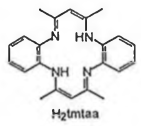
CHIMIA *50* (1996) Nr. 7/8 (Juli/August)

Chimie minérale et de coordination

85

The chemistry of the reduced species of the iron(II) macrocycle dibenzotetramethyltetraaza[14]annulene.

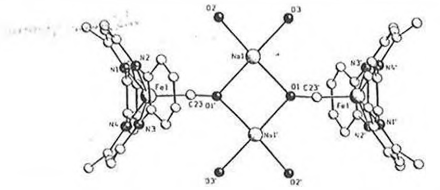
Alain Klose, Euro Solari and Carlo Floriani*, Institut de Chimie Minérale et Analytique, Université de Lausanne, BCH, 1015 Lausanne.



H_2tmtaa

Dibenzotetramethyltetraaza[14]annulene, tmtaaH_2, should be considered as providing an interesting chemical environment for studying the functionalization and the redox chemistry of transition metals.

The well known iron(II) tetraazaannulene can be easily reduced by sodium. This new compound is bifunctionnal and contains, in close proximity, two different reactive sites, namely iron and sodium. The nucleophilic iron shows an interesting reactivity with small molecules and organic functionalities. For example, the reaction with CO results in coordination of the carbon and oxygen to the iron and sodium respectively. Thus a nucleophilic form of CO is created. This compound was isolated and its structure determined by X-Ray analysis. The infrared spectrum consists of a characteristic band at lower frequency than the non-reduced product.



A new synthetic route for alkylation will be presented and involves treating the reduced iron species with different halogenoalkanes.

Anorganische-Koordinations Chemie

86

Pressure effects on the high-spin —> low-spin relaxation in some iron(II) complexes

Sabine Schenker, Andreas Hauser

Institut für anorganische, analytische und physikalische Chemie
Universität Bern, Freiestrasse 3, 3000 Bern 9

Because of the large difference in molecular volume between iron(II) complexes in the high-spin (HS) and the low-spin (LS) state, already moderate external pressures have a strong effect on the HS –> LS relaxation dynamics. For instance in the diluted spin-crossover system $[Zn_{1-x}Fe_x(mepy)_3tren](PF_6)_2$, where the zero-point energy difference between the two states is quite small, an external pressure of 1 kbar accelerates the low-temperature tunnelling process by one order of magnitude. In the LS systems $[M_{1-x}Fe_x(bpy)_3](PF_6)_2$ (M = Cd, Mn, Zn), where the zero-point energy difference is larger, the corresponding increase is only a factor of two.

In some iron(II) compounds a strong lattice dependence of the HS –> LS relaxation process has been noticed. In diluted mixed crystals, where the iron(II) complexes are surrounded by host complexes only, the influence of the host lattice can be understood as either a positive or a negative chemical pressure, which either destabilises or stabilises the HS state relative to the LS state.

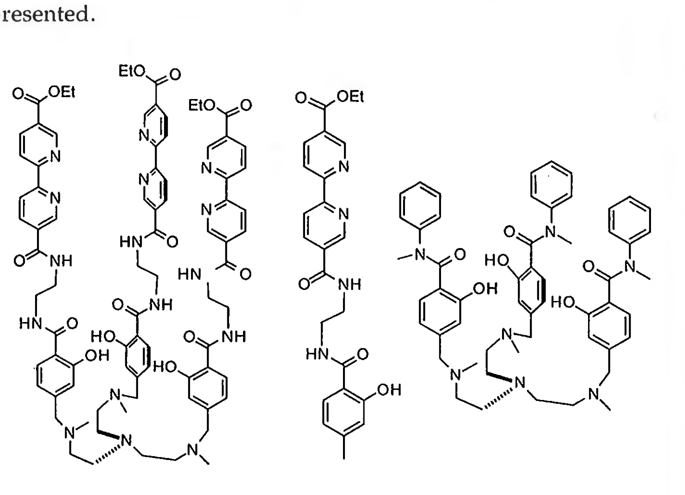
87

Anorganische Chemie/ Koordinationschemie

Synthesis of Salicylamide- and Bipyridine Containing Ligands For Iron(II) And Iron(III) Coordination

Andreas Lutz, Thomas R. Ward* and Martin Albrecht
Chemistry Department, University of Berne, 3000 Berne 9

The synthesis and characterisation of potential iron sequestering agents is reported. Both *single-stranded* ligands incorporating salicylamides for chelation of iron(III) and bipyridines for iron(II) as well as macrocyclic systems (*half-cages*) have been synthesized. Complexation studies with various transition metals will be presented.



Anorganische-Koordinations Chemie

88

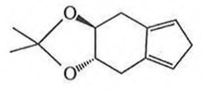
Homo-and Heteroleptic Ferrocenes Derived From C_2-Symmetrical Annulated Cyclopentadienes

Christoph Köllner, John Spencer, Antonio Togni
Laboratory of Inorganic Chemistry, Swiss Federal Institute of Technology, ETH-Zentrum, CH-8092 Zürich, Switzerland

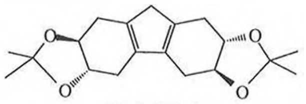
The already described literature preparation[1] of the mono annulated cyclopentadiene derivative, (*S*, *S*)-**1**, was also found to yield the C_2-symmetrical diannulated cyclopentadiene derivative, (*S*, *S*, *S*, *S*)-**2**, which was characterised by an X-ray diffraction study.

The obvious appeal of C_2 symmetry and potential water solubility, by appropriate deprotection and possible derivatisation of the resulting diol functions prompted us to employ (*S*, *S*)-**1** and (*S*, *S*, *S*, *S*)-**2** as precursors for the preparation of chiral ferrocenes.

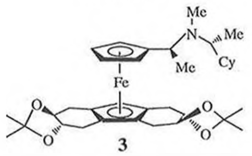
With the novel stereoselective route to heteroleptic ferrocenyl derivatives[2] we were able to synthesise the ferrocene **3** in 24% yield. It seems to be possible to form from **3** in four steps the new PP-Ligand **4** with four hydroxy groups following a well established protocol[2]. The hydrophilic groups of **4** may lead to water solubility without further derivatisation.



(*S*, *S*)-**1**



(*S*, *S*, *S*, *S*)-**2**



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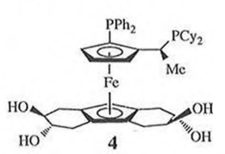

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[1] a) R.L.Haltermann, K.P.C.Vollhardt, *Organometallics* **1988**, 7, 883. b) R.L.Haltermann, K.P.C.Vollhardt, *Tetrahedron Lett.* **1986**, 27, 1461.

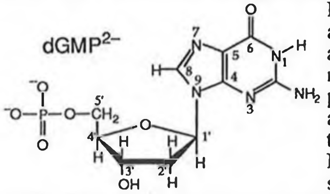
[2] H.C.L.Abbenhuis, U.Burckhardt, V.Gramlich, A.Togni, A.Albinati, B.Müller, *Organometallics* **1994**, 13, 4481.

Anorganische-Koordinations Chemie **89**

Metal Ion Complexes of 2'-Deoxyguanosine 5'-Monophosphate ($dGMP^{2-}$) Involving also *cis*-Diammine-Platinum(II)

Bin Song,[a] *Jing Zhao,*[a] *Gerda Oswald,*[b] *Bernhard Lippert,*[b] *& Helmut Sigel*[a]
[a] Institute of Inorganic Chemistry, University of Basel, Spitalstrasse 51, CH-4056 Basel, Switzerland; [b] Department of Chemistry, University of Dortmund, Otto-Hahn-Strasse 6, D-44227 Dortmund, Germany

Into our attempts to understand the effect of nucleobase-coordinated Pt^{2+} on the acid-base [1,2] and metal ion-binding [1] properties of other remaining sites we are including now $dGMP^{2-}$, which may be coordinated via N7 to *cis*-$(NH_3)_2Pt^{2+}$, an anticancer agent, to give *cis*-$(NH_3)_2Pt(dGMP)_2^{2-}$, abbreviated as $Pt(dG)_2^{2-}$. Clearly, this requires also knowledge of the complexing properties of $dGMP^{2-}$ itself, and thus, we have measured via potentiometric pH titrations (I = 0.1 M, $NaNO_3$; 25°C) the stability constants of several metal ion (M^{2+}) complexes (see Table, column 2). Purine-nucleotides may form macrochelates [3]; this 'backbinding' to N7 of a phosphate-bound M^{2+} must be reflected in an increased complex stability compared with that expected [4] on the basis of the basicity of the $-PO_3^{2-}$ group ($pK^H_{H(dGMP)}$ = 6.29). From these calculated [4] stabilities for the open isomers (column 3) follow the increased stabilities (column 4) and the formation degrees of the macrochelates (column 5). Such macrochelates cannot be formed anymore with $Pt(dG)_2^{2-}$; here M^{2+} binding is nearly solely governed by the basicity of the $-PO_3^{2-}$ group.



M^{2+}	$\log K^M_{M(dGMP)}$	$\log K^M_{M(dGMP)op}$	$\log \Delta_{M(dGMP)}$	%M(dGMP)
Cu^{2+}	4.05±0.04	2.91±0.06	1.14±0.07	93±1
Zn^{2+}	2.99±0.05	2.15±0.06	0.84±0.08	86±3

Supported by the Swiss Nat. Sci. Found. (H.S.), the Swiss Fed. Office for Educ. & Sci. (COST D1; H.S.), and the 'Deutsche Forschungsgemeinschaft' (B. L.).

[1] B. Song, G. Feldmann, M. Bastian, B. Lippert & H. Sigel, *Inorg. Chim. Acta* **235**, 99-109 (1995).
[2] G. Schröder, B. Lippert, M. Sabat, C. J. L. Lock, R. Faggiani, B. Song & H. Sigel, *J. Chem. Soc. Dalton Trans.*, 3767-3775 (1995).
[3] H. Sigel and B. Song, *Met. Ions Biol. Syst.* **32**, 135-205 (1996).
[4] H. Sigel, S. S. Massoud & N. A. Corfù, *JACS* **116**, 2958-2971 (1994).

Koordinationschemie **90**

Reaktionen von Dithiolopyrrol-Derivaten mit niedervalenten Platinkomplexen

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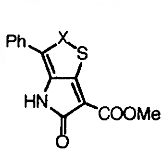
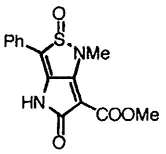
E-mail: Wei@anorg.chemie.uni-muenchen.de
[b]Institut für Pharmazie und Lebensmittelchemie, Ludwig-Maximilians-Universität München, D-80333 München, Sophienstraße 10, Deutschland.

Wir konnten zeigen, daß (a)cyclische Disulfide, Thiosulfinate und Thiosulfonate R-S(O)$_n$-S-R (n = 0,1,2) mit niedervalenten Platinkomplexen $L_2Pt(C_2H_4)$ (L = PPh_3, 1/2 dppe, 1/2 dppf) unter Insertion des Platinatoms in die S-S-Bindung reagieren; dabei entstehen neuartige Dithiolato-, Sulfenato-thiolato- und Sulfinato-thiolato-Komplexe [1].
Auch Dithiolopyrrole, die den Grundkörper wichtiger Antibiotika aus Streptomyces-Arten (Thiolutin, Holomycin, Aureothricin) bilden, und deren Mono- und Di-S-oxide sollten auf ihre Reaktivität gegenüber Platin(0)-Reagenzien getestet werden. **1** und **3** wurden durch eine Röntgenstrukturanalyse charakterisiert. Die Platin(0)-Kompexe $L_2Pt(C_2H_4)$ [L = PPh_3, 1/2 dppf, 1/2 (-)-DIOP] addieren sich oxidativ unter Spaltung der S-S-Bindung an die bicyclischen Disulfide **1**, Thiosulfinate **2** und die Sulfinamide **4**. Ein unerwartetes Reaktivitätsverhalten zeigt das Thiosulfonat **3**; hier erfolgt die Insertion des Platinatoms in die C-S-Bindung (**5**). Vom Thiosulfinato-Komplex **5** liegt eine Röntgenstrukturanalyse vor.



1: X = S
2: X = SO
3: X = SO_2



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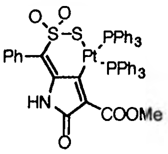

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[1] W. Weigand, G. Bosl, C. Robl, W. Amrein, *Chem. Ber.* **1992**, *125*, 39.

91

The chemistry of the Zr-C bond over an oxo surface: stepwise migratory insertion reactions of Carbon Monoxide and Isocyanides.

Alessandro Caselli, Luca Giannini, Euro Solari, Carlo Floriani.
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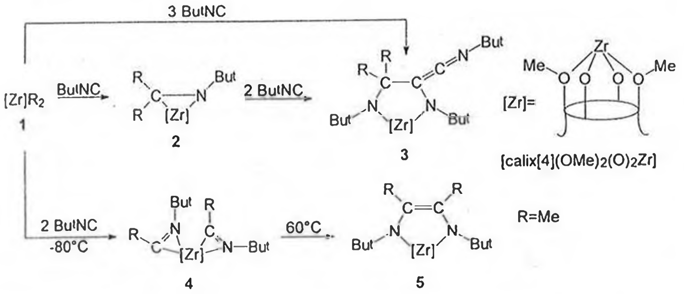
The chemistry of the Zr-C functionality is very versatile and has many applications in organic synthesis and industrial catalysis. We studied the migratory insertion reactions of isocyanides, using the bis-metoxy-calix[4] dianion as the ancillary ligand. A number of different migratory insertion pathways have been observed as a function of the temperature in the case of calix[4]$(OMe)_2(O)_2ZrMe_2$(1).



The reaction of 1 with Bu'NC at room temperature using a 1:1 Zr:Bu'NC molar ratio led to the η^2-imine complex 2. The metal carbon bond in 2 is still reactive in migratory insertion reactions, and can give 3, via a carbenoid intermediate.
The alternative pathway for 1, which as been singled out at low temperature (-80°C) shows the preferential migration of the second alkyl group to an incoming Bu'NC, thus forming a bis-η^2-iminoacyl (4), which, on heating (60°C), undergoes the well-known intramolecular coupling to the corresponding enediamide complex (5).

Anorganische Koordinationschemie **92**

FACILE OXYDATIVE ADDITION OF H_2O ON CHIRAL IRIDIUM(I) COMPLEXES

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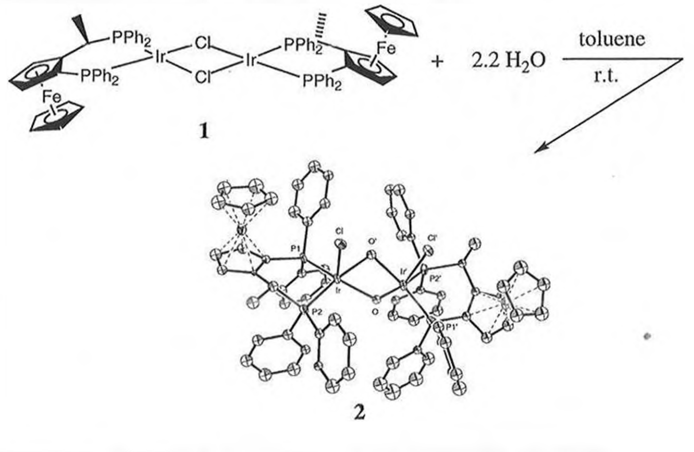
The chemistry of late transition metal (LTM) complexes of alkoxydes, hydroxydes and amides is a field of growing interest. The reactivity of this class of compounds towards unsaturated compounds[1] makes them ideal candidates for eventual catalytic C-O and C-N[2] bond forming processes. The use of LTM systems capable of activating O-H and N-H bonds may prove successful in the development of such catalysts. We report here on the activation of $PhNH_2$, $Ph(CO)NH_2$, NH_3, PhOH and H_2O by chiral ferrocenyl diphosphine chloro-bridged Ir(I) dimers. **1**, for example, reacts quantitatively with 2.2 eq of H_2O at room temperature affording two isomers of a bis-hydroxo bridged Ir(III) hydrido species (**2**).



(1) see e.g. Woerpel, K. A.; Bergman, R. G. *JACS* **1993**, *115*, 7888
(2) Casalnuovo, A. L.; Calabrese, J. C.; Milstein, D. *JACS* **1988**, *110*, 6738

Anorganische Chemie

93

Iridium Ferrocenyl Diphosphine Complexes: Megacatalysts for the Enantioselective Hydrogenation of N-Aryl Imines

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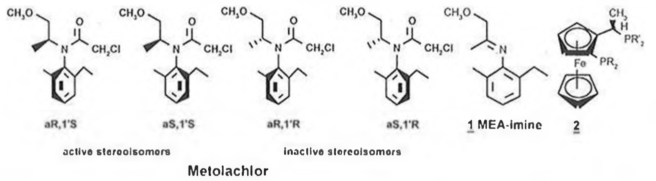
Recent years have witnessed impressive industrial applications of catalytic asymmetric hydrogenation reactions [1]. However, the enantioselective hydrogenation of imines remained a research topic with increasing interest [2]. Metolachlor, one of the most important herbicides, is a mixture of 4 stereoisomers. We have developed an efficient process for the biologically most active stereoisomers with the enantioselective hydrogenation of MEA-imine being the key step.



With a novel Ir-ferrocenyl diphosphine catalyst, generated in-situ from [Ir(COD)Cl]$_2$, **2**, iodide and an acid, *e.g.* CH_3COOH or H_2SO_4, MEA-imine was hydrogenated completely within 6 hrs. at 80 bar H_2/50°C with s/c up 1'000'000, while the optical yield was 78%. This catalyst showed an unprecedented high activity (TOF$_{initial}$: >1'800'000 h^{-1}) and is to our knowlegde the most active and productive enantioselective hydrogenation catalyst ever reported. The influence of various parameters on both activity and enantioselectivity will be presented.

References:

1 H.U. Blaser, B. Pugin, F. Spindler to be published in 1996 in B. Cornils, W.A. Herrmann (Eds.) Applied Homogeneous Catalysis by Organometallic Complexes.
2 H.U. Blaser, F. Spindler, ChimcaOggi, 13 (1995), 11.

Chimie Minérale et de Coordination

94

Tuning the Rate and Mechanism of Solvent Exchange at Rh(III) and Ir(III)

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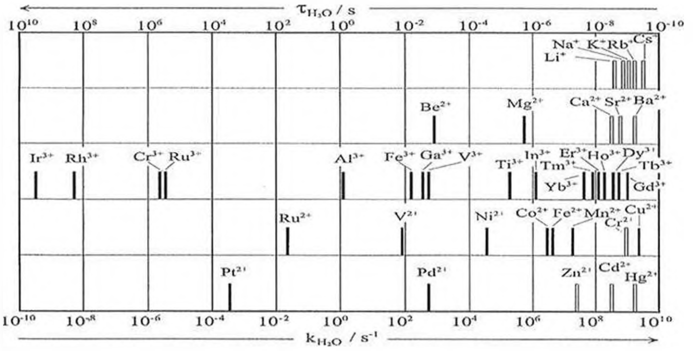
Quantitative kinetic studies on the hexaaqua complexes of Rh(III) and Ir(III), conducted in our laboratory, have led to water exchange rate constants of 2.2 × 10^{-9} and 1.1 × 10^{-10} s^{-1} respectively, and have thus necessitated a further expansion of the following figure.[1]



Interestingly, substitution of three ligated water molecules in the parent hexaaqua complexes by a Cp* moiety (M = Rh, Ir; S = H_2O) results in a dramatic 14-fold increase in the respective water exchange rate constants and, more importantly, this increase is also accompanied by a changeover in mechanism. Within this framework, we have also successfully extended the kinetic studies to organic solvents (S = MeCN, DMSO).

[1] Cusanelli, A.; Frey, U.; Richens, D. T.; Merbach, A. E. *J. Am. Chem. Soc. in press.*

Inorganic and Coordination Chemistry

95

Catalytic Hydrogenation of Benzene Derivatives under Biphasic Conditions Using Tetranuclear Ruthenium Clusters

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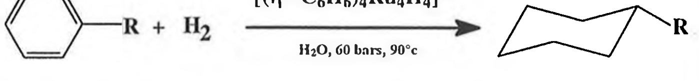
Water-soluble organometallics are particularly interesting with regard to catalytic applications in aqueous solution or under biphasic conditions, since water is a cheap and environmentally friendly solvent.

The tetranuclear ruthenium clusters $[(\eta^6\text{-}C_6H_6)_4Ru_4H_6]^{2+}$ and $[(\eta^6\text{-}C_6H_6)_4Ru_4H_4]^{2+}$ were found to be active for the catalytic hydrogenation of olefinic double bonds in aqueous solution [1]. We have now extended the catalytic potential of this system to the hydrogenation of various benzene derivatives . Under biphasic (water/substrate) conditions, the corresponding cyclohexane derivatives are obtained with catalytic turnover rates of more than hundred cycles per hour.



(R = H, Me, Pr, ^{i}Pr, ^{t}Bu)

The ^{1}H NMR study of the aqueous phase revealed the formation of the hexahydrido species $[(\eta^6\text{-}C_6H_6)_4Ru_4H_6]^{2+}$ and a ligand exchange process under catalytic conditions. The benzene ligands of both, the hexahydrido cluster $[(\eta^6\text{-}C_6H_6)_4Ru_4H_6]^{2+}$ and tetrahydrido cluster $[(\eta^6\text{-}C_6H_6)_4Ru_4H_4]^{2+}$ are successively substituted by the aromatic substrate.

[1] G. Meister, G. Rheinwald, H. Stoeckli-Evans and G. Süss-Fink, J. Chem. Soc., Dalton Trans. (1994), 3215.

Inorganic and Coordination Chemistry

96

Chiral Hydrophobic Recognition between Dibenzoyl Tartrate Ions and Ru-Complexes with Aromatic Ligands

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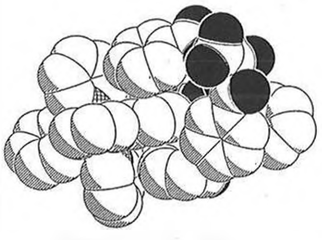
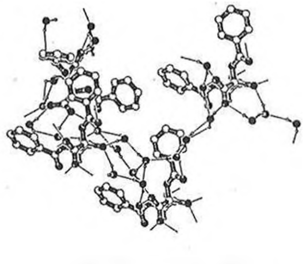
The successful resolution of *rac.*-[Ru(bpy)$_2$(py)$_2$]$^{2+}$ (bpy=2,2'-bipyridine, py=pyridine) with dibenzoyl tartrate was developed in our laboratory and has been recently described by X. Hua.[1]
The molecular structure and crystal packing mode of these chiral building blocks, Δ-[Ru(bpy)$_2$(py)$_2$][(+)-O,O'-dibenzoyl-D-tartrate]·12H$_2$O (**I**) and Λ-[Ru(bpy)$_2$(py)$_2$][(-)-O,O'-dibenzoyl-L-tartrate]·12H$_2$O have been determined by single crystal X-ray diffraction data. This study proposes a model of how the *(l)*-, respectively the *(d)*- Dibenzolytartrate anions, recognize the chirality of the hydrophobic [Ru(bpy)$_2$(py)$_2$]$^{2+}$ complex.
The monoclinic unit cell contains two complex cations, two tartrate anions and further twelve water molecules. Since there are no possibilities to form hydrogen bonds between the cations and the anions, chiral recognition is due to crystal packing. Two benzoyl rings of different tartrate anions are gripping in-between the two bpy-planes of the Ru-complex. Further one can see in special graphical presentations that a third benzoyl ring from a tartrate anion is packed between the two pyridine rings, favoring one enantiomeric form to crystallize from a water solution.



Packing mode of I
(Atoms with v. d. Waals Radii)



Packing mode of I
without the cation

(1) Hua, X.; von Zelewsky, A. *Inorg. Chem.*, **1995**, *34*, 5791-5797; Hua, X.; Lappin, A.G. *Inorg. Chem.*, **1995**, *34*, 992-994.

Anorganische und Koordinationschemie

97

Synthesis and Reactivity of Ru(IV) and Os(IV) Peroxo Complexes.

Arianna Martelletti and Antonio Mezzetti

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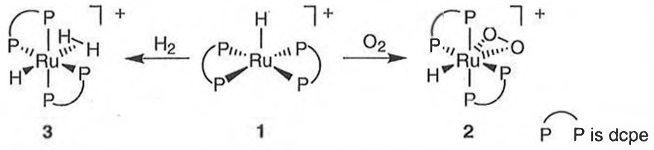
Recent results indicate that some formally unsaturated metal complexes form both dihydrogen and peroxo complexes.[1,2] We report here a further instance: the five-coordinate $[RuH(dcpe)_2]^+$ (**1**) (dcpe = 1,2-bis(dicyclohexylphosphino)ethane) reacts with O_2 yielding $[RuH(\eta^2\text{-}O_2)(dcpe)_2]^+$ (**2**), which is formally a Ru(IV) peroxo species. The binding of dioxygen is irreversible and the complex is stable in the solid state under N_2. Complex **1** also reacts with H_2 to give the already known dihydrogen complexes $[RuH(\eta^2\text{-}H_2)(dcpe)_2]^+$ (**3**), which is stable only under H_2 (1 atm).[3]



X-ray investigations of **1** and **2** will be reported, together with the reactivity of peroxo complex **2**, with particular emphasis on applications in homogeneous oxidation reactions.

References

1 Jiménez-Tenorio, M.; Puerta, M. C.; Valerga, P. *J. Chem. Soc. Chem. Commun.*, **1993**, 1750.
2 Mezzetti, A.; Zangrando, E.; Del Zotto, A.; Rigo, P. *J. Chem. Soc., Chem. Commun.* **1994**, 1597.
3 Mezzetti, A.; Del Zotto, A.; Rigo, P.; Farnetti, E. *J. Chem. Soc., Dalton Trans.* **1991**, 1525.

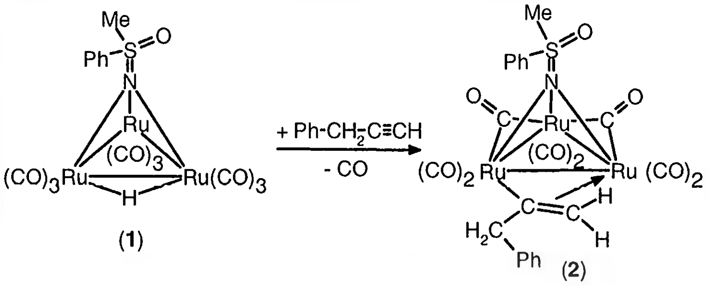
98

Chimie Minérale et de Coordination

Activation of Non-Functional Alkynes by the Electron-Deficient Cluster $(\mu_2\text{-H})Ru_3(CO)_9[\mu_3\text{-NS(O)MePh}]$

Vincent Ferrand and Georg Süss-Fink*

The reactivity of the electron-deficient cluster $(\mu_2\text{-H})Ru_3(CO)_9[\mu_3\text{-NS(O)MePh}]$ (**1**) towards non-functional alkynes was studied.



The reaction of **1** with the terminal alkyne benzyl acetylene proceeds with transfer of the hydride from the metal framework onto the incoming acetylene to give the vinyl complex **2**.

In the case of the internal alkyne diphenyl acetylene, **1** reacts with two acetylene equivalents to afford the cluster $(\mu_2\text{-H})Ru_3(CO)_6[\mu_3\text{-}\eta^2\text{-NS(O)MeC}_6H_4][\mu_2\text{-}\eta^2\text{-PhC=CHPh}][\mu_3\text{-}\eta^2\text{-PhC}\equiv\text{CPh}]$ (**3**).

99

Anorganische Chemie

Group 10 Metal Complexes with Sterically Demanding Nitrogen-Donor Ligands

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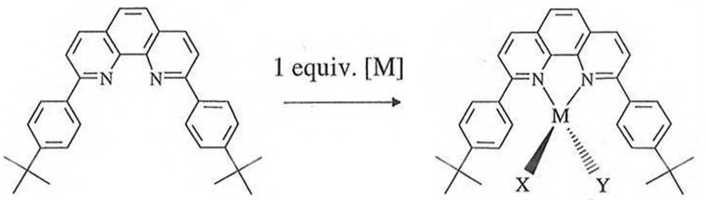
We have recently initiated a research program to develop synthetic access to group 10 d^8-metal complexes with sterically demanding derivatives of 1,10-phenanthroline and Schiff-base (diimine) donors. These complexes are sought as oxygen transfer catalysts to organic substrates. The syntheses and molecular structures of novel tetrahedral and square planar Ni(II)/Pd(II) containing additional oxygen donor ligands will be presented. A representative example for the synthetic access to these compounds is shown below.



$[M] = NiCl_2 \cdot dme, Pd(cod)Cl_2, Pd(cod)(Me)(Cl)$

100

Anorganische Chemie

Dinuclear Metal-Metal Multiple Bonded Halfsandwich Complexes of W(III) with Bridging Cyclopentadienyl Ligands

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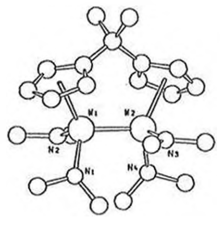
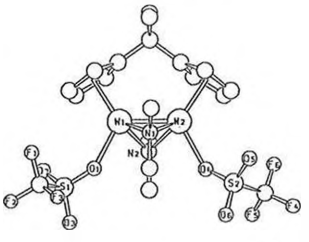
Anorg.-Chem. Institut, Universität Zürich, Winterthurerstr. 190, 8057 Zürich

The syntheses of dinuclear halfsandwich dimethyl amide and related complexes of W(III) with CMe_2- and $SiMe_2$-links between the two cyclopentadienyl rings will be presented. Representative X-ray crystal structures for the CMe_2 bridged tetraamide (Scheme 1, W-W 237.4 (2) pm)) and the corresponding diamide bis-triflate (Scheme 2) compounds provide support for W-W multiple bonds in these complexes.



Scheme 1



Scheme 2

Further ligand addition and reactions with electrophiles of these complexes will be described.

Anorganische Chemie

101

Coordination Chemistry of ansa-Magnesocenes

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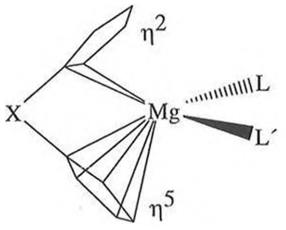
The syntheses and X-ray crystal structures of novel bridged magnesocenes with additional donor ligands will be presented. Typically, a pseudo-tetrahedral arrangement of the ligands around the Mg center is observed with distinct deviations from the bis-η^5-coordination mode of the cyclopentadienyl rings as most prominent structural feature (Scheme 1).



$X = CMe_2, SiMe_2, C_2Me_4$

L,L´ = THF; L,L´ = bipy; L = THF, L´ = MeNC

Scheme 1

Quantumchemical calculations have been performed on model compounds and support the dynamic behaviour of some of these complexes in solution.

Anorganische Chemie

102

Novel Halfsandwich Complexes of Tungsten(IV)

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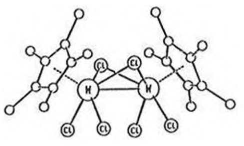
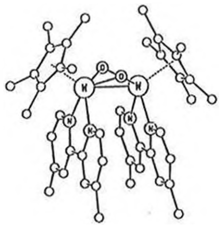
The synthesis of the novel paramagnetic tungsten-(IV)-chloro complex $[Cp^*WCl_2(\mu\text{-}Cl)]_2$ will be presented. In the X-ray crystal structure a four-membered ring of the tungsten and two bridging μ-Cl atoms with a W-W distance of 305.6(3) pm is observed (Scheme 1). EHT-calculations provide support for the observed paramagnetism and the diamagnetism of the essentially isostructural Re(IV) complex, $[(C_5Me_4Et)ReCl_2(\mu\text{-}Cl)]_2$, previously reported by Herrmann et al..



Scheme 1



Scheme 2

Bipyridyl ligand addition to the $[Cp^*WCl_2(\mu\text{-}Cl)]_2$ dimer leads to the weakly paramagnetic mononuclear W(IV) complexes $Cp^*W(4,4'\text{-}R,R\text{-}bpy)Cl_3$ (R = Cl, H, Me, t-Bu, MeO, NMe_2). Through controlled hydrolysis of the latter compounds, followed by ion exchange with PF_6^- the dicationic dimers, $[Cp^*W(4,4'\text{-}R,R\text{-}bpy)(\mu\text{-}O)]_2[PF_6]_2$, are obtained (Scheme 2, R = Me).

Chimie minérale et de coordination

103

The organometallic chemistry over a planar oxo surface: the organometallic functionalisation of tantalum calix[4]arene complexes

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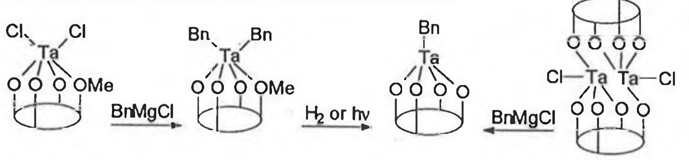
Of the alkoxo ligands studied as alternative Cp_2M- systems, the calix[4]arene moiety has some special features. This ligand can be considered a poly-oxo matrix on which is possible to control, by selective protection, the number of oxo groups available to bind the metal. In addition, the geometric constraint of this ligand allows the design of complexes bearing reactive functionalities in a *cis* relationship. These characteristics have been exploited in our initial work on the organometallic chemistry of the calix[4]arene tantalum complexes.



The starting materials, $[CalTaCl]_2$ and $CalMeTaCl_2$, are readily obtained by reacting *p-tert*-butyl-calix[4]arene ($CalH_4$) or dimethoxy-*p-tert*-butyl-calix[4]arene ($CalMe_2H_2$) with $TaCl_5$. In the latter reaction an *in situ* demethylation of the organic ligand takes place. The complexes $[CalTaCl]_2$ and $CalMeTaCl_2$ react with Grignard reagents RMgX (R= *p*-tolyl, benzyl) to give the corresponding alkyl derivatives CalTaR and $CalMeTaR_2$. Compounds $CalMeTaR_2$ react smoothly with CO and *tert*-buyl-*iso*-nitrile to give the migratory insertion of the two alkyl groups affording the η^2ketone derivative $CalMeTa(OCR_2)$ and the η^2imino derivative CalMeTa(*tert*-butyl-NCR_2). Photochemical activation or reaction with H_2 produce the transformation of $CalMeTaBn_2$, a complex with C_{2v} symmetry, to the more highly symmetric (C_{4v}) CalTaBn, through a process of dealkylation at the metal centre and demethylation of the organic ligand.

Chimie minérale et de coordination

104

Titanyl Functionality Stabilized Within a Pophyrinogen Cavity and Its Chemistry.

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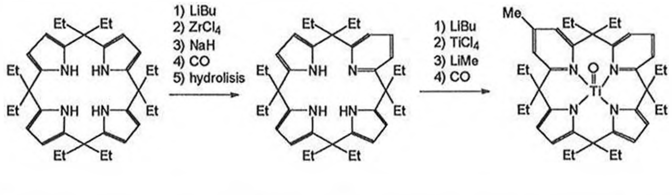
Metal complexes of porphyrins play a key role in biochemial processes and at present several researchers are actively involved in the investigation of this and related classes of macrocyclic compounds. We have recently developed an original procedure which allows the metal-assisted transformation of the porphyrinogen skeleton, which is the biological precursor of porphyrins. This conversion consists of the regioselective introduction of one carbon atom into one or two of the pyrrole rings, transforming them to pyridine. Such modifications have a considerable effect on the electronic and topological characteristic of the macrocyclic skeleton. The figure gives the overall scheme for these transformations.



The final product contains a titanyl moiety, as shown by X-ray analysis. This class of compounds is well known and has a rich and diverse chemistry. We consider this molecule as providing an excellent opportunity to study the chemistry and reactivity of the Ti=O functionality in a novel ligand enviroment.

CHIMIA 50 (1996) Nr. 7/8 (Juli/August)

Chimie Minérale et de Coordination

105

Synthetic Methodology Allowing the Interconversion of Titanium–Oxygen Single into Double Bond: the Self-Assembling of Bridging and Terminal Oxotitanium(IV) into Oligomeric and Polymeric Linear Titanoxanes

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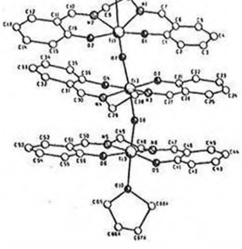
Bâtiment de Chimie, 1015 Lausanne

The controlled ionization of the linear skeleton Cl-Ti-O-Ti-Cl allowed the generation of the non-symmetrical dimer $[Cl–Ti–O=Ti]^+$, *via* a "push-pull synergy" determined by the extended Cl–Ti–O π-interactions. Such a fundamental step is responsible for the generation of the [Ti=O] unit which is made available as a building block for a variety of titanoxane structures. The stepwise $NaBPh_4$-assisted ionization of $[(Cl)(acacen)Ti]_2(\mu_2\text{-}O)$ and $[(Cl)(salen)Ti]_2(\mu_2\text{-}O)$ in THF led to the non-symmetrical dimer $[Cl–Ti–O=Ti]^+$ intermediate, which is the parent compound of a variety of linear titanoxanes. The monomer, trimer (see figure), tetramer and polymeric species containing the Ti=O unit have been isolated. A scheme is proposed for the genesis of all those species from a single, simple ionization of starting meterials, where the origin and the binding properties of the [Ti=O] unit play a major role.



Inorganic and Coordination Chemistry

106

Stereoselective Synthesis of New Optically Active Rhodium (III) Complexes

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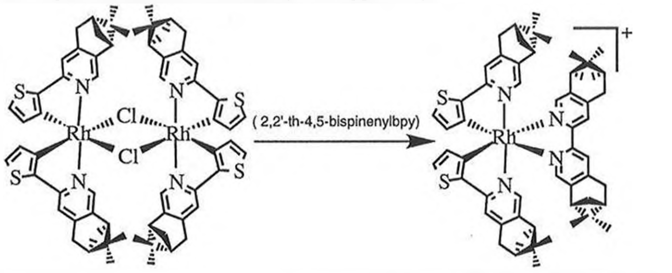
Institute of Inorganic and Analytical Chemistry, University of Fribourg, Pérolles; Fribourg, CH-1700, Switzerland

The desire to obtain complexes with a predetermined and controlled stereochemistry at the metal centre(s) is a source of great interest in coordination chemistry today. Here, we illustrate the synthesis and characterisation of a new series of chiral Rh(III) species, with ligand induced predetermined chirality. Cyclometallated Rh(III) complexes of the type $[Rh(C^\wedge N)_2(N^\wedge N)]^+$ have been prepared from the chlorobridged dinuclear precursor $[Rh(C^\wedge N)_2Cl]_2$ via a modified literature procedure.[1] As chelating ligands a range of α-pinene substituted 2,2'-(thienyl)pyridines and 2,2'-bipyridines were used.[2] The chirality of the ligands is developed by using the readily available natural products; (-)-myrtenal and (-)-α-pinene.

The complexation of 2,2'-(thienyl)-4,5-pinenyl-pyridine to rhodium is giving only one diastereoisomer in the case of the dinuclear complex. Upon cleavage of the chlorobridged complex with 2,2'-bipyridine and different substituted 2,2'-bipyridines, the metal helicity was apparently maintained.



[1] Mäder, U.; von Zelewsky, A.; Stoeckli-Evans, H.; *Helv. Chim. Acta* **1992**, *75*, 1320.
[2] Hayoz, P.; von Zelewsky, A.; *Tetrahedron Lett.* **1992**, *33*, 5165.

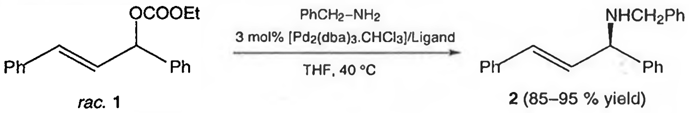
Anorganische und Koordinationschemie

107

A Remarkable Anion Effect on the Enantioselectivity of the Palladium-Catalyzed Allylic Amination

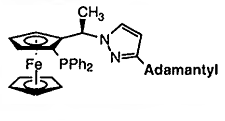
Markus Baumann, Urs Burckhardt and Antonio Togni
Laboratorium für anorganische Chemie, ETHZ, 8092 Zürich

Chiral pyrazole-containing ferrocenyl ligands have been shown to afford the highest known enantioselectivities (up to > 99% *ee*) in the Pd-catalyzed amination of 1,3-diphenylallyl carbonate **1** with benzylamine [1]. Structural studies, both in solution and in the solid state, of the intermediate cationic Pd-allyl complexes have given clues as to the origin of enantioselectivity of this reaction.



rac. **1**

2 (85–95 % yield)

(Ligand)	(anion added)	(observed *ee* in **2**)
	—	99.1 %
	$[PF_6^-]$	6.7 %
	$[F^-]$	**>99.5 %**

A subtle interplay between steric and electronic effects is responsible for the observed, unprecedented stereoselectivities in Pd-catalyzed allylic amination. Allyl configuration and site of nucleophilic attack are crucial. However, the interconversion rate of diastereoisomeric π-allyl complexes is also a decisive factor. Anions present in solution have been found to have a profound effect on stereoselectivity. The examples shown above illustrate this finding in a drastic manner.

The study of these effects will help elucidating important mechanistic details.

[1] A. Togni, U. Burckhardt, V. Gramlich, P.S. Pregosin, R. Salzmann, *J. Am. Chem. Soc.* **1996**, *118*, 1031.

Anorganische / Koordinations Chemie

108

Combustion of Methane over Palladium / Zirconia Derived from a Glassy Metal Alloy: Effect of Pd Particle Size on Catalytic Activity

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A $Pd_{25}Zr_{75}$ glassy metal has been activated by controlled oxidation in air, producing a highly active methane combustion catalyst. Several morphological and chemical changes, such as oxidation, crystallization, segregation, and rise in BET surface area, occurred during activation. After activation (oxidation) in air, the catalysts consisted of poorly crystalline palladium oxide on monoclinic and tetragonal zirconia. The fully oxidized catalyst was reduced in hydrogen at different temperatures resulting in metallic palladium supported on zirconia. The reduced materials showed marked differences in specific surface area of palladium and BET surface area after catalytic tests, both decreasing with increasing reduction temperature. The loss of surface area was accompanied by an increase of the palladium crystallite size. Catalysts reduced at low temperatures were faster reoxidized during controlled oxidation than catalysts reduced at high temperatures. Changes of the properties of palladium oxide supported on zirconia were reflected by different decomposition behavior and by its different reducibility with hydrogen and methane. Palladium oxide was thereby shown to become more reactive after reduction and subsequent reoxidation.

Kinetic measurements were carried out in a fixed-bed micro reactor using a reactant gas mixture containing 1% of methane and 4% of oxygen in a balance of He. Metallic palladium was reoxidized immediately, even at room temperature, under reaction atmosphere. Profound differences in catalytic activity were detected for catalysts reduced at different temperatures. Catalysts reduced at room temperature, 573 K, and 873 K were more active than the unreduced catalyst, whereas the catalyst reduced at 973 K was less active. Strong correlations between the catalytic activity and the crystallite size as well as the reducibility of palladium oxide with methane for catalysts reduced at different temperatures were found. Calculations of the turnover frequency implied that catalysts reduced at high temperatures with large particles exhibited higher activity per palladium atom exposed to the reaction atmosphere.

The correlation between the reduction with methane and the catalytic performance is explained by a redox mechanism involving palladium oxide. The influence of the particle size is attributed to a strong support effect.

Inorganic and Coordination Chemistry **109**

Structural Aspects of η^3-Allyl Palladium(II) Complexes with Chiral Phosphinoaryloxazolines

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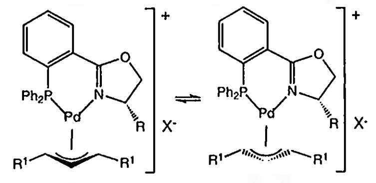
Palladium complexes of chiral phosphinoaryloxazolines have proved to be highly effective catalysts for enantioselective allylic substitution reactions. In order to get more information about the two possible (η^3-allyl)palladium(II) intermediates (*Fig. 1*) we prepared the 1,3-diphenyl derivatives (**2**) and their corresponding [Pd(η^3-C_3H_5)] complexes (**1**).



a R = CH_3
b R = CH_2CH_3
c R = $CH(CH_3)_2$
d R = $C(CH_3)_3$
e R = C_6H_5
f R = $CH_2C_6H_5$
X^- = PF_6^- *or* $B(C_6H_5)_4^-$

Fig. 1. *Isomers of* **1** (R^1 = H) and **2** (R^1 = Ph)

X-ray and ^{1}H-NMR investigations show, that the *hexafluorophosphates* of type **1** have a disordered allyl group with an *'endo'*:*'exo'* ratio of about 1:1. The corresponding 1,3-diphenylallyl complexes **2** exist only in the *'exo'* form in the solid state. In solution, NMR investigations demonstrate that the amount of the *'exo'* diastereomer increases with the bulk of the substituent at the oxazoline ring.

In ^{1}H-NMR studies of the *tetraphenylborate* **1e** at r.t. only one set of signals of the allylic protons and a significant upfield shift of the oxazoline protons with respect to the corresponding hexafluorophosphate is observed.

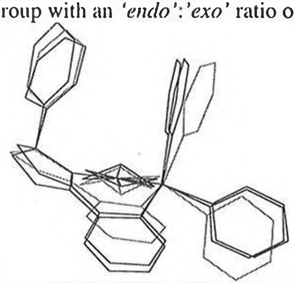


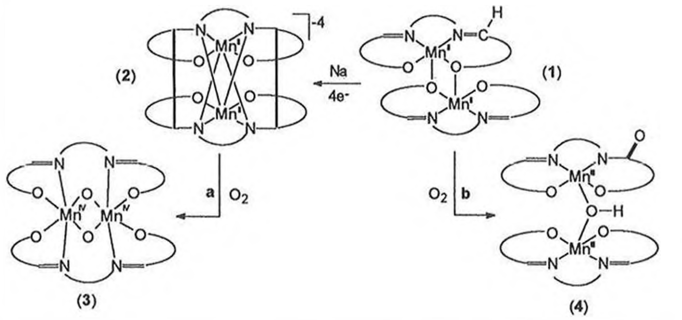
Fig. 2. *Superposition of the cations of the* PF_6^- *(·····) and the* $B(C_6H_5)_4^-$ *(—) salts*

Chimie minérale et de coordination **110**

The Ligand-Metal Synergism in the Redox Chemistry of Mn(II)-Schiff Base Complexes.

Gallo E.; Solari E.; Floriani C.*, Institut de Chimie Minérale et Analytique, Université de Lausanne, BCH, 1015 Lausanne (CH)

The present report deals with the reactivity of dioxygen with two Mn(II)-Schiff base complexes of different electron richness. In pathway a the electron rich complex (**2**) was acheived *via* the intramolecular reductive coupling of imino groups across two macrocyclic units of the complex (**1**). Complexes (**1**) and (**2**) have very distinct behaviours in their reaction with dioxygen.



The oxidation of electron-rich Mn(II) Schiff base complex (**2**) gave rise to a novel topology of di-μ-oxo-Mn(IV) dinuclear complex (**3**) while in pathway **b** the reaction of (**1**) with dioxygen led to the selective oxidation of a C-H functionality, thus resulting in an imino → amido transformation and the concomitant formation of the OH-bridged Mn(III)-dimer (**4**).

111

Metal-Metal and Metal-Carbon multiple bonds playing games over a Tungsten tetraoxo-calix[4]arene surface.

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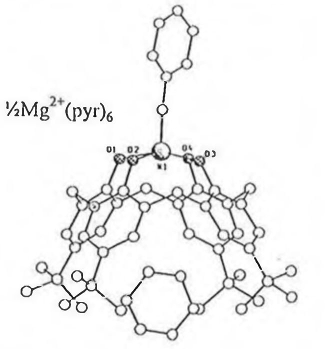
The chemistry of Tungsten in high oxidation states has been extensively studied in recent years (also for its industrial applications). Most often monodentate O-donor ancillary ligands have been used.
We decided to investigate the use of p-tert-Butylcalix[4]arene (Cal) as a polydentate oxo ligand; *cis*-Cl_2WCal (1) was used as the starting material.

Alkylation of 1 with 3 eqv of $LiCH_2SiMe_3$, Li^nBu or $MgBn_2$ led to the isolation of the corresponding negatively charged **carbyne** species **CalW≡CR$^-$ M$^+$** (R, M = $SiMe_3$, Li; ^{n}Pr, Li; Φ, ½Mg, respectively) (2) by double α-elimination.



Reduction of 1 with 3 eqv of $NaC_{10}H_8$ led to a bis anionic dimer where Na^+ counterions bridge the two calixarene units **CalW≡WCal(μ-Na)$_2$** (3).
It was also possible to isolate mono- and bis-reduced species:
i) **$KCalWCl_2$** (4) where K^+ is hosted in the cavity;
ii) **NaCalW=(μ-Cl)$_2$WCalNa** (5) where Na^+ is hosted in the cavity and the two Cl^- bridge the doubly bonded W atoms.

From these preliminary results it might be concluded that the calixarene ligand enhances the tendency of W to form "ate" complexes. In fact, complexes 1 - 5 can be rationalized in terms of the fragments represented by the general formula **$(CalWCl_n)^-$**, n = 0,1,2.

Anorganische Chemie - Koordinationschemie **112**

[Co^{III}(η^5-C_5H_5)$_2$]$^⊕$F$^⊖$ · 22 SiO_2, Cobalticiniumfluorid-Nonasil: Structure-Directed Synthesis of Strictly Aligned Metal-Organic Complex Chromophores in a Crystalline Silica Matrix

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An intriguing goal of materials chemists is the generation of composite structures that are organised on a molecular level and have been prepared by controlled nanoscale manipulation procedures. One approach uses the three-dimensional periodic void structure of zeolite-type host matrices to prepare ordered arrays of quantum-size metal or semiconductor particles, immobilised metal complexes, isolated electrically conductive polymer filaments or dispersions of dye molecules.

Here, we present investigations on a crystalline chromophore-silica nanocomposite that has been formed by direct hydrothermal synthesis using the cationic cobalticinium complex ($Cocp_2^⊕$) as structure-directing agent.[1] An X-ray single-crystal structure determination was performed at 220 K: $[Cocp_2F]_4 \cdot 88\ SiO_2$, orthorhombic, *Pccn*, $a = 22.125(2)$ Å, $b = 13.612(3)$ Å, $c = 14.889(2)$ Å, $Z = 1$.[2] The pure silica framework possesses the nonasil topology in which each large [5^86^{12}] cage is occupied by a $Cocp_2^⊕$ cation in staggered conformation. Due to effective C—H···O—Si interactions, e.g., hydrogen bridge bonds with $d_{O\cdots H} = 2.31$ Å, the $Cocp_2^⊕$ cations are completely fixed and show no orientational nor rotational disorder.[3] Fluoride anions that compensate the charge of the $Cocp_2^⊕$ cations reside in half of the small [4^15^8] cages. They coordinate to the neighbouring framework atom Si1 ($d_{Si1\text{-}F} = 1.836(6)$ Å), causing a distortion of the tetrahedral oxygen environment to a nearly ideal trigonal-bipyramidal penta-coordination at Si1.

Due to the special topology of the nonasil framework, the close fit between the $Cocp_2^⊕$ cation and the large nonasil cage and thus the rigid orientation of the $Cocp_2$ cations, a uniform supralattice of aligned cobalticinium chromophores is present. The strict parallel alignment is easily proved by polarisation microscopy, UV/Vis and IR spectroscopy showing distinct anisotropic absorption characteristics.[4]

[1] G. van de Goor, Thesis, Konstanz 1995. [2] G. van de Goor, C.C. Freyhardt, P. Behrens, Z. anorg. allg. Chem. 621 (1995) 311. [3] P. Behrens, G. van de Goor, C.C. Freyhardt, Angew. Chem. 107 (1995) 2895. [4] G. van de Goor, K. Hoffmann, S. Kallus, F. Marlow, F. Schüth, P. Behrens, Adv. Mater. 8 (1996) 65.

CHIMIA 50 (1996) Nr. 7/8 (Juli/August)

Inorganic and Coordination Chemistry **113**

Synthesis, Characterization and Chiroptical Properties of Metal Complexes with a Novel Chiral 5,6-substituted Terpyridine Ligand

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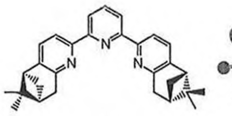
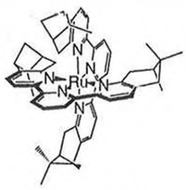
Université de Fribourg, Pérolles, 1700 Fribourg

Chiral 5,6-substituted terpyridine complexes can be used as building blocks to form stereochemically well defined chiral metal complexes which are of interest to design polynuclear supramolecular structures.[1]
With the enantiomerically pure ligand **1**, the 'chirality' of the ligand is strongly felt by the coordinating metal giving rise to Cotton effects in the metal to ligand charge transfer (MLCT) absorption.
1 has been synthesized in a 70% overall yield starting from 2,6-diacetylpyridine and 1*R*-(+)-α-pinene. Ru(II)-complexes $[Ru(\mathbf{trpy})(\mathbf{1})](PF_6)_2$ and $[Ru(\mathbf{1})_2](PF_6)_2$ were easily obtained (67% - 99% yield) by microwave heating (4 min, 375 W), which is a considerable improvement over syntheses of this type reported in literature.[2] Chiroptical data and the crystal structure of $Rh(\mathbf{1})Cl_3$ indicate that the ligand **1** is distorted in the metal complexes to form a left handed helix.



1

$Rh(\mathbf{1})Cl_3$



$[Ru(\mathbf{1})_2](PF_6)_2$

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[1] Sauvage, J.-P., Collin, J.-P., Chambron, J.-C., Guillerez, S., Coudret, C., and Balzani, V, Barigelletti, F., De Cola, L., Flamigni, L., *Chem. Rev.* **1994**, *94*, 993.

[2] (a) Rose, D., Wilkinson, G., *J. Chem. Soc.* **1970**, 1791 (b) Meyer, T.J., Braddock, J.N., *J. Am. Chem. Soc.* **1973**, *95*, 3158 (c) Stone, M.L., Crosby, G.A., *Chem. Phys. Lett.* **1981**, *79*, 78.

Anorganische Chemie **114**

Self-assembling metallodendrimers

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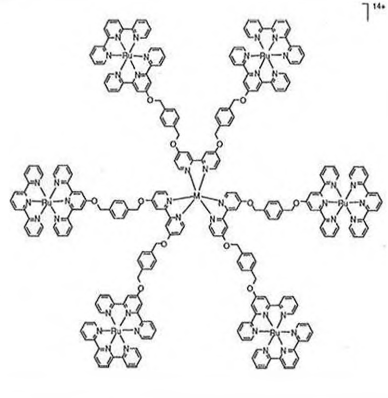
Metallodendrimers are dendrimers in which new generations arise as a result of interactions between metal ions and metal-binding domains as opposed to carbon-carbon or carbon-heteroatom bond formation reactions.

Various strategies for the assembly of such systems will be presented. These will range from highly programmed reactions of preorganised intermediates to genuinely self-assembling systems which form the desired products quantitatively simply upon mixing the reaction components.



Anorganische-Koordinations Chemie **115**

Organometallic Spirogermanium (or silicon) Compounds as new Electron-Donor-Systems for Charge-Transfer-Complexes.

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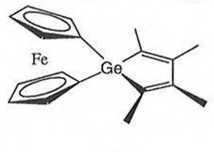
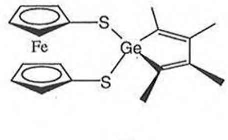
Charge-Transfer complexes containing ferrocene derivatives have been shown to display interesting conducting and magnetic properties[1]. However, although ferrocenophanes were used to form polymers by ring opening polymerisation, nothing is known about their ability to form CT-complexes. The two new spirogermanoles **A** and **B** show reversible redox processes (**A**: +150 mV; **B**: +250 mV (vs. ferrocene/ferrocenium couple)), and were characterized by X-ray diffraction.

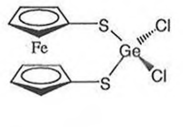
The derivative 1,3-Dithia-2,2-dichlorogermyl-[3]ferrocenophane[2] **C** is a useful starting material for the preparation of novel electron donors, e.g., the dmit derivative **D**, containing conjugated sulfur heterocycles.



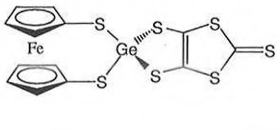
A



B



C



D

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[1] For a review, see: Togni, A. in *Ferrocenes*, Togni A.; Hayashi, T., Eds.; VCH, Weinheim, **1995**, 433-469.

[2] Osborne, A. G.; Blake, A. J.; Hollands, R. E.; *J. Organomet. Chem.* **1985**, *287*, 39-47.

Anorganische Chemie / Koordinationschemie **116**

Magnetic Neutron Scattering Experiments on the Two-Dimensional Networks $[MnCr(ox)_3]_n^{n-}$ and $[FeCr(ox)_3]_n^{n-}$

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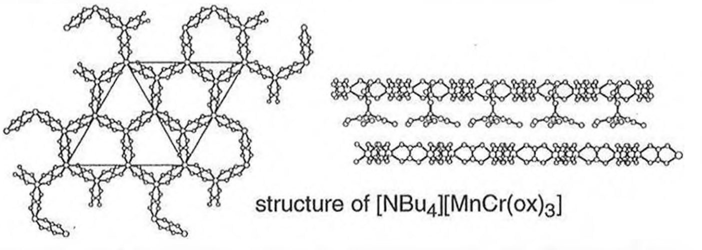
[1] Institut für Anorganische Chemie, Universität Zürich, CH-8057 Zürich
[2] Laboratorium für Neutronenstreuung, Eidgenössische Technische Hochschule Zürich & Paul Scherrer Institut, CH-5232 Villigen PSI
[3] Institut Laue-Langevin, F-38042 Grenoble Cedex 9
[4] Hahn-Meitner Institut, Abteilung für Neutronenstreuung, D-1000 Berlin

We are currently studying materials, that are formed by the interaction of transition-metal ions (as spin carrying centers) and the oxalate ions as bridging ligand units and mediators for magnetic exchange interactions. Based on different synthetic concepts either two- or three-dimensionally linked anionic chiral networks with stoichiometries $[M^{n+}M'^{m+}(ox)_3]^{(6-m-n)-}$ can be formed and crystallized. In particular XR_4^+ (X = P, N; R = alkyl or aryl) cations initiate the growth of layered structures with network stoichiometries $[M^{II}M^{III}(ox)_3]_n^{n-}$ (M^{II} = Cr, Mn, Fe, Co, Ni, Cu, Zn; M^{III} = V, Cr, Fe, Co).



structure of $[NBu_4][MnCr(ox)_3]$

Magnetic ordering (ferro- , ferri- or antiferromagnetic) of most of this compounds can be suggested from magnetic susceptibility measurements. Particularly, the compounds $[PPh_4][MnCr(ox)_3]$ orders ferromagnetically at T_c = 6 K and single crystal magnetisation shows the c-axis (perpendicular to the layers) to be the easy axis. Neutron diffraction experiments resulted in the determination of the magnetic structure which shows a 3D ferromagnetic ordering behavior of all spins along the c-axis. In contrast, the magnetic neutron diffraction experiments on $[PPh_4][FeCr(ox)_3]$ show evidence of a 2D spin alignement.

CHIMIA 50 (1996) Nr. 7/8 (Juli/August)

Anorganische Chemie

117

Reduktion von CO in $[W(CO)_2(NO)(Triphos)][BF_4]$

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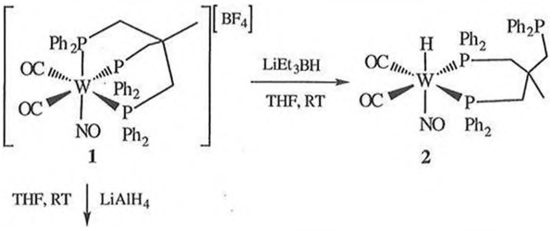
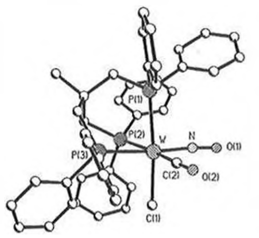
Die Umsetzung von **1** mit Hydrierungsreagenzien wie $NaBH_4$ und $LiEt_3BH$ führt zum Verlust eines Metall-koordinierten Phosphoratoms selektiv in trans-Stellung zum Nitrosylliganden unter Bildung der Hydridverbindung **2**.





Die Umsetzung von **1** mit $LiAlH_4$ dagegen führt zur vollständigen Reduktion eines koordinierten CO-Liganden zur entsprechenden Methyl-Verbindung. Der für ähnliche Systeme literaturbeschriebene Reaktionsverlauf über eine Formylspezies$^{1-4}$ kann mit Tieftemperatur-$^{31}P\{^1H\}$- und ^1H-NMR-spektroskopischen Untersuchungen bestätigt werden.

(1) Casey, C. P.; Neumann, S. M. *J. Am. Chem. Soc.* **1976**, *98*, 5396.
(2) Casey, C. P.; Neumann, S. M. *J. Am. Chem. Soc.* **1978**, *100*, 2545.
(3) Gladysz, J. A.; Merrifield, J. H. *Inorg. Chim. Acta* **1978**, *30*, L317.
(4) Winter, S. R.; et al. *J. Organomet. Chem.* **1977**, *133*, 339.

Anorganische/Koordinations Chemie

119

Aluminium-deficient zeolites as adsorbents for volatile organic compounds

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Eidgenössische Technische Hochschule, 8092 Zürich

Volatile organic compounds or VOCs constitute an important class of air pollutants commonly found in the atmosphere at ground level in all urban and industrial centres. They play a major role in a range of environmental problems such as stratospheric ozone depletion, ground level photochemical ozone formation and the global greenhouse effect and often have toxic or carcinogenic effects on health. Their emission is among others mainly a result of petrol storage and distribution, food manufacture, solvent evaporation from varnish, agriculture and landfilled wastes.

One possibility of avoiding emissions is the routinely used adsorption on activated charcoal. Alternatives of growing interest to these adsorbents are dealuminated, hydrophobic zeolites. While activated charcoal adsorbs large amounts of water, aluminium-deficient zeolites selectively adsorb VOCs, which is a great advantage for most applications.

At present, two zeolites are being investigated in our group, ZSM-5 and Y. While ZSM-5 can be synthesised with a Si/Al ratio of 1 to ∞, Y has to be dealuminated in a post-synthesis process which is accomplished by steaming and/or by $SiCl_4$-treatment. In this way, a set of zeolites with different pore structures and Si/Al ratios are produced.

The performance during adsorption is studied by the breakthrough behaviour of the solvents n-pentane, p-xylene, toluene, methanol and methyl-ethyl-ketone as well as water. These compounds have been adsorbed separately and as mixtures. Thus, displacement and diffusion effects can be investigated.

Regeneration is achieved by temperature-programmed desorption (TPD) which gives information about the ease of desorption.

Anorganische Chemie

118

Quantitative and qualitative analysis of the dealumination of zeolites

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Post-synthesis treatment of zeolites is an important step in the production of active, stable catalysts. Dealumination, the removal of framework aluminium atoms without destroying the micropore (3-7 Å) structure, is one of the most useful and widely used modifications. The most commonly used dealumination methods are acid leaching, complexation of the aluminium by oxalic acid or EDTA and the replacement of the framework aluminium directly with silicon by gaseous $SiCl_4$. Depending on the method used and on the zeolite type defect sites (hydroxyl nests) in the structure can be formed.

The extent of dealumination cannot be judged solely on the basis of bulk analysis because of the formation of extraframework aluminium (EFAl) but must be supported by spectrocopic methods such as FTIR and solid state NMR. FTIR of hydroxyl groups in dehydrated zeolites in the range 4000-3000 cm^{-1} has been subject of extensive research and peaks due to the presence of the protons associated with Brønsted acid sites, EFAl and different silanol groups have been identified. Signals due to the same hydroxyl groups can be observed by solid state ^1H NMR spectroscopy and it has been observed that the ^1H NMR chemical shift (δ_H) and the stretching vibration frequency (ν_{OH}) are correlated, aiding the interpretation of the MAS NMR signals.

Information about the number of Brønsted acid sites and therefore the number of framework aluminium atoms was obtained from the ^1H MAS NMR. It was also possible to quantify the number of silanols by means of ^{29}Si MAS NMR and to distinguish between isolated terminal silanols and hydrogen bonded silanols and therefore gain an estimate for the number of defect sites in the zeolite framework both before and after dealumination. At the same time the number of terminal silanol groups could be correlated with the extent of the external surface area. The results agreed with those from N_2 absorption.

The results showed that quantitative analysis of spectroscopic data can yield a great deal of information about the process occurring within a zeolite during modification.

120

Anorganische Chemie

Cs^+-exchange as a probe for the acid sites on the external surface of beta zeolites.

G. Harvey and M. Müller, Laboratorium für Technische Chemie, ETH-Zentrum, 8092-Zürich.

Brönsted acid sites on the external surface of zeolite catalysts may lower the selectivity when a reaction with product shape-selectivity is carried out. A test reaction such as tri-isopropylbenzene can establish the presence of such acid sites but gaining information about the number of acid sites on the external surface of a zeolite is difficult. For example measuring the amount of aluminium by spectroscopic methods such as XPS can be inaccurate when the surface area is high due to irregular texture or when the Si/Al ratio is high.

Beta zeolites often have very high external surface areas in relation to the total surface area due to the very small crystal size and irregular surface texture and the catalysts show correspondingly high catalytic activities for reactions involving large molecules such as substituted naphthalenes(1). We have developed a method to quantify the number of aluminium atoms and therefore the number of acid sites on the external surface by ion-exchanging the counter-cation of the tetrahedrally coordinated aluminium against cesium. When the ion-exchange is performed with an as-synthesised zeolite i.e. one that still has the internal micropore volume blocked by the presence of organic template molecules, the exchange capacity found is that of the external surface only.

We have found that the external surfaces of three beta zeolites provided by C.U. Uetikon contain substantial amounts of aluminium, but that the Si/Al ratio is always higher than in the bulk, indicating that aluminium deficiency in the crystallisation medium probably terminates crystal growth. Cs^+-exchange of modified as-synthesised zeolites shows that complete removal of the surface aluminium can be achieved by using oxalic acid solutions. ^{133}Cs MASNMR is used to gain information about the coordination sphere of the Cs^+ on the surface.

1. G. Harvey, G. Binder and R. Prins. Stud. Surf. Sci. Catal., **94**, 397, 1995.

CHIMIA *50* (1996) Nr. 7/8 (Juli/August)

Anorganische-Koordinations Chemie

121

Estimate of the Extent of Steric Inhibition by the 6-Amino Group on Metal Ion Coordination at N7 of the Adenine Residue

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Adenine: R = H

The adenine residue is an important metal ion binding site in adenine nucleotides and in nucleic acids as well. The related adenosine (Ado; R = ribose in the structure) is an ambivalent ligand [1,2] offering metal ions the N1 and N7 sites (the affinity of N3 is usually negligible). The steric inhibition of the 6-amino group on N1 was previously quantified via stabilities of metal ion complexes formed with tubercidin (= 7-deaza-adenosine) [3]. Now we are attempting to quantify this effect on N7 by employing 1-methylbenzimidazole (MBI; $pK^{H}_{H(MBI)} = 5.67$) and 1,4-dimethylbenzimidazole (DMBI; $pK^{H}_{H(DMBI)} = 5.78$) as ligands and by making the justified [3] assumption that the inhibitory effect of an amino group corresponds to that of a methyl group. Our preliminary results, obtained via potentiometric pH titrations (I = 0.5 M, $NaNO_3$; 25°C), are summarized below with some literature data. The inhibition, quantified via $\log \Delta_{N7} = \log K^{M}_{M(DMBI)} - \log K^{M}_{M(MBI)}$, varies for the metal ions and its extent also differs from that observed for N1 (see $\log \Delta_{N1}$; [3]). Further comparisons are possible with the data for $\log \Delta_{Ado}$ (column 8), which are based on the stability constants obtained for $M(MPu)^{2+}$ complexes (MPu = 9-methylpurine).

M^{2+}	$\log K^{M}_{M(DMBI)}$	$\log K^{M}_{M(MBI)}$	$\log \Delta_{N7}$	$\log \Delta_{N1}$ [a]	$\log K^{M}_{M(Ado)}$ [b]	$\log K^{M}_{M(MPu)}$ [b]	$\log \Delta_{Ado}$
Mn^{2+}	-0.10	0.77	-0.87	0.0			
Ni^{2+}	0.17	2.00	-1.83	-1.55	0.4	1.56	-1.2(-1.4)
Cu^{2+}	2.23	3.16	-0.93	-1.43	0.96	1.88	-0.9(-1.2)
Zn^{2+}	0.47	1.57	-1.10	-0.69	0.2	0.9	-0.7(-1.0)

[a] From [3]. [b] From table 5 in [2] (studies of J. Arpalathi and H. Lönnberg). The values given in parentheses for $\log \Delta_{Ado}$ are approximately corrected for the different basicities of N1 ($pK^{H}_{H(Ado)} = 3.86$ versus $pK^{H}_{H(MPu)} = 3.05$) by employing m = 0.33 as slope [1].

Supported by the Swiss Nat. Sci. Found., the Swiss Fed. Office for Educ. & Sci. (COST D1), and the Government of the Czech Republic (COST D1).

[1] H. Sigel, R. B. Martin, et al., *Comments Inorg. Chem.* **13**, 35-59 (1992).
[2] R. B. Martin, *Met. Ions Biol. Syst.* **32**, 61-89 (1996).
[3] L.-n. Ji, N. A. Corfù & H. Sigel, *J.C.S. Dalton Trans.*, 1367-1375 (1991).

122

Anorganische- und Koordinationschemie

Oligobipyridylpyrazine: Neue Liganden für die metallorganische supramolekulare Chemie

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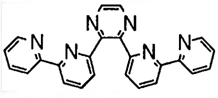
Über das Komplexierungsverhalten von Ligandensystemen, wo zwei Terpyridin-artigen Komplexierungszentren gegeneinander gerichtet sind, ist in der letzten Zeit ausführlich berichtet worden[1]. Bis-η^3-Liganden, die durch eine parallele Anordnung der beiden Bindungsdomänen gekennzeichnet sind, sind weniger untersucht worden[2]. Die Liganden **1** - **3** sind in 4 - 6 Schritten und in guten Gesamtausbeuten erhältlich[3]. In dieser Abhhandlung wird die Darstellung von diesen Liganden und ihren oligomeren Komplexen aus Eisen(II), Cobalt(II/III), sowie aus anderen Übergangsmetallen beschrieben.



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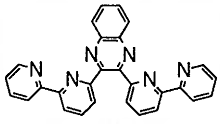

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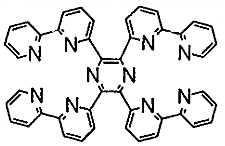

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1 Balzani, V.; Juris, A.; Venturi, M.; Campagna, S.; Serroni, S. *Chem. Rev.* **1996**, *96*, 759.
2 Hanan, G. S.; Arana, C. R.; Lehn, J.-M.; Fenske, D. *Angew. Chem.* **1995**, *107*, 1191.
3 Heirtzler, F. *Manuskript in Vorbereitung.*

123

Anorganische Chemie

Polypropylenimin als Ligand - Vergleich zu Polyethylenimin

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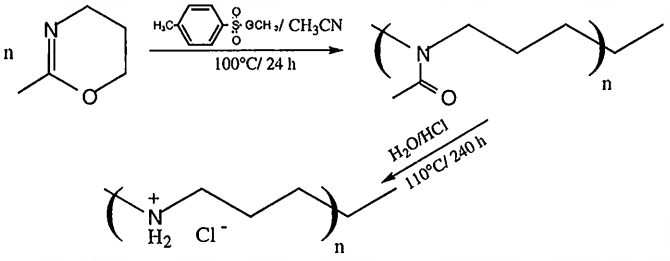
Synthese des Polypropylenimin:



Es wurden Polypropylenimine mit unterschiedlichen Molekulargewichten synthetisiert (n=10 bis n=30).

Die Reaktionsgeschwindigkeit der Polymerisation wurde mit ^{1}H-NMR-Messungen verfolgt. Als Initiatoren wurden Toluol-4-sulfonsäuremethylester und Bortrifluorid-ethyletherat verwendet.

Die Eigenschaften des Polyamins als Ligand für Ni(II) und Cu(II) wurden potentiometrisch und photospektrometrisch untersucht. Die Resultate wurden mit den Eigenschaften von Polyethylenimin als Ligand verglichen

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Anorganische Koordinationchemie

124

Modelling the Enantioselective C=N Hydrogenation of Industrially Relevant Substrates: New Imino and Amino Ir(I) Complexes

Romano Dorta, Antonio Togni
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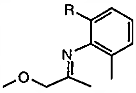
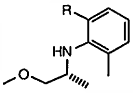
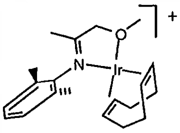
In view of the great commercial importance of the Iridium-mediated enantioselective (e.e. of ca 80%) and highly efficient (TON of up to 1,000,000) catalytic hydrogenation of imines **1a**,**b** to amines **2a**,**b**[1], we pursued the synthesis and characterization of Iridium complexes of **1a** and **2a**. **1a** and **2a** react with $AgBF_4$ in toluene to form the complexes $[Ag(\mathbf{1a})_2]BF_4$ and $[Ag(\mathbf{2a})_2]BF_4$. These transmetallate with $[Ir(COD)Cl]_2$ in CH_2Cl_2 affording [COD Ir **1a**]BF_4 (**3**) and optically active [COD Ir **2a**]BF_4 (**4**), respectively, in good yields. The substitution kinetics of **4** with **1a** to give **3a** has been studied. Compound **4** isomerizes when dissolved in THF: The bidentate ligand **2** in complex **4** adopts an η^6-arene coordination mode affording complex **5** in 82% isolated yield. X-ray studies of **3-5** will be presented.



1a R= CH_3
1b R= CH_2CH_3



2a R= CH_3
2b R= CH_2CH_3



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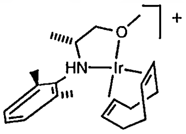

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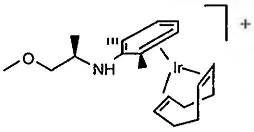

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[1] F. Spindler, B. Pugin, H.-P. Jalett, H.-P. Buser, U. Pittelkow, H.-U. Blaser, *Proceedings of the Conference on Catalysis of Organic Reactions*, Atlanta 1996, to appear in *Chem. Ind.* (Dekker) **1996**, Vol. 63.

Anorganische Koordinationschemie

125

The *fac*-Coordination of 1,4,7-Trithiacyclononane to Different Carbonyl- and Mixed Carbonyl-Nitrosyl-M(I)-Cores (M=Tc, Re)

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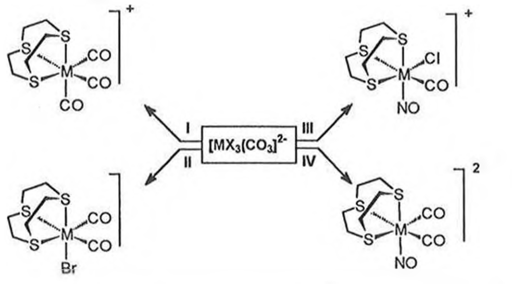
[2]Paul Scherrer Institute, Div. of Radiopharmacy, 5232 Villigen
[3]Institute of Inorg. Chem., University of Tübingen, 72076 Tübingen
[4]Institute of Inorg. Chem., University of Basel, 4056 Basel

$[MX_3(CO)_3]^{2-}$ (M=Tc,Re; X=Cl,Br) was nitrosylated with $NOBF_4$ or oxidized with Br_2 to yield the useful new precursor compounds $[MX_3(NO)(CO)_2]^-$ and $[MX_4(CO)_2]^-$. Subsequent substitution reaction with 1,4,7-trithiacyclononane [9-aneS3] gave novel complexes of the general composition $[MX_k(9\text{-aneS3})(NO)_m(CO)_n)]^{(1+m-k)+}$ (k,m=0,1; n=1,2) which structures could be elucidated. Reaction of $[MX_3(CO)_3]^{2-}$ with [9-aneS3] in water or polar organic solvents leads to known products of the type $[M(9\text{-aneS3})(CO)_3]^+$. All compounds are air stable in the solid state and in solution.



I; [9-aneS3] / MeOH II; i) Br_2 / CH_2Cl_2, ii) [9-aneS3] iii) DMSO Δ
III; i) $NOBF_4$ / CH_2Cl_2 ii) [9-aneS3], IV; $NOBF_4$ / CH_2Cl_2 ii) [9-aneS3] / THF

The complexes were investigated by means of X-ray-, IR- and ^{99}Tc NMR-spectroscopy. The X-ray structures revealed different conformations of coordinated [9-aneS3] depending on the over all charge of the complex and the ligands *trans* to the sulfur atoms.

Anorganische Chemie

126

From molecular wires to reversible cyclometallation

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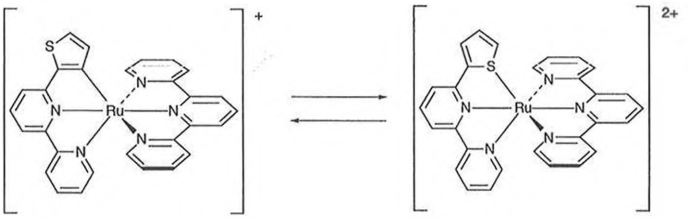
Ligands containing both thiophene and pyridine domains have a rich and useful chemistry. The poster will report studies on the synthesis of polythiophene linked oligopyridines and some aspectes of their coordination behaviour.

A unique reversible cyclometallation system will be described.



127

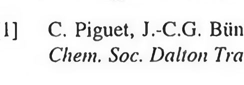
Chimie Minérale et de Coordination

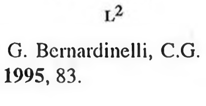
TRIDENTATE LIGANDS WITH CARBOXAMIDE SIDE ARMS FOR THE GENERATION OF ORGANIZED LANTHANIDE BUILDING BLOCKS

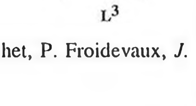
Fabien Renaud,[†] Claude Piguet,[‡] Gérald Bernardinelli,[‡] Jean-Claude G. Bünzli,[§] and Gérard Hopfgartner[†]

[‡] University of Geneva, Dept of Inorganic Chemistry and Laboratory for X-ray Cristallography, CH-1211 Geneva; [§] University of Lausanne, Chemistry Section, CH-1015 Lausanne; [†] Pharma Division, Hoffmann-La Roche, CH-4002 Basel

The tridentate ligand $\mathbf{L}^1$ is well-suited to produce light-converting devices with Ln^{III} (Ln=Eu, Tb) because stable D_3 complexes $[Ln(\mathbf{L}^1)_3]^{3+}$ are readily formed where the three ligands are wrapped around the metal ion. Strong intrastrand stacking interactions between the benzimidazole rings control the size of the cavity leading to promising discriminating effects between lanthanides of different sizes.[1] However, these complexes are only weakly luminescent as a result of internal quenching processes associated with the helical packing of the ligands.[1] Carboxamide groups are expected (i) to display a good affinity for lanthanide metal ions, (ii) to favor Ligand→Ln^{III} energy transfers and (iii) to remove intramolecular stacking interactions. The replacement of the benzimidazole groups of $\mathbf{L}^1$ by N,N'-diethylcarboxamide groups in $\mathbf{L}^2$ leads to stable and luminescent D_3 complexes $[Ln(\mathbf{L}^2)_3]^{3+}$. In these complexes, the wrapping of the ligand around Ln^{III} produces close contacts between the carboxamide side arms which strongly depend on the size of the lanthanide. NMR data show that rapid racemization between the two helical enantiomers occur at room temperature for the large lanthanides (Ln= La-Ce), while this exchange process is blocked on the NMR time scale for smaller ions (Ln = Y, Yb, Lu). Crystal and solution structures are discussed together with the influence of amide and ester groups on the electronic and structural properties of $[Ln(\mathbf{L}^2)_3]^{3+}$ and $[Ln(\mathbf{L}^3)_3]^{3+}$.


$\mathbf{L}^1$


$\mathbf{L}^2$


$\mathbf{L}^3$

[1] C. Piguet, J.-C.G. Bünzli, G. Bernardinelli, C.G. Bochet, P. Froidevaux, *J. Chem. Soc. Dalton Trans*. **1995**, 83.

128

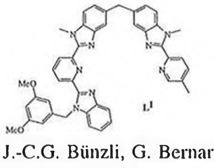
Chimie Minérale et de Coordination

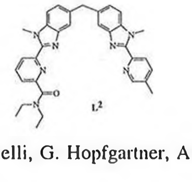
DESIGN OF SELF-ASSEMBLED NON-COVALENT LANTHANIDE PODATES WITH PREDETERMINED STRUCTURAL, PHYSICAL AND MAGNETIC PROPERTIES

Claude Piguet,[‡] Gérald Bernardinelli,[‡] Stéphane Rigault,[‡] Jean-Claude G. Bünzli,[§] and Gérard Hopfgartner[†]

[‡] University of Geneva, Dept of Inorganic Chemistry and Laboratory for X-ray Cristallography, CH-1211 Geneva; [§] University of Lausanne, Chemistry Section, CH-1015 Lausanne; [†] Pharma Division, Hoffmann-La Roche, CH-4002 Basel

The selective introduction of different metal ions into an organized architecture (for the design of functional devices) requires the development of non-symmetrical segmental receptors possessing different binding units coded for one particular metal ion.[1] The application of this principle for the preparation of the heterodinuclear d-f complexes $[LnM(\mathbf{L}^1)_3]^{5+}$ (Ln= La-Eu, M= Fe^{II}, Zn^{II}) leads to only limited selectivity since the aromatic tridentate unit diplays a significant affinity for both 4f and 3d metal ions.[2] The replacement of the terminal benzimidazole group by a N,N'-diethylcarboxamide leads to stable, water-resistant and strongly luminescent self-assembled complexes $[LnZn(\mathbf{L}^2)_3]^{5+}$ because carboxamide groups show a better selectivity for 4f ions. In these complexes the facial *pseudo*-octahedral d-block complex plays the role of a non-covalent tripod which controls the orientation of the remaining tridentate units for their coordination to Ln^{III}. Crystal structures and spectroscopic properties of the new non-covalent podates $[EuZn(\mathbf{L}^2)_3]^{5+}$ and $[LaFe(\mathbf{L}^2)_3]^{5+}$ are presented together with the complete characterization of the thermodynamic assembly processes in solution. The Fe^{II} ion in $[LnFe(\mathbf{L}^2)_3]^{5+}$ diplays unusual magnetic properties associated with a spin-crossover behaviour which can be controlled by the nature of the lanthanide.


L^1


L^2

[1] C. Piguet, J.-C.G. Bünzli, G. Bernardinelli, G. Hopfgartner, A.F. Williams, *J. Alloys and Compds* **1995**, *222*, 324.
[2] C. Piguet, E. Rivara-Minten, G. Hopfgartner, J.-C.G. Bünzli, *Helv. Chim. Acta* **1995**, *78*, 1541, 1651.

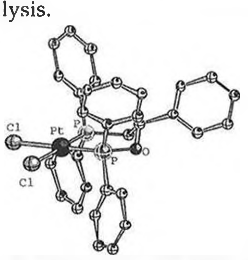
Anorganische Chemie / Koordinationschemie

129

An *Electronically Asymmetric* Bidentate Ligand for Enantioselective Catalysis: POP

Christof Brändli, Melanie Pilkington, Hans-Beat Bürgi and Thomas R. Ward
Chemistry Department, University of Berne, 3000 Berne 9

Electronically asymmetric ligands incorporating **P^N, P^S, P^O** donors have attracted much attention recently.[1-4] With such systems, a delicate interplay between steric and electronic effects determines enantioselection.[5] Chiral bidentate ligands incorporating phosphine and phosphinite donor sites are, to our knowlege, nonexistent. We have designed such a bidentate ligand, abbreviated **POP**, and report its coordination properties to late transition metals. Upon coordination, the chelate can be regarded as "achiral", thus allowing to investigate in detail the interplay between steric and electronic cooperativity in enantioselective catalysis.



1)Sprinz, J.; Helmchen, G. *Tetrahedron Lett.* **1993**, *34*, 1769. 2)Frost, C. G.; Williams, J. M. J. *Tetrahedron Lett.* **1993**, *34*, 2015. 3)Brown, J. M.; Hulmes, D. I.; Guiry, P. J. *Tetrahedron* **1994**, *50*, 4493. 4)Matt, P. v.; Pfaltz, A. *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 566. 5)Togni, A.; Burckhardt, U.; Gramlich, V.; Pregosin, P. S.; Salzmann, R. *J. Am. Chem. Soc.* **1996**, *118*, 1031.

Anorganische Chemie

130

Chemie und Reaktivität des $[W(NO)_2(dm\text{-}pybox)]^{2+}$-Fragmentes

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Universität Zürich, Anorganisch-Chemisches Institut,
Wintherthurerstrasse 190, CH-8057 Zürich

Lewis-saure Übergangsmetallkomplexe vermögen eine Vielzahl von organischen Reaktionen zu katalysieren. *Hersh*[1] zeigte, dass auch elektronenreiche Metallzentren wie Wolfram durch den Einsatz von Nitrosyl-Liganden und Liganden mit harten Donor-Atomen elektrophilen Charakter entwickeln können.

$$W(CO)_6 \xrightarrow[\text{(S)}]{\text{a) 2 Me}_3\text{NO, dm-pybox; b) 2 [NO](Y)}} [W(NO)_2(\text{dm-pybox})(S)](Y)_2$$

(1) $Y = BF_4, PF_6, SbF_6$
$(S) = EtCN, MeNO_2$

Der Solvenskomplex $[W(NO)_2(\text{dm-pybox})(S)](Y)_2$ ($S = EtCN, MeNO_2$; $Y = BF_4, PF_6, SbF_6$; dm-pybox = 2,6-Bis[4',4'-dimethyloxazolin-2'-yl]-pyridin) **1** konnte in einer zweistufigen Reaktion «in situ» hergestellt und spektroskopisch charakterisiert werden. Im Gegensatz zur von *Faller et al.*[2] beschriebenen organometallischen Lewis-Säure $[W(NO)_2(HCpy_3)(MeCN)](SbF_6)_2$ mit einem tripodalen N-Donor steht in Verbindung **1** das Solvensmolekül in trans-Position zu einer der beiden Nitrosylgruppen, was eine erhöhte σ- und π-Accidität erwarten lässt.
Die koordinationschemischen Eigenschaften und die Reaktivität des $[W(NO)_2(\text{dm-pybox})]^{2+}$-Fragmentes wurden untersucht. Die Röntgenstruktur des Halogenderivates $[W(NO)_2(\text{dm-pybox})(Cl)](SbF_6)$ konnte ermittelt werden.

(1) Hersh, W.H. *J. Am. Chem. Soc.* **1985**, *107*, 4599
(2) Faller, J.W.; Ma, Y. *J. Am. Chem. Soc.* **1991**, *113*, 1579

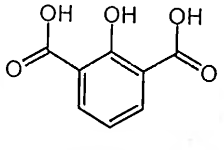
131

Chimie minérale et de coordination

A planar oxo matrix for binding transition metals

Alain Klose, Euro Solari and Carlo Floriani*, Institut de Chimie Minérale et Analytique, Université de Lausanne, BCH, 1015 Lausanne.

Designing buildings blocks for bi- and tri-dimensional arrays of oxygen atoms suitable for binding transition metals is particularly challenging. In this perspective we used the anion derived from the 2-hydroxyisonaphthalic acid, which has a rigorously planar geometry as shown by the X-Ray structure.



2-hydroxyisonaphthalic acid

The complexation of transition metals can be achieved using either the free acid or as the lithium or potassium salt. In the first approach clean products are obtained by reacting homoleptic aryl metals compounds with the free acid. This complexation reaction has been carried out with the following species: $[Fe_2(mes)_4]$, $[Mn_3(mes)_6]$, $[V(mes)_3(thf)]$ in the correct stoichiometry. Using the second approach an analogous vanadyl ion species was found by reacting the potassium salt with the $VOSO_4$ starting material. In both cases we were able to form the same polymeric layered species. A crystal structure and magnetic properties will be presented.

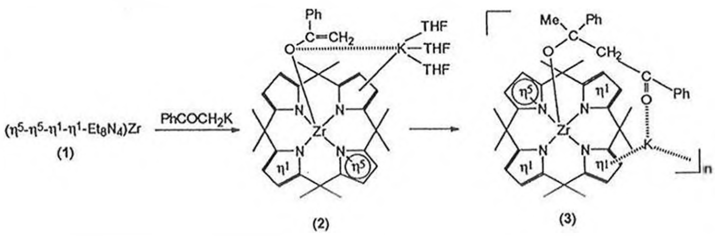
132

Chimie minérale et de coordination

Bifunctional carrier of alkali enolates: a novel approach to catalyzed aldol condensation

Giovanna Solari, E. Solari and C. Floriani* Institut de Chimie Minérale et Analytique, Université de Lausanne, BCH, 1015 Lausanne Switzerland.

The meso-octaalkylporphyrinogen-Zirconium (**1**), exemplifies the structural features of a bifunctional compound having in its structure two complementary reactive sites, which can assist the transformation of an organic substrate.
The ability of (**1**) to carry polar organometallics has been applied to the Zirconium-assisted enolate chemistry, with the added advantage that the porphyrinogen skeleton adapts its bonding mode depending on the electron request of the metal.
The following scheme summarizes the assistance of (**1**) in the aldol condensation reaction:



The displacement of the aldol adduct in (**3**) by the starting K-enolate is the key step towards the use of (**1**) as bifunctional catalyst.

CHIMIA 50 (1996) Nr. 7/8 (Juli/August)

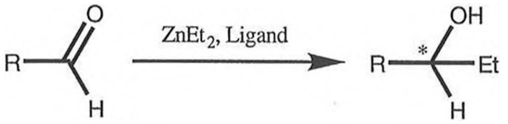
133

Chimie minérale et de coordination

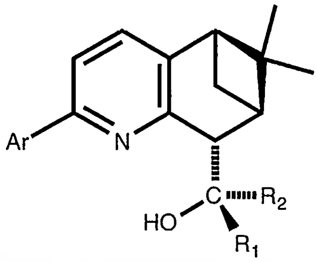
Synthesis and Use of Pyridyl-Alcohols in Asymmetric Catalysis

Philippe Collomb, Stefan Rupprecht and Alex von Zelewsky
Institut de Chimie Inorganique et Analytique, Université de Fribourg,
CH-1700 Fribourg

Optically active nitrogen / oxygen ligands have a broad use in various enantioselective catalytic reactions, including the addition of diethylzinc to aldehydes[1].



The optically active precursor for the synthesis of the catalysts is the inexpensive (-)-α-pinene[2]. The synthesis of the ligands and the results of the catalytic reactions will be presented.



Ar = phenyl, 2-pyridyl

R_1, R_2 = aryl, alkyl

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[1] A. Togni, L. M. Venanzi, *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 497.
[2] P. Hayoz, A. von Zelewsky, *Tetrahedron Lett.* **1992**, *33*, 5165.

Anorganische Chemie

134

Characterization of Iron Oxides used in the Reduction of Aromatic Nitro Compounds with Hydrazine Hydrate

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Aromatic amines are widely used as antioxidants, dye intermediates, as intermediates for photographic, pharmaceutical, and agricultural chemicals, and polyurethanes (via isocyanates). They are generally obtained by the reduction of nitroarenes. A promising alternative to the reduction with iron or sulfides is the reduction with hydrazine hydrate in the presence of iron oxide. Apart from the advantage of harmless co-products, hydrazine hydrate has the advantage that it does not reduce other groups, e.g., -OH, -OR, halogen, or azo groups.

In this work, several iron oxides were prepared by precipitation reactions and characterized by means of XRD, Mössbauer spectroscopy, and nitrogen adsorption measurements. Also supported iron oxides were prepared and characterized with the aim to increase activity, avoid deactivation by particle agglomeration and improve the filtration procedure.

Measurements of the kinetics of the reduction of 4-nitrotoluene were carried out in a jacketed thermostated vessel. Analysis was performed by GC. Except for 4-toluidine, no other products were observed. The rate constants were determined by fitting zero-order rate law. Supported catalysts were prepared by incipient wetness impregnation of silica with ammonium iron(III)citrate and subsequent thermal treatment in air at 300°C for 3h.

A reddish-brown precipitate formed by rapid hydrolysis of Fe(III)chloride solutions was found to be the most effective catalyst. Mössbauer spectroscopy showed this precipitate to be ferrihydrite ($Fe_5HO_8*4H_2O$). The high activity of this catalyst was concluded to be due to its high BET surface area (250 m^2/g) compared to other iron oxides. Mössbauer spectra of ferrihydrite reduced with hydrazine hydrate showed an increase in particle size and a small amount of Fe_3O_4. This new phase was tentatively assigned to a surface layer of Fe_3O_4. Under special conditions the catalyst showed deactivation mainly due to formation of α-Fe_2O_3. Iron oxides supported on silica showed an increase in activity that is comparable to that of ferrihydrite.

135

Anorganische Chemie

Darstellung und Reaktivität von Phosphordonor-substituierten trans-Carbinhydridwolfram-Komplexen

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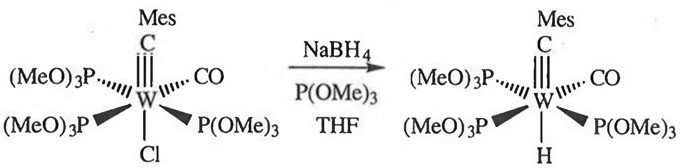
Wasserstoff-Substituenten in trans-Position zu einem mehrfach gebundenen Liganden lassen eine starke Aktivierung der Metall-Hydrid-Bindung bezüglich Insertionen und Carbonyl-Reduktionen erwarten.

Aus diesem Grund, um neue aktivierte Uebergangsmetallhydride herzustellen, wurde angestrebt, den synthetischen Zugang zu Carbinhydrid-Komplexen zu entwickeln. Für dieses Vorhaben wurden in Analogie zu trans-Nitrosylhydridwolfram-Komplexen Darstellungsmethoden mit Natriumborhydrid [1]-[3] in Betracht gezogen. Ausgehend von Carbinchloridwolfram-Verbindungen wurde deshalb versucht, isoelektronische Carbinhydrid-Komplexe darzustellen (Beispiel siehe Gleichung).



Die Umsetzungen weiterer Carbinchlorid-Verbindungen, sowie die Reaktivität der Produkte, wird beschrieben.

[1] H. Berke, P. Kundel, Z.Naturforsch., **B 1986**, *41*, 527
[2] G. L. Hillhouse, B. L. Haymore, Inorg.Chem. **1987**, *26*, 1876
[3] A. A. H. van der Zeijden, C. Sonntag, H. W. Bosch, V. Shklover; H. Berke, D. Nanz, W. von Philipsborn, Helv. Chim. Acta, **1991**, *74*, 1194

Computational Chemistry

136

Theoretical Study of the Structure and Reactivity of the $[Mo_3S_7]^{4+}$ Cluster and its Derivatives

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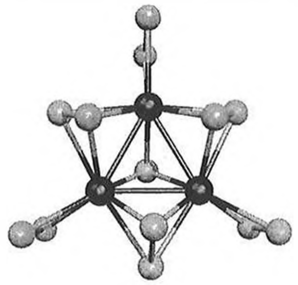
Calculations based on Density Functional (DF) and Extended-Hückel (EH) Theories have been performed on the $[Mo_3S_7]^{4+}$ core and its charged and neutral derivatives: $[Mo_3S_{13}]^{2-}$ (**1**), $[Mo_3S_7Cl_6]^{2-}$, $[Mo_3S_7(dtc)_3]ClO_4$ and $[Mo_3S_7(dtc)_3]Cl$ (where $dtc^- = (C_2H_5)_2NCS_2^-$). The purpose of the study was to rationalize the structure and reactivity of these complexes.



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The selectivity of the nucleophilic substitution reaction in the cluster core and the nature of the bonding in neutral compounds turned to be the central problems of our research. In particular, ligand substitution, sulfur elimination and anion binding have been investigated on a qualitative basis using the EH model and quantitatively using DF theory. Both approaches have been shown to be complementary and to lead to a coherent interpretation of the experimental results obtained for these systems.[1]

[1] M.D. Meienberger, K. Hegetschweiler, H. Rüegger and V. Gramlich, *Inorg. Chim. Acta* **213**, 157 (1993)

Chimie computationelle

137

The Structure of Transition States and Intermediates Formed in the Water-Exchange of the Hexa Aqua Ions of Scandium(III) through Zinc(II).

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The mechanism for the water-exchange reaction with the transition metal aqua ions from Sc^{III} through Zn^{II} has been investigated. The exchange mechanisms are analyzed on the previously reported model (Rotzinger, F. P. *J. Amer. Chem. Soc.* **1996**, in press.) that involves the metal ion with six or seven water molecules. The structures of the reactants/products, transition states and penta or hepta coordinated intermediates have been computed with Hartree-Fock or CAS-SCF methods. Each type of mechanism, associative, concerted or dissociative, proceeds via a characteristic transition state. The calculated activation energies agree with the experimental $\Delta G^{\ddagger}_{298}$ values, and the computed structural changes indicate whether an expansion or compression takes place during the transformation of the reactant into the transition state. These changes are in perfect agreement with the changes deduced from the experimental volumes of activation. The dissociative mechanism is always feasible, but it is the only possible pathway for high-spin d^8, d^9 and d^{10} systems. In contrast, the associative mechanism requires that the transition metal ion does not have more than seven 3d electrons. Thus, Sc^{III}, Ti^{III} and V^{III} react via the A, Ni^{II}, Cu^{II} and Zn^{II} via the D (or I_d) mechanism, whereas all pathways are feasible for the elements in the middle of the periodic table.

138

Computerunterstützte Chemie

Quantum-chemical calculations of harmonic and anharmonic force fields of small reactive molecules

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The equilibrium structures and the harmonic and anharmonic force fields of small reactive molecules have been determined by means of quantum-chemical ab initio calculations at different theoretical levels (SCF, MP2, CCSD, CCSD(T)) employing large polarized basis sets (TZ2Pf, cc-pVTZ, cc-pVQZ). The ab initio predictions for the rovibrational parameters have been used to facilitate the spectroscopic identification of the corresponding short-lived molecules and to guide the analyses of their high resolution infrared spectra. Applications that will be discussed include FCCF, F_2CC, $CH_2{=}SiH_2$, and related species.

139

Modeling of Lithium Thin-Film Electrochemical Cells

E. Deiss, Cl. A. Daul, J.-L. Barras

May 31, 1996

The energy density of a graphite/$LiMoO_2$, a graphite/$LiNiO_2$ and a graphite $LiMn_2O_4$ has been calculated from first principles for Li_xMoO_2 ($0 \leq x \leq 1$), Li_xNiO_2 ($0 \leq x \leq 1$) and $Li_xMn_2O_4$ ($0 \leq x \leq 2$). For each of these systems, the unit cell has been optimized and the reaction free energy has been integrated with reference to the graphite electrode. All the results are in good agreement with experimental data. We used density functional theory (Perdrew-Wang) and a linearized augmented plane waves basis set; this method is implemented in the WIEN95 package. The temperature dependence of this free energy has been calculated in the harmonic approximation.

Particular attention has been focused on maganese oxydes for obvious economical and environmental reasons. First principles calculations of the electrical conductivity, the optimization of the atomic positions and some substitution impurities have been achieved.

140

Computerunterstützte Chemie, Chemische Forschung

Calculation of water sorption in polymers

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Swiss Federal Institute of Technology, CH-8092 Zurich, Switzerland

The technological properties of many polymers are highly influenced by their ability to absorb small molecules. An example is polyamide 6 that takes up about 10 % water in moist environment accompanied by a drastic change in mechanical behaviour. To understand the underlying effects we have carried out an atomistic study on the solution thermodynamics of water in various amorphous polymers. By applying a combination of the thermodynamic integration and the Widom's insertion method we calculate the excess chemical potential of water in dense polymer matrices containing different number of water molecules. The comparison of these results to the excess chemical potential of water calculated for a pure water system gives an estimation of the water sorption behaviour of the polymer under investigation. Our results show clearly that amorphous polyamide 6 is able to absorb water up to high water content. In contrast amorphous polyamide 12 is not able to take up more than 2 % water in our simulations. Both results are in good agreement with experimental studies that measure the saturated water content of semi-crystalline polyamide 6 and polyamide 12 to 9.5 weight-% and 1.6 weight-%, respectively. Further simulations taking bisphenol-A-polycarbonate and polyvinylalcohol indicate that our method is appropriate to calculate the sorption behaviour of dense polymer. Since we investigated polymers exhibiting different sorption behaviour and we used no restrictions specific to water, a transfer of the method to other systems containing small molecules in polymer matrices is feasible.

CHIMIA 50 (1996) Nr. 7/8 (Juli/August)

Computational Chemistry **141**

Benzene-O_2 interaction potential from DFT calculations.

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The interaction potential in the $O_2..C_6H_6$ complex has been studied by means of two types of DFT based methods: the Kohn-Sham (KS) [1] equations and the "freeze-and-thaw" cycle of Kohn-Sham Equations with Constrained Electron Density (KSCED)[2]. Two different gradient dependent approximate exchange-correlation functionals (PW86/P86 [3] and PW91[4]) have been used in KS calculations. For the sake of comparison, MP2 calculations have also been performed. The KS calculations suffer from a large (1.0 kcal/mol) basis set superposition error (BSSE) which is of the order of the interaction energy and which is significantly larger than that in the MP2 calculations (0.3kcal/mol).

In the KSCED calculations, the PW91 exchange-correlation functional and the LC [5] kinetic energy functional have been used. The molecular fragments (ρ_1 and ρ_2) correspond to the benzene and the O_2 molecule. The BSSE is largely eliminated in KSCED calculations. The KSCED results are in better agreement with the MP2 ones than results obtained by means of KS calculations.

[1] W. Kohn and L.J. Sham (1965) Phys.Rev., **140**, A1133
[2] T.A.Wesolowski and J.Weber (1996) Chem.Phys.Lett, **248**, 71
[3] J.P. Perdew (1986) Phys. Rev. **B33**, 8822; *ibid* **B33**, 8800
[4] J.P. Perdew and Y. Wang in *Electronic Structure of Solids*'91, ed. P.Ziesche and H.Eschrig (Academie Verlag, Berlin, 1991), p. 11
[5] A. Lembarki and H. Chermette (1994) Phys.Rev. A,**50**, 5328

Computational Chemistry **142**

Accuracy of Approximate Kinetic Energy Functionals in the Model of Kohn-Sham Equations with Constrained Electron Density: the FH...NCH Complex as a Test Case.

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Ground-state properties of a linear hydrogen-bonded FH...NCH complex are studied by means of the "freeze-and-thaw" cycle of Kohn-Sham Equations with Constrained Electron Density (KSCED) [1]. For several geometries of the complex, the electron density and the total energy are compared to the ones obtained by means of the standard Kohn-Sham calculations. The comparisons are made to assess the accuracy of several gradient dependent approximate kinetic energy functionals applied in the KSCED equations. It is found that the closest results to the Kohn-Sham ones are obtained using the functional whose analytical form was proposed by Perdew and Wang for exchange energy [2] and parametrized by Lembarki and Chermette for kinetic energy [3]. In the region of the minimum of the interaction energy as well as for larger intermolecular distances, the "freeze-and-thaw" cycle of KSCED leads to a potential energy surface very similar to that of standard supermolecule Kohn-Sham calculations.

[1] T.A.Wesolowski and J.Weber (1996) Chem.Phys.Lett, **248**, 71
[2] J.P. Perdew and Y. Wang in *Electronic Structure of Solids*'91, ed. P.Ziesche and H.Eschrig (Academie Verlag, Berlin, 1991), p. 11
[3] A. Lembarki and H. Chermette (1994) Phys.Rev. A,**50**, 5328

Chimie Computationel **143**

A Density Functional study of magnetic coupling parameters: The nonempirical calculation of the ESR parameters of low spin planar Cobalt(II) complexes

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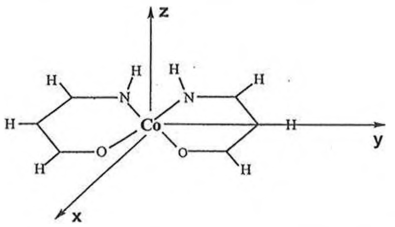
Evert Jan Baerends
Theoretical Chemistry Department, Vrije Universiteit, De Boelelaan 1083, NL-1081 HV Amsterdam, The Netherlands.

There is currently considerable interest in the calculation of magnetic coupling parameters and of ESR tensors in particular [1]. We present a first principle calculation of the Zeeman splitting (*g*-tensor) and of the hyperfine and superhyperfine (*A*)-tensors of the title compound (cf. Fig). The calculations will be performed using the Amsterdam Density Functional (ADF) package [2]. Various factors that affect the accuracy of the calculated ESR parameters are currently explored and will be discussed.



[1] V.G. Malkin, O.L Malkina, L.A. Eriksson and D.R. Salahub in Density Functional Calculations, Vol. 1 of Theoretical and Computational Chemistry; P. Politzer and J.M. Seminario, Eds., Elsevier, Amsterdam, The Netherlands, 1995
[2] E.J. Baerends, D.E. Ellis and P. Ros, Chem. Phys. 2:42, 1973
E.J. Baerends and P. Ros, Int. J. Quant. Chem. S12:169, 1978

144

Computational chemistry

A Density Functional (DF) Study on the Mechanism of Exchange in some Copper(II) Complexes

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University of Fribourg, Pérolles
CH-1700 Fribourg

The understanding of the mechanism of exchange coupling is very important in the perspective of the design of molecular ferromagnets. Therefore, we investigated on a non-empirical basis two compounds that exhibit exchange interaction in a different way.

On the one hand, we can consider two paramagnetic metal ions which are bridged by formally diamagnetic atoms, or groups of atoms. $[Cu_2Cl_6]^{2-}$ has been chosen as a relevant example of molecules which show this so-called superexchange.

On the other hand, direct exchange interactions can be studied in systems in which a transition metal ion is directly bound to a stable organic radical. We investigated a simplified model of $Cu(tfac)_2 \cdot NITMe$ [1], which shows a rather large ferromagnetic coupling of 65 cm^{-1}.

The relationship between the observed coupling and the electronic structure is discussed on the basis of DF calculations. The obtained results give also an indication of the accuracy and the predictive character of modern calculation techniques.

[1] A. Caneschi, D. Gatteschi, A. Grand, J. Laugier, L. Pardi, P. Rey, *Inorg. Chem.* **1988,** *27*, 1031

145

Chimie informatique

Density Functional Calculations on Organometallic Pt(II) Compounds: Molecular Structure and Some Excited States

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[b] Institut für Anorganische und Physikalische Chemie, Universität Bern, CH-3000 Bern

Coordination compounds of Pt(II) are the subject of extended experimental investigations. The photochemical properties of cyclometallated Pt(II) complexes are thereby of special interest because of their possible use as photosensitizers. Chemical modifications such as variations of the ligand or the substituents play an important role in this context.

In order to describe ground and excited state properties of some Pt(II) compounds [1,2] quantitatively, we performed first principle calculations, based on Density Functional Theory (ADF 1.1.4).
As results, we will show the modellized molecular structure of the ground state and the transition energies for some low lying excited states of substituted $Pt(thpy)_2$ compounds (thpy=2-thienylpyridine) and related complexes. The calculation models are compared to results from X-Ray structure analysis and optical spectroscopy.

[1] M. Gianini, A. Forster, P. Haag, A. v. Zelewsky, H. Stoeckli-Evans, *Inorg. Chem.*, submitted
[2] A. C. Stückl, *Thesis*, Regensburg 1993

146

Computational Chemistry

Calculation of Chiroptical Properties of Coordination Compounds

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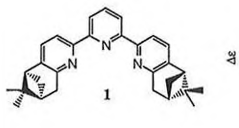
Université de Fribourg, Pérolles, 1700 Fribourg

CD-spectra can be used for the determination of the absolute configuration of chiral coordination compounds. Simple models such as the *exciton theory* where the absolute configuration can be determined by treating the non-interacting chromophores as charge dipoles can be successfully applied even to extended polynuclear metal complexes. For CD-spectra calculation of complexes with chiral ligands, we have developed a computer program (Fortran) that allows us to determine R-values from first principles taking result files from ZINDO[1] (INDO/1 hamiltonian) or ADF [2] (Amsterdam Density Functional package) as the only input.
Reasonable agreement between calculated and experimental spectra has been obtained for a number of metal complexes, such as Λ-/Δ-$Ru(bpy)_2(py)_2$, for metal complexes with the chiral terpyridine ligand **1**,[3] and also for organic molecules such as *M*-helicene[6].



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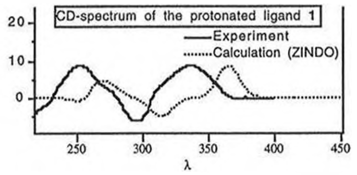

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[1] Anderson, W.P., Cundarai, T.R., Drago, R.S., Zerner, M.C., *Inorg. Chem.* **1990**, *29*, 1.
[2] te Velde, G., Baerends, E.J., *J. Comp. Phys.* **1992**, 99, 84.
[3] see poster by M. Ziegler, P. Belser, V. Monney and A. von Zelewsky

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147

Computerunterstützte Chemie

Thermoelastic Properties of Cellulose-Iβ

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Institut für Polymere, Departement für Materialwissenschaften, ETH Zürich

Composite materials are important both in natural and in technological structures. The understanding of their elastic behaviour is therefore of great theoretical and practical interest. Any analytical or numerical modeling of the elasticity needs information about the morphology and the complete matrix of the elastic constants of the constituent domains of the composite.

In the present work, the tensor of the elastic constants, *C*, of cellulose-Iβ, which is an important structural material in wood, cotton etc. was calculated from atomistic microcrystals using a fluctuation formula containing the strain ε and stress σ acting on the simulation cells:

$$C_{iklm} = \langle \varepsilon_{ik}\sigma_{nj} \rangle \langle \varepsilon_{nj}\varepsilon_{lm} \rangle^{-1}.$$

(The summation convention is applied for indices occuring twice).

A crystal of cellulose-Iβ of twice the size of a unit cell in each dimension - with 672 atoms in 8 chains - was built. An infinitely extended body was simulated through periodic continuation conditions and bonds across boundaries. To determine the thermoelastic behaviour, constant-stress Molecular-Dynamics simulations were performed at 150, 325 and 400 K. The highly charged groups of cellulose made an Ewald summation of the coulombic interactions necessary. A trajectory of 250 ps was used to calcuulate the matrices of the elastic constants.

Elastic constants at 150 K

$$\begin{bmatrix} \mathbf{19.4} & \mathbf{15.2} & \mathbf{6.8} & 0.2 & -0.1 & \mathbf{-1.2} \\ \mathbf{15.2} & \mathbf{37.0} & \mathbf{14.3} & -0.4 & 0.2 & \mathbf{-0.3} \\ \mathbf{6.8} & \mathbf{14.3} & \mathbf{158.3} & 0.0 & 0.1 & \mathbf{0.9} \\ 0.2 & -0.4 & 0.0 & \mathbf{7.2} & \mathbf{-0.4} & 0.0 \\ -0.1 & 0.2 & 0.1 & \mathbf{-0.4} & \mathbf{2.1} & -0.2 \\ \mathbf{-1.2} & \mathbf{-0.3} & \mathbf{0.9} & 0.0 & 0.2 & \mathbf{4.4} \end{bmatrix}$$

Elastic Constants at 325 K

$$\begin{bmatrix} \mathbf{17.2} & \mathbf{12.9} & \mathbf{6.8} & -0.1 & 0.1 & \mathbf{-0.5} \\ \mathbf{12.9} & \mathbf{34.3} & \mathbf{14.7} & 0.1 & 0.0 & \mathbf{-0.5} \\ \mathbf{6.8} & \mathbf{14.7} & \mathbf{162.0} & 0.1 & 0.0 & \mathbf{0.9} \\ -0.1 & 0.1 & 0.1 & \mathbf{5.0} & \mathbf{-0.2} & -0.1 \\ 0.1 & 0.0 & 0.0 & \mathbf{-0.1} & \mathbf{2.1} & 0.0 \\ \mathbf{-0.5} & \mathbf{-0.5} & \mathbf{0.9} & -0.1 & 0.0 & \mathbf{3.8} \end{bmatrix}$$

148

Organische Chemie

Regio- and Enantiocontrol in Palladium-Catalyzed Allylic Substitutions

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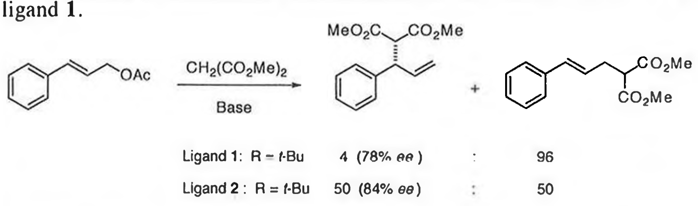
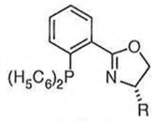
Chiral diphenylphosphino-oxazolines **1** have proven to be effective catalysts in the palladium-catalyzed allylic substitution reaction of symmetrically substituted allyl systems such as 1,3-diphenylpropenyl acetate [1]. Unfortunately, in analogous reactions of monosubstituted allylic acetates only small amounts of the desired chiral regioisomer have been obtained using ligand **1**.



We have found that the regioselectivity is strongly influenced by the electronic nature of the coordinating phosphorus atom. With ligand **2** which has a less electron-rich phosphorus atom the ratio of regioisomers could be shifted toward the chiral isomer. Further ligand variation has led to biarylphosphite-oxazoline ligands of type **3** which give even higher ratios of the chiral isomer and moderate to excellent enantioselectivities.



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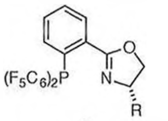

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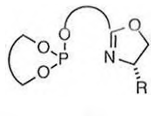

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[1] P. von Matt, A. Pfaltz, *Angew. Chem.* , **1993**, *105*, 614. P. von Matt, O. Loiseleur, G. Koch, A. Pfaltz, C. Lefeber, T. Feucht, G. Helmchen, *Tetrahedron: Asymmetry*, **1994**, *5*, 573. G. J. Dawson, C. G. Frost, J. M. J. Williams, S. J. Coote, *Tet. Lett.*, **1993**, *34*, 3149.

Organische Chemie **149**

New P-Chiral Diphosphines in Enantioselective Catalysis

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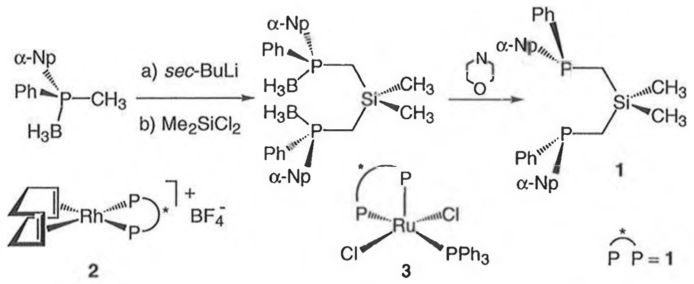
[a] LAC, ETHZ, 8092 Zürich, [b] Central Research Services, Ciba, 4002 Basel

Although general synthetic methods for P-chiral diphosphine ligands have become available lately, reports of catalytic applications of such ligands are still rare.[1] Thus, we prepared the new P-chiral ligand (*S,S*)-**1** and briefly investigated its ruthenium(II) and rhodium(I) coordination chemistry.



Z-α-Methylacetamidocynnamate is hydrogenated to (*R*)-*N*-acetylphenylalanin methylester in 86% e.e. with **2** as catalyst precursor, while **3** is active in the hydrogenation of pentane-2,4-dione to (*S,S*)-pentane-2,4-diol with up to 56 % e.e..

References

1 a) Jugé, S. *et al. Phosphorus, Sulfur, and Silicon*, **1993**, *77*, 199. b) Muci, A. R.; Campos, K. R.; Evans, D. A. *J. Am. Chem. Soc.*, **1995**, *117*, 9075. c) Genêt, J. P. *et al. Tetrahedron: Asymmetry*, **1994**, *5*, 665. d) Genêt, J. P. *et al. ibid.*, **1994**, *5*, 675.

Organic Chemistry **150**

Radical Cyclization Reactions with Chiral Cyclohexadienes Derived from Sequential Additions to Tricarbonyl Chromium Arene Complexes

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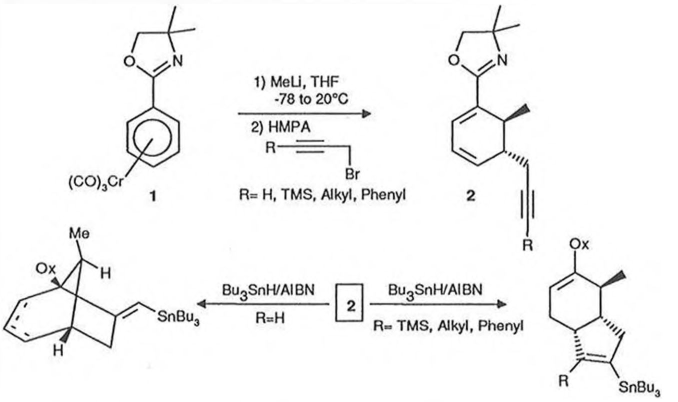
The *trans*-substituted cyclohexadienes **2** are readily obtained by a sequential C-nucleophile/C-electrophile addition to the tricarbonyl chromium arene complex **1**[1] and methodology has been developed to carry out this sequence to give highly enantioenriched compounds.[2] In this communication, we focus our attention on the transformation of the alkynyl moiety to generate a vinylic radical and the regioselectivity of the ensuing cyclization to the diene system. The preliminary results show that, depending on the starting material, different 5 *exo*-trig processes take place.



[1] E.P. Kündig, A.Ripa, R. Liu, G. Bernardinelli, *J. Org. Chem.*, **1994**, *59*, 4773 and ref. cited.

[2] D. Amurrio, K. Khan, E.P. Kündig, *J. Org. Chem.*, **1996**, *61*, 2258.

Organic Chemistry **151**

Synthesis of New Photo- and Thermochromic Systems Based on Cyclic Double Bond Shifts in Heptalenes

Sarah El Houar and Hans-Jürgen Hansen

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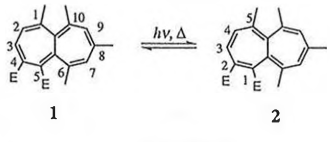
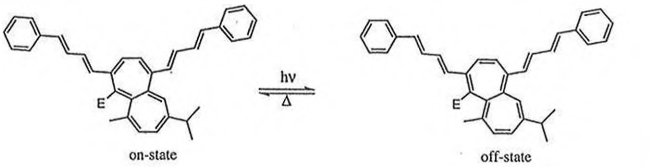
Heptalenes such as **1** and **2** are interconvertible by cyclic double bond shift which may be induced thermo- or photochemically. With appropriate conjugative substituents at position 1 and 4 in **1** there should exist an extended conjugation between both these substituents *via* the *s-cis*-butadiene subunit (C(1)-C(4)) of the heptalene π-skeleton. This extendend conjugation should be destroyed on thermal or photochemical double bond shift to a corresponding compound of type **2**. The conversion of **1** to **2** will therefore correspond to a negative thermo- or photochromism which will become positive for the reverse double bond shift **2**→**1**.



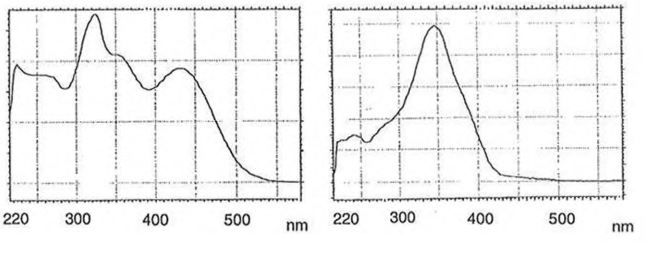
1 **2**

E = $COOCH_3$

To test these predictions and new type of thermo- and photochromism, we have synthetized the double bond shift isomers **3**/**4** starting from dimethyl 9-isopropyl-1,6-dimethylheptalene-4,5-dicarboxylate. Indeed, **3** shows an intense absorption band at 433 nm which is not present in **4**. Irradiation of **3** at 438±10 nm converts it into **4** which on standing at 25°, slowly rebuilds **3**.



on-state **3**   off-state **4**

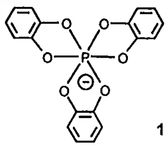


Organic and Inorganic Chemistry **152**

Synthesis and Applications of Enantiopure Hexacoordinated Phosphate Anions.

J. Lacour, C. Ginglinger, A. Londez
Département de Chimie Organique, Université de Genève, CH-1211 Genève

The octahedral geometry of pentavalent hexacoordinated phosphorus compounds allows the formation of chiral anions by complexation of the phosphorus with three bidentate ligands.[1] Tris(benzenediolato)phosphate anion **1**, easily prepared in one step from catechol, PCl_5 and an amine, is configurationally labile in solution.[2]



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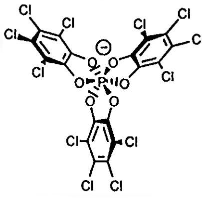

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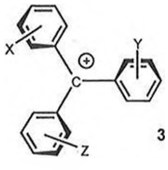

3

Herein, we report that introduction of electron-poor substituents on the chelate rings render the spirophosphate anion configurationally stable, *e.g.* tris(tetrachlorobenzenediolato)phosphate anion **2** (or TRISPHAT).

Complex of TRISPHAT and triarylcarbenium salts are readily available. The selectivity of the interaction between these two chiral molecular propellers (Δ-Λ or Δ-Δ) will be discussed.

[1] D. Hellwinkel, *Angew. Chem.* **1965**, *77*, 378-9.

[2] M. Koenig, A. Klaebe, A. Munoz, R. Wolf, *J. Chem. Soc., Perkin Trans. 2* **1979**, 40-4.

Chimie Organique **153**

Stereoselective catalytic Michael addition of a chiral Iminoglycinate

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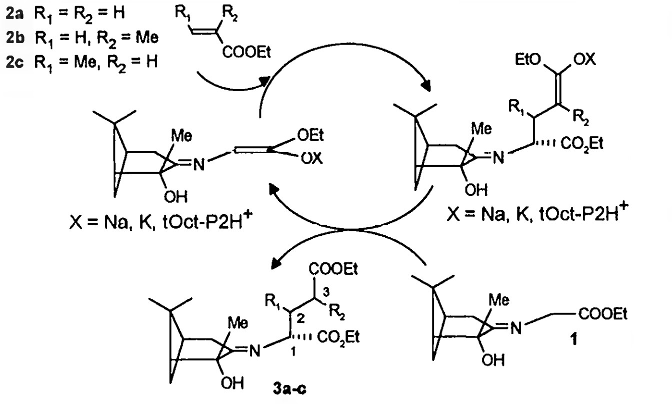
Clean (no trace of auto-condensation or other side products), highly *R*-diastereoselective (80-90% d.e.) and high yielded (80-95%) Michael additions have be performed with activated double bonds on chiral (*RRR*)-iminoglycinate 2 using catalytic amounts of base (NaH, KH or tOct-P2).



$R_1 = R_2 = H$ I(1S) / II(1R) = 10/90.
R_1 = Me, R_2 = H only 2 diastereomers over the 4 possible : I(1S,2 ?) / II(1R,2S) = 13/87
R_1 = H, R_2 = Me 3 diastereomers : I(1S) / II(1R,3R and 1R,3S) = 7/61,42

Application to methylcrotonate led to 87% of the (*RRR,1R,2S*) diastereomer in accord with a *substrate-directed approach* on a monomeric enolate.

Organische Chemie **154**

Synthese, Struktur und Reaktivität von Cycloalkadiinen

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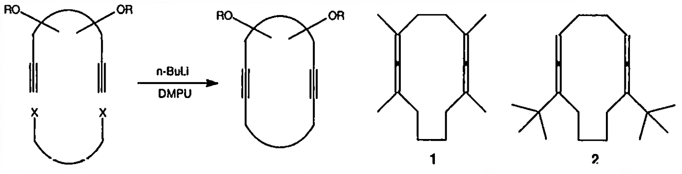
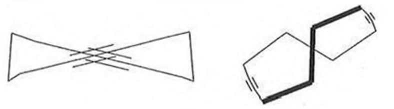
Symmetrisch angeordnete Funktionalitäten in mittleren Ringen sind für die transannulare Reaktivität von entscheidender Bedeutung. Retrosynthetische Ueberlegungen haben uns veranlasst, effiziente Synthesen zu entwickeln, mit denen in jeweils drei Stufen mono- und disubstituierte cyclische Dialkine aufgebaut werden können. Die zentrale Reaktion für den Ringschluss stellt die gleichzeitige Alkylierung der zwei terminalen Alkin-Funktionen dar, welche mit Ausbeuten bis zu 43% verläuft.



Transformation der funktionellen Gruppen und anschliessende S_N2'-Reaktion mit Cuprat-Reagenzien führte zu den beiden Cyclododeca-1.6-diallenen **1** und **2**. Der stereochemische Verlauf dieser Reaktionen wird durch sterische Faktoren der Produkte kontrolliert.

Information über die Struktur von propargylisch substituierten Cyclododecadiinen konnte mit Hilfe von Röntgenstrukturanalysen und AM1-Rechnungen erhalten werden. Es zeigte sich in allen von uns untersuchten Zwölfringen, dass die Alkin-Einheiten eine überkreuzte Anordnung aufweisen. Ob dadurch transannulare Cyclisierungen behindert werden, ist eine offene Frage.



155

Organic Chemistry

Stereoselective Reactions of 1-Amido Substituted Radicals

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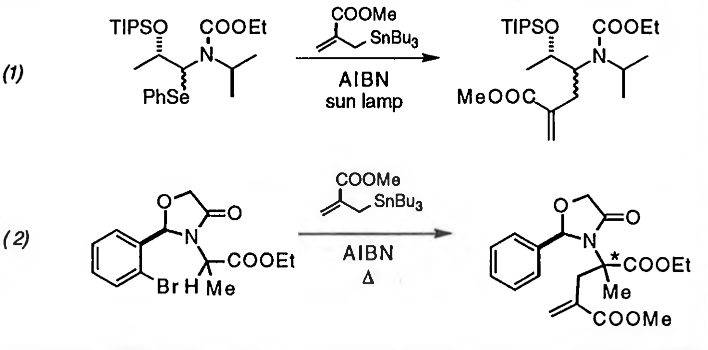
In the course of our investigations of nitrogen substituted radicals,[1] we prepared chiral radical precursors for the study of substrate control and of chiral auxiliary control. Two typical examples are represented in equations 1 and 2.



The factors which govern the asymmetric induction in these systems will be discussed and synthetic applications will be presented.

(1) (a) P. Renaud, A. Stojanovic, *Tetrahedron Lett.* **1996**, *37*, 2569. (b) S. Schubert, P. Renaud, P. A. Carrupt, K. Schenk, *Helv. Chim. Acta* **1993**, *76*, 2473. (c) P. Renaud, L. Giraud, *Synthesis* **1996**, in print.

156

Medizinische Chemie

Degrabloc, a Novel Radioopaque Polymer for Chemoembolization

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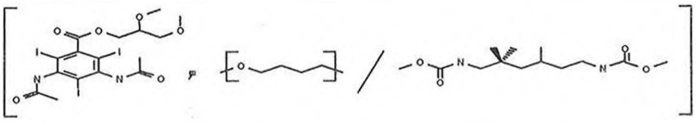
Institut für Polymere, Eidgenössische Technische Hochschule, CH-8092 Zürich, Switzerland / ** Forschungsabteilung des Departemente für Chirurgie, Universitätsspital Zürich, CH-8091 Zürich / *Klinik für Viszerale und Transplantationschirurgie Universität Bern CH-3010 Bern

We will report on the synthesis of a radiopaque block-*co*-polymer for medical occlusion purposes. Therefore 2,3-dihydroxypropyl-3,5-bis(acetylamino)-2,4,6-trijodobenzoate was prepared from the purchasable radiopaque substance 3,5-bis(acetylamino)-2,4,6-trijodobenzoic acid (diatrizoic acid). 2,3-dihydroxypropyl-3,5-bis(acetylamino)-2,4,6-trijodobenzoate was cocondensed with different hydroxy-terminated softsegments such as poly(tetramethylene ether glycol) (PTHF) and 2,2,4-trimethyl-hexamethylendiisocyanat (TMDI) as chain extender to give novel polyurethanes with a radiopaque moiety attached to the polymer backbone. The polymer IUPAC formula is given below:



The *in vitro* cell cultures of fibroblasts- and macrophage cell lines were performed on the polymer. In addition, compatability and degradation of the polymer was investigated *in vivo* in rats. First examples for applications are an animal model for chemoembolizations (Degrabloc/Doxorubicin) of hepatocellular carcinoma (occlusion of the arteria hepatica in pigs) and intraductal occlusion of the pancreas for tumor of exocrine cells (Degrabloc/Somatostatin).

CHIMIA 50 (1996) Nr. 7/8 (Juli/August)

Organische Chemie **157**

Matrizengesteuerte, nichtenzymatische Polymerisation von RNA

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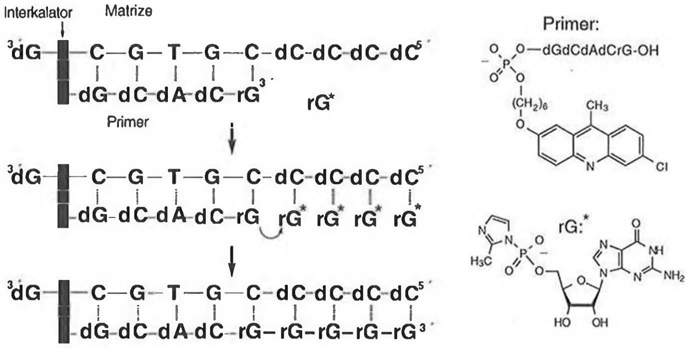
30, quai Ernest-Ansermet; CH-1211 Genève 4

Mit 6-Chlor-2-alkoxy-9-methylacridin markierte Oligonukleotide eignen sich als Primer zum Studium der nichtenzymatischen Polymerisation von RNA. Sie bilden stabile Duplexe mit komplementären Strängen (Abb. oben), deren überstehender Teil die Funktion einer Matrize übernimmt. Hieran binden thermodynamisch aktivierte Mononukleotide gemäß den Watson-Crick-Basenpaarungsregeln (Abb. Mitte). Durch nukleophilen Angriff der 3'-OH auf Phosphatgruppen der Nachbarnukleotide findet die eigentliche Kettenverlängerung statt (Abb. unten). Möglichkeiten und Grenzen dieses Systems im Hinblick auf eine Selbstreplikation von RNA werden diskutiert.



Organische Chemie **158**

Paarung unnatürlicher Nucleobasen: Untersuchung von Alanyl-PNA-Paarungskomplexen

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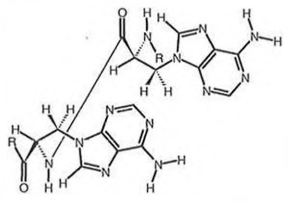
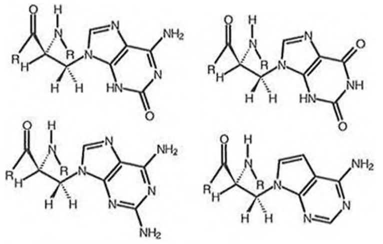
Institut für Organische Chemie und Biochemie der TU München, Lichtenbergstr. 4, D-85747 Garching

Peptidnucleinsäure-Oligomere, die aus alternierend konfigurierten, basensubstituierten Alanyl- oder Homoalanyleinheiten aufgebaut sind, bilden A-T und A-A Basenpaare [1] [2]. Die Alanyl-PNA-Paarungskomplexe sind vermutlich linear und stellen ein topologisch hervorragend geeignetes System dar, um neben den Purin-Pyrimidin- auch Purin-Purin-Paarungen in den jeweiligen Paarungsmodi zu beobachten.



Ausschnitt einer alternierend konfigurierten Alanyl-PNA



Alanylderivate mit den Basen Isoguanin, Diaminopurin, Xanthin und 7-Carbaadenin

Wir berichten über die Synthese und Paarungseigenschaften von PNA-Oligomeren, welche zusätzlich zu den kanonischen Basen Isoguanin, Diaminopurin, Xanthin und 7-Carbapurine enthalten.

[1] U. Diederichsen, *Angew. Chemie* **1996**, *108*, 458.
[2] U. Diederichsen, H.W. Schmitt, *Tetrahedron Lett.* **1996**, *37*, 475.

159

Organische Chemie

Triplex-Bildungseigenschaften von Oligonukleotiden enthaltend die Nukleoside 7-(2'-Deoxy-α/β-D-ribofuranosyl)-hypoxanthin.

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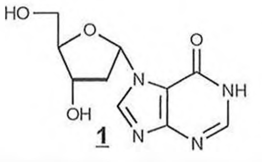
Institut für organische Chemie, Universität Bern, CH-3012 Bern

In der Erkennung von DNS-Duplexen mittels eines dritten Oligonukleotid-Stranges sind bis anhin zwei strukturelle Motive bekannt, welche beide eine strangweise Separation von Pyrimidin und Purinbasen im Zielduplex verlangen. Im einen (Pyrimidinmotiv; C^+×G·C und T×A·T Basentripels) ist der dritte Strang parallel zum Duplex-Purin-Strang orientiert, während er im zweiten (Purinmotiv; G×G·C, A×A·T und T×A·T Basentripels) antiparallel verläuft. Im Hinblick auf eine Verallgemeinerung der Duplexerkennung auf beliebige Basensequenzen, wurden die Nukleoside 7-(2'-Deoxy-α-D-ribofuranosyl)-hypoxanthin **1** und 7-(2'-Deoxy-β-D-ribofuranosyl)-hypoxanthin **2** hergestellt und in Oligonukleotide eingebaut. Die Paarungseigenschaften dieser Oligonukleotide wurden mittels der DNase-Footprinting-Technik untersucht [1]. Es konnte gezeigt werden, dass innerhalb des Pyrimidinmotivs nicht nur das β-Nukleosid **2** sondern erstaunlicherweise auch das α-Nukleosid **1** selektiv G·C Basenpaare erkennen können. Beide stellen somit ladungsneutrale Cytidin-Substitute dar.



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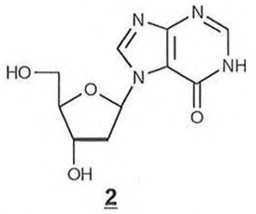


2

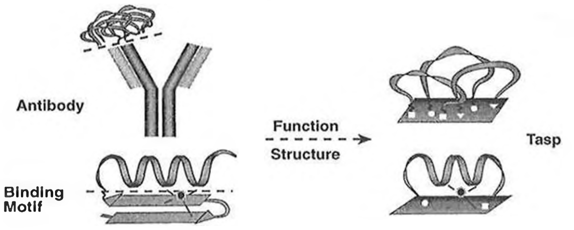
[1] E.S. Priestley, P.B. Dervan, *J. Am. Chem. Soc.* **1995**, *117*, 4761.

Organische Chemie **160**

Proteins as Templates for the Design of Functional Mimetics and Drugs

B. Rohwedder, P. Dumy, P. Garrouste, C. Lehmann, M. Mathieu, C. Peggion, S. Peluso, A. Razaname, G. Tuchscherer, T. Wöhr, M. Mutter, Institute of Organic Chemistry, University of Lausanne, BCH-Dorigny, CH-1015 Lausanne, Switzerland

The use of peptidomimetics and topological templates has become an important tool in protein design and mimicry. Recent progress in the design of regioselectively addressable templates and in the synthetic methodology for ligating peptide segments allows now to develop the full potential of this approach, i.e. the construction of template assembled synthetic peptide (Tasp) molecules acting as functional mimetics of protein receptors and ligands.



As a basic feature (Figure), the functional part of a protein, e.g. the binding loops of a receptor, is detached from the rest of the molecule and assembled on a topological template which mimicks the structural framework of the native protein. In particular, strategies for the chemoselective ligation of peptides disposing "sticky chain ends" to orthogonally protected templates are described. Moreover, novel structure inducing building blocks such as functional pseudo-proline derivatives are presented for accessing protein mimetics of nonnatural chain topology. In applying these methodologies, loop sequences derived from monoclonal antibodies and binding regions of receptors and ligands are covalently attached to templates via oxime, thioether or amide bond formation. Results of the chemical synthesis and first biostructural characterizations are in support of the template concept for accessing protein mimetics with novel functional properties for molecular recognition studies and potential therapeutic applications.

CHIMIA *50* (1996) Nr. 7/8 (Juli/August)

Organische Chemie **161**

Design and Synthesis of an Amide-Linked 4'-Homo-DNA

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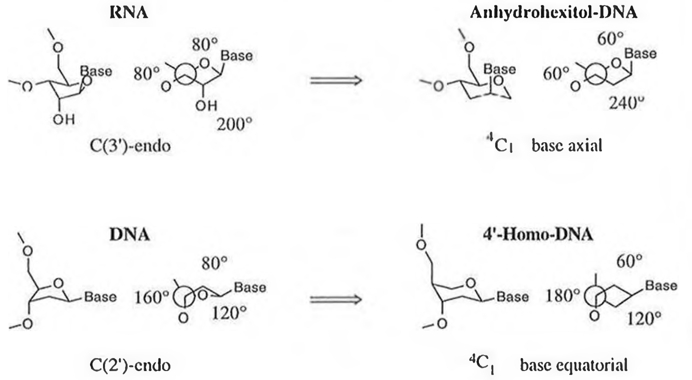
Preferential recognition of DNA over RNA – and vice versa – by synthetic and naturally occurring ligands is of prime interest not only in the development of antisense and antigene agents, respectively, but to the understanding of the phenomena governing the structure of DNA and RNA themselves. Recently, anhydrohexitol oligonucleotides have been described [1] which pair preferentially to complementary RNA. Based on a structural rationale for these findings we designed two novel oligonucleotide analogs (4'-homo-DNA and an amide-linked congener) that are expected to form stable duplex structures with complementary DNA but less stable complexes with complementary RNA.

We describe the synthesis of the respective monomer building blocks as well as molecular modeling studies testing the structural features and the dynamic behaviour of 4'-homo-DNA complexes with complementary DNA.



[1] A. Van Aerschot, I. Verheggen, C. Hendrix, P. Herdewijn, *Angew. Chem.* **1995**, *107*, 1483.

Organische Chemie **162**

Heterospirocyclische 3-Amino-2*H*-azirine als Synthone für α,α-heterocyclische α-Aminosäuren

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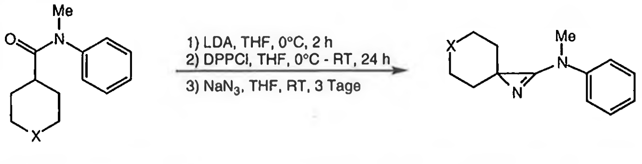
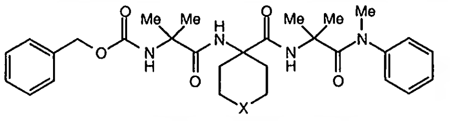
Durch die Verwendung von 3-Amino-2*H*-azirinen lassen sich α,α-distubstituierte α-Aminosäuren in guter Ausbeute in Peptide einführen [1]. Zur Synthese heterospirocyclischer 3-Amino-2*H*-azirine wurden die entsprechenden *N*-Methylcarbonsäureanilide mit LDA, Diphenylphosphorochloridat und Natriumazid umgesetzt [2].



Die so hergestellten heterospirocyclischen 3-Amino-2*H*-azirine wurden zur Synthese von Tripeptiden des Typs **1** verwendet, wobei auch die erste und die dritte Aminosäure variiert wurde (Phe, Val).
Mittels X-Ray-Kristallographie und NMR-Experimenten wurden die Strukturen dieser konformationell stark eingeschränkten Peptide bestimmt.



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[1] H. Heimgartner, *Angew. Chem.* **1991**, *103*, 271
[2] J. Villalgordo, H. Heimgartner, *Tetrahedron* **1993**, *49*, 7215

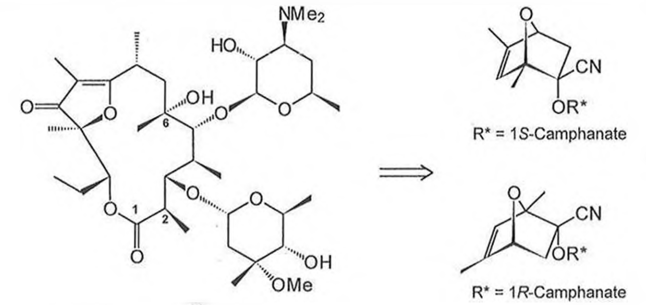
Organic Chemistry **163**

The Total Synthesis of Sporeamicin *via* the Optically Pure Diels-Alder Adducts of 2,4-Dimethylfuran and 1'-(*R*)- and 1'-(*S*)-Cyanovinyl Camphanates.

Simon W. Ainge and Pierre Vogel,

Section de Chimie de l'Université de Lausanne, BCH-Dorigny, CH-1015 Lausanne.

Sporeamicin A (**i**), discovered in 1992, is an erythromycin-like antibiotic isolated from a species of *saccharopolyspora* (L53 18-A). It has been found to be active *in vitro* against a wide variety of Gram-positive bacteria. Interesting structural features of this molecule include the 2,3-dihydro-3-oxofuran moiety, a rarity in polypropionate structures of this type.



(i)

Because of this latter-mentioned feature, sporeamicin A appeared to be an ideal synthetic target to demonstrate the application of our polypropionate methodology, which is based on optically pure Diels-Alder adducts of 2,4-dimethylfuran and 1'-(*R*)- and 1'-(*S*)-cyanovinyl camphanates (so-called *Second Generation Naked Sugars*).

P. Kernen and P. Vogel, *Helv. Chim. Acta*, 1995, **78**, 301.
A.-F. Sevin and P. Vogel, *J. Org. Chem.*, 1994, **59**, 5920.

Organische Chemie **164**

Zur Biosynthese von Bottromycin: Stereochemischer Verlauf der C-Methylierungsschritte

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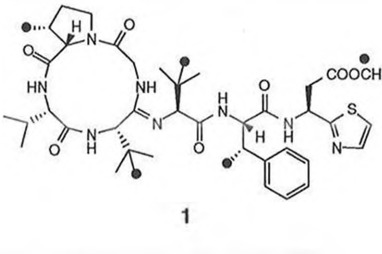
Bottromycin (**1**), ein antibiotisch wirksamer Metabolit aus *Streptomyces bottropensis*, enthält neben anderen ungewöhnlichen Aminosäurekomponenten zwei Einheiten *t*-Bu-Gly [1]. Mit Hilfe von [^{13}C-Methyl]-Met konnte gezeigt werden, dass die fünf in Formel **1** mit einem Punkt gekennzeichneten Methylgruppen aus diesem Vorläufer stammen; die sich daraus aufdrängende Hypothese, wonach die *t*-Bu-Gly-Einheiten aus der Methylierung einer dem Valin nahestehenden Zwischenstufe hervorgehen, konnte experimentell untermauert werden. Durch den Einsatz geeignet markierter Vorläufer wurde in vivo eine in ihren *t*-Butylgruppen chiral markierte Form von **1** erzeugt, deren nachträgliche stereochemische Analyse den Beweis für eine am alkylierten C-Atom erfolgte Inversion lieferte. Zudem konnte bewiesen werden, dass die Uebertragung der zusätzlichen Methylgruppe unter Netto-Retention stattfindet. Aehnliche Verhältnisse gelten auch für die Entstehung der β-Methyl-Phe-Einheit. Diese Befunde stimmen nicht mit denjenigen überein, die früher für den formal ähnlichen Fall der Bildung von β-Methyl-Trp in *S. griseus* gesichert worden sind [2] und verleiten zur Aufstellung eines in seinen Grundzügen vom Normalfall abweichenden Reaktionsmechanismus' für die biologische Alkylierungsreaktion.



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[1] D. Schipper *J. Antibiot.* **1983**, *36*, 1076-1077.
[2] R. W. Woodard, L. Mascaro, Jr., R. Hörhammer, S. Eisenstein und H. G. Floss *J. Am. Chem. Soc.* **1980**, *102*, 6314-6318.

Organische Chemie **165**

The First Active-Site Analogue of Chloroperoxidase - Synthesis and Catalytic Reactions

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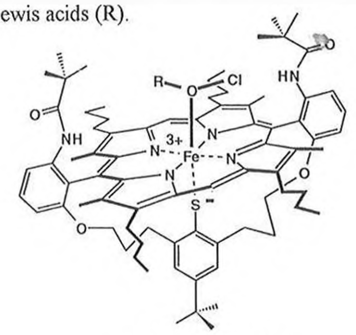
The heme-thiolate protein chloroperoxidase catalyzes the halogenation of aromatic compounds and activated C-H bonds employing H_2O_2 and Cl^- or Br^- [1]. It is believed that the reactive, X^+ donating intermediate is an iron(III)protoporphyrin(IX) complex, which contains S^- (cysteine) and ClO^- coordinating to the iron (S^--Fe(III)-OCl$^-$). This assumption, however, has never been verified neither by investigation of the enzyme nor by preparing model compounds.
We report here the synthesis of **1**, an active-site analogue of chloroperoxidase, which has been characterized and is capable of reactions resembling the enzymatic catalysis. The reactivity of **1** can be modulated using different Lewis acids (R).



1, R : H, Lewis Acid

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[1] M. C. R. Franssen, Biocatalysis **1994**, *10*, 87-111.

Organische Chemie **166**

Stereochemie der Inhibition von δ-Chymotrypsin mit optisch aktiven bicyclischen Organophosphaten

Walter Ganci, Eric. J. Meier, G. Przibille, U. Ringeisen und Peter Rüedi

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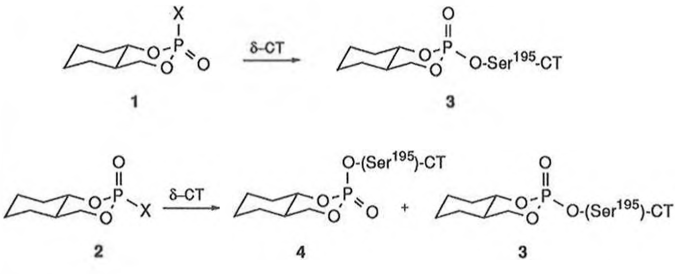
Der regio- und stereochemische Verlauf der Inhibition von δ-Chymotrypsin mit optisch aktiven, axial und äquatorial substituierten *trans*-3-(2',4'-Dinitrophenoxy)-2,4-dioxa-$3\lambda^5$-phosphabicyclo[4.4.0]decan-3-onen wurde mit ^{31}P-NMR Spektroskopie untersucht. Die Reaktion stöchiometrischer Mengen an Enzym und Inhibitor ergab im Falle der axialen Epimeren **1** und *ent*-**1** ausschliesslich Inversion der Konfiguration am Phosphor, während die äquatorialen Epimeren **2** und *ent*-**2** neben Inversion auch Retention der Konfiguration zeigten.



X = 2,4-Dinitrophenoxy

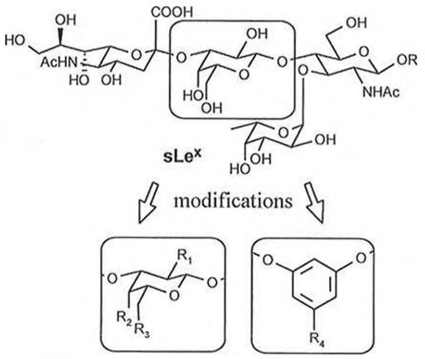
Die Reaktionsprodukte sind diastereoisomere, kovalent gebundene Phosphoenzyme (**3**,**4**), die aufgrund der unterschiedlichen chemischen Verschiebungen anhand von Modellverbindungen eindeutig zugeordnet werden konnten.

Organische Chemie **167**

Synthesis of Sialyl Lewis x Mimics with Modifications of the Galactose Unit

Rolf Bänteli, Hartmuth C. Kolb and Reinhold Oehrlein
Central Research Laboratories, CIBA, Postfach, CH-4002 BASEL

The carbohydrate binding proteins E-, P-, and L-selectin play a mayor role in the recruitment of leukocytes in acute and chronic inflammation[1]. The minimal structure which is recognized by the selectins is the tetrasaccharide sialyl Lewis x (sLe^x).



In the course of our research program to identify more potent and structurally simpler ligands for E-selectin we have investigated the importance of the many hydroxy groups in sLe^x. The syntheses and the biological activities of compounds with distinct modifications in the galactose unit will be presented. Furthermore the replacement of galactose by a resorcin moiety will be discussed.

[1] D. H. Boschelli, *Drugs of the Future* **1995**, *20*, 805

Organic Chemistry **168**

Herboxidiene: Relative and Absolute Configuration and Synthesis of an Aromatic Hybrid

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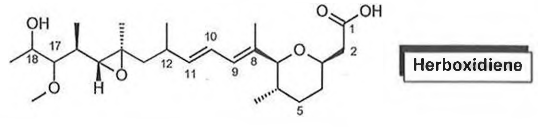
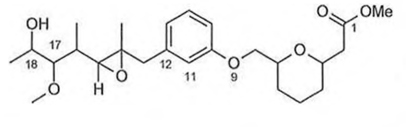
a) Sandoz Agro AG, CH-4002, Basel
b) Dept. of Organic Chemistry, University of Geneva, CH-1211 Geneva 4

The natural product herbicide, Herboxidiene [1], shows good control of broadleaf annual weeds and good selectivity in wheat. Although NMR studies enabled assignment of the relative stereochemistry at many of the centres, the configuration at carbons 12, 17 and 18 have hitherto remained unknown.



This paper reports on the relative and absolute configuration of the natural product which was determined by a combination of X-ray analysis, degradation, and asymmetric synthesis of the respective fragments. The asymmetric synthesis of an aromatic hybrid of Herboxidiene (**A**, in which the diene moiety is replaced by a phenol ring system) will also be presented.



A

[1] S.W. Ayer, B Isaccs, R.C. Elliot, and R. J. Stonard, *J.Org. Chem*, *57*, 7220, **1992**.

CHIMIA *50* (1996) Nr. 7/8 (Juli/August)

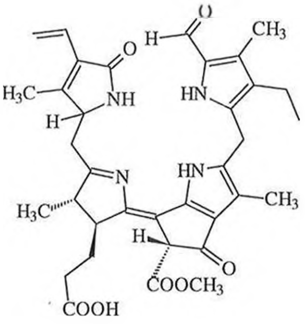
Organische Chemie **169**

A Fluorescing Chlorophyll Catabolite from Higher Plants

Walter Mühlecker[1], Karl-Hans Ongania[1], Stefan Hörtensteiner[2], Philipe Matile[2] and Bernhard Kräutler[1*]

[1]Institut für Organische Chemie, Universität Innsbruck, Innrain 52a, A-6020 Innsbruck, Austria
[2]Institut für Pflanzenbiologie, Universität Zürich, Zollikerstrasse 107, CH-8008 Zürich, Switzerland

Here we report on the elucidation of the constitution of Bn-FCC-2, a "fluorescing" chlorophyll catabolite (FCC) from senescent cotyledons of the dicot *Brassica napus*.[1] The catabolite Bn-FCC-2 is a trace intermediate of chlorophyll breakdown in rape (*Brassica napus*), where three nonfluorescing chlorophyll catabolites have been structurally characterized[2] and identified as final products of chlorophyll catabolism.[3]



[1] Hörtensteiner, S., Vicentini, F. and Matile, Ph. *New Phytol.* **1995**, *129*, 237
[2] Mühlecker, W. and Kräutler, B. *Plant Physiol. Biochem.* **1996**, *34*, 61
[3] Ginsburg, S., Matile, Ph. *Plant. Physiol.* **1993**, *102*, 521

Chimie organique **170**

Antifungal benzoic acid derivatives from *Piper dilatatum* L.C. Rich. (Piperaceae)

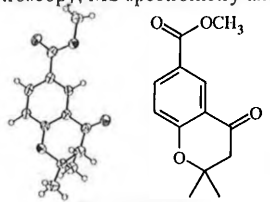
Christian Terreaux[1], Marc Maillard[1], Helen Stoeckli-Evans[2], Mahabir P. Gupta[3] and Kurt Hostettmann[1]

[1]Institut de Pharmacognosie et Phytochimie, Université de Lausanne, BEP, CH-1015 Lausanne, Switzerland; [2]Institut de Chimie, Université de Neuchâtel, Av. de Bellevaux 51, CH-2000 Neuchâtel, Switzerland; [3]CIFLORPAN, Faculdad de Farmacia, Universidad de Panama, Panama, Republica de Panama.

In the course of our investigations of plants from the Panamanian flora and our continuous search for new bioactive lead compounds, the extracts of the leaves of *Piper dilatatum* L.C. Rich. (Piperaceae) were studied. *P. dilatatum* is used by the Kuna Indians of Panama as a constituent of a mixture of plants applied as a tonic bath in various affections.

The dichloromethane extract from the leaves of *P. dilatatum* showed interesting antifungal activity in the direct bioautographic assay [1] against *Cladosporium cucumerinum*, a plant pathogenic fungus. Bioactivity-guided isolation yielded several prenylated benzoic acid derivatives. Compound **1** was obtained as colorless crystals with a molecular weight of 236 amu and showed significant activity against *C. cucumerinum*.

Structures of **1** and related compounds were elucidated by means of ^1H and ^{13}C NMR spectroscopy, MS spectrometry and X-ray analysis.



Compound **1**.

The isolation, structure determination and biological activity of compound **1** and other derivatives will be described.

[1] Homans, A.L. and Fuchs, A. (1970) *J. Chromatogr.* **51**, 327-329.

Organic Chemistry Section **171**

New NMR Experiments for the Determination of Long-Range Heteronuclear Spin-Coupling Constants

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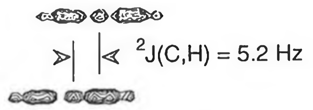
New gradient-assisted NMR experiments are presented that allow the accurate determination of long-range heteronuclear coupling constants, in particular, ^{13}C, ^1H *J*-coupling values. The presented methods base on the HETLOC sequence[1] designed to yield C,H-couplings between each proton-carrying carbon and the protons in the same proton spin system. However, they improve the resolution and signal dispersion in the F_1-domain, as well as the selection of the desired isotopomers. All sequences provide accurate values even in cases where the line width is comparable to the magnitude of the coupling, due to so-called E.COSY-type cross-peak patterns[2]. These display a two-fold symmetry instead of the four-fold symmetry characteristic for most 2D cross-peaks in experiments where a coupling evolves in both time domains. Accurate doublet splittings can thus be obtained by comparison of different rows of the 2D spectrum, irrespective of the line width, as is shown below for the case of a $^2J(^{13}C,^1H)$ coupling. Several applications will be presented.



Ref: 1. M. Kurz *et al. Angew. Chem.* **1991**, *103*, 1341.
2. C. Griesinger *et al. J. Am. Chem. Soc.* **1985**, *107*, 6394.

Organische Chemie **172**

Host-guest complexation linked to conformationally induced redox-type signal transduction

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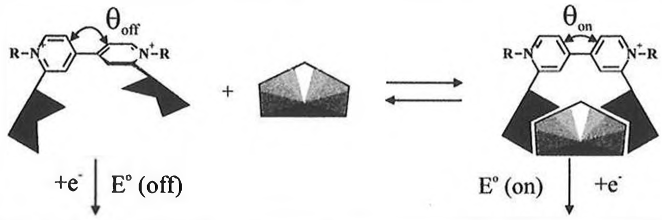
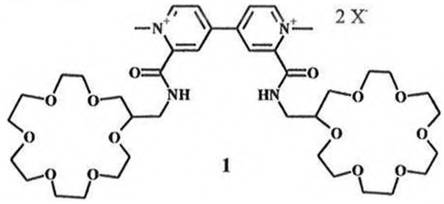
‡ *Institut für Chemie, Universität Osnabrück, D-49069 Osnabrück*
* *Institut für organische Chemie, Universität Bern*

With traditional electroactive hosts, the information (complexation of a ionic analyte) is transduced **via coulombic interaction** of the analyte and results in a shift of the reversible reduction potential of the host.

We have developed a new principle for such information transduction, that relies on a **conformational change within the host induced by complexation** of the guest. If the same conformational change can be linked to a shift of its reduction potential, the information (guest on or off) can be read out via a simple electrochemical measurement. Notably, this principle of signal transduction is not restricted to charged guests.



One possible realization is the two-point complexation of a guest by a 4,4-bipyridinium salt substituted in the 2 and 2'-positions with appropriate recognition sites, e.g.. **1**. The torsion due to the complexation shifts the reduction potential.



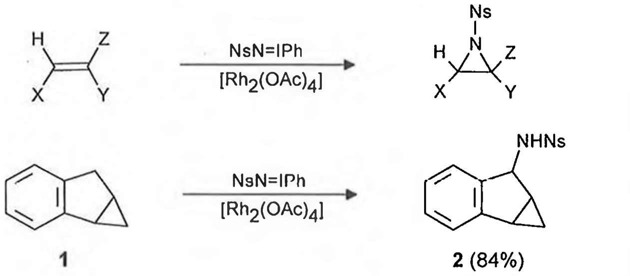
1

Chimie organique **173**

Rhodium(II)-Catalysed Aziridinations and CH-Insertions

Corine Baud, Ivo Nägeli, Paul Müller
Dpt de Chimie Organique, Université de Genève, 1211 Genève 4

Decomposition of NsN=IPh with $[Rh_2(OAc)_4]$ in presence of olefins affords aziridines in yields of up to 85%. The reaction is applicable to mono- and disubstituted olefins, although in some cases yields are reduced. The stereospecificity of the reaction was investigated with several alkenes. Both *cis*-β-methylstyrene and *cis*-2-hexene afforded only *cis*-aziridines while with *cis*-stilbene a 3:1 mixture of *cis* and *trans* aziridine was obtained in low yield. In the presence of the chiral catalyst $[Rh_2(R\text{-bnp})_4]$ *cis*-β-methylstyrene was aziridinated with 80% yield and 73% ee.



The NsN=IPh / $[Rh_2(OAc)_4]$ system is also efficient for allylic amination and for insertion into CH-bonds, activated by phenyl- or oxygen substituents. While simple olefins react via aziridination, cyclohexene undergoes reaction at the allylic position in 71% yield. The amination of cycloprop[*a*]inden (**1**) afforded only the insertion product **2** in 84% yield, while no products derived from ring-opening of an intermediate radical were observed. Reaction of indan with NsN=IPh / $[Rh_2(R\text{-bnp})_4]$ proceeded with 71% yield and 31% ee.

Organic Chemistry **174**

A New and Clean Source of $Fe(CO)_3$ at Intermediate Temperature

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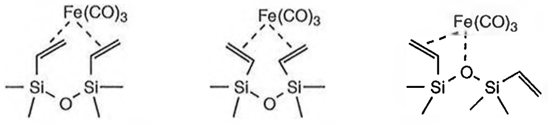
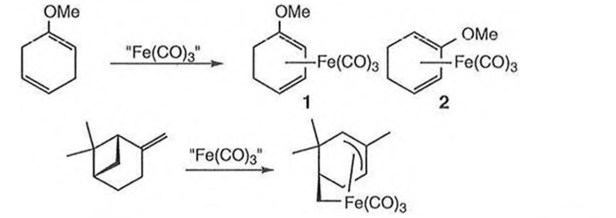
Reaction of 1,3-divinyl-1,1,3,3-tetramethyl-disiloxane with $Fe_2(CO)_9$ leads to a mixture of 3 to 4 tricarbonyliron complexes. Possible structures are depicted below.



These complexes promise to be useful tricarbonyliron transfer reagents to conveniently prepare (η^4-diene)$Fe(CO)_3$ complexes.
Unlike the well known BDA-$Fe(CO)_3$ complex, this new reagent transfers the $Fe(CO)_3$ unit not only to *s-cis*-1,3-dienes, but also to a series of other olefins which require isomerisation prior to complexation, *e.g.* 2,5-dihydroanisole, which is isomerised to a mixture of the 1,3-diene complexes **1** and **2** by migration of a double bond.

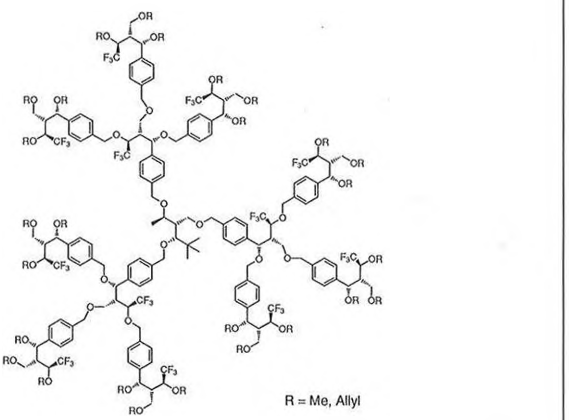


Higher temperatures (refluxing dioxane) allows the insertion of the ironcarbonyl unit into the four membered ring of verbenene, α- and β-pinene forming *σ-alkyl*, *π-allyl* complexes. Verbenene and β-pinene react faster than α-pinene. Probably the presence of a exocyclic double bond in verbenene and β-pinene favors the transfer of the $Fe(CO)_3$ unit, whereas in the case of α-pinene the double bond is sterically hindered.

Organische Chemie **175**

Fluorhaltige chirale Dendrimere: Synthese und ^{19}F-NMR-Untersuchungen

Guy Greiveldinger und Dieter Seebach
Laboratorium für Organische Chemie, Eidgenössische Technische Hochschule, ETH-Zentrum, Universitätstrasse 16, CH-8092 Zürich



Im Rahmen der in unserer Gruppe durchgeführten Strukturuntersuchungen chiraler Dendrimere wurden erstmals fluorhaltige, chirale Dendrimere synthetisiert. Dabei wurden auch chirale Dendrimere mit funktionalisierbaren Gruppen an der Oberfläche und solche, die Biphenyleinheiten als Spacer enthalten, hergestellt.
Anschliessend wurden diese Strukturen mit ^{19}F-NMR untersucht.

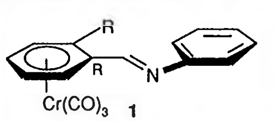
[1] P. Murer und D. Seebach, *Angew. Chem.* **1995**, *107*, 2297; Teil der geplanten Dissertation von G. Greiveldinger, ETH Zürich.

Organische Chemie **176**

Diastereoselektive Aza-Cycloadditionen mit Planar-Chiralen η^6-Benzyliden-Amin $Cr(CO)_3$-Komplexen

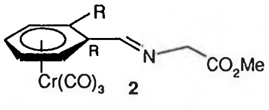
E. P. Kündig, B. Schnell und L.-H. Xu, Département de Chimie Organique, Université de Genève, 1211-Genève 4

Hetero-[4+2] und [3+2]-Cycloadditionen gehören zu den effizientesten Methoden zur Darstellung 6- und 5-gliedriger Heterozyklen. Asymmetrische Cycloadditionen beruhen im Allgemeinen auf Chiralität im Dien (resp. Dipolarophile) oder Dienophil (resp. Dipolarophil). In Kombination mit chiralen Lewis Säuren ergeben sich oft sehr hohe Diastereoselektivitäten.



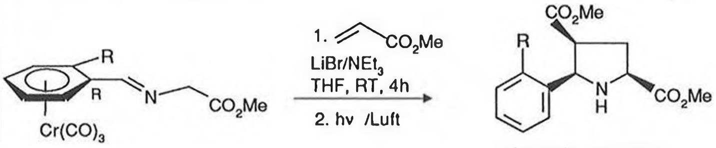
1

Wir berichten hier über inter-und intramolekulare diastereoselektive Hetero-[4+2] und [3+2]-Cycloadditionen der planar-chiralen η^6-Benzyliden- Komplexe **1** und **2**.[1]



2

In Gegenwart von Lewis-Säuren geht Komplex **1** als 2-Aza-Dien mit elektronenreichen Dienophilen Cycloadditionsreaktionen ein.[2] Komplex **2** reagiert unter basischen Bedingungen als chiraler 1,3-Dipol mit sehr guter diastereofacialer Selektiviät.



>95 % de, >98% ee

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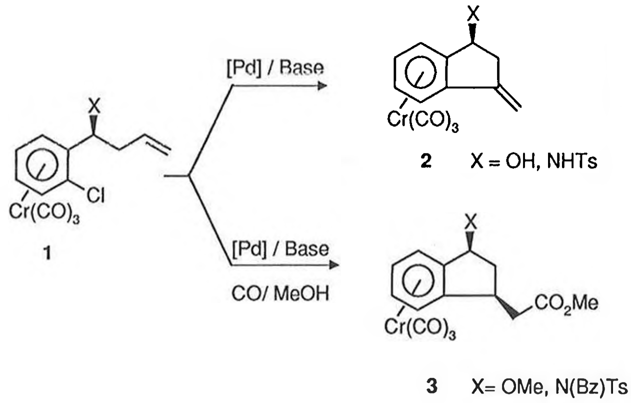
[1] siehe auch L.-H. Xu und E.P. Kündig, *Synlett* **1996**, 270.
[2] vgl. S. Laschat, R. Noe und M. Riedel, *Organometallics* **1993**, *12*, 3783.

Organic Chemistry **177**

Intramolecular Heck Reactions with Planar Chiral Tricarbonyl Chromium Arene Complexes

B. Crousse, E. P. Kündig, L.-H. Xu
Département de Chimie Organique, Université de Genève, 1211-Genève 4

The palladium-catalyzed arylation (Heck reaction)[1] of alkenes is a powerful method for the preparartion of functionalized aromatics. In this communication we report the first application of the intramolecular Heck reaction with planar chiral tricarbonyl chromium complexes. By its electron withdrawing effect, the $Cr(CO)_3$ group modifies the reactivity of the arene while the planar chirality of **1** induces a perfect diastereoselectivity in the Pd-olefin insertion step and creates the new stereogenic center as shown in **3**.



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[1] (a) Heck, R. F. *Org. React.* (N.Y.) **1982**, *27*, 345.
(b) Tsuji, J. *Palladium Reagents and Catalysts*, Wiley, New York, 1995.

Organische Chemie **178**

Potential Reagents for the Multiplication of Chiral Information: Crystallographic and Ab Initio Studies of Optically Active Dilithiosulfoximines

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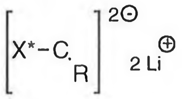
Institut für Anorganische Chemie der Universität Basel, Spitalstrasse 51, CH-4056 Basel

Although organolithium compounds with a chiral environment count to the most useful reagents for diastercoselective C-C bond formations the further development to polilithiated chiral systems is restricted only to a few examples. About chiral heteroatom stabalized dilithiocarbanions, where both lithiums are attached to the same carbon atom nothing is known about there existence, structure and chemical behavior.


$$\left[X^{*}-\underset{R}{C}\right]^{2\ominus}\ 2\,Li^{\oplus}$$

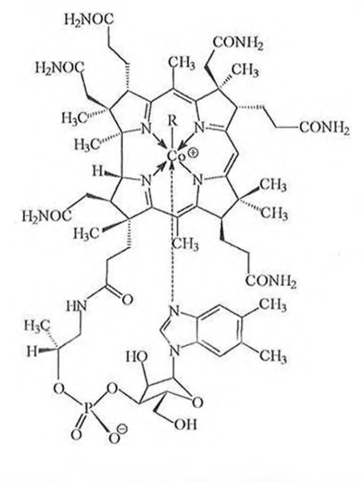
We report here about ab initio calculations of dilithiated Sulfoximines and give some direct evidence by their X-ray structure determination .

Organische Chemie **179**

On Neocoenzyme B_{12}

D. Riether, M. Tollinger, R. Hannak, B. Kräutler*
Institute of Organic Chemistry, University of Innsbruck, Innrain 52a, A-6020 Innsbruck, Austria

By electrochemical synthesis neocoenzyme B_{12} (Co_β-5'-deoxyadenosyl-13-epicobalamin, **1**), a stereoisomer of coenzyme B_{12} known from work of Hogenkamp et al.[1], was prepared with high yield (89%) from neovitamin B_{12} (Co_β-cyano-13-epicobalamin, **2**) and 5'-deoxy-adenosyltosylate.
The structure of neocoenzyme B_{12} in aqueous solution was investigated by extensive analysis based on modern 2D nuclear magnetic resonance spectroscopy. Exploratory experiments concerning the homolytic thermal decomposition of this stereoisomer of coenzyme B_{12} were carried out.



Structural formulae of
1: neocoenzyme B_{12}
R = 5'-deoxyadenosyl
2: neovitamin B_{12}
R = CN

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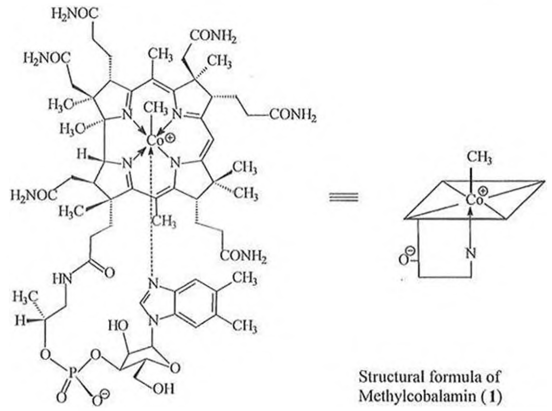
[1] Richard D. Tkachuck, Michael E. Grant, and Harry P. C. Hogenkamp, *Biochemistry*, Vol.13, No. 12, **1974**, 2645

Organic Chemistry **180**

Structural Analysis of Methylcobalamin in Aqueous Solution by means of NMR Spectroscopy

M. Tollinger, R. Konrat, B. Kräutler*
Inst. of Organic Chemistry, University of Innsbruck
Innrain 52a, A-6020 Innsbruck, Austria

Nuclear magnetic resonance (NMR) spectroscopy has been developed lately to investigate the structure of cobalamins in solution. The present work describes the analysis of the structure of methylcobalamin (**1**) in aqueous solution by means of high-resolution NMR spectroscopy. Comparison of these NMR data with results from X-ray diffraction studies reveal remarkable conformational differences between the solution structure and the crystal structure of **1**. In addition, this work has helped to localise a series of solvent water molecules, one of them a "bound" water molecule linking the polar phosphate group and the hydroxyl group located at R2 of the ribose moiety, which appears to be "conserved" from the X-ray structures of cobalamins.



Structural formula of
Methylcobalamin (**1**)

CHIMIA 50 (1996) Nr. 7/8 (Juli/August)

181

Organische Chemie

Die Reaktionssequenz der nukleophilen Addition / Hydridabstraktion an Aren Chromtricarbonylkomplexen

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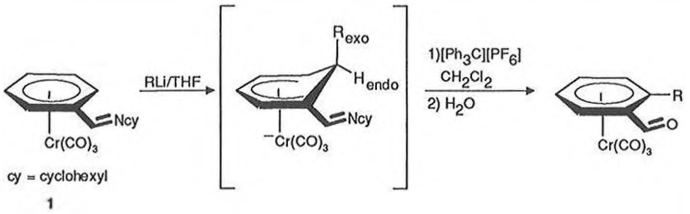
Als attraktive Ausgangsubstanzen für die aymmetrische Synthese können *ortho*-substituierte (η^6-Benzaldehyd)Cr(CO)$_3$ Komlexe durch die Titelreaktionsfolge aus (η^6-Benzyliden(cyclohexyl)amin)Cr(CO)$_3$ (**1**) erhalten werden.[1]
Über das grosse Potential dieser Reaktion in der organischen Synthese hinaus, handelt sich um das einzige Literaturbeispiel, in dem formel eine *endo*-Hydridabstraktion an einem (η^6-Aren)Cr(CO)$_3$ Komplex erfolgt.



Die Ergebnisse mechanistischer Studien sollen vorgestellt werden:
Mögliche Isomerisierungsprozesse, die einen Angriff des Trityl Kations an ein *exo*-Hydrid ermöglichen würden, werden diskutiert. Gleichzeitig werden Experimente vorgestellt, die die Annahme einer "echten" *endo*-Hydridabstraktion bekräftigen.

---

[1] E.P. Kündig, A.Ripa, R. Liu, *Helv. Chim. Acta* **1992**, *75*, 2657.

182

Chimie organique

Asymmetric Synthesis of Enantiomerically Pure Disubstituted Cyclopropanes

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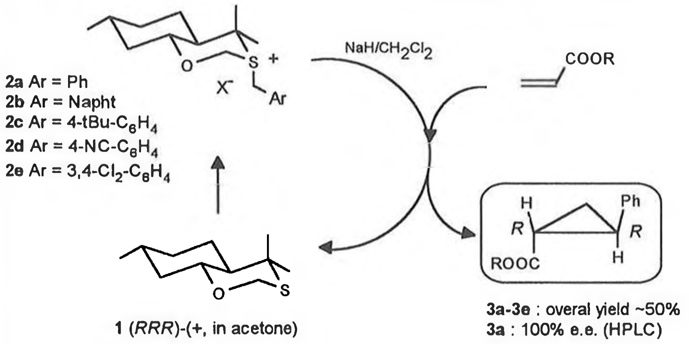
We have schown that Eliel's oxathiane **1**, which allowed us to synthezise in two steps mono and diarylepoxides of high enantiomeric purities (ranging from 90 to 99% ee)[1], can be used efficently in the synthesis of disubstituted cyclopropanes.

It was found that, while in the case of compounds **3a-c**, only traces (5%) of *cis* cyclopropanes were obtained, when the phenyl ring was substituted with a nitrile function or a chlorine atom (**3d-e**), about 20% of the *cis* compounds was also formed. But the separation is easily done by chromatography. The enantiomeric purity of compound **3a** having the *trans* configuration has been determined to be 100% ee by HPLC.



1) A. Solladie-Cavallo, A. Diêp-Vohuule *J. Org. Chem.* **1995**, *60*, 3494-3498.

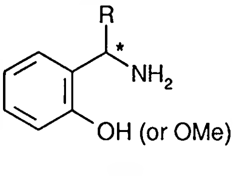
183

Organic Chemistry

ortho-Hydroxy-α-Alkylbenzylamines as New Chiral Auxiliaries in Asymmetric Synthesis

R. Gosmini, E. P. Kündig, P. Meier, A. Ripa, L. Saudan, P. Schüpfer, and B. Treptow, Département de Chimie Organique, Université de Genève, CH-1211-Genève 4.

Unlike the readily accessible enantiomerically pure 1,2-aminoalcohols which are widely used in asymmetric synthesis, chiral 1,3-aminoalcohols are scarcely used as auxiliaries despite their obvious potential. We here present two new chiral amino phenols which can efficiently be obtained highly enantio-enriched by either racemic synthesis / resolution or by asymmetric synthesis. Preliminary applications of these auxiliaries are in the fields of diastereoselective aldol reactions, diastereoselective transformation of arenes into substituted alicyclic compounds, and in the synthesis of new bi- and tridentate chiral ligands.



R = Me, *t*-Bu

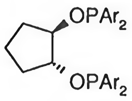
184

Organic Chemistry

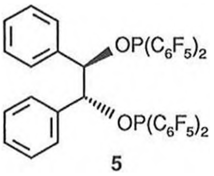
Electron-Poor Chiral C$_2$-Symmetric Bidentate Phosphorus Ligands and their use in Transition Metal Catalyzed Diels-Alder Reactions

M.E. Bruin, K. Khan, E.P. Kündig and I. Stary
Département de Chimie Organique, Université de Genève, 1211 Genève 4

The cationic complex [CpFe(CO)$_2$]$^+$ has been shown to catalyze the Diels-Alder reaction between substituted dienes and enals. [1] By substituting the two CO ligands by electron poor phosphorus ligands, the complex maintains its Lewis acid character and remains an active catalyst. We have previously reported the synthesis and use of the chiral complex [CpFe(PP)L]BF$_4$ (PP=**1**, L=acrolein) as a catalyst for Diels-Alder reactions resulting in highly enantio-enriched products. [2]



1: Ar = C$_6$F$_5$
2: Ar = C$_6$H$_3$F$_2$
3: Ar = C$_6$H$_3$(CF$_3$)$_2$
4: Ar = C$_6$H$_5$



5

Herein we report our continued studies in this area and present the synthesis of a range of complexes of the same type, with PP = **1-5**. All complexes are active catalysts. Ligand modification affects the stability of the catalyst, as well as its activity and the enantioselectivity of the cycloaddition reactions between enals and dienes.

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[1] P.V. Bonnesen, C.L. Puckett, R.V. Honeychuck and W.H. Hersh, *J. Am. Chem. Soc.*, **1989**, *111*, 6070.

[2] E.P. Kündig, B. Bourdin and G. Bernardinelli, *Angew. Chem. Int. Ed. Engl.*, **1994**, *33*, 1856.

CHIMIA 50 (1996) Nr. 7/8 (Juli/August)

Organische Chemie **185**

Oligomere Carbonylierungsprodukte bei der enantioselektiven Copolymerisation von Styrol mit Kohlenmonoxid

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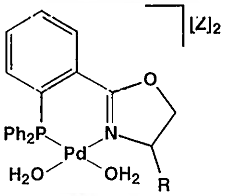
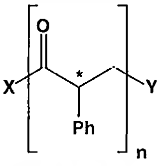
[1] *Laboratorium für Technische Chemie, ETH-Zentrum, CH-8092 Zürich*
[2] *Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, 45470 Mülheim a.d. Ruhr*

Kationische Palladium-Komplexe **1** mit koordinierten Phosphandihydrooxazol-Liganden ergeben katalytisch aktive Systeme für die Bildung von optisch aktiven, alternierenden Styrol-Kohlenmonoxid Copolymeren **2**. Abhängig von der Symmetrie der Liganden besitzen die gebildeten Copolymere entweder eine hoch isotaktische oder eine ataktische Mikrostruktur. Eine eingehende Endgruppen-Analyse der Copolymere durch ^{1}H-^{13}C-NMR-Korrelationsspektroskopie erlaubte die Identifizierung der gebildeten Endgruppen (**2**; X, Y), die Rückschlüsse auf die Initiierung, Propagation und den Kettenabbruch erlauben. Die Einflüsse des CO-Druckes, des Oxidationsmittels, der Reste R sowie der Anionen Z des Katalysatorvorläufers **1** auf die Copolymerisation wurden untersucht.



1



2

Hinweise über Faktoren, welche die Regio- und Enantioselektivität der Copolymerisation beeinflussen, konnten aus den Cooligomeren (**2**; n=1, 2) und der Natur der Endgruppen (**2**; X, Y) gewonnen werden. Die Cooligomere wurden nach Abfiltrieren der Copolymere direkt aus dem Reaktionsgemisch isoliert und eindeutig charakterisiert. Die Enantiomeren- resp. Diastereomerenverhältnisse dieser niedermolekularen Verbindungen weisen analog zu den Diastereomerenverhältnissen der entsprechenden Endgruppen in den isotaktischen Copolymeren auf eine im allgemeinen geringe Enantioselektivität der ersten Styrolinsertion hin.

Organic and Inorganic Chemistry **186**

Tris(tetrachlorobenzenediolato)phosphate Anion. Resolution and Asymmetric Synthesis.

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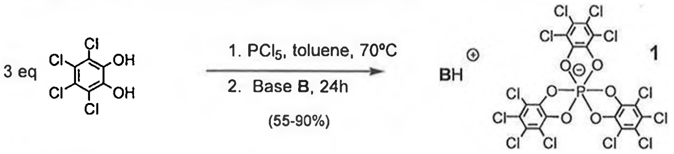
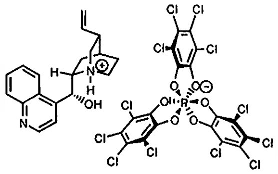
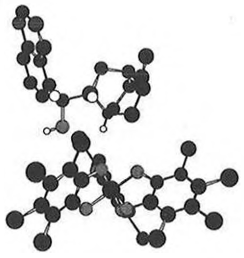
Département de Chimie Organique, Université de Genève, 1211 Genève

Herein, we report a one-pot procedure for the synthesis of configurationally stable tris(tetrachlorobenzenediolato)phosphate anion **1** (or TRISPHAT). Treatment of PCl_5 with 3 eq. of tetrachlorocatechol, followed by the addition of an amine leads to the precipitation of the corresponding *N*-H-ammonium-TRISPHAT salt.



Resolution of TRISPHAT is currently being achieved by the selective precipitation of the *N*-H-cinchonidinium-(Δ)-TRISPHAT.





The extent of the induction using an enantiopure base in the asymmetric synthesis of TRISPHAT will be presented.

Organische Chemie **187**

Enantioselective hydrogenation of ketopantolactone on Pt/alumina

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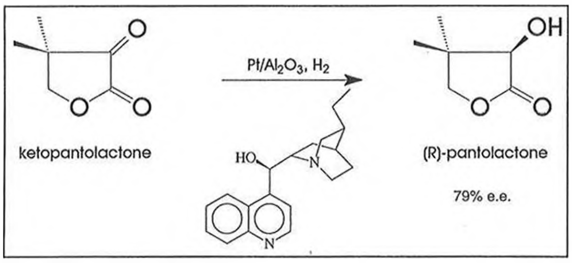
The heterogeneous enantioselective hydrogenation of α-ketoesters has become a field of considerable attention. Most of the studies focused on the reduction of ethyl pyruvate over cinchonidine-modified Pt, and only a few attempts have been made to broaden the scope of reactants. Here we report an industrially important reaction: the hydrogenation of ketopantolactone to R-(-)-pantolactone, as shown below.



A detailed study of the influence of reaction conditions on the enantiomeric excess (ee) revealed that crucial parameters are the catalyst pretreatment, solvent, temperature, surface hydrogen concentration, modifier and reactant concentrations. Good ee can be obtained only in an oxygen- and waterfree system. Apolar medium (toluene), moderate temperature (10°C), high hydrogen pressure (> 70 bar) and medium substrate concentration (0.5 M) are advantageous for enantio-differentiation. Pt/alumina has to be treated in flowing hydrogen at 300-400 °C before reaction. The nature of the reactant-modifier interaction has been studied using molecular mechanics calculations.

Organische Chemie **188**

Enantioselective hydrogenation of an α,β-unsaturated carboxylic acid on Pd/alumina

K. Borszeky, T. Mallat, A. Baiker
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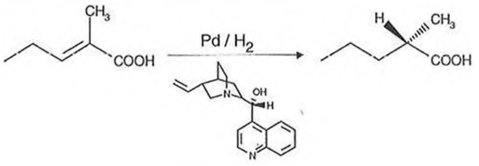
The enantioselective hydrogenation of α,β-unsaturated carboxylic acids has received great attention due to the pharmaceutical importance of some chiral carboxylic acids. Unfortunately, there is no preparatively useful solid catalyst available for the enantioselective hydrogenation of olefins. There have been reported a few attempts to hydrogenate cinnamic acid derivatives and isophorone over cinchonidine-modified Pd catalysts, but the enantiomeric excesses achieved (ee's) are moderate. The aim of our study was to gain some basic information concerning the nature of interaction between Pd, cinchonidine and reactant. The enantioselective hydrogenation of 2-methyl-2-pentenoic acid (MPA) was used as a model reaction (Scheme 1).



Scheme 1

A kinetic analysis of the hydrogenation of MPA revealed that the reactor should be operated in the kinetic regime for obtaining the maximum enantioselection. In agreement with this observation, high surface hydrogen concentration (at least 60 bar hydrogen pressure) favours the enantioselection. Other important parameters of the reaction are the solvent, catalyst pretreatment and cinchonidine concentration. The highest ee obtained until now is 52 % to the (S) product (apolar solvent, room temperature, catalyst prehydrogenation at 400 °C, >0.4 mol% cinchonidine/MPA ratio).

Molecular modelling calculations, combined with NMR and FTIR studies, were also performed (molecular mechanics, MM+ force field) for obtaining information about the nature of cinchonidine - MPA interaction.

189

rganic Chemistry

nantioselective Radical Reactions Using Chiral luminum Based Lewis Acids

nna-Reine Fhal and Philippe Renaud
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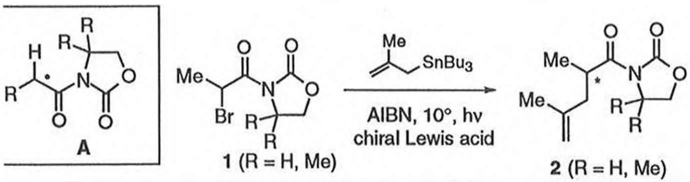
ibourg, Suisse

our approach to devise enantioselective radical reactions,[1] we decided, by ıalogy to cycloaddition reactions, to investigate radicals of type **A**. The *cis/s-trans* isomerism of these radicals and the stereofacial approach are pected to be controlled by *Lewis* acid additives. During our previous work ith *Lewis* acids, we have observed that aluminum derivatives are particulary ficient in radical reactions.[2] So, we decided to focus on chiral *Lewis* acids ntaining aluminum as metal center.



, R = H) and 3-(2-bromopropionyl)-4,4-dimethyl-1,3-oxazolidin-2-one (**1**, = ME) were used for a first screening of Lewis acids of types $(R^*X)_2AlMe$ ıd $(R^*X)_2AlCl$ (X = O, N). A moderate selectivity (er 62:38) has been ›served with methylaluminum TADDOLate. Other The allylation reaction of (2-bromopropionyl)-1,3-oxazolidin-2-one systems will be presented.

) Murakata, M.; Tsutsui, H.; Hoshino, O. *J. Chem. Soc., Chem. Com.* **1995,** 481-482. Urabe, H.; Yamashita, K.; Suzuki, K.; Kobayashi, K.; Sato, F. *J. Org. Chem.* **1995**, 3576-3577. Porter, N. A.; Radinov, R.; Wu, J. H. *J. Am. Chem. Soc.* **1995**, *117*, 11029-11030.
!) Moufid, N.; Renaud, P. *Helv. Chim. Acta* **1995**, *78*, 1001-1005. Renaud, P.; Gerster, M. *J. Am. Chem. Soc.* **1995,** *117*, 6607.

190

Organic Chemistry

Stereoselectivity in Reactions of 1,2-Disubstituted Cyclic Radicals.

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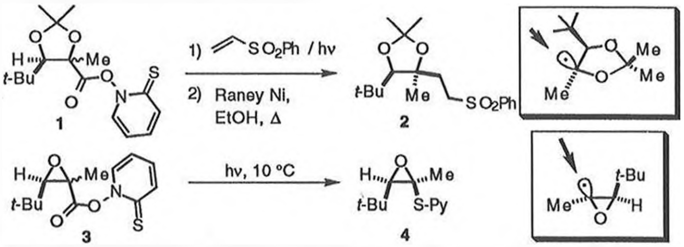
Our investigations of acyclic 1,2-dialkyl-1-alkoxy-2-hydroxy substituted radicals under chelation control showed that *anti-Cram*-cyclic products were preferentially formed.[1] This unexpected result is caused by pyramidalization of the radical intermediates. We report here, that similar effects are governing the stereochemistry of 1,2-disubstituted cyclic radicals. Systems such as for instance 1,3-dioxolan-4-yl and oxiranyl radicals have been investigated.[2] Irradiation of the Barton ester **1** in the presence of phenyl vinyl sulfone affords **2** as a single diastereoisomer. Interestingly, the reaction is occuring *syn* to the very bulky *t*-butyl group. Similar results were observed with oxiranyl radicals generated from **3**.



The stereochemical outcome of these reactions can be explained by pyramidalization of the radical intermediates. We are actually trying to demonstrate that such effects are also important for planar radical intermediates due to transition state pyramidalization.

(1) Renaud, P.; Gerster, M. submitted for publication.
(2) Giese, B. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 969-1146.

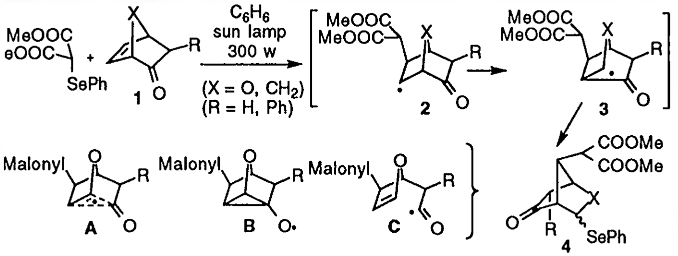
191

;ganic Chemistry

2-Acyl migration in bicyclic systems: A mechanistical study

›kol Abazi, Pierre-Alain Carrupt, Juliette Fitremann et Philippe Renaud
ıiversité de Fribourg, Institut de Chimie Organique, CH-1700 Fribourg

ıe radical addition of dimethyl (phenylselanyl)malonate on bicyclic tones of type **1** affords mainly products of 1,2-acyl migration **4**. This ıaction is the key step of a the synthesis of 12-*epi*-prostaglandins.[1] The act mechanism of the rearrangement **2**→**3** is related to the radical ːdiated one carbon atom ring expansion of monocyclic ketones and has t yet been firmly established.[2]



ısed on calculations and experiments, we have been able to demonstrate ıt a concerted mechanism via a transition state of type **A** is certainly ɾolved. The mechanism going through a tricyclic cyclopropyloxy radical which seems to prevail with monocyclic ketones is strongly disfavored by ıg strain as shown by calculations. At third mechanism, i.e. fragmentation an acyl radical **C** followed by cyclization could not be ruled out by lculations. This possibility could be ruled out by performing the reaction th 3-phenylbicyclo-[2.2.1]hept-5-en-2-one (X = CH_2, R = Ph). In this ʒe, decarbonylation of the putative acyl radical **C** is expected to be much ›re rapid than the cyclization reaction. Since no decarbonylation product observed, we can exclude the fragmentation-cyclization mechanism.

P.Renaud, J-P. Vionnet, J.Org.Chem., **1993**, *58*, 5895-5896
J-P.Vionnet, P.Renaud, Helv.Chim.Acta, **1994**, *77*, 1781-1790
P.Dowd, W.Zhang, Chem. Rev. **1993**, *93*, 2091-2115

192

Organic Chemistry

New Chiral Diselenides in Selective Cyclisation Reactions

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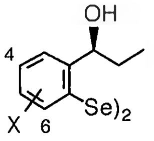
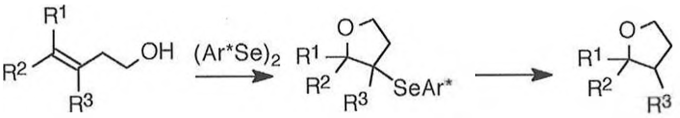
Stereoselective functionalizations of not activated C=C double bonds can be performed efficiently with the help of chiral selenium electrophiles. To increase the electrophilicity of the unsubstituted diselenide **1** (X=H) we have synthesized acceptorsubstituted diaryl diselenides **2** (X=4-NO_2) and **3** (X=6-CF_3). We applied these diselenides to addition reactions with alkenes and obtained the products with diastereomeric ratios up to 95 : 5.



1 X = H
2 X = 4-NO_2
3 X = 6-CF_3

With alkenes bearing internal nucleophiles (e.g. OH) intramolecular cyclisation reactions are possible. After the cleavage of the selenium group chiral substituted tetrahydrofurans are obtained with good stereoselectivities. By variation of the substituents R^1, R^2, and R^3 we are investigating the mechanism of this reaction.

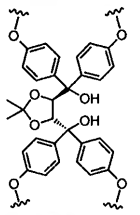


CHIMIA 50 (1996) Nr. 7/8 (Juli/August)

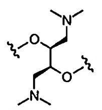
Organische Chemie **193**

Versuche zur Anwendung von chiralen Dendrimeren in der Katalyse

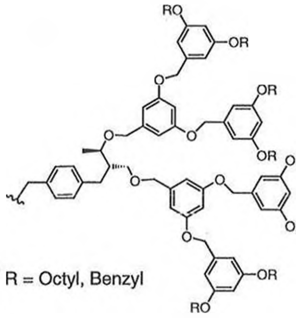
P. Beat Rheiner, Peter Murer und Dieter Seebach
Laboratorium für Organische Chemie, Eidgenössische Technische Hochschule, ETH-Zentrum, Universitätstrasse 16, CH-8092 Zürich



1



2



R = Octyl, Benzyl

In unserer Gruppe wurde der Einfluss chiraler Bausteine auf die Struktur von Dendrimeren untersucht. Während aus CD-, ^{13}C-Relaxations- und Viskositätsmessungen bereits interessante Informationen erhalten werden konnten [1], wurden nun mit neu synthetisierten, chiralen dendritischen Liganden erster bis dritter Generation deren Eigenschaften in der Katalyse untersucht. Dazu wurden von TADDOL und DDB abgeleitete Liganden wie **1** oder **2** eingesetzt.

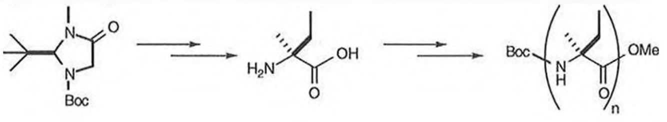
[1] P. Murer und D. Seebach, *Angew. Chem.* **1995**, *107*, 2297; Teil der Dissertation von P. Murer, ETH Zürich, **1996**.

Organic Chemistry **194**

Homooligopeptides Derived from (*S*)-(+)-Isovaline: Studying Their Conformations in the Solid State and in Solution

Masakazu Tanaka, Christine Braun, Florian N.M. Kühnle, Paul Seiler, Bernhard Jaun and Dieter Seebach
Laboratorium für Organische Chemie, Eidgenössische Technische Hochschule, ETH-Zentrum, Universitätstrasse 16, CH-8092 Zürich

The synthesis of (*S*)-(+)-isovaline ((*S*)-(+)-Iva) **2** from *t*-butyl (*S*)-2-*t*-butyl-1,3-imidazolidin-4-one ((*S*)-Boc-BMI) **1** has been carried out on a large scale (up to 0.3 mol) using methods developed within our group [1].



1 **2** **3**

Standard peptide coupling procedures resulted in the formation of several homooligopeptides **3** (n = 2 - 6). X-Ray crystal structure analysis of three of these peptides **3** (n = 3, 4, 6) showed two independent molecules in the asymmetric unit - one right-handed and one left-handed 3_{10}-helix. Previous work in this field had identified only one helix in the asymmetric unit of similar oligopeptides [2]. Variable temperature NMR spectroscopy of the hexamer has confirmed the presence of both types of helix in solution.

---

[1] D. Seebach, A. Sting, M. Hoffmann, *Angew. Chem*, **1996**, In Press.

[2] F. Formaggio, M. Crisma, G.M. Bonora, M. Pantano, G. Valle, C. Toniolo, A. Aubry, D. Bayeul, J. Kamphuis, *Peptide Research*, **1995**, *8*, 6.

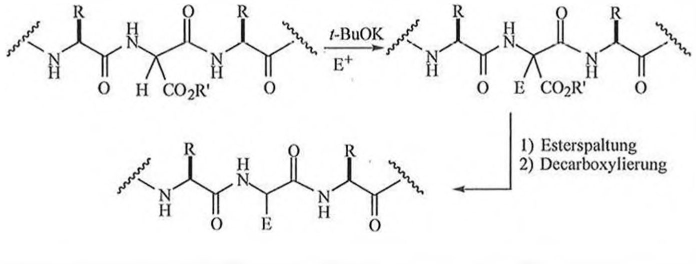
195

Organische Chemie

Herstellung und *C*-Alkylierung von Peptiden mit Aminomalonsäure-Bausteinen

Thomas Matt und Dieter Seebach
Laboratorium für Organische Chemie, Eidgenössische Technische Hochschule, ETH Zentrum, Universitätstrasse 16, CH-8092 Zürich

In früheren Arbeiten haben wir gezeigt, dass sich Oligopeptide über polylithiierte Derivate an Sarkosin- oder Glycin-Bausteinen alkylieren lassen [1]. Dabei werden zuerst alle aciden HX-Protonen entfernt und danach wird eine CH_2-Gruppe unter Enolatbildung deprotoniert. Dieses Prinzip haben wir nun umgekehrt. Durch den Einbau eines Aminomalonsäuremonoester-Bausteines wird die zu substituierende Position zur acidesten Stelle im Molekül [2].



Die aminomalonsäurehaltigen Peptide können so unter milden Bedingungen mit verschiedenen Elektrophilen in sehr guten Ausbeuten und mit zum Teil beachtlichen Diastereoselektivitäten umgesetzt werden.
Die Verseifung des Aminomalonester-Bausteines und nachfolgende Decarboxylierung liefern die entsprechend modifizierten Peptide.

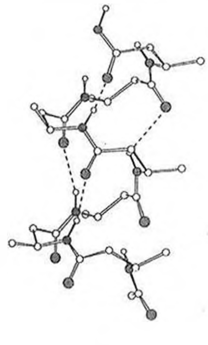
[1] H.G. Bossler, D. Seebach, *Helv. Chim. Acta* **1994**, *77*, 1124.

[2] H.G. Bossler, P. Waldmeier, D. Seebach, *Angew. Chem.* **1994**, *106*, 455.

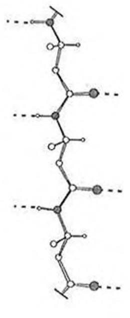
Organische Chemie **196**

Synthese kurzkettiger β-Peptide und Untersuchungen zur Sekundärstruktur

Dario Rigo, Tobias Hintermann, Bernhard Jaun, Jennifer Matthews und Dieter Seebach
Laboratorium für Organische Chemie, Eidgenössische Technische Hochschule, ETH-Zentrum, Universitätstrasse 16, CH-8092 Zürich



1



2

In unserer Gruppe wurde die Bildung helicaler Strukturen (1) in β-Hexapeptiden mittels NMR-Messungen nachgewiesen [1]. Di Auswirkungen von Substitutionen an verschiedenen Stellen des Rückgrate auf die Sekundärstruktur wurden untersucht. Wir wollen den Einflus intramolekularer Disulfidbrücken oder Coulomb-Wechselwirkungen de Seitenketten auf die Stabilität der Helix studieren. Ausserdem soll di Sekundärstruktur von α,β-disubstituierten β-Peptiden studiert werden Durch diese synthetischen Variationen suchen wir ander Sekundärstrukturen wie Schleifen und Faltblätter (2).

[1] D. Seebach, M. Overhand, F. M. N. Kühnle, B. Martinoni, L. Oberer, U. Hommel, H. Widmer, *Helv. Chim. Acta* **1996**, *79*, im Druck

Organische Chemie **197**

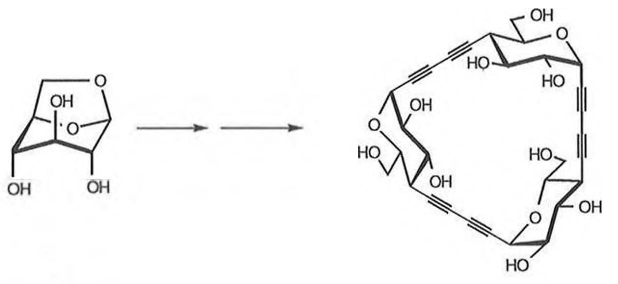
SYNTHESIS OF A CYCLODEXTRIN ANALOGUE

by Roland Bürli and Andrea Vasella*

boratorium für Organische Chemie, ETH-Zentrum, Universitätsstrasse 16,
CH-8092 Zürich

study the influence of weak interactions, particularly of intra- and inter-olecular hydrogen bonds, on the structure and properties of oligo- and lysaccharides, we are preparing analogues of the native glucanes, in which me or all glycosidic oxygens are substituted by 1,3-butadiyne-1,4-diyl oieties [1].

e describe the synthesis of the cyclic trimer **2** from levoglucosane **1**.



1 2

] C. Cai, A. Vasella, *Helv. Chim. Acta* **1996**, *79*, 255; and earlier papers in the series.

Organische Chemie **198**

Me$_3$Si/Me$_3$Ge: Orthogonal Protecting Groups for Dialkynes

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Laboratorium für Organische Chemie, ETH Zentrum, Universitätstr. 16
CH-8092 Zürich

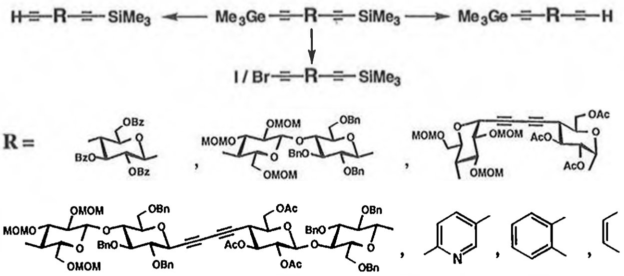
We are preparing polysaccharide analogues where some or all glycosidic oxygens are replaced by butadiynediyl units.

The synthesis of these analogues is based on the cross coupling of saccharide derived dialkynes and requires orthogonally protected ethynyl moieties [1].

The first orthogonally protected dialkynes possess Me$_3$Si and [*d*imethyl(*o*xy)-*p*ropyl]dimethyl*s*ilyl (DOPS) groups [2].

The replacement of the DOPS group by Me$_3$Ge is shown to be advantageous.

We report the synthesis of several Me$_3$Si/Me$_3$Ge-protected dialkynes [3] [4] and methods for their regioselective protodemetallation and bromo-/iododegermylation.



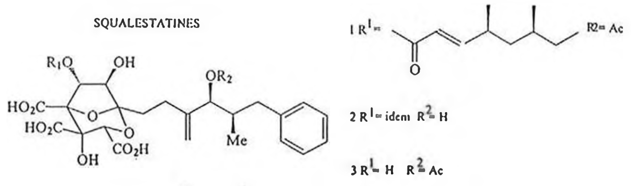
[1] J. Alzeer, C. C., A. Vasella, *Helv. Chim. Acta* **1995**, *78*, 242.
[2] C. Cai, A. Vasella, *Helv. Chim. Acta* **1995**, *78*, 732.
[3] L. Gobbi, Diplomarbeit WS 1996, ETH Zürich, 1996.
[4] A. Ernst, R. Bürli, A. Vasella, *unpublished results*

199

organic chemistry

toward a total synthesis of squalestatine 1

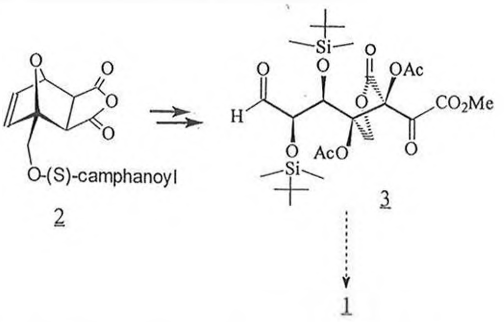
Nathalie Jotterand and Pierre Vogel *
institute of organic chemistry (ICO)
University of Lausanne , CH-1015 Lausanne



1

qualestatine (1) is a potent inhibitor of squalene synthase, an enzyme hich takes part in the biosynthesis of cholesterol.

elted maleic anhydride adds to furfuryl (1S)-camphanate to give the ptically pure adduct 2[1] .We shall describe the conversion of 2 into dehyde 3, a potential synthetic precursor of 1 .



2 3 1

[1] V. Theurillat-Moritz, Univ. of Lausanne, unpublished

200

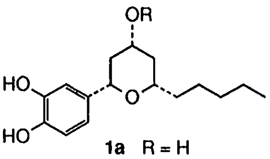
Organische Chemie

Synthese von optisch aktiven n-Alkyloxycatecholen als Inhibitoren von Lipoxygenase

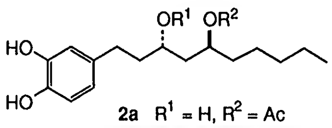
Mathias Juch und Peter Rüedi

Organisch-chemisches Institut der Universität, 8057 Zürich

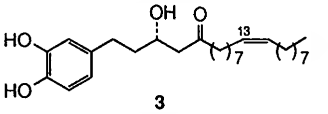
Die nach dem Leitkriterium der antioxidativen Aktivität aus *Plectranthus sylvestris* (Labiatae) isolierten Alkyloxycatechole konnten in enantiomerenreiner Form hergestellt werden. Die offenkettigen Verbindungen wurden nach Aldolkondensation und enantioselektiver Reduktion, die cyclischen Komponenten durch Phenoloxidation von **2b** erhalten.



1a R = H
1b R = Ac



2a R^1 = H, R^2 = Ac
2b R ^{1}= Ac, R^2 = H



3

Neben ihrer antioxidativen Aktivität (Grössenordnung BHA, BHT) sind die Verbindungen *in vitro* Inhibitoren der Lipoxygenase mit IC$_{50}$-Werten im µMol- (**1** und **2**; Grössenordnung NDGA), bzw. nMol-Bereich (**3**).

Organic Chemistry **201**

Total Synthesis of Bauhinin

Guillaume Desmares and Claude Le Drian
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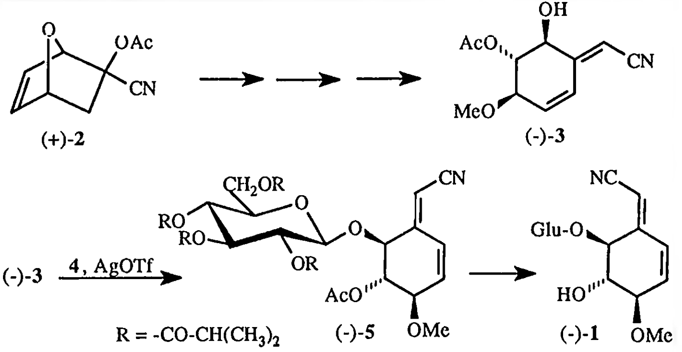
3, rue Alfred Werner F-68093 MULHOUSE Cedex.

Bauhinin (-)-**1** (**1**), a cyanoglucoside, has been isolated from roots of a leguminous plant from Taiwan, *Bauhinia Championii*. Cyanoglucosides are relatively rare compounds, found in plants showing biological activity. Only one cyanoglucoside, Simmondsin, has been synthetized so far.
We report here the first total synthesis of Bauhinin. The starting material was the optically pure Diels-Alder adduct (+)-**2** [2] from which the aglycone (-)-**3** was prepared in several steps including functionalization of the double bond, Wittig-Horner reaction and cleavage of the oxa bridge [3].
A new reagent, bromotetraisobutyrylglucose (**4**), had to bee used in the Koenigs-Knorr reaction to obtain selectively in fair yield the ß-glucoside (-)-**5**, which was then easily transformed in naturally occuring Bauhinin.
We are now studying the selective formation of ß-glucosides from several secondary alcohols with this new reagent (**4**). The first results show a significant improvement over existing procedures.



[1] C.C. Chen et al., *J. Nat. Prod.* **1985**, *48*, 933.
[2] A. Warm, P. Vogel, *Helv. Chim. Acta* **1987**, *70*, 690.
[3] E. Vieira, Ph. D. Thesis, Lausanne, **1986**.

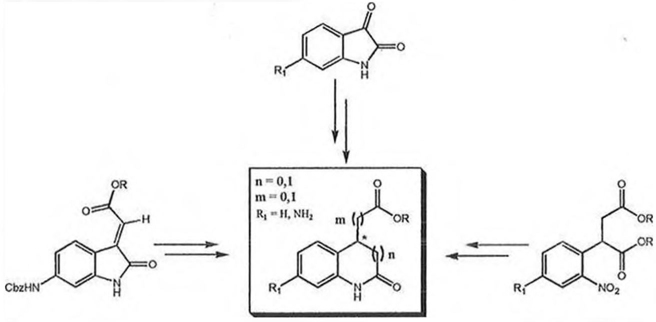
Organic Chemistry **202**

ASSEMBLING NOVEL BIOLOGICALLY ACTIVE-ALKALOID-CATABOLITES RELATED TO INDOLE ACETIC ACID

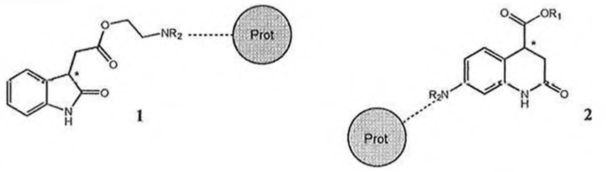
Catherine P. Fankhauser and Ulrich Burger

Dept of Organic Chemistry, University of Geneva, quai E.-Ansermet 30, 1211 Genève 4, Switzerland.

Oxindole acetic acid and related ring-enlarged dihydroquinolines have attracted considerable attention for their plant growth properties (auxin) and more recently for their antineoplastic activities. We report on efficient regioselective syntheses of various analogues *via* Knoevenagel condensation or reductive cyclization (Scheme).



Protein bound structures **1** and **2** have been synthetized for further biological evaluation.



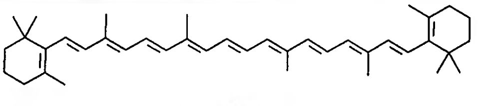
Organische Chemie **203**

Kinetic Study of the Thermal Isomerization of β,β-Carotene.

Martin Brunner and Hanspeter Pfander
Institute of Organic Chemistry, University of Berne, Freiestrasse 3, CH-3012 Berne, Switzerland

It is known that physiologically significant levels of (*Z*)-isomers of (all-*E*)-β-carotene **I**, formed during common food processing procedures, are consumed by humans [1]. It was postulated that either the (15*Z*)- or the (13*Z*)-isomer or both are acting as anticarcinogenic agents [2]. Therefore the interest in the *E*/*Z*-isomerization of carotenoids increased during the last few years.

We report on our kinetic investigation of the thermal isomerization of β-carotene. All experiments were performed at 50°C in degassed ethyl acetate containing 2,2,6,6-tetramethylpiperidin-1-yloxyl (TEMPO) as radical trapping agent to prevent any radical degradation of β-carotene. By using HPLC with a RP-C_{30} column connected to a DAD it was possible to detect simultaneously (all-*E*), (9*Z*), (13*Z*) and (15*Z*)-β-carotene. Rate constants for all isomerization processes were calculated based on the four isomerization reactions, each starting from the pure isomer.



I

While the fast isomerization reactions of (15*Z*)- and (13*Z*)-β-carotene resulted in the formation of (all-*E*)-β-carotene, the slow isomerization reaction of (9*Z*)-β-carotene yielded three di-(*Z*)-isomers and only a small amount of (all-*E*)-β-carotene.

[1] L.A. Chandler and S.J. Schwartz, *J. Agric. Food Chem.* **36**, 129-133 (1988).
[2] W. von E. Doering, C. Sotitiou-Leventis and W.R. Roth, *J. Am. Chem. Soc.* **117**, 2747-2757 (1995).

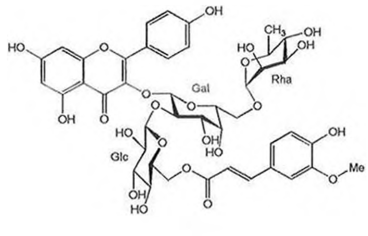
Organic Chemistry **204**

APPLICATION OF TWO-DIMENSIONAL NMR METHODS AT 14 TESLA TO THE STRUCTURE DETERMINATION OF A COMPLEX GLYCOSIDE

Gerhard Brunner[1], Pierre Castioni[2] and Ulrich Burger[1]

1- Dept. of Organic Chemistry, 2- Dept. of Pharmacognosy, University of Geneva, quai Ernest-Ansermet 30, 1211-Geneva-4, Switzerland

We report on the structure elucidation of a novel glycoside isolated from *Brunfelsia grandiflora*, a Solanacea growing in South America, which shows highly anti-inflammatory properties. COSY-DQF reveiled that the glycoside **1** is made up of five building blocks. Three of them are hexoses, *i. e.* glucose, galactose and rhamnose, all being present in the pyranoid form. The two aglycone building blocks are shown to be the flavonoid kaempferol, and ferulate, a disubstitued cinnamate. Full assignment of all ^{13}C-resonances was made. The interconnection of the five subunits was established by means of GRASP-HMQC experiments optimised for the detection of C,H long range couplings. GRASP-HMQC moreover completed information not available from COSY-DQF experiments due to overcrowded spectral areas. Finally ROESY spectroscopy was exploited to unveil the link between kaempferol and galactose, wich could not be dedected by HMQC because of a nearly zero scalar 3J coupling.



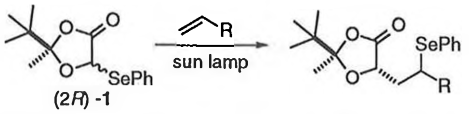
1

Organic Chemistry **205**

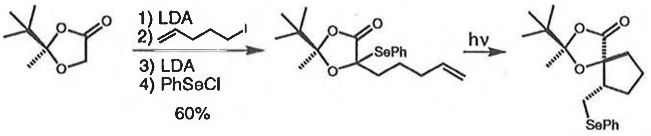
Highly Stereoselective Radical Alkylation of a Chiral Derivative of Glycolic Acid

Sokol Abazi and Philippe Renaud
Université de Fribourg, Institut de Chimie Organique, Pérolles, 1700 Fribourg, Suisse

Recently, Byers and others have reported the formation of C-C bonds by transfer of a phenylselanyl group.[1] We have already reported that the selenium transfer method allow to perform radical addition with alkoxy-substituted ester radicals despite their captodative stabilization.[2] We report here a general method for the preparation of enantiopure α-hydroxy acids using the (2*S*)- and (2*R*)-5-phenylselanyl-2-tert-butyl-2-methyldioxolane-4-one **1**. The influence of the stereoelectronic effects will be discussed.



Combination of classical enolate alkylation and radical cyclization procedure an be used for the preparation of cyclic α-hydroxy ester with high yield and xcellent stereocontrol. The effect of temperature on product distribution radical cyclization versus radical dimerization) will be discussed.



1) Byers, J.H.; Lane, G.C. *J. Org. Chem.* **1993**, *58*, 3355; Curran, D. P.; Martin-Esker, A. A.; Newcomb, M. *J. Org. Chem.* **1993**, *58*, 4691; Renaud, P.; Vionnet, J. P. *J. Org. Chem.* **1993**, *58*, 5895.
2) Renaud, P.; Abazi, S. *Synthesis* **1996**, *2*, 253.

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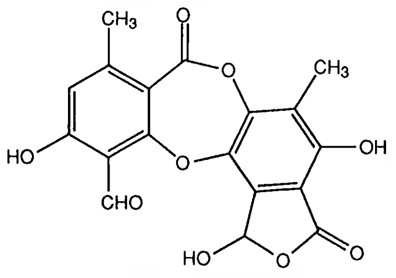
rganic Chemisty **207**

hytochemical study of the lichen *Bryoria fuscescens* and attempt synthesize natural lactonic depsidones

. Rama, A. Fkyerat and R. Tabacchi
stitut de Chimie de l'Université de Neuchâtel
v. de Bellevaux 51, CH-2000 Neuchâtel

The plant material of the lichen *Bryoria fuscescens* was tracted with hexane, ether, acetone and methanol. After romatographic separations and purifications, we obtained veral typical lichen compounds consisting of monophenolic rivatives, depsidones, sterols, fatty acids and sugars.

Among these depsidones, we isolated norstictic acid which a depsidone containing a hydroxy-phthalide cycle.



Norstictic acid

An original method for total synthesis of this product will discussed.

Organic Chemistry **206**

Isolation of Phytotoxic Metabolites from culture medium of *Stereum hirsutum*

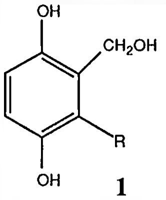
G.-M. Dubin, R. Tabacchi

Institut de Chimie de l'Université de Neuchâtel,
Av. de Bellevaux 51, CH-2000 Neuchâtel

Esca is a vine disease. It is caused by five fungii : *Stereum hirsutum, Phialophora parasitica, Phellinus sp., Cephalosporium* or *Acrimonium* and *Eutypa lata*.

In the course of the analysis of the culture medium of pathogenic agents, several metabolites were isolated.

Some of these compounds are described belows :



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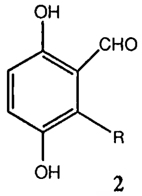

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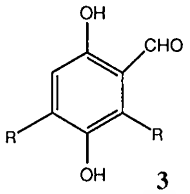


3

Frustulosin (1) and frustulosinol (2) were reported as metabolites from *Stereum frustulosum* [1,2].

Compounds (2), (3) and other derivatives isolated from toxic fractions are now in investigation.

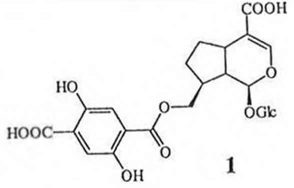
[1,2] Nair M. S., Anchel M., *Tetrahedron Lett.* 1975, 2641-2642; *Phytochemistry* 1977, **16**, 390-392.

Chimie organique **208**

Search for antioxidants in higher plants - blumeoside A, a new iridoid glucoside with free radical scavenger properties from *Fagraea blumei*

Muriel Cuendet[1], Kurt Hostettmann[1], Wahjo Dyatmiko[2] and Olivier Potterat[1]
1 Institut de Pharmacognosie et Phytochimie, Université de Lausanne, BEP, 1015 Lausanne, Switzerland
2 Fakultas Pascasarjana, Universitas Airlangga, Surabaya, Indonesia

Oxygen reactive species are now recognized to be involved in a great variety of diseases and even in normal aging. In this context, natural antioxidants are receiving increasing attention as leads for the development of new drugs and as an alternative to the use of synthetic compounds in food technology. When searching for new leads in plant extracts, it is of crucial importance to dispose of assays allowing rapid identification of the active constituents in order to avoid repeated isolation of well-known compounds. Our screening strategy is based on tests enabling visualization of the active constituents in crude mixtures. Bleaching of β-carotene [1] and reduction of the free radical diphenylpicrylhydrazyl (DPPH) [2] have been used for the systematic TLC screening of plant extracts.
As part of this screening, we detected in the methanol extract of *Fagraea blumei* (Loganiaceae) a strongly fluorescing compound with free radical scavenging properties against DPPH radical. Activity-guided fractionation afforded the new iridoid glucoside blumeoside A (**1**). In addition, a related compound, blumeoside B, in which two iridoid moieties are linked together with a hydroxyterephthalyl acid unit, was isolated and characterized. Activity of blumeoside A was comparable to that of the synthetic antioxidant butylhydroxytoluene (BHT). Detailed characterization of the antioxidative properties of **1** is in progress.



1

[1] Pratt, D.E., Miller, E.E. (1984) *J. Am. Oil Chem. Soc.* **61**, 1064.
[2] Takao, T., Kitatani, F., Watanabe, N., Yagi, A., Sakata, K. (1994) *Biosci. Biotech. Biochem.* **58**, 1780.

CHIMIA *50* (1996) Nr. 7/8 (Juli/August)

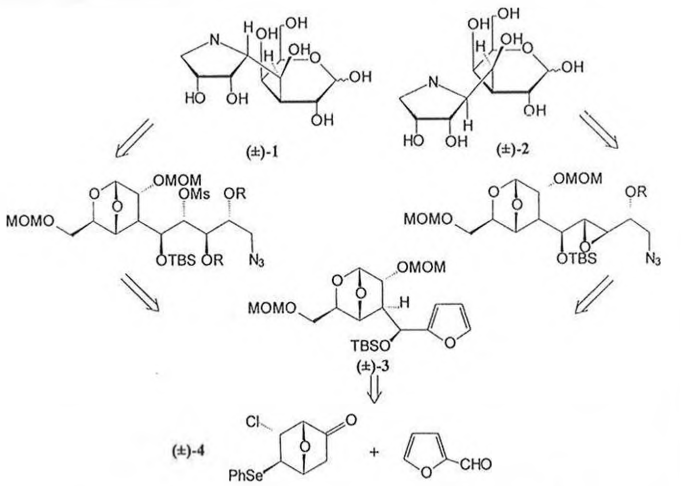
Organic Chemistry

209

Total Synthesis of Sugar Mimics Bearing a Polyhydroxylated Pyrrolidine Subunit C-linked to Galactose

K. Kraehenbuehl, P. Vogel*
Section de chimie de l'Université de Lausanne, BCH, CH-1015, Lausanne-Dorigny, Switzerland.

Inhibitors of the enzyme-promoted hydrolysis of C-O glycosidic bonds have potential applications as antibacterial, antiviral and anticancer agents.[1] Disaccharide mimics (±)-**1** and (±)-**2** were designed to combine some of the features thought to bring about good inhibition properties. The target molecules were synthesised via two routes (6, 7 steps) starting from a common intermediate, the anhydrosugar (±)-**3**[2] itself derived from "naked sugar" (±)-**4** and furfural.



1. Legler, G. *Adv. Carbohydr. Chem. Biochem.*, **1990**, *48*, 319-384.
2. Kraehenbuehl, K.; Vogel, P. *Tetrahedron Lett.*, **1995**, *36*, 8595-98.

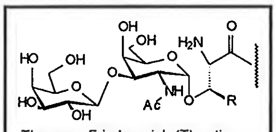
Organic Chemistry

210

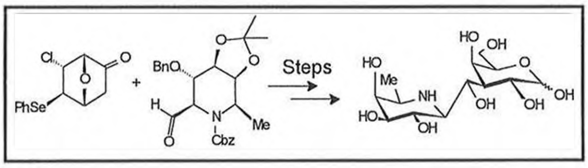
Synthesis of a β-(1→3)-*C*-linked Trideoxy-1,5-iminogalactoside of D-Galactose Derivative, Mimic of the Thomsen-Friedenreich (T) antigen.

Alain Baudat and Pierre Vogel

Section de Chimie de l'Université de Lausanne, BCH-Dorigny,
CH-1015 Lausanne


Thomsen-Friedenreich (T) antigen

As cellular carbohydrate structures are involved in multiple cellular functions, alterations in these structures have been studied in an effort to find markers and predictors of the clinical course of disease in human cancers. The Thomsen-Friedenreich (T) antigen and its disaccharide component D-Gal-β-*O*-(1→3)-D-Gal*N*Ac, have been proposed as useful tumor markers because of their apparently specific occurrence in certain types of carcinomas[1].
We report here the synthesis of a non-hydrolysable analogue, the 3-deoxy-3-*C*-[(1'*S*)-2',6',7'-trideoxy-2',6'-imino-β-D-*glycero*-L-*manno*-heptitol-1'-yl]-β-D-galactose, which was obtained through a highly stereoselective cross-aldolisation of a 2,6,7-trideoxy-2,6-imino-D-*glycero*-L-mannose and a 7-oxanorbornanone derivative[2].



[1] G.F. Springer, *Science*, **1984**, *224*, 1198-1206.
[2] A. Baudat, P. Vogel, *Tetrahedron Lett.*, **1996**, *37*, 483-484.

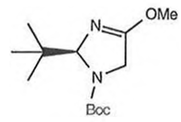
Organische Chemie

211

Synthese von nicht-proteinogenen Aminosäuremethylestern mit hydrolyseempfindlichen Seitenketten

Matthias Hoffmann und Dieter Seebach
Laboratorium für Organische Chemie, Eidgenössische Technische Hochschule, ETH-Zentrum, Universitätstrasse 16, CH-8092 Zürich

In unserer Gruppe wurde im Hinblick auf eine neue, milde Methode zur Synthese von nicht-proteinogenen Aminosäureestern der chirale Glycinbaustein **1** und dessen Enantiomer hergestellt [1]. Man fand, dass der chirale Baustein **1** mit verschiedenen Elektrophilen in guten bis sehr guten Ausbeuten diastereoselektiv alkyliert werden konnte. Neben Monoalkylierungen (→ **2**, R^1=H) konnten in einer "Eintopfreaktion" auf einfache Art und Weise auch Dialkylierungen (→ **2**) durchgeführt werden. Dabei zeigte sich, dass auch die Zweitalkylierungen hoch diastereoselektiv verliefen. Die so erhaltenen mono- und disubstituierten Glycinbausteine konnten unter sauren Bedingungen in guten Ausbeuten zu den entsprechenden Aminosäureestern **3** gespalten werden. Dank der im Vergleich zu anderen Methoden [2] relativ milden Hydrolysebedingungen wurde so eine breite Palette von enantiomerenreinen, nicht-proteinogenen Aminosäuremethylestern mit hydrolyseempfindlichen Seitenketten leicht zugänglich.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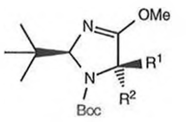
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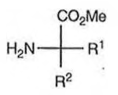
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[1] S. Blank, D. Seebach, *Angew. Chem.* **1993**, *105*, 1780, *ibid. Int. Ed. Engl.* **1993**, *32*, 1765.
[2] R. M. Williams, 'Synthesis of Optically Active α-Amino Acids', Pergamon Press, Oxford, 1989; R. O. Duthaler, *Tetrahedron* **1994**, *50*, 1539.

Organische Chemie

212

Design und Synthese eines DNS-Analogons mit Polyamidrückgrat ("Distamycin-NA")

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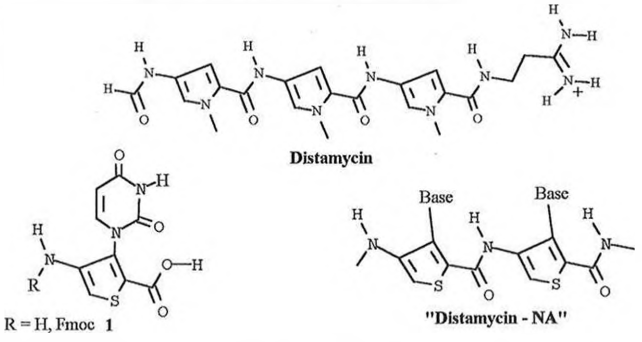
Nucleinsäureanaloga mit Peptidrückgrat sind vielversprechende Kandidaten im Rahmen der Antisensestrategie (vgl.[1]). Strukturelle Vorbilder des hier beschriebenen DNS-Analogons "Distamycin-NA" bilden die natürlichen Antibiotika der Netropsin- und Distamycin- Familie, welche aufgrund ihrer helicalen Gestalt DNS-Doppelhelices effizient in der kleinen Furche komplexieren [2]. In der "Distamycin-NA" sind somit intrinsische Helizität und Basenerkennung strukturell miteinander vereint.



Wir berichten hier über Synthese sowie strukturelle Eigenschaften der Monomereinheit **1** sowie eines Dimeren enthaltend die Base Uracil.

[1] M.Egholm, O.Burchardt, P.E.Nielsen, R.Berg, Science, 1991, 254, 1497-1500 und J.Am.Chem.Soc., 1992, 114, 1895-1897.
[2] P.B. Dervan et al. J.Am.Chem.Soc., 1987, 109, 7564-7566.

213

ıysikalische Chemie

Femtosecond lifetime investigations of hot electrons trapped by adsorbates on a metal surface

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Many photo-induced reactions between adsorbed species and metal rfaces are induced by hot carriers rather than by thermal activation. A ıssible mechanism is that photoexcited electrons in the substrate tunnel rough the surface and become attached to the adsorbed molecules to form temporary, negative molecular ion (hot electron mechanism). The hot ectron is inelastically scattered back into an unoccupied electronic state of e metal substrate, leaving the adsorption system excited with some energy. ne can, therefore, regard negative ion formation as the initiator of a variety photon-stimulated surface dynamical processes.

An important parameter for understanding this mechanism is the lifetime the hot electron inside the adsorbate. This so-called resonance time is rectly related to the energy gain by the adsorbate. Using time-resolved 2-ıoton-photoemission we were able to resolve, for the first time, an increase the lifetime of excited electrons due to an adsorbate resonance; electrons ıpped by an unoccupied Cs-induced state on a Cu(111) surface show an crease in their excitation lifetime of about 11 fs in comparison to the ectrons in the bulk. In contrast, we found no increase in lifetime due to an ıoccupied electronic state, induced by the adsorption of oxygen on ı(111). A simple model to explain the surprisingly high resonance time lue for the Cs-state will be presented.

Physical Chemistry **214**

PICOSECOND TRANSIENT GRATING SPECTROSCOPY

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A transient grating (TG) experiment can be described as a holographic counterpart to flash-photolysis, because information is contained as well in the amplitude as in the phase of the probe light. A TG is created by exciting the sample with two spatially crossed and time coincident laser pulses producing an interference pattern on the sample. This spatially modulated excitation generates grating-like distributions of ground state and excited state, intermediate or product populations. This TG is probed by a third time-delayed laser pulse striking the grating at Bragg angle.

As it is impossible to obtain spectral information by probing with a single frequency laser, we developed an experimental setup for ps transient spectroscopy using white light generated by self-phase modulation for probing.

According to Kogelnik's coupled wave theory, the intensity of the TG signal depends quadratically on changes of both absorbance (amplitude grating) and refractive index (phase grating). Moreover, as the signal is diffracted in a unique direction and has a zero background, this technique is much more sensitive than linear transient spectroscopies (figure 1).

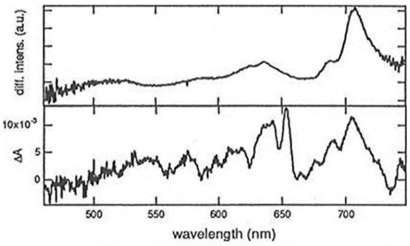

Figure 1: Diffracted spectrum (top) and transient absorption spectrum (bottom) of 9, 10-dicyanoanthracene with 0.5 M anisole in acetonitrile measured 250 ps after excitation using same experimental conditions.

Recent results on the dynamics of photoinduced electron transfer reactions, obtained with this technique, will be presented.

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ysikalische Chemie **215**

ıotophysical Properties and Stark Effect of Single Perylene Molecules

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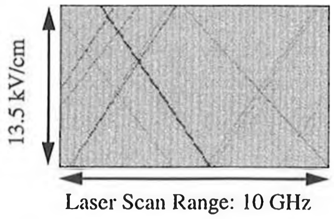
Fluorescence excitation and emission spectroscopy of single molecules MS) at liquid helium temperature allows to determine photophysical paneters of molecules, and reveals information about short-range guest-host eractions.

Laser induced fluorescence emission ($S_1 \rightarrow S_0$) from a molecule is interıted, when the molecule is trapped in its triplet state T_1. A dark period with photon emission occurs, until the molecule relaxes to its electronic ground te S_0, where it is accessible for further excitation-emission cycles. This lving of the molecule in its triplet state can be monitored *directly* by SMS. e statistical evaluation of the "on"- and "off"-periods reveals photophysical ormation about the triplet lifetime, the intersystem crossing rate and the insystem crossing quantum yield for each individual molecule.



The spectral position of a single molecule absorption line is highly sensitive to changes of the matrix or to externally applied perturbations, such as hydrostatic pressure or static electric fields. The Stark effect causes a shift of the absorption line of a molecule on the frequency axis upon aping an electric field. The dark lines in the figure represent the resulting tracıf single molecule excitation profiles in the frequency-electric field plane. analysis allows to estimate internal electric fields and the difference of the tric dipole moment between S_0 and S_1.

Physikalische Chemie **216**

Photoinduced Bimolecular Reactions in Clusters

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The photodissociation of homogeneous methyl nitrite clusters $[CH_3ONO]_n$ was investigated in a supersonic jet using laser excitation to the $S_1(n\pi^*)$ state. Previous work showed that the dissociation of a cluster bound CH_3ONO molecule leads to the formation of two different energy distributions of $NO(X^2\Pi)$ fragments depending on its site in the cluster [1]. Recently also nitroxyl $HNO(X^1A')$ and formaldehyde $H_2CO(X^1A_1)$ have been observed as the products of the photoinduced cluster reaction. The state selective detection of the NO fragments and the products HNO and H_2CO was accomplished by LIF spectroscopy. The reaction mechanism leading to the formation of HNO and H_2CO is a bimolecular reaction of the photofragments NO and CH_3O mediated by a cluster cage effect. The fragments collide with the surrounding solvent molecules giving rise to a prompt recoil and subsequent recombination and disproportionation.

Primary process : $CH_3ONO \xrightarrow{h\nu} CH_3O + NO$
Recombination : $CH_3O + NO \longrightarrow CH_3ONO$
Disproportionation : $CH_3O + NO \longrightarrow H_2CO + HNO$

This reaction scheme can also be applied to explain the results of previous photodissociation experiments with methyl nitrite in solid matrices, which yielded exclusively H_2CO and HNO [2].

[1] E. Kades, M. Rösslein and J. R. Huber, *J. Phys. Chem.* **97** (1993) 989 and **98** (1994) 13556.
[2] R. P. Müller and J. R. Huber, *Rev. Chem. Intermed.* **5** (1984) 423.

Physical Chemistry **217**

Accurate van der Waals and hydrogen bond energies between 1-naphthol and several solvent partners

C. Wickleder, T. Bürgi, T. Droz and S. Leutwyler
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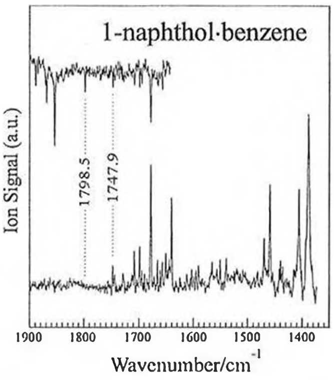
Mass-selective vibronic spectra of the ground state of jet cooled 1-naphthol•S complexes were obtained using pump-dump-probe spectroscopy (PDP). The ground state dissociation energy $D_0(S_0)$ of the van der Waals or hydrogen-bonded complex can be bracketed to within typically ± 2%. Taking into account the spectral shift of the origin of the cluster relative to that of bare 1-naphthol the first excited state dissociation energy $D_0(S_1)$ can be obtained. The investigation included hydrogen-bonded complexes (S = water, alcohols, ammonia or benzene) [1] as well as van der Waals type complexes (S = alkanes and cyclohexane).

The dissociation energy in hydrogen bonded complexes should be related to the proton affinity of S in the gas phase. We actually observed a nearly linear dependence between these two properties with oxygen or nitrogen as the proton acceptor.



PDP spectra of 1-naphthol•benzene showing the upper and the lower limit of the dissociation energy

[1] T. Bürgi, T. Droz, S. Leutwyler, Chem. Phys. Lett. 246 (1995) 291.

Physical Chemistry **218**

Dynamics of NIR-to-VIS upconversion in $RbGd_2Br_7$: 1% Er^{3+}

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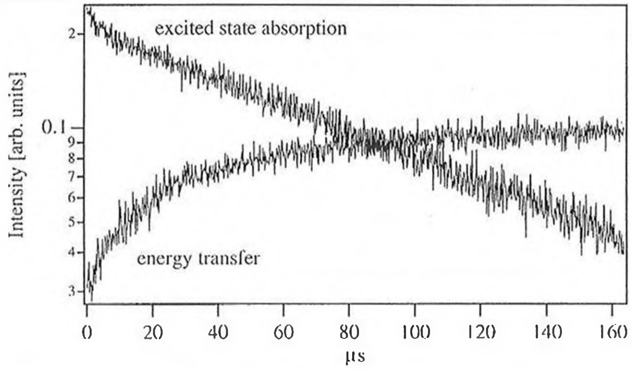
Institut für anorganische Chemie, Universität Bern
Freiestr. 3, 3000 Bern 9

Stepwise addition of near infrared photons followed by luminescence in the visible — known as upconversion — is an ubiquitous phenomenon among Er^{3+} containing compounds. Several processes are known to lead to highly excited states. Most of them rely on excited state absorption (ESA) or a radiationless energy-transfer (ET). Time-dependent measurement of the upconverted luminescence (see Fig.) serve as a fingerprint and can be used to distinguish between these two mechanisms.

The Figure shows the time-dependence of the $^4F_{7/2} \rightarrow {}^4I_{15/2}$ visible luminescence intensity at 10 K after 10 ns excitation pulses into the $^4I_{15/2} \rightarrow {}^4I_{11/2}$ transition of Er^{3+} at 10172 cm^{-1} (ET) and 10289 cm^{-1} (ESA). For these specific excitation energies relatively clean ET and ESA behaviour, respectively, is observed. In general the two processes compete, and the observed time dependence is a superposition of the two. Their relative contributions are strongly temperature dependent.



Chimie physique **219**

Long-lived photoinduced charge separation in heterosupramolecular systems. Redox-type photochromism.

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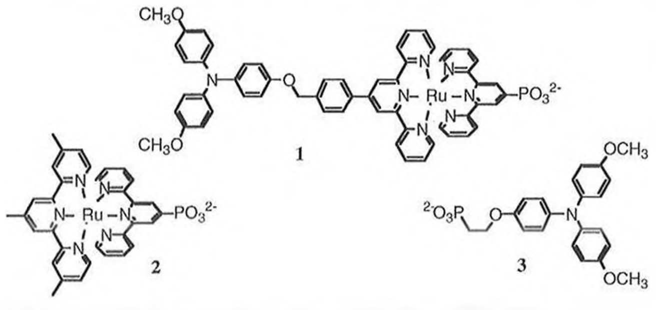
Lorenz Walder and Michael Grätzel
Laboratoire de photonique et interfaces, EPFL, 1015 LAUSANNE

Nanocrystalline TiO_2 electrodes of high specific surface area were derivatized with two entities, a sensitizer (S) and an electrochromophore (D), either linked in a supramolecular assembly or coadsorbed.

The sensitizer is a Ru(II)-polypyridine complex which, after excitation by visible light, injects one electron into the TiO_2 conduction band ($S^* | TiO_2 \rightarrow S^+ | (e^-) TiO_2$). The electrochromophore is a triarylamine, colorless in the reduced state and strongly absorbing red light in the oxidized state (D^+). D is easily oxidized by S^+.

When S and D are linked to the TiO_2 surface, by a phosphonate group, light-induced charge separation (eq. 1) takes place in less than 10 ns, in an intramolecular way (diad **1**) or in an intermolecular way (between **2** and **3**).

$$D{-}S^* | TiO_2 \rightarrow D{-}S^+ | (e^-) TiO_2 \rightarrow D^{+}{-}S | (e^-) TiO_2 \qquad (1)$$



Kinetics of charge separation and recombination will be discussed.

Under positive polarization of the electrode, charge recombination is blocked and photochromism is observed (the electrode turns from orange to green when illuminated). Applications for information storage and self-adaptating filters will be considered.

220

Physical Chemistry

Electron Transfer-induced Mesomorphism in the Ferrocene-Ferrocenium Redox System

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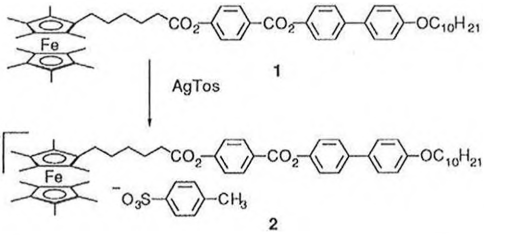
The oxidation of the non-mesomorphic ferrocene derivative **1** produces the paramagnetic ferrocenium salt **2**, which exhibits a monotropic S_A-liquid-crystalline phase (polarised optical microscopy, differential scanning calorimetry, x-ray-diffraction)[1]. This is explained by the electrostatic intermesogen interactions between the ferrocenium-group and its counterion.



A permethylated ferrocene derivative was selected as an electron-dono because of the ease of oxidation of such a species in comparison with les substituted structures {$Fe(cp)_2$ +0.44 V, Fecpcp* +0.13 V, $Fe(cp^*)_2$ -0.1 V}[2]. The cyclic voltamogramm obtained from **1** shows a reversible redo behaviour.

Mesogenic ferrocene and ferrocenium derivatives can be used as redox active molecular units.

[1] R. Deschenaux, M. Schweissguth and A.-M. Levelut, *J. Chem. Soc., Chem. Commun.*, **1996**, 1275.
[2] A. Togni in *Ferrocenes*, ed. A. Togni and T. Hayashi, VCH, Weinheim, ch. 8, 1995.

ıysical Chemistry

221

ɣe Molecules in Zeolites as Artificial Antenna

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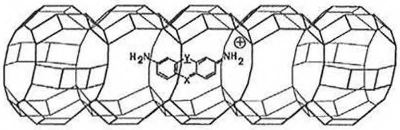
eiestrasse 3, CH-3000 Bern 9, Switzerland

ɣe molecules in zeolite L are able to mimic the reactions of the antenna stem in natural photosynthesis. Concentrations of up to ~0.1 M of dyes :e thionine, pyronine or oxonine inside zeolite L have been reached. The stricted geometry of the zeolite channels excludes aggregation of dye olecules inside zeolite L [1]. The electronic transition dipole moments of : S1←S0 are all parallel.



Schematic view of a dye molecule in the large channel of zeolite L.
Py: Y=O, X=C-H
Ox: Y=O, X=N
Th: Y=S, X=N

ıe short distances between the dye molecules in zeolite L and their spectral operties allow fast energy transfer reactions. We have shown that the ometrical arrangement of the dye molecules supports very efficient isotropic energy migration [2]. The probability that an excitation inside the olite microcrystal will reach traps adsorbed at different places on the outer rface is calculated based on the Förster's theory of energy transfer. The fluences of different parameters on this probability are discussed, namely : microcrystals shape, the spectral properties of the dye, and its concentra- ın in the microcrystal.

] G. Calzaferri and N. Gfeller, J.Phys.Chem. **96** (1992), 3428-3435
] F. Binder, G. Calzaferri and N. Gfeller, Proc. Indian Acad.Sci. 'hem.Sci), **107** (1995), 1-15

Physikalische Chemie

222

Resonant and Phonon-Assisted Energy Transfer within the R_1-line of $[Cr(ox)_3]^{3-}$ in three-dimensional oxalato-networks

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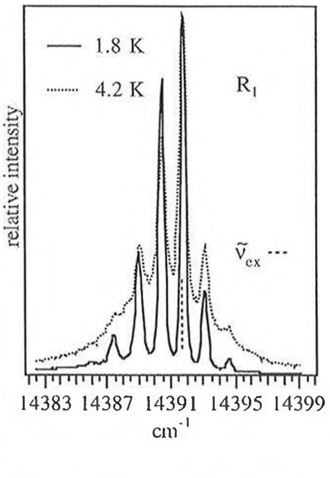
a) Institut für anorg. und physik. Chemie, Universität Bern, 3012 Bern
b) Research School of Chemistry, Australian National University, Canberra
c) Anorganisch-Chemisches Institut der Universität Zürich, 8057 Zürich

The three-dimensional network structures $[Rh(bpy)_3][NaCr(ox)_3]ClO_4$ and $[Ru(bpy)_3][LiCr(ox)_3]$ are singularly suited for studying a number of excitation energy transfer processes in the solid state.

In both compounds the expected luminescence from the lowest excited state, the ^2E state, of the $[Cr(ox)_3]^{3-}$ chromophore is observed. Resonant and phonon-assisted energy transfer processes within the R_1 line of the $^2E \rightarrow {}^4A_2$ transition can be unambiguously distinguished, using the technique of resonant fluorescence line narrowing. At 1.8 K the former is dominant, with increasing temperature the latter becomes more efficient.



Resonant Fluorescence Line Narrowing spectra of $[Ru(bpy)_3][LiCr(ox)_3]$

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hysikalische Chemie

223

MR Studies and MD Simulations of the Hydration of Proteins and ucleic Acids in Aqueous Solution.

urt Wüthrich, Martin Billeter, Peter Güntert, Peter Luginbühl, Roland iek and Gerhard Wider
ıstitut für Molekularbiologie und Biophysik, Eidgenössische :chnische Hochschule-Hönggerberg, CH-8093 Zürich, Switzerland.

uclear magnetic resonance (NMR) information on the hydration of oteins and nucleic acids in aqueous solution[1] is largely ımplementary to the information obtained by diffraction experiments ith single crystals, which is the only other approach available for udies of hydration at atomic resolution. This presentation will focus on MR studies of the rate processes governing the exchange of water olecules between the bulk solvent and the hydration sites on the ological macromolecules. The use of diffusion filters in NMR :periments for observation of hydration water molecules[2,3] will be :scribed, and results of a long-time molecular dynamics (MD) mulation used to support the analysis of NMR data on hydration water the intermolecular interface of protein–DNA complexes[3,4] will be 'esented.

eferences

Otting, G., Liepinsh, E. and Wüthrich, K. (1991) *Science* **254**, 974–980: Protein hydration in aqueous solution.
Wider, G., Riek, R. and Wüthrich, K. (1996) *J. Am. Chem. Soc.*, submitted: Diffusion filters for separation of solvent–protein and protein–protein NOEs (HYDRA).
Wüthrich, K., Billeter, M., Güntert, P., Luginbühl, P., Riek, R. and Wider, G. (1996) *Faraday Discussions*, in press: NMR studies of the hydration of biological macromolecules.
Billeter, M., Güntert, P., Luginbühl, P. and Wüthrich, K. (1996) *Cell*, in press: Hydration and DNA recognition by homeodomains.

224

Physikalische Chemie

Chemical Reactivity of Nonperiodic Surface Structures in Graphite

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[2] Fritz Haber Institut der Max Planck Gesellschaft, D-14195 Berlin.

Surface and bulk nonperiodic structures in graphite play an essential role in many processes involving this material. They influence strongly chemical (reactivity, activation of adsorbed molecules) and physical (electronic and thermal conductivity, electronic structure) properties of graphite. Superperiodicity observed by STM is attributed to the existence of such structures either in the bulk or on the surface.

In order to study in detail the effect of these structures on the above phenomena, especially the carbon oxidation reaction mechanism, it is important to characterize the fine structure of the surface in real space. However, due to the fact that graphite in bulk samples is a very poor emitter of secondary electrons and therefore essentially black for SEM, small lateral and vertical variations originating for instance from nonperiodic features are very difficult to resolve. This renders it difficult to obtain by SEM meaningful images with sufficient contrast to recognize the fine structure of the graphite surface. One technique of choice which allows even atomic resolution in real space with very simple sample preparation is STM.

Here we present different kind of nonperiodic structures with a resolution up to atomic scale. Bubble-like structures, with a few nanometer width and less than 1nm height, ribbons and prismatic loops were resolved. Vacancy lines and dislocations on graphite are presented with atomic resolution. Monoatomic steps on the surface as well as bended graphite layers with height differences less than 0.1nm originating from steps in the bulk, have been uncovered. The chemical reactivity of such structures towards molecular oxygen at elevated temperatures (550-750°C) is discussed.

Russbildung bei dieselmotorischer Verbrennung

225

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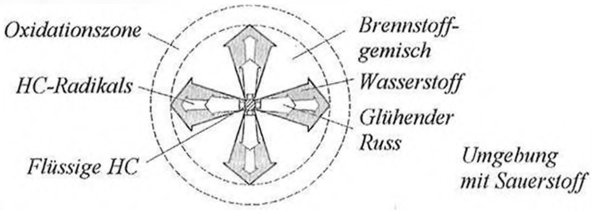
Eidg. Amt für Messwesen, Lindenweg 50, 3084 Wabern

Ein neues Modell wird zur Erklärung der Russbildung bei der Verbrennung von Kohlenwasserstoffen (HC), insbesondere bei dieselmotorischer Verbrennung, vorgestellt.



Bei der Verbrennung werden flüssige HC zuerst verdampft. Dabei findet nicht nur die Pyrolyse der HC mit H-Abspaltung, sondern auch die Rekombination unterschiedlicher HC-Moleküle/Radikals mit Dehydrierung statt. Der dabei freigesetzte Wasserstoff mit dem grössten Diffusionskoeffizienten unter allen Spezies verbraucht den anwesenden Sauerstoff vor allem über die diffusionskontrollierte Reaktion $\mathbf{H\cdot + O_2 \rightarrow \cdot OH + \cdot O\cdot}$, so dass die HC-Moleküle/Radikals nicht rechtzeitig oxidiert werden können. Ausserdem führen die schnelle Diffusion und die hohe mittlere Geschwindigkeit des Wasserstoffes auch dazu, dass die Konzentration des Sauerstoffes durch die Reaktion zwischen Wasserstoff und Sauerstoff schon bereits an der Front des gasförmigen Brennstoffgemisches stark abgebaut wird. Erst unter dieser O_2-Isolation werden durch Rekombination der ungesättigten kurzen HC zuerst PAK und anschliessend Russpartikel gebildet.

Durch die Russbildung wird der Wasserstoff in HC schnell freigesetzt. Eine höhere Russbildungsrate hat zur Folge, dass in kürzerer Zeit vermehrt Wasserstoff durch die Kettenreaktion zwischen Wasserstoff und Sauerstoff oxidiert wird. Dabei werden sowohl physikalische als auch chemische Voraussetzungen für eine effizientere Nachoxidation des Russes bereit gestellt. Demzufolge liegt der hohe Energieumsatz des Dieselmotors in der verstärkten Reaktion zwischen Wasserstoff und Sauerstoff durch die rasche Dehydrierung bei der Russbildung.

226

Physikalische Chemie

Investigating the Process of Plastic Deformation of Amorphous Polymers by Solid State NMR Spectroscopy

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[2] *Laboratorium für Physikalische Chemie, Eidgenössische Technische Hochschule*
8092 Zürich, Switzerland

Plastic deformation processes are the origin of many important properties of glassy polymers such as impact and fracture behaviour, toughness, and ductility. In contrast to the case for metals, the mechanism of plastic deformation is not yet well understood for polymer glasses. NMR spectroscopy is capable of revealing structural changes with atomic specificity and can be advantageously employed for the investigation of polymer deformation. In this work, samples of bisphenol-A polycarbonate ^{13}C-enriched either at the carbonate group or at the phenyl carbon joined to it have been subjected to extensive plastic compression. The orientation distributions of the molecular segments surrounding the label have been determined by recording chemical-shielding-anisotropy (CSA) powder spectra at various orientations of the samples with respect to the magnetic field and by the sample reorientation technique introduced by Grant and Henrichs. It was found that the local director of the polymer chains and the phenyl rings tend to align perpendicular to the axis of deformation. The C=O bond, on the other hand, tends to align parallel to the axis of deformation. A new NMR probe assembly for slow sample rotation at variable temperature has been designed and built for this purpose.

227

Physical Chemistry

Laser Induced Thermal Desorption of Organic Molecules: A Time Resolved Study

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Although laser-induced thermal desorption techniques are widely used for intact vaporization of large nonvolatile and fragile molecules, the mechanism of energy transfer during desorption from the surface remains largely unknown.

Submonolayer coverages of aniline have been desorbed intact from silica surfaces in classical temperature programmed desorption (TPD) experiments and using pulsed laser-induced thermal desorption (LITD). In the latter case, heating rates of 10^{10} K/s are achieved. Transient detection of the black-body emission allowed us to trace the exact time evolution of surface temperature induced by ps and ns laser pulses [1].

Currently we are exploring pump-probe methods to monitor the depletion of the aniline layer with ps time resolution. Partitioning of the thermal energy supplied by the laser radiation into kinetic and internal (rovibronic) energy of the desorbing molecules is probed by time-of-flight-measurements combined with resonant multiphoton ionization (REMPI-TOF). The results are discussed using different models for laser-induced thermal desorption from surfaces.

[1] S. Nettesheim and R. Zenobi, accepted for publication, Chem. Phys. Lett. (22.03.96).

Physical Chemistry

228

Structural Chemistry of Organic-Inorganic Mesophases

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Since the discovery of highly ordered silicates mesoporous materials of the MCM41 family in 1992[1] (pore size in the range 2-10 nm), much effort has been devoted to the study of organic-inorganic supramolecular self-assemblies of the generic type $nRS^{+/-}I^{-/+} + mMO_x$ ->structured mesophase, where R=aliphatic tail, S ionic head group, I the associated counterion, and MO_x a polymerizable metal oxyde and of their subsequent polymerization leading to highly structured mesoporous materials.

The research in this field is largely fueled by the search of new materials to be used as heterogeneous catalysts, ultraselective molecular sieves, mesoscopically structured hosts, for optically or biologically active guests, or more marginally, as substrates to enter into the realm of mesoscale electronic devices. A thorough understanding of the various molecular forces acting cooperatively for the formation of organic-inorganic mesophases is crucial in order to improve the quality and increase the variety of the targeted mesoporous materials.

We present a model based on the aggregation colloids chemistry and on the lyotropic liquid crystal physico-chemistry[2]. Some aspects, specific to the unique ability of silicates to polymerize must also be included to get a coherent picture. This model provides insight into how the various synthesis conditions favor a particular morphology and also suggests possible synthesis modifications to enhance the quality of the final material. Recent diffraction experiments revealing various phase transitions occurring during the synthesis of the mesoporous material are presented. The occurrence of these phases transitions is discussed within the frame of the above proposed model.

[1] J.S.Beck et al.,J.Am.Chem.Soc.114,10834(1992)
[2] A.Monnier et al, Science,261,1299(1993)

CHIMIA 50 (1996) Nr. 7/8 (Juli/August)

ıysikalische Chemie

229

Supramolecular Materials: NLO Molecules in Channels of Perhydrotriphenylene (PHTP)

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Single crystalline inclusion compounds allow a control of the
ometrical confinement of non-linear optical (NLO) molecules. Depending
ı the supramolecular architecture, the guests may be arranged either along
annels or within layers, as well as in isolated cages. Inclusion lattices
oviding a simple channel-like framework are likely to promote polar tensor
operties: for geometrical reasons parallel alignment of NLO molecules will
sult in, for example, an optimized electro-optic effect. Although a host
tice such as perhydrotriphenylene (PHTP) reduces the density of active
ecies to about 0.1 as compared to pure compounds, the supramolecular
proach is particularly of interest because it permits the inclusion of NLO
olecules whose native crystals are *centrosymmetric* or exhibit a packing in
ıich the dipoles are *not fully parallel*.

Racemic all-*trans* PHTP forms continuous channel-type inclusion
tices with a variety of guest molecules and polymers [1]. Recently, [2,3]
demonstrated that different types of linearly shaped NLO molecules could
included into the channels of (racemic) PHTP. By application of
ystallization techniques discussed earlier [4], spontanuous nucleation has
elded macroscopically polar materials (SHG powder test at 1.06 and 1.3
n [5]) for *ca.* 90% of the [PHTP-NLO] systems.

As compared to other host materials [6], PHTP seems to be ideally
ited to tailor the linear frame and terminal groups of guest molecules. This
ens up a new field for the synthesis of single crystalline supramolecular
aterials which demonstrate pronounced electro-optic and photorefractive (in
case of photoconduction along channels)[7] effects.

M. Farina in Inclusion Compounds Vol. 2, 1984, p. 69-95; [2] J. Hulliger, O. König,
Hoss, *Adv. Mater.* 1995, **7**, 719-721; [3] R. Hoss, O. König, V. Kramer-Hoss, U.
rger, P. Rogin, J. Hulliger, *Angew. Chem.*, in press; [4] J. Hulliger, *Angew. Chem.*
. *Ed. Engl.* 1995, **33**, 143-163; [5] we thank Ch. Bosshard (ETH) for the use of SHG
ıipment; [6] V. Ramamurthy, D. Eaton, *Chem. Mat.* 1994, **6**, 1128-1136; [7] J.
lliger, K. Sutter, Y. Schumacher, B. Brezina, V. A. Ivanshin, *J. Cryst. Growth*, 1993,
8, 886.

230

Physical Chemistry

Multilayered thin films of frequency selective samarium doped alkaline-earth fluorohalides.

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The obtention of chromophores with a high inhomogeneous over homogeneous bandwidth ratio (IHBR) of the active optical absorption band is crucial when considering applications related with hole burning photophysics.

In this respect, mixed alkaline earth fluorohalides (AEFH) of the Matlokite structure are very effective hosts to increase the IHBR of rare earth ion intrashell f-f transitions. This ratio increase is such that spatial sequences of permanent spectral holes may be burned and observed in $^5D_1$<-$^7F_0$ and $^5D_0$<-$^7F_0$ Sm^{2+} transitions even at room temperature[1].

To further increase the IHBR of AEFH, a molecular beam deposition technique has been developed to produce multilayered AEFH structures. The equipement realized in our laboratory permits to grow films with alkaline earth and halogen compositions varying in a controlled manner across the film depth z according to the following equation:

$$Sr_{x(z)}Ca_{1-x(z)}FCl_{y(z)}Br_{1-y(z)};Sm^{2+}$$

Films with a « square wave » x composition profile have been produced using this technique. The IHBR of these films is larger by a factor 3 in comparison to the bulk material. Moreover, the films have a higher burning rate than bulk material at the same burning power. The influence of various parameters on the final lineshape have been studied. An estimate of the alkaline earth diffusion constant in AEFH is given from this study.

[1] H.Bill et al,Opt.Eng.,34,8,2333-2338 (1995)

231

ıysikalische Chemie

eparation and Characterization of Metal Oxide films on ı(111)/mica

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Recently it was shown that highly dispersed gold on specific metal
pports exhibits a remarkable activity in low temperature CO-oxidation
hough the metal or oxide itself are almost inactive. To make the interface
ıenable to surface science methods we prepared a flat, electrically
nducting gold/oxide model system which was analyzed by XPS, ISS,
M, STM, SEM, Raman spectroscopy and XRD. Different methods,
cluding PVD and wet chemical procedures, e.g. dip and spin coating, were
plied for depositing the metal oxides TiO_2 and ZrO_2 on a highly orientated
ı(111)/mica film.

In the case of electron beam evaporation, interdiffusion of the
ld/titania species and different amounts of reduced titanium were
served depending on the substrate temperature (293 K - 593 K), the
ygen partial pressure (4 x 10^{-7} - 4 x 10^{-5} mbar) and the film thickness (1.0
ı - 10.0 nm). Considering the reduced titania films on gold, XPS and ISS
owed that the film consists of flat islands with a TiO_x core covered with a
n TiO_2 layer.

In contrast, with wet chemical preparation methods, a highly porous
rface was obtained. The morphology of the titania films changed during
lcination as followed by AFM and SEM. Titania recrystallized at higher
nperatures to anatase which could be elucidated by XRD and Raman
ectroscopy (characteristic bands at 400 cm^{-1}, 515 cm^{-1} and 637 cm^{-1}). XPS
owed a significant decrease of the surface titanium content at higher
lcination temperatures and revealed the presence of a substantial amount
carbon on the surface of the porous model systems. This carbon
ntamination could be strongly reduced by appropriate post-treatments.

Physikalische Chemie

232

Preparation and Characterization of Fullerene Thin Films using AFM, XRD and XANES

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Studies on physical and chemical properties of C_{60} and C_{70} in the solid state are carried out using film samples prepared by vacuum deposition or crystals prepared by sublimation. Several results concerning the nucleation, growth, structure, and interactions of fullerenes (C_{60}, C_{70}) with various metal and semiconductor surfaces have been reported. Many of these studies, however, are restricted to either thin films, with a coverage ranging between submonolayer and 100nm, or to single crystals in millimeter size range.

In this study we focused on the morphology and structure (geometric and electronic) of films with thicknesses in the range of a few micrometers, which are of interest for technical applications, such as coatings, lubricants, and catalysts, as well as for studying physical (electronic structure, electrical conductivity) and chemical (reaction with O_2) properties of modified and unmodified fullerene films. In our previous study [1] we addressed the morphological and crystallographical properties of C_{60} films with thicknesses in the range from 0.2μm to 10μm, focussing on the influence of substrate temperature and deposition rate. Here we have extended this study to C_{70} films with thicknesses of 0.1-10μm. The films prepared using a substrate temperature of 80°C consisted of crystallites with preferred [111] orientation. Increasing substrate temperature (200°C) led to suppression of the [111] orientation and favored the [220] orientation. Morphological characterization of the films by AFM confirmed this behavior. XANES was applied to follow changes in the electronic structure. The relation between substrate temperature and film growth will be discussed.

[1] F. Atamny, A. Baiker, H-J Muhr and R. Nesper, Fresenius J. Anal. Chem. 353 (1995) 433.

CHIMIA 50 (1996) Nr. 7/8 (Juli/August)

Physical Chemistry **233**

Femtosecond Interfacial Electron Transfer in the Dye-Sensitization of Nanocrystalline Semiconductors

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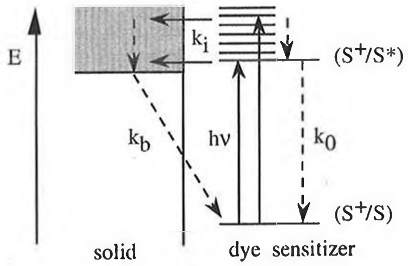
Femtosecond transient absorption spectroscopy and fluorescence up-conversion are used to probe the dynamics of the interfacial electron transfer reaction from the excited state of an adsorbed molecular dye into the conduction band of a wide bandgap semiconductor. This type of process is of widespread technological importance due to its application to photographic and xerographic systems, and in the photochemical solar energy conversion.

Transparent films supported by a glass substrate and liquid dispersions, both constituted of nanocrystalline colloidal particles of TiO_2 and ZrO_2, are employed in order to increase the effective surface area, and therefore the optical density of the samples. Upon light excitation, electron injection from adsorbed ruthenium(II)-complexes, coumarin, alizarin, and merocyanine dye molecules is monitored. On titanium dioxide, the charge transfer processes appears to occur in a time scale as short as 100 fs.



A $k_i = 10^{13}$ s^{-1} rate constant as well as the observation of an excitation wavelength dependent efficiency of the charge injection suggest that in the systems used the reaction proceeds adiabatically prior to the relaxation of the dye excited state. Other important mechanistic and theoretical implications of this remarkably fast processes will be discussed.

Physikalische Chemie **234**

Photodissociation of liquid surfaces

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A technique was developed to prepare clean and continuously renewed liquid surfaces in vacuum, similar to a previously used method [1]. A wheel rotating at 0.6 Hz is partially immersed in the liquid. It drags a liquid layer with it which is scraped to a thickness of 0.1 mm. The liquid film is exposed to the vacuum chamber through a 4x10 mm² hole. A tunable pulsed laser beam is directed at the surface, initiating photodesorption and photodissociation at the gas-liquid interface and in the bulk of the liquid. The identity and velocity distribution of the ejected molecules and fragments is studied using photofragment translational spectroscopy. First results are presented for the liquid dodecyl iodide, as well as dodecyl iodide dissolved in polar (glycerol) and apolar (squalane) liquids. The upper part of the velocity distribution of the photoproducts I and I_2 can be modelled with a Maxwell-Boltzmann distribution assuming an almost complete equilibration with the surrounding solvent molecules. The slow velocity tail, which is particularly pronounced in highly viscous solutions, is attributed to photoproducts which have to diffuse through a liquid layer of several µm prior to evaporation. Mechanistic features of the variation of photodissociation wavelength, intensity, as well as the polarity and temperature of the solvent are discussed in comparison with results from gas-phase photodissociation.

[1] M.E. Saecker and G. M. Nathanson, *J. Chem. Phys.* **99**, 7056 (1993).

Chimie physique **235**

New photochromic devices for information storage and optical filters

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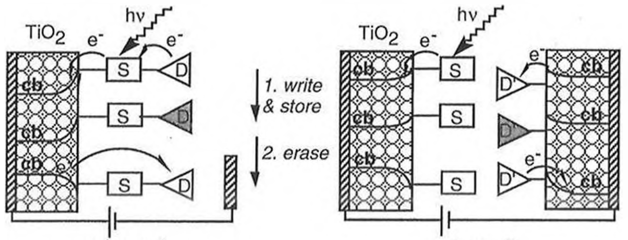
Redox-type photochromism is observed when a sensitizer and an electrochromophore (D) are present either simultaneously on a single nanocrystalline TiO_2 electrode or separately on two such electrodes, electrically and electrochemically connected.

In both cases, light absorption causes S to inject one electron into the TiO_2 conduction band ($S^* \mid TiO_2 \rightarrow S^+ \mid (e^-)\ TiO_2$).

In the first case (scheme 1), S^+ oxidizes the electrochromophore D which is colorless in the reduced state and colored in the oxidized state (D^+). The process can take place within a supramolecular assembly of S and D or between S and D coadsorbed. Positive polarization prevents charge recombination and allows to keep D oxidized.

In the second case (scheme 2), the electron in the conduction band is carried by the electric circuit to the second electrode where it reduces an electrochromophore D' which is colorless in the oxidized state and colored in the reduced state.



scheme 1

scheme 2

In both cases, the system can be returned to its initial state by reversing the applied voltage.

Other systems based on these principles will be presented and their application for information storage and self-adaptating optical filters will be discussed.

Physikalische Chemie **236**

Electrochromism of nanocrystalline TiO_2 film electrodes derivatized with organic electrochromophores.

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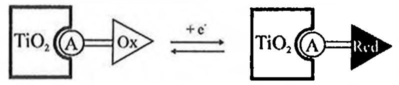
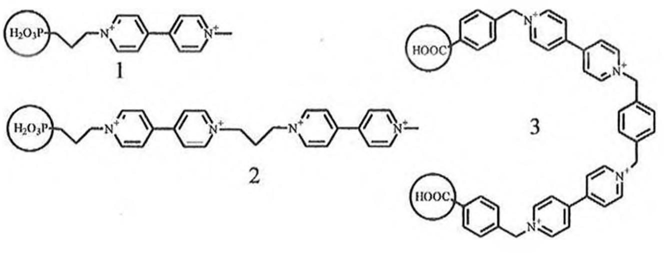
Thin film nanocrystalline TiO_2 electrodes were modified with monolayers of organic electrochromophores equipped with anchoring groups (A). Reversible redox chemistry and accompanying color change is observed for redox systems with $E^\circ_{(Red/Ox)} <= E_{flat\ band}\ (TiO_2)$.



Organic electrochromophores, such as **1-3**, have been optimized

- for **reversible electron exchange** (adjustment of $E_{flat\ band}$ and $E^\circ_{(Red/Ox)}$);
- for **irreversible anchoring** (introduction of different anchoring functionalities and cross-linking of the anchored modifier);
- for **large color changes** (oligomeric and thin polymeric layers as well as dendrimeric structures);
- for **different colors** (dialkyl- and diphenyl-4,4'- and 2,2'-bipyridinium salts, aromatic tetracarboxylic acid diimides).



iimie physique **237**

ew electrochromic devices for display and filter applications

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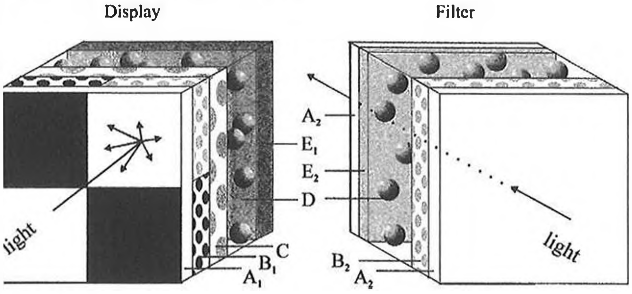
in film electrodes of nanocrystalline TiO_2 (B) on conducting glass (A) re surface modified with electrochromic compounds and used for the nstruction of flat electrochromic displays and filters. Fast switching times, ;h coloration efficiencies, no current leakage and low operation voltage ve been achieved and explained on the basis of:

the inherent properties of TiO_2-electrodes (large surface area, transparency for vis. light, electric conductivity, surface affinity);

specifically designed electrochromic compounds (with suitable extinction coefficient, and anchoring irreversibly to TiO_2 (B_1, B_2));

cell construction (small electrode gap, two surface confined redox systems, isolating spacers and an optimized electrolyte-solvent ;tem (D)).

e display device is equipped with individually addressable segments ild into a single cell. Good reflectivity contrasts are produced by a thin ous diffusive layer C. **The filter device** can be switched in 1 sec from nsparent to colored (A_{in}<0.2, A_f>2).



Physikalische Chemie **238**

Defect Segregation in Graphite: STM and STS Study

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The extensive use of graphite as a moderator in nuclear reactors in the sixties has fostered the great interest in this material. The effects of neutron damage on physical and chemical properties of graphite and the origin, structures and formation energy of different kind of defects have been intensively investigated. Defects on the basal plane are generally considered as active sites in chemical reactions. Optical microscopy as well as the more powerful techniques SEM and TEM have been used for studying the above phenomena. Although very valuable findings emerged from these studies fundamental physical (light wave lenght) and experimental (decoration) restrictions excluded further progress. After the invention of the STM in 1982 the interest in defects in graphite has been renewed, due to the possibility of studying such phenomena in more details and in real space. Furthermore, observation of different anomalous STM images as well as giant corrugation amplitudes and superperiodicities of graphite surfaces has led to a great interest concerning the interpretation of the experimental data. Imaging of nonperiodic surface structures (point defects, steps, dislocations etc.) in graphite is still one of the most interesting theoretical and experimental challenges, not only by virtue of its importance for clarifying the STM imaging mechanism but also due to its relevance for studying chemical reactions initiated at defects.

In this study we present for the first time a sequence of STM images showing segregation of defects forming defect lines on atomic scale. The defect lines are several microns long and only 1-3 atoms in width. Successive application of mechanical stress (cleaving, bending) on the sample led to diffusion of differently located defects in the graphite layer, creating defect lines with different vacancy density. A possible source for the atomic resolution of such defects and the driving force for the defect segregation and defect line formation will be discussed.

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ysical Chemistry **239**

Systematic Raman Studies on Mixed Alkaline Earth Fluorohalides

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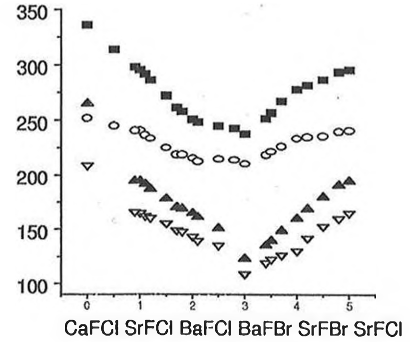
the course of our extensive studies on Sm(II)-doped PbFCl-type mixed 'stals as materials for room temperature hole-burning, [1,2], we prepared ny mixed Matlockite-structure crystals MFX where M=Ca,Sr,Ba,Sm and Cl,Br,I. The binary subsystems (eg SrFCl-SrFBr) present Raman quencies that shift practically linearly with composition, as shown in the ure below. The two highest frequency Raman bands are assigned to inly fluoride involving vibrations. The comparison of their linewidth as a ction of composition yields additional insight into the vibrational perties of these crystals.Their temperature dependence was further died.



ig.1. Room temperature Raman shifts (in cm^{-1}) of mixed MFX crystals.

erences [1] H. Bill et al., Opt. Eng. **34** (1995) 2333.
[2] R. Jaaniso et al., Chimia **46** (1992) 133.

Physikalische Chemie **240**

Spectroscopic Investigations on Novel Host-Guest Compounds Based on Microporous Silica Frameworks and Inorganic Guest Species

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An intriguing goal of materials chemists is the generation of composite structures that are organised on a molecular level and have been prepared by controlled nanoscale manipulation procedures. One approach uses the three-dimensional periodic void structure of zeolite-type host matrices to prepare ordered arrays of (uniform sized) metal and semiconductor clusters or wires , immobilised metal complexes, isolated electrically conductive polymer filaments or dispersions of dye molecules.[1]

In this study we used crystalline microporous pure silica frameworks (porosils) as host materials and inserted the bulk semiconductor iodine via the gas phase.[2] The host structures used include so-called deca-dodecasil 3R (abbrev. DDR), silica-ZSM-22 (TON), silica-ferrierite (FER) and silicalite-1 (MFI). They possess pore dimensionalities ranging from zero (cages in DDR) to three (3D-intersecting channel system in MFI) and pore openings from 3.5 Å to 5.5 Å (8- and 10-membered rings) and thus allow to control the geometric arrangement, steric confinement and electronic interactions between the inserted iodine species. From spectroscopic experiments (UV/Vis, Raman, EXAFS, XANES) or simply from the colour of the inserted porosils, the change in the electronic properties is evident and correlates well with the steric limitations imposed by the host (see Table).

Beside iodine we succeeded to insert other halogens, interhalogens, sulfur, selenium, mercury halides (e.g. HgI_2) and mixed mercury halides (e.g. HgBrI).[3]

I_2-porosil	dimensionality	composition	I_2/1000 Å^3	colour
I_2-DDR	0	$120\ SiO_2 \cdot 6.0\ I_2$	0.886	violet
I_2-TON	1	$24\ SiO_2 \cdot 1.2\ I_2$	0.989	blue-violet
I_2-FER	2	$36\ SiO_2 \cdot 3.2\ I_2$	1.63	red-violet
I_2-MFI	3	$96\ SiO_2 \cdot 11.5\ I_2$	2.15	reddish brown

[1] G.A. Ozin, Adv. Mater. 6 (1994) 71. [2] G. Wirnsberger, H.P. Fritzer, A. Popitsch, G. van de Goor, P. Behrens, Angew.Chem., submitted. [3] G. van de Goor, Thesis, University of Konstanz, Konstanz 1995.

241

Physikalische Chemie

Study on the Mechanism of Combustion of Methane Over Palladium/ Zirconia

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The reaction of gaseous molecules with lattice oxygen of a solid catalyst is widely accepted as a possible mechanism for oxidations over oxidic materials. Investigation of such redox mechanisms are based on the comparison of the reduction and oxidation rates of the catalyst or, more reliably, on the labelling of the catalyst with isotopes of oxygen. However, not much effort has been dedicated so far to elucidate the role of the isotopic exchange (scrambling) of oxygen between gas phase and solid catalyst, which masks the real influence of a redox mechanism.

As a model reaction, the catalytic combustion of methane over a catalyst prepared by oxidation of a Pd-Zr amorphous alloy has been investigated. The catalysts used have been previously reduced and thereafter oxidized with ^{18}O giving $Pd^{18}O$ supported on zirconia. The experiments, carried out by combined pulse thermal analysis and mass spectrometric techniques, are based on the detection of labelled species such as water and carbon dioxide in the products of the reaction upon pulses of reaction mixture.

During pulses of a feed mixture consisting of 1% methane and 4% oxygen ($^{16}O_2$) in a balance of helium, substantial amounts of labelled reaction products (CO_2 and H_2O) were found. These findings, which indicated a lattice oxygen contribution to the catalytic reaction, were masked by scrambling of molecular oxygen and carbon dioxide from the gas phase with ^{18}O of the solid phase. The effects of oxygen scrambling could be neglected due to its small extent. The scrambling of CO_2 on the other hand proved to be of such importance that at 500°C, a redox mechanism could not be shown. For 300°C, a minimum amount of 20% CO_2 totally produced was formed through a redox (Mars & van Krevelen) mechanism, taking into account the amount of CO_2 scrambled over the catalyst.

The results obtained provide a reasonable explanation for the correlations found between bulk properties of palladium oxide and the catalytic combustion of methane.

Physical Chemistry

242

New luminescent materials doped with the $(3d)^1$ ions CrO_4^{3-} and MnO_4^{2-}

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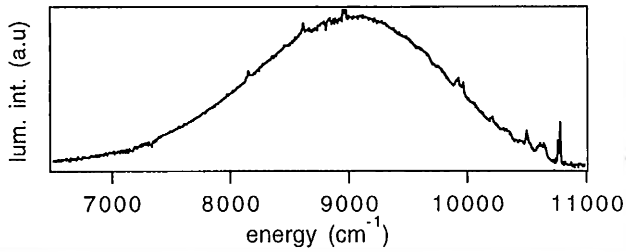
The absorption and luminescence properties of two new near-infrared (NIR) luminophors are reported and discussed. The CrO_4^{3-} ion can be stabilised in phosphate, vanadate and arsenate lattices and the MnO_4^{2-} ion in sulphate, selenate, chromate and molybdate host lattices. The luminescence of these ions, which is due to the $^2T_2 \text{-->} {}^2E$ (d-d) transition, is very broad. The figure shows the luminescence at 10 K of CrO_4^{3-} doped in Li_3PO_4 as an example. The energy of the luminescence depends on the crystal field strength and on the distortion of the host tetrahedron. Hence, the energy of the luminescence maximum can be "tuned" between about 9300 cm^{-1} and 7800 cm^{-1} by choosing a suitable combination of host lattice and dopant ion. The possibility to use these ions in tunable NIR laser materials is discussed as well.



243

Physical Chemistry

A Study of Manganese Dioxide surfaces using Atomic Force Microscopy and Adsorption Techniques

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Manganese Dioxide (MnO_2) is used as a cathode component in Leclanché type alkaline cells, where it functions as a depolarizer[1]. It is known that battery performance of MnO_2 depends on its origin, (natural, synthetic, activated). It would seem that these differences can be related to surface characteristics of MnO_2. We present results of a systematic study of several MnO_2 samples. Adsorption isotherms and immersion calorimetry provide information about the external surface area and micropore distribution. Using Atomic Force Microscopy (AFM), the surface was imaged down to atomic level. These images were correlated with the information obtained by adsorption and immersion to provide a complete description of the surface. The AFM images were also investigated for information on their fractal character. The numerical data is analyzed in one dimension (profile analysis) or two dimensions using a Fourier transform method[2] which yields the mean fractal dimension D (≈2.2 for a typical MnO_2 sample), and its dispersion σ_D, which parameters can be considered as 'fingerprints' of the surface.

1 N. C. Cahoon, *The Primary Battery*, Vol II, Wiley, New York 1976.
2 H.F. Stoeckli, L. Currit, *Carbon*, **33**, 338, 1995.

Chimie-physique

244

Caractérisation et applications de noirs de carbone pour des piles

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Les noirs de carbone constituent un élément important dans la fabricatio de la masse cathodique d'une pile Leclanché. Leurs caractéristiques physico-chimiques (oxydation de surface, aires spécifiques, caractère fractal d masse, etc.) ont une grande influence sur les performances des piles. L'étude de la décharge globale conduit aux équations suivantes, pour l'intensité I, l capacité totale C_∞ et l'énergie totale E_∞ dissipée à travers une résistance R.

$$I(t) = I_o \cdot \exp\{-a \cdot t^n\} \qquad C_\infty = \int_0^\infty I(t)\,dt = [I_o / n \cdot a^{1/n}] \cdot \Gamma(1/n)$$

$$E_\infty = \int_0^\infty R \cdot I^2(t)\,dt = [R \cdot I_o{}^2 / n \cdot (2a)^{1/n}] \cdot \Gamma(1/n)$$

Ces grandeurs sont reliées aux paramètres principaux AS et DBP, décrivan différentes capacités d'absorption, polaire et apolaire. De plus, le courant d court-circuit de la pile, I_K, une caractéristique industrielle très importante dépend également des propriétés du noir utilisé (notamment le caractèr fractal de surface, obtenu par l'analyse des isothermes d'adsorption[1,2] ou l diffusion X aux petits angles).

1. H. Van Damme et J.J. Fripiat, J. Chem. Phys., 82(6), 2785 (1985)
2. H.F. Stoeckli, A. Laederach, J. Affolter et A.V. Athalye, Progress in Batteries & Battery Materials, 15, 81 (1996)

CHIMIA 50 (1996) Nr. 7/8 (Juli/August)

imie physique **245**

W EVIDENCE FOR THE IMPORTANCE OF CHARGE UTRALIZATION IN FLOCCULATION

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cculation plays an important role in the transport of colloidal particles associated pollutants in aquatic systems as well as in water treatment. have studied the aggregation kinetics of hematite particles induced by rly monodisperse polyacrylic acid of two different molecular weights A, $M_w = 1.36 \times 10^6$, $M_w/M_n = 1.53$ and $M_w = 3.69 \times 10^4$, $M_w/M_n = 1.60$) using Photon Correlation Spectroscopy (PCS) to follow the evolution of regate sizes over a long period of time. The aggregation rate increases a maximum value at certain polymer/hematite ratio and then decreases the PAA concentration is increased. The maximum rates for the two ymers are exactly the same, which are in turn identical to that of fusion limited aggregation (DLA) induced by simple electrolytes. In the A regime, scaling of the aggregate size with time yields the same fractal nension of aggregates for both polymers and simple salts. Moreover, the adth of flocculation zone is independent of polymer molecular weights. wever, the optimal dosage, in terms of total polymer concentration, fts slightly to a lower value for the larger polymer. This shift, responding exactly to a displacement in the zero electrophoretic bility, is most likely due to the higher adsorption affinity of the longer ymer chains. These results clearly demonstrate that polymer bridging is important as compared to the charge neutralization mechanism. In lition, the observation that the maximum rates are identical in the sence of polymers and simple salts suggests that the macromolecules do form distinguished patches as described in the "electrostatic patch" del. Because of their relatively small charge density, the cromolecules overlap on the hematite surface, resulting in a quasi-form charge neutralization.

Physikalische Chemie **246**

Photodegradation of Carbon Tetrachloride in Aqueous Solutions

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Recently, the use of the Advanced Oxidative Processes (AOP) for the treatment of contaminated ground water and industrial waste waters has been receiving more attention with respect to conventional methods. However, radical generation upon direct excitation of a C-X bond is complementary to processes where degradation initiated by hydroxyl radicals is found to be rather inefficient [1]. Rates of such a photooxidations depend on the absorbed photon rate at the wavelengths of excitation, on the concentration of dissolved molecular oxygen and on the temperature of the reaction mixture.
The objective of the present work is to illustrate the photodegradation of carbon tetrachloride in water. Solutions of carbon tetrachloride (5,5 L), prepared in tridistilled water, were irradiated using a high-intensity short wavelength medium pressure mercury lamp. This light source shows a broad emission band in the UV-C region from 210 to ca. 230 nm. To follow the course of degradation of the substrate, samples were taken at different time intervals during the irradiation and analyzed by gas chromatography. On the other hand, ion chromatographic analyses were performed to monitor the formation of the chloride anion as degradation product.

The present results proves that high degradation efficiency may be achieved upon electronic excitation of such pollutants as the primary photochemical step since after 9 minutes of irradiation, analysis of CCl_4 confirmed the elimination of 99.3 % of the substrate. The efficient degradation of CCl_4 may be explained by the high incident photon rate emitted from the light source in the UV-C spectral region, where CCl_4 is exhibiting considerable absorbance between 200 and 250 nm. The results shows the necessity of developing light sources those emit sufficiently in the UV-C region where highly chlorinated saturated aliphatics may be efficiently eliminated.

[1] O. Legrini, E. Oliveros, A.M. Braun, Photochemical processes for water treatment. *Chem. Rev.*, **93**, 671-698.(1993)

247

sikalische Chemie

-ESR-Studien des Abbauverhaltens einer Huminsäure während Vakuum - Ultraviolett (VUV) - Photolyse

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Oxidation von im Wasser gelösten Huminsäuren mit Hilfe der VUV - tolyse und die nachträgliche Zugabe des stabilen Radikals Cu^{2+} zu den tandenen Photolyseprodukten ermöglichen interessante Einblicke in n chemische Struktur, Topologie und chemischen Eigenschaften. rbei erwies sich die Abhängigkeit des CW-ESR - Spektrums von Cu^{2+} dessen Koordinationssphäre als hilfreich.

Verlaufe der VUV - Photolyse, die schließlich zur vollständigen Mine-sation führt, konnten verschiedene chemische Umgebungen von Cu^{2+}, aus dem organischen Material der Huminsäure stammten, identifiziert den. Es gelang u. a. der Nachweis des Vorliegens von Porphyrinen in em organischen Material biologischen Ursprungs.

Authors, Index

CHIMIA 50 (1996) Nr. 7/8 (Juli/August)

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European Cooperation in the Field of Scientific and Technical Research

1st Swiss COST Chemistry Symposium

Wednesday, 20th November 1996
Basel

ILMAC 96
Convention Center of the Basel Fair
Messeplatz 21

Sponsored by:
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CHIMIA *50* (1996) Nr. 7/8 (Juli/August)

What is COST?

COST (a French acronym for 'Coopération Européenne dans le domaine de la recherche Scientifique et Technique') was set up in 1971 to stimulate and to give a framework for the European cooperation in the field of science and technology. This forum of research brings now together 25 European countries including the members of the European union, of the EEE and seven central and eastern European states. COST is oriented towards pre-competitive research (unlike EUREKA) and has launched activities in Information Technology, Telecommunications, Transport, Oceanography, Materials, Environment, Meteorology, Agriculture, Food Technology, Social Sciences, Medicine, Civic Engineering and Forestry.

COST Chemistry?

Surprisingly chemistry was missing. Chemistry is a central basis science with distinguished history and success in Europe (23 of the 55 *Nobel*-Prizes for chemistry in 1960–1993 are European). Chemical Industry is one of Europe's most international, competitive and successful industries (eight of the ten largest chemical companies in the world are based in Europe) and contributes to the prosperity and quality of life of modern European society. In order to maintain and even to improve this position it was decided to use the COST forum to elaborate a strategic scientific scheme for basic research in chemistry in Europe. In this respect, a Technical Committee (TC) in chemistry was built in 1990. In 1992, through a proposition of the TC, COST decided to launch seven actions in the field of chemistry. The COST CHEMISTRY activities of these seven actions correspond to 86 collaborative projects in which 391 European groups (among them, 38 Swiss groups) are involved. Among the characteristic and philosophy of the COST systems are: the bottom-up approach (the initiative comes from the researcher) and the funding of the research is national. In Switzerland the main sources of funding for COST CHEMISTRY is the Office of Education and Science, and partially the Swiss National Science Foundation.

Why a 1st Swiss COST Chemistry Symposium ?

The goal of this symposium is to present to the Swiss scientific public the progress of the research of the Swiss group in this European collaboration after three years of activities. The program consists of seven invited lectures by prominent European and Swiss scientists and more than 50 posters communications from Swiss scientists active in COST CHEMISTRY.

Scientific Program

Kongressraum SINGAPORE – 2nd Floor

Welcome

10.00	Opening by Prof. ***André Merbach***, Lausanne, Switzerland
10.05	Introduction by the Chairman of the Technical Committee Chemistry: Prof. ***Gilbert Balavoine***, CNRS, Toulouse, France

Lectures – Morning Session

Chairman:	Prof. ***Alexander von Zelewsky***, Fribourg, Switzerland
10.15	Prof. ***Jan Reedijk***, Leiden, The Netherlands 'Heavy Metal Compounds as Useful Drugs' *Abstract 1*
10.55	Prof. ***Bernd Giese***, Basel, Switzerland 'Selectivity of Photochemical Cyclization Reactions with Amino Acids and Peptides' *Abstract 2*
11.35	Prof. ***Jürgen Brickmann***, Darmstadt, Germany 'Modelling and Computer Simulation of Large Chemical Systems' *Abstract 3*

Posters – Sandwich Session

12 .15	
Action D1	'Coordination Chemistry in the Context of Biological and Environmental Studies' *Abstracts 8–15*
Action D2	'Selective Synthesis' *Abstracts 16–35*
Action D3	'Theory and Modelling of Chemistry Systems and Processes' *Abstracts 36–50*
Action D4	'Design and Preparation of New Molecular Systems with Unconventional Electrical, Optical and Magnetic Properties' *Abstracts 51–53*
Action D5	'Chemistry at Surfaces and Interfaces' *Abstracts 54–61*
Action D6	'Chemical Processes and Reactions under Extreme or Non-Classic Conditions' *Abstracts 62–64*
Action D7	'Molecular Recognition Chemistry' *Abstracts 65–68*

Lectures – Afternoon Session

Chairman:	Prof. ***Hans-Ulrich Güdel***, Bern, Switzerland
14.15	Prof. ***Michael Grätzel***, Lausanne, Switzerland 'Molecular Photovoltaics Devices Mimick Photosynthesis' *Abstract 4*
14.55	Prof. ***Bernard Delmon***, Louvain-la-Neuve, Belgium 'From the Molecular Level to Chemical Engineering Models in Heterogeneous Catalysis. New Discoveries and Their Impact' *Abstract 5*
15.35	Coffee Break
16.00	Prof. ***Richard R. Ernst***, Zürich, Switzerland 'Nuclear Magnetic Resonance, a Powerful Tool for the Study of Biomolecular Dynamics' *Abstract 6*
16.40	Prof. ***Jean-Paul Behr***, Illkirch, France 'The Proton Sponge: a Trick to Enter Cells the Viruses Did not Exploit' *Abstract 7*
17.20	End of the Symposium

Organizing Committee:
T. Kaden (Basel), A. Merbach (Lausanne, chairman),
I. Portner (OFES, Bern), H.-P. Schelling (Sandoz, Basel),
J. Weber (Geneva), J.-B. Weber (SNSF, Bern)

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1

HEAVY METALS AS USEFUL DRUGS

n Reedijk
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niversity, P.O.Box 9502, 2300 RA Leiden, The Netherlands

After a brief introduction on "heavy metals" some examples will
e discussed of commonly used drugs that contain heavy metals.
ost attention will be given to the use and mechanism of Platinum
mpounds as anticancer drugs.

Questions dealt with will be:
How dangerous are heavy metals and their compounds?
What are the common metals in biological systems?
Is the chemical form of heavy metals crucial or not?

In fact all metals are poisons, depending on the dose; however,
rtain very toxic metals are nevertheless crucial for life.

Well-known examples of metal-containing drugs are:
Lithium salts in treatment of manic depression
Bismut salts in treatment of ulcers
Copper salts in treatment of radiation damage
Gold compounds in treatment of rheumatic arthritis
Mercury compounds as a diuretic
Platinum compounds als antitumor agents

The last topic will be dealt with in some more detail with
tention to the development of new drugs based on earlier
echanistic investigations.

ference:
Reedijk, Improved Understanding in Platinum Antitumour
Chemistry, Chem. Comm. (1996) 801-806.

2

SELECTIVITY OF PHOTOCHEMICAL CYCLIZATION REACTIONS WITH AMINO ACIDS AND PEPTIDES

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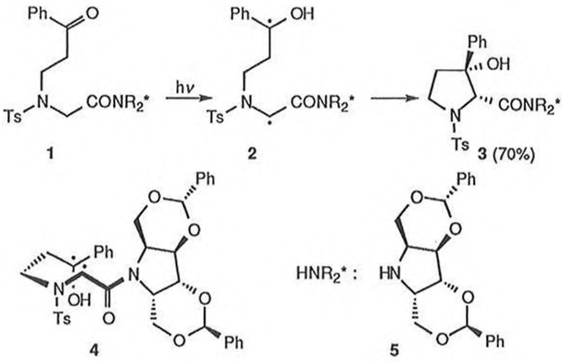
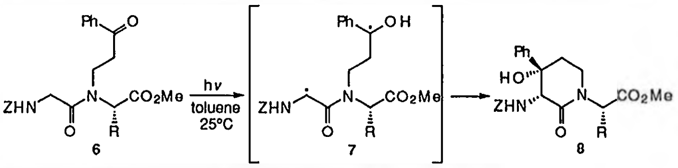
In this decade the rules that govern the stereoselectivity in reactions between radicals and non-radicals have been elucidated. Much less is known about selective radical-radical reactions. Recently, we have demonstrated, that control by auxiliary **5** gives rise to a stereoselective cyclization of glycine derivative **1** to proline **3**. Biradical **2** is the intermediate that cyclizes *via* transition state **4**.



It has now turned out that also substrate control by the stereogenic centers of amino acids induces stereoselective cyclizations in dipeptides (**6**→**8**).



The application of this photocyclization will be described.

3

MODELLING AND COMPUTER SIMULATIONS

OF LARGE CHEMICAL SYSTEMS

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itute of Physical Chemistry and Darmstadt Center of Scientific
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rsenstr. 20 D-64287 Darmstadt, Germany

Already now, advanced computational chemistry underpins rational
design, contributes to the selection and synthesis of new compounds,
guides the design of catalysts. *Computational Chemistry* is considered
natural outgrowth of *Theoretical Chemistry*, the role of which should
lve the creation and dissemination of penetrating conceptional
structure for the chemical sciences. There are numerous methodologies
ntum chemistry at all levels of complexity, molecular dynamics and
te Carlo type simulations, mixed quantum classical dynamics) available
he treatment of chemical systems and the applications of these methods
led to the solution of many problems in particular when the systems
of limited complexity. For systems of increasing complexity the
itional tools can be applied only in exceptional cases just because of the
natical increase of the computational effort with increasing size. This is
onstrated by a few examples from the group of the author:
The simulation of crystal phases of cellulose.
The simulation of phospolipid bilayers in contact with water.
The treatment of proton transfer processes in aqueous solution.
The modelling of organic molecules in zeolites.
computational methods used in these simulations are still based on
tional concepts but it is demonstrated that new approximative model
egies can drastically enhance the applicability of these methods.
ertheless, there are new concepts and new tools needed in this field.
e speculations for future developments are presented.

4

MOLECULAR PHOTOVOLTAIC DEVICES MIMICK PHOTOSNYTHESIS

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Photoinduced charge transfer processes involving molecules adsorbed at interfaces are a fascinating topic which is presently attracting wide attention.

Our investigations have focused on the identification of the factors that control the dynamics of such processes. The goal is to design molecular electronic devices that achieve light induced charge separation. The systems investigated consist of a monolayer of charge transfer sensitizer grafted to the surface of mesoporous semiconductor films. Surface coordination plays a primordial role in the electron transfer from an excited sensitizer into the conduction band of the oxide film. The sensitizer is endowed with interlocking groups such as carboxylates, whose role is to graft the chromophore to the surface of the solid and to couple its excited state wavefunction efficiently to the conduction band manifold. Suitable molecular engineering of transition metal complexes allows the electron transfer to occur on a femtosecond time scale. Judicious molecular design retards on the other hand the undesired thermal back electron transfer. The latter process has been investigated over a large temperature range by laser photolysis and the kinetic results have been interpreted in terms of a quantum mechanical model. Photovoltaic and photochromic applications of these systems will be briefly discussed.

References:
B. O'Regan and M. Grätzel, Nature **353**, 737, 1991.

CHIMIA *50* (1996) Nr. 7/8 (Juli/August)

5

FROM THE MOLECULAR LEVEL TO CHEMICAL ENGINEERING MODELS IN HETEROGENEOUS CATALYSIS. NEW DISCOVERIES AND THEIR IMPACT.

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Important phenomena in catalysis are attributed to surface mobility, changes of surface structure and spillover processes.

In the oxidation of CO dissociatively adsorbed oxygen on Cu(111) can trigger the reaction with molecular oxygen of CO adsorbed on Pt(111), in conditions where pure Pt(111) is otherwise inactive (1). A reaction front expands from Cu to the whole Pt surface. Small amounts of O crossing the Cu/Pt border trigger the process.

A different effect is the creation of new catalytic sites by a mobile surface species flowing from one type of surface to another (2). The most conspicuous result is a strong catalytic synergy between two or several distinct solids. This corresponds to a **remote control**. Some part of the catalyst (usually a given phase) dissociates a molecule (O2 or H2) to form surface species. These flow, namely "spillover", over the other part to create active sites, namely surface atoms in the correct coordination (2).

A remote control takes place in numerous reactions (e.g. oxidations and hydrotreatments). Many fields are likely to be influenced by consideration of this concept : activity and selectivity, catalyst formulation and "architecture", ageing processes, kinetic modelling, and process operation (3).

References
1. M. Kolodzejczyk, R.E.R. Colen, M. Berdau, B. Delmon, J.H. Block, *submitted*
2. B. Delmon, Surf. Rev. and Lett., 1995, 2, 25-41
3. B. Delmon, G.F. Froment, Cat. Rev.-Sc. Engg, 1996, 38, 69-100.

6

NUCLEAR MAGNETIC RESONANCE, A POWERFUL TOOL FOR THE STUDY OF BIOMOLECULAR DYNAMICS

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Laboratorium für Physikalische Chemie,
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The nuclear spins are nearly ideal reporters built by nature into virtually all matter and allow one to monitor, on a molecular basis, structural and dynamical features relevant in chemistry and in biology. It can be utilized under a variety of external conditions, including also extreme and nonclassical conditions. In this lecture, some selected aspects of the study of molecular dynamics by NMR will be covered.

The intramolecular dynamics and flexibility of peptides and proteins, that is important for their biological function, can be elucidated in great detail by NMR relaxation measurements. This will be demonstrated for the cyclic decapeptide antamanide which exhibits backbone and sidechain dynamics as well as water exchange dynamics in a non-aqueous solvent.

Proteins can be unfolded and refolded under variable high pressure conditions. NMR allows one to monitor the dynamic processes that are occurring during folding and unfolding. This will be exemplified by experiments on the protein human ubiquitin.

A fascinating dynamical phenomenon is hydrogen tunneling in organic and inorganic molecules. It is relevant for numerous chemical processes. A high pressure study of hydrogen tunneling in transition metal hydrogen complexes has been undertaken. The pressure dependence of the tunneling frequency will be discussed and rationalized.

7

THE PROTON SPONGE: A TRICK TO ENTER CELLS THE VIRUSES DID NOT EXPLOIT.

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Non-viral vectors for gene therapy still need to be improved. The rational development of new delivery systems would benefit from an increased control over the supramolecular DNA/vector assembling process, as well as from a better understanding of the cellular events behind the gene transfer process itself.

We recently noticed that several polycationic weak bases possessing substantial buffering capacity below physiological pH, such as lipopolyamines and polyethylenimines, are efficient transfection agents *per se*, i.e. without the addition of lysosomotropic bases, or cell targeting or membrane disrupting agents. These vectors have been shown to deliver genes as well as oligonucleotides to cells both *in vitro* and *in vivo*. Our hypothesis is that their efficiency is a consequence of proton-mediated endosome swelling and rupture that provides an escape mechanism for the polycation/DNA particles.

8

ISOMERIC EQUILIBRIA IN COMPLEXES INVOLVING Cu^{2+} AND TH AMP^{2-} ANALOGUE 9-[2-(PHOSPHONOMETHOXY)ETHYL]-ADENIN (PMEA) OR ITS DEAZA DERIVATIVES

Claudia A. Blindauer,[a] *Elin Anvedsen,*[b] *Antonín Holý,*[c] *Einar Sletten,*[b] *and Helmut Sigel*[a]
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[b] Department of Chemistry, University of Bergen, N-5007 Bergen, Norwa
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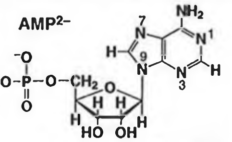
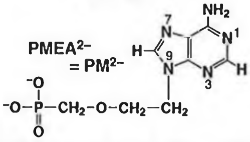
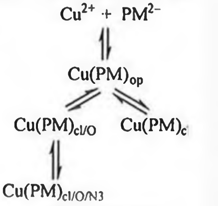

AMP^{2-}


$PMEA^{2-} = PM^{2-}$

$PMEA^{2-}$, an acyclic analogue of adenosine 5'-monophosphate (AMP^{2-} owns antiviral activity [1]. Since metabolic processes involving nucleotid are metal ion-dependent its coordinating properties are studied. Besides bi ding to the phosphonate group ($M(PM)_{op}$) t alkaline earth and divalent 3d ions also intera with the ether O atom leading to 5-member chelates ($M(PM)_{cl/O}$) [2]. Ions like Cu^{2+} bind addition to the nucleobase residue [2], either v N7 ($Cu(PM)_{cl/N7}$) or via N3; in the latter ca the 5-membered chelate may remain intact and further 7-membered chelate to N3 may for ($Cu(PM)_{cl/O/N3}$) (Scheme). Based on ^{1}H-NM line broadening experiments [3] we could co firm [4] that Cu(AMP) forms a macrochelate to N7 (strong broadening of the signal of H8) whereas in the PMEA system the $Cu(PMEA)_{cl/O/N3}$ isomer is important (overwhelming broadening of the H2 signal); that the latter result is not due to an interaction with N1 could be proven with 1-deaza-$PMEA^{2-}$. The species distributions [2] for $Cu(PMEA)_{op}$, $Cu(PMEA)_{cl/O}$ and $Cu(PMEA)_{cl/O/N3}$ are about 17, 34 and 49%, respectively; hence, the solution structures of M(AMP) a M(PMEA) complexes differ significantly.



Supported by the Swiss Fed. Office for Educ. & Sci. (COST D1), the Swiss Nat. S Found., and the Governments of the Czech Rep. (COST D1) and of Norway (COST D

[1] A. Holý, E. De Clercq, I. Votruba, *ACS Symp. Ser.* **401**, 51-71 (198
[2] H. Sigel, *Coord. Chem. Reviews* **144**, 287-319 (1995).
[3] E. Sletten & N. Å. Frøystein, *Met. Ions Biol. Syst.* **32**, 397-418 (199
[4] H. Sigel & B. Song, *Met. Ions Biol. Syst.* **32**, 135-205 (1996).

9

DERIVATIVES OF BENZIMIDAZOLE AS TOOLS TO EVALUATE THE IETAL ION-BINDING PROPERTIES OF THE ADENINE (Ade) RESIDUE

Larisa E. Kapinos,[a] *Bin Song,*[a] *Antonín Holý,*[b] *Matthias Bastian,*[a] *and Helmut Sigel*[a]
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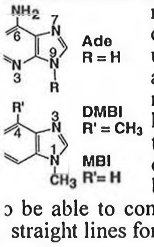
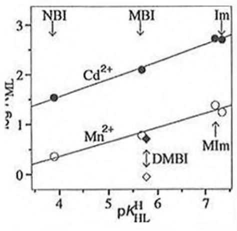


Nucleobase residues and phosphate groups are the main metal binding tes of nucleotides and nucleic acids [1]. However, the roles nucleobase moieties are playing in selectivity and discrimination as observed upon complex formation are relatively poorly understood [1]. For example, it is known [2] that the 6-amino group of the adenine residue inhibits complex formation at N1 as well as at N7, but only the effect on N1 has so far been quantified [3] for various metal ions. As the steric inhibition of an amino group corresponds to that of the methyl group [3], we are now using 1,4-dimethylbenzimidazole (DMBI) as a model for the Ade residue. o be able to construct log K^{M}_{ML} *versus* pK^{H}_{HL} plots, which should result straight lines for a family of related ligands [4], we are presently studying the stabilities of the complexes (via potentiometric pH titrations; $I = 0.5$ M, $NaNO_3$; 25°C) formed with the ligands (L), 1-methylbenzimidazole (MBI), 5(6)-nitrobenzimidazole (NBI), imidazole (Im), and 1-methylimidazole (MIm). Some preliminary results are shown in the Figure; it is evident that the point due to Cd(DMBI) (◆) is more below its reference line (●) than the one due to Mn(DMBI) (◇). This proves that (i) in both instances steric inhibition occurs but that (ii) this is larger for the first ample. More such data should finally permit to evaluate quantitatively the 1 versus N7 metal ion dichotomy [2] of the Ade residue.



Supported by the Swiss Fed. Office for Education & Science (COST D1), the Swiss Nat. Science Foundation, an d the Government of the Czech Republic (COST D1).

] H. Sigel, *Chem. Soc. Rev.* **22**, 255-267 (1993).
] R. B. Martin, *Met. Ions Biol. Syst.* **32**, 61-89 (1996).
] L.-n. Ji, N. A. Corfù, H. Sigel, *J.C.S. Dalton Trans.* 1367-1375 (1991).
] R. B. Martin, H. Sigel, *Comments Inorg. Chem.* **6**, 285-314 (1988).

10

Dynamic parameters of MRI Contrast Agents

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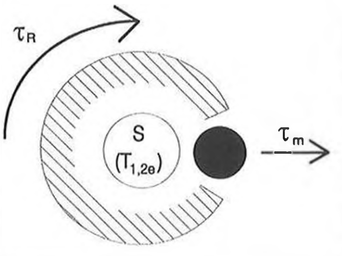
e University of Coimbra, Portugal, f University of Mons, Belgium

Current developments in MRI (3D-time-of-flight, micro and blood vessel imaging) call for very-high-relaxivity contrast agents. The dynamic parameters governing the relaxivity of today's (poly(amino carboxylate) complexes of Gd^{3+} or other paramagnetic metals) and most probably also of tomorrow's contrast agents are the rates of molecular tumbling, of the exchange of the inner sphere water molecule, and of electronic relaxation.



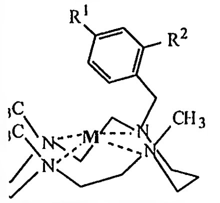
While it seems straightforward to freeze out rotation by attachment of the complexes to macromolecules, tuning the rates of water exchange and of electronic relaxation is less evident. Over the last four years we have gained considerable insight into the mechanisms determining these rates using ^{17}O NMR, EPR, and NMRD studies. Changing field strength, temperature, pressure, ligands, and complexed metals in an integrated approach we were able to separate the different contributions to relaxivity and to determine their values with certainty.
We present a review of our results and of the conclusions that can be drawn for the design of future high-relaxivity contrast agents.

11

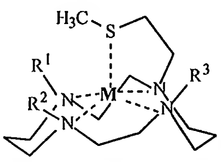
ACTIVITY OF MACROCYCLIC Ni^{II} AND Cu^{II} COMPLEXES TH THIOETHER AND ETHER SIDE CHAINS

Schmid and Thomas. A. Kaden
itute of Inorganic Chemistry, Spitalstr. 51, 4056 Basel, Switzerland

To investigate the role played by cofactor F430 in the production of hane, we prepared a series of macrocyclic Ni^{II} and Cu^{II} complexes and lied their structure and reactivity. Compounds **1-4** have either a thioether n ether group in the side chain, which does not bind to M^{2+} (CN=4), ereas compounds **5-7** have a variable number of thiomethyl side chains, of which coordinates to M^{2+} (CN=5).



R^1=SCH_3 R^2=H
R^1=H R^2=SCH_3
R^1=OCH_3 R^2=H
R^1=H R^2=OCH_3



5: R^1=R^2=R^3=CH_3
6: R^1=$(CH_2)_2$-SCH_3 R^2=R^3=CH_3
7: R^1=R^2=R^3=$(CH_2)_2$-SCH_3

Cyclic voltammetry shows the reversible Ni^{II}/Ni^{I} pair (-0.7V *vs.*), the cleavage of the thiomethyl group (-2.0V to -2.4V *vs.* SCE) and the nation of the corresponding thiol (+0.7V *vs.* SCE for GCE and 0V *vs.* for HMDE); no similar behaviour could be observed for compounds **3** **4** since, under similar conditions, no breaking of the O-CH_3 bond takes e. All complexes were reduced with Na/Hg in DMF and the production nethane was monitored by GC: only complex **2** liberates small amounts ethane.

12

FORMATION OF MIXED METAL COMPLEXES WITH *cis*-$(NH_3)_2Pt(dGuo)(dGMP)$;

dGuo = 2'-Deoxyguanosine, $dGMP^{2-}$ = 2'-Deoxyguanosine 5'-Monophosphate

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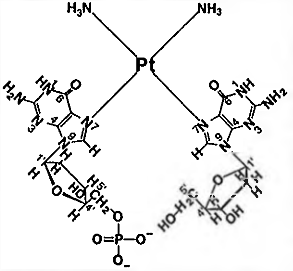
Under natural conditions nucleotides and nucleic acids interact with *labile* [1] metal ions, whereas in therapeutic agents, like in the anticancer drug Cisplatin, *cis*-$(NH_3)_2PtCl_2$, often *inert* [2] metal ions are employed. We are studying both kinds of interactions [1,2] and joined now our forces to evaluate also the effect of nucleobase-coordinated Pt^{2+} on the metal ion-binding properties of phosphate groups. The depicted structural formula of *cis*-$(NH_3)_2Pt(dGuo)(dGMP)$, abbreviated as Pt(G)(GP), indicates that this system is ideal for studying such mixed metal ion complexes. By potentiometric pH titrations (I = 0.1M, $NaNO_3$; 25°C) we measured the stability constants given in column 2 of the Table. Application of log K *vs* pK_a straight-line plots [3] allows to calculate the uninfluenced affinity of a -PO_3^{2-} group (column 3); for phosphate monoprotonated $H[Pt(G)(GP)]^+$, p$K^{H}_{H[Pt(G)(GP)]}$ = 5.85 ± 0.04 [compare with p$K^{H}_{H(dGMP)}$ = 6.29 of free $H(dGMP)^-$]. Column 4 demonstrates that the effect of the N7-coordinated Pt^{2+} on the metal ion-binding properties of the phosphate group of the same $dGMP^{2-}$ is small; an important result regarding platinated nucleic acids!



M^{2+}	log $K^{M}_{M[Pt(G)(GP)]}$	log $K^{M}_{M[Pt(G)(GP)]calc}$	log $\Delta_{M[Pt(G)(GP)]}$
Mg^{2+}	1.21±0.04	1.49±0.03	-0.28±0.05
Cu^{2+}	2.65±0.08	2.71±0.06	-0.06±0.10
Zn^{2+}	1.81±0.06	2.00±0.06	-0.19±0.08

Supported by the Swiss Fed. Office for Educ. & Sci. (COST D1; H.S.), the Swiss Nat. Sci. Found. (H.S.), and the 'Deutsche Forschungsgemeinschaft' (B.L.).

[1] H. Sigel and B. Song, *Met. Ions Biol. Syst.* **32**, 135-205 (1996).
[2] B. Lippert, *Met. Ions Biol. Syst.* **33,** 105-141 (1996).
[3] H. Sigel, S. S. Massoud & N. A. Corfù, *JACS* **116**, 2958-2971 (1994).

13

WATER EXCHANGE AND ROTATIONAL DYNAMICS ON DIMERIC GD(III) COMPLEXES*

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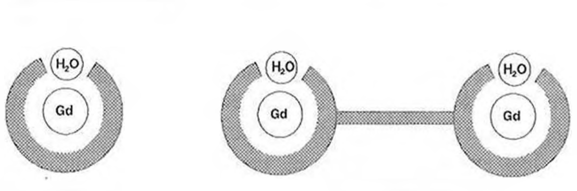
Rapid water exchange and slow rotation are essential for high relaxivity MRI contrast agents. Dimeric Gd(III) complexes are of relevance to MRI as attempts to gain higher ^{1}H relaxivity by slowing down the rotation of the molecule, compared to the monomers already used as contrast agents.

A variable temperature and pressure ^{17}O NMR study at different fields has been performed on the Gd(III) complexes of three dimeric ligands, all containing DOTA-type macrocyclic chelating units.

The parameters characterizing water exchange and rotational dynamics are very similar for the three complexes. The rate constants of the water exchange, k_{ex}^{298}, are (1.0-1.5) $\times 10^6 s^{-1}$, the activation volumes, $\Delta V^{\neq}$, of the process indicate an interchange mechanism. The rotational correlation time becomes about two times longer compared to monomeric polyamino-polyacetate Gd(III) complexes studied so far: τ_R= 220-270 ps, which results in an enhanced proton relaxivity by raising the correlation time for the paramagnetic interaction.



τ_R= 90 ps
(monomers)

τ_R= 250 ps
(dimers)

*E.Toth, S.Vauthey, D. Pubanz and A.E. Merbach, *Inorg. Chem.* **1996**, *35*,3375.

15

BINUCLEAR METAL COMPLEXES OF BIS-MACROCYCLES WITH A PYRAZOLE BRIDGING UNIT

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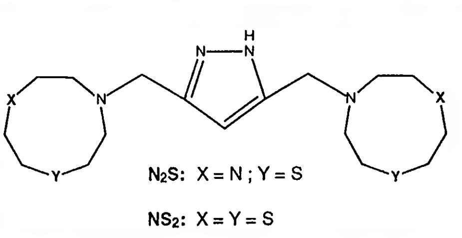
Two pyrazole bridged binucleating ligands N_2S and NS_2 were prepared by alkylation of the corresponding macrocycles with 3,5-bis-(chloromethyl)-pyrazole.



The equilibria in solution were studied for N_2S and Cu^{2+} using potentiometric titrations, which were evaluated with the program TITFIT. Besides mononuclear species, binuclear complexes were also identified and their stability was determined. In addition a series of binuclear complexes of N_2S and NS_2 with copper(II) and nickel(II) have been synthesized and characterized (elemental analysis, FAB-MS, IR, X-ray).

The binuclear copper(II) complexes exhibit a pentacoordinate geometry. In contrast the binuclear nickel(II) complexes prefer hexacoordination, which is achieved by binding additional solvent molecules. In all complexes the pyrazole group is deprotonated and bridges the two metal centres.

In case of the copper(II) complexes various exogenous bridging molecules can also be incorporated (for N_2S: pyrazolide, sulfate, azide and for NS_2: chloride, bromide).

14

DENDRIMER -BASED GD(III) COMPLEXES: A PROMISING CLASS OF MRI CONTRAST AGENTS

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Dendrimer-based macrocyclic Gd(III) complexes represent a new class of potential MRI contrast agents. They have high proton relaxivities and extended lifetime in blood pool, which are indispensable for safe and efficient application in Magnetic Resonance Angiography.

We performed a variable temperature and pressure ^{17}O NMR study on water exchange and rotational dynamics on the macrocyclic Gd(DO3A-bz-N{CS}) complex attached to three different generations of PAMAM dendrimers in aqueous solution, as well as on the Gd(III) complex of the monomer macrocyclic unit with the linker group.

The water exchange rates, k_{ex}^{298}, are practically the same on the complexes of the different dendrimer generations and on the monomer uni (1.0-1.6$\times 10^6$ s^{-1}), which makes possible to *predict water exchange rates fo complexes attached to polymers* prior to the tedious synthesis of the whol macromolecule. The activation volumes indicate dissociatively activate processes.

The rotational correlation times, τ_R, and consequently proto relaxivities of the dendrimers are much higher than for any monomeric o dimeric Gd(III) complexes. However, slow water exchange prevents th relaxivities from attaining the values expected from the increase in τ_R.

These dendritic complexes represent the first example where *proto relaxivity is mainly limited by water exchange rate*. Therefore, furthe development towards high relaxivity contrast agents inevitably require complexes with increased water exchange rate.

16

DESYMMETRISATION OF DIENYLSILANES.

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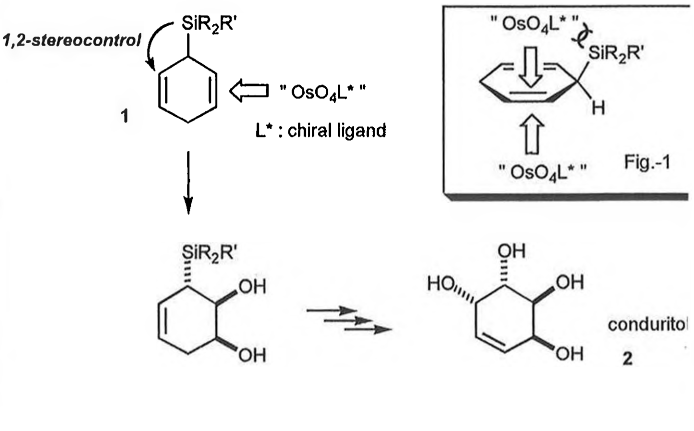
Collège Propédeutique, CH-1015 Lausanne-Dorigny.

The potential of polyhydroxylated cyclohexanes such as conduritols **2** an analogues as inhibitors of glycosidases has recently stimulated enormou synthetic efforts. We wish to describe a new strategy which can afford acce to both enantiomers of such cyclitols, using the desymmetrisation of silyl-2, cyclohexadienes such as **1**. We have demonstrated that the Sharples dihydroxylation reagent (*i.e.* AD-mix) efficiently differentiates the tw enantiotopic double bonds of **1**. The silicon moiety is particularly convenien to control the diastereofacial selectivity (*1,2-stereocontrol*) (Fig.-1) befor unmasking using the classical Tamao-Kumada-Fleming oxidation. The scop and limitations of our methodology along with an application to the tot synthesis of potent glycosidase inhibitors will be presented.



CHIMIA 50 (1996) Nr. 7/8 (Juli/August)

17

RADICAL DEUTERATION OF β-SILYL- AND β-HYDROXYSULFOXIDES.

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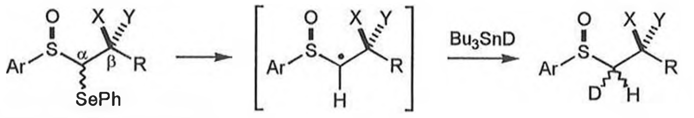
ɔllège Propédeutique, CH-1015 Lausanne-Dorigny.
'nstitut de Chimie Organique, Université de Fribourg
'rolles, CH-1700 Fribourg.

2-Stereocontrol using sulfoxides in acyclic radical reactions has recently racted a great deal of interest. High level of diastereoselectivity can be ained with the chirality at sulfur being transferred to the vicinal prochiral ntre during allylation or deuteration. Several models, supported by lculations, have been proposed to rationalise the 1,2-stereocontrol served during these radical reactions. Addition of a second chiral centre in position relative to the sulfur centre introduces both steric and electronic ects which led to unexpected diastereoselectivities (Scheme 1).



ır Y = OH, OR, SiR$_3$, t-Bu, H

Scheme 1

discussion of the factors which are likely to control this diastereoselective lical process will be presented. For instance, the nature of the substituents β-position (*i.e.* SiR$_3$ or OR) has a dramatic effect on the stereochemical tcome of the deuteration. Semi-empirical calculations have been formed which support our proposed conclusion of a co-operative effect ween the chirality at sulfur and the chirality at the β-carbon centre.

19

IE TRANS-INFLUENCE OF THE CARBYNE LIGAND AND ITS POTENTIAL TO STABILIZE THE 16 e$^-$ CONFIGURATION

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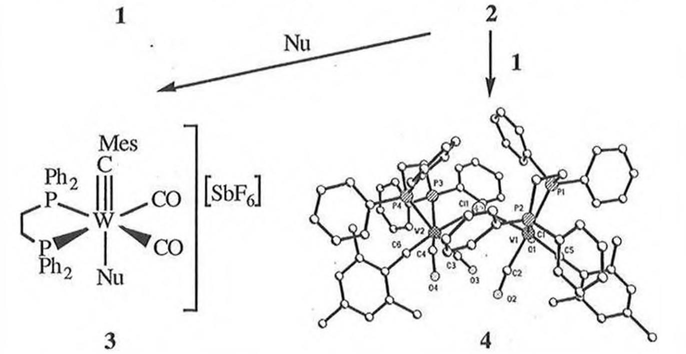
, CH-8057 Zurich, Switzerland

multiply bonded carbyne ligand displays a strong trans influence. We efore decided to use known trans carbyne chloride tungsten complexes as a precursor for Lewis acidic cations.

ogen abstraction from a trans carbyne chloride tungsten complex **1** ilized by a chelating phosphine donor leads to a quite stable five-rdinated 16 e$^-$ cation **2**. Reactions of **2** with anionic or neutral nucleo-es offer a great potential for the synthesis of new carbyne complexes **3**. A ial nucleophile, the starting chloride complex **1**, reacts with the cation to dinuclear complex [(dppe)(CO)$_2$(CMes)W]$_2$Cl[SbF$_6$] **4**.

$$/(CO)_2(CMes)(Cl)(dppe)] \xrightarrow[- AgCl]{AgSbF_6} [W(CO)_2(CMes)(dppe)][SbF_6]$$



3 **4**

G. A. McDermott, A. M. Dorries, A. Mayr, Organometallics, **1987**, *6*, 925

18

ASYMMETRIC SYNTHESIS OF OPTICALLY ACTIVE TRICARBONYLIRON DIENE COMPLEXES BY LIGAND EXCHANGE FROM CHIRAL VINYL OXAZOLINE-IRON COMPLEXES.

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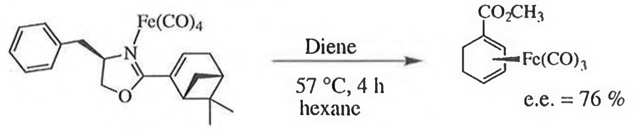
Tricarbonyliron diene complexes have considerable potential as useful intermediates in organic synthesis, because of the sterical and electronical properties of the tricarbonyl-iron moiety [1].

Although only modest degrees of asymmetric induction have been achieved by complexation via ligand exchange using optically active enones derived from the chiral pool, this approach showed a promising general access to optically active diene complexes [2][3]. As tricarbonyliron complexes of 1-aza-1,3-butadienes were found to be excellent transfer reagents for the complexation of 1,3-dienes [4] it was obvious to continue the quest for better transfer ligands by replacing oxygen by nitrogen in the heterodiene [5][6][7].

The best enantiomeric exesses were obtained so far by using chiral vinyl oxazolines of the type depicted below:



It is important to note that highest enantioselective inductions were observed using isolated and purified heterodienic-σ-*N*-Fe(CO)$_4$ complexes.

[1] R. Grée, J.-P. Lellouche, *Adv. in Metal-Organic Chem.*, L. S. Liebeskind Ed. **1994**, *4*.
[2] A. J. Birch, W. D. Raverty, G. R. Stephenson, *Organometallics* **1984**, *3*, 1075.
[3] T. A. Jenny, V. Schmid, *Chimia* **1993**,*47*, 296.
[4] H.-J. Knölker, P. Gonser, *Synlett* **1992**, 517.
[5] T. A. Jenny, P. Aspari, *Chimia* **1995**, *49*, 268.
[6] H.-J. Knölker, H. Hermann, *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 341.
[7] F. Maywald, P. Eilbracht, *Synlett*, **1996**, 380.

20

INVESTIGATIONS ON POTENTIAL RHENIUM BASED LEWIS ACIDS - THE NITROSYL LIGAND AND THE RHENIUM TRIFLATE BOND

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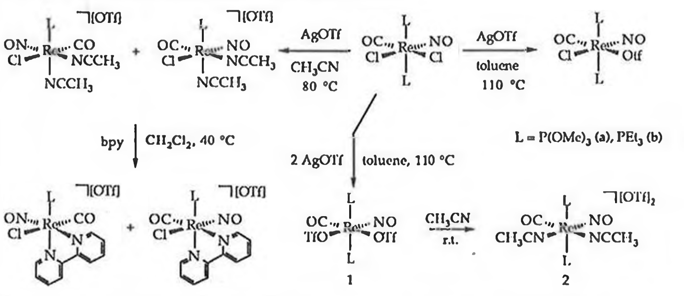
Transition metal Lewis acids require a vacant or loosely filled coordination site and desirably also a positive charge on the metal center. However, systems with complete vacancy of one ligand position are presumably for many practical cases not appropiate. The triflate anion turned out to be an excellent protecting group for such sites, but its lability is known to be strongly dependent on the electronic nature of the metal.

According to the Scheme different triflate chemistry has been explored starting from Re(NO)(CO)L$_2$Cl$_2$ complexes.[1]



In order to trace the triflate effect the reaction from **1** to **2** has been investigated in greater detail. Two parallel regioselective reactions and stepwise substitution processes have been found. From this it was possible to draw conclusions on the mutual electronic influence of the triflate and the nitrosyl ligand.

[1] D.Veghini and H. Berke, Inorg. Chem., 1996 (in press)

CHIMIA *50* (1996) Nr. 7/8 (Juli/August)

21

ENANTIOSELECTIVE HYDROGENATION OF 2-METHYL-2-PENTENOIC ACID

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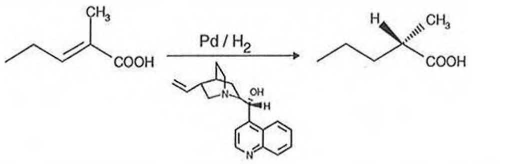
The enantioselective hydrogenation of α,β-unsaturated carboxylic acids has received great attention due to the pharmaceutical importance of some chiral carboxylic acids. Unfortunately, there is no preparatively useful solid catalyst available for the enantioselective hydrogenation of olefins. There have been reported a few attempts to hydrogenate cinnamic acid derivatives and isophorone over cinchonidine-modified Pd catalysts, but the enantiomeric excesses achieved (ee's) are moderate. The aim of our study was to gain some basic information concerning the nature of interaction between Pd, cinchonidine and reactant. The enantioselective hydrogenation of 2-methyl-2-pentenoic acid (MPA) was used as a model reaction.



A kinetic analysis of the hydrogenation of MPA revealed that the reactor should be operated in the kinetic regime for obtaining the maximum enantioselection. In agreement with this observation, high surface hydrogen concentration (at least 60 bar hydrogen pressure) favours the enantioselection. Other important parameters of the reaction are the solvent, catalyst pretreatment and cinchonidine concentration. The highest ee obtained until now is 52 % to the (*S*) product.

Molecular modelling calculations, combined with NMR and FTIR studies, were also performed for obtaining information about the nature of cinchonidine - MPA interaction.

22

SYNTHESIS AND INVESTIGATION OF TRIFLUOROMETHYL SUBSTITUTED COMPOUNDS

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D. Michel, F. Mongin and M. Schlosser
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By virtue of the COST concept, a network has been established at the European level that devotes considerable research efforts to the synthesis and application of organofluorine compounds in general and focuses on "CF_3 chemistry" in particular. Annual workshops and symposia are held to share ideas or know-how and to generate synergies by practical collaborations. The partner laboratories and their principal activities are :

K. Burger (Leipzig)	Unnatural Aminoacids and Peptidomimetics
A. Commeyras (Montpellier)	New Materials Having Perfluoroalkyl Tails
W. Dmowski (Warsaw)	Reactions with Sulfur Tetrafluoride
R. Ruzziconi (Perugia)	Oxidation Promoted Diene Coupling
M. Schlosser (Lausanne)	Halogenated Analogs of Bioactive Substances
L. Töke (Budapest)	Chiral, Chrysanthemate-Like Cyclopropanes
C. Wakselman (Versailles)	Steroids and Phytohormones

New results dealing with the selective preparation and transformation of aliphatic, aromatic and heterocyclic "CF_3-doped" compounds will be presented. Model reactions to be described will probe the reactivity and selectivity modulating effects of trifluoromethyl substituents.

23

ELECTRON-POOR BIDENTATE PHOSPHORUS LIGANDS IN TRANSITION METAL CATALYZED DIELS-ALDER REACTIONS

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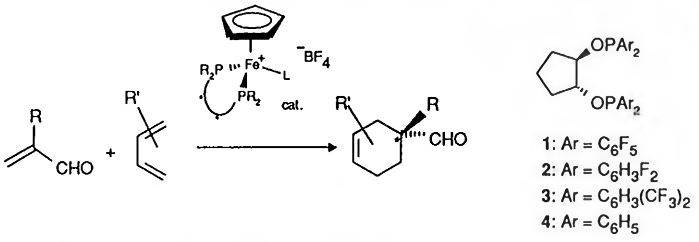
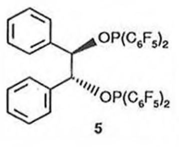
30, Quai Ernest Ansermet, CH-1211 Genève 4

Previous work from this laboratory showed that the chiral complex $[CpFe(PP)L]BF_4$ (PP=**1**, L=acrolein) acts as a catalyst for asymmetric Diels-Alder reactions to give highly enantioenriched products.[1] The essential new feature of the catalyst is the presence of an electron poor, chiral, bidentate phosphorus ligand which maintains the Lewis acidity of the metal center and generates the required chiral pocket for asymmetric induction.



1: Ar = C_6F_5
2: Ar = $C_6H_3F_2$
3: Ar = $C_6H_3(CF_3)_2$
4: Ar = C_6H_5



5

Herein we report our continued studies in this area and present the synthesis of a range of complexes of the same type, with PP = **1**-**5**. All complexes are active catalysts. Ligand modification affects the stability of the catalyst, as well as its activity and the enantioselectivity of the cycloaddition reactions between enals and dienes.

---

[1] E.P. Kündig, B. Bourdin and G. Bernardinelli, *Angew. Chem. Int. Ed. Engl.*, **1994**, *33*, 1856.

24

DEVELOPMENT OF A TRIPODAL PHOSPHANE SUBSTITUTED LEWIS ACID BASED ON THE {Re(NO)} - FRAGMENT

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Winterthurerstr. 190
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Many C-C bond forming reactions, preferably stereoselective ones, can be enhanced or catalysed by Lewis acids. Up to now main group Lewis acids have found only limited use in enantioselective catalysis, mainly due to restricted possibilities for chiral modifications. On the contrary transition metal based compounds are expected to have a higher flexibility in this regard. Most promising are complexes with low-spin d^6 centers because of their usually high configurational stability.
Our approach to new potentially chiral transition metal systems is based on the tripodal unit tris(diphenylphosphinomethyl)ethane (tdppme), which is known to represent a quite rigid ligating moiety shielding a facial side of the resulting complex. Among other aspects the nitrosyl and carbony substituents are sought to enforce the Lewis acidity of our systems.
Based on these considerations we intended to develop complexes containing the $[(tdppme)Re(NO)(CO)_n]^{2+}$ (n=1,2) motif.
The high-yield synthesis of $[(tdppme)Re(NO)(CO)_2][BF_4]_2$ was achieved in two steps starting from easily available $Re(CO)_5X$ (X=Cl, Br).

$$Re(CO)_5X \xrightarrow{a)} [LRe(CO)_2X] \xrightarrow{b)} [LRe(NO)(CO)_2][BF_4$$

X = Cl, Br
L = tdppme

a) tdppme, toluene
b) $NOBF_4$, CH_2Cl_2

This rhenium nitrosyl precursor offers two routes to the desired Lewis acids
1. oxidative elimination of one CO ligand with iodosobenzene.
2. conversion of a carbonyl group into a methyl or a hydride ligand and subsequent elimination of the latter with a Brønsted acid.
The results of these efforts are described.

25

LEWIS ACIDS IMPROVED STEREOCONTROL IN SULFOXIDE BASED RADICAL REACTIONS.

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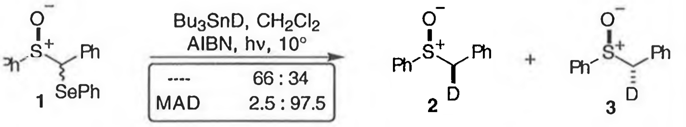
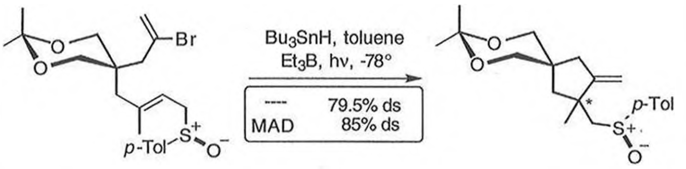
our study of sulfinylated benzyl radicals we demonstrated that the sense id degree of stereoselectivity can be efficiently controlled by using *Lewis* ids. Radical deuteration of the selenylated precursor **1** afforded the rresponding α-deuterosulfoxides **2** and **3** in a ratio of 66 : 34. Running the action in the presence of a bulky *Lewis* acid such as the methylaluminum (2,6-di-*tert*-butyl-4-methylphenoxide) (MAD) leads exclusively to **3**.



the presence of the same bulky MAD we were able to increase the ereocontrol of the cyclizations using vinylsulfoxide as radical trap.



conclusion, we demonstrated that sulfoxides complexed by bulky *Lewis* ids are good templates for controlling the stereochemistry of radicals ictions.

26

EXPERIMENTAL AND THEORETICAL STUDIES OF AN OLEFIN-BRIDGED DINUCLEAR ZIRCONIUM COMPLEX

Heiko Jacobsen†, Heinz Berke†, Francisco J. Fernández‡, Pilar Gómez-Sal‡, Antonio Manzanero‡, and Pascual Royo‡
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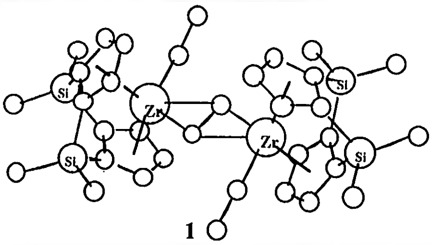
'Narrow angle' early transition metal metallocene fragments play an important role in the tuning of Lewis acidic catalysts. Herein, we report on the structure of $[Zr(CpSi_2Cp)Et]_2(\mu\text{-}CH_2{=}CH_2)$ **1**, ($CpSi_2Cp$ = 1,1',2,2'-$(SiMe_2)_2(\eta^5\text{-}C_5H_3)_2$), an olefin-bridged dinuclear complex in which the zirconium fragment has a bite angle of only 119°.



1

Characteristic structural features of **1** are the two significantly different C-Zr distances of 230 pm and 253 pm between the bridging ethene and the metal fragments.

Although the Zr centers in **1** have the formal oxidation number +III, quantum chemical calculations, based on density functional theory (DFT), suggest that the system is better described as Zr^{+IV}. The geometry around the CH_2CH_2 unit has been optimized ($d_{Zr\text{-}C}$ = 233 pm, 251 pm), and results in a pyramidal coordination of the carbon atoms. In contrast, when a planar coordination around the carbon centers is enforced, the resulting Zr-C distances are shorter and almost equal ($d_{Zr\text{-}C}$ = 240 pm, 243 pm).

27

TOTAL SYNTHESIS OF AN AZA-C-DISACCHARIDE

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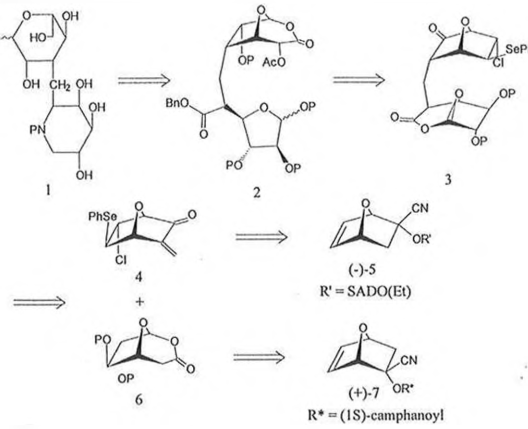
ction de chimie de l'Université de Lausanne, BCH, CH-1015 Lausanne-Dorigny, Switzerland

Specific inhibitors of glycosidases, may be useful for the treatment of eases such as diabetes, cancer, viral and bacterial infections and ammations[1].

We present here a total synthesis of a new aza-C-disaccharide (**1**), ential inhibitor of glycosidases. It is obtained through the Michael lition of lactone **6** to enone **4**. Both are derived from optically pure 7 - bicyclo[2.2.1]hept-5-en-yl (+)-**7** and (-)-**5** ("naked sugars of the first eration")[2]



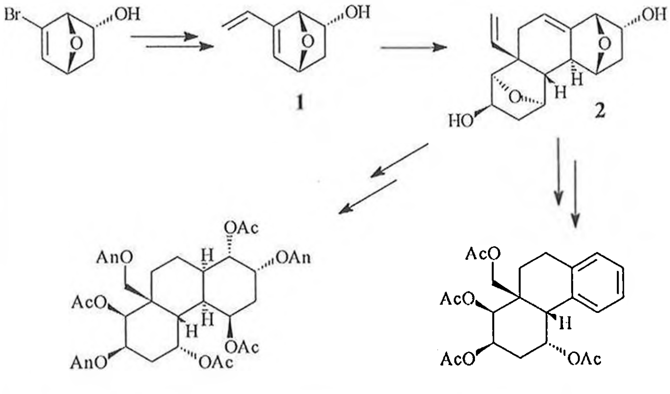
See e.g. Karlsson *et al. J. Biol. Chem.* **1993**, *268*, 570.
E. Frérot *et al. Tetrahedron Lett.*, **1996**, *37*, 2026.

28

SYNTHESIS OF POLYHYDROXYLATED PERHYDROPHENANTHRENES VIA STEREOSPECIFIC DIELS-ALDER DIMERISATION OF SEMICYCLIC DIENES

Hervé Mosimann, Pierre Vogel.
Section de Chimie de l'Université de Lausanne, BCH-Dorigny, CH-1015 Lausanne, Switzerland.

An efficient synthesis of 6-vinyl-7-oxabicyclo[2.2.1]hept-5-en-2-ol (**1**) by a Sonogashira coupling of the corresponding vinyl bromide and ethynyltrimethylsilane has been developed. As expected [1], this semicyclic diene dimerises by a stereospecific Diels-Alder addition affording **2** as the only product. This dimer has been further transformed into different highly functionalised octahydro-and perhydrophenanthrenes by two successive regio- and stereoselective oxa-bridge opening reactions.



[1] Meerpoel, L.; Vrahami, M.-M.; Ancerewicz, J.; Vogel, P.; *Tetrahedron Lett.* **1994**, *35*, 111-114.

29

STRUCTURAL DIVERSITY OF LEWIS ACIDIC COMPLEXES CONTAINING THE W(NO)$_2$-FRAGMENT

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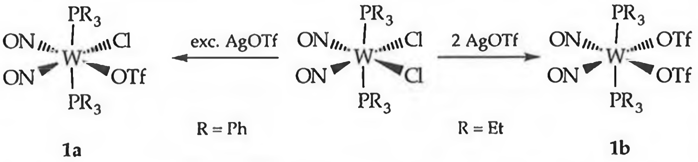
Winterthurerstr. 190, CH-8057 Zürich

The compounds $[M(NO)_2(NCCH_3)_4][BF_4]_2$ (M = Mo, W) are known to catalyze polymerisations, oligomerisations and isomerizations of olefins [1]. In a previous communication Johnson and his co-workers [2] showed, that cations like cis-$[M(NO)_2(NCCH_3)_4]^{2+}$ (M = Mo, W) undergo stereospecific dissociative exchange of the CH_3CN ligands. Johnson assumed, that the two labile CH_3CN ligands are those disposed trans to the two NO groups.



We now report synthetic pathways for neutral $W(NO)_2L_2X_2$ complexes with one **1a** (L = PPh_3) or two **1b** (L = PEt_3) labile OTf ligands in trans position to the NO groups as a precursor for Lewis acids. Derivatives with L_2 = dmbipy or L = THF will be presented, as well. ^{19}F-NMR monitoring of the triflate exchange reaction of these complexes demonstrated high reaction rates in substitution processes with CH_3CN. In addition to this the structural parameters of these complexes will be discussed.

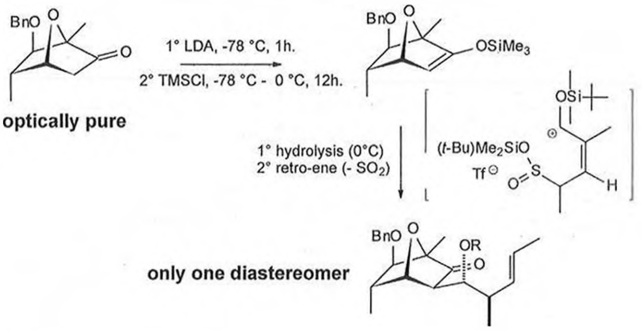
[1] Sen, A.; Thomas, R. R. *Organometallics* **1982**, 1, 1251
Sen, A. *Acc. Chem. Res.* **1988**, 21 ,421
[2] Johnson, B. F. G.; Khair, A.; Savory, C. G.;Walter, R. H. *J.C.S. Chem. Comm.* **1974**, 744

30

SULFUR DIOXIDE IN ORGANIC SYNTHESIS. ALLYLATION OF A BICYCLIC ENOL ETHER: THREE CONTIGUOUS STEREOGENIC CENTRES IN ONE STEP REACTION.

Jean-Michel Roulet and Pierre Vogel*, Institute of Organic Chemistry, University of Lausanne, BCH-1015 Lausanne-Dorigny.

We have developped an unusual method for the synthesis of polypropionate chain through the chemistry of sulfur dioxide. The key reaction of our new strategy is the catalytic allylation of an intermediate resulting from the cycloaddition of sulfur dioxide to substituted alkoxydienes[1]. Through this reaction, we obtain an unstable allylsulfinic acid, which readily eliminates sulfur dioxide by a sterecontrolled retro-ene process[2], providing in one step three contiguous stereogenic centres.



[1]B. Deguin, P. Vogel, *Tetrahedron Lett.* **1993**, *34*, 6269. [2]J.-B. Baudin, S Julia, *Bull. Soc. Chim. Fr.* **1995**, *132*, 196.

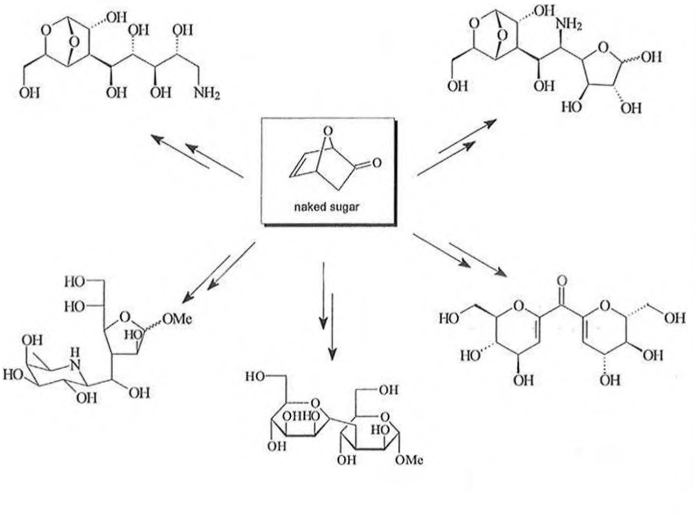
31

SYNTHESIS OF SUGAR MIMICS, POTENTIAL SWEETENERS

C. Schaller, A. Baudat, P.Gerber, V. Jeanneret, K. Krachenbuchl, M. Khaldi, C. Marquis, C. Pasquarello, A. Stimac, Y.H. Zhu et P. Vogel*

Section de chimie de l'Université de Lausanne, BCH, CH-1015 Lausanne-Dorigny, Suisse

There is considerable interest at present in the design of synthetic sweeteners. Concomitantly, there has been intense investigation of the structural and mechanistic aspects associated with sweeteness; however, it is still not possible to predict a priori whether a novel structure will be sweet.
In our laboratories we are developing, starting from furane, the synthesis of sugars mimics, potential non-metabolisable sweeteners, through the "naked sugar" methodology.



32

HETEROGENEOUS ENANTIOSELECTIVE HYDROGENATION OF KETOPANTOLACTONE

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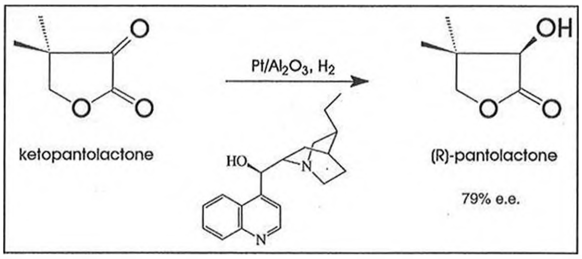
Departement of Chemical Engineering and Industrial Chemistry, Swiss Federal Institute of Technology, ETH Zentrum, CH-8092 Zürich, Switzerland.

The heterogeneous enantioselective hydrogenation of α-ketoesters has be come a field of considerable attention. Most of the studies focused on th reduction of ethyl pyruvate over cinchona-modified Pt, and only a fe attempts have been made to broaden the scope of reactants. Here we repo an industrially important reaction: the hydrogenation of ketopantolactone t R-(-)-pantolactone, as shown below.



A detailed study of the influence of reaction conditions on the enantiomer excess (ee) revealed that crucial parameters are the catalyst pretreatmen solvent, temperature, surface hydrogen concentration, modifier and reacta concentrations. Good ee can be obtained only in an oxygen- and waterfr system. Apolar medium (toluene), moderate temperature (10°C), high h drogen pressure (> 70 bar) and medium substrate concentration (0.5 M) a advantageous for enantio-differentiation. Pt/alumina has to be treated flowing hydrogen at 300-400 °C before reaction. The nature of the reactan modifier interaction has been studied using molecular mechanics calcul tions.

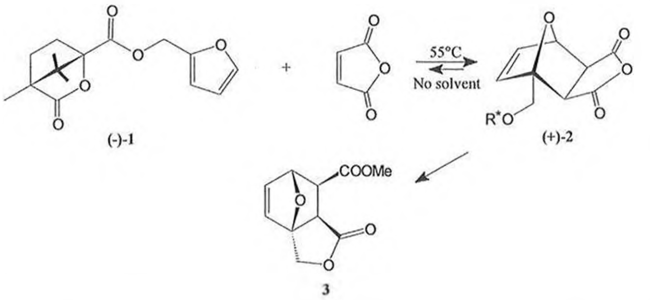
CHIMIA 50 (1996) Nr. 7/8 (Juli/August)

33

SYNTHESIS OF OPTICALLY PURE 7-OXABICYCLO[2.2.1]HEPT-2-ENES PRECURSORS IN THE PREPARATION OF TAXOL ANALOGUES.

viane Theurillat-Moritz, Pierre Vogel.
ction de Chimie de l'Université de Lausanne, BCH, CH-1015 Lausanne-
›rigny, Switzerland.

)-Camphanate of furfuryl alcohol undergoes Diels-Alder addition in elted maleic anhydride giving one major crystalline adduct **(+)-2** (1*S*,1*S*', ,3*S*,4*R*)-1-[(camphanoyloxy)methyl]-7-oxabicyclo[2.2.1]hept-5-ene-2*exo*, *xo*-dicarboxylic anhydride) the absolute configuration of wich was ablished through chemical correlation. Adduct **(+)-2** was converted into optically pure intermediate of the Yadav's approach to the synthesis of ol derivatives[1].



Yadav, J. S.; Renduchintala, R.; Samala, L.; *Tetrahedron Lett.* **1994**, *35*, 17

35

Aryl Sulfoxides as Chiral Templates for Radical Reactions

Zahouily and P. Renaud
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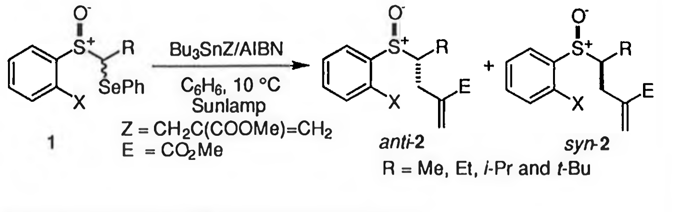
bourg, Suisse

dical reactions and in particular cyclization and multiple cyclization ctions are becoming more and more popular in organic synthesis. The stereoselectivity of such processes is easily predictable. In order to access enantiomerically pure compounds, the use of a chiral auxiliary is highly ractive. We are currently investigating the use of sulfoxides as chiral nplates to control the absolute stereochemistry of compounds prepared m acyclic alkyl radicals. We report here the scope and limitation of ›stituted aryl sulfoxides in intermolecular reactions. A comparison with the ssical alkylation of sulfinylated carbanion will be presented.



analysis of the results shows two tendencies:
arge R groups tend to favor the *syn* configuration.
he presence of an *o*-chlorine atom favors the *anti* configuration.
results presented here are presently used in our laboratory to control the eoselectivity of simple and multiple cyclization reactions.

34

CHEMISTRY AND REACTIVITY OF THE $[W(NO)_2(DM\text{-}PYBOX)]^{2+}$ FRAGMENT

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Winterthurerstrasse 190, CH-8057 Zürich

Transition metal based Lewis acids can catalyze a multitude of organic reactions. It has been shown by *Hersh*[1] that the electrophilicity of low valent tungsten metal centers can be enhanced by the introduction of NO^+ ligands in conjunction with appropriate hard donor ligands.

Solvent complexes of the type $[W(NO)_2(\text{dm-pybox})(S)](X)_2$ (S = EtCN, $MeNO_2$; X = BF_4, PF_6, SbF_6; dm-pybox = 2,6-Bis[4',4'-dimethyloxazolin-2'-yl]pyridin[2]) **1** were synthesized «in situ» in a simple two step reaction and were characterized spectroscopically.

$$W(CO)_6 \xrightarrow[\text{(S)}]{\text{a) 2 Me}_3\text{NO, dm-pybox} \quad \text{b) 2 [NO](X)}} [W(NO)_2(\text{dm-pybox})(S)]\,(X)_2$$

(1) X = BF_4, PF_6, SbF_6
(S) = EtCN, $MeNO_2$

In contrast to *Fallers*[3] tungsten Lewis acid $[W(NO)_2(HCpy_3)(CH_3CN)](SbF_6)_2$ with the facially arranged tris-pyridylmethane ($HCpy_3$), *dm-pybox* is a meridionally bound ligand. Therefore the coordinated solvent molecule in compound **1** is in trans position to one of the two nitrosyl ligands which leads to the assumption of an increased σ- and π-accidity of the tungsten metal center.

The coordination chemistry and reactivity of the $[W(NO)_2(\text{dm-pybox})]^{2+}$ fragment has been examined. $[W(NO)_2(\text{dm-pybox})Cl](SbF_6)$ has been studied by X-ray diffraction.

(1) Hersh, W.H. *J. Am. Chem. Soc.* **1985**, *107*, 4599
(2) Nishiyama, H.; Kondo, M.; Nakamura, T.; Itoh, K. *Organometallics*, **1991**, *10*, 500
(3) Faller, J.W.; Ma, Y. *J. Am. Chem. Soc.* **1991**, *113*, 1579

36

STRUCTURE AND REARRANGEMENTS OF ORGANIC ION-MOLECULE COMPLEXES

T. Bally,[a] P. Čársky,[b] V. Hrouda,[a,b] P. Jungwirth,[a,b] M. Roeselova[a,b]

[a] *Institut de Chimie Physique, Université de Fribourg, Pérolles, CH-1700 Fribourg, Switzerland*
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Ion-molecule reactions are studied both in the gas phase and in condensed phase. These studies differ especially with regard to the dissipation of excess energy imparted onto the incipient ion-molecule complexes (which is rapid in condensed phase and slower or completely absent in gas-phase experiments).

We have attempted to provide a theoretical framework for understanding both types of experiments by carrying out state-of-the art *ab-intio* quantum chemical calculations on the potential energy surfaces for the formation, rearrangement and eventually the fragmentation of ion-molecule complexes formed from pairs of π-systems.

Such complex cations distinguish themselves from other ion-molecule complexes by the presence of substantial *covalent* interactions which can be thought to arise from the interaction between the HOMOs of the two species. We have examined the formation and the subsequent rearrangement of homo- and heterocomplexes formed from ethylene and acetylene and their radical cations, where much experimental information is available and is partially waiting to be fully understood.

Interestingly, the incipient ion-molecule complexes formed from ethylene and acetylene are different in nature: whereas the former is of the expected π-complex type, the latter is bound (albeit more weakly) by a H-bridge of the ionized moiety to the π-cloud of the neutral one, analogous to the neutral dimer. Both species rearrange over small activation barriers to tightly bound linear or cyclic stable products.

The continuation of the project is dedicated to the elucidation of the more complicated potential energy surface of the ethylene$^{\cdot+}$ + acetylene reaction and to the exploration of the dissociation channels to the fragments observed in various gas-phase studies.

37

WATER EXCHANGE FROM SECOND COORDINATION SHELL: EXPERIMENTS AND MD SIMULATION ON HEXAAQUACHROMIUM(III) SOLUTION.

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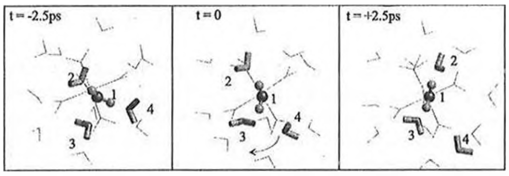
[a] Institut de Chimie Minérale et Analytique University of Lausanne, BCH, CH-1015 LAUSANNE
[b] Deparment of Physical Chemistry, University of Geneva, 30, quai Ernest-Ansermet, CH-1211 GENEVA

The $[Cr(H_2O)_6]^{3+}$ is the most inert paramagnetic cation towards its bound water exchange. Thus it represents the most favorable case for the study of a second coordination sphere water molecule exchange by ^{17}O NMR spectroscopy. Since Taube[1] has determined the exchange rate for the first coordination sphere water exchange ($k_{1st} \approx 10^{-6} s^{-1}$), X-ray diffraction[2] and neutron scattering[3] measurements have shown the existence of a well-defined second sphere.



The exchange of second sphere water molecules on $[Cr(H_2O)_6]^{3+}$ with bulk water has been studied both by ^{17}O NMR spectroscopy and by molecular dynamics simulations. The exchange rate determined experimentally ($k_{2nd} = 7.8 \times 10^9 s^{-1}$) is in good agreement with the simulated one. Furthermore, the simulations support a mechanism for the second sphere water exchange where the leaving and the incoming water molecules participate both in the transition state.

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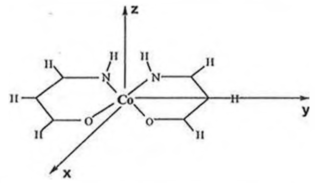
[1] J.P. Hunt; H. Taube *J. Chem. Phys.*, **1951**, *19*, 602.
[2] M.C. Read ; M. Sandström *Acta Chem. Scand.*, **1992**, *46*, 1177. R. Caminiti.; G. Licheri; G. Piccagula; G. Pinna *Chem. Phys.* **1977**, *19*, 371.
[3] R.D. Broadbent ; G.W. Neilson ; M. Sandström *J. Phys.:Condens. Matter*, **1992**, *4*, 639.

38

A DENSITY FUNCTIONAL STUDY OF MAGNETIC COUPLING PARAMETERS : NONEMPIRICAL CALCULATION OF ESR PARAMETERS OF LOW SPIN PLANAR COBALT(II) COMPLEXES

Raf Bruyndonckx[a)], Claude Daul[a)] and Evert Jan Baerends[b)]
[a)] Institut de Chimie Inorganique et Analytique, Université de Fribourg, Pérolles, CH-1700 Fribourg, Suisse.
[b)] Theoretical Chemistry Department, Vrije Universiteit, De Boelelaan 1083, NL-1081 HV Amsterdam, The Netherlands.

There is currently considerable interest in the calculation of magnetic coupling parameters and of ESR tensors in particular [1]. We present a first principle calculation of the Zeeman splitting (*g*-tensor) and of the hyperfine and superhyperfine (*A*)-tensors of the title compound (cf. Fig). The calculations will be performed using the Amsterdam Density Functional (ADF) package [2]. Various factors that affect the accuracy of the calculated ESR parameters are currently explored and will be discussed.



[1] V.G. Malkin, O.L Malkina, L.A. Eriksson and D.R. Salahub in Density Functional Calculations, Vol. 1 of Theoretical and Computational Chemistry; P. Politzer and J.M. Seminario, Eds., Elsevier, Amsterdam, The Netherlands, 1995
[2] E.J. Baerends, D.E. Ellis and P. Ros, Chem. Phys. 2:42, 1973
E.J. Baerends and P. Ros, Int. J. Quant. Chem. S12:169, 1978

39

Non-empirical, dynamical, DFTcalculation of the Berry Pseudo Rotation (BPR) of PF_5

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University of Fribourg (Switzerland)

A. Selloni
Department of Physical Chemistry
University of Geneva (Switzerland)

Abstract

The pseudorotation of PF_5 has been investigated using both static and dynamic Density Functional Theory (DFT) methods. The lowest energy path is the Berry pseudoratation, corresponding to the concerted exchange of two apical and two equatorial ligands. The potential energy surface has been derived and the transition state localized.

In the ab-initio molecular dynamics the BPR has been observed and occurs within 0.6 ps at 750K. Analysis of the trajectories and comparison of the spectral density with the vibrational frequencies is presented.

4

A DENSITY FUNCTIONAL (DF) STUDY ON THE MECHANISM OF EXCHANGE IN SOME COPPER (II) COMPLEXES

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University of Fribourg, Pérolles
CH-1700 Fribourg

The understanding of the mechanism of exchange coupling is ver important in the perspective of the design of molecular ferromagnets Therefore, we investigated on a non-empirical basis two compounds tha exhibit exchange interaction in a different way.

On the one hand, we can consider two paramagnetic metal ion which are bridged by formally diamagnetic atoms, or groups of atoms $[Cu_2Cl_6]^{2-}$ has been chosen as a relevant example of molecules which shov this so-called superexchange.

On the other hand, direct exchange interactions can be studied i systems in which a transition metal ion is directly bound to a stable organi radical. We investigated a simplified model of $Cu(tfac)_2 \cdot NITMe$ [1], whic shows a rather large ferromagnetic coupling of 65 cm^{-1}.

The relationship between the observed coupling and the electroni structure is discussed on the basis of DF calculations. The obtained resul give also an indication of the accuracy and the predictive character (modern calculation techniques.

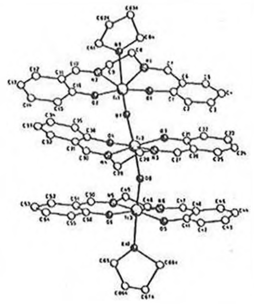
[1] A. Caneschi, D. Gatteschi, A. Grand, J. Laugier, L. Pardi, P. Rey, *Inor Chem.* **1988**, *27*, 1031

41

SYNTHETIC METHODOLOGY ALLOWING THE INTERCONVERSION OF TITANIUM–OXYGEN SINGLE INTO)OUBLE BOND: THE SELF-ASSEMBLING OF BRIDGING AND TERMINAL OXOTITANIUM(IV) INTO OLIGOMERIC AND POLYMERIC LINEAR TITANOXANES

Federico Franceschi, Emma Gallo, Euro Solari and Carlo Floriani
Université de Lausanne
Institut de Chimie Minérale et Analytique
Bâtiment de Chimie, 1015 Lausanne

e controlled ionization of the linear skeleton Cl-Ti-O-Ti-Cl allowed the
ıeration of the non-symmetrical dimer [Cl–Ti–O=Ti]$^+$, *via* a "push-pull
ıergy" determined by the extended Cl–Ti–O π-interactions. Such a
ıdamental step is responsible for the generation of the [Ti=O] unit which
made available as a building block for a variety of titanoxane structures.
e stepwise NaBPh$_4$-assisted ionization of [(Cl)(acacen)Ti]$_2$(μ_2-O) and
:l)(salen)Ti]$_2$(μ_2-O) in THF led to the non-symmetrical dimer [Cl–Ti–
Ti]$^+$ intermediate, which is the parent
npound of a variety of linear titanoxanes.
e monomer, trimer (see figure), tetramer
l polymeric species containing the Ti=O
t have been isolated. A scheme is proposed
the genesis of all those species from a
gle, simple ionization of starting meterials,
ere the origin and the binding properties of
[Ti=O] unit play a major role.

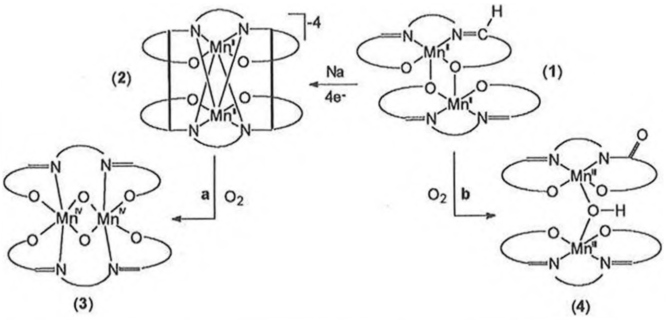


42

THE LIGAND-METAL SYNERGISM IN THE REDOX CHEMISTRY OF Mn-SCHIFF BASE COMPLEXES.

Gallo E.; Solari E.; Floriani C.*, Institut de Chimie Minérale et Analytique, Université de Lausanne, BCH, 1015 Lausanne (CH)

The present report deals with the reactivity of dioxygen with two Mn(II)-Schiff base complexes of different electron richness. In pathway **a** the electron rich complex **(2)** was acheived *via* the intramolecular reductive coupling of imino groups across two macrocyclic units of the complex **(1)**. Complexes **(1)** and **(2)** have very distinct behaviours in their reaction with dioxygen.



The oxidation of electron-rich Mn(II) Schiff base complex **(2)** gave rise to a novel topology of di-μ-oxo-Mn(IV) dinuclear complex **(3)** while in pathway **b** the reaction of **(1)** with dioxygen led to the selective oxidation of a C-H functionality, thus resulting in an imino → amido transformation and the concomitant formation of the OH-bridged Mn(III)-dimer **(4)**.

43

MECHANISMS OF WATER EXCHANGE BETWEEN NTHANIDE(III) AQUA IONS [Ln(H$_2$O)$_N$]$^{3+}$ AND BULK WATER: A ID-SIMULATION STUDY INCLUDING WATER POLARIZATION

Ielm, T. Kowall, F. Foglia, A. E. Merbach,
itut de Chimie Minérale et Analytique University of Lausanne, BCH,
-1015 LAUSANNE

ng molecular dynamics simulations we have investigated the
chanistic aspects of the water exchange reaction for aqueous solutions of
hanide(III) ions (Ln^{3+} = Nd^{3+}, Sm^{3+} and Yb^{3+}).

ing into account the mean polarization of water molecules in the first
ration shell using a new 3-body potential function we were able to
oduce the experimentally known change in the structural hydration
ıber from 9 (Nd^{3+}) to 8 (Yb^{3+}) along the lanthanide series as well as the
ilibrium between nine- and eightfold coordination in the middle of the
es (Sm^{3+}). [1]

lifetime of the coordination polyhedron between two internal
rangements comes out as 2 ps for Nd^{3+} (tricapped trigonal prism) and as
s for Yb^{3+} (square antiprism). [2]

water exchange for [Yb(H$_2$O)$_8$]$^{3+}$ exhibits the characteristics of an
ciative interchange I$_a$ mechanism. First a 9-coordinated transition state
icapped trigonal prismatic geometry is formed that then initiates the
ing of a water molecule from the first shell. For Sm^{3+} a ninth water
ecule is frequently exchanging between the first hydration shell and the
and maintains the coordination equilibrium between a [Sm(H$_2$O)$_8$]$^{3+}$
a [Sm(H$_2$O)$_9$]$^{3+}$ aqua ion. For [Nd(H$_2$O)$_9$]$^{3+}$ the exchange mechanism is
rly dissociative involving an eight-fold coordinated intermediate of
re antiprismatic geometry. [3]

h. Kowall, F. Foglia, L. Helm and A.E. Merbach *J. Am. Chem. Soc.* **1995**, *117*, 3790.
h. Kowall, F. Foglia, L. Helm and A.E. Merbach *J. Phys. Chem.* **1995**, *99*, 13078.
h. Kowall, F. Foglia, L. Helm and A.E. Merbach *Chem. Eur. J.* **1996**, *2*, 285.

44

METAL-METAL AND METAL-CARBON MULTIPLE BONDS PLAYING GAMES OVER A TUNGSTEN TETRAOXO-CALIX[4]ARENE SURFACE.

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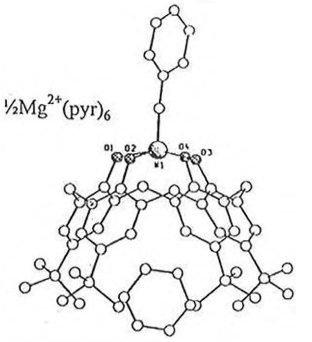
The chemistry of Tungsten in high oxidation states has been extensively studied in recent years (also for its industrial applications). Most often monodentate O-donor ancillary ligands have been used.
We decided to investigate the use of p-tert-Butylcalix[4]arene (Cal) as a polydentate oxo ligand; *cis*-Cl$_2$WCal (1) was used as the starting material.

Alkylation of 1 with 3 eqv of LiCH$_2$SiMe$_3$, Li^{n}Bu or MgBn$_2$ led to the isolation of the corresponding negatively charged **carbyne** species **CalW≡CR$^-$ M$^+$** (R, M = SiMe$_3$, Li; ^{n}Pr, Li; Φ, ½Mg, respectively) (2) by double α-elimination.

Reduction of 1 with 3 eqv of NaC$_{10}$H$_8$ led to a bis anionic dimer where Na$^+$ counterions bridge the two calixarene units **CalW≡WCal(μ-Na)$_2$** (3).
It was also possible to isolate mono- and bis-reduced species:
i) **KCalWCl$_2$** (4) where K$^+$ is hosted in the cavity;
ii) **NaCalW=(μ-Cl)$_2$WCalNa** (5) where Na$^+$ is hosted in the cavity and the two Cl$^-$ bridge the doubly bonded W atoms.



From these preliminary results it might be concluded that the calixarene ligand enhances the tendency of W to form "ate" complexes. In fact, complexes 1 - 5 can be rationalized in terms of the fragments represented by the general formula **(CalWCl$_n$)$^-$**, n = 0,1,2.

45

BIFUNCTIONAL CARRIER OF ALKALI ENOLATES: A NOVEL APPROACH TO CATALYZED ALDOL CONDENSATION

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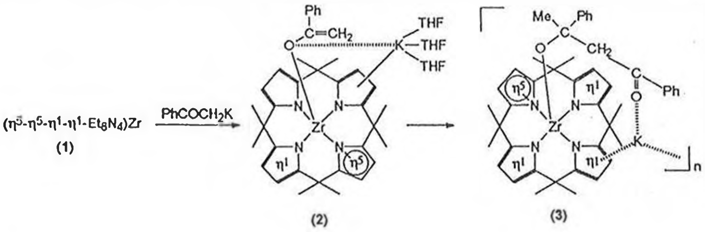
The meso-octaalkylporphyrinogen-Zirconium (**1**), exemplifies the structural features of a bifunctional compound having in its structure two complementary reactive sites, which can assist the transformation of an organic substrate.

The ability of (**1**) to carry polar organometallics has been applied to the Zirconium-assisted enolate chemistry, with the added advantage that the porphyrinogen skeleton adapts its bonding mode depending on the electron request of the metal.

The following scheme summarizes the assistance of (**1**) in the aldol condensation reaction:



The displacement of the aldol adduct in (**3**) by the starting K-enolate is the key step towards the use of (**1**) as bifunctional catalyst.

46

DENSITY FUNCTIONAL CALCULATIONS ON ORGANOMETALLIC PT(II) COMPOUNDS: MOLECULAR STRUCTURE AND SOME EXCITED STATES

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Coordination compounds of Pt(II) are the subject of extended experimental investigations. The photochemical properties of cyclometallated Pt(II) complexes are thereby of special interest because of their possible use as photosensitizers. Chemical modifications such as variations of the ligand or the substituents play an important role in this context.

In order to describe ground and excited state properties of some Pt(II) compounds [1,2] quantitatively, we performed first principle calculations, based on Density Functional Theory (ADF 1.1.4).

As results, we will show the modellized molecular structure of the ground state and the transition energies for some low lying excited states of substituted $Pt(thpy)_2$ compounds (thpy=2-thienylpyridine) and related complexes. The calculation models are compared to results from X-Ray structure analysis and optical spectroscopy.

[1] M. Gianini, A. Forster, P. Haag, A. v. Zelewsky, H. Stoeckli-Evans, *Inorg. Chem.*, submitted
[2] A. C. Stückl, *Thesis*, Regensburg 1993

47

Accuracy of Approximate Kinetic Energy Functionals in the Model of Kohn-Sham Equations with Constrained Electron Density: the FH...NCH Complex as a Test Case.

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Ground-state properties of a linear hydrogen-bonded FH...NCH complex are studied by means of the "freeze-and-thaw" cycle of Kohn-Sham Equations with Constrained Electron Density (KSCED) [1]. For several geometries of the complex, the electron density and the total energy are compared to the ones obtained by means of the standard Kohn-Sham calculations. The comparisons are made to assess the accuracy of several gradient dependent approximate kinetic energy functionals applied in the KSCED equations. It is found that the closest results to the Kohn-Sham ones are obtained using the functional whose analytical form was proposed by Perdew and Wang for exchange energy [2] and parametrized by Lembarki and Chermette for kinetic energy [3]. In the region of the minimum of the interaction energy as well as for larger intermolecular distances, the "freeze-and-thaw" cycle of KSCED leads to a potential energy surface very similar to that of standard supermolecule Kohn-Sham calculations.

[1] T.A.Wesolowski and J.Weber (1996) Chem.Phys.Lett, **248**, 71
[2] J.P. Perdew and Y. Wang in *Electronic Structure of Solids*'91, ed. P.Ziesche and H.Eschrig (Academie Verlag, Berlin, 1991), p. 11
[3] A. Lembarki and H. Chermette (1994) Phys.Rev. A,50, 5328

48

Intermolecular interactions studied by Kohn-Sham equations with constrained electron density.

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The recent developments of the formalism of Kohn-Sham Equations with Constrained Electron Density (KSCED) [1,2] are reported together with their applications to studies of potential energy surfaces in several molecular complexes.

In the KSCED approach, the ground-state electron density of a molecular complex is represented as a sum of densities of fragments. The electron density of each fragment (ρ_1) is obtained by solving Kohn-Sham-like equations where the effective potential contains terms present in standard Kohn-Sham equations and an additional term ($\delta T^{nadd}(\rho_1,\rho_2)/\delta\rho_1$; where $\rho_2 = \rho - \rho_1$) which is expressed using the approximate kinetic energy functional ($T^{app}[\rho]$). It was found [3,4] that the most accurate KSCED results are obtained with the functional whose analytical form was proposed by Perdew and Wang [5]. Provided the T^{app} is sufficiently accurate, the KSCED formalism forms a computationally robust framework for modeling large molecular systems, esp. solvent effects and surface phenomena. Studies of several relevant molecular complexes are reported here. They include:

- hydrated ions $Me(H_2O)_8$ ($Me=Cd^{2+},Ca^{2+}$)
- complexes of small diatomic molecules and benzene
  ($X...C_6H_6$, where $X=H_2$, O_2, CO, N_2, CO, NO), (the first step towards modeling the adsorption phenomena at the graphite surface)
  $Cr(CO)_6$ and its interactions with fragments of the MgO surface.

[1] T.A.Wesolowski and A.Warshel (1993) J.Phys.Chem., 97, 8050
[2] T.A.Wesolowski and J.Weber (1996) Chem.Phys.Lett, **248**, 71
[3] T.A.Wesolowski and J.Weber (1996) Int.J.Quant.Chem. *in press*
[4] T.A.Wesolowski, H. Chermette, and J.Weber (1996) J.Chem. Phys. *submitted*
[5] J.P. Perdew and Y. Wang in *Electronic Structure of Solids*'91, ed. P.Ziesche and H.Eschrig (Academie Verlag, Berlin, 1991), p. 11

49

SELF ASSEMBLING OF CALIX[4]ARENE IN JPRAMOLECULAR STRUCTURES USING ORGANOMETALLIC HEMISTRY OF TITANIUM OVER AN OXO SURFACE DEFINED BY A CALIX[4]ARENE MOIETY

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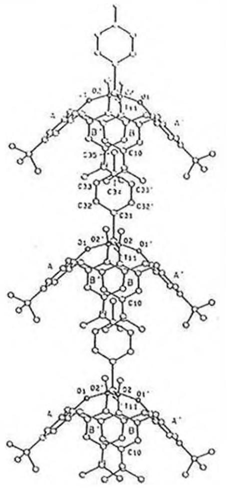
e dimethoxy-*p-tert*-butylcalix[4]arene ($CalMe_2H_2$) dianion has been used a tetra oxo matrix for binding the [$Ti^{(III)}Cl$] and the [$Ti^{(IV)}Cl_2$] fragments. e Lewis acid assisted demethylation of the ligand makes also available [$Ti^{(IV)}Cl$] fragment. The complexes of $Ti^{(III)}$ and $Ti^{(IV)}$ are the starting terials for the investigation of two major aspects of the transition metal-ix[4]arene chemistry.

Reactivity of the organometallic fragments. e organometallic complexes $CalMe_2Ti^{(III)}R$ l $CalMeTi^{(IV)}R$ (R=methyl, *p*-tolyl, benzyl) ve been synthetized via alkylation of the responding chloro derivatives $lMe_2Ti^{(III)}Cl$ and $CalMeTi^{(IV)}Cl$. sproportionation reactions have been served in the reactions of $CalMe_2Ti^{(III)}R$ h O_2 and CO.

Self assembling into supramolecular uctures. The presence of an appropriate stituent in the complexes $CalMe_2Ti^{(III)}R$ l $CalMeTi^{(IV)}R$ (R= *p*-tolyl) produces, in the id state, a self organisation of the nomeric units into a columnar structure. is host-guest interaction can be interpreted terms of alkyl/π interaction between the *p*-yl group and the calix[4]arene cavity.



$CalMe_2Ti^{(III)}$(*p*-tolyl)

50

Calculation of Chiroptical Properties of Coordination Compounds

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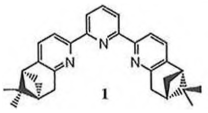
CD-spectra can be used for the determination of the absolute configuration of chiral coordination compounds. Simple models such as the *exciton theory* where the absolute configuration can be determined by treating the non-interacting chromophores as charge dipoles can be successfully applied even to extended polynuclear metal complexes. For CD-spectra calculation of complexes with chiral ligands, we have developed a computer program (Fortran) that allows us to determine R-values taking result files from ZINDO[1] (INDO/1 hamiltonian) or ADF [2] (Amsterdam Density Functional package) as the only input.
Reasonable agreement between calculated and experimental spectra has been obtained for a number of metal complexes, such as Λ-/Δ-$Ru(bpy)_2(py)_2$, for metal complexes with the chiral terpyridine ligand **1**,[3] and also for organic molecules such as *M*-helicene[6].



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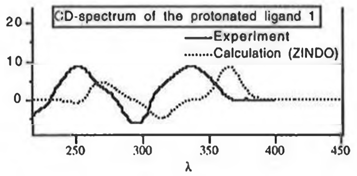

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[1] Anderson, W.P., Cundarai, T.R., Drago, R.S., Zerner, M.C., *Inorg. Chem.* **1990**, *29*, 1.

[2] te Velde, G., Baerends, E.J., *J. Comp. Phys.* **1992**, 99, 84.

[3] M. Ziegler, P. Belser, V. Monney and A. von Zelewsky, submitted to *Inorg.Chem.*

51

STUDY OF AN ANOMALOUS FERROELECTRIC PHASE RANSITION IN POLY(VINYLIDENE-*CO*-TRIFLUOROETHYLENE)

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in.

The ferroelectric phase transition in random copolymers of vinylidene oride (VDF) and trifluoroethylene (TrFE), with a molar ratio of 60:40, has n studied to clarify the thermodynamic nature of this transition.

Although the crystalline structure and properties of both, ferroelectric and aelectric phases in melt-quenched samples of these copolymers, have been ll characterized,[1] not much information is available about the properties of ns prepared from diluted solutions.

The virgin material of solution cast films behaves differently from already ted materials. First heating scans in calorimetric experiments performed in e films of VDF-TrFE copolymers show step-like increases in Cp that point ne existence of a phase transition. Subsequent scans, after melting the crys-exhibit the characteristic endothermic peak of the ferroelectric to paraelec-transition as previously reported.[1] Simultaneous measurements of WAXS SAXS using synchrotron radiation and dielectric spectroscopy confirm the urrence, in the first heating scan of a continuous phase transition from a fer-ectric to a paraelectric state.

The transition was also optically monitored by measuring UV spectra of a t-host systems. The copolymers was used as a matrix wherein 4-tricyano-l-4'-[N,N-di(2-ethylbenzoate)]azobenzene, a compound with high dipole nent, was dispersed. Again, all indications pointed to a ferroelectric-parac-ic transition that exhibits a continuous rather than first-order character.

F.J. Baltá-Calleja, A. Gonzalez Arche, T.A. Ezquerra, C. Santa Cruz, F. llan. B. Frick and E. López Cabarcos, Adv. Polym. Sci. 1, (1993).

52

PHOTOCONDUCTIVITY IN POLED POLYMERS FOR PHOTOREFRACTIVE APPLICATIONS

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Photorefractive polymers are multifunctional materials exhibiting an electro-optic effect and photoconductivity. There has been considerable interest in such materials because of their potential application in electro-optic devices such as optical storage materials and optical amplifiers.

Based on the well-known nonlinear optical chromophore DDANS [2',5'-di-amino-4-(dimethylamino)-4'-nitrostilbene], the hole transport agent DDEH (the 1,1-diphenylhydrazone of 4-[N,N-bis-(2-hydroxyethyl)]-aminobenzal-dehyde) and aliphatic acid dichlorides we have prepared different types of polymer systems, including doped polyamides, polymer blends, random copolymers and block-copolymers. Photoconductivity was achieved by doping these polymers with the sensitizer TNF (2,4,7-trinitro-9-fluorenone).

We have investigated some photophysical properties of these materials and relate them to their composition and morphology. Photoconductivity was determined in the range of 700 nm to 900 nm. Depending on the composition, some polymers show extraordinarily high ratios of photocurrent to dark current. Additionally, the mobility of charges was measured, using the time-of-flight method.

Because of the high ratios of photocurrent to dark current at 800 nm, the high mobility of charges and the easy processability these polymers might also be suitable for laser printers and other xerographic applications.

53

NONLINEAR OPTICAL PROPERTIES FOR METHACRYLAMIDIC GUEST-HOST SYSTEMS AND POLYMERS

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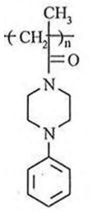
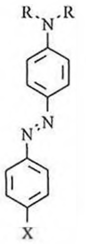
In recent years great interest has been focused on the study of second-order nonlinear optical properties of compounds with extended conjugation and high dipole moment; these structures might be used in devices based on phenomena such as second harmonic generation (SHG) and electrooptical effect. In this work guest-host systems have been investigated as useful models for studying the relaxation behaviour of polymeric materials.

Several azobenzene dyes were synthesized with different structure of the electron-acceptor group, steric hindrance and hydrogen bonding capability. Second-order hyperpolarizabilities and dipole moments showed that the presence of a second electron acceptor substituent enhances very much the SHG response, while decreasing the dipole moment. Substitution of an acyclic structure with a cyclic one, or of an ester group with a nitrile moiety did not cause large changes in the second order hyperpolarizabilities.

All investigated dyes were dispersed poly(1-methacryloyl-4-phenylpiperazine) as a host, at a fixed molar ratio with the monomeric units, and oriented by electric poling. The dependence of orientability and polar-order stability on the chemical structure was studied monitoring the SHG response of these systems; the results were compared with those obtained from similar polymers bearing the same chromophoric structures in the side chains.





54

THREE-DIMENSIONAL ORDERING OF MOLECULES IN ALIGNED SINGLE CRYSTAL ZEOLITES

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Large efforts have been undertaken to use zeolites as guest hosts in the development of new optical, electronic and magnetic material. For nanoscale devices based on zeolites an ordered arrangement of crystals is required.

We have realised a technique to align synthetic single crystal zeolites on an area of several millimeters by means of surface structures which are artificially produced. Two different types of ZSM-5 crystals were fixed to the substrate with tetramethoxysilane. Accessibility of the microporous system is checked with N_2 adsorption measurements and controlled by Scanning Probe Microscopy. This system allows a quasi three dimensional orientation of suitable molecules. Naphthalene and p-nitroaniline have been chosen as guests.

X-ray diffraction and UV/vis spectroscopy indicate clearly, that naphthalene molecules have entered into the channels. Coupled Thermo-Gravimetry/FTIR reveals a loading of p-nitroaniline in ZSM-5 with 8 weight-%. FTIR spectra of PNA adsorbed into ZSM-5 ressemble best to single crystal PNA.

Polarisation dependent photoluminescence experiments from 4.5 K up to roomtemperature reveal the high degree of orientation of the molecules within the channels. Different places of PNA in the twodimensional channelstructure could be identified. Slight difference in synthesis conditions of the two types are responsible for different peak positions in the emission spectra.

55

LOCAL DYNAMIC PROPERTIES OF SYNTHETIC OXIDE FILM/LIQUID INTERFACES

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The initiation of local breakdown of passive films on metals is in many cases caused by heterogeneity's such as MnS inclusions. It was found that most initiation processes are not fatal when - after a breakdown event- a fast reformation kinetics of the passive film is provided. This repassivation process is essential for the high corrosion resistance of many technical alloys. However often a main difficulty in direct passive film investigations is the separation of film properties from influences from the underlying metal. Therefore parameters involved in the local activation/repassivation process were modelled for the passive film on iron using sputter deposited iron oxide layers.

The oxide layers and the passive film on iron were investigated with impedance spectroscopy and photoelectrochemistry in order to determine the semiconductive properties. The dissolution kinetics and mechanism were studied with in-situ X-ray near edge absorption (XANES) measurements. Experiments were performed in borate buffer (pH 8.4) using a standard three electrode configuration.

The comparison of data determined from the model systems and from the passive film on iron resulted in a clear evidence for the applicability of bulk semiconductor models for thin polycrystalline highly doped systems. The doping concentration of the passive film on iron could be reliably determined in the range of 10^{27} m^{-3}. The doping species was identified as Fe(II). Variation of doping concentration by thermal treatment of oxide layers and by anodic polarisation of passive films allowed the investigation of the influence of doping concentration on the photocurrent efficiency. It was found that an increasing doping concentration results in a decrease in photocurrent efficiency. XANES experiments with Fe-oxides with a different Fe(II) content showed that the higher the Fe(II) content the lower the stability of the oxide against dissolution. The comparison of the sputtered films with the native passive film allowed the identification of parameters and mechanisms responsible for local breakdown of passive materials.

5

PLANAR BILAYER AND VESICLE LAYER FORMATION FROM PHOSPHOLIPID VESICLES

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Supported planar phospholipid bilayers are used in many areas. Th most widely used method to produce them is the Langmuir-Blodge technique, which involves an intermediate monolayer at the air/wate interface. When the technique is used to incorporate large transmembran proteins into bilayers by mixing them with the intermediate monolayer denaturation may ensue due to exposure of part of the protein to the air. T evade this problem, the proteins may be pre-incorporated into unilamell vesicles, and the formation of the bilayer from the vesicles may be attempte

Previously this formation has been looked at using total intern reflexion fluorescence microscopy, but this method has the disadvantages requiring fluorescently labelled lipids and yields no structural informatio about the lipid layers.

Here we report experiments made with a rather new techniq (optical waveguide mode spectroscopy) to investigate how vesicles different sizes, made from different phospholipids and by different metho differ from each other in their ability for producing a bilayer. This techniq has the advantages of good time resolution and yielding thickness a refractive index data on the layers formed.

We were able to show that under many conditions, a layer of inta adsorbed vesicles is formed, rather than a bilayer membrane.

57

MPROVED DETECTION EFFICIENCY FOR HIGH MASS IONS IN MASS SPECTROMETRY

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many mass spectrometric methods, the signal is detected via an ion-to- ctron conversion, using secondary electron multiplier or micro-channel tes (MCP). These are fast and low-noise but their detection efficiency is ongly dependent on the incident ion velocity (and therefore on mass), due a smaller ion-to-electron conversion probability at lower velocity (higher ss). In modern MS methods, such as MALDI-TOF-MS, where the ected mass range is up to 1 MDa, this is particularly problematic.

e performed a study to characterise the response of an MCP with the aim increase its high mass performance. We found an exponentially decreasing ss dependence. To improve this response, grids can be placed in front of MCP to promote secondary ion formation by impact of the primary ion m on the mesh. Those small secondary ions were found to have low rgy but can be post-accelerated easily and used to increase the primary signal. Their formation yield was determined for different grid materials, tings, and sizes.

addition, two new home-built detectors were tested, based on different nciples. The first one is a non-destructive direct current measurement of secondary ions created on such a grid. The second is an ion-to-photon version detector. Both detectors, even if they are not presently ready for tine use, have detection efficiencies with much lower mass dependence n MCPs and therefore could be used for very high mass detection.

58

Real-time imaging of a surface reaction with nano-scale spatial resolution

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Field ion microscopy can provide structural information on the atomic scale of solid surfaces either clean or adsorbate-covered. We have applied the same method in order to trace the course of a catalytic surface reaction under reaction conditions of gas pressures and temperatures. Samples used in field ion microscopy resemble a small hemispherical particle (field emitter tip) which exposes a number of crystallographically well-defined surface planes with different catalytic activity. Our studies of the catalytic reduction of nitric oxide (NO) with hydrogen on platinum to yield nitrogen and water have revealed an explosive concerted ignition in regions which are of {210} plane symmetry before reaction. Using NO ions as imaging species we have observed that reaction-diffusion fronts can propagate along the ⟨100⟩ zone lines towards the central (001) plane. The catalytic cycle stops after about 0.2-0.3 seconds but returns periodically in times of some ten seconds and with the appearance of identical reaction patterns. The oscillatory behaviour is driven by an autocatalytic step which consists in the liberation of a number of empty sites after occasional water formation. A similar reaction behaviour was observed in the catalytic reduction of NO_2. In that case the imaging conditions (field strength) could be varied over a large range without provoking changes in the reaction patterns. Low-temperature noble gas imaging have shown considerable reaction-induced structural changes of the platinum sample after both NO and NO_2 reduction. The oscillatory reaction behaviour and the different patterns associated with reaction-diffusion fronts will be demonstrated in a video.

59

ater exchange on Mn^{2+} adsorbed on SiO_2 (Aerosil 300)

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bourg, Switzerland

e water exchange on Mn^{2+} adsorbed on SiO_2 (Aerosil 300) was idied in situ by the temperature dependence of the ^{17}O relaxation the solvent H_2O. The relaxation rate of ^{17}O in H_2O is strongly uenced by the exchange of H_2O in the coordination sphere of $^{2+}$ in solution. This relaxation and its temperature dependence anges strongly, if Mn^{2+} is adsorbed on SiO_2. The number of changing H_2O decreases from 6 to 4 per Mn^{2+} and exchange rate accelerated by a factor of 2 to 3. No trans effect of the surface gen is observed. The four H_2O in the coordination sphere change with the same rate. Interpretation of the results by the thod of Swift and Connick (1) yields the following activation ameters (values for Mn^{2+} in solution (2) in brackets) k_{298} 7.3(2.1) s^{-1}, ΔH^* 22(35.9) $kJmol^{-1}$, ΔS^* -20(5.7) $Jmol^{-1}$, T_{1e}^{-1} 5(80) 10^6 s^- The effect increases with increasing surface coverage however proportional to the Mn^{2+} adsorbed. The analyses of the deviation n linearity shows, that the latter is caused by a change in the ctronic relaxation time of Mn^{2+}, which is due to a fast movement the Mn^{2+} at the surface or a heterogeneous distribution of the sorbed Mn^{2+}. The measurements indicate in addition, that the axation behaviour of the ^{17}O is a very sensitive probe for any nges of the surface structure of SiO_2.

T. J. Swift and R.E. Connick, J. Chem Phys., (1962) **37**, 397
A.E. Merbach, Y. Ducommun and K.E. Newman,
Inorg. Chem., (1980) **19**, 3696

60

INFLUENCE OF PARTICLE MORPHOLOGY ON SURFACE CHARGE AND COAGULATION BEHAVIOR OF HEMATITE COLLOIDS

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Synthetic hematite particles (α-Fe_2O_3) are often used as model colloids for adsorption and stability studies in colloid, material and environmental sciences. But only few studies have been conducted combining proton adsorption, electrophoretic mobility and colloidal stability of hematites. Although hematites vary widely in particle morphology, similar adsorption, mobility, and aggregation behavior is commonly assumed.

In this study, synthetic hematites differing in particle morphology were compared in terms of their charging behavior and colloidal stability. The hematites had similar narrow size distributions (d ≈100 nm, TEM), but one sample had a larger surface roughness, microporosity and specific surface area (N_2-BET) compared to the other samples. The charging behavior was obtained by measuring the proton adsorption at different ionic strengths using potentiometric titrations. The electrophoretic mobility of the particles was measured as a function of pH and ionic strength using electrophoretic light scattering. The kinetics of coagulation was followed by measuring the mean particle radius as a function of time using photon correlation spectroscopy (PCS) where the rate of coagulation was determined from the slope of the initial increase in particle radius over time.

61

SURFACTANT GELS AS TRANSPARENT MATRICES FOR THE ENTRAPMENT OF BIOMATERIALS

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A few years back in our group in Zürich it was found that the solubilization of gelatin in AOT reverse micelles lead to the formation of highly transparent microemulsion gels which possess a continuous gelatine network in a mobile oil phase. These so-called organogels or microemulsion based gels (MBG) were the starting point for the preparation of novel composite materials via an *in-situ* polymerization of alkoxides, which provided a polymeric network probably interpenetrating with the gelatine macromolecules. These materials are very hard and, depending upon conditions, transparent. The temperature and time stability of these materials have been studied as a function of various parameters, like the initial concentration conditions of water, alkoxide, pH, AOT usw. The time progress of the reaction was followed by proton- NMR, as the resonances of the hydroxyl groups bound to the alkoxide ($Si(OR)_3OH$ or $Si(OR)_2(OH)_2$ are clearly different from each other. Biomolecules can be incorporated into the nanocomposites, and we have studied in details the enzymatic activity of lipases towards the synthesis of water insoluble esters. Since the enzyme-containing nanocomposites are stable in organic solvents, the enzymatic reaction could be carried out in non-aqueous solvents, and gave very high yields. Bacteriorhodopsin and cytochrome-C were also incorporated and their spectroscopic properties studied directly on the transparent material.

63

FAST WATER EXCHANGE ON $[Pt\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}(OH_2)]^+$: VARIABLE TEMPERATURE AND PRESSURE ^{17}O NMR STUDY AT 14.1 TESLA

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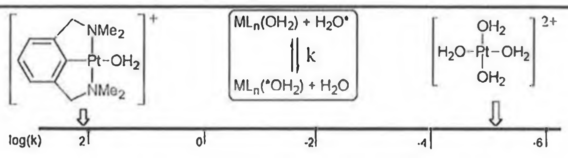
The water-soluble ionic aryl platinum species $[Pt\{C_6H_3(CH_2NMe_2)\text{-}2,6\}(OH_2)]^+$ undergoes water exchange at a rate 10^7 times faster than the coordination complex $[Pt(OH_2)^4]^{2+}$; a clear-cut example of the trans effect of the C-bonded organic group. Lineshape analysis of high pressure ^{17}O NMR data acquired in a 14.1 Tesla magnet are indicative for an associative mode of activation for this water exchange.



Frey, U.; Grove, D.M.; van Koten, G., submitted for publication.

62

HIGH PRESSURE NMR MICRO-REACTOR: KINETICS OF COMPLEX FORMATION REACTION OF $[Ru(H_2O)_6]^{2+}$ WITH C_2H_4 IN WATER

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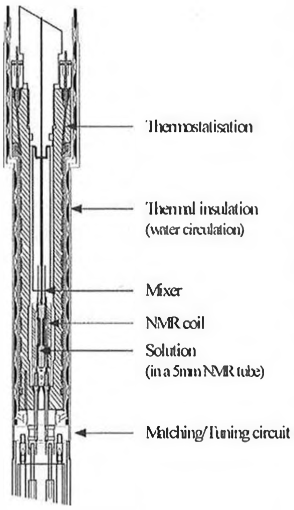
Institut de Chimie Minérale et Analytique, Université de Lausanne, BCH, 1015 Lausanne, Switzerland.



NMR at elevated pressure has been used for studying various physical and chemical phenomena. Several research groups have demonstrated the possibility of performing NMR measurements at relatively high resolution and pressures in wide-bore or superwide-bore cryomagnet. We now present a high pressure micro-reactor (see Figure) constructed to fit in to a standard bore, 9.4 Tesla cryomagnet, which can be used for either ^1H and/or multinuclear NMR. This probe can be used at pressures up to 200 MPa and temperatures up to 180°C.

As example is presented the study of complex formation reactions of $[Ru(H_2O)_6]^{2+}$ with C_2H_4 at variable temperature and pressure followed by ^1H(400 MHz) NMR spectroscopy.

64

Electronic Structure Determination at High Temperatures and Vapour Pressures by Photoelectron Spectroscopy

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Institute of Physics, University of Basel, Klingelbergstrasse 82, CH-4056 Basel, Switzerland

An experimental method has been developed in order t determine the electronic structure (valence band and core electro states) of condensed matter at high temperatures. The method i based on pulsed laser excitation of the sample surface followed b time resolved photoelectron spectroscopy measurements. Th vapour pressure limitations of standard steady state experiment are no longer relevant in the new dynamic measuring techniqu and as a consequence fundamentally new studies became possible

In order to illustrate the new method experimental result obtained from liquid silicon at temperatures close to 2000 K, liqui nickel and liquid gold-tin alloys investigated as a function of tem perature will be presented. In addition, a study performed on al kali metal-group IVB alloys (alloys of type Li-Sn) will be discusse These alloys are of particular interest because of the metal-insu lator transition in the liquid state.

65

PYRIDOXAL - 5' - PHOSPHATE - DEPENDENT CATALYTIC ANTIBODY

amatikova, S. I. [1], *Mahon, M. M.* [2], *Fitzpatrick, T. B.* [2], *Malthouse, J. G.* [2], *Christen, P.* [1], [1] *Biochemisches Institut der Universität Zürich, interthurerstrasse 190, CH-8057, Switzerland,,* [2] *Department of ochemistry, University College Dublin, Belfield, Ireland*

factors might efficiently extend the catalytic potential of tibodies. Monoclonal antibodies against Nα-phosphopyridoxyl-L-ine were screened for (1) binding of 5'-phosphopyridoxyl amino ids, (2) binding of Schiff base of pyridoxal-5'-phosphate (PLP) d amino acids, the first intermediate of all PLP-dependent actions, and (3) catalysis of PLP-dependent α,β-elimination with β-loro-D/L-alanine. Antibody 15A9 was selected and found to talyze cofactor-dependent stereospecific exchange of the pro-2S oton of glycine, α,β-elimination with β-chloro-D-alanine, and nsamination of hydrophobic D-amino acids and oxo acids (k'_{cat} = 2 min^{-1} with D-alanine). No other reactions with either D- or L-ino acids were taking place. PLP markedly contributes to talytic efficacy, being a 10^4 times more efficient acceptor of the ino group than pyruvate. The antibody ensures reaction, stereo-, well as substrate specificity and further accelerates the reaction $_{cat (ab)}$ /$k'_{cat (PLP)}$ = 5 x 10^3).

66

SELF-REPRODUCTION OF CHIRAL FATTY ACID VESICLES

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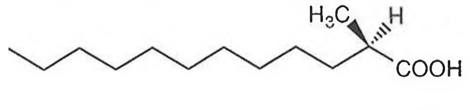
In the context of the origin of life and prebiotic cells, we have been conducting studies on the autopoietic self-reproduction of fatty acid vesicles. The vesicles are able to reproduce themselves due to a reaction that takes place within their boundary (hydrolysis reaction of fatty acid anhydride). We have now extended the autopoietic self-reproduction to chiral fatty acids with the aim to combine autocatalytic self-reproduction and stereoselectivity. Various chiral fatty acids which bear an asymmetric carbon atom in alpha-position to the carboxylic group were synthesized and their vesicle forming properties were examined. 2-Methyldodecanoic acid (2ML) was found to form stable vesicles at room temperature within the pH range 7.3 and 8.5. We have conducted the hydrolysis reaction of 2ML anhydride in the presence of 2ML vesicles. The influence of slightly different physico-chemical properties of the enantiomeric vesicles and the racemic vesicles (for example, phase transition temperatures) on the self-reproduction kinetics will be discussed.



(R)-2ML

67

POSOMES FROM PHOSPHATIDYL-NUCLEOSIDES

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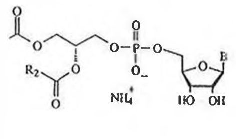
Ten different phosphatidyl-nucleosides have been prepared from three ferent 1,2-diacyl-*sn*-glycerol-3-phosphoryl-cholines and four different ribo-cleosides. The aggregation properties in aqueous solution of all these npounds have been investigated by electron microscopy and dynamic light ttering. Using the pure lipids, it was found that liposomes with a high bility can only be formed from **1**. In the case of **2** liposomes tend to gregate with time, **3** spontaneously assembles into superhelical fibres or sed superhelical rings. Liposomes prepared from **1** have been characterized circular dichroism and ^{1}H-NMR spectroscopy, which allowed to get insight the molecular orientation of the cytidine head group on the surface of the somes. Stable liposomes could also be prepared from equimolar mixtures **1** and **2** or **4** and **5**. In this case, head group interactions most likely tribute to the liposome stability.



	Base (B)	R_1COOH	R_2COOH
1	cytosine	C 16:0	C 18:1
2	hypoxanthine	C 16:0	C 18:1
3	cytosine	C 16:0	C 16:0
4	uracil	C 16:0	C 18:1
5	adenine	C 16:0	C 18:1

68

CHEMICAL PROPERTIES AND APPLICATIONS OF NATURAL AND SYNTHETIC POLYPEPTIDES

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Protein-protein recognition and protein oligomerization functions are among the important roles played by the x-helical coiled coil motif. As part of a study into the equilibrium and kinetic aspects of the folding of model coiled coils, an investigation into the stoichiometry and magnitude of the associative constants by sedimentation equilibrium in the ultracentrifuge has been initiated. A series of interrelated model peptides, with sequence lengths of about 30 residues, has been designed, synthesized and characterized. Each of the peptides has been subjected to conventional sedimentation equilibrium analysis under a variety of conditions. The stoichiometry of self-association has been established and it has been shown that, contrary to the expected result, most of the peptides formed trimeric systems of varying stability. The effect of substituting large hydrophobic constituents of the interacting interfaces of the systems with other similar residues has been shown to have minimal effect on trimer formation. However, substitution of such residues in the central sequence positions with either alanine or asparagine leads to a marked decrease in the stability of the trimeric state.

†FZ	Ac-K	FEALEGK FEALEGK FEALEGK FEALEGK-FEALEG-$CONH_2$
LZ	Ac-E	YEALEKK LAALEAK LQALEKK LEALEHG-$CONH_2$
LZ12A	Ac-E	YEALEKK LAAAEAK LQALEKK LEALEHG-$CONH_2$
LZ16A	Ac-E	YEALEKK LAALEAK AQALEKK LEALEHG-$CONH_2$
LZ16N	Ac-E	YEALEKK LAALEAK NQALEKK LEALEHG-$CONH_2$
LZVNV	Ac-E	YEALEKK VAALEAK NQALEKK VEALEHG-$CONH_2$
LZVVV	Ac-E	YEALEKK VAALEAK VQALEKK VEALEHG-$CONH_2$
Acid-LZ	Ac-E	YQALEKE VAQLEAE NQALEKE VAQLEHE-$CONH_2$
Basc-LZ	Ac-E	YQALKKK VAQLKAK NQALKKK VAQLKHK G-$CONH_2$
GCN4-pl	Ac-R	MKQLEDK VEELLSK NYHLENE VARLKKL VGER-$CONH_2$

Authors, Index

Name Abstract No.

Leitartikel zum CHIMIA-Jubiläum 1996

Leading Articles on the Occasion of the CHIMIA Anniversary 1996

Aus Anlass des 50. Jahrgangs der CHIMIA werden zusätz- ch zu den üblichen Aktivitäten über das ganze Jubiläumsjahr ɔ96 Leitartikel von ausgewählten Persönlichkeiten zu wissen- ;haftlichen, industriellen, technologischen, ökologischen, so- alen, politischen und wirtschaftlichen Aspekten erscheinen, e im Zusammenhang mit Chemie stehen.

Das Editorial Board der CHIMIA dankt allen Autorinnen ıd Autoren, die hierzu spontan ihre Bereitschaft bekundet ıben. Mögen die verschiedenen Beiträge auch zu Diskussionen ıregen, unser 'Leserforum' steht zur Verfügung.

During 1996, on the occasion of the 50th volume, in addition to the usual activities, CHIMIA will publish leading articles by selected personalities on scientific, industrial, technological, ecological, social, political, and economical aspects connected with chemistry.

The Editorial Board of CHIMIA is grateful to all authors for their spontaneous readiness to write a contribution. Active participation of our readers is welcomed and the discussion forum is open for 'letters to the editor'.

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·rüherkennung, Technikfolgen- ıbschätzung und die Fullerene

of. Dr. **Verena Meyer***
äsidentin des Schweizerischen Wissenschaftsrats

Der Schweizerische Wissenschaftsrat t, gestützt auf das Bundesgesetz über ː Forschung, die Aufgabe, den Bundes- in Fragen der Wissenschaftspolitik zu raten. In diesem Rahmen ist er zurzeit eder daran, neben den 'Zielvorstellun- n über die künftige Entwicklung der ɔchschulen' Vorschläge für die 'Ziele r Wissenschaftspolitik' für die Periode 00–2003 vorzubereiten. Die Ideen dazu ıgt sich der Rat nicht aus den Fingern, d sie entspringen auch nicht allein den hirnen der Ratsmitglieder, wiewohl die- in der Mehrzahl selber Wissenschaftler d Forscherinnen und über ihre Diszipli- ı bestens auf dem Laufenden sind. Zur üllung seiner Aufgaben arbeitet der t vor allem in sogenannten Leitungs- ;schüssen, die sich mit verschiedenen pekten seines breiten Tätigkeitsgebie- befassen. Von diesen sollen hier die üherkennung' und die 'Technikfolgenabschätzung' (engl: Technology Assessment oder kurz TA) zur Sprache kommen.

Wissenschaftspolitik hat die Aufgabe, die Wissenschaft des Landes zu fördern mit dem Ziel, dem Staat bei der Erfüllung seiner Aufgaben nach innen und nach aussen beizustehen und ihn in seiner Rolle in der Staatengemeinschaft sowohl als Partner wie als Konkurrent zu stärken.

Heute, wo die Wissenschaften sich bekanntlich besonders schnell entwickeln und namentlich in ihren technischen Anwendungen auf unser Leben immer stärker einwirken, sind Früherkennung und Folgenabschätzung gefragt, sollen sie doch der Wissenschaftspolitik dazu verhelfen, den besten Weg in die Zukunft zu weisen.

Für die Schweiz gilt das in besonderem Mass. Ein *kleiner* Staat kann sich nicht die einfache Devise 'Überall an der Spitze sein' auf die Fahne schreiben. So ist er darauf angewiesen, neue und zukunftsträchtige Wissenschaftszweige frühzeitig zu entdecken und gezielt zu fördern. Ein *demokratischer* Staat kann in neue Richtungen nicht blindlings mit- oder gar vorausfahren, sondern er ist seiner Öffentlichkeit Rechenschaft schuldig über Chancen oder Gefahren, die mit jeder Weichenstellung verbunden sind.

Der Bedarf nach Früherkennung und Technikfolgenabschätzung braucht somit nicht weiter begründet zu werden. Die Frage stellt sich vielmehr, ob und wie sie durchführbar sind. Es ist hier nicht der Ort, darüber tiefgründige Gedanken zu entwickeln. Ich beschränke mich auf einige zugegeben subjektiv ausgewählte Erfahrungen und Eindrücke.

Früherkennung kann verschiedene Ziele haben und auf verschiedene Weise angegangen werden. Dies zeigen grosse 'Forecast'-Übungen, wie sie in den letzten Jahren beispielsweise in Australien, Deutschland, England, Holland und den USA durchgeführt wurden. Auch die Europäische Union befasst sich im übrigen laufend mit Früherkennung.

An der englischen 'Foresight'-Übung – ganz auf das Ziel 'wealth creation' ausgerichtet – waren schliesslich insgesamt 10 000 Leute beteiligt in Delphi-Umfragen, regionalen Workshops, Konferenzen usw. In Japan finden Delphi-Umfragen seit 1975 alle fünf Jahre und mit einem Zeithorizont von 30 Jahren statt, wobei ausgewählte Fachleute jeweils in ihrem Fachgebiet abschätzen, *bis zu welchem Zeitpunkt* gewisse 'Durchbrüche' zu erwarten sind. Dieselbe Umfrage wurde im Jahr 1992 probeweise auch in Deutschland durchgeführt. Ein grosser Delphi-Report liegt von dort vor. In der Schweiz wurde eine derartige Übung bisher nicht durchgeführt, doch dürften die Ergebnisse nicht allzu verschieden ausfallen.

Und was sind diese Ergebnisse? Überblickt man die in verschiedenen Ländern resultierenden Listen zukunftsträchtiger und somit förderungswürdiger Technolo-

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gien, so fällt vor allem ihre weitgehende Übereinstimmung auf. Biotechnologie, Mikro-und Optoelektronik, Nanowissenschaften sind nur einige vielgenannte Beispiele. Einerseits stärkt diese Einhelligkeit der Prognosen zwar das Vertrauen in ihre Zuverlässigkeit. Auf der andern Seite drängen sich damit an ihrer *Originalität und Spezifizität* gewisse Zweifel auf. Schliesslich wird erst die ferne Zukunft zeigen, wie weit solche Voraussagen richtig oder falsch waren. Wenn im Rückblick auf die früheren japanischen Berichte eine Trefferquote von 20% genannt wird, so klingt das nicht schlecht. Noch schöner wäre es allerdings, *im voraus* zu wissen, *welches* denn die jeweils richtigen 20% der Voraussagen sind!

Doch Spass beiseite: Unbestritten und den meisten Übungen wiederum gemeinsam ist, dass der Erfolg solcher Voraussage-Studien nicht nur an den publizierten Erkenntnissen und Empfehlungen gemessen werden darf, sondern dass es vor allem der *Prozess* ist, der zählt. Gemeinsame Zieldiskussionen, verbunden mit einer Erweiterung des Horizontes aller Beteiligten und anderen ähnlichen Wirkungen, werden in den Schlussberichten sicher zu recht als wichtige Ergebnisse solcher aufwendiger Unternehmen gewertet.

Die Früherkennungsgruppe unseres Wissenschaftsrates hat ein Verfahren gewählt, welches eben diesem Prozess grosses Gewicht beimisst. Dies betrifft nicht nur ihre Arbeitsweise, sondern auch die Wahl der Objekte. Neben der eher traditionellen, nämlich disziplinorientierten Diskussion von Themen wie Biologie oder Asienwissenschaften, jeweils mit Blick auf deren künftige Entwicklung in der Schweiz, – um nur einige der kürzlich abgeschlossenen Arbeiten zu nennen – bildeten auch Abläufe und Wechselwirkungen z.B. im Bereich 'Forschung – Unternehmen – Arbeitswelt' Gegenstand von Studien und Workshops.

Die Technikfolgenabschätzung hat ebenfalls eine längere Geschichte. Und die Frage, welche Chancen und Risiken mit der Verwissenschaftlichung und Technisierung unserer Welt verbunden sind, wird gerade mit den grossen Erfolgen dieser Entwicklung immer dringender. So überrascht es nicht, dass unser Parlament vor wenigen Jahren seine Zustimmung zu den stark technisch orientierten Schwerpunktprogrammen des Bundes an die Bedingung knüpfte, dass sie durch eine Technikfolgenabschätzung begleitet würden. Der Wissenschaftsrat hat diese Aufgabe übernommen, auch hier im Bewusstsein, dass die Folgen technischer Entwicklungen auf lange Frist nicht voraussehbar sind. Ein Blick in die Geschichte genügt ja, um zu sehen, auf welchen oft krummen Wegen technische Produkte sich durchgesetzt oder tot gelaufen haben und wieviele falsche Erwartungen damit verbunden waren. Dennoch ist der Versuch zur Technikfolgenabschätzung sinnvoll, so z.B. als Mittel der Informationsbeschaffung, zur Förderung des Verantwortungsbewusstseins bei Forschern und Anwendern und zur Anregung des Gesprächs zwischen Wissenschaft und Öffentlichkeit.

Was haben die **Fullerene** mit dem hier abgehandelten Thema zu tun? Nun, sie sind ein wunderbares Beispiel dafür, welche Überraschungen die Forschung immer wieder bereit hält. Nicht etwa mit dem Ziel, ein neues Molekül zu synthetisieren, sondern im Bestreben, die Molekülspektren interstellaren Staubes besser zu verstehen, wurde das Molekül aus 60 Kohlenstoffatomen entdeckt. Und aus der Diskussion über die mögliche Gestalt des eben entdeckten C_{60}-Moleküls wie aus seiner Namengebung darf man – ohne die frühere Literatur abgesucht zu haben – schliessen, dass bis dahin die Vorstellung von einem räumlichen Kohlenstoff-Molekül niemanden im Traum eingefallen war. Nicht dem Chemiker *Kékulé*, als ihm – wenn ich mich recht an meinen Chemie-Unterricht erinnere – im Dämmerschlaf die Gestalt des Benzol-Rings vor Augen trat und nicht den zahllosen Chemikern, denen seither viel komplexere Strukturen aufzuklären gelang. Und wer hätte somit denn auch auf die Idee verfallen können, etwa in einem Delphi-Verfahren zur **Früherkennung** die Frage zu stellen, wann wohl ein solches Molekül entdeckt werden würde? Und wer ist heute, immerhin gut zehn Jahre nach ihrer Entdeckung, imstande, die **Folgen abzuschätzen,** welche die Nanokäfige und Nanoröhren aus Kohlenstoff in technischen Anwendungen noch mit sich bringen werden?

Reflexion über die Forschung, Forschungspolitik und Forschungsplanung sind nötig, gerade dann, wenn die Geldquellen nicht mehr reichlich fliessen unc die Aufnahmebereitschaft der Öffentlichkeit an ihre Grenzen stösst. Auf der anderen Seite ist es immer wieder erfreulich wenn der Forschergeist des Menschen unc die Macht der Tatsachen unserer Voraussicht ein Schnippchen schlagen.

Auch wenn zuzugeben ist, dass Entdeckungen wie das C_{60}-Molekül – ode die Hochtemperatur-Supraleitung – nich zum Forschungsalltag gehören, so dar doch die Möglichkeit dazu durch allz ziel- und anwendungsorientierte Forschungsplanung niemals unterdrückt ode auch nur behindert werden.

Chimie et Fonds national

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Prof. Dr. **André Aeschlimann***, Président du Conseil de la recherche

Dr. **Jean-Bernard Weber**, Secrétaire scientifique de la division II

La chimie: troisième par ordre d'importance

La chimie est la troisième discipline scientifique au Fonds national suisse de la recherche scientifique (FNS) par ordre d'importance des moyens financiers qui y sont engagés. Elle se place derrière la physique et la biologie. Cette définition rigoureusement disciplinaire a-t-elle aujourd'hui encore un sens, alors que tous les domaines scientifiques interagissent et que l'interdisciplinarité, la transdisciplinarité ou encore la multidisciplinarité devraient être les championnes du développement scientifique futur?

Aujourd'hui, la chimie vit probablement tout autant sinon plus par son interaction et ses apports aux sciences de l vie, aux sciences des matériaux, celles d l'environnement et de la médecine, qu sous la seule et spécifique appellation d

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chimie'. S'il était possible de faire un lassement en tenant compte de ces interactions, il se pourrait fort bien que la himie se retrouve encore mieux placée.

Dans l'éditorial du numéro de juin du nagazine *Horizon* publié par le Fonds iational, le professeur *H.-U. Güdel*, proesseur de chimie à l'Université de Berne t membre du Conseil de la recherche du NS, illustre bien ce rôle 'multifacette' de a chimie.

C'est donc à une discipline scientifiue de toute première importance que ous avons à faire. De plus, c'est une iscipline de base, donc essentielle.

n fait-on assez?

Oui et non. Oui, si l'on tient compte es sommes absolues investies. Non, peut-tre, si l'on se réfère à l'importance de la elève scientifique qui est formée au conict des recherches encouragées par le NS et qui en est, en fin de compte, le roduit le plus tangible. Car le FNS conentre son effort principal sur la recherche ondamentale. Or, les résultats de celle-ci e consistent pas en des brevets ou des roduits commercialisables, mais bien en es cerveaux formés au contact de la reherche. Là pourrait d'ailleurs se situer le lon d'Achille du FNS. En effet, en périoe de difficultés financières, l'on est tenté e mettre l'accent sur le concret et le court rme au détriment des efforts porteurs à lus long terme. Or, le rôle du FNS consis principalement à mettre sur le marché e jeunes chercheurs créatifs et innovaurs qui apporteront leur imagination à urs employeurs, industriels (pour la pluart), mais aussi académiques.

es sciences de base, dont la chimie, nt l'une des priorités du FNS!

La politique scientifique du FNS est andée par un rythme quadriannuel. En fet, tous les quatre ans, le FNS élabore s options scientifiques, qui fixent d'une anière globale les lignes majeures selon squelles il orientera sa politique d'enuragement de la recherche. Ces proains mois, le FNS va s'attacher à la daction de ses options pour la période 00–2003. Il est intéressant de noter qu'il fait alors que la période quadriennale écédente, qui va de 1996 à la fin de ce ècle, vient à peine de démarrer. C'est re si la préparation de ces options exige s qualités de visionnaire, particulièreent difficile dans la recherche fondaentale, qui vit de la découverte et donc de l'imprévu. Ultérieurement, le FNS rédigera un plan pluriannuel pour la même période, plan dans lequel il sera plus concret, connaissant entre-temps aussi les plans de développement des universités et hautes écoles suisses. Il y fixera ses priorités scientifiques et y définira des domaines à plafonner, voire à arrêter; il définira aussi des priorités au niveau de la relève ou de la collaboration internationale.

Pour la période en cours (1996/99), le FNS a donné la priorité à l'encouragement de la recherche fondamentale, à la recherche libre, afin de maintenir au côté des encouragements orientés prodigués par les programmes prioritaires et les programmes nationaux, un espace suffisant dans lequel les chercheurs peuvent donner libre cours à leur esprit de création et d'invention. Ce message s'exprime de la manière suivante au niveau de la division II du FNS, qui est responsable des sciences: elle 'mettra l'accent sur des recherches fondamentales dans les sciences de base et dans leurs contributions aux sciences de l'ingénieur et de l'environnement. Chimie, physique et mathématiques constituent la base de la biologie et de la médecine, et permettent à la recherche sur le climat, l'environnement, la santé ou l'énergie de fournir des résultats crédibles'.

Le ton est donné; la chimie jouit donc d'une haute priorité. Il s'agit d'une affirmation globale, car tout ce qui vient de la chimie n'est pas forcément encouragé. Chaque initiative, toute demande pour l'octroi d'un subside de recherche ou d'une bourse, est soumise à une évaluation rigoureuse, le critère d'évaluation premier étant la qualité scientifique de l'initiative. L'originalité et l'actualité du thème choisi, mais aussi la manière de l'aborder, ainsi que les compétences du ou des chercheurs impliqués, sont d'autres valeurs déterminantes pour bénéficier du soutien du FNS. Ces facteurs sont évalués par le Conseil de la recherche, l'un des trois piliers du FNS, les autres étant le Conseil de fondation et le secrétariat du FNS situé à Berne.

Constitué de chercheurs de toutes les disciplines scientifiques, élus par une commission électorale et issus des milieux de la recherche universitaire et industrielle, le Conseil de la recherche évalue tous les projets qui sont présentés au FNS. Il est organisé en quatre divisions qui siègent une fois par mois et dont les présidents et vice-présidents constituent le Bureau du Conseil. Dans son travail d'évaluation, le Conseil de la recherche consulte souvent des experts externes. Il va sans dire que de tels experts sont recrutés dans leur grande majorité à l'étranger.

La division II du FNS

La chimie relève de la compétence de la division des mathématiques, des sciences naturelles et de l'ingénieur du Conseil de la recherche, appelée plus communément division II. Actuellement, le quart des 21 membres de celle-ci sont des chimistes. La charge et les responsabilités des conseillers sont importantes. Il ne faut pas perdre de vue que le Conseil de la recherche est un organe de milice et la plupart de ses membres sont des chercheurs actifs. On peut estimer à 1 jour par semaine le temps qu'un conseiller consacre au FNS. Ce travail consiste en l'étude et l'évaluation des dossiers (10–15 par semestre), la discussion des projets avec leurs responsables (ce contact est une tradition en division II), la participation aux séances du Conseil ou chaque conseiller présente et défend les dossiers qui lui ont été confiés. Il participe aux décisions collégiales sur tous les autres projets à évaluer par la division. Le Conseil de la recherche suit aussi l'avance des projets accepté par le contrôle des rapports scientifiques qui sont adressés tous les 12 mois au FNS par les chercheurs. Enfin, le Conseil traite de dossiers d'une portée plus étendue, tels que la formulation d'avis sur l'opportunité de construire en Suisse une source de lumière synchrotronique (Swiss Light Source), et s'exprime sur des dossiers tels que les nouvelles Hautes Ecoles Spécialisées (HES).

La chiralité: un effort particulier du FNS

Le FNS dispose d'un instrument, l'action thématique, dont il use rarement pour encourager plus spécifiquement un domaine de la recherche. Actuellement une seule action thématique est en cours, en chimie précisément, dans le domaine de la synthèse chimique sélective: CHiral2. En cinq ans, 4 fois CHF 2,5 mio seront investis dans de telles recherches. Il ne s'agit pas de recherche programmatique proprement dite, au sens de programmes nationaux ou prioritaires, mais d'un faisceau de projets parallèles menés dans un encadrement administratif minimal. Les chercheurs, qui proposent eux-mêmes les sujets qu'ils souhaitent aborder dans le domaine de la chiralité, et dont les demandes de subsides sont examinées par un groupe de spécialistes constitué par le Conseil de la recherche, sont convoqués une fois l'an pour un workshop de deux jours. Ils y présentent et confrontent leurs résultats, ce qui permet des synergies inattendues.

L'action durera jusqu'en 1998 et aura permis un renouveau dans ce domaine traditionnellement fort de la recherche suisse et d'une très grande actualité, mais dans lequel on observait un certain tassement. Cette injection de moyens dans un esprit de compétition aura non seulement permis de développer un potentiel important de groupes de chercheurs, mais aussi de sensibiliser une cinquantaine de jeunes chercheurs aux problèmes de la chiralité dans le cadre d'une thèse de doctorat ou d'un postdoc.

Les actions thématiques sont appréciées des chercheurs. Preuve en est ce conférencier américain qui, invité comme conférencier à un récent workshop et impressionné par l'enthousiasme des participants et l'encadrement administratif efficace mais minimal, souhaite que le modèle soit repris par le FNS américain! Le FNS souhaite toutefois utiliser cet instrument de l'encouragement avec parcimonie, considérant que la recherche orientée est déjà suffisamment encouragée par le biais des programmes nationaux, prioritaires et autres, et qu'il convient de laisser à la recherche dite libre un espace suffisamment vaste (y compris financier ...) pour lui permettre de développer toute son imagination.

Quelques chiffres

250 projets en cours, de durées diverses, sont actuellement enregistrés en chimie; ils représentent un volume financier total de CHF 41.7 mio. L'encouragement annuel du FNS à la chimie ressort à CHF21 mio. C'est le cinquième du budget des sciences, sciences de la vie exceptées. Les subsides alloués permettent de rétribuer quelque 460 collaborateurs. Mis à part la vingtaine de techniciens (laborants, électroniciens, *etc.*), tous ces collaborateurs se forment au contact de la recherche. C'est là, comme indiqué précédemment, que se situe l'effort principal du FNS et le résultat le plus immédiatement tangible de l'action du FNS: contribuer à la formation de jeunes chercheurs pour l'industrie et pour la recherche et la relève académique. Comme ces collaborateurs sont en formation, ils sont soumis à un rapide turn-over. Les candidats au doctorat (env. 320) peuvent être rétribués pendant 3, voire 4 ans à charge d'un subside FNS. Les postdocs et ingénieurs (env. 130) – pour lesquels une limite d'âge est fixée à 35 ans à l'engagement – peuvent figurer pendant 2, voire 4 ans dans un projet. On peut donc estimer qu'une centaine de doctorants et une quarantaine de postgradués sortent annuellement des projets en chimie dont une partie importante démarrent leur carrière professionnelle.

Programmes spéciaux et efforts ciblés

Dans les sciences – la chimie ne constitue pas une exception – la proportion des femmes est peu élevée. De gros efforts sont consentis par les universités et hautes écoles, pour motiver de jeunes femmes à suivre une filière scientifique. Le FNS, se situant en aval, ne peut intervenir par des mesures influençant le nombre d'étudiantes. Il fournit de ce fait un effort au niveau post-diplôme: il donne la possibilité à des femmes, ayant dû interrompre ou fortement réduire leur activité scientifique pour des raisons familiales, à retrouver un poste dans la recherche. Ce programme, appelé *Marie Heim Voegtlin* du nom de la première femme médecin de Suisse, est mis au concours par voie de presse et d'affiche. Les candidates soumettent un bref dossier au FNS. Celles dont le dossier est retenu sont invitées à un entretien.

Afin d'identifier de jeunes scientifiques de très haut niveau, la division II met chaque année cinq subsides PROFIL au concours. L'on essaie d'identifier des personnes dont les qualités de chercheur, mais aussi d'enseignant, devraient en faire des candidats de premier plan pour la relève académique. Le subside qui leur est alloué, généralement assorti d'un subside pour des recherches indépendantes, doit leur permettre de se 'profiler' en vue de postulations lors de mises au concours de postes universitaires, voire dans l'industrie. Usuellement, 50–70 candidatures sont présentées: une quinzaine de candidats sont invités pour un hearing suite à un examen sur dossier. Depuis 1992, année de lancement du concours, 5 chimistes en ont bénéficié. Deux d'entre eux se sont d'ores et déjà vu attribuer une chaire universitaire.

L'encouragement du Fonds national ne se limite pas à la Suisse

Chaque année, le FNS envoie 500 boursiers à travers le monde. L'an passé, une quarantaine d'entre eux portaient un diplôme de chimiste, généralement complété d'un doctorat ès sciences. La bourse prévoit un soutien pendant 12 ou 24 mois, ce séjour dans une université étrangère étant souvent prolongé par des ressources que le jeune boursier obtient sur place. On notera que la plupart des boursiers choisissent les Etats-Unis comme lieu de postformation, même si une légère augmentation des séjours dans les pays européens est constatée. L'Australie et le Canada se trouvent en bonne place, tandis que seuls deux jeunes chimistes suisses se sont rendus au Japon l'an passé.

Une analyse des dossiers soumis au FNS montre qu'en sciences, plus des trois quarts des projets de recherche sont réalisés avec des partenaires d'autres pays. Ceci vaut aussi pour la chimie, où l'on constate que la plupart des partenaires sont situés, comme il fallait s'y attendre, aux Etats-Unis, puis en Allemagne et en France. Les interactions sont de types divers, allant d'un vrai projet commun à des contacts ponctuels ou des échanges de services. On notera que les subsides de recherche alloués prévoient une somme destinée à la participation à des conférences, colloques et workshops à l'étranger, ce qui permet une interaction permanente avec le monde de la recherche.

Où va-t-on?

Les chiffres des étudiants optant pour la chimie sont préoccupants. Ils sont dangereusement bas. Il faut veiller à ce que la relève ne tombe pas au-dessous d'un certain seuil. La recherche en chimie dépend beaucoup de l'existence de forces vives. Cela est d'autant plus important que la chimie participe au développement, comme nous l'avons dit d'entrée, des domaines de recherche les plus divers. Dans une mesure importante, les progrès de la biologie moléculaire, de la médecine, notre compréhension des systèmes environnementaux et l'avance dans les sciences des matériaux dépendent des nouvelles découvertes de la chimie. Gymnasiens: la chimie est une science qui mérite votre attention. Pensez-y lorsque vous devrez choisir l'orientation de vos études universitaires.

Reçu le 7 juillet 1996

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Ecoles d'ingénieurs Information Ingenieurschulen

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bteilung Chemie

ReseaChem GmbH
Chemical Research Laboratory

ienstleistungen für Dritte an der Abteilung Chemie ler ISB

uth Weber und **Franz Baumberger***

Die Chemieabteilung der ISB hat seit ngerer Zeit versucht, gute Kontakte zur dustrie zu pflegen. Dies hat dazu ge- ihrt, dass der Anteil der Diplom- und emesterarbeiten, die an unserer Abtei- ng in Zusammenarbeit mit der Industrie d/oder der öffentlichen Hand entstan- n sind, stetig gestiegen ist und sich omentan bei 80–85% eingependelt hat. elbst bei erfolgreichen Arbeiten hat sich mer wieder gezeigt, dass die zur Verfü- ng stehende Zeit (fünf Wochen) meist cht ausreicht, um sämtliche Probleme zu sen. Zum einen kommt es vor, dass die omplexität eines Themas sowohl von n Auftraggebern als auch von der Schu unterschätzt wird, zum andern treten teressante Aspekte häufig erst im Ver- uf einer Arbeit auf. Gelegentlich war es öglich, solchen Fragen durch kurzfristige Anstellung des neu diplomierten Absolventen weiter zu verfolgen, häufiger war aber die etwas unbefriedigende Situation, dass man mangels Personal den Auftraggeber auf die nächste Semesterarbeit vertrösten musste.

Im Zusammenhang mit der Umwandlung der Ingenieurschulen in Fachhochschulen hat das Thema Industriekontakte neue Impulse erhalten. So schreibt das Fachhochschulgesetz den künftigen Fachhochschulen vor, angewandte Forschung und Entwicklung zu betreiben (Art. 9) und Dienstleistungen für Dritte zu erbringen (Art. 10). Da eine Abteilung mit fünf Dozenten und zwei Assistenten nie auf dem ganzen Gebiet der Chemie kompetent sein kann, haben wir uns entschlossen, Analytik im weitesten Sinn als Ausbildungsschwerpunkt zu wählen. Dies aus den folgenden Gründen: 1. die Abteilung Chemie der ISB verfügt über einen gut und modern ausgerüsteten Gerätepark; 2. der Kanton Bern hat keine chemische Grossindustrie aber viele kleinere Firmen und Labors, denen Dienstleistungen auf unserem Gerätepark nützen könnten; 3. die Umfrage bei der chemischen Industrie im Vorfeld der Lehrplanrevision zum neuen Fachhochschul-Lehrplan 95 zeigte, dass bevorzugt kleine und mittlere Unternehmen (KMU) grosses Interesse an einer Zusammenarbeit mit den Ingenieurschulen haben. Zudem wissen wir aus einer Umfrage bei den Ehemaligen, dass ein Grossteil unserer Absolventen in der Region bleibt und heute in der Analytik tätig ist.

Aufgrund all dieser Tatsachen haben wir uns im Frühjahr 1995 entschlossen, die Kontakte zu Firmen in der Region Bern zu intensivieren. Unsere beiden (damaligen) Assistenten Herr *Stefan Berger* und Herr *Beat Keller*, haben sich mit sehr viel Engagement dieser Aufgabe angenommen. In Zusammenarbeit mit den Dozenten haben sie Know-how-Schwerpunkte festgelegt und ein mögliches Dienstleistungsangebot erstellt. Ende Juni 1995 wurden über 200 Faltprospekte an Firmen der Region Bern-Solothurn-Fribourg versandt, die im Bereich Chemie tätig sind. Der erfreuliche Antwort-Rücklauf von *ca.* 40% bestätigte unsere Hypothese, dass von Seiten der KMUs ein Bedürfnis nach Dienstleistungen dieser Art besteht. Sehr schnell wurden erste Anfragen an uns gerichtet und daraus folgend Dienstleistungsaufträge erteilt. Bald mussten wir aber unsere Grenzen erkennen, die sich aus den knappen personellen Kapazitäten sowie der Administration ergaben. Wollten wir unseren Lehrauftrag nicht

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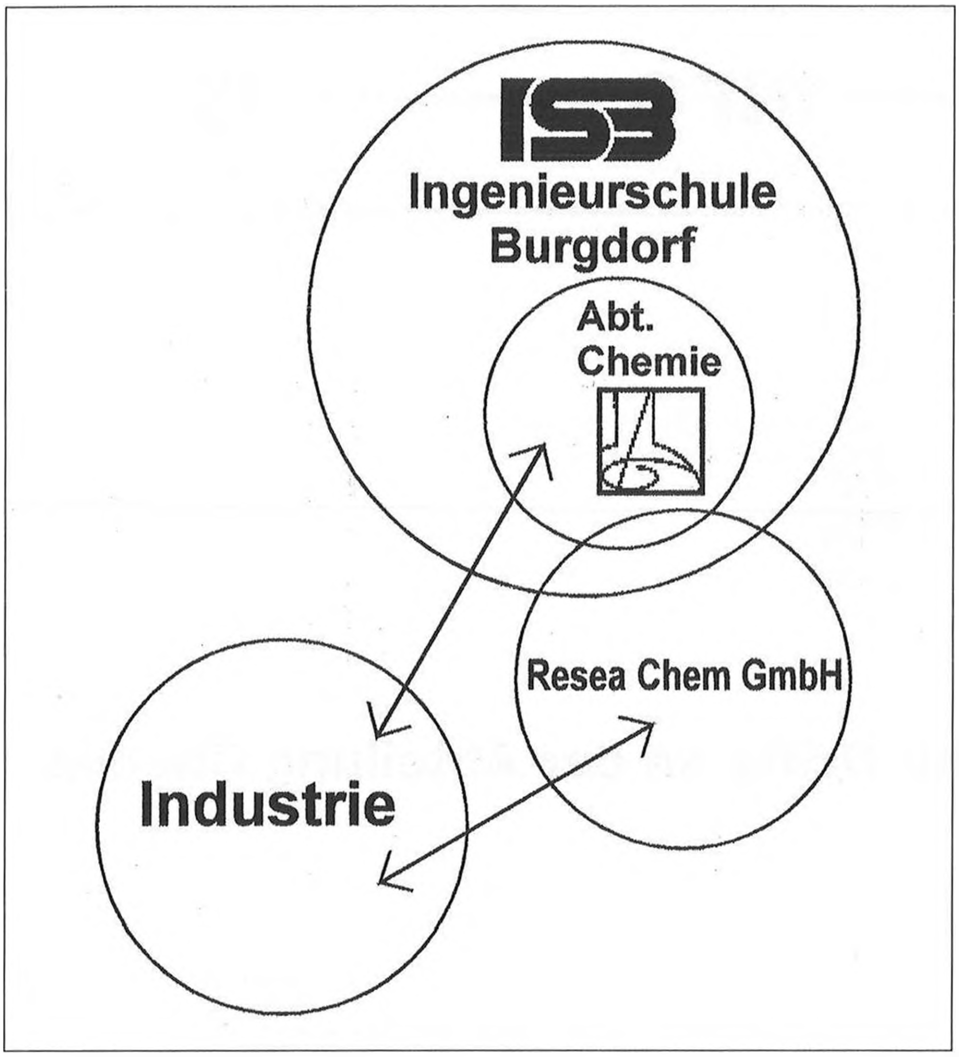
CHIMIA 50 (1996) Nr. 7/8 (Juli/August)



vernachlässigen, so fehlten uns die Arbeitskräfte für die praktische Ausführung dieser Dienstleistungsaufträge; zudem mussten solche Aufträge/Anfragen auch administrativ bewältigt werden. Dem Personalproblem begegneten wir, indem die eingegangenen Aufträge in Abend- und Wochenendarbeit erledigt wurden. Dass dies keine Lösung auf die Dauer sein konnte, wurde uns sehr schnell klar. Kreative Lösungen waren somit gefragt und verschiedene Möglichkeiten wurden erörtert. Da Assistenten bei uns befristet angestellt sind und die beiden Verträge mit den damaligen Assistenten auf das Frühjahr 1996 ausliefen, stellte sich für beide Seiten die Frage, wie es weiter gehen würde. Nachdem *Stefan Berger* den Vorschlag machte, die Dienstleistungsaufträge in eigener Regie zu übernehmen, musste für das Dreieck Industrie-Schule-Dienstleistung eine für alle Partner akzeptable Lösung gefunden werden. Als Möglichkeiten boten sich die Gründung einer AG oder einer GmbH an. Letztlich erwies sich die GmbH zum einen aus finanziellen Gründen (geringeres Stammkapital), zum andern dank der kurzen Entscheidungswege (nur zwei Gesellschafter nötig) als die geeignetste Gesellschaftsform. So gründeten per 1. Januar 1996 Herr *Stefan Berger*, Chem. HTL, und Dr. *F. Baumberger* die *ReseaChem GmbH* mit Sitz in Burgdorf.

Die *ReseaChem GmbH* ist eine wirtschaftlich eigenständige Firma und als spin-off aus der Abteilung Chemie entstanden. Sie ist in den Gerätepark und die Räumlichkeiten der ISB eingemietet. Dadurch ist sie noch eng mit der Abteilung Chemie verknüpft, kann jedoch unabhängig mit der Industrie Kontakte pflegen (s. *Abb.*) Interessant ist diese enge Zusammenarbiet sowohl für die Schule, die Industrie und die *ReseaChem GmbH*. Die Schule profitiert durch die direkten Kontakte der *ReseaChem GmbH* mit der Industrie durch Knwo-how-Transfer und der Möglichkeit angewandte F+E-Projekte an die Schule zu holen (es sollen ja nur die Dienstleistungsaufträge ausgegliedert werden). Sie profitiert aber auch, indem die *ReseaChem GmbH* dem Kanton die für die Laborbenützung im Raum Burgdorf übliche Gewerbemiete bezahlt und der Gerätepark besser ausgenützt wird als früher. Die Industrie kann *via ReseaChem GmbH* oder Abteilung Chemie zu Dienstleistungen kommen und kann so den gut ausgebauten Gerätepark der Abteilung nutzen. Die *ReseaChem GmbH* schliesslich hatte durch diese Zusammenarbeit ideale Startbedingungen ohne hohe Risiken und kann vom 'Know-how' und dem kreativen Umfeld der Schule profitieren. Und last, but not least, ist die Abteilung Chemie am Erfolg der *ReseaChem GmbH* beteiligt, indem diese sich verpflichtet hat, 20% ihres Reingewinnes wieder in den Gerätepark der Abteilung zu investieren.

Die *ReseaChem GmbH* ist ein Teil der Neuorientierung der Abteilung Chemie bei der Umwandlung der ISB in eine Fachhochschule. Wir sind überzeugt, mit den neugeschaffenen Strukturen, die an uns gerichtete Forderung nach 'Dienstleistungen für Dritte' erfüllen zu können.

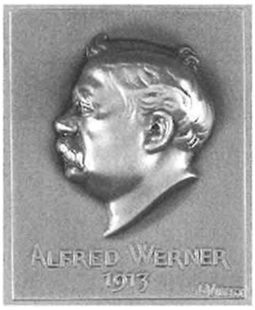
CHIMIA 50 (1996) Nr. 7/8 (Juli/August)

Vissenschaftliche Auszeichnungen der NEUEN SCHWEIZERISCHEN CHEMISCHEN GESELLSCHAFT

Ausschreibung für die Verleihung 1997

istinctions scientifiques de la NOUVELLE SOCIÉTÉ SUISSE DE CHIMIE

Mise au concours pour 1997



Werner-Preis

Der *Werner*-Preis wird an schweizerische oder in der Schweiz tätige Nachwuchswissenschafter für ausgezeichnete Forschungsarbeiten auf dem Gebiet der Chemie verliehen. Die Auswahl umfasst Kandidaten und Kandidatinnen aus Hochschulen und Industrie.
Die Preisverleihung findet im Herbst 1997 statt.
Einreichefrist: 31. Oktober 1996.

Prix _Werner_

Le prix *Werner* sera attribué à un jeune chercheur suisse ou un jeune chercheur exerçant son activité en Suisse, pour un travail de haute qualité dans le domaine de la chimie. Les candidats et candidates peuvent être issus d'une Haute École ou de l'industrie.
La remise du prix aura lieu en automne 1997.
Délai de présentation: 31 octobre 1996.

ındmeyer-Preis

er *Sandmeyer*-Preis wird für hervorragende
rbeiten auf einem Gebiet der industriellen oder
ıgewandten Chemie an ein Arbeitsteam oder
nen Einzelnen verliehen. Die Arbeit soll in der
egel in der Schweiz oder im Ausland von einem
rbeitsteam mit Beteiligung von Schweizer Bür-
rn und Bürgerinnen ausgeführt worden sein.
ie Preisverleihung findet im Frühjahr 1997 statt.
nreichefrist: 31. Oktober 1996.

Prix _Sandmeyer_

Le prix *Sandmeyer* sera attribué à un groupe de travail ou à un candidat unique pour un travail de haute qualité dans le domaine de la chimie industrielle ou appliquée. Le travail doit avoir été réalisé en suisse ou à l'étranger par un groupe de travail comprenant des citoyens et citoyennes suisses.
La remise du prix aura lieu au printemps 1997.
Délai de présentation: 31 octobre 1996.

Dr.-_Max-Lüthi_-Preis

Die Dr.-*Max-Lüthi*-Auszeichnung wird für ausgezeichnete Diplomarbeiten verliehen, die an Chemieabteilungen von höheren technischen Lehranstalten der Schweiz ausgeführt werden.
Anträge der Abteilungsvorsteher der Chemieabteilungen müssen bis Ende Dezember 1996 an den Geschäftsführer der NSCG eingereicht werden.
Die Preisverleihung findet im Frühjahr 1997 statt.

Prix Dr.-_Max-Lüthi_

Le prix Dr.-*Max-Lüthi* est attribué à l'auteur d'un travail de diplôme de qualité exceptionelle effectué dans le département de chimie d'une école technique supérieure suisse.
Les propositions des directeurs des départements de chimie des écoles techniques supérieures suisses doivent être soumises à l'administrateur de la NSSC avant la fin décembre 1996.
La remise du prix aura lieu au printemps 1997.

racelsus-Preis

r *Paracelsus*-Preis kann Wissen-
ıaftern, die im internationalen
rgleich Hervorragendes in der
ssenschaftlichen Forschung
dem Gebiet der Chemie ge-
stet haben, zuerkannt werden.
r *Paracelsus*-Preis wird im Tur-
von 2 Jahren verliehen, das
hste Mal im Frühjahr 1998.
reichefrist: 31. Oktober 1997.

Prix _Paracelse_

Le prix *Paracelse* est attribué à des scientifiques qui ont effectué des travaux de recherche exceptionnels et reconnus sur le plan international dans le domaine de la chimie.
Le prix *Paracelse* sera remis tout les 2 ans, la prochaine fois au printemps 1998.
Délai de présentation: 31 octobre 1997.

schläge und Bewerbungen sind mit den not-
ıdigen Unterlagen an den Geschäftsführer der
CG einzureichen.

Propositions et candidatures doivent être adressées à l'administrateur de la NSSC avec un dossier complet.

NEUE SCHWEIZERISCHE CHEMISCHE GESELLSCHAFT
NOUVELLE SOCIÉTÉ SUISSE DE CHIMIE

Prof. A. von Zelewsky
Präsident/Président
Dr. R. Darms
Geschäftsführer/Directeur

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CH–4002 Basel

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Prof. C. Ganter
Laboratorium für Organische Chemie
ETH-Zentrum
CH–8092 Zürich, Switzerland

Correspondence concerning submitted manuscripts should be mailed to the same address, quoting the manuscript reference number.

3. Types of Manuscripts

The autors should consider the fact that the heterogenous readership of CHIMIA, although trained in fundamentals, may not have extensive knowledge in specialized topics.

3.1. *Review Articles*. Preference will be given to creative reviews that are timely, critical, and comprehensive. For clarity, divisions and subdivisions should be used like 1. ..., 1.1. ..., 1.1.1. ... with appropriate titles. A short scientific portrait of the author is also requested (text and photo).

3.2. *Short Communications*. Only contributions that have not been (except in the form of an abstract or a brief preliminary remark) and are not to be published elsewhere will be considered. For clarity, they should be subdivided into labeled sections *e.g.* **Introduction**, **Results**, **Discussion**, **Experimental**.

4. Preparation of Manuscripts

4.1. *General Considerations*. Authors are strongly encouraged to submit manuscripts in English; however, manuscripts in German or French can also be accepted for publication. They must be typewritten, double-spaced, on substantial paper of A4 or similar format. Special characters not available on a typewriter should be clearly indicated in ink and explained unambiguously in the margin on their first appearance. Authors are requested to reserve margins of at least 3 cm at the top and bottom of each page and at least 4 cm on the left-hand side. Copies made by a clearly legible duplication process are preferred. For computer-generated manuscripts, *Times* font is preferred.

Pages should be numbered consecutively beginning with the title page. References, tables, figure legends, formula collections, schemes, and figures *must* be grouped together *in this order* at the end of the manuscript and numbered accordingly. Original drawings of formulae, schemes, and figures should be furnished together with the manuscript.

4.2. *Title Page*. A current issue of CHIMIA should be consulted.

Attention is drawn to the following points:

a) The title of a manuscript should reflect concisely the purpose and findings of the work in order to provide maximal information for a computerized title search. Abbreviations, symbols, chemical formulae, references, and footnotes should be avoided. First letters of nouns and adjectives are capitalized.

b) The authors' full first names, middle initials, and last names should be given, followed by the address (or addresses) of the contributing institution. The author to whom correspondence and/or inquiries should be directed should be indicated by an asterisk (*).

The complete address, *including phone number* (telefax number if any), of the correspondence author should also be given.

4.3. *Abstract*. The second page of the manuscript should be reserved for a summary in English, independent of the language of the main text. If this is German or French, the summary should be preceeded by an English translation of the title. The summary should be self-explanatory and intelligible without reference to the text and should not exceed 200 words.

4.4. *References* and *Footnotes* should be numbered sequentially in the order they are cited in the text. The numbers should be set in brackets, thus [2] or [3][14]. References and footnotes typed with double spacing are to be collected in numerical order at the end of the main text. Titels of journals must be abbreviated according to *Chemical Abstracts* (*cf.* Chemical Abstracts Service Source Index (CASSI)).

Attention is drawn to the following conventions:

a) Names of all authors of cited publications should be given. Use of '*et al.*' in the list of references is not acceptable.

b) Only the initials of first and middle names should be given.

c) Whenever possible, composite references should be used, instead of a series of individual ones. The abbreviation '*ibid.*' may only be used within such a compositie reference.

d) In references described as 'personal communications', an affiliation should follow the name(s) of the person(s).

In the text, reference to author(s) of cited works should be made without giving initials, *e.g.* '... as shown by *Jones* and *Smith* [7]'. If the reference carries the names of three or more authors, it should be quoted as '... *Smith et al.* [3]', if *Smith* is the first author, or as '*Jones* and coworkers [3]', if *Jones* is the senior author.

4.5. *Tables*. Tables should be used only in case they will present information more effectively than running text. Numbered tables with suitable captions at the top should be typed on separate sheets and placed after the references. Each table must be referred to in the text.Column headings should be as short as possible but must define units unambiguously. When necessary, an abbreviated or symbolic column heading should be used and explained in the table-heading or in a footnote. Footnotes to tables should be labeled [a]), [b]), [c]), *etc.*, and typed at the bottom of the table.

4.6. *Structural Formulae, Schemes, and Figures*. Line drawings or sharp glossy photographs (no *Xerox* or similar copies) of the figures and structural formulae should be submitted with the manuscript. Copies must be included with each copy of the manuscript.

Original drawings of standard size A4 are preferred. In any case, drawings should not exceed the standard size A3 (about 30 x 40 cm) and must contain all necessary symbols and lettering, *i.e.*, they must be usable without additional art work by the CHIMIA printers.

Line thickness, line spacings, and size of lettering should be planned for optimal reproduction (*cf. Appendix I*). Computer-plotted drawings must satisfy the same criteria.

Original drawings or photographs should be identified with the author's name and numbered to agree with the figure legends.

Structural formulae will not be type-set and must, therefore, be provided by the authors ready for reproduction. They should be combined in suitable schemes to reduce the cost of block-cutting. In general, only displayed formulae should be given key numbers; compounds mentioned only in the text should be referred to by their complete names.

For authors using the *ChemDraw* program, the following preference items are recommended: fixed length, 25 pt; line width, 1pt; bold width, 3 pt. Single-width bold and dashed lines are preferred to wedges for stereochemical notation: 14-pt *Helvetica* font should be used for text material, and 12-pt *Helvetica* font for atom labels. Drawings should be prepared with the page setup at 70% and printed in this manner with a laser printer on a good quality *white paper*.

4.7. *Chemical Equations and Physical or Mathematical Expressions*. Chemical equations and physical or mathematical expressions should be numbered sequentially on the righthand side with arabic numerals in parentheses. Physical quantities and variables that have to be defined in the text should be written in *italics* (wavy line). It is recommended to use the symbols proposed by IUPAC (*cf. Pure Appl. Chem.* **1979**, *51*, 1).

Fractional expressions should be written using a slant, *e.g.* $h\nu/kT$.

5. Nomenclature

All new compounds should be named in accordance with IUPAC nomenclature rules. As an additional guideline, the *Index Guide of Chemical Abstracts* can also be consulted. Some special conventions peculiar to CHIMIA are:

For common solvents, reagents, or other compounds, the molecular formulae or accepted abbreviations may be used: *e.g.* $CHCl_3$, NaCl, $SOCl_2$, CH_3OH (or MeOH), DMF, DMSO, THF, Py.

Different alkyl or aryl substituents should be designated by superscripts: R^1, R^2, R^3, *etc.* (Subscripts denote the number of substituents.)

Individual atoms should be referred to as C(2), N(5) (not C-2 and N-5), *etc.* For 'hydrogen atom attached to carbon atom 4' *etc.*, CHIMIA prefers the notation H–C(4).

An *ad hoc* abbreviation may be used for a name or formula that occurs repeatedly. This has to be clearly defined, *e.g.* THC = tetrahydrocannabinol.

Some symbols and abbreviations are listed in *Appendix II*.

6. Units and Their Symbols

SI units are to be used, especially in contributions dealing with physical chemistry. However, some non-SI units are acceptable, *e.g.* ml, min, h, d, Hz, g, mg, Torr, eV, °C.

7. Proofs and Corrections

Authors will be provided with two sets of proofs, one of which should be returned to the editor within the indicated deadline.

Corrections of errors other than those due to the printers or editors will be charged. Standard correction marks should be used.

Together with the proofs the authors will receive a form for key-words. The completed form must be returned with the proofs.

Key-words are entries in the annual subject index. Well-chosen key-words will help a reader to find articles of potential interest. Key-words should consist of not more than three words. Very general words or phrases (*e.g.* organic compounds, synthesis, instability, color, *etc.*) are clearly unsuitable as key-words.

Appendix I. *Line Thickness and Size of Lettering for Original Drawings*

The thinnest lines in a printed figure or formula should not be narrower than 0.15 mm.

The following table will serve as a guide in preparing original drawings.

Line thickness required [mm]

Format of original drawing [cm x cm]	Main part of drawing	Emphasized lines	Secondary lines
7.5 x 10.5	0.3–0.5	0.5–0.9	0.25–0.3
10.5 x 14.8	0.4–0.6	0.6–1.2	0.3 –0.4
14.8 x 21	0.6–0.9	0.9–1.8	0.5 –0.6
21.0 x 30.5	0.8–1.2	1.2–2.4	0.6 –0.8
30.5 x 42	1.0–1.5	1.5–3.0	0.8 –1.0

Distances between parallel lines or between letters should not be smaller than the line thickness.

The minimum height of lettering depends on the required linear reduction, as indicated in the following table.

Format of original drawing [cm x cm]	Height of capitals Main lettering [mm]	 Secondary lettering [mm]
7.5 x 10.5	3	2
10.5 x 14.8	4	2.5
14.8 x 21	6	4
21.0 x 30.5	8	5
30.5 x 42	10	6

Appendix II. *Some Symbols and Abbreviations Used by CHIMIA*

Disignation	Symbol	Remarks
Amount-of-substance concentration or 'molarity'[a])	M	in mol/dm^3; *e.g.* 1M NaOH
Molality[a])	*m*	in mol/kg; *e.g.* 1*m* HCl
Normality[a])	N	in equiv./dm^3; *e.g.* 1N H_2S
Percentage by mass	%	*e.g.* 15%
Percentage by volume	% (*v/v*)	*e.g.* 10% (*v/v*)
Melting point	m.p.	*e.g.* m.p. 157–158°
Boiling point	b.p.	*e.g.* b.p. 111–112°
Boiling point under a certain pressure	b.p./Torr	*e.g.* b.p. 65/4 Torr
Freezing point	f.p.	*e.g.* f.p. 3°
Refractive index	*n*	*e.g.* $n_d^{20} = 1.643$
Relative density	*d*	*e.g.* $d_4^{20} = 1.1811$
Optical rotation[b])	α	*e.g.* $\alpha_D^{25} = 0.73$ ($l = 0.1$, neat)
Specific optical rotation[b])	$[\alpha]$	*e.g.* $[\alpha]_D^{25} = 108$ ($c = 3.42$, $CHCl_3$)
Molecular optical rotation[b])	$[M]$	*e.g.* $[M]_{598}^{23} = 380$ ($c = 1.52$, H_2O)
Thin-layer chromatography	TLC	
Gas-liquid chromatography	GLC	
Liquid chromatography	LC	
Column chromatography	CC	
High-pressure (performance) liquid chromatography	HPLC	
Paper chromatography	PC	
Ultraviolet	UV	
Visible	VIS	
Circular dichroism	CD	
Optical rotatory dispersion	ORD	
Infrared (absorption) spectrum	IR	
Nuclear magnetic resonance of ^{1}H	^{1}H-NMR	
Nuclear magnetic resonance of ^{13}C	^{13}C-NMR	
Electron paramagnetic resonance	EPR	
Electron spin resonance	ESR	
Mass spectrum	MS	
Photoelectron spectroscopy	PES	
X-Ray photoelectron spectroscopy	XPES, ESCA	
Shoulder	sh	
Broad	br.	
Strong IR absorption	*s*	
Medium IR absorption	*m*	
Weak IR absorption	*w*	
Singlet	*s*	
Doublet	*d*	
Triplet	*t*	
Quadruplet	*q*	
Quintuplet	*quint.*	
Sextuplet	*sext.*	
Septuplet	*sept.*	
Multiplet	*m*	

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[a]) For a comprehensive discus
sion on the usage of the term
'equivalent' and 'normal
see, *Pure Appl. Chem.* **197**
50, 325.

[b]) The symbol c is used in co
nection with the specific o
tical rotation $[\alpha]$; it is d
fined as mass of substanc
(in g) in 100 ml of solutio
The quantities l and d in [
= 100 · $\alpha/l \cdot c$ or $[\alpha] = \alpha/$
d are given in dm and g/
(kg/m^3), respectively.

CHIMIA 50 (1996) Nr. 7/8 (Juli/August)

INFORMATION

Neue Schweizerische Chemische Gesellschaft
Nouvelle Société Suisse de Chimie
New Swiss Chemical Society

Sektion Analytische Chemie
Section Chimie Analytique

Jahresversammlung der Mitglieder der Sektion Analytische Chemie Assemblé annuelle des membres de la Section Chimie Analytique

Donnerstag, 21. November 1996 / Jeudi, 21 novembre 1996

1.00–11.15
Kongresszentrum Messe Basel: Kongresssaal Rio
Centre de Congrès de la Foire de Bâle: Salle de congrès: Rio

Traktanden/Ordre du jour

1. Protocol of the annual meeting of the Section held October 20, 1995
2. Annual report of the chairman
3. Annual report of the treasurer
4. Release of the committee and treasurer
5. Election of new committee members
6. Membership fees 1997
7. Future activities of the section
8. Miscellaneous

Prof. H.M. Widmer
Chairman of the Section
Analytical Chemistry

Sektion Chemische Forschung
Section Recherche Chimique

Jahresversammlung der Mitglieder der Sektion Chemische Forschung Assemblé annuelle des membres de la Section Recherche Chimique

onnerstag, 21. November 1996 / Jeudi, 21 novembre 1996

.00–11.15
ongresszentrum Messe Basel: Kongresssaal Montréal
entre de Congrès de la Foire de Bâle: Salle de congrès: Montréal

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6. Future activities of the section
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Prof. J. Weber
Chairman of the Section
Chemical Research

Sektion Medizinische Chemie
Section Chimie Thérapeutique

ahresversammlung der Mitglieder der ektion Medizinische Chemie ssemblé annuelle des membres de la ection Chimie Thérapeutique

onnerstag, 21. November 1996 / Jeudi, 21 novembre 1996

00-11.10
ongresszentrum Messe Basel: Kongresssaal Singapur
ntre de Congrès de la Foire de Bâle: Salle de congrès: Singapur

Traktanden/Ordre du jour

1. Annual report of the chairman
2. Annual report of the treasurer
3. Future activities of the section
4. Miscellaneous

Dr. R. Giger
Chairman of the Section
Medicinal Chemistry

Homepage der Section for Medicinal Chemistry (SMC):

http://sgich1.unifr.ch/smc.html

Homepage der European Federation for Medicinal Chemistry (EFMC):

http://sgich1.unifr.ch/EFMC.html

News

Alusuisse-Lonza übernimmt Biotechnologieunternehmen

Die *Alusuisse-Lonza* Gruppe hat mit der *Celltech Group plc.* eine Vereinbarung zur Übernahme der Tochtergesellschaft *Celltech Biologics plc.* (*'Bologics'*) unterzeichnet. *Biologics* ist spezialisiert auf die biotechnologische Herstellung von Wirkstoffen für führende Unternehmen aus der Pharma- und Biotechnologie-Industrie. Die Übernahme unterliegt noch der Zustimmung der Aktionäre der *Celltech Group plc.* Mit dem Abschluss der Transaktion, die voraussichtlich Ende Juni stattfindet, wird *Biologics* neu unter dem Namen *Lonza Biologics* firmieren und in das Feinchemikaliengeschäft der *Lonza* integriert. Der Kaufpreis beträgt £ 42 Mio., zusätzlich werden Schulden von rund £ 10 Mio. übernommen. Sofern die Umsatzentwicklung in den nächsten drei Jahren besser ist als geplant, werden zusätzliche Zahlungen fällig.

Biologics ist der führende Hersteller von komplexen therapeutischen Proteinen auf Basis tierischer Zellkulturen. Das Unternehmen beschäftigt rund 300 Mitarbeiterinnen und Mitarbeiter. Es verfügt über eine Forschungs- und Entwicklungsabteilung, einen Produktionsstandort in Slough (UK) und eine neue Produktionsstätte in Pease, New Hampshire (USA). Das Unternehmen hat seit seiner Gründung vor 10 Jahren die Geschäftsaktivitäten kontinuierlich ausgebaut und besitzt heute ein bedeutendes Know-how und eigene Verfahren, um für Kunden Exklusivprodukte zu entwickeln und kommerziell herzustellen. 1996 wird *Biologics* voraussichtlich einen Umsatz von etwa 45 Mio. CHF erwirtschaften. Für die nächsten Jahre wird ein Umsatzwachstum von jährlich rund 15% erwartet.

Lonza besitzt bei der Exklusivherstellung von chemischen Produkten für weltweit führende Unternehmen der 'Life Science'-Industrie langjährige Erfahrung. Die Gründung der in den letzten Jahren laufend verstärkten Biotechnologie-Forschungsgruppe geht auf Anfang der 80er Jahre zurück. 1992 akquirierte *Lonza* ein Fermentationswerk in Tschechien.

Die *Lonza* Gruppe ist schwerpunktmässig in der Forschung, Entwicklung, Herstellung und Vermarktung einer breiten Palette von komplexen Feinchemikalien, Zwischenprodukten, Polymeren und Additiven sowie chemischen Spezialitäten tätig. Auf dem Gebiet der Exklusivsynthesen, die für die weltbesten Life Science Unternehmen durchgeführt werden, ist *Lonza* Marktleader. Die *Lonza* Gruppe verfügt über 17 Produktionsstandorte in den USA, der Schweiz, Italien, Deutschland und Tschechien und beschäftigt rund 5 000 Mitarbeiterinnen und Mitarbeiter. 1995 erzielte sie einen Umsatz von über 1,7 Mrd. CHF.

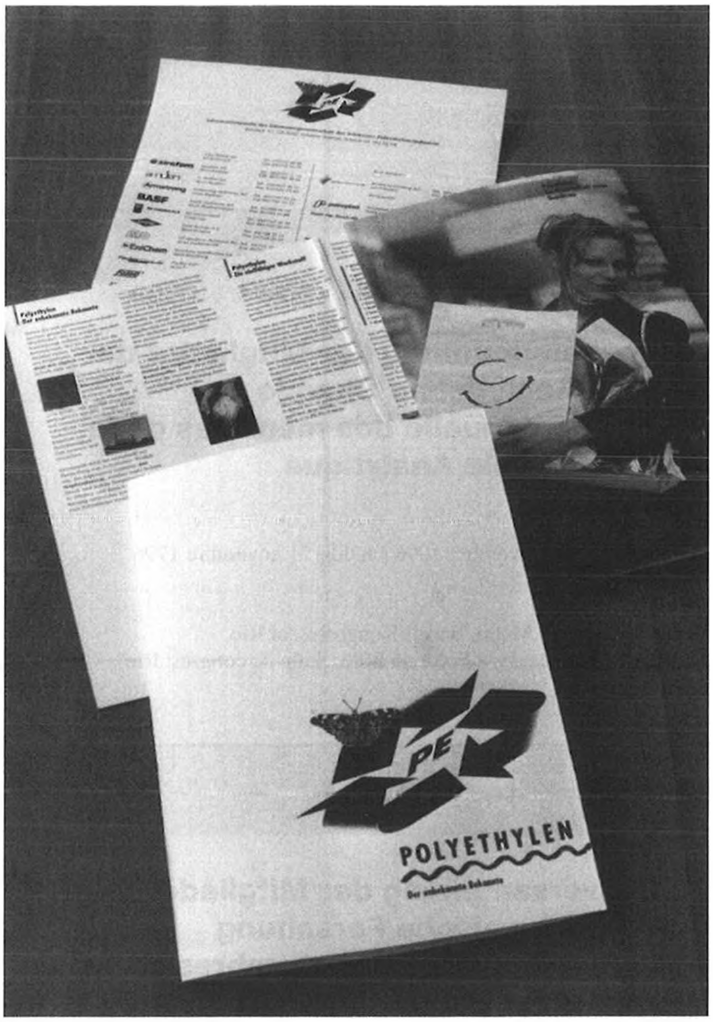
Die *Alusuisse-Lonza* Gruppe ist ein diversifizierter, internationaler Industriekonzern mit 31 000 Mitarbeiterinnen und Mitarbeitern und einem Jahresumsatz 1995 von 7,5 Mrd. CHF. Die unternehmerischen Aktivitäten konzentrieren sich auf die Bereiche Aluminium, Chemie und Verpackung und sind auf die Marktsegmente mit hoher Wertschöpfung ausgerichtet.

Weitere Auskünfte:
Dr. Walter Eschenmoser
Telefon +41 61 316 83 63
Telefax +41 61 316 82 20

Die Schweizer Polyethylen-Industrie stellt sich vor

Die Schweizer Polyethylen-Industrie stellt sich in einer neuen, reich illustrierten Broschüre vor. Die in drei Landessprachen herausgegebene Publikation vermittelt Wissenswertes über den Werkstoff Polyethylen, dessen Herstellung, Verarbeitung und Einsatz, bis hin zur Wiederverwertung respektive Entsorgung.

Die neue Broschüre wird von der Interessengemeinschaft der Schweizer Polyethylen-Industrie (IGPE), einer Vereinigung von Herstellern, Verarbeitern, Importeuren und Händlern von Polyethylen, herausgegeben. Sie soll in erster Linie einen Einblick in die Welt des Polyethylens vermitteln, eines Werkstoffes, mit dem jedermann täglich in Berührung kommt, von dem der Durchschnittsverbraucher im allgemeinen jedoch nur sehr wenig weiss. Dabei nimmt die Bedeutung von Polyethylen z.B. im Verpakkungssektor, aber auch mit Blick auf die Umweltverträglichkeit, laufend zu.



Die neue Broschüre der Interessengemeinschaft der Schweizer Polyethylen-Industrie (IGPE) ist ab sofort in drei Landessprachen erhältlich.

Die IGPE stellt die neue Broschüre interessierten Firmen aber auch Einzelpersonen, Schulen, *etc.* für deren Informationsveranstaltungen zur Verfügung. Die Publikation soll zur Verbesserung des Informationsstandes in der Bevölkerung beitragen und damit das Verständnis für den Werkstoff PE – und für den Kunststoff allgemein – erhöhen.

Die im Jahre 1992 gegründete IGPE will einen konstruktiven Dialog zwischen Produzenten und Konsumenten fördern. Durch ständige Forschung und Entwicklung sollen der Einsatz des Werkstoffes Polyethylen in der Praxis optimiert und gleichzeitig Wege zu einem sinnvollen Recycling aufgezeigt werden.

Für weitere Informationen wenden Sie sich bitte an:

Informationsstelle IGPE
Eric W. Zeller
Postfach 17
CH–8702 Zollikon-Station
Telefon: 01/392 02 08
Telefax: 01/391 38 78

Neues Forschungszentrum ICSI eingeweiht

Am 20. Juni wurde in Mulhouse, Frankreich, im Beisein von Politikern und Meinungsbildnern das neue Forschungszentrum 'Institut de Chimie des Surfaces et Interfaces' (ICSI) vom französischen Erziehungsminister *François Bayrou* eingeweiht.

Das führende Forschungszentrum, geleitet von Prof. *Jacque* *Schultz*, Direktor des Instituts, is weltweit bekannt für innovativ Forschung auf dem Gebiet der physikalischen Chemie von Oberflächen. Das Institut konzentriert sic

CHIMIA *50* (1996) Nr. 7/8 (Juli/August)

auf Molekularaspekte sowie makroskopische Eigenschaften von Verbundwerkstoffen (Komposits). Die Prioritäten der Forschungsarbeit sind:
- Adhäsion
- Oberflächenchemie
- Kolloide
- Keramik

Seit 1994 besteht zwischen dem nstitut und der Forschung und Entwicklung Schweiz der Firma *MBT Master Builders Technologies*), ein weltweit führendes Unternehmen in der Bauchemie und Tochtergesellschaft der *Sandoz AG*, eine wissenschaftliche Zusammenarbeit. Erste Resultate dieser Kooperation werden demnächst publiziert.

Für Rückfragen:
Anita Lösch
Corporate Communications
Telefon 01/438 23 34
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EURO CHLOR
REPRESENTING THE CHLOR-ALKALI INDUSTRY

Gewaltiger Chlorausstoss der Natur und seine Bedeutung für die belebte Welt

Die grösste Quelle organisch gebundenen Chlors in der Umwelt sind die Weltmeere. Mit jedem Wellenbrecher wird ein Aerosol von Meersalz erzeugt, wobei jährlich 5000 bis 15000 Mio. t Chlor in die Atmosphäre der Erde eingetragen werden. Das meiste kehrt wieder in die Ozeane zurück, aber man schätzt, dass sich 3–35% davon in Form anorganischer Chlorverbindungen verflüchtigen.

Die natürliche Rolle des Chlors in der Umwelt – ein Gebiet mit vielversprechenden Ansätzen für Sekoren wie z.B. das Gesundheitsween – ruft ein wachsendes Interesse n der Wissenschaft hervor. Die Veröffentlichung *The Natural Chemstry of Chlorine in the Environment* ‘Die natürliche Chemie des Chlors n der Umwelt’) ist von einem Gremium von zehn führenden Wissenchaftlern aus sieben Ländern verasst.

Lebende Organismen, darunter Bakterien, Pilze, Landpflanzen und Meeresorganismen, stellen mehr als 200 verschiedene chlororganische hemische Stoffe her. Meerespflanen synthetisieren mindestens 400 nterschiedliche Halogenorganika, on denen viele Chlor enthalten. ine pazifische Tangart, die besoners auf Hawaii vorkommt und essbar ist, produziert allein *ca.* 50 erschiedene Chlorverbindungen. Das Phyto-Plankton (Kleinalgen der Meere) spielt wegen seiner Verbreiung über alle Weltmeere eine wichge Rolle, während die meisten Tange vorwiegend im küstennahen Beich vorkommen.

Man kennt bisher 300 chlorhaltie Verbindungen, die von Landflanzen produziert werden. Diese ichen von einfachen Stoffen wie hlormethan, das z.B. von Pilzen zeugt wird, die die Verrottung von olz bewirken, bis zu komplexen hlorierten Polyacetylenen, die in er Gattung der Astern vorkommen. hlor kommt von Natur aus im Erdboden vor, wo es eine Schlüsselrolle beim Abbau von abgestorbenem festem Pflanzenmaterial wie Lignin spielt. Pilze, die Holz verrotten lassen, können bis zu 90% des anorganischen Chlorids, das im Holz enthalten ist, in Form von Chlormethan verflüchtigen. Dieser Vorgang macht sicher einen bedeutenden Anteil der 4 Mio. t Chlormethan aus, die jedes Jahr aus natürlichen Quellen in die Atmosphäre gelangen.

Chlor wird in der lebenden Natur für viele verschiedene Funktionen eingesetzt, so unterschiedlich wie der Reifungsprozess von Samen und der Informationsaustausch. Die Hausschabe (*Blattella germanica*) benutzt zwei chlorhaltige Steroide zur Kommunikation. In der Erbsenpflanze findet sich Chlor in einem Pflanzenhormon (Auxin), welches vermutlich die Zufuhr von Nährstoffreserven zu den Erbsensamen während der Reifung steuert. Viele chlorhaltige Naturstoffe schützen Pflanzen vor Insekten oder Pflanzenfressern. Andere spielen eine wichtige biochemische Rolle wie 3,5-Dichlorhexanophenon, das bei Schimmelpilzen die Umformung von undifferenzierten Zellen zu Sporen (Fruchtkörpern) auslöst.

Die Chlorierung ist ein natürlicher Vorgang. Im Immunsystem des Menschen hilft die Umwandlung des im Blut gelösten Salzes in aktives Chlor, Infektionen durch Mikroben, wie Bakterien und Pilze, zu bekämpfen und sogar Tumorzellen abzutöten. Viele natürliche Organochlorverbindungen werden für die menschliche Gesundheit genützt, wie die gebräuchlichen Antibiotika Chloramphenicol, Aureomycin, Griseofulvin und Vancomycin.

Zu kürzlich entdeckten natürlichen Chlororganika gehören vielversprechende Chemotherapeutika gegen Krebs, z.B. Spongistatin (ein chlorhaltiger Stoff aus einem Schwamm, der im Indischen Ozean wächst), Ansamitocin (von Felsen in einem Douglastannenwald in Oregon und von Felsen und Bäumen eines Waldes in West-Virginia isoliert) und Rebeccamycin (aus einer Bodenmikrobe in Panama). Andere natürlich vorkommende Chlorverbindungen haben ein antivirales Potential wie, z.B. Ambigol. Dies natürliche polychlorierte Biphenyl (PCB) wird aus einer blaugrünen Alge isoliert und zeigt im Labor Wirkung gegen den Aids-Virus.

Bedeutung für die Umwelt...

Mit fortschreitender Forschung über das natürliche Chlor und seine Verbindungen wird es zunehmend deutlich, dass Chlor aus industrieller Produktion nur sehr wenig zu den in der belebten Umwelt vorkommenden Mengen dieses Elements beiträgt. Organisches Material aus einer tiefen Wasserader, dessen Alter mit der Kohlenstoff-14-(^{14}C) Methode zu mehr als 35000 Jahren ermittelt wurde, enthielt doch organisch gebundenes Chlor, Brom und Jod. In einem 8000 Jahre alten Sediment aus Japan wurden polychlorierte Dibenzo-*p*-dioxine (PCDD) nachgewiesen. Organisch gebundene Halogene wurden auch in organischem Material aus Wassersedimenten gefunden, wie in einem 4000 Jahre alten Meererton und in Torf, der sich vor rund 1000 Jahren abgesetzt hatte. Bodenproben, die vor 100–150 Jahren in Grossbritannien gezogen worden waren, enthalten PCDD und polychlorierte Dibenzofurane (PCDF) in Konzentratiaonsbereichen, die rund ein Drittel der heute gefundenen Werte betragen. Auch in Gletschereis aus vorindustrieller Zeit wurden Chlororganika analytisch nachgewiesen.

Im Regenwasser, in Oberflächengewässern und im Boden kann man nur eine Minderheit des gefundenen organisch gebundenen Halogens durch die bekannten industriellen Verschmutzungen erklären. Es gibt auch deutliche Hinweise darauf, dass heute in Flüssen wie dem Rhein natürliches Chlor einen grossen Teil des organisch gebundenen Chlors ausmacht. Die Konzentrationen im Rhein sind seit 1986 um 80–90% gefallen. Obwohl somit die industriellen Emissionen in den Fluss praktisch beseitigt sind, bleibt ein niedriges konstantes Niveau von Chlororganika übrig. Die Wissenschaftler meinen, dass dieses vom organisch gebundenen Chlor im Erdboden herrührt, welches in die Oberflächengewässer ausgeschwemmt wird.

Organohalogene in der Umwelt, gleichgültig, ob sie aus natürlichen oder industriellen Quellen stammen, können selbstverständlich Grund für Besorgnisse sein. Weitere Forschungsarbeiten über die natürlichen Bildungs- und Abbauprozesse dieser Stoffe können dazu beitragen zukünftige Lösungen zu finden.

Hinweis:

Das Ziel von *Euro Chlor* ist in allen Industriezweigen die besten Sicherheits-, Gesundheits- und Umweltverfahren zu fördern (Konzept des verantwortlichen Handelns). Es wird ausserdem darauf geachtet, wichtigen Interessenverbänden ausgewogene, wissenschaftlich fundierte Informationen zukommen zu lassen, um sachlich getragene Entscheidungsprozesse zu gewährleisten. *Euro Chlor*, die alle westeuropäischen Chlorproduzenten repräsentiert, ist eine der einflussreichen Fraktionen im Europäischen Rat der Chemischen Industrie (CEFIC).

Die Broschüre ‘*The Natural Chemistry of Chlorine in the Environment*’ ist erhältlich bei:
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Neue Biotechnologie – Perspektiven für die Schweiz

Zusammenfassung des gleichnamigen Syntheseberichts des Technologie-Abschätzungs-Programms Schweiz des Schweizerischen Wissenschaftsrats (SWR).

Die Zukunft der Gentechnik in der Schweiz hängt unter anderem von politischen Entscheidungen ab. Wenn es das Ziel ist, die Gentechnik in der Schweiz sozialverträglich zu gestalten, so müssen drei Bedingungen erfüllt werden: *Mitbeteiligung* der Gesellschaft bei Entscheidungsprozessen über die Anwendung, klare *Wahlmöglichkeiten* beim Konsum sowie Verbesserung der Bedingungen zur *wirtschaftlichen Nutzung* der Gentechnik in der Schweiz. Zu diesem Schluss kommen die Autoren der Studien über Gentechnologie des TA-Programms Schweiz.

Der Synthesebericht fasst die Ergebnisse der Studien zusammen, die im Auftrag des Programms für Technologiefolgen-Abschätzung (TA-Programm Schweiz) des Schweizerischen Wissenschaftsrats (SWR) entstanden sind. Die eine (Biotechnologie-Standort Schweiz) ist den politisch-ökonomischen Rahmenbedingungen gewidmet, die andere befasste sich in sieben Teilstudien mit der neuen Biotechnologie bei Lebensmitteln. Der Synthesebericht behandelt in einem ersten Teil den Stand der Technik, die Akzeptanz und das wirtschaftliche Umfeld. In einem zweiten Teil zeigen die Autoren Wege zu einem zukunftsträchtigen und gesellschaftlich mitgetragenen Gentechnologie-Standort Schweiz auf.

Einstellung, Akzeptanz und Wissen

Die Haltung der Bevölkerung gegenüber der Gentechnologie hängt nach Einschätzung der Autoren deutlich vom Einsatzbereich ab. Anwendungen zur Medikamentenherstellung werden überdurchschnittlich gut aufgenommen. Transgene Nutztiere stehen am anderen Ende der Skala. Die Kriterien der Konsumentenseite lassen sich wie folgt zusammenfassen: Ein mit Hilfe von Gentechnologie hergestelltes Produkt muss

- auch dem Konsumenten einen deutlichen Nutzen bringen;
- gesundheitsfördernd sein;
- in der Produktion tier- und umweltgerecht und sicher sein;
- insbesondere wenn es um Lebensmittel geht, klar als solches gekennzeichnet sein, damit die Wahlmöglichkeit gewährleistet bleibt.

Unterschiede gibt es auch je nach Landesteil und Geschlecht. Frauen sind skeptischer als Männer, die Deutschschweiz gibt sich zurückhaltender als die Romandie. Prinzipielle Ablehnung aus ethischen, religiösen oder weltanschaulichen Gründen findet sich nach Erkenntnis der Autoren nur bei einem kleinen Teil der Bevölkerung.

Obwohl der Synthesebericht der Information einen hohen Stellenwert einräumt, halten die Autoren fest, dass Wissen über Gentechnologie allein nicht zwingend die Akzeptanz erhöht, sondern zu einer differenzierten Wahrnehmung führt. Ausserdem kommt es darauf an, wer informiert. Den Verlautbarungen der Industrie wird kaum geglaubt. Am meisten Vertrauen besitzen die Umwelt- und Konsumentenschutzorganisationen.

Die Schweiz als Biotechnologie-Standort

Die Bedeutung der neuen Biotechnologie/Gentechnologie für die pharmazeutisch-chemische Industrie wächst. Hält der Abwanderungstrend an, hat das schwerwiegende wirtschaftliche Folgen für unser Land. Die Gründe für die Abwanderung der Biotechnologie/Gentechnologie können aber nicht allein in der Schweiz gesucht werden. Die Autoren verweisen auch auf globale Veränderungen wie den Strukturwandel in der Pharmabranche.

Mit folgenden Linien charakterisiert der Synthesebericht die aktuelle Situation des Biotechnologie-Standorts Schweiz:

- die Biotech-Forschung der Pharmakonzerne wird teilweise ins Ausland verlagert;
- kaum Neugründungen kleiner Biotech-Firmen, z.B. für die direkte wirtschaftliche Nutzung neuer Resultate der Hochschulforschung;
- risikofreudige und wachstumsstarke Biotechnologie-Firmen fehlen weitgehend.

Als *Stärke* des Biotechnologie-Standorts Schweiz führt der Bericht das im internationalen Vergleich hohe *Niveau der Forschung* an. Zudem könnte auch die dichte *Konzentration von Pharma-Konzernen* dazu beitragen, dass neue Firmen im Bereich der Biotechnologie gegründet werden. Allerdings sind die Anstrengungen der Hochschulen, den Technologie-Transfer und die Neugründung von Firmen zu unterstützen, noch zu bescheiden. Ungünstige Finanzierungsbedingungen, unter anderem ein mangelnder Zugang zu Risikokapital, erschweren es zusätzlich, dass neue Arbeitsplätze im Bereich der Biotechnologie entstehen.

Die Autoren halten die Verbesserung der Gesamtsituation aber für wahrscheinlich. Gerade die angespannte finanzielle Lage bei Bund und Kantonen fördere den Technologie-Transfer von den Universitäten, und die gespannte Lage am Arbeitsmarkt erhöhe die Anreize zu Firmengründungen.

Anwendungen

Gesundheit und Sauberkeit haben der Gentechnologie die Türen zu den Schweizer Haushalten geöffnet. So wird der grösste Teil der Waschmittelenzyme mittels Gentechnologie hergestellt. Das zurzeit bedeutendste Anwendungsgebiet in der Schweiz ist aber die *Medizin*. 16 mit Hilfe von Gentechnologie hergestellte Wirkstoffe sind bisher zugelassen, vier davon finden sich unter den zehn Medikamenten mit den weltweit grössten Umsätzen. Gentechnologie kommt aber auch in der medizinischen Forschung sowie für neue Vorsorge-, Diagnose- und Voraussagemöglichkeiten zum Einsatz. Für Teilbereiche der Medizin stellt sie eine eigentliche Schlüsseltechnologie dar, für welche keine ebenbürtigen Ausweichmöglichkeiten in Sicht sind.

Im *Lebensmittelbereich* dagegen stehen in der Schweiz für alle derzeit möglichen gentechnischen Anwendungen technische Alternativen zur Verfügung. Zunehmend an Bedeutung gewinnt die Gentechnologie vor allem bei der Herstellung von Lebensmittelzusatzstoffen (z.B. Vitamine) und Produktionshilfsmittel (vor allem Enzyme) sowie von Nutzpflanzen.

Besonders beleuchtet, da für die Schweiz von grosser Bedeutung, wurde der Bereich *Milchproduktion und Milchverarbeitung*. Auffallend: Fast in allen Bereichen der Milchproduktion und -verarbeitung ist die Schweizer Gentechnologie bezüglich Forschung und Entwicklung gegenüber dem Ausland im Rückstand. Selbst Anwendungen, die im Ausland zum Standard gehören, spielen in der Schweiz kaum eine Rolle. Beispielsweise wird der grössere Teil der Weltkäseproduktion nicht mehr mit Lab aus Kälbermagen hergestellt, sondern mit einem gentechnisch hergestellten Enzym (Chymosin). In der Schweiz findet dieses Enzym kaum Verwendung.

Konkurrenzdruck von aussen wird nach Einschätzung der Autoren aber dennoch dazu führen, dass im Verlauf der nächsten Jahrzehnte immer mehr Produkte der neuen Biotechnologie in der Milchwirtschaft eingesetzt werden. Für den Konsum wird das möglicherweise eine verstärkte Marktteilung zur Folge haben; einerseits preisgünstigere Angebote aus Produktionen unter Anwendung von Gentechnologie, andererseits eine Stärkung des Segmentes naturnah hergestellter Milchprodukte.

Optionen

Sollen die Vorzüge der Bio- und Gentechnik wahrgenommen und ihr wirtschaftliches Potential genutzt werden, schreiben die Autoren im zweiten Teil des Syntheseberichtes unter dem Titel Optionen, dann im Rahmen der gesellschaftlichen Akzeptanz und unter Berücksichtigung des Schutzes von Bevölkerung und Umwelt. Dazu nennen sie Handlungsoptionen nach drei Gesichtspunkten:

- **Partizipation:** Mitbeteiligung verschiedener Gruppierungen an Entscheidungsprozessen über die anwendung der Gentechnik.

  Optionen:
  - Repräsentative Studie über Wahrnehmung und Akzeptanz in der Bevölkerung;
  - Institutionalisierung einer Kommunikationsplattform für die verschiedenen Gruppierungen (z.B. Konsensus-Konferenzen);
  - Aufbau eines Beratungsangebots für die F&E-Planung in Firmen unter Berücksichtigung der Konsumbedürfnisse.

- **Transparenz:** Klarheit über die Wahlmöglichkeiten beim Konsum.

  Optionen:
  - Ausdrücklicher Ausschluss der Gentechnik in den Biorichtlinien des Bundes;
  - Überprüfung und Verbesserung der rechtlichen Grundlagen für die Information durch die Bundesverwaltung;
  - Förderung der Kompetenz der KonsumentInnen-Organisationen in Bezug auf die Gentechnik.

- **Wettbewerbsfähigkeit:** Verbesserung der Bedingungen zur wirtschaftlichen Nutzung der Gentechnik in der Schweiz.

  Optionen:
  - Grundsätzliche Verbesserung jener Rahmenbedingungen, welche die Entwicklung der Biotechnologie begünstigen;
  - Intensivierung des Wissens- und Technologie-Transfers durch die Hochschulen;
  - Verbesserung der Ausbildung und der Grundlagenforschung an den Hochschulen;
  - Verbesserung der Regulierungssituation.

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Gentechnologie 1995 in der Schweiz

Jahresbericht der Interdisziplinären Schweizerischen Kommission für Biologische Sicherheit in Forschung und Technik (SKBS/CSSB).

Im vergangenen Jahr hat die Interdisziplinäre Schweizerische Kommis- ion für Biologische Sicherheit in Forschung und Technik (SKBS) vier Forschungsvorhaben zur somatischen Gentherapie sowie zwei Impfversu- he am Menschen gutgeheissen. Die Geschäftsstelle der SKBS registrierte 995 über 150 Gentechnik-Projekte. Freisetzungen von gentechnisch ver- nderten Organismen haben wiederum keine stattgefunden.

Gentherapie und Impfversuche am Menschen

Die Kommission befürwortete 1995 vier Gentherapie-Anträge. Bei drei Anträgen ging es um die Behandlung verschiedenartiger Krebskrankheiten. m vierten Fall war das Ziel, die zystische Fibrose zu behandeln. Die Kommission stimmte zudem dem ersten Schweizer Versuch mit einem DNA-Impfstoff zu. Bei diesem Projekt des Universitätsspitals Zürich andelte es sich um eine Impfung gegen Aids. Schliesslich wurde der Durchführung einer Studie mit einem gentechnisch veränderten Lebend- npfstoff gegen die Dysenterie (Bakterienruhr) zugestimmt. Eine ähnliche tudie war schon 1993 durchgeführt worden, nun soll ein verbesserter npfstoff verwendet werden. In allen sechs Projekten besteht weder für die Patienten noch für die Umwelt ein zusätzliches Risiko.

Projekte mit gentechnisch veränderten Organismen im geschlossenen ystem

Die Zahl der Arbeitsgruppen in der Schweiz, die Gentechnik-Verfahren nwenden, war 1995 weiter angestiegen und erreichte insgesamt 653, erteilt auf 15 Kantone (*Fig. 1*). Die Zuwachsrate war jedoch im Vergleich u den Vorjahren wesentlich geringer (*Fig. 2*). 28% der Projektleiterinnen nd Projektleiter arbeiten in der Industrie, der Rest an Universitäten oder an orschungsanstalten des Bundes. Projekte mit gentechnisch veränderten Organismen lassen sich jeweils aufgrund ihres Risikos bestimmten Sicher- eitsstufen zuordnen. Gentechnische Arbeiten, die mit bewährten Wirts- Vektorsystemen und Spenderorganismen aus der Risikogruppe 1 in klei- em Massstab ausgeführt werden, unterliegen keinen Auflagen. Solche rbeiten stellen nach dem Stand der Wissenschaft kein Risiko für Mensch nd Umwelt dar. Alle übrigen Vorhaben müssen dem Sekretariat der SKBS emeldet werden (*Tab.*). Die Registrierung von Projekten im kleinen Massstab ergab für 1995 in der Sicherheitsstufe 2 eine Zunahme von 99 auf 15. Auf der Sicherheitsstufe 3 erfolgten wie schon im Vorjahr nur gerade inf Projekte. Auf der höchsten Sicherheitsstufe 4 hat bis heute in der Schweiz noch nie eine gentechnische Arbeit stattgefunden. Projekte von grossem Massstab sind in jedem Fall meldepflichtig. Die SKBS registrierte deren 32 in der Sicherheitsstufe 1.

abelle. *Anzahl gentechnischer Projekte in der Schweiz 1995*

Kanton	Projekt im kleinen Massstab				Projekt im grossen Massstab			
	Risikogruppe				Risikogruppe *			
	1	2	3	4	1	2	3	4
Basel-Stadt	x	23	2	–	21	–	–	–
Bern	x	18	1	–	–	–	–	–
Freiburg	x	3	–	–	3	–	–	–
Genf	x	11	–	–	–	–	–	–
Luzern	x	–	–	–	2	–	–	–
Neuenbrug	x	1	–	–	–	–	–	–
Waadt	x	18	2	–	4	–	–	–
Wallis	x	–	–	–	2	–	–	–
Zürich	x	41	–	–	–	–	–	–
Total	x	115	5	–	32	–	–	–

= nicht erfasst

= keine Projekte durchgeführt

eisetzungen

Die Tollwutzentrale beabsichtigte, in ihrer Sommerimpfung gegen die ollwut den gentechnisch veränderten Lebendimpfstoff 'Raboral' einzu- zen.

Die Gesamtkommission stimmte der Durchführung des Versuches zu, llte aber die Bedingung, dass die Wohnbevölkerung in der Impfregion eingehend informiert würde. Schlussendlich verzichtete die Tollwutzentrale auf den Versuch, und es fanden im vergangenen Jahr keine Freisetzungsversuche mit gentechnisch veränderten Pflanzen oder Mikroorganismen statt.

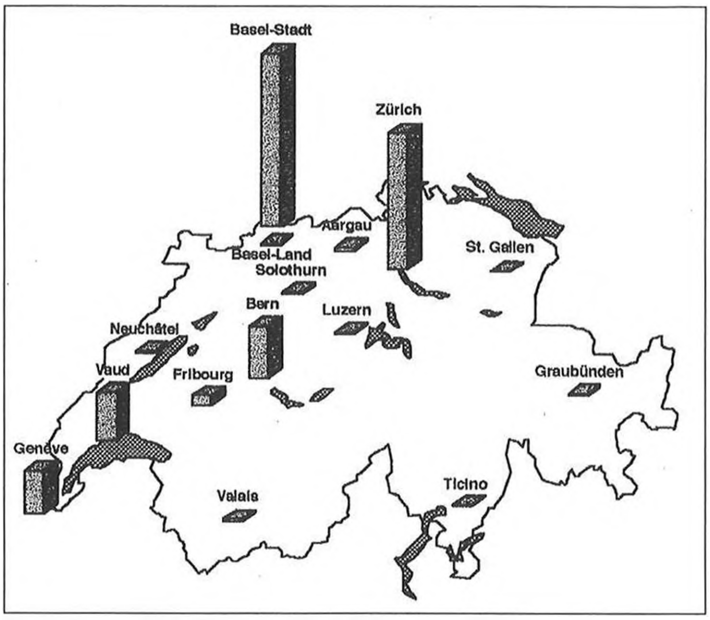

Fig. 1. *Geographische Verteilung der Arbeitsgruppen 1995*

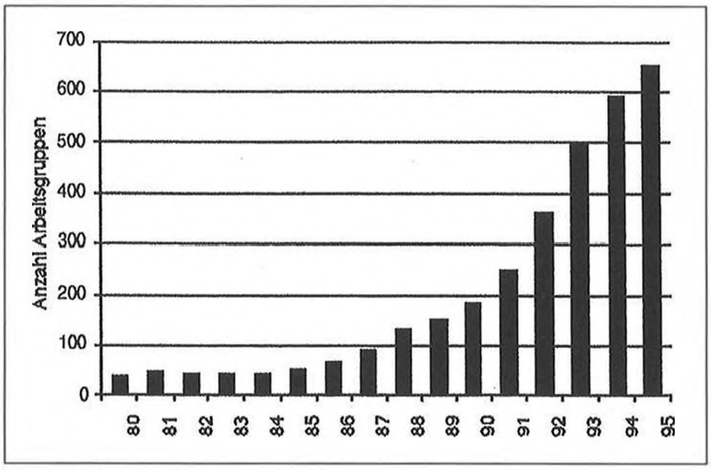

Fig. 2. *Arbeiten mit gentechnisch veränderten Organismen in der Schweiz, 1980–1995*

Regelung des Exportes von gentechnisch veränderten Organismen

Der Export von gentechnisch veränderten Organismen ist gesetzlich noch nicht geregelt. Auf Wunsch von Industrie und Forschung hat die SKBS diese Lücke vorübergehend gefüllt und eine entsprechende Regelung in ihre Richtlinien aufgenommen.

Die Kommission

Die Interdisziplinäre Schweizerische Kommission für Biologische Sicherheit in Forschung und Technik (SKBS/CSSB) besteht seit 1986 und befasst sich in erster Linie mit Fragen der Sicherheit bei Arbeiten mit gentechnisch verändertem biologischen Material. Sie wird von der Schweizerischen Akademie für naturwissenschaften und von den Schweizerischen Akademien für medizinische und für technische Wisssenschaften getragen. Der Kommission gehören 21 Vollmitglieder (neun aus Universitäten, fünf aus der Industrie und sieben aus Behörden) und acht assoziierte Mitglieder an. Ein Ausschuss leitet die Geschäfte, welche den Themenbereichen 'Experimentelle Genetik', 'Technologie' und 'Ökologie' zugeordnet sind. Prof. *Heidi Diggelmann* gab 1995 nach fünf Jahren ihr Amt als Präsidentin ab. Prof. *Riccardo Wittek* von der Universität Lausanne hat die Nachfolge übernommen.

Die Grundlage der Arbeit der SKBS/CSSB sind die seit 1992 geltenden 'Richtlinien für das Arbeiten mit gentechnisch veränderten Organismen'.

CHIMIA *50* (1996) Nr. 7/8 (Juli/August)

Die SKBS-Richtlinien (deutsche, französische und englische Version) sind beim Sekretariat der SBKS/CSSB erhältlich (c/o Dr. *Karoline Dorsch-Häsler*, Apfelbaumstrasse 43, CH–8050 Zürich, Telefon/Telefax 01/312 08 40, E-mail: skbsdorsch@access.ch). Im Rahmen der Störfallverordnung hat das BUWAL die SKBS mit der Registrierung der Gentechnik-Projekte in der Schweiz beauftragt. Die SKBS informiert die kantonalen Behörden regelmässig über die gemeldeten Projekte.

Mit der Annahme der Änderungen des Umweltschutzgesetzes und des Epidemiengesetzes am 21. Dezember 1996 durch die eidgenössischen Räte wird nun auch in der Schweiz ein gesetzliches Instrument entstehen, welches den Umgang mit gentechnisch veränderten Organismen sowohl im geschlossenen wie auch im offenen System regelt. Das Gesetz tritt voraussichtlich 1997 in Kraft. Demzufolge wird der Bundesrat eine eidgenössische Fachkommission bestellen, in welcher Schutz- und Nutzungsinteressen angemessen vertreten sein müssen. Diese eidgenössische Kommission soll die SKBS ablösen.

Dr. Karoline Dorsch-Häsler
Geschäftsführerin der SKBS

Prof. Dr. Riccardo Wittek
Präsident der SKBS/CSSB

Herausforderung im politischen Bereich:

Die Gen-Schutz-Initiative

Philippe Baechtold*

Am 25. Oktober 1993 wurde die Gen-Schutz-Initiative mit 111 063 Unterschriften eingereicht. Sie strebt nebst einer umfassenden Regelung der Missbräuche und Gefahren der ausserhumanen Gentechnologie auch eine verfassungsrechtliche Verankerung des Verbots der Patentierbarkeit von gentechnisch veränderten Pflanzen und Tieren an. Dieses Verbot würde namentlich auch dazu führen, dass die Schweiz in Widerspruch zu ihren völkerrechtlichen Verpflichtungen treten würde. Der vorliegende Beitrag fasst die Konsequenzen einer Annahme der Initiative in patentrechtlicher Hinsicht für die Schweiz zusammen.

Die Gentechnologie hat sich in den letzten Jahren zu einem bedeutenden politischen Thema entwickelt. Nicht zuletzt ist dies auch der Gen-Schutz-Initiative zu verdanken, die der schweizerischen Bevölkerung im Rahmen unserer demokratischen Mitwirkungsrechte Gelegenheit bietet, zur Zukunft der Gentechnologie in der Schweiz Stellung zu nehmen. Unabdingbare Voraussetzung für eine fruchtbare Auseinandersetzung über die Gentechnologie, die in der Bevölkerung grosse Ängste weckt, ist aber das Vorhandensein des notwendigen Wissens. Dies gilt besonders auch bezüglich der Frage der Patentierbarkeit der entsprechenden Erfindungen, an dem sich ein Teil der Gentechnologie-Diskussion entzündet. Die Gen-Schutz-Initiative sieht in der Tat unter anderem auch ein weitgehendes Verbot der Patentierbarkeit gentechnisch veränderter Tiere und Pflanzen vor.

Die patentrechtlichen Aspekte der Gen-Schutz-Initiative

Die Initiative strebt die Schaffung eines neuen Artikels 24*decies* der Bundesverfassung an. Nebst verschiedenen Gesetzgebungsaufträgen an den Bund zur Einführung von Vorschriften auf dem Gebiet der ausserhumanen Gentechnologie enthält sie drei Verbotstatbestände: Untersagt sind Herstellung, Erwerb und Weitergabe gentechnisch veränderter Tiere, die Freisetzung gentechnisch veränderter Organismen in die Umwelt und schliesslich die Erteilung von Patenten für gentechnisch veränderte Tiere und Pflanzen sowie deren Bestandteile, die dabei angewandten Verfahren und für deren Erzeugnisse. Damit soll ein weitgehendes Verbot der Patentierbarkeit im Bereich der ausserhumanen Gentechnologie auf verfassungsrechtlicher Stufe angesiedelt werden, von dem gemäss den Initianten bloss die Mikroorganismen ausgeschlossen sein sollen.

Das Patentrecht im allgemeinen ...

Das Patentrecht bezweckt die Förderung von Forschung und Entwicklung, indem es ein höchstens 20 Jahre dauerndes Ausschliesslichkeitsrecht an einer Erfindung gewährt. Erfindungen sind Lehren zum technischen Handeln; sie sind patentierbar, sofern sie neu sind, eine erfinderische Tätigkeit aufweisen und gewerblich anwendbar sind. Ein Erfindungspatent gewährt dem Berechtigten die Befugnis, Dritte von der gewerbsmässigen Benützung der patentierten Erfindung auszuschliessen. Es gewährt also nicht das positive Recht, die Erfindung auch zu benützen. Dies bedeutet, dass Entwicklungen, die vom Gesetzgeber verboten werden, nicht gestützt auf das Patent trotzdem durchgeführt werden dürfen. Das Patentrecht erfüllt zudem eine bedeutsame Offenbarungsfunktion, indem die Erfindung ab der Patenterteilung öffentlich zugänglich ist.

... und im Zusammenhang mit gentechnischen Erfindungen

Ob eine gentechnische Erfindung patentierbar ist, beurteilt sich in der Schweiz nach den allgemeinen Kriterien der Patentfähigkeit, das heisst Neuheit, erfinderische Tätigkeit und gewerbliche Anwendbarkeit. Fällt diese Prüfung positiv aus, ist weiter zu untersuchen, ob der Patentierung gesetzliche Ausschlussgründe entgegenstehen. In der Schweiz sind Tierarten und Pflanzensorten (nicht aber Tiere und Pflanzen allgemein) sowie im wesentlichen biologische Verfahren zur Züchtung von Pflanzen und Tieren von der Patentierbarkeit ausgenommen. Hingegen sind mikrobiologische Verfahren und die damit gewonnenen Erzeugnisse patentierbar. Weiter sind Erfindungen, deren Verwertung gegen die öffentliche Ordnung oder die guten Sitten verstösst sowie Verfahren der Chirurgie, Therapie und Diagnostik, die am menschlichen oder tierischen Körper angewendet werden, von der Patentierbarkeit ausgeschlossen.

Von besonderer Tragweite auf dem Gebiet der gentechnischen Erfindungen ist, nebst dem Ausschlussgrund der Tierrassen und Pflanzensorten, insbesondere der allgemeine Ausschlussgrund für die Patentierbarkeit von Erfindungen, deren Verwertung gegen die öffentliche Ordnung oder die guten Sitten verstösst. Er erlaubt eine Güterabwägung im Einzelfall und gegebenenfalls die gerichtliche Feststellung der Nichtigkeit des Patentes.

Im Erfindungsbegriff ist auch das Erfordernis der Wiederholbarkeit enthalten: Weil es sich bei der Erfindung um eine Regel handelt, muss sie auch wiederholbar sein. Dies bedeutet nicht, dass die Erfindung bis in das letzte Detail wiederholt werden können muss, aber doch, dass mindestens ein Weg angegeben wird, wie die Erfindung wiederholt werden kann. Bis zum Aufkommen der modernen Biotechnologie waren die Ergebnisse der Biologie und biologische Verfahren vom Zufall geleitet und wurden als nicht wiederholbar angesehen. Heute aber sind gentechnische Verfahren reproduzierbar, ihre technischen Ergebnisse voraussehbar. Das Bundesgericht hat dazu in einem kürzlich ergangenen Entscheid (BGE 121 III 125 ff) festgehalten, dass Technik und Biologie nicht in grundsätzlichem Gegensatz zueinander stehen. Nahrungsmittel und Arzneimittel zum Beispiel können seit langem patentiert werden.

Zusammenfassend kann gesagt werden, dass in der Schweiz und in den meisten europäischen Industrieländern Erfindungen auf dem Gebiet der Tiere und Pflanzen patentierbar sind, sofern es sich um eine technische Lehre handelt und sie den obengenannten Patentierbarkeitsvoraussetzungen genügen, ausser es handle sich um Tierrassen oder Pflanzensorten oder die Verwertung der entsprechenden Erfindungen verstosse gegen die guten Sitten oder die öffentliche Ordnung. In den USA und in Japan hingegen gehen die Patentierungsmöglichkeiten weiter. Bereits durch die Erfindungsdefinition von der Patentierbarkeit ausgeschlossen sind indessen reine Entdeckungen, z.B. Gene, wie sie in der Natur vorkommen und ohne Angabe ihres Zweckes.

Die Schweiz im Verhältnis zum Ausland

Nebst der nationalen Gesetzgebung auf dem Gebiet des Patentrechts ist die Schweiz auch an internationale Verpflichtungen gebunden. Nachstehend werden zwei für die Schweiz bedeutende Beispiele dargestellt, nämlich das Europäische Patentübereinkommen (EPÜ) und das WTO/TRIPS-

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**Korrespondenz*: P. Baechtold
Leiter Rechtsdienst Patente
Eidgenössisches Institut für Geistiges Eigentum
Einsteinstrasse 2
CH–3003 Bern

Abkommen über handelsbezogene Aspekte der Rechte an geistigem Eigentum. Erwähnt werden schliesslich auch die Entwicklungen in der Europäichen Union.

- Die Schweiz ist seit 1978 einer der 18 Vertragsstaaten des EPÜ (SR 0.232.142.2). Das Europäische Patentamt erteilt im Rahmen des EPÜ europäische Patente, die einer gemeinsamen Erteilung bei diesem Amt unterliegen. Nach der Erteilung werden die europäischen Patente von den Vertragsstaaten, in denen sie Wirkung entfalten, verwaltet. Das Europäische Patentübereinkommen, an das die Schweiz gebunden ist, enthält die gleichen Patentierungsvoraussetzungen und Ausschlussgründe wie das schweizerische Patentrecht. Obschon der Wortlaut der Gen-Schutz-Initiative nur schweizerische Patente erfasst, ist davon auszugehen, dass die Initianten auch die Erteilung europäischer Patente mit Wirkung für die Schweiz verhindern wollen.

  Bei einer Annahme der Initiative und bei Zugrundelegen eines politischen Auftrages, auch keine europäischen Patente zuzulassen, wäre das Verbot der Patentierung von gentechnisch veränderten Tieren und Pflanzen generell (mit Ausnahme der Tierrassen und Pflanzensorten), von Teilen von Tieren und Pflanzen (darunter können auch Gene fallen) sowie von nicht im wesentlichen biologischen und von mikrobiologischen Verfahren zur Züchtung von Pflanzen und Tieren (Art. 53 Bst. b EPÜ) nicht kompatibel mit dem EPÜ, da keine entsprechenden europäischen Patente mehr Wirkungen in der Schweiz entfalten könnten. Damit würde die Schweiz in Widerspruch zum EPÜ treten.

  Seit dem 1. Juli 1995 ist die Schweiz der Welthandelsorganisation (WTO) und damit auch dem in diesem Rahmen ausgehandelten Abkommen über handelsbezogene Aspekte der Rechte an geistigem Eigentum (dem sogenannten TRIPS-Abkommen) beigetreten. Die dort vorgesehenen Ausschlussgründe sind etwas weiter gefasst als im schweizerischen Recht, indem die Vertragsstaaten Pflanzen und Tiere generell von der Patentierbarkeit ausschliessen dürfen. Dennoch hätte eine Annahme der Initiative Inkompatibilitäten mit diesem Abkommen zur Folge, indem dieses das Verbot der Patentierbarkeit von nicht im wesentlichen biologischen und von mikrobiologischen Verfahren zur Züchtung von Pflanzen und Tieren (Art. 27 Abs. 3 Bst. b TRIPS-Abkommen) nicht zulässt. Eine nicht abschliessend beantwortete Frage ist, ob das TRIPS-Abkommen den Ausschluss der Patentierung von Teilen von Tieren und Pflanzen gestattet.

  Schliesslich ist auf die laufenden Arbeiten in der Europäischen Union hinzuweisen. Nach dem Scheitern eines ersten Entwurfs für eine Richtlinie zum rechtlichen Schutz biotechnologischer Erfindungen im Frühjahr 1995 hat die Europäische Kommission im Dezember 1995 einen neuen Entwurf vorgelegt. Darin werden entsprechende Erfindungen dem Patentrecht unterstellt und festgehalten, dass die Patentierbarkeit nicht allein deshalb ausgeschlossen sei, weil eine Erfindung biologische Materie betrifft. Ferner sind Pflanzen und Tiere patentierbar, sofern es sich nicht um Pflanzensorten oder Tierrassen handelt. Sollte die Gen-Schutz-Initiative in der Schweiz angenommen werden, so würde die Schweiz signalisieren, patentrechtlich einen anderen Weg als die Europäische Union gehen zu wollen.

sgewählte Fragen zur Patentierbarkeit gentechnischer findungen

Anstelle einer umfassenden Darstellung der Argumente, die von den gnern der Patentierbarkeit gentechnischer Erfindungen vorwiegend aus ischen, religiösen und umweltpolitischen Gründen vorgebracht werden, d der Gründe, die deren Befürworter aus gesundheitlicher, wirtschaftlier und politischer Motivation ins Feld führen, wird nachstehend auf zelne Fragen zur Patentierbarkeit gentechnischer Erfindungen eingegen:

das Patentrecht ein Monopolrecht?

Oft wird am Patentrecht kritisiert, es gewähre ein Monopol, das seinem aber weitgehende Rechte einräume, was sich gerade im Bereich der ebten Natur besonders nachteilig auswirke. In diesem Zusammenhang ss klargestellt werden, dass ein Patent keine positiven Rechte (zum ispiel Verfügungs- oder Benutzungsrechte) gewährt. Es erlaubt dem entinhaber lediglich, Dritten die gewerbliche Benützung der patentier- Erfindung zu verbieten. Der Patentinhaber ist dabei an die geltende Rechtsordnung gebunden und darf keinesfalls mit oder an der Erfindung Handlungen vornehmen, die ihm beispielsweise die Tierschutzgesetzgebung verbietet. Genausowenig dürfte er eine Erfindung auf den Markt bringen, wenn eine Rechtsnorm eine solche Vermarktung untersagt oder einer Zulassung unterstellt, selbst wenn sie patentiert wäre.

Können durch ein Patentierungsverbot Missbräuche der Gentechnologie verhindert werden?

Das Patentrecht ist nicht der richtige Ansatzpunkt, um die gentechnischen Aktivitäten zu kontrollieren. Zunächst ist das Patentrecht nur eine Reflexwirkung der damit geschützten Tätigkeiten; regulatorische Massnahmen müssten daher im Rahmen einer Missbrauchsgesetzgebung betreffend die gentechnischen Entwicklungen selbst getroffen werden. Im Gegenteil kann argumentiert werden, dass nur über die erteilten Patente, die ja öffentlich zugänglich sind, gentechnische Entwicklungen überprüft werden können. Weiter ist die Gentechnologie ein weltweit rasant wachsender Sektor, dessen Weiterentwicklung auf internationaler Ebene kaum durch die Abwesenheit patentrechtlichen Schutzes in der Schweiz aufgehalten werden kann. Schliesslich wird ein gentechnisch veränderter Organismus gegebenenfalls einen Schaden anrichten, ob er patentiert ist oder nicht. Aus diesen Gründen würde ein blosses Patentierungsverbot nur dazu führen, dass eine Erfindung von jeder Person vermarktet werden darf, nicht aber, dass das Risiko von Missbräuchen der Gentechnik vermindert wird.

Wird Leben patentiert?

Das Patent schützt Erfindungen. Darunter ist die technische Lösung zu verstehen, die im Rahmen der Aufgabenstellung gefunden worden ist. In bezug auf gentechnische Erfindungen bedeutet dies beispielsweise, dass ein Patent, das ein pflanzliches Gen in die Problemlösung einbezieht, nicht das Gen in seinem natürlichen Umfeld, sondern nur das in den Kontext der Aufgabenlösung gestellte Gen erfasst. Dasselbe gilt für menschliche Zellen: wird eine menschliche Zelle entnommen und damit eine Substanz gewonnen, so heisst dies nicht, dass die Menschen an den entsprechenden Zellen in ihrem Körper Patente dulden müssen. Es bedeutet einzig, dass Konkurrenten im wirtschaftlichen Wettbewerb die entsprechenden Zellen für die gewerbsmässige Benützung der patentierten Erfindung nicht verwenden dürfen. Die Rechte aus dem Patent erstrecken sich nicht auf Zellen im menschlichen Körper. Der Mensch kann nicht patentiert werden.

Verletzt das Patentrecht die Würde der Kreatur?

An sich verletzt das Patentrecht die Würde der Kreatur nicht, denn es gewährt weniger weitgehende Rechte als beispielsweise das sachenrechtliche Eigentum. Die korrekte Fragestellung muss daher vielmehr lauten, ob der gentechnische Eingriff als solcher die Würde der Kreatur verletzen könnte. Wenn der Eingriff selber so gravierend ist, dass die Verwertung in schwerwiegender Weise gegen die guten Sitten oder die öffentliche Ordnung verstösst, so soll auch kein Patent für eine solche Tätigkeit erteilt werden. Schliesslich stellt sich die Frage, ob angesichts der Ziele der Gentechnik, dem Menschen ein würdiges Dasein dank Verbesserungen in den Arzneimittel-, Lebensmittel- und Umweltsektoren zu ermöglichen, der Vorwurf der Verletzung der Würde der Kreatur durch den Schutz gerade dieser Ziele gerechtfertigt sein kann.

Behindert das Patentrecht die Forschung?

Der Aussage, dass das Patentrecht die Forschung behindert, kann nicht zugestimmt werden. Zunächst enthält das Patentrecht eine sogenannte Forschungsausnahme, die es Dritten erlaubt, auf der Grundlage der patentierten Erfindung Forschung zu betreiben und sie beispielsweise weiterzuentwickeln, sofern es sich dabei nicht um gewerbsmässige Handlungen handelt. Sollte eine Weiterentwicklung zu einer Verletzung eines bestehenden Patents führen, so hätte der Inhaber des jüngeren Patents das Recht, vom Inhaber des älteren Patents eine Zwangslizenz zu erhalten. Zweitens hindert das Patentrecht die Forschung insofern nicht, als eine Publikation der Forschungsergebnisse unschädlich ist, sobald eine Patentanmeldung vorgenommen worden ist.

Die Folgen einer Annahme der Initiative für den Standort Schweiz ...

In patentrechtlicher Hinsicht müsste die Annahme der Initiative ernste Konsequenzen für die Schweiz nach sich ziehen, indem der schweizerische Forschungs- und Produktionsstandort Schweiz empfindlich geschwächt würde. Das weitgehende Patentierungsverbot von gentechnischen Erfindungen betreffend Pflanzen und Tiere würde zum Rückgang der Forschungs- und Entwicklungstätigkeiten der Industrie, aber auch der Hochschulen beitragen. Weil die ausländische Industrie keine Patentierungsmöglichkeit in der Schweiz mehr erhielte, wären ferner gegenüber der schweizerischen Industrie im Ausland Reaktionen, ja vielleicht Retorsionsmassnahmen nicht ausgeschlossen.

... und im Rahmen ihrer völkerrechtlichen Verpflichtungen

Auf internationaler Ebene betrifft dieses Verbot in erster Linie das Europäische Patentübereinkommen (EPÜ). Da die Annahme der Initiative wohl den politischen Auftrag enthalten würde, mit dem vorgesehenen Patentierungsverbot auch europäische Patente mit Wirkung für die Schweiz zu erfassen, müsste die Schweiz im Rahmen des EPÜ zunächst eine Änderung des Abkommens anstreben und in zweiter Linie eine Sonderlösung auszuhandeln versuchen. Sollte auch das nicht gelingen, ist nicht auszuschliessen, dass die übrigen Vertragsparteien der Schweiz den Austritt aus der Europäischen Patentorganisation nahelegen würden. Aber auch bezüglich des TRIPS-Abkommens ergäben sich Probleme, weil dieses nicht so weite Ausschlussgründe von der Patentierbarkeit zulässt, als sie die Initiative vorsieht. Im Rahmen dieses Abkommens sind Retorsionsmassnahmen gegen die Schweiz nicht auszuschliessen. Schliesslich ist aber auch mit negativen Reaktionen auf bilateraler Ebene zu rechnen. In der Tat dürfte ein Patentierungsverbot in der Schweiz gerade von Ländern, die dem Patentschutz eine hohe Bedeutung beimessen, wie die USA oder Japan, als Handelsverzerrung qualifiziert werden.

Wie weiter?

Um allfällige Missbräuche der Gentechnik effizient anzugehen, müssen zunächst Forschungs- und Entwicklungstätigkeiten einer wirksamen Kontrolle durch bestehende oder neu zu schaffende Instanzen unterworfen sein. Die Patentierbarkeit entsprechender Erfindungen ist dabei in einer ersten Phase grundsätzlich zuzulassen, denn sie tritt in einem sehr frühen Zeitpunkt der Entwicklung der Erfindung ein. Sollte sich indessen im Rahmen einer Güterabwägung erweisen, dass die Verwertung der Erfindung von vornherein schwerwiegenden ethischen oder sittlichen Prinzipien zuwiderlaufen würde, könnte auf der Grundlage des patentrechtlichen Vorbehaltes der Sittenwidrigkeit und des Verstosses gegen die guten Sitten gegebenenfalls die Patentierbarkeit verneint werden. Auch später besteht die Möglichkeit, die Nichtigkeit eines bereits erteilten Patentes durch die Gerichte feststellen zu lassen. Bei der Güterabwägung ist denkbar, dass Kontrollorganismen wie Ethikkommissionen einbezogen werden.

Mit diesem Vorgehen kann dreierlei erreicht werden: die Patentierbarkeit von Erfindungen, deren Verwertung gegen die guten Sitten verstösst, kann vor der Patenterteilung verhindert, aber auch nachträglich rückgängig gemacht werden. Zweitens wird vermieden, dass die Verwertung einer Erfindung erlaubt wird, nicht aber deren Patentierung, und damit der Erfinder leer ausgeht. Schliesslich kann aufgrund einer Konkretisierung der postulierten Güterabwägung eine sachlich befriedigende Lösung für die Patentierbarkeit gentechnischer Erfindungen gefunden werden, was erlauben würde, den nicht mehr zeitgemässen, sektoriellen Patentausschlussgrund der Tierrassen und Pflanzensorten aufzuheben. Dieses Vorgehen müsste ebenfalls auf internationaler Ebene, namentlich im Europäischen Patentübereinkommen, verankert werden.

Schlusswort

Das weitgehende Patentierungsverbot der Gen-Schutz-Initiative würde der Schweiz ernsthafte Schwierigkeiten bereiten, ohne dass dem Anliegen der Initianten, allfällige Missbräuche gentechnischer Eingriffe einzudämmen, gedient wäre. Die Schweiz würde sich aussenpolitisch vermehrt isolieren und ihre eigene Wirtschaft schwächen, ohne dass im benachbarten Ausland eine ähnliche Entwicklung abzusehen ist. Es muss daher vermehrt Aufklärungsarbeit geleistet und bestehenden Ängsten begegnet werden, um zu verhindern, dass auf Jahre hinaus Gültigkeit beanspruchende, forschungsbehindernde Bestimmungen Eingang in die Verfassung finden. Es ist andererseits auch notwendig, gerade im Rahmen neuer Technologien wie der Gentechnik den betroffenen Forschungsanstalten, Hochschulen und Industrien ein gewisses Verantwortungsbewusstsein zuzubilligen. Dabei ist es durchaus angebracht, diese Veranwortungsüberlassung mit verbesserten Kontrollmechanismen auf der Stufe der Entwicklung und Verwertung der betroffenen gentechnischen Entwicklungen zu begleiten. Damit kann am richtigen Ort angesetzt werden, ohne zugleich das Kind mit dem Bad auszuschütten. Der Weg in die Zukunft kann nicht darin bestehen, jeder neuen Technologie und ihren Schutzmöglichkeiten absolute Verbote entgegenzusetzen. Wir sollten vielmehr danach streben, gangbare Lösungen im Rahmen anerkannter Leitplanken zu finden.

Tagungen, Veranstaltungen, Weiterbildung

ANAKON '97

6.–8. April 1997 in Konstanz

- Gesellschaft Deutscher Chemiker, Fachgruppe Analytische Chemie
- Österreichische Gesellschaft für Analytische Chemie der Gesellschaft Österreichischer Chemiker
- Sektion Analytische Chemie der Neuen Schweizerischen Chemischen Gesellschaft

Vorträge
Aus der Breite und Vielfalt der Analytik werden aktuelle Schwerpunkte ausgewählt:

- Möglichkeiten und Probleme bei der Entwicklung von analytischen Geräten
- Neuere methodische Entwicklungen und deren Anwendungen in der Massenspektrometrie (insbesondere weiche Ionisierungstechniken)
- Analytik und Steuerung von chemischen sowie biotechnologischen Prozessen
- Analyse und Charakterisierung von Biopolymeren

Forum Analytikum
Das Forum Analytikum gibt dem akademischen Nachwuchs Gelegenheit, seine Arbeitsgebiete und Forschungsergebnisse vorzustellen.

Anfragen an:
GDCh, Abt. Tagungen/ANAKON '97
Postfach 900440
D–60444 Frankfurt am Main
Tel. (069)7917-358/-360/-366
Fax (069)7917-475

Studenten im wissenschaftlichen Austausch

Vom 4.–6. Januar 1995 fand der 4. Workshop des *Fördervereins Chemie-Olympiade e.V.* für Studenten, Doktoranden und Mitglieder des Vereins in Würzburg statt. Voraussetzung für die Teilnahme an dem Workshop war lediglich, ein wenig Faszination für Chemie mitzubringen. Interessierte aus dem gesamten deutschsprachigen Raum (Österreich, Deutschland, Schweiz) waren nach Würzburg gekommen. Kernpunkt der Veranstaltung war die Vortragsreihe der Teilnehmerinnen und Teilnehmer am Freitag und Samstag.

Wollten Sie immer schon wissen was spektrales Lochbrennen ist, ode was für faszinierende Eigenschaften Tenside aufweisen? Solche un viele weitere Vorträge hielten die i der Regel sehr jungen Teilnehmerinnen und Teilnehmer. Mit den Thema 'Kolloide' führte *Franzisk Gröhn* vom Max-Planck-Institut fü Kolloidforschung, Berlin-Teltow, i die Welt in Nanometerdimensione ein. Ganz andere 'Welten' berührt *Gunnar Jeschke*, ETH-Zürich, un *Thomas Fuhrmann*, Universitä Marburg, mit ihren themenübergreifenden Vorträgen 'Sind Rationalitä

)ie Teinehmerinnen und Teilnehmer des 4. Workshops in Würzburg

ınd Spiritualität geborene Feinde – lie Weltbilder des Buddhismus und ler Quantenmechanik' und 'Alchenie: Geschichte – Symbolik – Myhos'. *Florian Heupel*, Merton Colege, war extra aus Oxford angeeist, um den Weg zur biomimetichen Synthese der Manzamin-Alaloide den Teilnehmerinnen und 'eilnehmern des Workshops aufzueigen.

Kein Wunder, dass alle von dieem vielfältigen Programm begeitert waren! Die Diskussionsbereitchaft und Offenheit der Teilnehıerinnen und Teilnehmer war beeits am ersten Abend sehr gross, nachdem sich jeder in einer geschlossenen Runde von etwa 40 Personen vorgestellt hatte. Abgerundet wurde das Programm durch einen Bericht über die Chemie-Olympiade 1995 von Chemie-Olympiade-Teilnehmern sowie den Delegationsleitern.

Möchten Sie auch beim nächsten Mal dabei sein? Dann merken Sie sich jetzt schon das erste Januarwochenende 1997 vor. Der Schriftführer des o.g. Vereins, *Christoph Kiener*, Marbachstrasse 3, D-81369 München, schickt Ihnen gerne weitere Unterlagen, auch das Vortragsprogramm über den beschriebenen Workshop.

'aul Scherrer Institut

2. PSI-Tagessymposium Elektrochemische Energiespeicherung

aum WLGA/E26/28, PSI-West, Villigen
l. September 1996, 10.30–16.15 Uhr

hema: Bipolarer Zellenbau

Die bipolare Zellenanordnung in Elektrolyseapparaturen, Brennstoffzeln, Batterien und Kondensatoren erlaubt eine kompakte Bauweise mit heblichen Gewichts- und Volumeneinsparungen. Sie ermöglicht auch das rbeiten mit höheren Spannungen, was der Umrichtertechnik entgegenımmt. Trotzdem ist dieses Konzept bis jetzt nur in wenigen elektrochemihen Speichern und Wandlern zur Anwendung gekommen. Die Thematik :s bipolaren Zellenbaus wird am bevorstehenden 12. Tagessymposium sführlich diskutiert.

'ogramm

.30–10.35	Begrüssung
.35–11.00	Bipolare Zellen für die Elektrochemieprojekte am PSI Dr. *O. Haas*, PSI
.00–11.35	Fundamental Aspects and Engineering Concepts of Bipolar Electrochemical Cells Prof. Dr. *F. Walsh*, University of Porthsmouth
.35–11.45	Diskussion
45–12.10	Kaffeepause
12.10–12.45	Materialprobleme des bipolaren Bleiakkumulators Prof. Dr. *J. Garche*, ZSW, Ulm
12.45–12.55	Diskussion
13.00–14.10	Mittagessen im Personalrestaurant Oase
14.15–14.50	Bipolare Konzepte für PEM-Brennstoffzellen Dr. *M. Waidhas*, *Siemens AG*, Erlangen
14.50–15.00	Diskussion
15.00–15.25	Kaffeepause
15.25–16.00	Bipolare Zellen für die elektrochemische Synthese Dr. *P.M. Bersier*, Riehen
16.00–16.10	Diskussion
16.10–16.15	Schlussbemerkungen
Organisation:	Dr. *O. Haas*
Anmeldungen:	Frau *U. Grütter* Paul Scherrer Institut CH-5232 Villigen PSI Fax 056/310 21 99 E-mail: ursula.gruetter@psi.ch

FECS
Federation of European Chemical Societies

Working Party on Food Chemistry

Eingereicht von Prof. Dr. *R. Amadò*, nationaler Delegierter

EuroResidue III – Third Conference on Residues of Veterinary Drugs in Food (FECS No. 213)

Veldhoven (The Netherlands), 6–8 May 1996

In 1990 and 1993, the EuroResidue I and II conferences were organized in The Netherlands with the aim to cover all aspects related to residues of veterinary drugs with special emphasis on recent developments and applications of various analytical techniques. The WPFC decided that a third EuroResidue conference should be held in 1996, again in The Netherlands.

The scope of ER III was broader than in 1990 and 1993, as a result of the cooperation with the EU Community Reference Laboratories for residues (CRLs) and with Prof. *C. Van Peteghem* who organized the Ghent conferences on anabolics in 1988, 1990, 1992, and 1994. Anabolic and other growth promotors were included now, and much attention was focused upon quality assurance in inspection systems. The last-mentioned field was highlighted by several speakers from the European Commission and from the CRLs. Apart from this, experts from the USA and Canada were invited to report on the way in which drug residue monitoring is planned and performed overseas.

Nearly 200 abstracts were submitted to the Scientific Committee of the conference, of which 165 appeared in the programme either as an oral or as a poster presentation. About 45 presentations were devoted to anabolics, corticosteroids and beta agonists. The majority of the contributions, however, reported studies on antibacterial drugs. Like in the other conferences, considerable attention was paid to pharmacokinetic aspects as well. The large amount of contributions stressed the function of the EuroResidue conferences as a forum where all aspects regarding veterinary drug residues can be discussed and information can be exchanged.

The conference, which attracted 388 subscribers from many countries in and outside Europe, was opened by Mrs. *Erica Terpstra*, the Netherlands State Secretary of Health, Welfare, and Sports. She stressed the need for international cooperation with regard to the protection of public health, to which the EuroResidue conferences also contribute.

The conference was shaded by the decease of Dr. *Nel Haagsma* who was the driving force behind the EuroResidue conferences. She was commemorated with a moment of silence.

Seven speakers were invited to present their view on the following topics: Antimicrobials – a strategy for linking screening and confirmatory methods; Recent develoments in methods for residue control of some growth promoting substances; The use of *in vitro* systems in metabolism and safety studies; MS-MS – applications and tentative quality criteria; Bound residues – developments on their release from matrices and methods of analysis; Biosensors and their potential applications; and Analysis of drug residues in fish. Further, the programme included a plenary workshop on validation and recovery, and a general discussion on consumer perception of residues and on self-control systems. Reports of these discussions will be published as an appendix to the Proceedings.

It was agreed that the next EuroResidue conference will be held in 2000, again in The Netherlands, and that the WPFC will contribute to the Ghent conference which is scheduled in 1998 in Bruges. It was also agreed that the EuroResidue conferences and the Ghent conferences will be held alternately every two years. The Proceedings of the conference (ISBN 90-6159-023-X), consisting of two volumes with in total 1000 pages, can be regarded as a document that provides ample information on a number of topics with respect to veterinary drug residues in food of animal origin. They contain all contributions to ER III, author and subject indexes and the programme. Contributions are listed alphabetically but, for convenience's sake, are also classified into nine categories.

Copies of the Proceedings can be obtained by deposition of NLG 125, plus NLG 15 for transfer costs, to the RSBO Bank, De Bilt, The Netherlands (account number 30.83.85.217 in the name of *A. Ruiter* inz. Proceedings EuroResidue). After receival of this sum the Proceedings will be mailed to the address given in a separate letter. A limited number of the Proceedings of EuroResidue II is still available for which an additional NLG 75 have to be paid.

Berichterstatter: Prof. Dr. *A. Ruiter* (Universität Utrecht, NL)

Ehrungen

Prof. Dr. *Vladimir Prelog*, *Nobel*-Preisträger für Chemie des Jahres 1975, erhielt von der Universität Sarajevo den Titel eines Ehrendoktors. Prof. *Prelog* wurde 1906 in Sarajevo geboren und lehrte von 1942 bis 1976 an der ETH-Zürich Organische Chemie. Die Universität Sarajevo ehrt *Prelog* 'für seinen ausserordentlichen Beitrag an die Wissenschaft allgemein, an den Fortschritt der Wissenschaften an der Universität Sarajevo sowie an die moralische Unterstützung und an die Wahrung der Integrität der Bürgerschaft der Republik Bosnien und Herzegowina'.

Bücher

Bei der Redaktion eingetroffene Bücher

'Bestimmen der Brenn- und Explosionskenngrössen von Stäuben'
ISSA Prevention Series No. 2016 (G)
Internationale Sektion der IVSS für Maschinensicherheit
D-68165 Mannheim, 1995

Neue Mitglieder

Neue Schweizerische Chemische Gesellschaft

Meier, Roland, 3008 Bern

Sauter, Guido, 3005 Bern

Schmid, Gabrielle, 1297 Founex

Senn, Hans Martin
8173 Riedt-Neerach

Die Neue Schweizerische Chemische Gesellschaft
trauert um ihr Ehrenmitglied

Tadeus Reichstein

20.7.1897–1.8.1996

Eine Würdigung des Verstorbenen wird in einer späteren
Ausgabe erfolgen

Wir trauern um unseren hochgeschätzten Kollegen
und ehemaligen Institutsvorsteher

Tadeus Reichstein

Prof. Dr. ing., Dr. pharm. h.c., Dr. sc. techn. h.c.
Nobel-Preisträger für Medizin 1950

der in seinem 100. Lebensjahr am 1. August verstorben ist.
Wir werden dem Verstorbenen ein ehrendes
Andenken bewahren.

Die Dozenten, Assistenten und Mitarbeiter
des Instituts für Organische Chemie der Universität Basel

CHIMIA-REPORT

Sehr geehrte Inserenten

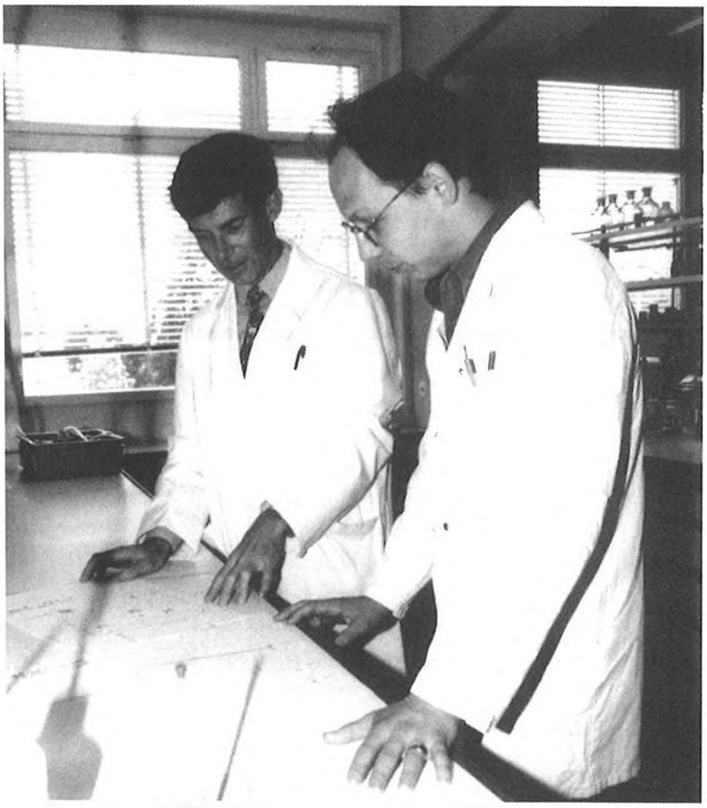
Bitte senden Sie Ihre Beiträge für diese Rubrik ausschliesslich an *ofa*Zeitschriften, CHIMIA, Sägereistrasse 25, CH–8152 Glattbrugg.

Besten Dank!

ReseaChem GmbH – ein Kurzporträt

Kaum ein Gebiet der Chemie hat in den letzten Jahren eine so innovative Phase durchgemacht wie die instrumentelle Analytik. Die *ReseaChem GmbH* ist eine junge dynamische Firma, die Dienstleistungen auf dem Gebiet der instrumentellen Analytik anbietet, mit dem Ziel, dem Kunden so nahe wie möglich zu stehen. In diesem Sinn gründeten die beiden heutigen Geschäftsführer *Stefan Berger* und *Franz Baumberger* die *ReseaChem GmbH* mit Sitz in Burgdorf.

Analytik im weitesten Sinne beherrscht unseren Alltag im privaten wie im Geschäftsbereich. Analytik verschafft uns Sicherheit und erlaubt uns, in unserer Umwelt zu agieren, statt nur zu reagieren. Die *ReseaChem GmbH* begegnet diesem Bedarf durch das Angebot der Auftragsuntersuchung. Hier werden organische Analysen angewendet, um Substanzstrukturen aufzuklären und/oder Inhaltstoffe von Proben qualitativ/quantitativ zu bestimmen. Auf Wunsch wird auf der Basis der Messergebnisse eine Dokumentation erstellt, die neben den Resultaten auch eine Bewertung der Daten, eine Interpretation derselben und Vorschläge zur Umsetzung beinhaltet.



ranz Baumberger (links) und Stefan Berger (rechts) bei der Auswertung von Dienstleistungs-^{1}H-NMR-Spektren

Die *ReseaChem GmbH* entstand Anfang 1996. Die immer häufiger gestellten Anfragen nach Dienstleistungsaufträgen an die Abteilung Chemie der Ingenieurschule Burgdorf konnten dadurch ausgegliedert werden. Das Dienstleistungsangebot der *ReseaChem GmbH* hat zum Ziel, den Unternehmen der Region Bern–Mittelland–Burgdorf–Emmental Analysemöglichkeiten und Beratungs-Know-how anzubieten. Die junge Firma hat sich in die Räumlichkeiten und den Gerätepark der ISB Abteilung Chemie eingemietet. Durch diese enge Zusammenarbeit und die breitgefächerte Ausbildung der *ReseaChem*-Mitarbeiter wird grösstmögliche Verlässlichkeit der Resultate geboten. Das kreative Umfeld trägt somit zu originellen und optimierten Lösungsvorschlägen für unsere Kunden bei. Durch gute Kundenbetreuung und eine aktive Beratung will die *ReseaChem GmbH* massgeschneiderte Problemlösungen offerieren.

Das Dienstleistungsangebot der *ReseaChem GmbH* unfasst insbesondere die Schwerpunkte instrumentelle Analytik und reaktionstechnische Untersuchungen.

Zu den Kunden der *ReseaChem GmbH* zählen heute bevorzugt kleine und mittlere Unternehmen (KMU), die einerseits Routineuntersuchungen in Auftrag geben, andererseits aber auch einmalige Auftragsuntersuchungen erteilen. Unternehmen wie die *ReseaChem GmbH* sind letztlich eine Unterstützung für den Innovationsstandort Schweiz und im besonderen für den Standort Bern-Mittelland. Durch Kreativität und Schnelligkeit bei der Problemlösung will die junge Unternehmung die Effizienz einbringen, die für ihre Kunden überlebenswichtig ist. Wir stehen am Anfang unseres Weges – begleiten Sie uns!

- ReseaChem GmbH
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  Pestalozzistrasse 16
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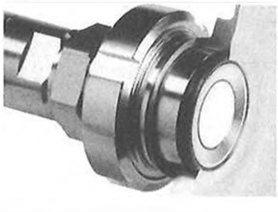
  Telefon 034 424 03 10
  Telefax 034 424 03 12

Leserdienst Nr. 10

Messevorschau SAW 1996
VEGA Messtechnik AG

Die VEGA Messtechnik AG zeigt auf der SAW in Basel vom 17.–20.9.96 einen Querschnitt aus den Programmbereichen Füllstand und Druck. Es werden viele Neuheiten vorgestellt. Vor allem wurden viele bewährte Messmethoden durch neue Technologien in ihren Einsatzbereichen erweitert.

Das neue PC-Bedienprogramm VEGA Visual Operating mit welchem die Programmierung von verschiedenen Geräten der unterschiedlichen physikalischen Messmetho-



den wie Radar, Ultraschall, Druckaufnehmer, etc. auf einfache und gut verständliche Art möglich ist. Über die Windows-Oberfläche können so Grundeinstellungen, Eichungen, Messwertkontrollen und Korrekturen vorgenommen werden.

Im weiteren werden die neuen Auswertegeräte der Bauformen 600 mit Aufbaugehäuse und Bauform 500 in 19" Europakartenformat vorgestellt. Auch kann die neue Auswertezentrale VEGALOG 571 in Funktion beobachtet und getestet werden. Lassen Sie sich von den intelligenten Möglichkeiten überzeugen.

Bei den Schwingstabgrenzschaltern VEGASWING ist vor allem für die chemische Industrie eine neue emaillierte Version für den Einsatz in sehr aggressiver Atmosphäre zu sehen. Damit ist der Einsatz als Überfüllsicherung in diesen Medien und an emaillierten Tanks kein Problem mehr.

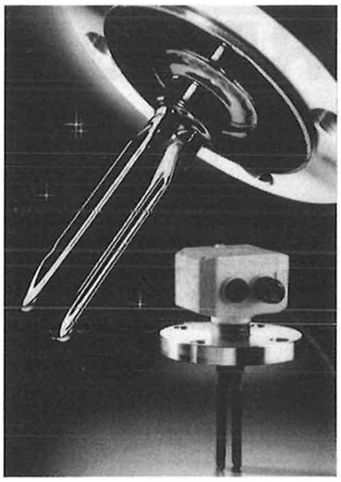
Mit dem VEGASWING 70 bietet VEGA einen sehr kompakten und preiswerten Flüssigkeitsgrenzschalter an, der für die Zukunft die Sorgen mit Schwimmschaltern vergessen lässt.

Bei der immer wieder für viele Einsätze zuverlässigen und preiswerten kapazitiven Messmethode, wird ein komplett neu überarbeitetes Sondenprogramm gezeigt. Duch ein verbessertes Messverfahren, sind jetzt viele Messungen bei anhaftenden Produkten möglich, die bisher problematisch waren.

Im Bereich Radar und Ultraschall sind die neuen Ausführungen der Geräte mit der Echofox-Software zu sehen. Dazu komen bei den Radargeräten die neuen, sehr attraktiven Gehäuseversionen, womit jetzt auch dem Einsatz in der gekapselten Ex-Version, wo dies erwünscht wird, nichts mehr im Wege steht.

Auch das neue Programm der hydrostatischen Druckaufnehmer, wo nun alle Aufnehmertypen je nach Einsatzgebiet mit keramischer oder metallischer Messzelle ausgerüstet werden, ist auf der SAW zu sehen. Vor allem sind dabei die neuen Anschlussversionen für die Papierindustrie und den Lebensmittelbereich zu erwähnen.

Im Prozessdruck sehen Sie verschiedene Typen des neuen VEGABAR 20. Verschiedene Prozessanschlüsse und eine Vielzahl von Möglichkeiten in der Auswertung machen den VEGABAR zum anwendungsspezifischen Gerät. Aus dem Baukastensystem kann der Kunde den genau für seinen Einsatzfall richtigen Typ der VEGABAR zusammenstellen.



Sicher durch Email

Für den Einsatz in besonders aggressiven Medien bietet die Firma VEGA Messtechnik AG den Vibrationsgrenzschalter VEGASWING jetzt auch mit hochbeständiger Emaillierung an.

Alle medienberührten Teile sind mit einer Emailschicht überzogen, die gegen nahezu jedes Medium resistent ist. Durch seine hohe Stabilität ist Email unempfindlich gegen stark oxidierende oder reduzierende Einwirkungen. Ausserdem besitzt das Material hohe Schlag- und Verschleissfestigkeit sowie Temperaturschocksicherheit.

Typische Anwendungsbereiche für den emaillierten VEGASWING sind z.B.: Hydrolyse, Chlorierung, Sulphorierung, Nitrierung, Bromverarbeitung, Rauchgasentschwefelung und die Chrom- oder Schwefelsäure-Rückgewinnung.

Email ist zudem leicht keimfrei zu halten und wirkt durch seine hohe Oberflächengüte antiadhäsiv. Aus diesen Gründen eignet sich dieser Werkstoff auch für die Lebensmittel- und Pharmaindustrie. Der emaillierte VEGASWING ist auch für den Einsatz in explosionsgefährdeten Bereichen der Zone 0 oder als Überfüllsicherung nach WHG und VbF zugelassen. Durch diese Weiterentwicklung kann der tausenfach bewährte Vibrationsgrenzschalter auch Füllstandmessaufgaben in problematischen Medien lösen.

Wer sich über den neusten Stand der Technik im Füllstand und Druck orientieren will, ist in der Halle 214, Stand F73 der VAGA Messtechnik AG genau am richtigen Ort. Lassen Sie sich die vielen Neuheiten vorführen und Sie sehen, dass Sie diese Technologien, an vielen Orten, zu Ihrem Vorteil einsetzen können.

- VEGA Messtechnik AG
  CH–8330 Pfäffikon

Leserdienst Nr. 11

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CHIMIA-Leserdienst 7/8 – 96

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Ihre Anfragen werden sofort an die einzelnen Firmen weitergeleitet, die Ihnen die gewünschten Auskünfte gerne zur Verfügung stellen werden.
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ProMinent Ex-Pumpen jetzt auch mit Schlagwetterschutz

EX-Schutz hört nicht beim Antrieb auf. Die neuen EXtronic® Magnetdosierpumpen von ProMinent haben rundum EX-Schutz und können in Zonen mit Schlagwettergefahr eingesetzt werden. Sie erfüllen alle Vorgaben für den EX-Schutz der Gruppe I. Der Vorteil dieser Pumpen liegt darin, dass die gesamte Pumpe, inklusiv des Dosierkopfes, EX-geschützt ist und BVS-Zulassung besitzt. Das Gehäuse ist für diese Ausführung aus Bronze, Gefahrenmomente der Funkenbildung sind somit ausgeschlossen. Die Antriebsspannung beträgt in diesem Bereich 500 V und nicht wie üblich 230 V. Die gesamte Pumpe ist in der Schutzart IP 65 ausgelegt. Der Eintritt von Staub und Strahlwasser ist nicht möglich.

Die neuen ProMinent EXtronic® Dosierpumpen basieren wie ihre Schwestermodelle der EX-Gruppe I, auf der vieltausendfach bewährten Kurzhub-Magnet-Membran-Dosierpumpe von ProMinent. Ihre mechanischer Aufbau ist denkbar einfach, da der wartungs- und verschleissfreie Magnetanker das einzig bewegte Teil des Antriebes ist. Dieser lenkt dierekt die Dosiermembrane bis maimal 1,25 mm aus. Der Leistungsbereich reicht von 0,23 l/h bis 60 l/h bei deinem Gegendruck bis 25 bar.

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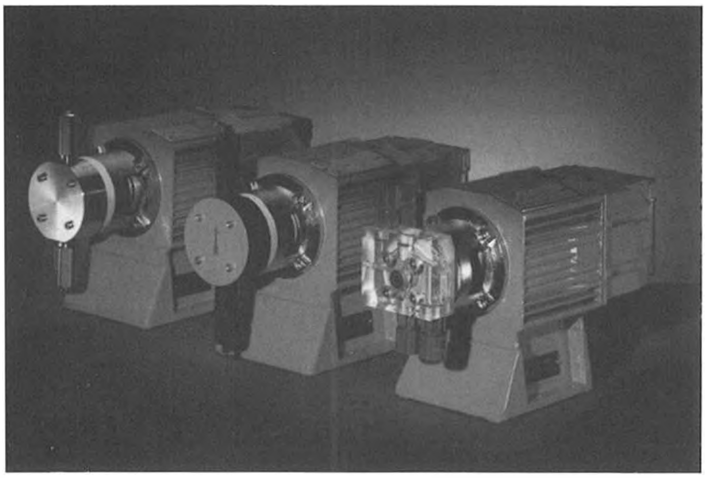
Die Ansteuerung dieser Pumpen kann unter drei Varianten gewählt werden. Erster Steuerungstyp 'Intern': Hublängeneinstellung 1:10, Hubfrequenzeinstellung 1:25, Gesamteinstellbereich 1:250, zweiter 'extern Contact': 'Hublängeneinstellung 1:10, Hubfrequenzregelung in Abhängigkeit von externen Schaltkontakten; dritter 'Analog': ebenfalls Hublängeneinstellung 1:10, Hubfrequenzregelung proportional zu Analogsignalen 0/4-20 mA. Die Fremdansteuerungs-Varianten sind in den Ausführungen 'eigensicher' und 'nicht eigensicher' erhältlich.

- ProMinent Dosiertechnik AG
  Trockenloostrasse 85
  Postfach
  CH-8105 Regensdorf/Watt
  Telefon 01 870 61 11
  Telefax 01 841 09 73

Leserdienst Nr. 12



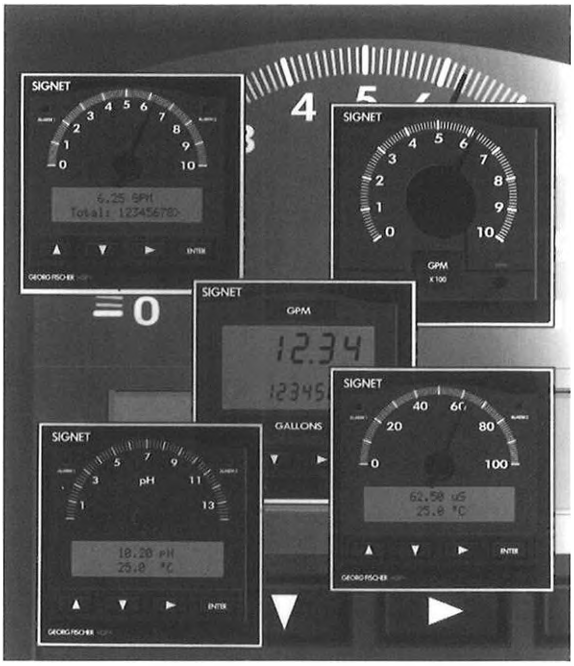
SIGNET Seroe 5000 – Technik par excellence

Die neue SIGNET Serie 5000 ietet innovative Anzeige- und Auswertetechnik par excellence. Messwerte verarbeiten, anzeigen, überwachen und übertragen sind Aufgaben, ie in verschiedenen Einrichtungen nd Anlagen in der Industrie vielfach vorkommen. Die Auslegung von Mess-Systemen ist von zentraler edeutung, und die Anforderungen n Messgeräte vom 'Alleskönner' s zum einfachsten Gerät werden etig erhöht.

Die neuen SIGNET Serie 5000 nzeigegeräter wurden unter diesen spekten entwickelt und präsentieren eine Familie von Anzeigegeräten r Durchfluss, pH/Redox und Leithigkeit. Diese neue Anzeigegeräte-Familie besticht durch ein einzigartiges Design, ausgereifte Technik, einfachste Handhabung und universelle Einsatzmöglichkeiten.

Die Innovation in der Darstellung von Prozesswerten

Ob Analog- oder Digitalanzeige ist nicht mehr eine Frage des Geschmacks eines Anlagenbauers oder Anwenders: die SIGNET Serie 5000 bietet beide Anzeigen im gleichen Gerät! Schnelle Änderungen und Tendenzen im Prozess werden durch die Analoganzeige unverzüglich angezeigt, und diese Information kann durch den roten Zeiger auch von weiterer Entfernung abgelesen werden. Genauste Ablesung des Messwertes wird durch die digitale Anzeige präsentiert. Weitere wichtige Informationen über den Prozess können über Tastendruck an die Digitalanzeige aufgerufen werden.



SIGNET Serie 5000 – für einfache bis komplexe Messaufgaben

Der logische Aufbau der SIGNET Serie 5000 bietet Lösungen für einfache wie auch komplexe Messaufgaben. Für Anwendungen, in denen beispielsweise der Durchfluss angezeigt werden soll, jedoch keine weiteren Ausgangssignale gebraucht werden, steht ein netzunabhängiges, analoges Anzeigegerät oder ein batteriegespeistes, digitales Durchfluss-Anzeigegerät mit Zähler zur Verfügung.

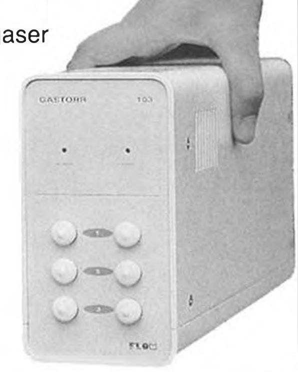
Für komplexere Messaufgaben mit Regel- und Überwachungsaufgaben bilden die SIGNET Serie 5000 Anzeigegeräte mit integrierten Grenzwerten, digitalen und analogen Ausgängen die idealen Komponenten. Einfachste Bedienbarkeit durch die frontseitige Tastatur und Flexibilität in der Gerätekonfiguration erlauben die individuelle Verknüpfung mit aussenstehenden Komponenten oder übergeordneten Systemen.

Einfache Installation von Mess-Systemen – vielfältige Anwendungen

Mess-Systeme von SIGNET sind einfach und schnell zu installieren, und die Inbetriebnahme erfolgt dank modernster Technologie innert weniger Minuten. Die neue SIGNET Serie 5000 fügt sich nahtlos in das bestehende Sortiment von Sensoren und Transmittern ein und bildet eine weitere wichtige Komponente leistungsfähiger Mess-Systeme von Georg Fischer. Erfolgreiche Anwendungen sind daher in vielen Industrien zu finden: Wasseraufbereitung, Verteilnetze von Trinkwasser, Schwimmbadanlagen, chemische Industrie und Landwirtschaft, um nur einige wenige zu nennen.

- Georg Fischer
  Rohrleitungssysteme AG
  CH-8201 Schaffhausen
  Telefon 052 631 11 11

Leserdienst Nr. 13



Meeting point Rhine Valley.

- Internationaler Kongress mit hochkarätigen Referenten
- Kombinierte Eintrittskarten für Messe und Kongress
- Erweitertes High-Tech-Angebot im Bereich Analytik und Biotechnologie

Infos neu über Internet:
http://www.messebasel.ch/ilmac
e-mail:
ilmac@messebasel.ch

The picture shows a combination of biomolecular and semiconductor structures.

Internationale Messe und Kongress für chemische Technik, Analytik und Biotechnologie.

19.–22. Nov. 1996

ilmac 96

Messe Basel.

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so weit das Auge reicht.

Rufen Sie uns an

RC G

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Switzerland

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