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CHIMIA

Assemblée d'automne 1997
Herbstversammlung 1997

NEUE SCHWEIZERISCHE CHEMISCHE GESELLSCHAFT
NOUVELLE SOCIETE SUISSE DE CHIMIE
NEW SWISS CHEMICAL SOCIETY

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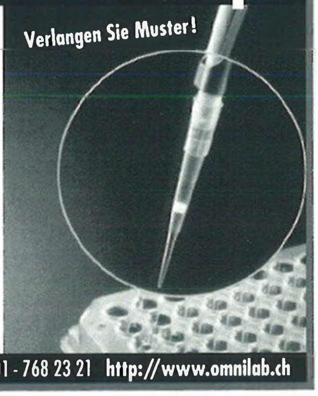
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CHIMIA *51* (1997) Nr. 8/9 (August/September)

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PREISAUSSCHREIBUNGEN

NSCG/NSSC/NSCS

NFORMATION

CHIMIA-REPORT

CHIMIA

Journal for Chemistry
covering scientific, industrial, technological, ecological, social, political and economical aspects

Official Membership Journal
of the New Swiss Chemical Society (NSCS) and its sections

Sections
Chemical Research, Medicinal Chemistry, Industrial Chemistry, Analytical Chemistry

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für Wissenschaft, Technik und Wirtschaft im Bereich der Chemie

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Sektionen
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SSCI	Swiss Soc. of Chemical Industries
SGLUC	Swiss Soc. of Food and Environmental Chemistry
SGMS	Swiss Group for Mass Spectrometry
SGPP	Swiss Photochemistry and Photophysics Soc.
SVCT	
VSN	Swiss Association of Science Teachers

Kollektivmitgliedgesellschaften

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VSN	Vereinigung Schweiz. Naturwissenschaftslehrer

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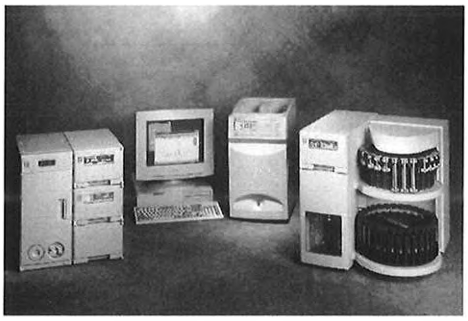

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Leserdienst Nr. 33

CHIMIA *51* (1997) Nr. 8/9 (August/September)

Invitation to Attend the Fall Meeting of the New Swiss Chemical Society in Lausanne, Wednesday, October 15, 1997

EDITORIAL

On behalf of the New Swiss Chemical Society (NSCS) and the Local Organizing Committee, it is our pleasure to invite you to attend the next Fall Meeting of the NSCS. We are particularly delighted and honoured that this meeting takes place in Suisse Romande. Indeed, after many years during which traditionally the Fall Meeting took place in Bern, the Committe of the NSCS was faced with the problem of finding larger venues due to the growing attendance at these events. It was by no means easy to take this decision, as Bern is obviously the most central place in Switzerland for organizing such meetings, but the facilities offered by the University had definitely become too tight. This is why, after two Fall Meetings organized in Basel (1993, 1996), in the context of ILMAC, and the last ones in Bern (1994, 1995), they move this year to Lausanne and to the comfortable facilities of the Collège Propédeutique and the Ecole de Pharmacie of the University.

It is now undisputed that the Fall Meeting of the NSCS is the largest yearly event in Switzerland where graduate students in chemistry, post-docs and chemists of all levels have the opportunity to present results they have been achieving in their research projects. In addition, this meeting is by tradition a nice occasion to meet friends and colleagues so as to develop or strengthen social and scientific connections. In this context, these meetings have proved indispensable within the swiss chemical community, and we know by experience that many fruitful collaborations between research groups of our country have been initiated by discussions in front of a poster or after a scientific communication of the Fall Meeting! We, therefore, look forward to having well attended and lively sessions in Lausanne next October.

'Never change a winning team'! This elementary principle of football coaches will apply without restriction to the 1997 Fall Meeting: the scientific program will be very similar to that of previous years, with the opening ceremony and lecture(s) by *Werner* Prize laureate(s) as the only plenary session, followed by the parallel ones in organic (three of them), inorganic (minisymposium), physical, computational, medicinal and analytical chemistry. Last but not least, this program would be incomplete without the usual poster sessions. All the ingredients are, therefore, present so as to make this 1997 Fall Meeting as successful as the previous ones. We already welcome you in Lausanne and hope that you will enjoy the 1997 Fall Meeting both on scientific and social grounds!

Professor Jacques Weber
Chairman of the Section
Chemical Research of the NSCS

Professor André Merbach
Chairman of the Local
Organizing Committee

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NEUE SCHWEIZERISCHE CHEMISCHE GESELLSCHAFT
NOUVELLE SOCIETE SUISSE DE CHIMIE
NEW SWISS CHEMICAL SOCIETY

SECTION CHIMIE ANALYTIQUE
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SECTION RECHERCHE CHIMIQUE

SEKTION ANALYTISCHE CHEMIE
SEKTION MEDIZINISCHE CHEMIE
SEKTION CHEMISCHE FORSCHUNG

Assemblée d'automne 1997
Herbstversammlung 1997

Mercredi 15 octobre 1997
Mittwoch 15. Oktober 1997

Lausanne

Université de Lausanne, Dorigny
Collège Propédeutique
Ecole de Pharmacie

CHIMIA 51 (1997) Nr. 8/9 (August/September)

Organizing Committee:

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Jean-Luc Marendaz – University of Lausanne
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Informations:

L'inscription n'est pas nécessaire.

Les étudiants membres de la NSSC peuvent demander le remboursement des frais de voyage sur la base du billet de train Lausanne et retour, 2e classe, 1/2 tarif (pour les membres qui viennent de l'étranger, seuls 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 la formation continue et des congrès de la NSSC, Mme *B. Köchli*, Département de Chimie et Biochimie, Université de Berne, Freiestrasse 3, CH–3012 Berne.

Informationen:

Keine Anmeldung erforderlich.

Studierende, die Mitglied der NSCG sind, erhalten folgende Reisekosten zurückerstattet: Bahnbillett nach Lausanne, 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 unter Beilage eines Einzahlungsscheines beim Sekretariat für Weiterbildung und Symposien der NSCG, Frau *B. Köchli*, Departement für Chemie und Biochemie, Universität Bern, Freiestrasse 3, CH–3012 Bern, einzureichen.

Transportation:

With the new timetable of the CFF it is now more convenient for people coming from Basel (BS), Bern (BE), Fribourg (FR) and Zürich (ZH) not to stop in Lausanne, but rather to continue with the same train until Renens (next stop after Lausanne) and then to take the tramway TSOL from Renens to the Lausanne University at Dorigny (stop UNI/Sorge); for people coming from Geneva (GE), stop at Renens (one stop before Lausanne) and take the TSOL from Renens to UNI/Sorge. Unfortunately, this facility does not apply for people coming from Neuchâtel (NE). They should stop at Lausanne, then take the underground from Lausanne train station to Place du Flon and then the TSOL from Place du Flon to UNI/Sorge. A short timetable showing this facilities is given below:

Morning:
Tramway train station – UNI/Sorge (each 10 min)

Evening:
Tramway UNI/Sorge – Renens train station (each 10 min)

Train:	Departure	Arrival Renens	Lausanne	Departure Renens	*via*	Arrival	
BS	7.03	9.43		17.49	Yverdon	20.38	BS
BE	8.21	9.43		17.48		19.11	BE
FR	8.44	9.43		17.48		18.47	FR
GE	8.40	9.15		17.44		18.22	GE
NE	8.00		8.50	17.49	Yverdon	18.59	NE
ZH	7.03	9.43		17.48		20.26	ZH

For those coming by car, follow Lausanne-Sud, exit UNIL-EPFL, then turn to the right at the sign EPFL/UNIL. Parking facilities will be available at the Collège Propédeutique.

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Programm der Herbstversammlung 1997
Programme de l'assemblée d'automne 1997

10.00–10.40 **Eröffnung / Cérémonie d'ouverture**
Collège Propédeutique: Auditorium B
Prof. *A. von Zelewsky*

Verleihung des *Werner*-Preises 1997
Remise du Prix *Werner* 1997

Vortrag des *Werner*-Preisträgers 1997
Conférence du lauréat du Prix *Werner* 1997
Dr. ***Yannick Landais***
Institut de Chimie Organique, Université de Lausanne
'Desymmetrisation of Dienylsilanes. Stereocontrolled Access to Cyclitols and Carba-sugars'

Analytische Chemie / Chimie analytique
Mitgliederversammlung / Assemblée des membres:
Ecole de Pharmacie: Auditorium C
Vorträge / Conférences: *Ecole de Pharmacie: Auditorium C*
Postersession / Session de posters:
Main Hall of Collège Propédeutique
Programm s. Seite 583 / Programme v. page 583
Abstracts s. Seite 589 / Abstracts v. page 589

Medizinische Chemie / Chimie thérapeutique
Mitgliederversammlung / Assemblée des membres:
Ecole de Pharmacie: Auditorium B
Vorträge / Conférences: *Ecole de Pharmacie: Auditorium B*
Postersession / Session de posters:
Main Hall of Collège Propédeutique
Programm s. Seite 584 / Programme v. page 584
Abstracts s. Seite 594 / Abstracts v. page 594

Chemische Forschung / Recherche chimique
Mitgliederversammlung / Assemblée des membres:
Collège Propédeutique: Auditorium B

- **Anorganische Chemie und Koordinationschemie / Chimie minérale et de coordination**
  Vorträge / Conférences:
  Collège Propédeutique: Auditorium D
  Postersession / Session de posters:
  Main Hall of Collège Propédeutique
  Programm s. Seite 585 / Programme v. page 585
  Abstracts s. Seite 598 / Abstracts v. page 598

- **Computerunterstützte Chemie / Chimie computationnelle**
  Vorträge / Conférences:
  Collège Propédeutique: Salle CP 321
  Postersession / *Session de posters:*
  Main Hall of Collège Propédeutique
  Programm s. Seite 585 / Programme v. page 585
  Abstracts s. Seite 619 / Abstracts v. page 619

- **Organische Chemie / Chimie organique**
  Vorträge / Conférences:
  Collège Propédeutique: Auditorium A, B, C
  Postersession / Session de posters:
  Main Hall of Collège Propédeutique
  Programm s. Seite 586 / Programme v. page 586
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- **Physikalische Chemie / Chimie physique**
  Vorträge / Conférences: *Ecole de Pharmacie: Auditorium A*
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  Main Hall of Collège Propédeutique
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Analytische Chemie
Chimie analytique

10.45–11.15 **Mitgliederversammlung**
Assemblée des membres
Ecole de Pharmacie: Auditorium C
Appreciation of the activities of late Prof. *H.-M. Widmer* in the SACh

Vorträge / Conférences: *Ecole de Pharmacie: Auditorium C*
Abstracts: 1, 3, 5, s. Seite 589 / v. page 589
Chairman: PD Dr. *U. Spichiger*

11.15–11.45 ***J.-L. Veuthey***
Laboratoire de Chimie Analytique Pharmaceutique, Université de Genève
Le Centre de Compétence en Chimie et Toxicologie Analytique

11.45–12.10 ***J.-L. Wolfender***, *K. Hostettmann*
Institut de Pharmacognosie et Phytochimie, Université de Lausanne
LC/NMR, a Powerful New Tool for LC On-line Structural Identification
Abstract 1

12.10–12.35 ***V. Deckert***, *D. Zeisel, R. Stöckle, R. Zenobi*
Laboratorium für Organische Chemie, ETH-Zürich
Non-Destructive Molecular Analysis with 100 nm Lateral Resolution
Abstract 5

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Paul Scherrer Institut, Elektrochemie, Villigen PSI
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Abstract 3

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Medizinische Chemie
Chimie thérapeutique

10.45–10.55 **Mitgliederversammlung**
Assemblée des membres
Ecole de Pharmacie: Auditorium B

Vorträge / Conférences: *Ecole de Pharmacie: Auditorium B*
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Chairman: *R. Giger*

11.10–11.20 ***G. Caravatti***, *P. Furet, B. Gay, C. Garcia-Echeverria, H. Fretz, J. Rahuel, J. Schoepfer*
Novartis Pharma AG, Basel
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Abstract 22

11.20–11.40 ***S. Cottens***, *R. Sedrani, J. Kallen, W. Schuler, G. Zenke*
Novartis Pharma AG, Transplantation Research, Basel
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11.40–12.00 ***W. Froestl***, *B. Bettler, H. Bittiger, K. Kaupmann, S.J. Mickel*
Novartis Pharma AG, Research Department, Therapeutic Area Nervous System, Basel
Ligands for Expression Cloning of GABA_B Receptors
Abstract 24

12.00–12.20 ***P. Furet***, *P. Peterli, H.-G. Capraro, S. Ruetz, T. Meyer, J. Zimmermann*
Novartis Pharma Inc., Oncology Research Department, Basel
Structure-Based Optimization of Olomoucine, a Cyclin-Dependent Kinase 2 (CDK2) Inhibitor
Abstract 25

12.20–12.40 ***T. Godel***, *C. Riemer, D.S. Hartman*
Pharmaceutical Research, Preclinical Neurosciences, Hoffmann-La Roche, Basel
Discovery and Synthesis of Three Chemical Classes of Selective Dopamine D4 Ligands
Abstract 26

12.40–13.00 ***A. von Sprecher***
Novartis Pharma AG, Research Department, Basel
Neurokinin Antagonists as Potential New Drugs for the Treatment of Asthma
Abstract 27

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Chairman: *W. Froestl*

14.00–14.20 ***A. Heppeler***, *M. Béhé, E. Jermann, P. Powell, S. Froidevaux, H.R. Mäcke*
Institute of Nuclear Medicine, University Hospital, Basel
New Somatostatin Analogues for Spect, Pet and Internal Radiotheraphy
Abstract 35

14.20–14.40 ***G. Caron***[a]), *P.-A. Carrupt*[a]), *B. Testa*[a]) *R. Fruttero*[a]), *E. Fornatto*[b]), *D. Boschi*[b]), *G. Ermondi*[b]), *A. Gasco*[b])
[a]) *Institut de Chimie Thérapeutique, Université de Lausanne*
[b]) *Dipartimento di Scienza e Tecnologia del Farmaco, Facoltà die Farmacia, Università di Torino*
Drug-Membrane Interactions as Described by Partitioning in Liposome/Water Systems
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14.40–15.00 ***I. Raynaud***[a]), *P. Weber*[a]), *P.-A. Carrupt*[a]), *J. Paris*[b]) *D. Gerlier*[c]), *C. Rabourdin-Combe*[d]), *L. Ettouati*[b]), *B. Testa*[a])
[a]) *Institut de Chimie Thérapeutique, Université de Lausanne*
[b]) *Laboratoire de Chimie Thérapeutique, Faculté de Pharmacie, Lyon*
[c]) *Immunité et Infections Virales, IVMC, UMR30, CNRS-UCBL, Lyon*
[d]) *Immunobiologie Moléculaire, UMR 49, CNRS-ENS, Lyon*
Etude par modélisation moléculaire du complexe d'une protéine MHC de classe II I-A^k et du peptide HEL (52–61)
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15.00–15.20 ***A. Pagliara***, *P.-A. Carrupt, G. Caron, P. Gaillard, B. Testa*
Institut de Chimie Thérapeutique, Université de Lausanne
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15.20–15.40 ***A.L. Marzinzik***, *E.R. Felder*
Novartis Pharma AG, Core Technology Area, Combinatorial Chemistry, Basel
Diversity Platform in Combinatorial Chemistry: Transformation of α,β-Unsaturated Ketones on Solid Phase
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Chemische Forschung
Recherche chimique

10.45–10.55 **Mitgliederversammlung**
Assemblée des membres
Collège Propédeutique: Auditorium B

Anorganische Chemie / Chimie inorganique

Minisymposium: *Collège Propédeutique: Auditorium D*
Chairman: *E. Constable*

11.00–12.00 Prof. *J. McCleverty*
School of Chemistry, University of Bristol
Manipulating Molecules for Magnetism

12.00–13.00 Prof. *A. Togni*
Laboratory of Inorganic Chemistry, Swiss Federal Institute of Technology, Zürich
What Can an Organometallic Chemist Offer to Materials Science?

14.00–17.00 **Postersession / Session de posters**
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Computerunterstützte Chemie / Chimie computationnelle

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Abstracts: 128–137, s. Seite 620 / v. page 620
Chairman: *J. Weber*

12.00–12.20 ***A. Selloni***a)c), *A. Vittadini*b), *M. Grätzel*c)
a) *Département de Chimie Physique, Université de Genève*
b) *CSSRCC-CNR, Padova*
c) *Institut de Chimie Physique, EPF-Lausanne*
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Institut für Physikalische Chemie, Universität Basel
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Institut de Chimie Inorganique, Université de Fribourg
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Organisch-chemisches Institut, Universität Zürich
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14.20–14.40 ***E. Sidorenkova***b), *N. Aebischer*a), *G. Laurenczy*a), *J. Weber*b), *A.E. Merbach*a)
a) *Institut de Chimie Minérale et Analytique, Université de Lausanne*
b) *Département de Chimie Physique, Université de Genève*
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Institut de Chimie Inorganique et Analytique, Université de Fribourg
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15.00–15.20 ***V. Musolino***a)b), *A. Selloni*c), *R. Car*a)b)
a) *IRRMA, EPF-Lausanne*
b) *Département de Physique de la Matière Condensée, Université de Genève*
c) *Département de Chimie Physique, Université de Genève*
Atomic and Electronic Structure of Cu Clusters on MgO
Abstract 134

15.20–15.40 ***A. Dyson***, *J. Solca, H. Huber*
Institut für Physikalische Chemie, Universität Basel
Determination of the Melting Curves of Argon and Neon from Pure Theory
Abstract 135

15.40–16.00 ***H.H. Günthard, T.-K. Ha***, *R. Gunde, H.-J. Keller*, *Physical Chemistry Laboratory, ETH-Zürich*
Quantum Chemistry Based Set of Additive Contributions to Conversion Energies of All Geometric Isomers and Tautomers of the Nucleic Acid Bases Cytosine, Isocytosine, Uracil, Thymine, Adenine, Xanthine and Guanine
Abstract 136

16.00–16.20 ***E. Migliavacca***, *P.-A Carrupt, B. Testa*
Institut de Chimie Thérapeutique, Université de Lausanne
Theoretical Parameters as Tools to Characterize Antioxidants
Abstract 137

Organische Chemie / Chimie organique

Vorträge / Conférences:
Collège Propédeutique: Auditorium A, B, C
Abstracts: 148–170, s. Seite 625 / v. page 625

11.00–12.00 **Posters: Short presentations**
Abstracts: 138–189, s. Seite 623 / v. page 623

Auditorium A, B, C: the results described in each poster will be presented by the main author; 2 slides / 3 min max. each presentation

Auditorium A: Chairman: *J.A. Robinson*
E. Serrano, P.B. Rheiner, M. Mayor, A. Londez, J. Lacour, S. Heinen, C. Ginglinger, M. Zürcher, H. Mosimann, J. Stichler-Bonaparte, F. Monnat, P. Meier, P. Kraft, A. Forster/L. Giraud, L. Giraud, I. Mergelsberg, S. Pache

Auditorium B: Chairman: *E.P. Kündig*
C. Baud, K. Borszeky, E. El-Sayed, G. Fragale, J.F.K. Müller, K. Neuschütz, H. Ratni, L. Saudan, T.P. Sieber, F. Villar, A.K. Beck, M. Dusi, I. Fenger, T. Mallat, I. Nägeli, B. Spingler, D. Zeller

Auditorium C: Chairman: *M. Mutter*
A. Boog, H. Imogaï, V. Priyadarshanie Bulugahapitiya, S. Abele, G. Kontaxis, Y. Yokokawa/S. Peluso, L.C. Scheibler, G. Tuchscherer, A. Rieder, W. Fieber, A. Ratnatilleke, F. Stauffer, T. Engeloch, R. Epple, C. Poliart, P. Schaeffer, H. Trafelet, A. Kogelbauer

12.00–14.00 **Postersession / Session de posters**
Main Hall of Collège Propédeutique
Abstracts: 138–189, s. Seite 623 / v. page 623

Vorträge / Conférences: *Collège Propédeutique: Auditorium A*
Chairman: *E.P. Kündig*

14.00–14.20 ***A. Fretzen***, *E.P. Kündig*
Département de Chimie Organique, Université de Genève
A New Route to Highly Enantionenriched Planar-Chiral Arene Complexes – Precursors in Asymmetric Synthesis
Abstract 190

14.20–14.40 ***A.K.H. Knöbel***, *G.C. Lloyd-Jones, A. Pfaltz*
Max-Planck-Institut für Kohlenforschung, Mülheim an der Ruhr
Enantioselective Copper-Catalyzed 1,4-Addition of Organometallic Reagents to Enones
Abstract 191

14.40–15.00 ***M. Juch***, *P. Rüedi*
Organisch-chemisches Institut, Universität Zürich
Enantioselektive Synthese von n-Alkyloxycatecholen als Inhibitoren von Lipoxygenase
Abstract 192

15.00–15.20 ***T. Wirth***
Institut für Organische Chemie, Universität Basel
Catalytic Reactions with Chiral Selenium Compounds
Abstract 193

15.20–15.40 ***P. Suter***, *G. Fortier, Y.-X. Cheng, J. Boukouvalas*
Département de Chimie, Université Laval, Québec
Progrès vers la synthèse énantiosélective du plakortone A
Abstract 194

Chairman: *P. Rüedi*

15.40–16.00 ***F. Glarner***, *E.A. Acar, U. Burger*
Département de Chimie Organique, Université de Genève
6-Azabicyclo[3.1.0]hex-3-en-2-ol Derivatives, Photochemically Generated Building Blocks for Cyclopentanoids
Abstract 195

16.00–16.20 ***S. Lemaire-Audoire***, *P. Vogel*
Institut de Chimie Organique, Université de Lausanne
Total Synthesis of Long Chain Sugars
Abstract 196

16.20–16.40 ***A. Studer***
Laboratorium für Organische Chemie, ETH-Zürich
Intramolecular Homolytic Substitution Reactions at Silicon as Unimolecular Chain Transfer Steps in the Formation of 5-Membered Cyclic Silyl Ethers
Abstract 197

16.40–17.00 ***C. Fehr***
Firmenich SA, Corporate R&D Division, Genève
Diastereofacial Selectivity in Epoxidation Depends on Reagent Electrophilicity
Abstract 198

Vorträge / Conférences: *Collège Propédeutique: Auditorium B*
Chairman: *R. Neier*

14.00–14.20 ***J. Raemy***, *T. Jenny*
Institut de Chimie Organique, Université de Fribourg
Reaction of Olefin Iron Complexes with Alkyl Lithium Reagents
Abstract 199

14.20–14.40 ***V. Helbing***, *R. Keese*
Departement für Chemie und Biochemie, Universität Bern
$ZrCp_2$-induzierte Cyclisierungen
Abstract 200

14.40–15.00 ***A. Fkyerat***, *G.-M. Dubin, R. Tabacchi*
Institut de Chime, Université de Neuchâtel
The Synthesis of Natural Acetylenic Compounds from *Stereum hirsutum*
Abstract 201

15.00–15.20 **F. Flachsmann**, *W. Oppolzer*
Département de Chimie Organique, Université de Genève
Synthesis of (–)-Erythrodiene *via* a Highly Diastereoselective Intramolecular Palladium-Catalysed Zinc-Ene Reaction
Abstract 202

15.20–15.40 **J. Fässler**, *S. Bienz*
Organisch-chemisches Institut, Universität Zürich
1-Hydroxyallylsilane: Herstellung, Oxidation und Folgereaktionen
Abstract 203

Chairman: *S. Ainge*

15.40–16.00 **J. Velker**, *V. Linder, P.-Y. Eschler, A. Franz, R. Neier*
Institut de Chimie, Université de Neuchâtel
A New Stereocontrolled Tandem Reaction of Butadienyl Ester Enolates
Abstract 204

16.00–16.20 **R.E. Martin**a), *J. Bartek*a), *R.R. Tykwinski*a), *F. Diederich*a), *E. Meister*b), *A. Hilger*c), *H.P. Lüthi*c)
a) *Laboratorium für Organische Chemie, ETH-Zürich*
b) *Laboratorium für Physikalische Chemie, ETH-Zürich*
c) *Swiss Center for Scientific Computing, ETH-Zürich*
Photochemical *trans/cis* Isomerization of Functionalized Tetraethynylethenes and 1,5-Hexenediynes
Abstract 205

16.20–16.40 **R. Boehlen**, *N. Molisho, L. Walder*
Institut für Chemie, Universität Osnabrück
Two-Point Molecular Recognition Linked to Redox Type Signal Transduction
Abstract 206

16.40–17.00 **C. Zumbrunn**, *D. Obrecht, K. Müller*
F. Hoffmann-La Roche AG, Basel
Carbonyl-Alkine Exchange (CAE) Reaction of Dihydropyranthione Derivatives with Acetylenic Ketones: A Convergent Synthesis of Highly Substituted Aromatic Sulphides
Abstract 207

Vorträge / Conférences: *Collège Propédeutique: Auditorium C*
Chairman: *J.L. Reymond*

14.00–14.20 **P. Dumy**, *M. Keller, C. Sager, M. Mutter*
Institut de Chimie Organique, Université de Lausanne
Pseudo-Prolines: New Tools in Peptide Mimicry
Abstract 208

14.40–15.00 **E. Meggers**, *D. Kusch, B. Giese*
Institut für Organische Chemie, Universität Basel
Electron Transfer in DNA from Guanine Bases to the Sugar-Phosphate Backbone during C-4' Radical Induced Strand Cleavage
Abstract 209

15.00–15.20 **L. Peng**, *M. Goeldner*
Laboratoire Chimie Bio-organique, Université Louis Pasteur, Strasbourg
Photoregulation of Cholinesterases Activites with Photolabile Ligands
Abstract 210

15.20–15.40 **J.L. Matthews**, *J. Schreiber, T. Hintermann, D. Seebach*
Laboratorium für Organische Chemie, ETH-Zürich
Delving Further into β-Peptide Chemistry
Abstract 211

15.40–16.00 **R. Konrat**, *G. Kontaxis, C. Eichmüller, R. Weiskirchen*a), *K. Bister*a), *B. Kräutler*
Institute of Organic Chemistry, a) *Institute of Biochemistry, University of Innsbruck, Austria*
NMR Structural Studies of the Zinc-Binding LIM Motif
Abstract 212

Chairman: *H. Heimgartner*

15.40–16.00 **J. Lehmann**, *A. Linden, H. Heimgartner*
Organisch-chemisches Institut, Universität Zürich
Selektive Einführung einer Thioamid-Gruppe in Aib-haltide Peptide über eine Variante der 'Azirin/Oxazolon-Methode'
Abstract 213

16.00–16.20 **T. Carell**, *R. Epple, J. Butenandt*
Laboratorium für Organische Chemie, ETH-Zürich
Model Compounds to Investigate DNA Repair Processes
Abstract 214

16.20–16.40 **D. Kaufmann**, *J.-L. Reymond*
The Scripps Research Institute, La Jolla, CA
New Photostable Fluorescent Labels for Proteins Using the Quinacridone Chromophore
Abstract 215

16.40–17.00 **U. Diederichsen**, *H.W. Schmitt, D. Weicherding*
Institut für Organische Chemie und Biochemie II, Garching
Alanyl, Homoalanyl and β-Homoalanyl Nucleo Amino Acids (PNA)
Abstract 216

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Physikalische Chemie / Chimie Physique

Vorträge / Conférences: *Ecole de Pharmacie: Auditorium A*
Abstracts: 217–224, s. Seite 643 / v. page 643

Postersession: ganztags
Session de posters: pendant toute la journée
Main Hall of the Collège Propédeutique
Abstracts: 225–234, s. Seite 645 / v. page 645

Vorträge / Conférences: *Ecole de Pharmacie: Auditorium A*
Chairman: Prof. *U.P. Wild*

11.00–11.20 ***M. Schildenberger***, *Y. Bonetti, M. Aeschlimann, R. Prins*
Laboratorium für Technische Chemie, ETH-Zürich
Investigation of Size Effects in Heterogeneous Catalysis Using Nanostructured Multilayer Systems
Abstract 217

11.20–11.40 ***P. Bonhôte***, *E. Gogniat, N. Vlachopoulos, M. Grätzel*
Laboratoire de Photonique et Interfaces, EPF-Lausanne
Efficient Lateral Electron Transport Inside a Monolayer of Aromatic Amines Anchored on Nanocrystalline Metal Oxide Films
Abstract 218

11.40–12.00 ***I. Fischer***, *H.-J. Deyerl, T. Schultz, T. Gilbert, P. Chen*
Laboratorium für Organische Chemie, ETH-Zürich
The Photochemistry of the Allyl Radical
Abstract 219

Vorträge / Conférences: *Ecole de Pharmacie: Auditorium A*
Chairman: Prof. *S. Leutwyler*

14.00–14.20 ***H.-P. Brack***[a]), *L. Bonorand*[b]), *H.G. Bührer*[b]), *G.G. Scherer*[a])
[a]) *Paul Scherrer Institut, Elektrochemie, Villigen PSI*
[b]) *Technikum Winterthur Ingenieurschule, Winterthur*
Reaction Rates and Yields in the Radiation Grafting Processing of Polymers: Base Polymer and Irradiation Effects
Abstract 220

14.20–14.40 ***D. Reiss***, *U.P. Wild*
Laboratorium für Physikalische Chemie, ETH-Zürich
Nondestructive Read-out of Two-Colour Photon-gated Spectral Holeburning Holograms at Helium Temperatures
Abstract 221

14.40–15.00 ***M. Croci***, *U.P. Wild*
Laboratorium für Physikalische Chemie, ETH-Zürich
Frequency Shifts of Single Molecules in Solids
Abstract 222

15.00–15.20 ***F. Reymond***[a]), *G. Steyaert*[b]), *P.-A. Carrupt*[b]), *B. Testa*[b]), *H.H. Girault*[a])
[a]) *Laboratoire d'Electrochimie, EPF-Lausanne*
[b]) *Institut de Chimie Thérapeutique, Section de Pharmacie, Université de Lausanne*
Transfer Mechanisms of Ionizable Drugs and Solvatochromic Analysis of the Water/1,2-Dichloroethane Solvent System
Abstract 223

15.20–15.40 ***S. Pawlik***, *M. Bauer, M. Aeschlimann*
Laboratorium für Technische Chemie, ETH-Zürich
Substrate Optimization for Hot Electron Induced Reactions on Surfaces
Abstract 224

CHIMIA *51* (1997) Nr. 8/9 (August/September)

Analytical chemistry **1**

LC/NMR, a powerful new tool for LC on-line structural identification.

J.-L. Wolfender and K. Hostettmann

Institut de Pharmacognosie et Phytochimie, Université de Lausanne, BEP,
CH-1015 Lausanne, Switzerland

Proton detected high-performance liquid chromatography / NMR (LC/^{1}H-NMR), despite being known for over fifteen years, has not been yet a widely accepted technique, mainly because of its lack of sensitivity. However, the recent progress in pulse field gradients and solvent suppression, the improvement in probe technology and the construction of high field magnets have given a new impulse to this technique. LC/NMR has been recently added to our HLPC setup which already included LC/DAD-UV and LC/MS detection. LC/UV/MS is routinely used since several years in our laboratory in association with biological screening for a rapid survey of plant extract composition. The implementation of LC/NMR represents an ideal complement to LC/UV/MS for in depth on-line identification.

Crude extracts as well as enriched fractions of plants belonging to various families have been analysed by LC/NMR in both on-flow and stopped-flow modes. These samples were analysed in reversed phase HPLC, non-deuterated solvents such as MeOH or MeCN were used, while water was replaced by D_2O. Well resolved ^{1}H-NMR spectra were obtained on-line for the major compounds (flavones, flavanones, xanthones, naphthoquinones, secoiridoids and alkaloids) of the extracts. In the stopped-flow mode, proton-proton correlations (COSY, NOESY), selective experiments (NOE, TOCSY) as well as indirect proton-carbon correlations (HMBC, HSQC) were performed. Around 20 µg per peak (MW ca. 400) were needed for on-line measurements on a 500 MHz instrument. 1D and 2D LC/NMR in combination with LC/UV/MS data permit a complete structure identification 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.

Chimie analytique **2**

Influence de la structure et de la polarité des polymères sur la sélectivité en GC chirale

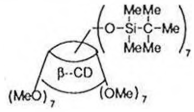
S.G. Claude and R. Tabacchi
Institut de Chimie de l'Université de Neuchâtel, 2000 Neuchâtel

A. Saxer
Departement für Chemie + Biochemie der Universität Bern, 3012 Bern

Une pratique courante en GC chirale est la dissolution d'une cyclodextrine dérivée au moyen d'entités alkyles, acétoxy, etc. dans un polymère.
L'OV 1701 demeure par son aptitude à dissoudre les différentes cyclodextrines utilisées à ce jour, le polymère usuel.

Il a été toutefois observé que le recours à d'autres polymères tels que:
PS 347.5, PS 264, SE 54, PS 086 [1], [2], dont la polarité varie de faible à moyenne, permet, dans nombre de cas, une meilleure sélectivité.

Afin de mieux cerner ces comportements, des polysiloxanes de composition et structure déterminées ont été synthétisés, puis comparés en fait d'incidence sur la sélectivité chirale à certains des polymères commerciaux précités.
La cyclodextrine retenue pour cette étude est le :
2,3-Di-O-méthyl-6-O-*ter*.-butyldiméthylsilyl-β-cyclodextrine



D'intéressantes conclusions découlent de cette approche comparative.

[1] A. Dietrich, B. Mass, G. Brand, V. Karl, A. Kauzinger, A. Mosandl, J. *High Resolut. Chromatogr.* 1992, **15**, 769.
[2] C. Bicchi, A. D'Amato, V. Manzin, A. Galli, M. Galli, *J. Chromatogr. A*, 1996, **742**, 161.

Analytische Chemie **3**

FT-Infrared and FT-Raman Investigations of the Monomer Distribution and Extent of Reaction in Radiation Grafted Films

Hans-Peter Brack[1], Olivier Schweizer[2], Dieter Jahn[2], Günther G. Scherer[1]

[1]Paul Scherrer Institut, Elektrochemie, CH-5232 Villigen PSI
[2]Ingenieurschule beider Basel, Abteilung Chemie, CH-4132 Muttenz

Radiation grafting can combine the desirable properties of two dissimilar polymers together in a graft copolymer. If more than one monomer is used, differences in the monomer diffusion and reaction rates may result in differences in the distribution of the grafted monomers through the base polymer film thickness. FT-IR Attenuated Total Reflectance (ATR) and transmission measurements have been used to investigate these effects. FT-Raman spectroscopy has been used to examine the extent of reaction of the crosslinker divinyl benzene (DVB) in radiation grafted films and in poly(styrene-*co*-DVB) copolymers prepared in solution.

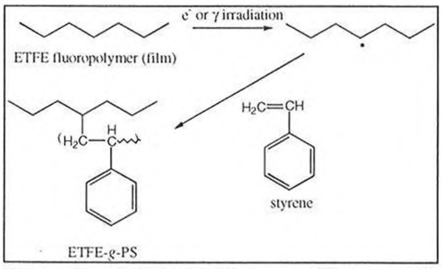


Fig. 1 Pre-irradiation grafting method

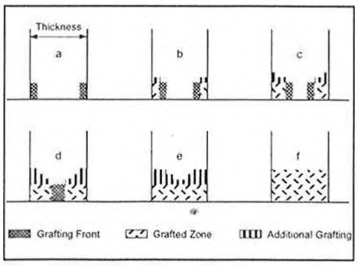


Fig. 2 Grafting Front Mechanism

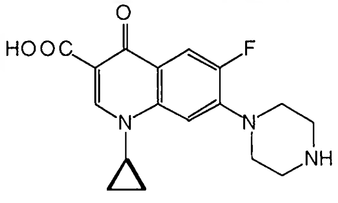
Analytische Chemie **4**

Determination of the Antibiotic Ciprofloxacin in Wastewaters by Solid-Phase-Extraction and HPLC

Alfredo C. Alder[1], Eva Golet[1], Andreas Hartmann[2], Theo Koller[2], and Rosa M. Widmer[2]

[1] Swiss Federal Institute for Environmental Science and Technology (EAWAG), CH-8600 Dübendorf and [2] Institute for Hygiene and Applied Physiology, Environmental Hygiene Group, Swiss Federal Institute of Technology (ETH), CH-8092-Zürich

Hospital wastewaters are known sources for potentially genotoxic (DNA-damaging), mutagenic or carcinogenic chemicals entering the aquatic environment. The fluorquinolone antibiotic Ciprofloxacin, used for the inhibition of bacterial, DNA unwinding enzyme gyrase, was determined in aqueous samples from hospital wastewaters and wastewater treatment plants using solid-phase extraction and high-performance liquid chromatography with fluorescence detection. The concentrations of Ciprofloxacin in hospital waste waters ranged from 3 to 90 µg/L. No enrichment procedure was needed because of the high concentrations. A solid-phase extraction method for the enrichment from wastewaters was developed to study the elimination of Ciprofloxacin from the aqueous phase in wastewater treatment.



Ciprofloxacin

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Analytical Chemistry **5**

Non-Destructive Molecular Analysis with 100 nm Lateral Resolution

Volker Deckert, Dieter Zeisel, Raoul Stöckle, Renato Zenobi.
ETH Zürich, Laboratorium für organische Chemie, ETH Zentrum,
Universitätsstr. 16, CH-8092 Zürich, Switzerland.

Analysis of small sample areas or volumes is getting more and more important for technical areas such as semiconductor and data storage technology or microbiology. Most of the well-established analytical tools have distinctive limitations which one has to overcome to obtain information in the sub-micrometer or nanometer domain. For instance, many consume the sample or yield only elemental composition (SIMS, SEM, Auger) or the information content is very limited (AFM, STM). Conventional optical spectroscopic techniques (UV, IR) are restricted by the diffraction limit to a lateral resolution of λ/2 that corresponds to ~ 200 - 400 nm.

We will demonstrate that the combination of Raman spectroscopy and scanning near-field optical microscopy (SNOM) can yield true chemical information on a subwavelength scale. By using subwavelength sized apertures instead of conventional optics we illuminate an area whose size is basically determined by the size of the aperture. If we excite the sample through this aperture with monochromatic laser light we can investigate the inelastically scattered light (Raman signal) from this sample spot. Because the Raman spectrum of every compound is unique one can easily distinguish between different compounds on a surface. We will show Raman spectra of CVD deposited diamond with a lateral resolution of < 200 nm.

Additionally, the SNOM technique yields precise topographic data of the surface. This enables one to correlate Raman signal intensities with the surface morphology, which we will demonstrate by showing how the lateral surface enhanced Raman spectra (SERS) of laser dyes on a silver island substrate depend on the surface morphology. Furthermore this novel SERS technique allows us so detect less than 300 molecules below our aperture.

Analytical Chemistry **6**

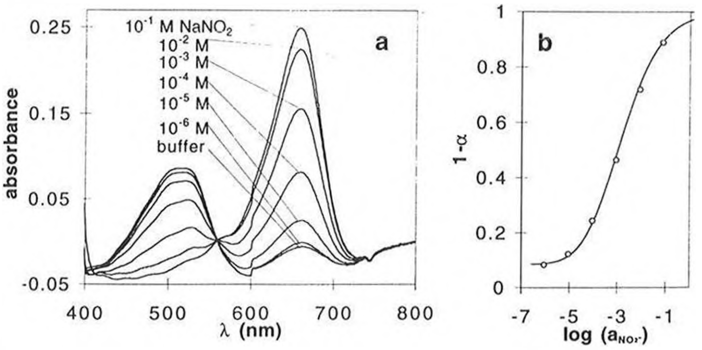
Response function and analytical parameters of nitrite-selective optode membranes in absorbance and fluorescence mode

C. Demuth and U.E. Spichiger

Centre for Chemical Sensors/Biosensors and bioAnalytical Chemistry
ETH Technopark, Technoparkstrasse 1, CH-8005 Zürich

Cobyrinates show characteristic extraction capabilities for anions when incorporated into solvent polymeric membranes. The ligand aquacyano-cobalt(III)-hepta(2-phenylethyl)-cobyrinate, dissolved in such a membrane, discriminates Cl^-, HCO_3^-, NO_3^-, $H_2PO_4^-$ and SO_4^{2-} and favours the extraction of nitrite from an aqueous specimen.

Optode membranes consist of a ligand and a H^+-selective chromoionophore dissolved in a plasticized poly(vinyl chloride) bulk medium. Four different nitrite-selective optodes are studied and compared with respect to their analytical parameters such as selectivity, dynamic range and detection limit. The response functions of the optical sensors, derived from the changes in the absorbance and/or fluorescence of the membranes with varying nitrite concentration, are described by a theoretical model based on coextraction equilibria.



Absorbance spectra (**a**) and response function (**b**) of a nitrite-selective optode membrane for aqueous sodium nitrite concentrations between 10^{-1} and 10^{-6} M.

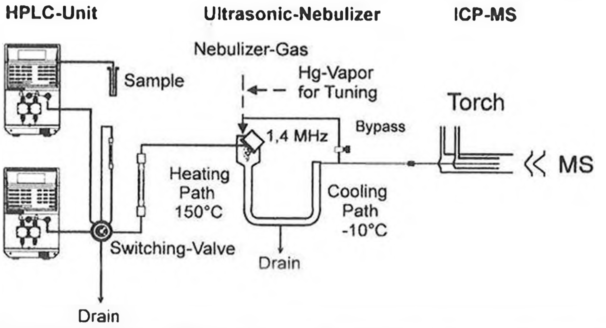
Analytische Chemie **7**

Determination of the abiotic mercury methylation potential of humic substances by using stable mercury isotopes combined with methyl mercury determination by HPLC-ICP-MS

R. Falter and R.-D. Wilken

ESWE-Institute for Water Research and Water Technology, D-65201 Wiesbaden-Schierstein, Söhnleinstrasse 158, Germany

The application of HPLC-ICP-MS technology and the use of stable enriched mercury isotopes ($^{200}Hg^{2+}$, $^{202}Hg^{2+}$) has shown, that methyl mercury was formed due to inorganic mercury within short time by heating up sediment samples to 45°C in the presence of diluted acid[1,2]. Up to 50% of the methyl mercury contained in the sample was formed during the procedure. The consequence was a change of the methyl mercury content during the sample preparation, for example by applying the water-vapor-distillation method.



The results have shown that acetone and acetonitrile extracts of sediment, soil and green leaves possess a high methylation potential to form methyl mercury in an abiotic way. Seven mercury mass traces can be detected by using the new developed HPLC-ICP-MS method.

[1] H. Hintelmann, R. Falter, G. Ilgen, R. D. Evans, Fres. J. Anal. Chem 358 (1997) in press.

[2] H. Hintelmann, R. Falter, Mercury as a Global Pollutant, August 4-8 (1996) Hamburg 284.

Analytical Chemistry **8**

Nanosecond and Picosecond Desorption Kinetics: Impact on Modern Mass Spectrometric Techniques

M. Handschuh, S. Netteshein, and R. Zenobi
Department of Chemistry, ETH-Zürich, Switzerland

Although laser induced thermal desorption techniques are widely used to gain access to gas phase species of non-volatile and fragile molecules for high resolution mass spectrometry, the desorption mechanism remains largely unknown.

In this context, a systematic study on the desorption and dissociation kinetics of submonolayer coverages of ethylene glycol and poly- (ethylene glycol) oligomers (PEG) with masses ranging from 62 to 35000 Da from a silica surface was undertaken. The measurements include characterization of the PEG-silica adsorption system using temperature programmed desorption, investigation of the surface coverage, and chemical composition during slow surface heating by real time X-ray photoelectron spectroscopy and determination of translational energy distributions following nanosecond CO_2 as well as picosecond Nd-YAG laser heating.

Our findings indicate that a thermal equilibrium model can be used to describe nanosecond as well as picosecond laser induced thermal desorption of PEGs at heating rates of $\geq 10^9$ K/s and $\geq 10^{13}$ K/s, respectively.

PEG 1000 is the highest mass oligomer that can be desorbed intact from silica if classical heating is applied, whereas under nanosecond and picosecond laser heating conditions only oligomers with masses $\leq$ 600 Da and $\leq$ 300 Da can be desorbed intact.

Novel strategies to enhance the accessible mass range of large polar molecules like biopolymers and a large range of synthetic polymers in LITD applications will be presented.

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Analytische Chemie **9**

MALDI Mechanisms: Spectroscopy and excited-state properties of 2,5 dihydroxybenzoic acid in a supersonic jet

Volker Karbach, Richard Knochenmuss
Laboratorium für Organische Chemie, Universitätsstr. 16, ETH Zentrum,
8092 Zürich

Certain molecules like 2,5 dihydroxybenzoic acic (DHB) have proven to be very effective as MALDI (Matrix Assisted Laser Desorption / Ionization) matrices. The molecular properties relevant to MALDI suitability are, however, still largely unknown. Generation of primary MALDI ions must involve excited electronic states of matrix molecules, and or matrix aggregates. We have begun to investigate the spectroscopy of $(DHB)_n$ n=1-3 in a supersonic molecular beam. This allows detailed study of excited state properties, as well as the effects of intermolecular interactions leading to the condensed phase.

We report initial studies of the S_1 state of DHB via 2-color resonant two-photon ionization, fluorescence excitation and dispersed fluorescence spectroscopies. Several conformers were found, of which two are apparently nearby in energy. The spectra are in all cases rather different from other benzoic acids, which are poor MALDI matrices. The S_1 appears to undergo a remarkable geometric distortion compared to the ground state. Unusual fluorescence spectra from higher S_1 vibrational levels are observed as a result.

Analytical Chemistry **10**

Ionization Mechanisms in MALDI Mass Spectrometry

Edda Lehmann, Richard Knochenmuss, and Renato Zenobi

Laboratorium für Organische Chemie, ETH Zentrum,
Universitätstr. 16, CH-8092 Zürich

Different ionization mechanisms are currently being discussed in MALDI. Ions may be pre-formed in the condensed phase and simply desorb after laser desorption, or they may form through ion-molecule reactions after desorption. Studies have mainly been performed reactions in the MALDI plume, i.e. after desorption [1]. Only few experiments on pre-formed ions have been carried out [2].
In this context, we investigated the contribution of pre-formed ions in MALDI in different matrix-cation systems and in the cation-polystyrene system. Transition metal ions were chosen as cations,. DHB and dithranol as matrices. The solution, the solid, and the gas phase were investigated by visible, infrared, proton nuclear magnetic resonance spectroscopy, and MALDI mass spectrometry. The contribution of pre-formed ions was found to be predictable from condensed-phase thermodynamics.
The experiments also gave insight into the mechanisms of charge compensation. All the ions detected were singly charged although divalent cations were used. The excess charges are compensated by deprotonation of the polar matrix in the matrix adducts, and by reduction of the cation in the polystyrene adducts.

[1] B. H. Wang, K. Dreisewerd, U. Bahr, M. Karas and F. Hillenkamp, *J. Am. Soc. Mass Spectrom.* **4**, 393 (1993).
[2] R. W. Nelson and T. W. Hutchens, *Rapid Commun. Mass Spectrom.* **6**, 4 (1992).

Analytische Chemie **11**

Validierte gas- und flüssig-chromatographische Analysenmethoden zur Epimerentrennung in einer komplexen Matrix

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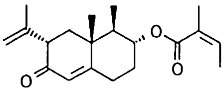
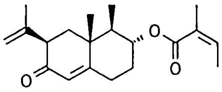
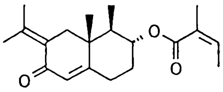
Max Zeller Söhne AG, CH-8590 Romanshorn

Mittels neuen NP- und RP-HPLC- und on column-GC-Methoden gelang es, die pharmakologisch wirksamen Hauptinhaltsstoffe von *Petasites hybridus* (L.) G., M. et SCH. (Gemeine Pestwurz, Petasin-Chemovarietät) aus Pflanzenextrakten zu trennen. Dabei handelt es sich um die zwei epimeren Sesquiterpenester Petasin und Neopetasin sowie um das dazu isomere Isopetasin.


Petasin


Neopetasin


Isopetasin

Die Extrakte wurden entweder mit mittelpolaren organischen Lösungsmitteln (z. B. Ether, Dichlormethan) oder durch superkritische CO_2-Extraktion aus getrockneten Pflanzenteilen (Wurzeln, Blätter, Blüten) erhalten.

Die Normalphasen-HPLC-Methode basiert auf einer Trennung an 3µm-Kieselgel mit einem ternären Laufmittelgradienten. Dieser Gradient erwies sich als robust, wobei sich die drei Verbindungen unter 20 Minuten basisliniengetrennt eluieren liessen.

Eine Umkehrphasen-Trennung des Pflanzenextraktes gelang auf einer kurzen (33mm) 1.5µm-C_{14}-Phase.

Die Trennung der thermolabilen Naturstoffe konnte mit on column-Kapillarsäulen-GC ebenfalls unter 15 Minuten realisiert werden.

Analytical Chemistry **12**

Automatic Evaluation of ^{1}H-NMR Spectra of Combinatorial Libraries

Renate Bürgin Schaller,[a] Pius Portmann,[a] Reinhard Neudert,[b]
Bernd Follmeg,[b] Ernö Pretsch[a]

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New flow-through NMR probeheads and the use of robots allow to automatically record ^{1}H-NMR spectra of combinatorial libraries. The time needed for a spectrum of submicrogram samples is in the order of minutes. This may lead to an enormous data flow and, hence, requires automatic storage and processing of the information.

The system presented here has been developed in connection with the SpecInfo database [1] using the Proton Shift program [2] for spectra estimation. First, a database of all the experimental spectra is generated automatically together with the structures proposed and entered by the chemist by means of a structure drawing program of his choice. The evaluation module described then uses the spectra and the corresponding structures. Chemical shifts, on the one hand, are estimated from the structures and, on the other, approximately derived from the measured spectra by using a heuristic procedure. Comparison of these two sets of chemical shifts provides a measure for the quality of agreement. If necessary, a whole set of proposed structures can be compared with a single spectrum, or vice versa, and ranked accordingly [3].

[1] SpecInfo V 3.1. Chemical Concepts, P.O. Box 10 02 02, D-69442 Weinheim.

[2] R. Bürgin Schaller, E. Pretsch, *Anal. Chim. Acta* **1994**, 290, 295-302.

[3] R. Bürgin Schaller, M.E. Munk, E. Pretsch, *J. Chem. Inf. Comput. Sci.* **1996**, 36, 239-243.

Analytical Chemistry **13**

Automatic Structure Elucidation

Hans Schriber, Renate Bürgin Schaller, Ernö Pretsch

Department of Organic Chemistry, Swiss Federal Institute of Technology,
CH-8092 Zürich

Computer-aided structure elucidation of organic compounds is a three-step process according to the customary approach: (1) Generation of the molecular formula and derivation of structural information from spectra, (2) from these, creation of all possible isomers, and (3) estimation of the spectra for the structures thus obtained and comparison with the experimental ones. In ideal cases, module 1 should provide sufficient information to constrain the number of possible solutions to less than about ten thousand entries so that step 3 efficiently produces a manageable number of candidate structures.

Here, we present a new rule-based system named SpecInt as module 1. It is capable of reducing the solution space to a few percent of the possible isomers defined by the molecular formula alone. Robust and conservative rules simultaneously coping with ^{1}H-NMR, ^{13}C-NMR, and IR spectra, have been designed and tested against a large number of reference data (10 000–100 000). The performance of module 1 in combination with different structure generators is shown.

Estimation of ^{1}H- and ^{13}C-NMR chemical shifts and automatic comparison with manually entered values have been used to rank the structures generated (module 3, cf. [1]). For a set of 80 examples, the performance of the system combining modules 1 and 3 is presented. The correct structure is always among the 15 best-ranked solutions or better.

[1] R. Bürgin Schaller, M.E. Munk, E. Pretsch, *J. Chem. Inf. Comput. Sci.* **1996**, 36, 239-243.

Analytical chemistry **14**

Use of LC/UV and LC/MS for the targeted isolation of dimeric monoterpenes from *Lisianthius* species (Gentianaceae)

S. Rodriguez[1], J.-L. Wolfender[1], H. Stoeckli-Evans[2] and K. Hostettmann[1]

[1] Institut de Pharmacognosie et Phytochimie, Université de Lausanne,
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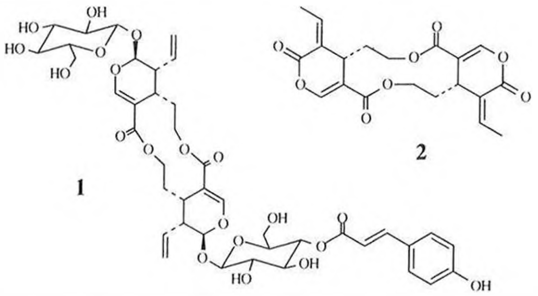
[2] Institut de Chimie, Université de Neuchâtel, 51, Avenue de Bellevaux,
CH-2000 Neuchâtel, **Switzerland**

The isolation and the structure elucidation of a novel type of dimeric secoiridoid glycoside, called lisianthioside, from *Lisianthius jefensis* has previously been described [1]. A further investigation of the plant was undertaken, together with two other species of *Lisianthius* from Panama. Chemical screening performed by liquid chromatography with on-line UV photodiode-array detection (LC/UV) and thermospray mass spectrometry (LC/TSP-MS) was performed. The presence of more lipophilic compounds than lisianthioside, presenting relatively high mass ions in the TSP spectra, was observed. Moreover, the dichloromethane extracts of the three species exhibited antifungal activity in a direct bioautographic assay against *C. cucumerinum*. The targeted isolation of the compounds presenting unusual spectroscopic features or antifungal activity was undertaken. Structure determination of the high molecular weight compound **1** and the antifungal compound **2**, established by UV, MS, X-ray, ^{1}H- and ^{13}C-NMR data, in combination with chemical reactions, will be presented.



[1] Hamburger, M., Hostettmann, M., Stoeckli-Evans, H., Solis, P.N., Gupta, M.P. and Hostettmann, K. (1990), *Helv. Chim. Acta*, 73, 1845.

Analytical Chemistry **15**

Improved performance of oxygen sensors based on new lipophilic ruthenium(II) complexes

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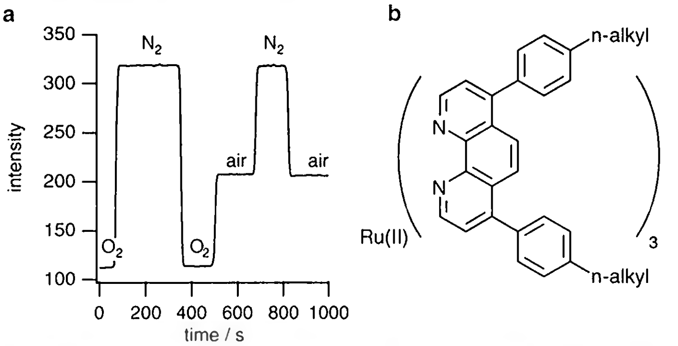
Ruthenium(II) complexes have found wide-spread use in oxygen sensors due to their long luminescence lifetimes, high quantum yields and their chemical stability. Oxygen selectively quenches the luminescence of these complexes and thereby allows oxygen quantification in gaseous or aqueous samples. For sensor applications ruthenium(II) complexes with the ligands 2,2'-bipyridine or 4,7-diphenyl-1,10-phenanthroline are the most widely used, usually dissolved in a membrane, i.e. a thin polymer layer.

To overcome their limited solubility in apolar membranes and subsequent restrictions for membrane materials encountered with these relatively hydrophilic complexes, we work with the self-synthesized complex tris-(4,7-bis(4'-propylphenyl)-1,10-phenanthroline)ruthenium(II) perchlorate and some of its alkyl homologues.



Typical sensor response to gases at atmospheric pressure for tris(4,7-bis (4'-propylphenyl)-1,10-phenanthroline)ruthenium(II) perchlorate in a polystyrene membrane (**a**) and the formula of the complex (**b**).

Analytical Chemistry **16**

Matrix-assisted Laser Desorption/Ionization of Noncovalent Dye-Peptide and Dye-Protein Complexes

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Many dyes, especially those that contain sulfonyl groups, show an affinity for proteins. Dyes can be immobilized on polymeric beads or membranes for protein separation. If water insoluble polymeric metarials are used, proteins can be separated from the aquous media. The support material can be used repeatedly in adsorption-desorption cycles. However, the interactions between dyes and proteins are very complex and not well defined [1].

Matrix-assisted laser desorption/ionization (MALDI) time-of-flight mass spectrometry provides a convenient method for mass analysis for biopolymers. In this study, we used different MALDI matrices, i.e, acidic, neutral, and basic ones, and a range of peptides, proteins, and sulfonyl dyes (especially cibacron Blue F3GA) to characterize noncovalent biopolymer-dye complexes. In acidic matrices, biopolymer complexes could not be detected by MALDI, in agreement with solution data [2]. With basic MALDI matrices, complexes of up to eight dye molecules with medium size proteins were observed. Every sulfonic acid group of a dye molecule can bind to one small peptide via its N-terminus. To higher molecular weight proteins, dye molecules are attached via one sulfonic acid group binding with the N-terminus as well as with other positively charged sites. These sites of interaction depend on the tertiary structure and the number of amino acid residues that can be protonated (Arg, Lys, His, Pro, Trp, and Gln). If two or more of these residues are very close to each other, charge repulsion may occur and the stochiometry of the complexes can change according to the location of basic amino acids in the protein chain.

[1] A. Denizli, B. Salih, E. Piskin, J. Chromatogr. **1996**, 731, 57.
[2] A. S. Woods, J. C. Buchsbaum, T. A. Worrall, J. M. Berg, and R. J. Cotter, Anal. Chem. **1995**, 67, 4462.

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Analytische Chemie **17**

Einführung der Analytik gentechnisch veränderter (GVO) Futtermittel mittels PCR in einem nach EN 45001 akkreditierten Labor

Michael Gilgen*, Jean-Yves Deru+, Jean-Louis Gafner+,
Toni Rihs+ und Beat Schmitter+

+ Eidgenössische Forschungsanstalt für Nutztiere, Sektion Analytik
1725 Posieux
* Labor für Lebensmittelchemie der Universität Bern, 3012 Bern

Mit der Zulassung von gentechnisch veränderten Produkten im Lebens- und Futtermittelbereich stellt sich die Frage nach deren Nachweis und Kontrolle. Die Sektion Analytik der Eidgenössischen Forschungsanstalt für Nutztiere betreibt das amtliche Futtermittellabor der Schweiz und analysiert die Proben aus der amtlichen Futtermittelkontrolle. Selber erhobene oder von Dritten eingesandte Futtermittel und Proben landwirtschaftlicher Produkte werden mit der vom Bundesamt für Gesundheit für Lebensmittel vorgeschriebenen „Screening"-Nachweismethode [1], bzw., mit spezifischen Nachweismethoden [2] auf nicht bewilligte, oder nicht deklarierte, Bestandteile von gentechnisch veränderten Organismen geprüft und gegebenenfalls beanstandet.

Die Einführung der „Polymerase Chain Reaction" (PCR-Analytik") bietet in einem akkreditierten, analytischen Dienstleistungslabor wegen der im pg-Bereich liegenden Empfindlichkeit und der sich daraus ergebenden Kreuzkontaminationsgefahr erhebliche Probleme. In Zusammenarbeit mit dem Labor für Lebensmittelchemie der Universität Bern wurde ein Konzept erarbeitet und umgesetzt, welches sowohl den wissenschaftlichen als auch den organisatorischen Anforderungen eines akkreditieren Labors zu genügen vermag.

[1] K.Pietsch et al., Dtsch. Lebensm. Rundsch. [93], 35-38 (1997).
[2] Esther Köppel et al., Mitt. Gebiete Lebensm. Hyg. [88], 164-175 (1997).

Analytical Chemistry **18**

Heavy Metal Sensors for Environmental Analysis

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Ernö Pretsch[b]

[a] Departament de Quimica, Universitat de Girona, E-17071 Girona
[b] Department of Organic Chemistry, Swiss Federal Institute of Technology,
CH-8092 Zürich
[c] On leave from University of Warsaw, Department of Chemistry,
PL-02093 Warsaw

A series of Pb^{2+}-selective ionophores are investigated in optode membranes and their relative complex formation constants with Pb^{2+} in the membrane phase are determined. The optimal ligand for environmental monitoring is selected. With Cd^{2+} as the only important interfering ion, the resulting optode or a corresponding test strip may be used for screening purposes for the two toxic ions. The applicability of the approach is validated by comparing optode measurements in drinking water to data obtained by ICP-MS spectroscopy.

Since the lower detection limit of ion-selective electrodes (ISEs) is worse, by orders of magnitude, than that of bulk optodes based on the same ionophore, ISEs currently are not adequate for environmental monitoring. However, there is no fundamental reason for this difference which is thought to be a consequence of ISE membrane components leaching into the sample. Various ISE designs are investigated in view of substantially improving the detection limits.

Analytical Chemistry **19**

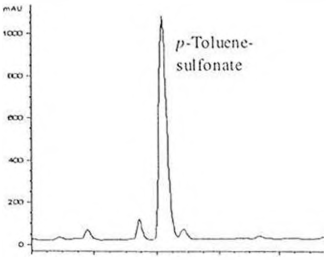
Determination of Benzene- and Naphthalenesulfonates in Landfill Wastewater and Groundwater

Sonja Riediker, Marc J.-F. Suter and Walter Giger

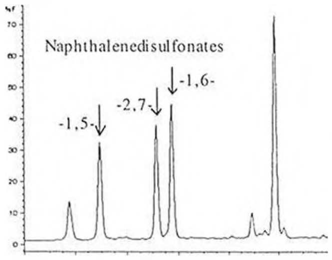
Swiss Federal Institute for Environmental Science and Technology (EAWAG), CH-8600 Dübendorf

Benzene- and naphthalenesulfonates are used in many industrial processes and are intermediates for a wide varity of products such as azo dyes, superplasticisers, herbicides etc. These ionic xenobiotics have high water solubilities and thus are very mobile in aquatic systems. Compounds substituted with a nitro, hydroxy, sulfo or amino group are hardly or not biodegradable.

The focus of this work is the determination of benzene- and naphthalenesulfonates in wastewater of landfills and in groundwater by solid-phase enrichment with graphitized carbon black and ion-pair reversed phase HPLC coupled with diode array and fluorescence detection. Liquid chromatography with electrospray mass spectrometry detection was used to qualitatively confirm the results of HPLC analyses.



Diode array detection: wastewater



Fluorescence detection: groundwater

Analytische Chemie **20**

Determination of Nitrophenols in Water with HPLC

Alfred Reichert and Markus Zehringer
Gewässerschutzamt Basel-Stadt , Hochbergerstrasse 158, CH-4019 BASEL

Nitrophenols are used mainly as educts and intermediates in chemical synthesis (e.g. dinitrophenols) and as pesticides (e.g. dinoseb). Therefore they are present in the environment (e.g. in effluents from manufacturing plants, in drainage waters from cultivated lands). The International Commission for the Protection of the Rhine Against Pollution (IKSR) has integrated some nitrophenols into its analytical program: dinoseb, dinoterb, 2,4-dinitrophenol and 3,5-dinitro-ortho-cresol (DNOC).

Nitrophenols are also of high relevance at sanitary landfills, especially sites of war industries are often contaminated with nitrophenols and other nitroaromatics. In the new Swiss regulation for the restoration of landfills [1] there are limiting values for leachates or groundwater (e.g. for 2,4-dinitrophenol).

Our lab has therefore optimated a robust analytical method with HPLC for the determination of nitrophenols. A complicated derivatization step used in common gc-methods is not necessary.

One liter of filtered water (0.45µm) is adjusted with hydrochloric acid to pH=2 and internal standard (2,6-dinitro-p-cresol) added. The nitrophenols are enriched by solid phase-extraction (200 mg Lichrolute EN from Merck). The cartridge is dried with nitrogen for 30 minutes, then eluted with 6 mL of methanol/tert.-butylmethylether (7:3). The solution is concentrated with nitrogen to a volume of 200 µL.

HPLC-conditions:
Column: C-18-column (250 x 4 mm, 5µm LiChrosphere 60 from Merck)
Mobile phase: A: 1% acetic acid, B: 1% acetic acid in acetonitrile. Program: Start at A:B = 70:30, 10 minutes isocratic, then linear to A:B = 20:80 during 28 minutes. Flow: 1 mL/minute. Wavelength of detection: 365 nm.

Recovery tests were made in drinking- and Rhine-water. Recoveries were for all nitrophenols more than 90%, the relative standard deviation was between 3 and 15 % for 4 separate analysis.

[1] Eidgenössisches Departement des Innern: Verordnung über die Sanierung von belasteten Standorten (Altlasten-Verordnung; AltlV), Entwurf vom 18.4. 1997.

Analytical Chemistry **21**

Transport Processes in Sensor Membranes

Titus Zwickl,[a] Tomasz Sokalski,[b] Monia Fibbioli,[a] Bernhard Schneider,[a] Ernö Pretsch[a]

[a] Department of Organic Chemistry, Swiss Federal Institute of Technology, CH-8092 Zürich
[b] On leave from University of Warsaw, Department of Chemistry, PL-02093 Warsaw

Various time-dependent processes in the bulk of solvent polymeric membranes are analyzed by using a flow-through cell mounted on a microscope equipped with optical filters and a CCD camera to record pictures at selected wavelengths with a resolution of ca. 2 µm.
The water uptake of dry membranes based on 2-nitrophenyl octyl ether (o-NPOE)/poly(vinyl chloride) (2:1) is investigated with the help of a lipophilic water indicator, thus determining an apparent water diffusion coefficient, $D^*_{H_2O}$, of 2×10^{-8} cm^2 s^{-1}. In contrast to results of Harrison et al. obtained with hydrophilic water indicators, $D^*_{H_2O}$ is found to be independent of time, and no light scattering due to water droplets occurs in the bulk of the membrane. On the other hand, by using a custom-built cell in connection with a Karl Fischer titrator, true diffusion coefficients of water-saturated membranes of various compositions have been shown to be about 100 times larger.
Cation interference in H^+-selective electrode membranes based on a chromoionophore induces long-term potential drifts. Simultaneous measurements of the concentration profiles of the protonated and unprotonated forms of the chromoionophore allow to evaluate the rate-determining process and to correlate the diffusion processes with non-monotonic potential-time transients.
As an additional application of the new technique, the coextraction of acids into H^+-selective membranes is studied. The diffusion processes observed in this case can be correlated with the response times of optode membranes of the same composition.

Medicinal Chemistry **22**

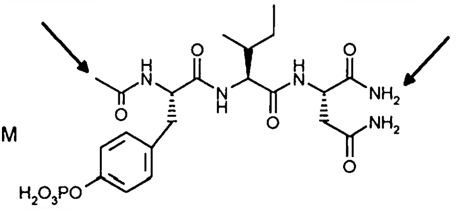
Antagonists of the SH2 Domain of Grb2

Pascal Furet, Brigitte Gay, Carlos García-Echeverría, Heinz Fretz, Joseph Rahuel, Joseph Schoepfer and Giorgio Caravatti

Oncology Research, Novartis Pharma Inc., CH-4002 Basel

Activation of the ras proteins is a key step in the biochemical pathways triggered by ligand bound cell surface receptors which are tyrosine kinases or associated with tyrosine kinases. The activation of ras proteins is triggered by a family of guanine nucleotide releasing factors (GRFs) which are themselves regulated by an SH2 (Src homology 2) domain containing adaptor protein referred to as Grb2 (growth factor receptor bound protein 2). Therefore, Grb2 appears to be an important link between activated growth factor receptors and the ras pathway.
Deregulations at the growth factor or growth factor receptor level lead to deregulation of ras signaling. This is known to be central to many tumors. Grb2-SH2 antagonists, as modulators of ras, would be potentially attractive antitumor agents and could also have potential in other indications in which regulation of signal transduction through SH2-phosphoprotein interactions is required.
We have designed antagonists of Grb2-SH2 starting from the natural 1068-sequence of the EGF receptor. We report on modifications at the N- and C-terminus of the minimum binding sequence, Ac-pY-I-N-NH_2 which have led to nano-molar compounds.

Minimum sequence:
Ac-pY-I-N-NH2: IC_{50} 10 µM



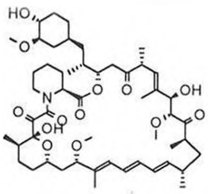
Medicinal Chemistry **23**

Rapamycin Chemistry: Manipulation of The Cyclohexyl Subunit and of The Triene Region

S. Cottens, R. Sedrani, J. Kallen, W. Schuler, G. Zenke
Transplantation Research, Novartis Pharma AG, CH-4002, Basel

Rapamycin **1** has attracted a lot of interest in recent years because of its potential use in the prevention of allograft rejection or in the treatment of autoimmune diseases. Like the structurally related macrolide FK506, rapamycin binds to a family of intracellular proteins, termed FK506-binding proteins (FKBPs). Despite this similarity, the mechanisms by which these natural products exert their immunosuppressive activity are clearly distinct, indicating that binding to FKBP is not sufficient for immunosuppressive activity. Indeed, whereas the complex FKBP-FK506 binds to and inhibits the serine-threonine phosphatase calcineurin, the complex FKBP-rapamycin binds to another target protein called FRAP.

We will describe transformations of the cyclohexyl subunit of rapamycin leading to the analogue **2** and derivatives thereof. These analogues retain a high affinity to FKBP but display a reduced immunosuppressive activity. These results indicate that the cyclohexyl moiety of rapamycin is involved not only in the interaction with FKBP as assumed so far, but also in the interaction of the FKBP-rapamycin complex with FRAP. In addition we will describe the preparation of a series of 16-demethoxy-16-(alk-2-ynyl)oxy analogues **3** which possess an FKBP-binding affinity comparable to rapamycin but are up to 10 fold more immunosuppressive.



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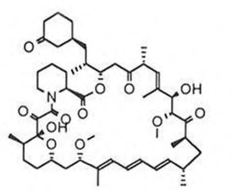

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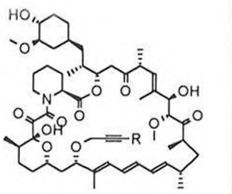

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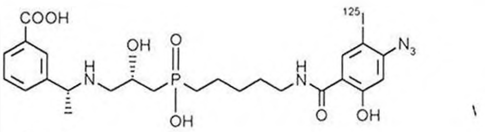
Medicinal Chemistry **24**

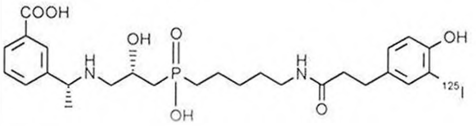
Ligands for Expression Cloning of GABA$_B$ Receptors

Wolfgang Froestl, Bernhard Bettler, Helmut Bittiger, Klemens Kaupmann and Stuart J. Mickel
Novartis Pharma AG, Research Department, CH-4002 Basel

Although GABA$_B$ receptors were characterized pharmacologically already in 1980 [1] the cloning of these G-protein coupled (metabotropic) receptors - attempted by several groups since 1988 - proved to be very difficult. We developed two radioligands, which allowed finally the cloning of the splice variants GABA$_B$ R1a and -b [2]. The photoaffinity ligand [^{125}I]CGP71872 revealed two putative GABA$_B$ proteins of 130K and 100K in rat cerebral cortex membranes. Autoradiography using [^{125}I]CGP64213 allowed to pick up a GABA$_B$ receptor clone from a cDNA library of 2 million clones after transfection in COS-1 cells. The rationale behind and the syntheses of the ligands will be presented.



[^{125}I]CGP71872



[^{125}I]CGP64213

[1] Bowery, N.G., Hill, D.R., Hudson, A.L., Doble, A., Middlemiss, D.N., Shaw, J., Turnbull, M. *Nature* (1980), 283, 92-94.
[2] Kaupmann, K., Huggel, K., Heid, J., Flor, P.J., Bischoff, S., Mickel, S.J., McMaster, G., Angst, C., Bittiger, H., Froestl, W., Bettler, B. *Nature* (1997), 386, 239-246.

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Medicinal Chemistry **25**

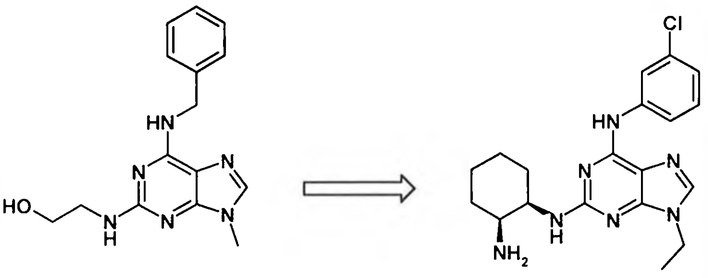
Structure-Based Optimization of Olomoucine, a Cyclin-Dependent Kinase 2 (CDK2) Inhibitor

Pascal Furet, Patricia Peterli, Hans-Georg Capraro, Stephan Ruetz, Thomas Meyer and Juerg Zimmermann

Novartis Pharma Inc., Oncology Research Department, CH-4002 Basel

Cyclin-dependent kinases play a critical role in regulating the cell cycle [1]. By blocking cell-cycle progression, inhibitors of these enzymes have the potential to become new interesting antitumor agents. In particular, we have initiated a medicinal chemistry program aiming at the discovery of potent and selective inhibitors of CDK2.

As part of this effort, we report here our work to improve the potency of the micromolar inhibitor olomoucine [2] following a molecular modeling approach based on the X-ray structure of the enzyme. The result of this work is examplified by CGP 74514 which is two orders of magnitude more active than olomoucine while maintaining high selectivity.



OLOMOUCINE

CGP 74514

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Medicinal Chemistry **26**

Discovery and Synthesis of Three Chemical Classes of Selective Dopamine D4 ligands

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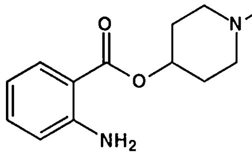
The dopamine D4 receptor (D4R) has been implicated in affective and emotional disorders including schizophrenia. Using CHO cells expressing the human D4R, novel potent and selective ligands were identified. Optimization of these lead compounds led to the synthesis of the antagonists Ro 61-6270 and Ro 62-4599, which inhibited DA-induced GTPγS binding to CHO-D4 cell membranes. Ro 62-4599 has subnanomolar affinity and over 10,000-fold selectivity vs. D2R.

In addition, the 1-phenoxy-3-(4-phenyl-piperazin-1-yl)-propan-2-ol derivative Ro 10-4548, was identified as a selective, high-affinity agonist.

These compounds are currently being used in behavioural studies to investigate potential roles of the D4R in dopaminergic disorders.



Ro 61-6270

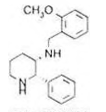
Medicinal Chemistry **27**

Neurokinin Antagonists as Potential New Drugs for the Treatment of Asthma

Andreas von Sprecher

Research Department, Novartis Pharma AG, CH-4002 Basel

The neurokinins substance P (SP) and neurokinin A (NKA) are present in human airway sensory nerves. Activation of these nerves leads to the local release of neuropeptides within the lung , notably SP and NKA, which cause an acute inflammatory response referred to as "neurogenic inflammation". This response includes bronchoconstriction and bronchial hyperreactivity (principally via NK2 receptor activation), vasodilation, microvascular leak, recruitment of inflammatory leukocytes and mucus hypersecretion (principally via NK1 receptor activation). For the last few years many pharmaceutical companies engaged in research programs aimed at the development of neurokinin antagonists as anti-asthma drugs. The first clinical trials with FK 224 a peptide with dual NK1/NK2 antagonist activity and CP-99994, a nonpeptide NK1 selective antagonist were negative. As a consequence the role of neurokinins in asthma was questioned. However clinical trials with more potent second and third generation neurokinin antagonists might still demonstrate a crucial role for the neurokinins in airway inflammation and asthma. Recent developments in the field of neurokinin antagonists will be discussed.



CP-99994

FK 224

Medicinal Chemistry **28**

5-Aminomethyl-quinoxalinediones: a Novel Class of Ionotropic Glutamate Receptor Antagonists

Y. Auberson, P. Acklin, H. Allgeier, S. Bischoff, R. Moretti, S. Ofner, S. Veenstra

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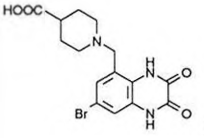
L-Glutamate is the major excitatory neurotransmitter in the mammalian brain, acting at ionotropic and at metabotropic receptors. Excessive activation of a number of these receptors has been shown to be involved in the neurodegeneration occuring after cerebral ischemia [1] and to play a role in triggering seizures associated with epilepsy [2]. Compounds preventing this excessive stimulation are expected to be of therapeutic interest [3].

Several quinoxalinediones acting as antagonists at the ionotropic glutamate receptors have been described in the literature [4,5], but most suffer of a low solubility or of a lack of selectivity. We report here the structure-activity relationship of amino-acid derivatives of 5-aminomethyl-quinoxalinediones, derived from the lead structure **1**, and the identification of water-soluble, selective antagonists with good *in vitro* potencies at AMPA receptors (e.g. **2**) or at the glycine-binding site of NMDA receptors (e.g. **3**).



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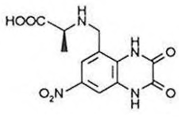

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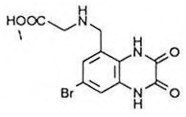

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Medicinal Chemistry **29**

Kinetic Studies of Nitrogen Monoxide Induced Oxidation of Oxymyoglobin and Oxyhemoglobin

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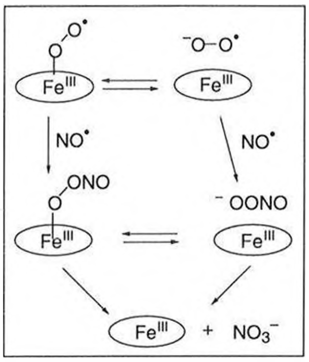
Nitrogen monoxide ($NO^{\bullet}$) has been found to be involved in a variety of physiological functions such as transmission of nerve impulses, smooth muscle relaxation, inhibition of platelet aggregation, regulation of blood pressure, and immune response to bacterial infection.

Despite the physiological importance of the reaction between nitrogen monoxide ($NO^{\bullet}$) and oxyhemoglobin, considered to be the major pathway for $NO^{\bullet}$ depletion and the cause of vasoconstriction when extracellular hemoglobin-based dioxygen carriers are administered, its mechanism is not well understood [1]. In particular, it has been proposed that this reaction might proceed via a peroxynitrite ($ONOO^-$) intermediate, free or coordinated to the iron center, which then isomerizes to nitrate. This powerful oxidant is also formed *in vivo* by the diffusion-limited reaction of superoxide ($O_2^{\bullet -}$) with $NO^{\bullet}$ and is likely to be responsible for much of the cytotoxicity originally attributed to $NO^{\bullet}$ or oxygen-derived species [2].



To get a better understanding of the mechanism of this reaction, we have measured by stopped-flow the kinetics of the $NO^{\bullet}$-mediated oxidation of horse heart myoglobin under different conditions. Preliminary result show that the bimolecular rate constant raises with increasing pH and varies from about 30 to 60 $\mu M^{-1} s^{-1}$ in the range of pH = 5-9.

[1] Eich, R. F. et al. *Biochemistry* **1996**, *35*, 6976-6983.
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Medicinal Chemistry **30**

Preserving Molecular Diversity for Drug Discovery

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What prices diversity? We argue that molecular diversity consists both chemical information and chemical substances of molecules.
Chemists contribute not only new knowledge but also new substances. However, more than 90% of compounds recorded in literature exist only on paper; they were discarded by chemists. With the development of high throughput screening technology in recent years, the acquisition of chemical samples by samples collection and combinatorial synthesis now become the bottleneck in the process of new drug discovery. The high quality of a chemical library relies on the distinct differences of both the structures and properties of the collected samples [1]. These compounds in isolated form are traditionally and still routinely prepared in the laboratories and isolated from natural sources. Among other strategies, the first journal of organic chemistry and natural product chemistry, *Molecules* (visit http://www.mdpi.org/molecule/), was launched by MDPI in 1995 to encourage authors to deposit their compound samples at MDPI center in Switzerland and distribute at reasonable prices worldwide. This example has been followed by six other chemistry journals so far (http://www.mdpi.org/forum.htm). The idea [2] of this program is to supply both chemical information as well as the chemical substances themselves.

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Medicinal Chemistry **31**

Diversity Platform in Combinatorial Chemistry: Transformation of α,β-Unsaturated Ketones on Solid Phase

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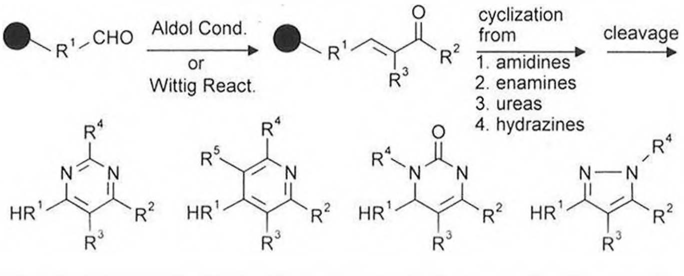
The search for new valuable drug candidates not only demands that numerous structural subunits (building blocks) are combined on a particular backbone or template, but also that a rich variety of such scaffolds is provided. Occasionally, reports in the literature have indicated that from certain intermediate structures grafted on the solid phase, it is possible to derive more than one type of heterocyclic compound libraries, e.g. dioxopiperazines and dioxomorpholines from α-bromo substituted dipeptides [1], or pyrazoles and isoxazoles from β-diketones [2].



Here we discuss the value of α,β-unsaturated ketones as key intermediates for the combinatorial assembly of 4 different templates on solid phase, namely pyrimidines, dihydropyrimidinones, pyridines and pyrazoles.

[1] B. O. Scott, A. C. Siegmund, C. K. Marlowe, Y. Pei, K. L. Spear, *Mol. Diversity* **1996**, *1*, 125.
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Medicinal Chemistry **32**

A NOVEL TRICYCLIC DIKETOPIPERAZINE-BASED TEMPLATE TO STABILIZE LOOP CONFORMATIONS IN A CYCLIC PEPTIDE CONTAINING THE NPNA MOTIF

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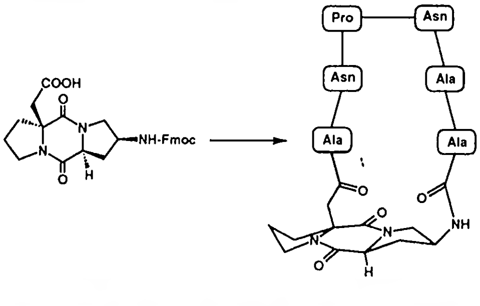
Organic templates are currently of interest in the design of small molecule peptide and protein mimetics. They are also of interest as scaffolds upon which a variety of pharmacophore groups may be attached in a combinatorial chemistry approach to ligand discovery. Here we describe the synthesis of the tricyclic dipeptide template *(2S, 5aS, 10aS)-5,10-Dioxoperhydro-2-{[(9*H*-fluoren-9-yl)methoxycarbonyl]amino}pyrrolo[1,2-*a*]pyrrolo[1,2-*d*]pyrazine-5a-acetic acid*, which was incorporated into the cyclic molecule cyclo(-Ala^1-Asn^2-Pro^3-Asn^4-Ala^5-Ala^6-template-) according to solid-phase peptide synthesis using Fmoc chemistry.



The conformations of this cyclic peptide mimetic in water was studied by NMR methods. Average solution structures derived by restrained dynamic simulated annealing (SA) point to a highly populated βI-turn within the Asn-Pro-Asn-Ala motif, and also indicate which conformations are preferred by the template itself. At present syntheses of more functionalised diketopiperazine-type templates are being developed and their use in the design of protein loop mimetics of defined conformation and biological activity are being explored.

Medicinal Chemistry **33**

Attemped mimicry of a conformational epitope on the human interferon gamma receptor with cyclic peptides

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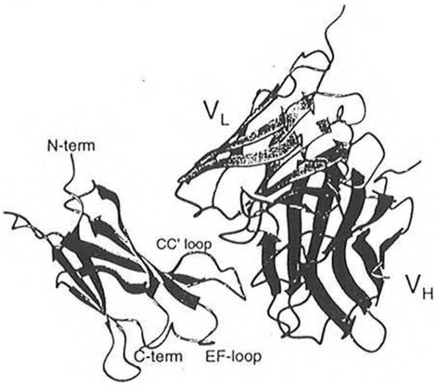
The extracellular interferon γ receptor α-chain (IFNγR) compromises two immunoglobulin-like domains [1]. In each domain, the chain forms two antiparallel β-sheets composed of β-strands A, B, E and G, F, C and C'. The epitope recognised by the neutralising antibody A6 has recently been characterised by homologue scanning mutagenesis and by X-Ray crystallography [2], and shown to comprise primarily the CC' surface loop of the receptor. Attempts have been made to mimic this surface epitope using disulfide-bridged, cyclic and template-bound peptides. The biological activity of the conformationally constrained peptides was assessed using a BIAcore instrument. Binding assays with analogues containing modified peptide sequences have given insights into which groups in the protein loop are important for recognition by the antibody.



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[2] Sogabe, S. et al. submitted.

Chimie thérapeutique **34**

Synthèse et Modélisation d'Analogues Hydrosolubles du GalCer, Récepteur du VIH-1.

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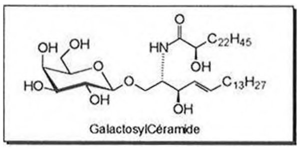
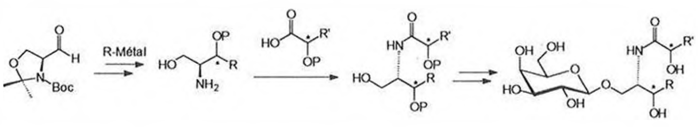
Le GalactosylCéramide (GalCer) est un récepteur glycosphingolipidique permettant au virus d'immunodéficience humaine(VIH)-1 de pénétrer dans des cellules dépourvues du récepteur CD4.[1]



La conformation fondamentale du GalCer a été établie par mécanique moléculaire. Nous avons montré qu'une longueur minimale des deux chaînes hydrocarbonées était nécessaire pour conserver cette conformation caractéristique.
Une série d'analogues du GalCer à chaînes écourtées a alors été préparée suivant une voie générale de synthèse stéréosélective que nous présentons.



Ces analogues sructuraux se sont avérés suffisament hydrosolubles pour permettre d'étudier expérimentalement, *in vitro* et *in vivo*, la reconnaissance moléculaire entre la gp120, protéine de surface du virus, et le GalCer.

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[1] "HIV Infection in $CD4^-$ Cells" *Perspectives in Drug Discovery and Design, Vol.5*; J. Fantini et J.-M. Sabatier Ed.; ESCOM : Leiden, 1996.

Medicinal Chemistry **35**

NEW SOMATOSTATIN ANALOGUES FOR SPECT, PET AND INTERNAL RADIOTHERAPHY

A. Heppeler, M. Béhé, E. Jermann, P. Powell, S. Froidevaux, H. R. Mäcke
Institute of Nuclear Medicine, University Hospital Basel, Switzerland

A variety of tumors show an overexpression of receptors for somatostatin (SRIF). For the visualization of such tumors radiolabeled SRIF analogues have been used successfully. These conjugates show sufficient stability only for diagnostic radionuclides and are not promising for internal radiotherapy. We designed DOTA (1,4,7,10-tetraazacyclododecane-1,4,7,10-tetraacetic acid) derivatized somatostatin analogues (tyr^3-octreotide and octreotide) to study if DOTA serves as a unique chelator for a multitude of hard radiometals for diagnosis and therapy with regard to high in vivo stability and preservation of biological integrity and applicability in patients.
The two new conjugates were labelled with Ga-67, In-111 and the β-emitter Y-90 with high specific activity and high radiochemical purity. Radiolabelled **DOTATOC** and **DOTAOCT** show high stability in human serum. In vitro binding studies demonstrate that the two labelled conjugates are highly specific radioligands for the SRIF receptor (sst_2). In vivo biodistribution studies in a tumor bearing nude mice model show high uptake in SRIF receptor positive tissues and the fast background clearance of the two radiolabelled derivatives. First human studies with ^{111}In-**DOTATOC** (6 patients) confirm the superior tumor uptake and background clearance in comparison to the commercial ^{111}InOctreoScan.
The presented data show clearly that **DOTATOC** and **DOTAOC** are two new promising conjugates, whereby ^{111}In-**DOTATOC** appears to be superior to ^{111}In-OctreoScan. The new tracer ^{90}Y-**DOTATOC** with its low kidney uptake and retention delineates a new modality for receptor-mediated radiotherapy.

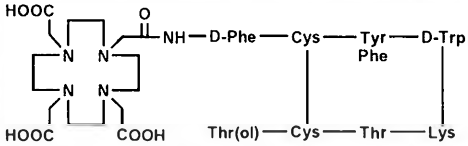

Fig. 1 DOTA-octreotide (**DOTAOC**)
DOTA-tyr^3-octreotide (**DOTATOC**)

Medicinal Chemistry **36**

Drug-Membrane interactions as described by partitioning in liposome/water systems

Caron Giulia$. Carrupt Pierre-Alain$, Testa Bernard$, Fruttero Roberta*, Fornatto Elisa*, Boschi Donatella*, Ermondi Giuseppe* and Gasco Alberto*

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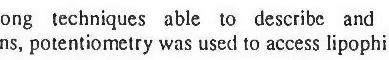
$Institut de Chimie Thérapeutique, BEP, UNIL, CH-1015 Lausanne.

The human body can be visualized as a very large series of aqueous compartments separated by lipid membranes that control the distribution of xenobiotics. The partitioning of molecules into biological membranes is governed by their lipophilicity, which is thus the major factor determining their pharmacokinetic behaviour.

For complex compounds such as drugs, the traditional isotropic two-phase solvent systems (such as *n*-octanol/water) are not always a good indicator of biodistribution. In addition, all cell membranes do not possess the same biophysical characteristics. Thus anisotropic systems such as liposome/water are an interesting field to explore.

In this work a series of (*p*-methylbenzyl)alkyl-amines (I) were synthetized to compare their lipophilic behaviour in octanol/water and in liposome/water, and to verify whether in the liposome/water system the mechanisms governing the partitioning of neutral and cationic forms remain constant in a congeneric series of compounds (I).


$CH_3-C_6H_4-CH_2-NH-(CH_2)_n-CH_3 \cdot HCl$ n = 1-10 (I)

Among techniques able to describe and quantify drug-membrane interactions, potentiometry was used to access lipophilicity behaviour, and NMR spectroscopy clarified the mechanisms of interaction between compounds and liposomes.

The findings indicate that partitioning in isotropic and anisotropic media gives different information and demonstrates the relevance of electrostatic

Chimie thérapeutique **37**

Etude par modélisation moléculaire du complexe d'une protéine MHC de classe II I-A^{k} et du peptide HEL (52-61)

Isabelle Raynaud[1], Peter Weber[1], Pierre-Alain Carrupt[1], Joelle Paris[2], Denis Gerlier[3], Chantal Rabourdin-Combe[4], Laurent Ettouati[2] et Bernard Testa[1]

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2. Laboratoire de Chimie thérapeutique, Faculté de Pharmacie, F-69373 Lyon Cedex 08
3. Immunité et infections virales, IVMC, UMR30, CNRS-UCBL, F-69373 Lyon Cedex 08
4. Immunobiologie Moléculaire, UMR 49, CNRS-ENS Lyon, F-69364 Lyon Cedex 07

Les molécules du complexe majeur d'histocompatibilité (MHC) sont des glyco-protéines qui lient des peptides pour les présenter ensuite aux cellules T. Les récepteurs situés sur les cellules T (TcR) vont reconnaître les peptides non-désirables pour l'organisme, et induire la prolifération des cellules T. Lorsqu'un peptide appartenant au soi est reconnu par les cellules T, cela produit des maladies auto-immunes. L'étude de la fixation des peptides sur les protéines MHC est donc d'un grand intérêt.

Le complexe peptide/MHC HEL(52-61)/I-Ak étudié ici est constitué d'un décapeptide issu du lysosyme du blanc d'oeuf de poule ou de ses dérivés substitués et d'une protéine MHC de classe II appartenant au système immunitaire de la souris. Le complexe est construit par homologie à la structure cristalline du complexe constitué de la protéine humaine MHC de classe II HLA-DR1 et du peptide du virus de la grippe HA(306-318) [1]. Pour contruire le site actif du complexe, nous avons utilisé des résultats expérimentaux provenant de tests de reconnaissance fonctionnelle par les cellules T [2].

Nous décrirons la détermination de la géométrie de ce complexe par dynamique moléculaire et minimisation de l'énergie ainsi que l'étude des surfaces en contact avec les récepteurs TcR par cartographie de Potentiel de Lipophilie Moléculaire(MLP).

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Medicinal Chemistry **38**

Lipophilicity Profiles of Ampholytes

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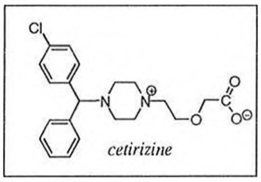
Experimental and computational advances have now demonstrated the significance of the lipophilicity of ionised species, whose partitioning in organic solvents and permeation into biological membranes can no longer be neglected and are in fact of great biological significance.

One particular class of ionised solutes is that of amphoteric compounds (i.e., ampholytes), which are frequently encountered in pharmaceutical research either as actual drugs or as metabolites. They can be classified conveniently into two main categories, namely the *ordinary* and the *zwitterionic ampholytes*.

As far as their lipophilicity is concerned, zwitterionic ampholytes exhibit incompletely understood intramolecular effects which increase their lipophilicity, such as charge delocalization, internal electrostatic bonds and folding. The most recent results (e.g., *cetirizine*) will be examined to clarify the factors at play in controlling the lipophilicity of zwitterions. The issues are to find a rational explanation to the pH-dependent lipophilicity behaviour of zwitterions, and to relate their partitioning to pharmacological properties and pharmacokinetic behaviour.



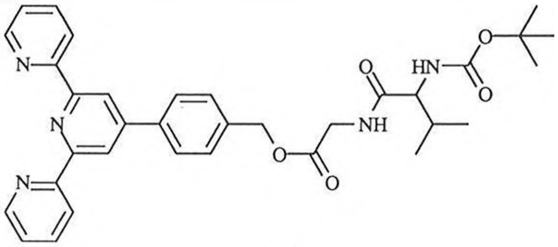
Inorganic Chemistry **39**

Biofunctionalized metal-complexes

Reza-Ali Fallahpour, Edwin C. Constable, Catherine E. Housecroft, Stefan Mundwiler and Amina Wirth

Laboratory for Supramolecular Chemistry, Institute of Inorganic Chemistry, University of Basel, CH-4056 Basel

The facile formation of bis(2,2':6',2"-terpyridine)metal complexes incorporating hetero- or homoleptic ligands makes this an attractive motif for assembly of molecular recognition motifs. In this poster, this use of 2,2':6',2"-terpyridine ligands bearing biological recognition sites will be presented. Ligands bearing peptide **1** or nucleotide **2** substituents will be discussed.



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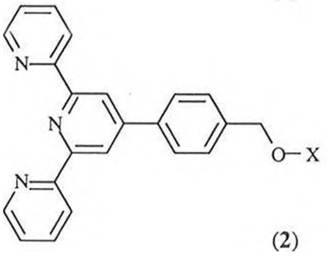

X = thymine or uracil

(2)

Inorganic and Coordination Chemistry **40**

SYNTHESIS OF NEW DINUCLEAR COMPLEXES OF RU(II) AND OS(II)

Gabriella Albano and Peter Belser

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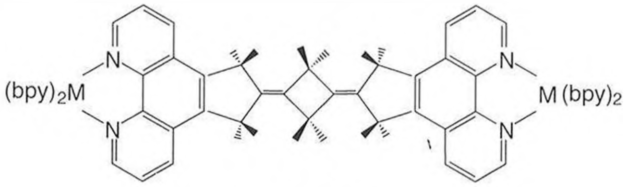
Complexes of Ru(II) and Os(II) can be used as building blocks in supramolecular species in view of the construction of sensors, light-harversting and charge separation devices. Experiments have shown that the best connectors between the metal centers are rigid bridging ligands with a C_2-axis [1].

Here we present the synthesis [2] of a new bridging ligand (PCP) based on two 1,3-dihydro-1,1,3,3-tetramethyl-7,8-diazacyclopenta-(1)-phenanthrene units connected by a tetramethylcyclobutane unit.



M= Ru, Os

The syntheses of the dinuclear complexes Ru-PCP-Ru, Os-PCP-Os, Ru-PCP-Os are presented. The compounds are characterized by ^{1}H-NMR, ^{13}C-NMR, MS(FAB), UV-vis spectra and cyclovoltammetry.

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CHIMIA 51 (1997) Nr. 8/9 (August/September)

Inorganic and Coordination Chemistry

41

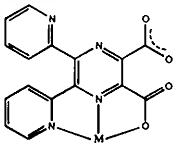
Zn(II), Co(II), & Mn(II) COMPLEXES OF A NEW SUBSTITUTED PYRAZINE LIGAND : 5,6-BIS(2-PYRIDYL)-PYRAZINE-2,3-DICARBOXYLIC ACID

M. Alfonso, Y.Wang, H. Stoeckli-Evans

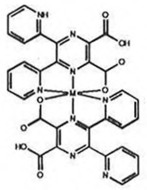
Institut de Chimie, Université de Neuchâtel, Avenue de Bellevaux,51,
CH-2000 Neuchâtel, Switzerland

The new pyrazine-based ligand, 5,6-bis(2-pyridyl)-pyrazine-2,3-dicarboxylic acid (H_2L) has been synthesized in order to study the formation of coordination compounds with first row transition metals and Zinc.
H_2L has proved to be an extremely versatile ligand as up to four different binding modes have been observed to date.

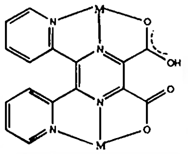
I ($M^{2+} = Zn^{2+}$)



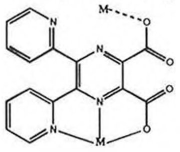
II ($M^{2+} = Co^{2+}$)



III ($M^{2+} = Co^{2+}$)



IV ($M^{2+} = Mn^{2+}$)



Further coordination modes are expected for this unusual "aminoacid".

Inorganic-Coordination Chemistry

42

Synthesis of Methylamines from CO_2, NH_3 and H_2 over Cu/Mg-Al Mixed Oxides Derived from Cu-Mg-Al LDHs

S.M. Auer, S.V. Gredig, R.A. Köppel and A. Baiker
Laboratorium für Technische Chemie, ETH Zentrum, 8092 Zürich

The synthesis of methylamines from CO_2, NH_3 and H_2 over Cu/Al_2O_3 has recently been studied in our group in order to investigate the potential of CO_2 as a starting material for the production of valuable chemicals [1]. Lamellar double hydroxides (LDHs) are often used as precursors for metal/mixed oxide catalysts in order to increase the thermal stability of highly dispersed metals. In this study, the relation between structural and chemical properties of Cu/Mg-Al mixed oxides, derived from Cu-Mg-Al LDHs, and their catalytic behavior in the synthesis of methylamines from CO_2, NH_3 and H_2 has been investigated.

Catalysts containing 33 at% of Cu, related to the total metal content, with different ratios of Mg(II) and Al(III) were prepared by precipitation of metal nitrates with Na_2CO_3. The thoroughly washed precipitates were calcined for 4 h at 673–873 K in vacuo. Amination was carried out in a fixed-bed microreactor at 473–553 K and 0.6 MPa pressure. The feed gas mixture contained 20% CO_2, 20% NH_3 and 60% H_2 (total flow rate 150 ml min^{-1}). In all experiments, 3 g of catalyst were used, which were reduced in a H_2/N_2 stream at 473 K before reaction.

Crystalline phases of the samples were determined by XRD. After precipitation, all samples contained a hydrotalcite phase, the typical crystalline phase of LDHs. After reaction, metallic Cu was observed. The corresponding Cu particle sizes, estimated from XRD line broadening, amounted to 15–35 nm for the Cu/Mg-Al mixed oxides. Cu surface areas, determined by N_2O titration, ranged from 14 to 7 $m^2\ g^{-1}$.

The amine production rate of the Cu/Mg-Al mixed oxides decreased with increasing Mg content (0.3–0.1 mol $kg_{cat}^{-1}\ h^{-1}$ at 513 K). Selectivity to monomethylamine, related to total amines, increased with increasing Mg content (87–100%). Compared to Cu/Al_2O_3, Cu/Mg-Al oxides exhibited similar amine production rates and significantly higher selectivities to monomethylamine.

[1] S.V. Gredig, R.A. Köppel, A. Baiker, *Catal. Today* **1996**, 29, 339.

Inorganic and Coordination Chemistry

43

Palladium-Catalyzed Asymmetric Heck-Arylation with Pyrazole-Containing Ferrocenyl Ligands

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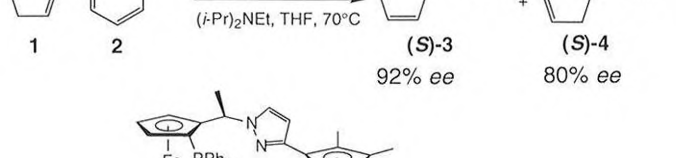
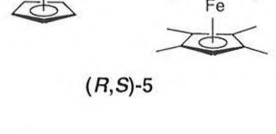
Chiral phosphanyldihydrooxazole ligands has been shown to afford a very high enantio- (up to 97% *ee*) and regioselectivity in the palladium-catalyzed Heck-type reaction of 2,3-dihydrofuran (**1**) with phenyltriflate (**2**) obtaining the two isomeric products **3** and **4** [1].
Therefore, it was interesting for us to apply our P,N pyrazole containing ferrocenyl ligands. The highest enantioselectivity for both isomers **3** and **4** (92% *ee*, 80% *ee* resp.) was achieved with ligand **5**. The influence of the substituents attached to phosphorus and to the pyrazolyl fragment on stereo- and regioselectivity was studied.





(*R*,*S*)-5

[1] O. Loiseleur, P. Meier, A. Pfaltz, *Angew. Chem.* **1996**, *108*, 218

Technische Chemie

44

Electrochemical reduction of thiophenes - a first step towards a molecular mechanism of the thiophene hydrodesulfurization reaction

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Catalytic hydrodesulfurization (HDS) of crude is carried out in refineries all over the world. During the HDS reaction, molecules containing sulfur are converted at moderately high pressures of H_2 and ca. 400°C into hydrogenated compounds and H_2S, typically employing Co- or Ni-promoted MoS_2-type phases supported on γ-Al_2O_3 as the catalyst. Although this reaction has been used successfully over many years, significant improvements will be necessary to satisfy the requirements of the planned environmental legislation. At present, this is almost impossible, because many aspects of the catalytic reaction, such as the precise surface structure of the catalyst, the relationship between surface structure and reactivity as well as the mechanism of the HDS reaction are still unclear. Using a systematic approach to obtain a molecular mechanism of the HDS reaction, we studied the electrochemical reduction of thiophene on different electrode materials. Cyclic voltammetry measurements with Pt, Mo, and microcrystalline MoS_2 on Mo as the electrode materials provided valuable knowledge about the surface affinity of thiophene towards the different electrode materials. Since MoS_2-type electrodes are of great importance for the technical HDS-process, we prepared them according to different methods that is by decomposition of molecular molybdenum sulfide compounds and by electrochemical deposition from an aqueous solution of K_2MoS_4. The latter results in a highly textured film of MoS_2 after annealing at 550°C in inert gas. In a next step we will combine cyclic voltammetry with infrared and Raman spectroscopy. Infrared and Raman spectra, measured during the electrochemical experiment, will provide unique structural information on the catalyst-thiophene system, i.e. the structural changes of the catalyst surface upon reduction and of thiophene while being coordinated to the electrode as well as the structural evolution of thiophene during its reaction to H_2S and C_4 products.

Inorganic and Coordination Chemistry **45**

TRIPTYCENE A VERSATILE SPACER FOR BRIDGING LIGANDS

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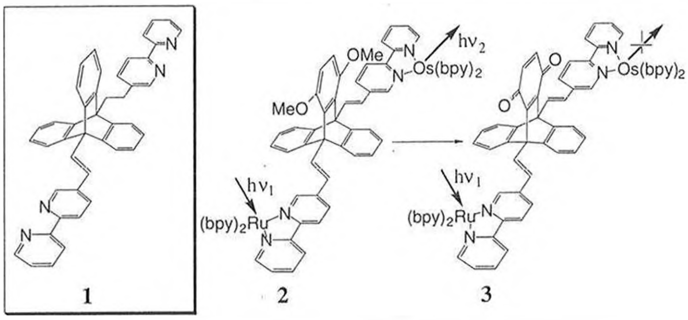
University of Fribourg, CH-1700 Fribourg, Switzerland

The synthesis and study of bridged dinuclear metal complexes that can act as light driven molecular devices (PMD's) are of great interest. By means of such molecular machines, we can study energy and electron transfer reactions[1]. Molecular switches are an extension of such PMD's. The switches themselves can fulfill the functions YES/NO, AND/OR or can be used as photon-reading or -writing systems [2].

Triptycene is a versatile spacer. An oxidized form of the triptycene can act as a pH dependent electron trap (see the following molecules 1-3).



Prepared metal complexes: Ru/Ru, Os/Os and Ru/Os.

Here, we report the preparation of the different bridging ligands and the corresponding homo and hetero dinuclear metal complexes. We have used the Ruthenium-tris-diimine part as a photosensitizer unit and the Osmium-tris-diimine part as a light emitting acceptor unit. The ground state and photophysical properties were studied in detail.

[1] a) Bernhard, S.; Belser, P. *Synthesis* **1996**, 192. b) De Cola, L.; Balzani, V.; Barigelletti, F.; Flamigni, L.; Belser, P.; Bernhard, S. *Recl. Trav. Chim. Pays-Bas* **1996**, *114*, 534.
[2] De Silva, A.; Gunaratne, H.; McCoy C. *Nature* **1993**, *364*, 42.

Anorganische/Koordinations-/Chemie **46**

Intramolecular Stacking Interactions in the Ternary Complex Cu(bpy)(PMEC) in Aqueous Solution

(bpy = 2,2'-Bipyridyl; PMEC = 9-[2-(Phosphonomethoxy)ethyl]cytosine)

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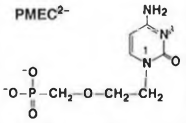
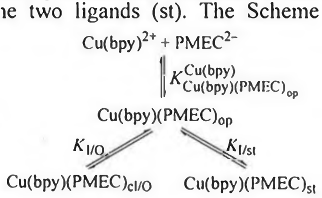
[a] *Inst. of Inorg. Chem., University, Spitalstr. 51, CH-4056 Basel, Switzerland;*
[b] *Inst. of Org. Chem. & Biochem., Acad. of Sci., CZ-16610 Prague, Czech Rep.*



Within our studies of the proton- and metal ion-binding properties of acyclic nucleotide analogs [1] we are evaluating presently the stability of binary and ternary complexes of $PMEC^{2-}$, which may be considered as an analog of cytidine 5'-monophosphate (CMP^{2-}). The ternary complex Cu(bpy)(PMEC) was studied in order to establish the ability of PMEC to interact via π-stacking with a second ligand, as ligand-ligand interactions are crucial for numerous biochemical reactions [2]. Cu(bpy)(PMEC) ($\log K^{M(bpy)}_{M(bpy)(PMEC)} = 4.26\pm0.06$) is considerably more stable than the binary complex Cu(PMEC) ($\log K^{M}_{M(PMEC)} = 3.73\pm0.03$). Comparisons with the calculated stability constant based on a pure phosphonate coordination [3] and with the value due to the Cu(bpy)(PME) complex, where $PME^{2-} = CH_3CH_2\text{-}O\text{-}CH_2\text{-}PO_3^{2-}$, reveal the formation of five-membered chelates involving the ether O (cl/O) as well as a direct stacking interaction between the two ligands (st). The Scheme shows the equilibria involved. The respective constants were determined; they allow to calculate the percentages of the three isomeric complexes: The 'open' form (with Cu^{2+} solely coordinated via the $-PO_3^{2-}$ group) occurs with 10±2%, whereas the $Cu(bpy)(PMEC)_{cl/O}$ and $Cu(bpy)(PMEC)_{st}$ species form to 28±8 and 63±9%, respectively. The latter value may be compared with 51±9% for $Cu(bpy)(CMP)_{st}$ [2].



Supported by the Swiss Nat. Sci. Found., the Swiss Fed. Off. for Educ. & Sci. (COST D1 & D8), and the Min. of Educ. of the Czech Rep. (COST D1 & D8).

[1] H. Sigel, D. Chen, N. A. Corfù, F. Gregáň, A. Holý, and M. Strašák, *Helv. Chim. Acta 75* (1992) 2634-2656.
[2] O. Yamauchi; H. Sigel, et al., *Met. Ions Biol. Syst. 32* (1996) 207-270.
[3] D. Chen, M. Bastian, F. Gregáň, A. Holý, and H. Sigel, *J. Chem. Soc. Dalton Trans.* (1993) 1537-1546.

Inorganic and Coordination Chemistry **47**

A NEW BRIDGING LIGAND PHENANTHROLINE-STELLANE-PHENANTHROLINE

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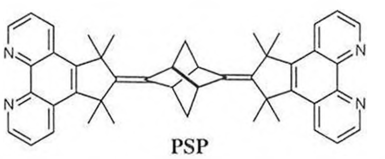
The synthesis of the phenanthroline-stellane-phenanthroline (PSP) bridging ligand offers the possibility to prepare homo and hetero dinuclear complexes with Ruthenium and Osmium as metal centers. With such compounds we are able to study electron and energy transfer reactions after irradiation into the donor part of the metal complex [1].



PSP

The nature of the stellane spacer between the two phenanthroline moieties determines the dihedral angles (45°). Such an arrangement of the complexing units must influence the energy or electron transfer properties. In addition, the corresponding PES measurements of the stellane unit show that the two exo double bonds of the spacer are strongly electronically coupled [2].

We discuss the synthesis of the bridging ligand and of the homo- and heteronuclear metal complexes. The prepared compounds are characterised by ^{1}H-NMR, MS, UV-vis and PES.

[1] De Cola, L.; Balzani, V.; Barigelletti, F.; Flamigni, L.; Belser, P.; Bernhard, S. *Recl. Trav. Chim. Pays-Bas* **1996**, *114*, 534.
[2] a) Gleiter, R.; Borzyk, O. *Angew. Chem.* **1995**, *107*, 1094.
b) Siegwart, Ch. Dissertation, University of Heidelberg, **1992**.

New Sugar-Ligands in Homogenous Catalysis **48**

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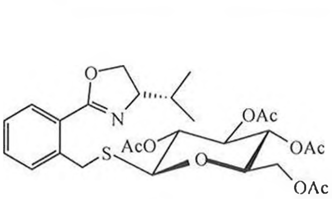
Laboratory of Inorganic Chemistry, Swiss Federal Institute of Technology,
ETH Zentrum, CH-8092 Zürich, Switzerland

Oxazolines derived from readily available amino acids have found widespread use as chiral ligands in asymmetric catalyses [1].

New chiral N,S-ligands **1** based on oxazolines and thioglucose were prepared and characterised.



1

The application of **1** as chiral auxiliary in the Pd(II) catalysed enantioselective allylic alkylation will be shown.

[1] Pfaltz, A. *Acta Chem. Scand.* **1996**, *50*, 189;
Sprinz, J.; Helmchen, G. *Tetrahedron Lett.* **1993**, *34*, 1769;
Frost, C. G.; Williams, J. M. J. *Tetrahedron Lett.* **1993**, *34*, 2015;
Frost, C. G.; Williams, J. M. J. *Tetrahedron: Asymm.* **1993**, *4*, 1785.

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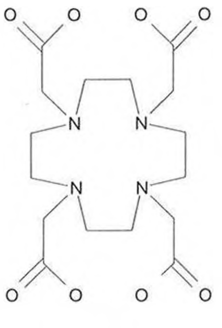
Inorganic chemistry **49**

Molecular dynamics simulations of Gd^{3+} complexes in aqueous solution

Alain Borel, Lothar Helm, André E. Merbach

Institut de Chimie Minérale et Analytique, Université de Lausanne, CH-1015 Lausanne, Switzerland



$DOTA^{4-}$

The effect of Gd^{3+} complexes such as $[Gd(DOTA)(H_2O)]^-$ on magnetic relaxation of surrounding protons is usually divided in two contributions, namely *inner-sphere* (regarding metal-coordinated water molecules) and *outer-sphere relaxivity* (other molecules in the solution) [1]. While factors influencing the former at a molecular level are relatively well understood, the latter is only described by semi-macroscopic models such as Freed's [2]. We use molecular dynamics simulations to study the structure and dynamics of water around Gd^{3+} complexes.

[1] Lauffer R. B., *Chem. Rev.* **1987**, *87*, 901-927.

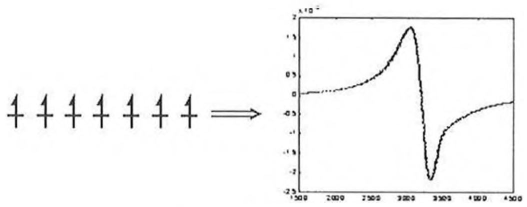
[2] Freed J. H., *J. Chem. Phys.* **1978**, *68*, 4034-4037.

Inorganic chemistry **50**

Electron spin relaxation of MRI contrast agents

Alain Borel, Lothar Helm, André E. Merbach

Institut de Chimie Minérale et Analytique, Université de Lausanne, CH-1015 Lausanne, Switzerland



Gd(III) complexes used as Magnetic Resonance Imaging contrast agents have a 7/2 electron spin. We report variable temperature and field Electronic Paramagnetic Resonance measurements of several Gd(III) chelates in solution and interpret the results using the idea of a transient zero-field splitting (ZFS) induced by distortions of the complexes [1,2]. Lineshapes analysis gives us access in a novel approach to the three parameters governing the electron spin relaxation rate: Δ^2, the trace of the square of the ZFS tensor, the correlation time τ_v for its modulation and the associated activation energy E_v.

[1] Hudson A., Lewis J. W. E, *Trans. Faraday Soc.*, **1970**, *66*, 1297-1301

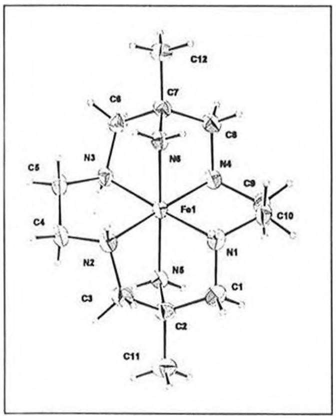
[2] Powell D. H. et al., *Helv. Chim. Acta*, **1993**, *76*, 2129-2146

Anorganische Chemie **51**

Coordination of the Pendant Arm Macrocycle 6,13-dimethyl-1,4,8,11-tetraazacyclotetradecane-6,13-diamine to Iron[II]

Heidi Börzel, Peter Comba and Hans Pritzkow

Anorganisch-Chemisches Institut der Universität Heidelberg,
Im Neuenheimer Feld 503 D-69120 Heidelberg



The hexadentate polyamine macrocycle 6,13-dimethyl-1,4,8,11-tetraazacyclotetradecane-6,13-diamine (trans-diammac) reacts with iron[II] in aqueous deoxygenated solution to form the low-spin iron[II] complex $[Fe(diammac)]^{2+}$. This is one of the few examples of a true low-spin Fe[II] coordination compound with a fully saturated polyamine ligand which has been fully characterized by UV-VIS- and NMR-spectroscopy in solution. We also report the X-ray analysis of the $[Fe(diammac)](PF_6)_2$. Spectroscopic, magnetic and structural properties will be discussed in detail and compared with those of analogous systems.

Inorganic Chemistry **52**

Water exchange on diamagnetic ions using Tb^{3+} as chemical shift agent.

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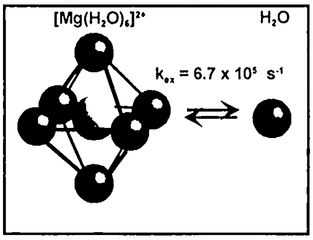
Université de Lausanne, BCH, CH-1015 Lausanne

Variable temperature and pressure ^{17}O nuclear magnetic relaxation studies of water exchange on 2+ and 3+ ions in aqueous solution allowed the assignment of the mechanism for a variety of these reactions.[1] Only a few diamagnetic cations could be studied directly by NMR. Because of the relatively slow ($k < 10^4$ s^{-1}) water exchange rate on these ions a direct observation of the bound water ^{17}O NMR resonance is possible for Ru(II), Rh(III), Pd(II), Ir(III) and Pt(II). For solutions of Be(II), Al(III) and Ga(III) the large free water signal had to be broadened artificially by adding Mn^{2+}, a strong relaxation agent, to the solution.



Another method to separate the free and bound water NMR signals is the addition of a chemical shift agent ($[Tb(H_2O)_8]^{3+}$). If the free water signal is shifted very much from its normal resonance frequency it is broadened due to fast exchange between the diamagnetic bound site and the bulk water.

We have shown for the case of water exchange on Mg^{2+} that both methods led, within experimental error to the same exchange rate constants. The chemical shift technique under fast exchange condition extends the measurable rate constant for water exchange on diamagnetic cations up to 10^7 s^{-1}. Water exchange on other diamagnetic cations (Zn^{2+}, Th^{4+}) was studied using this new method.

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[1] S. L. Lincoln and A. E. Merbach, *Adv. Inorg. Chem.* **42,** 1 (1995).

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Inorganic and Coordination Chemistry **53**

Kinetics and Mechanism of Water Exchange at the Eu(II) Aquaion

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BCH, 1015-Lausanne, CH

Solvent exchange is the fundamental reaction in inorganic solution chemistry. The simplicity of the exchange reaction, *ie.* like for like, allows the unambiguous assignment of the reaction mechanism from variable pressure measurements. ^{17}O NMR has proved an exceedingly useful tool

$$[M(OH_2)_n]^{x+} + H_2O^* \longrightarrow [M(^*OH_2)(OH_2)_{n-1}]^{x+} + H_2O$$

in the direct study of water exchange on a host of aquated metal ions [1]. One class of metal ions that has escaped direct scrutiny are large dipositive ions with no ligand field stabilization energy, such as Ca(II). The low charge to radius ratio, high coordination number, and lack of covalent bonding ability of such ions leads to very fast exchange rates. Europium(II), unlike the group II ions, is strongly paramagnetic and is isoelectronic with gadolinium(III). The theory and methodology developed for obtaining the rates and mechanisms of water exchange on gadolinium complexes [2] can be applied to Eu(II). Variable temperature, field, and pressure ^{17}O NMR and variable temperature and field EPR measurements on the Eu(II) aquo ion will be reported. These measurements afford the kinetic parameters, k^{298}, $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, $\Delta V^{\ddagger}$, which enable the postulation of a mechanism.

[1] S.F. Lincoln and A. E. Merbach, *Adv. Inorg. Chem.* **1995**, *42*, 1.
[2] D.H. Powell *et al.*, *J. Am. Chem. Soc.* **1996**, *118*, 9333.

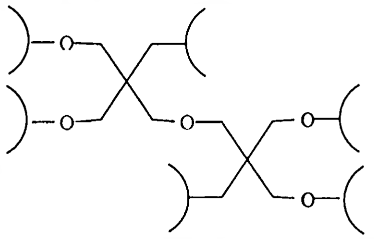
Inorganic Chemistry **54**

Metallodendrimers and metallocuriosities

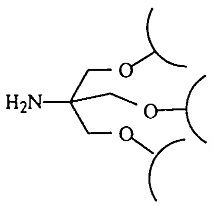
Marco Cattalini, Edwin C. Constable, Catherine E. Housecroft, Oliver Eich, Chiara Lazzarini, David Phillips and Caroll Pohl-Ferry

Laboratory for Supramolecular Chemistry, Institute of Inorganic Chemistry, University of Basel, CH-4056 Basel

Ligands containing two or more 2,2':6',2"-terpyridine metal-binding domains are the key building blocks for the metal-directed assembly of high-nuclearity metallodendrimers and topologically novel compounds. In this poster, new dendrimers incorporating **1** or **2** will be presented together with a discussion of the consequences of incorporating long flexible spacers which allow the assembly of novel species.



(1)



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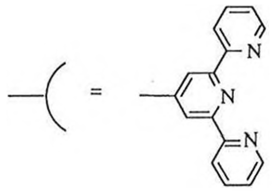

Chimie minérale et de coordination **55**

Influence de la déprotonation d'un site éloigné sur le potentiel d'oxydation du Co^{II}.

S. Clemente, A. Sour, A. F. Williams.

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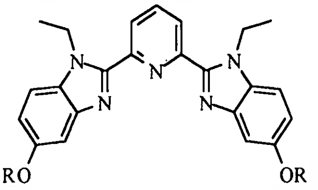
L'utilisation du ligand tridentate L de type bisbenzimidazolpyridine, permet la formation de complexes octaédriques $[M(L)_2]^{n+}$, par réaction d'un équivalent de métal avec deux équivalents de ligand.



L_1 R=H
L_2 R=Me

Le ligand étant fonctionnalisé en position 5 des benzimidazoles, il peut être utilisé pour des réactions de substitutions nucléophiles et le complexe octaédrique formé peut donc servir de précurseurs dans la synthèse de caténates.

Le complexe $[Co(L_1)_2]^{2+}$ a été synthétisé et montre une vague d'oxydation à 0,64V/ ENH.

Le complexe anionique $[Co(L_2\text{-}2H)_2]^{2-}$ formé in situ en solution basique, est rapidement oxydé par l'air.

Inorganic and Coordination Chemistry **56**

Catalytic Chemistry of Gases in Aqueous and Alcohol Media

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CH-1015 Lausanne, Switzerland

During the past several years, the remarkable ability of the ruthenium hexaaqua ion $[Ru(H_2O)_6]^{2+}$ **(1)** to form complexes with carbon-based ligands, notably olefins, in water or alcohol has been recognized [1]. Accordingly, preliminary studies conducted in Lausanne, demonstrated that **1** can also efficiently coordinate ethene and subsequently dimerize two molecules of this olefin to yield a mixture of butenes [2]. Using high gas pressure NMR systems, developed in-house, we now report the mechanistic details associated with this ecologically important reaction which, in turn, have allowed us to dramatically improve the catalytic efficiency of this process to *ca.* 1000 turnovers of butene per hour at 363 K and 60 bar ethene. In addition, the coordination chemistry of **1** with other gaseous reactants such as butadiene and 1,1-difluoroethene in water and methanol media has also been explored (Figure 1).

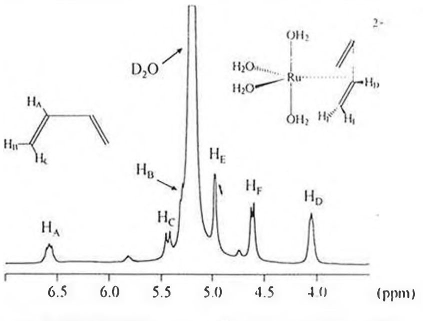


Figure 1. ^1H NMR (400 MHz) spectrum of a Ru^{2+} solution (0.1 m in D_2O) containing free and coordinated butadiene at 275 K and 1.0 MPa gas pressure

[1] Novak, B. M.; Grubbs, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 960.
[2] Laurenczy, G.; Merbach, A. E. *J. Chem. Soc., Chem. Commun.* **1993**, 187.

CHIMIA 51 (1997) Nr. 8/9 (August/September)

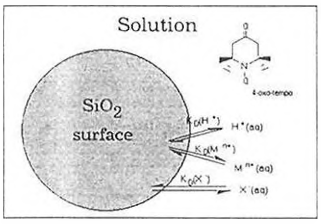
Chimie minérale et de coordination **57**

The Dynamics of a Spin-Label Spin Probe in Water Adsorbed on a Oxide Surface Studied by ESR.

David De Corte and Carl Wilhelm Schläpfer
Institut de Chimie Inorganique et Analytique, Université de Fribourg, Pérolles, CH-1700 Fribourg, Suisse.

It has been widely demonstrated that the study of the electron spin relaxation of paramagnetic labels (stable organic radicals) and spin probes (paramagnetic transition metal ions) in solution provides direct information on the distribution and the dynamics of the probe in the system.

In the present work the adsorption of the transition metal ions, Ni^{2+} and Cu^{2+}, and a charged nitroxide radical, $TPOCA^{\cdot}$, on the surface of amorphous silica gel has been studied. Observation of the relaxation of the neutral 4-oxo-tempo and the charged $TPOCA^{\cdot}$ spin labels at different temperatures and pH's in the microheterogeneous solution gives information about the distribution of the metal ions on the surface and the topology of our surface.



[1] The dynamics of a nitroxide radical in water adsorped on porous supports studied by ESR.; Martini G.;Ottaviani M.F.. Romanelli M.;*Journal of Colloid and Interface Science*;1982.94.105

[2] Reviews in Mineralogy; Mineral-Water Interface Geochemistry; M.F. Hochella, Jr. and Art F.White; *Mineralogical Society of America*; Washington, 1990

Inorganic and Coordination Chemistry **58**

The [IrCl(Josiphos)]2 / Fluoride System. An Efficient and Enantioselective Catalyst for the Intermolecular Olefin Hydroamination

Romano Dorta, Antonio Togni
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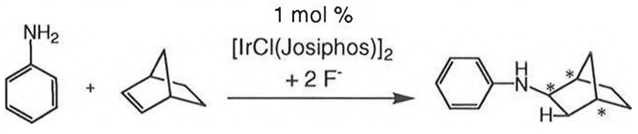
The asymmetric catalytic olefin hydroamination is a virtually unknown reaction [1]. The design of efficient catalyst systems not requiring high temperatures and/or high pressures is a big challange. Transition metal catalysts for the intermolecular hydroamination of unactivated olefins hardly afford turnover numbers (TON) of more than ca. 0.08 h^{-1} at ambient pressure and medium temperature (*ca.* 350 K)[2]. We report the selective (*exo*-addition and up to 64% ee at 298 K) and efficient (TON up to 1.11 h^{-1} at 348 K) condensation of aniline with norbornene catalyzed by Iridium. A decisive fluoride ion effect on activity and selectivity has been found. We also present a general synthesis of chiral dinuclear Ir(I) diphosphine complexes.



[1] Giardello, M. A.; Conticello, V. P.; Brard, L.; Gagné, M. R.; Marks, T. J. *J. Am. Chem. Soc.* **1994**, *116*, 10241.

[2] (a) Casalnuovo, A. L.; Calabrese, J. C.; Milstein, D. *J. Am. Chem. Soc.* **1988**, *110*, 6738. (b) Brunet, J.-J.; Neibecker, D.; Philippot, K. *J. Chem. Soc. Chem. Commun.* **1992**, 1215.

Anorganische Chemie und Koordinationschemie **59**

Elektrochemie in Cu-bpy-Polyethylenglykol Schmelzen

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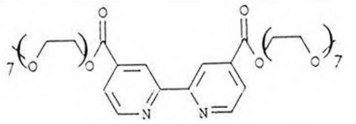
†Kenan Laboratories of Chemistry, University of North Carolina Chapel Hill, NC, USA

Mit Cyklischer Voltammetrie, Chronoamperometrie und Leitfähigkeitsmessungen wurde der Mechanismus der elektrischen Leitung in Raumtemperatur-Schmelzen des Komplexsalzes $CuL_2(ClO_4)_2$ untersucht.

L =



Es wurde gefunden, dass die ionische Leitfähigkeit der Schmelze durch die Bewegung des Perchlorations bestimmt wird. Dennoch haben Proben, die zusätzliches $LiClO_4$ enthalten, geringere Leitfähigkeit, weil die Ätherketten durch die Koordination mit Lithium versteift werden und darum die Viskosität stark zunimmt.

Bei 298 K ist der heterogene Elektronenaustauch viel langsamer als der homogene ($k_{hetero} = 6.5 \cdot 10^{-7}$ $cm \cdot s^{-1}$, $k_{homo} = 2.3 \cdot 10^{4}$ $M^{-1}s^{-1}$), hat aber eine etwas kleinere Aktivierungsenergie ($E_{A,hetero} = 37$ $kJmol^{-1}$, $E_{A,homo} = 50$ $kJmol^{-1}$).

Der homogene Elektronenaustausch des Cu(II/I)-Komplexes ist nahezu adiabatisch (Frequenzfaktor der Arrhenius-Gleichung $A = 10^{13}$ $M^{-1}s^{-1}$). Seine Aktivierungsenergie ist etwas grösser als für einen inner-sphere Elektronenaustausch erwartet würde, was mit der Kopplung von Ligandsphäre und "Lösungsmittel" (Polyätherkette des bpy) zu erklären ist. Die Bewegung der metallischen Zentren innerhalb der Polyäther-Hülle ist schneller, aber die Bewegung des ganzen Komplexes ist langsamer als der homogene Elektronenaustausch.

Chimie Minérale et de Coordination **60**

Electron storage and release through formation and cleavage of carbon-carbon bonds: the redox chemistry of titanium and vanadium Schiff bases complexes

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Institut de Chimie Minérale et Analytique, Université de Lausanne

The reduction of Ti^{III} and V^{III} salophen [salophen = *N,N'*-phenylene-bis(salicylideneiminato) dianion] complexes led to the formation of C-C bonded dimers via the coupling of imino groups. These bonds act as a reservoir of 2 e^- which can be released upon C-C bond cleavage. Reduction of [M(salophen)(Cl)(thf)] with sodium metal in a 1:1 molar ratio led to the formation of the dimers $[M_2(salophen_2)(thf)_2]$, where two salophen units are joined by a single C-C bond. Further reduction led to the introduction of an additional C-C bridge between the two salophen units thus forming $[M_2(^*salophen_2^*)(Na_2)(thf)_6]$, where $^*salophen_2^*$ functions as a dinucleating, octadentate, octaanionic ligand (see figure). The reactivity of the reduced complexes with oxidizing agents such as $Cp_2Fe^+BPh_4^-$, $PhCH_2Cl$, quinones, O_2 and PhN_3 showed the reversibility of the formation of these C-C bonds, whose electrons were used in the oxidation process, thus restoring the imino functionality of the ligands.

Inorganic and Coordination Chemistry **61**

New Chiral Mononuclear Rh(III) Complexes Containing Diamines

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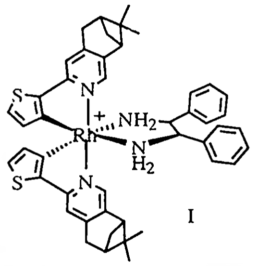
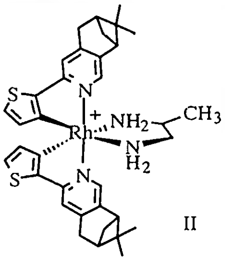
Institute of Inorganic and Analytical Chemistry, University of Fribourg,
Pérolles; Fribourg, CH-1700, Switzerland

In analogy to previously reported cyclometallated Rh(III) complexes [1], here we illustrate the synthesis and characterisation of new Rh(III) compounds with controlled stereochemistry at the metal center(s). Upon complexation of 2,2'-thienyl-4,5-pinenyl-pyridine with rhodium, a dinuclear homochiral (ΔΔ from (-)-myrtenal as precursor) complex $[Rh(C^\wedge N)_2Cl]_2$ is obtained. Cleavage of the dinuclear complex by (-)-α-pinene substituted 2,2'-bipyridines and several diamines, yields mononuclear complexes of the type $[Rh(C^\wedge N)_2(N^\wedge N)]^+$ (e.g. I and II).



I



II

It was found that in the case of all the mononuclear complexes the metal centers helicity is maintained.

Readily available natural products such as (-)-myrtenal and (-)-α-pinene have been employed in order to develop the chirality of the above ligands.[2]

[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 Chemie **62**

Dealumination behavior of mordenite: a comparison of nitric and oxalic acid

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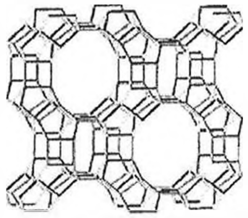
Laboratorium für Technische Chemie, Eidgenössische Technische
Hochschule, Universitätstrasse 6, CH-8092 Zürich

Mordenite is a well-known zeolite used in a wide range of applications, for instance in hydroisomerisation and hydrocracking processes. The structure of this zeolite consists of 12-ring elliptic channels interconnected by 8-ring channels. Although mordenite has a two-dimensional pore system, large molecules can be adsorbed only in the bigger pores.



A novel field of application of zeolites could be the adsorption of volatile organic compounds (VOC) currently adsorbed over active charcoal. The main advantages of zeolites are that they can be easily regenerated, they are not combustible, and they are temperature-resistant up to 1000°C. Another advantage is that they show a hydrophobic character depending on the aluminium content: the lower the Si/Al ratio the more hydrophobic the zeolite; they can then be employed for the purification of humid exhaust fumes. To achieve a low aluminium content mordenite must be dealuminated by a post-synthesis treatment.

The aim of this work is to compare the dealumination behavior using two different acids: nitric acid, a mineral acid, and oxalic acid, an organic acid. The samples were first natrium-exchanged using a solution of hydrochloric acid followed by a solution of ammonium nitrate. After high temperature calcination, aluminium was removed by acid leaching at reflux temperature, and samples were collected after different times of contact. The obtained mordenites were then calcined and characterized: the crystallinity was checked by powder XRD, the bulk Si/Al ratio determined using atomic absorption spectrometry, the surface measured by nitrogen adsorption, and the different aluminium species formed were investigated by ^{27}Al MAS NMR.

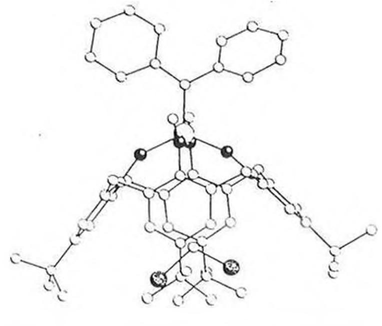
The results showed a good dealumination capability for both acids. However, oxalic acid is more effective even when diluted. Nitric acid, contrary to oxalic acid, leads to the formation of meso- and macropores in the zeolite structure.

Organometallic Chemistry **63**

A High Spin Alkilidene Complex: the synthesis, structure, magnetic properties and reactivity of [dimethoxy-p-Bu^{t}calix[4]arene]Fe(CPh$_2$)

Giusti, M.[a]; Crescenzi, R.[a]; Floriani, C.[a]; Giannini, L.[a]: Solari, E.[a]
Chiesi-Villa, A.[b]; Re, N.[a]; Rizzoli, C.[b]

a: Institut de Chimie Minerale et Analitique, Université de Lausanne,
BCH, CH-1015 Lausanne
b: Dipartimento di Chimica, Università di Parma, I-43100 Parma, Italy



M-C double bond compounds are well known metathesis polimerization catalysts; further, diazo-compounds are powerful synthons for obtaining carbene complexes

Using Ph_2CN_2, we succeeded in preparing an iron-carbene complex supported by the almost planar oxygen environment of calix[4]arene.

This represents the first example of a Fe-carbene supported by an alkoxo ligand. The molecule shows an unusual magnetic behaviour (μ_{eff}=5.1) together with an interesting reactivity.

Organometallic Chemistry **64**

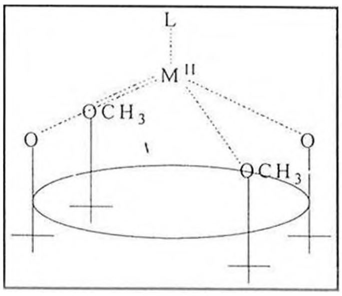
[M^{II} dimethoxy-p-Bu^{t}calix[4]arene] (M^{II} = Mn^{II}; Fe^{II}; Co^{II}): novel starting materials for organometallic synthesis

Giusti, M.[a]; Crescenzi, R.[a]; Floriani, C.[a]; Giannini, L.[a]; Solari, E.[a]
Chiesi-Villa, A.[b]; Re, N.[a]; Rizzoli, C.[b]

a: Institut de Chimie Minerale et Analitique, Université de Lausanne,
BCH, CH-1015 Lausanne
b: Dipartimento di Chimica, Università di Parma, I-43100 Parma, Italy

The number of reports concerning Mn^{II}, Fe^{II}, Co^{II} alkoxo derivatives in the literature is nearly non-existent.

Calix[4]arene-dimethylether provides a square planar set of oxygen atoms suitable for the coordination of late transition metals, and can be easily transformed into its dianionic form.



We have succeeded in preparing compounds of this type with M^{II} = Mn^{II}, Fe^{II}, Co^{II}; their syntheses, solid state structures and magnetic properties are described.

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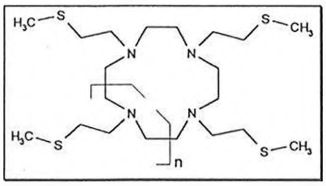
Inorganic Coordination Chemistry **65**

SYNTHESIS OF N_4S_4 AND N_3S_3 MACROCYCLIC LIGANDS FOR NEW TRANSITION METAL COMPLEXES OF GROUP 11 ELEMENTS: SPECIAL FOCUS ON SILVER(I) COMPLEXES

THOMAS GYR[a], HELMUT R. MAECKE[a], M. HENNIG[b]

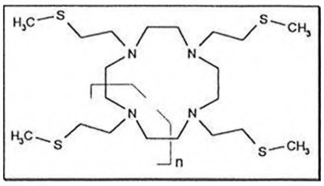
[a] Institute of Nuclear Medicine, University Hospital, 4031 Basel, Switzerland
[b] Hoffmann-La Roche, Basel, Switzerland

Metal complexes are used in different diagnostic and therapeutic medical applications. High kinetic and/or thermodynamic stability is necessary for this type of application because of competition with ligating biomolecules and excess metal ions like Ca^{2+}, Fe^{2+}, Zn^{2+} etc. *in vivo*. A special challenge is the design of bifunctional ligands for metallic radionuclides for internal therapy (such as ^{111}Ag and ^{198}Au) to target tumors by use of specific biomolecules. To better understand the coordination chemistry of group 11 metal complexes we have synthesized two new tetra- and triazamacrocycles with (2-methyl-thio)ethyl pendant arms (Fig., n=1,0) and studied their solid state and solution chemistry.



The structures showed hexacoordination about the Ag^+. The solution structure was studied by ^{13}C and ^1H-NMR at variable temperatures. Fluxional behavior is seen in these complexes in terms of the conformation of the ethylene groups bridging the nitrogens. The stability constants were determined by pH potentiometry. For **Ag(DOTETE)$^+$** (n=1), a lower limit of **$\log K_{AgL^+}$ = 19.05** and a deprotonation constant $\log K_{AgLH^{2+}}$ = 2.8 was found. The complex is the most stable Ag^+ complex known to date. The kinetic data of transfer of $^{110m}Ag^+$ to serum proteins is somewhat equivocal. About 40% of radiolabel is transferred to proteins within 2 - 3 h. The remaining complex is stable over 24 h under these conditions.

The presented ligands form a good starting point to investigate the binding affinity of group 11 elements to N_xS_y-ligands. DOTETE forms the most stable Ag^+ complex known todate and opens new pathways for the immobilization of Ag^+ ions in biological fluids.


Inorganic Coordination Chemistry **66**

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Inorganic Chemistry **67**

Synthesis, Molecular Structure and Reactivity of the New Mixed-Metal Cluster Anion $[Ru_3Ir(CO)_{13}]^-$

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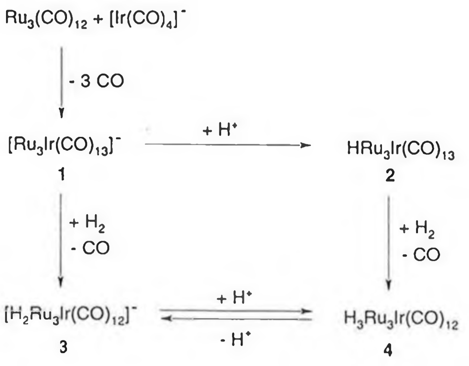
Institut de Chimie, Université de Neuchâtel, CH-2000 Neuchâtel

In the series of tetranuclear mixed-metal carbonyl clusters of ruthenium with d^9 metals, only the complexes $[Ru_3Co(CO)_{13}]^-$ [1], $[Ru_2Rh_2(CO)_{12}]^{2-}$ [2] and $[Ir_3Ru(CO)_{12}]^-$ [3] are known so far. The missing link, $[Ru_3Ir(CO)_{13}]^-$ (**1**), is accessible from the reaction of $Ru_3(CO)_{12}$ with $[Ir(CO)_4]^-$. The crystal structure of **1** and its reactivity towards protonation agents and molecular hydrogen will be presented.



[1] P. C. Steinhardt, W. L. Gladfelter, A. D. Harley, J. R. Fox, G. L. Geoffroy, *Inorg. Chem.* **1980**, *19*, 332.
[2] A. Fumagelli, D. Italia, M. C. Malatesta, G. Ciani, M. Moret, A. Sironi, *Inorg. Chem.* **1996**, *35*, 1765.
[3] A. Fumagelli, F. Demartin, A. Sironi, *J. Organomet. Chem.* **1985**, *279*, C33.

Anorganische- und Koordinationschemie **68**

Supramolekulare Komplexe von Oligo-(2,2'-bipyridyl)pyrazinen mit Co(II) und Ru(II) und die Synthese von nichtsymmetrischen 2,3-Bis-(oligopyridyl)pyrazinen

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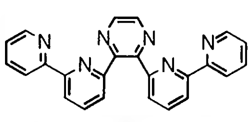
Wir berichteten vor kurzem über die Synthese von einigen Oligo-(2,2'-bipyridyl)pyrazinen als Liganden für die suprametallorganische Chemie[1].

Der Komplex von 2,3-Bis-(2,2'-bipyridyl)pyrazin **1** und Kobalt(II) weist eine 1:1-Liganden:Metall-Zusammensetzung auf. Vor kurzem ist es uns gelungen, die Struktur davon durch eine entsprechende Kristallstrukturanalyse aufzuklären[2].

Wir haben weiterhin die Darstellung der Ruthenium(II)terpyridinyl Komplexe ausgehend von dem Liganden **1** oder dem entsprechenden Quinoxalin-Derivat **2** untersucht. Für **1** wird -je nach experimentellen Bedingungen- die *ausschliessliche* Bildung der entsprechenden mono- oder dimetallischen Komplexen beobachtet. Die Metallatome der dimetallischen Verbindung weisen eine ausserordentlich starke elektrochemische Kopplung auf. Für **2** läßt sich der entsprechende Monoruthenium(II)-Komplex darstellen, dessen Struktur durch eine Kristallstrukturanalyse abgesichert worden ist[3]

Wir interessieren uns weiterhin für die Synthese von Pyrazin-Derivaten, die zwei unterschiedliche Oligopyridin-Reste auf die 2,3-Stellungen tragen. Wir berichten ebenfalls über unsere Ergebnisse in diesem Gebiet.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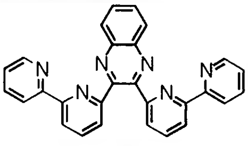
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[1] F. R. Heirtzler, M. Neuburger, M. Zehnder, E. C. Constable *Liebigs Ann./Recueil* **1997**, 297-301.
[2] F. Heirtzler, T. Weyhermüller, *Chemical Communications*, Manuskript eingereicht.
[3] F. Heirtzler, P. G. Jones, Manuskript in Vorbereitung.

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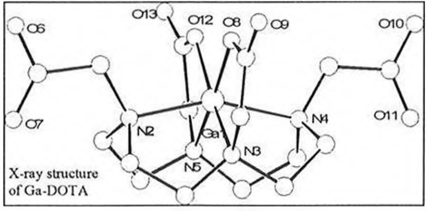
Inorganic Coordination Chemistry **69**

COORDINATION CHEMISTRY AND TUMOR TARGETING OF A NEW SOMATOSTATIN ANALOGUE

A.Heppeler[a], M. Béhé[a], E. Jermann[a], P. Powell[a], M. Hennig[b], S. Froidevaux[a], H.R. Mäcke[a]
[a] Institute of Nuclear Medicine, University Hospital Basel; [b] Hoffmann-La Roche, Basel

The aim of our investigations was to show that DOTA (1,4,7,10-tetraazacyclododecane-1,4,7,10-tetraacetic acid), coupled to a bioactive peptide serves as a unique chelator for a multitude of hard radiometals with regard to high in vivo stability and preservation of biological integrity and to compare it to a commercial DTPA-conjugated peptide. For this reason we designed a DOTA derivatized somatostatin (SRIF) analogue **DOTATOC** (DOTA^0- tyr^3-octreotide). SRIF analogues are known for their high affinity to a variety of tumors and are used as carrier molecules for tumor-targeting. The conjugated peptide was synthesized by use of the orthogonal protected DOTA derivative 2-[4,7,10-tri(tert-butyl-oxycarbonyl-methyl)-1,4,7,10-tetraazacyclododecanyl]-acetic acid. Although the chelate is remote from the receptor binding site, it strongly influences the binding affinity and biodistribution of the tumor targeting peptide. This was studied in receptor binding assays and in biodistribution studies in a tumor bearing nude mouse model. Y-90-, In-111-,Ga-67-**DOTATOC** show high stability under physiological conditions. The binding affinity to the SRIF receptor is a factor of 5 higher for Ga-67-**DOTATOC** compared to the other two. Biodistribution in a tumor bearing mouse model show a clear advantage with regard to tumor accumulation and background clearance for the Ga-67 labelled peptide. All three show higher uptake than In-111-DTPA-octreotide. Obviously coordination chemistry aspects cause this difference which allows improved tumor targeting in humans. X-ray analysis of the M^{3+}-DOTA complexes ($M = Y^{3+}$, In^{3+}, Ga^{3+}) were used to explain the different properties. Y-and In-DOTA show octacoordination and antiprismatic geometry whereas Ga-DOTA has a pseudooctahedral geometry with pendant carboxylates.



X-ray structure of Ga-DOTA

Anorganische Chemie **70**

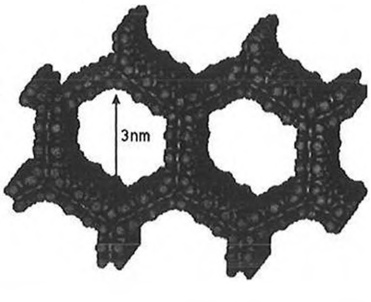
Influence of pH-adjustments on structure, stability and catalytic activity of MCM-41 mesoporous molecular sieves

S. Hitz, C. Beck and R.Prins

Laboratory of Technical Chemisty, Eidgenössische Technische Hochschule,
Universitätstrasse 6, CH-8092 Zürich

MCM-41 is a mesoporous molecular sieve consisting of a hexagonal array of uniform pores. The MCM-41 pores (≈28Å) are significantly larger than zeolite pores (5.5 bis 7.5 Å). This makes Al-MCM-41 a promising catalyst for conversion of bulky molecules in fine chemistry.

MCM-41 is synthesized in a hydrothermal process under basic conditions. With the polymerization of silicate species, the pH value of the synthesis mixture rises, and a further reaction is hindered by the high pH value. If the pH value of the synthesis gel is repeatedly adjusted to 11.3, then the polymerization proceeds further, and the resulting material is expected to be more stable than a MCM-41 obtained without pH-adjustment.



In our work, Al-MCM-41 samples were prepared at 100°C using the pH adjustment procedure. The untreated parent sample was compared to samples that underwent 1, 2 or 3 pH adjustments of intervals of 24 h.

The chemical composition changed dramatically: Si/Al as well as Na/Al ratios increased with repeated adjustments by factors between 2 and 10 respectively. The structural properties, characterized by powder XRD and nitrogen adsorption data, show clearly that a pH adjustment stabilizes the mesopore structure. Repeated pH adjustments have no further stabilizing effect. ^{27}Al-NMR reveals an increase in tetrahedrally coordinated Al-species with repeated pH-adjustment.

All these effects can be explained by the increasing degree of polymerization of silanol groups with repeated pH-adjustments. The catalyst structure is stabilized and the dehydratisation of Brønsted sites to Lewis sites is hindered.

Anorganische Chemie **71**

Clusters of main-group elements from crown-ether melts: A novel synthetic procedure for polyanions of Group 14-16.

Thomas F. Fässler and Rudolf Hoffmann

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Ligand-free ("naked") anionic main-group element clusters have been known for over 100 years. However, the "Zintl-anions" still suprise by their structural and preparative chemistry [1-4]. The classic synthesis utilizes the extraction of binary and ternary alloys with polar, aprotic basic solvents.

We report here a novel procedure which allows the synthesis of homoatomic polyanions directly from the elements in melts of crown-ethers at temperatures between 40 and 80°C. The reductive power of alkalides and electrides which are easily obtained in solution and melts from crown-ethers and alkali metals is well documented [5].

So far we have applied this method for generating polyanions of Te, Sb, As and Sn. The work-up of the melts yielded crystals suitable for single-crystal structural analysis. The structures of these compounds show direct bondage of alkali metal atoms to the polyanions.

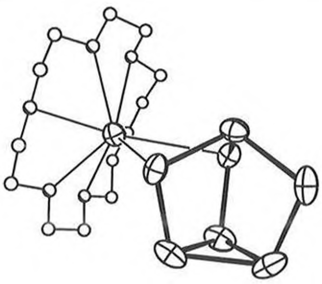

Fig.1: Direct binding of a [K(18-crown-6)]-unit on a Sb_7^{3-}-anion.

[1] J.D. Corbett; *Chem. Rev.* **1985**, *85*, 383.
[2] T.F. Fässler, M. Hunziker; *Inorg. Chem.* **1994**, *33*, 5380.
[3] T.F. Fässler, M. Hunziker; *Z. Anorg. Allg. Chem.* **1996**, *622*, 837.
[4] T.F. Fässler, U. Schütz; *J. Organomet. Chem.* **1997**, *in press.*
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Inorganic and Coordination Chemistry **72**

Substituent, Solvent, and Chelating Effects on the Oxygenation of tris-(2-Pyridylmethyl)amino Cu(I) Complexes

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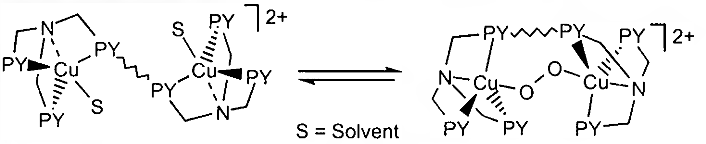
With the Cu(I) complex of tris-(2-pyridylmethyl)amine (TMPA) stepwise and pseudoreversible formation of superoxo and μ-η^1:η^1 peroxo species has been observed with full kinetic characterisation of all relevant mechanistic steps [1]. Tethered binucleating derivatives and a less coordinating solvent have been used to significantly increase peroxo adduct stability with full formation even at room temperature [2].



L_1: ∼∼ = $-CH_2CH_2-$; L_2: ∼∼ = $-CH_2OCH_2-$

Substitution of the pyridyl residues in 4-position by electron donating groups (R=-Me, t-Bu, -OMe) leads to significant, but relatively weak increase in thermodynamic stability and to some decrease in reactivity for adduct formation in Cu(I) coordinating solvents like EtCN. This is related to competing effects of solvent and O_2, both having significant Lewis acid properties. Non-coordinating solvents like acetone dramatically increase kinetic reactivity and room temperature stability for most complexes studied. Full kinetic analysis is hampered by dimerisation pre-equilibria, especially with the most strongly electron donating pyridine substituents.

[1] K.D. Karlin, N. Wei, B. Jung, S. Kaderli, P. Niklaus, A.D. Zuberbühler, *J. Am. Chem. Soc.* **1993**, 115, 9506.
[2] K.D. Karlin, D.-H. Lee, S. Kaderli, A.D. Zuberbühler, *Chem. Commun.* 1997, 475.

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Inorganic and Coordination Chemistry **73**

Oxygenation of Mono- and Dinuclear Cu(I) Complexes with bis-(2-Pyridylethyl)amino Chelating Units

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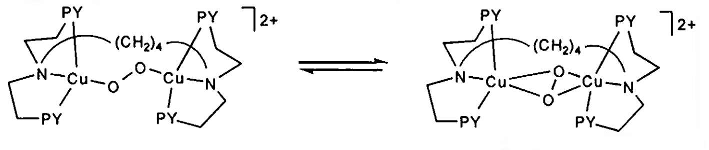
Based on the bis-(2-pyridylethyl)amino chelating unit the first Cu(I) complex with pseudoreversible dioxygen binding properties has been characterized and its kinetics studied several years ago [1]. Recently, interconversion of an initial end-on μ-η^1:η^1 peroxo complex into a thermodynamically more stable side-on μ-η^2:η^2 isomer has been observed using a binucleating ligand linking two bis-(2-pyridylethyl)amino units by a 4 carbon $-(CH_2)_4-$ aliphatic tether [2].



μ-η^1:η^1-peroxo μ-η^2:η^2-peroxo

In order to more fully understand the oxygenation kinetics and in view of the potential significance of this interconversion for oxygen binding and cooperativity effects in hemocyanin, we have extended our studies to analogous mononuclear complexes as well as to binuclear species with tethers of different chain length. Reactivity towards O_2 is significantly reduced with the mononuclear compounds, indicating a rapid preequilibrium lying over to the left for the first oxygen binding step. No end-on μ-peroxo intermediate is observed with a shorter $-(CH_2)_3-$ linker and the adduct spectra reveal subtle, but significant, influences imposed by steric restrictions.

[1] K.D. Karlin, M.S. Nasir, B.I. Cohen, R.W. Cruse, S. Kaderli, A.D. Zuberbühler, *J. Am. Chem. Soc.* **1994**, 116, 1324.
[2] B. Jung, K.D. Karlin, A.D. Zuberbühler, *J. Am. Chem. Soc.* **1996**, 118, 3763.

Anorganische/Koordinations-/Chemie **75**

Relation between Ligand Basicity and Metal Ion-Complex Stability for Imidazole and Derivatives

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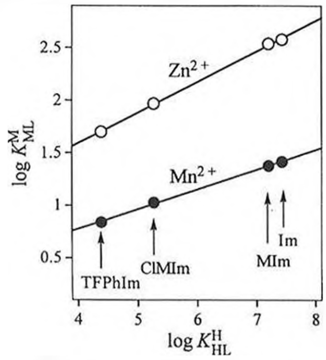

The imidazole residue is one of the most important binding sites for metal ions in proteins [1] and it may also undergo stacking interactions [2]. Considering this it is surprising that so far no detailed study on the interrelation between ligand basicity and complex stability has been carried out for imidazole and sterically unhindered derivatives thereof (= L). We have now measured via potentiometric pH titrations (I = 0.5 M, $NaNO_3$; 25°C) the stability constants of the binary complexes formed between imidazole (Im), 1-methylimidazole (MIm), 5-chloro-1-methylimidazole (ClMIm), or N-(2,3,5,6-tetrafluorophenyl)imidazole (TFPhIm) and metal ions, like Mg^{2+}, Mn^{2+}, Cu^{2+}, or Zn^{2+} (= M^{2+}). From the results shown in the Figure it is evident that plots of log K^{M}_{ML} versus pK^{H}_{HL} result -- as one might expect -- in straight lines. Based on such *reference* lines it will now be possible to evaluate steric effects which metal ions experience, e.g., upon coordination to benzimidazole and related ligands, like 1,4-dimethylbenzimidazole. Eventually, this research should also enable us to reevaluate the metal ion-binding properties of the various N sites present in purines [3].

Supported by the Swiss National Science Foundation and the Swiss Federal Office for Education & Science (COST D1 & D8).

[1] H. Sigel, B. E. Fischer & B. Prijs, *J. Am. Chem. Soc. 99*, 4489-4496 (1977); H. Sigel, *Inorg. Chem. 19*, 1411-1413 (1980).
[2] H. Sigel, R. Tribolet & O. Yamauchi, *Comments Inorg. Chem. 9*, 305-330 (1990).
[3] (a) R. B. Martin, *Met. Ions Biol. Syst. 32*, 61-89 (1996). (b) H. Sigel, N. A. Corfù, L.-n. Ji & R. B. Martin, *Comments Inorg. Chem. 13*, 35-59 (1992).

Anorganische Chemie **74**

Modeling of Redoxpotentials of Hexaaminecobalt(III/II) Couples via Molecular Mechanics

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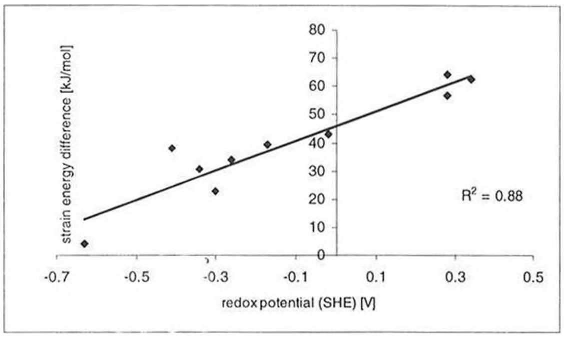

Redox potentials of transition metal compounds depend on various parameters, and most have been used in correlations with the redox properties. These include electronic effects (e.g. ligand field stabilisation energies), steric effects (e.g. strain energies), solvation and entropic effects. We have modeled redox properties of hexaaminecobalt(III/II) couples by molecular mechanics calculations. Due to the large difference in the Co-N bond lengths between the oxidized and reduced form (~0.2 Å), steric effects are of major importance. This also emerges from the figure.

Solvation and entropic effects are now included to improve the quality of the correlation, and modeling of electronic effects helps to extend the computations to systems different from hexaaminecobalt(III/II) couples.

Inorganic Chemistry **76**

MOLECULAR ARCHITECTURE - NOVEL CHIRAL TRIPOD LIGANDS

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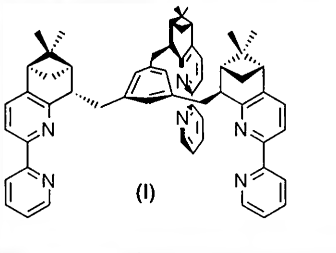
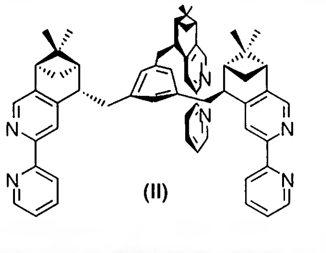
The pool of chiral ligands is extended by the novel tripod ligands (**I**) and (**II**) shown below. Both are available via a stereospecific synthesis in over 90 % yield.



(I)



(II)

The concept of chiral predetermination is well established for mono- or bis-didentate ligands [1],[2] but considerably less is known for tris-didentate substances. Ligands (**I**) and (**II**) could help to fill this gap. Molecular structures containing up to three chiral metal centers within one molecule can be generated in a controlled way. No separation of diastereomers is necessary and no problems with "fuzzy" stereochemistry are encountered.

Special emphasis will be given on the discussion of diastereoselective synthesis and characterisation of (I) and (II) and its trinuclear Zinc and Ruthenium complexes.

[1] P. Hayoz, A. von Zelewsky, Tetrahedron Lett. **1992**, *33*, 5165.
[2] H.-R. Mürner, P. Belser, A. von Zelewsky, *J. Am. Chem. Soc.* **1996**, *118*, 7989.

Inorganic and Coordination Chemistry **77**

Chiral Ferrocenyl Diphosphine Ligands Bound On Dendrimers

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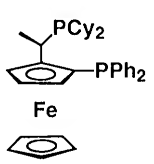
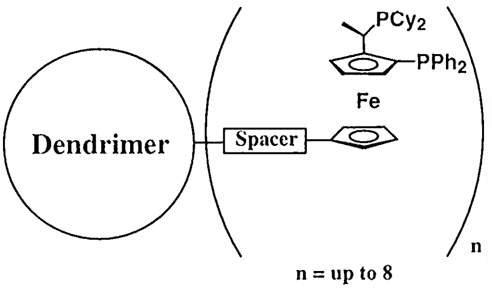
Since Vögtle et al.[1] reported the first synthesis of a „cascade" molecule nearly 20 years ago, the field has attracted increasing attention and importance. Dendrimers covered with catalytically active centres on the surface are of interest in terms of recovering expensive catalysts.[2] As an interface between heterogeneous and homogeneous catalysis, these catalysts react in a homogeneous solution and might be recycled by virtue of their molecular size (membrane reactor) and their altered solubility.
We report how to bind our well established[3] ligand system **1** on a dendritic core via ester or amide functions. The synthesis of dendrimers such as **2** with up to 8 diphosphine units is described. Analytical data und catalytical results in the enantioselective hydrogenation, allylic alkylation and hydroboration reactions are presented.



1



2

[1] E.Buhleier, W.Wehner, F.Vögtle, *Synthesis* **1978**, 155.
[2] a) J.W.J.Knapen, A.W.van der Made, J.C.de Wilde, P.W.N.M.van Leeuwen, P.Wijkens, D.M.Grove, G.van Koten, *Nature* **1994**, 372, 659. b)P.J.Davies, D.M.Grove, G.van Koten, *Organometallics* **1997**, 16, 802.
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Inorganic and Coordination Chemistry **79**

(η^2-Acrylate)benzenedicarbonylchromium(0): a Complex with a Highly Labile η^6-Arene Metal Bond

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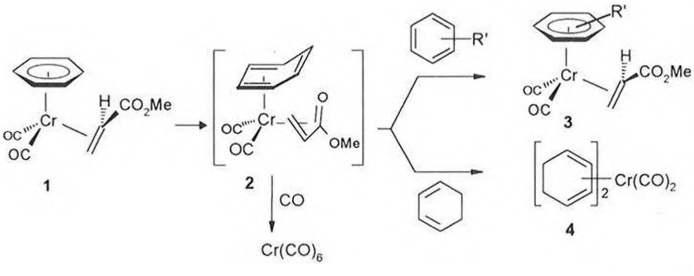
In stark contrast to the parent complex [(benzene)Cr(CO)$_3$], the metal-arene bond in the acrylate complex **1** is highly labile. Complex **1** undergoes arene exchange reactions at room temperature, it reacts with CO to give Cr(CO)$_6$ and with cyclohexadiene to provide a high yield synthesis of the bis-diene complex **4**.



Both, the acrylate and the arene in **1** are labile but, surprisingly, the first bond to be cleaved is the metal-arene bond. We believe that the driving force for these unprecedented reactions is the labilization of the arene by the acrylate. This presumably occurs via a haptotropic shift of the acrylate from $\eta^2 \rightarrow \eta^4$ concomitant with a $\eta^6 \rightarrow \eta^4$ shift of the coordinated arene to give intermediate **2** which is then expected to rapidly lead to arene loss. Arene lability varies with the donor strength of the arene.

Inorganic Chemistry **78**

PREPARATION OF PT(II)-COMPLEXES WITH CHIRAL BIPYRIDINE DERIVATIVES AS LIGANDS

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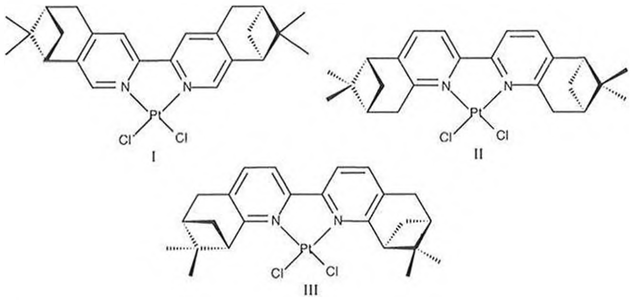
The preparation and characterization of three Pt(II) complexes with chiral bipyridine derivatives (**I**, **II**and **III**) are reported.



The sterically demanding chiral ligands prevent the formation of bis-bipyridine complexes. The two relatively labile chloride ions of these two complexes make them versatile precursors for a wide class of substitution reactions.
A special focus is given on substitution reactions with chiral didentate ligands. The products are characterized in detail by ^{1}H-, ^{13}C- and ^{195}Pt- NMR as well as by CD spectroscopy.

Anorganische Chemie **80**

X-Ray Structure and Superconducting Property of K_5Pb_{24}

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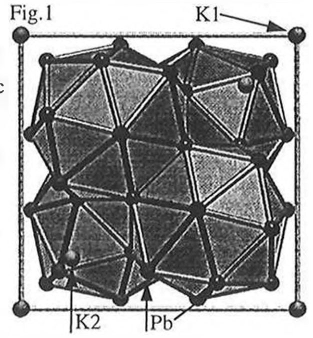
There are many intermetallic compounds that exhibit the α–Mn structure type (χ–Phases[1]), however only a few with non–transition metals[2,3] are known. K_5Pb_{24} (Tab.1) provides a new example of a main group element compound with such a structure type. The phase crystallizes in space group I$\bar{4}$3m (cubic, a=12.358(1)Å, V= 1887.32 Å^3). The lead substructure can be described as containing "supertetrahedral" units of 48 lead atoms (Fig.1), leading to new insights about the complex α–Mn structure type. The analysis of the chemical bonding in K_5Pb_{24} in terms of the Electron Localization Function (ELF) shows the concentration of lone pairs in cavities around the K atoms.
SQUID magnetometer measurements reveal the superconducting property of the phase. Here the structural, magnetic and electronic properties are discussed.

Fig.1



Tab.1 Atomic Positional and Isotropic Displacement Parameters [Å^2*10^3]

atom	x	y	z	U(iso)
Pb1	5949(1)	5949(1)	7925(2)	27(1)
Pb2	8615(1)	5399(2)	8615(1)	29(1)
K1	0	0	0	30(12)
K2	818(1)	818(1)	818(1)	21(3)

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[1] Pearson's Handbook of Crystallographic Data for Intermetallic Phases, ed. P. Villars, L.D. Calvert, 2nd edition 1991
[2] $Mg_{17}Al_{12}$: P.Schobinger–Papamantellos, P.Fischer, Naturwissenschaften 3(1970)123
[3] $Li_xMg_{17-x}Al_{12}$: R.Nesper, Habilitationsschrift Universität Stuttgart, 1988; R.Nesper, Angew. Chem. **103** (1991) 805

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Inorganic and Coordination Chemisty **81**

Aromatic Hydroxylation Catalised By Copper (II)

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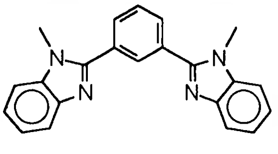
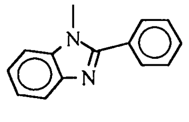
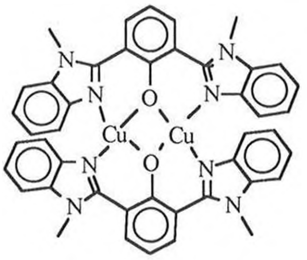
Ligand **1** is hydroxylated in the presence of Cu(II)/ O_2 in DMF to give the complex $[Cu_2(\mathbf{2})_2]$ characterised by X-ray crystallography. Hydroxylation is faster if H_2O_2 is used as the oxidant.



1



3



$[Cu_2(\mathbf{2})_2]^{2+}$

The analogous mononucleating ligand **3** is not hydroxylated in these conditions. The reaction may be explained according to the mechanism proposed by Karlin [1] involving a μ-η^2:η^2 peroxo intermediate. Our results show that a dinuclear system is essential but that no particular coordination environment is required to activate the copper.

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Anorganische Chemie **82**

Dynamics of Helical Dicopper(I) Complexes

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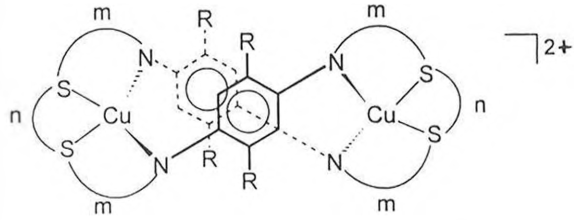
The [2+2] condensation of primary α,ω-diamines and aromatic dialdehydes yields macrocyclic ring systems with a large variability both in ring size and in donor atoms. Macrocyclic ligands with two N_2S_2 (thioether and imine) donor sets and various spacer groups were synthesized.



1 R = H
2 R = Me
3 R = OMe
4 R = Ethylen
m = n = Ethylen

The dinuclear copper(I) complexes have a double helical topology in the solid state as well as in solution. In acetonitril solutions of **1-3** we observe a temperature dependent isomerization involving the two stereoisomeric helical forms. The paracyclophane derivative **4** is a rigid preorganized chiral ligand, which does not isomerize. The racemization was monitored by ^{1}H-NMR.

Inorganic Chemistry **83**

Through a Glass Darkly: The World of Chiral Helicates

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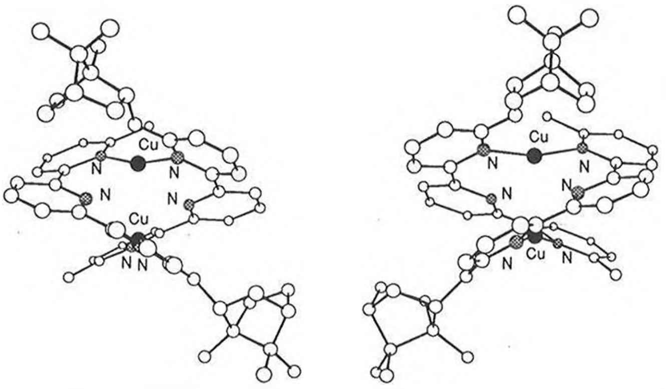
Helices are inherently chiral and may possess left- or right-handed conformations. The spontaneous assembly of dinuclear double helicates from the interaction of oligopyridines with metal ions leads to racemic mixtures of the left- or right-handed helicates. When chiral ligands are used, diastereomeric excesses depending upon the absolute *R* or *S* chirality of the ligand are expected. With simple 2,2':6',2"-terpyridine and 2,2':6',2":6",2'''-quaterpyridine derivatives, high diastereomeric excesses are obtained. NMR spectroscopic studies combined with X-ray structural studies allow the assignment of absolute configuration of the products.



See: E.C. Constable, T. Kulke, M. Neuburger and M. Zehnder, *Chem. Commun.* 1997, 489.

Anorganische Chemie **84**

Modelling Phase Transitions with Periodic Nodal Surfaces - The Transformation of Silicon Networks from $SrSi_2$ to α-$ThSi_2$

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Topologies related to a particular space group can be best recognized by means of short Fourier summations, if they are developed over only a few fundamental reflections, which are next to the origin of reciprocal space and characteristic for the group. The traces of the roots of such functions (PNS, Periodic Nodal Surfaces) define in many cases continuous curved objects which are closely related to periodic minimal surfaces[1].The properties of PNS are defined only by the symmetry elements and their concerted interactions. The generated continuous forms however, allow for different sets of tilings on each surface corresponding to different structures along the surface which in general are open frameworks. On the other hand, point configurations of space groups can be described as continuous networks, situated in the labyrinths which are generated by the continuous space partitioning of PNS. Smooth topological changes between two different networks can be modeled if such functions are considered as limiting structures in a structural transition. The transition itself can then be modeled simply by a linear interpolation.

The silicon network in the structure type $SrSi_2$ (SG $P4_332$) can be fitted using sets of plane waves of two different supergroups; a suitable choice of the phases shows the chiral character of that space group. The cubic heritage of the silicon network of the tetragonal high-pressure modification (α-$ThSi_2$ type, SG $I4_1$/amd) can be recognized in a reflection set corresponding to a tetragonal distortion of the cubic D*-surface [2] (SG Fd3m). Both the limiting SG's contain screw axes with different orientation and frequency; under the transition there is a continuous vanishing of one set and rotation of another set of screw axes. The representation by PNS in the linear interpolation of suitably chosen limiting functions shows on one hand a plausible atomic displacement, on the other hand the necessary changes in the metrical parameters from cubic to tetragonal become clear. However, the complete topological transformation can now be formulated by a concerted movement of the positions.

[1] H.G.v.Schnering, R.Nesper, Z.Phys. B83,407(1991)
[2] H.G.v.Schnering, R.Nesper, Angew. Chem. Int. Ed. Engl. 26, 1059(1997)

Coordination Chemistry **85**

Anionic Derivatives of $Ir_4(\mu\text{-}CO)_3(CO)_7(\mu\text{-}Ph_2PCH_2PPh_2)$

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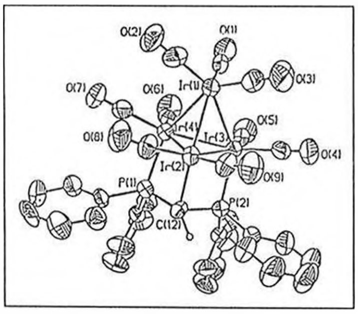
Several anionic derivatives of $Ir_4(\mu\text{-}CO)_3(CO)_7(\mu\text{-}Ph_2PCH_2PPh_2)$ [1] (1) have been synthesised: $[Ir_4(\mu\text{-}CO)_3(CO)_7(\mu_2\text{-}Ph_2PCHPPh_2)][PPN]$ ($PPN^+ = (Ph_3P)_2N^+$) (2) obtained by deprotonation of 1; $[Ir_4(CO)_9(\mu_3\text{-}Ph_2PCHPPh_2)][PPN]$ (3) by decarbonylation of 2 in strongly basic medium and $[Ir_4(\mu\text{-}CO)_3(CO)_6H(\mu_2\text{-}Ph_2PCH_2PPh_2)][PPN]$ (4) from 1 with a base in alcoholic solution. In 2 the $[Ph_2PCHPPh_2]^-$ ligand is symmetrically coordinated in bis–axial position. In compound 3 the carbanion is coordinated to one of the Ir atoms of basal face. This structure has been confirmed by X-ray diffraction (see Figure). This compound is fluxional in solution, the activation parameters for the rotation of the apical carbonyls have been determined. In 4 the H^- ligand is coordinated in axial position, replacing the unique axial CO in 1. Preliminary studies on $[Ir_4(\mu\text{-}CO)_3(CO)_7(\mu_2\text{-}dpam)]$ and $[Ir_4(CO)_9(\mu_3\text{-}tripod)]$ with a strong base show similar reactions with anionic cluster formations.



[1] a) Ros, R. et. al., *J. Chem. Soc. Dalton* **1986**, 2411.
b) Roulet, R. et. al., *Helv. Chim. Acta* **1986**, *76*, 2210.

Inorganic Chemistry **86**

Influence of the Host Lattice on the Electronic Structure of Er^{3+} in $Cs_3Lu_2Cl_9$, $Cs_3Lu_2Br_9$, and $Cs_3Y_2I_9$

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[3] Chemical Science and Technology Division, Los Alamos National Laboratory, Los Alamos, NM 87545, USA

Single crystals of $Cs_3Lu_2Cl_9$: 1% Er^{3+}, $Cs_3Lu_2Br_9$: 1% Er^{3+}, and $Cs_3Y_2I_9$: 1% Er^{3+} were grown using the Bridgman technique. The crystal-field levels of the $^{2S+1}L_J$ ($4f^{11}$) multiplets of Er^{3+} were assigned from highly resolved absorption and luminescence spectra at 10*K* and 4.2*K*. A Hamiltonian including 16 atomic, 6 crystal-field, and 1 correlation crystal-field parameter was fitted to the experimental data and gave rms standard deviations of less than 20cm^{-1}. Trends of atomic interactions and crystal-field effects are discussed for the different host lattices.

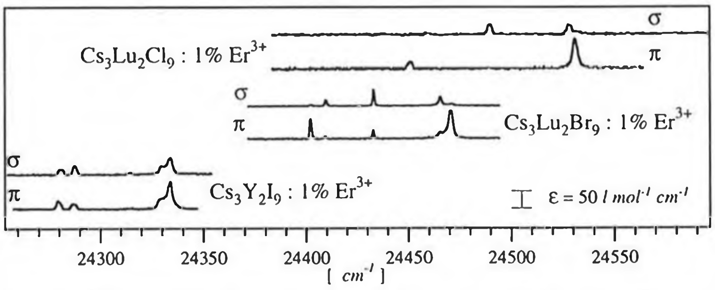

Figure: Highly resolved polarized absorption spectra of $^4I_{15/2} \rightarrow {}^2H_{9/2}$ at 10*K* for Er^{3+} in the three host lattices $Cs_3Lu_2Cl_9$, $Cs_3Lu_2Br_9$, and $Cs_3Y_2I_9$.

Inorganic and Coordination Chemistry **87**

A Potentially Tetradentate O-P-P-O Ligand with Stereogenic P Atoms

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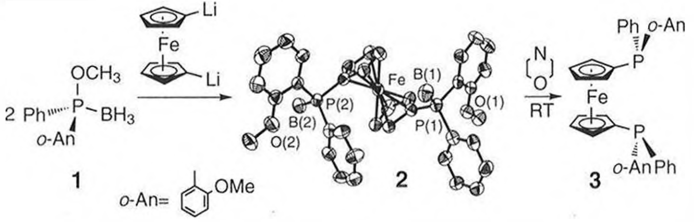
The potentially tetradentate ligand **3**, bearing stereogenic P atoms, is prepared in high enantiomeric purity according to the following reaction sequence:



Phosphinite borane (*R*)-**1** [1] reacts with 1,1'-dilithioferrocene with inversion of configuration at the P atom to give the enantiomerically pure diphosphine borane (*S,S*)-**2**, whose absolute configuration is established by X-ray crystallography. Deprotection of **2** with morpholine yields the enantiomerically pure diphosphine (*S,S*)-**3**.

Ligand (*S,S*)-**3** reacts with $[RuCl_2(PPh_3)_3]$ in a 1:1 molar ratio to give a complex formulated as $[RuCl_2(2)]$ (**4**): ^1H NMR spectroscopic data indicate that at least one of the methoxy groups coordinates to the metal. The Re and Rh coordination chemistry of **2** will be also reported, as well as preliminary applications in enantioselective catalysis.

[1] S. Jugé, M. Stéphan, J. A. Laffitte, J. P. Genet, *Tetrahedron Lett.* **1990**, 31, 6357.

Inorganic Chemistry **88**

DINUCLEAR HELICAL METAL COMPLEXES WITH PREDETERMINED CHIRALITY

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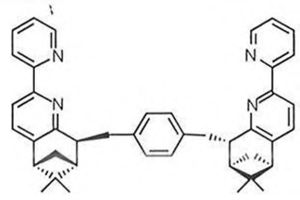
University of Fribourg, CH-1700, Switzerland

Self-assembling processes leading to double or triple helicale structures have found widespread interest in supramolecular chemistry. These inherently chiral structures are always formed as racemates if achiral compounds are used as starting materials. Often it is quite difficult to resolve these racemates into the corresponding enantiomers.

We will present the stereoselective formations of dinuclear helical Cu(I) and Ag(I) complexes. The use of chiral derivatives of 2,2' bipyridine ligands predetermines the chirality at the metal centers [1, 2].

CD, ^1H-NMR and ES-MS measurements proove the proposed structures with homochiral configuration at the metal centers.



[1] Mürner, H.; von Zelewsky, A.; Stoeckli-Evans,H. *Inorg. Chem.* **1996**, *35*, 3931.
[2] Hayoz, P.; von Zelewsky, A.; Stoeckli-Evans, H. *J. Am. Chem. Soc.* **1993**, *115*, 5111.

Inorganic and Coordination Chemistry **89**

Electrochemistry of O_2-Activating Complexes of Ru(II) and Os(II)

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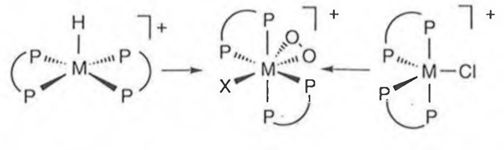
The unsaturated d^6 complexes $[MH(dcpe)_2]^+$ (dcpe=1,2-bis(dicyclohexylphosphino)ethane) (**1a,b**) react instantaneously with O_2 forming the stable peroxo derivatives **3** [1]. By contrast, **2b** forms an unstable peroxo intermediate, whereas **2a** reacts with O_2 giving a yet unidentified paramagnetic species. We find now that the electrochemical properties of **1** and **2** suggest a rationale for the different reactivity of **1,2**.



1 **3** **2**

	M	X
1a	Ru	H
1b	Os	H
2a	Ru	Cl
2b	Os	Cl

Cyclic voltammetry studies show **1,2** to undergo irreversible (or quasireversible) Ru(II)→Ru(III) oxidation in CH_2Cl_2: **1a** and **1b** are oxidized at lower potentials (anodic peak potentials E_a=0.43 and 0.57 V *vs.* $FeCp_2/FeCp_2^+$, scan rate 0.1 V s^{-1}) than the chloro analogs **2a** and **2b** (E_a=0.83 and 0.80 V). Thus, the reactivity of **1,2** toward O_2 increases with the reducing power of the five-coordinate fragment. Accordingly, the complex with the highest E_a, i.e. **2a**, does not form a detectable peroxo complex **3**.

[1] (a) M. Jiménez-Tenorio, M. C. Puerta, P. Valerga, *Inorg. Chem.* **1994**, 33, 3515. (b) A. Mezzetti, E. Zangrando, A. Del Zotto, P. Rigo, *J. Chem. Soc., Chem. Comm.* **1994**, 1597.

Anorganische/Koordinations Chemie **90**

Interpretation and Simulation of the Adsorption Behaviour of Solvents on Zeolites

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Laboratorium für Technische Chemie
Eidgenössische Technische Hochschule, 8092 Zürich

Volatile organic compounds or VOCs can cause a number of severe environmental problems and often have toxic or carcinogenic effects. They are routinely adsorbed on activated charcoal. As alternatives to these adsorbents there is increasing interest in dealuminated, hydrophobic zeolites. Their advantage is low water adsorption with a high selectivity for VOCs.

Breakthrough and isothermal desorption are measured with the apparatus shown in Figure 1. Two types of zeolites were investigated: ZSM-5 and Y. While ZSM-5 can be synthesised with Si/Al ratios of 10 to ∞, Y zeolite has to be dealuminated by a post-synthesis treatment which is accomplished by steaming and/or $SiCl_4$-treatment .

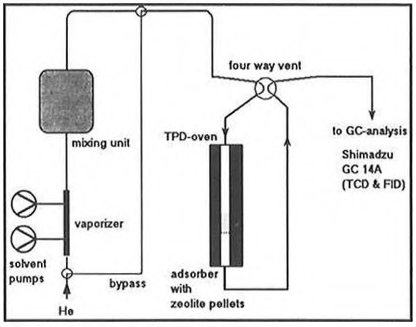

Figure 1: Adsorption Apparatus

The breakthrough and isothermal desorption curves of selected VOCs and water were measured, analysed and simulated. To achieve this, one has to solve the partial differential equation related to the mass balance of the adsorber. Diffusion limitation is introduced with the linear driving force model. To take axial dispersion into account, a Peclet number of 100 is assumed. The described method enables rapid scale up of adsorbers.

Inorganic and Coordination Chemistry **91**

^{13}C NMR Studies of Cyanide Exchange Kinetics on Square-planar Tetracyanometalate Complexes

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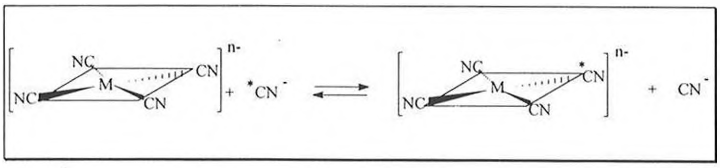
We have recently reviewed the kinetics of the dioxotetracyanometalate complexes of Re(V), Tc(V), W(IV) and Mo(IV) [1]. We now extend the study to the cyanide exchange on the tetracyanometallate complexes $[M(CN)_4]^{n-}$ where M= Au(III), Pd(II) and Pt(II), which are thermodynamically stable yet kinetically labile complexes.



As a first approach, the proton exchange study on cyanide was reviewed followed by the determination of the rate law for these square-planar CN/HCN substitution reactions. The exchange kinetics were monitored using ^{13}C NMR line-broadening and isotopic exchange using fast injection techniques[2] , including variable pressure experiments [3].

[1] Root, A. ; Leipoltd, J.G. ; Helm, L. ; Abou-Hamdan, A. ; Merbach A. E. *Inorg Chem.* **1995**,*34*,560
[2] Bernhard P. ; Helm L. ; Ludi, A. ; Merbach, A.E. *J. Amer. Chem. Soc.* **1985**,*107*,312
[3] Frey U. ; Merbach A. E. *High Pressure Research* **1990**, *2*, 237

Anorganische Chemie **92**

Dealumination behaviour of beta, ZSM-5 and mordenite zeolites

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Hochschule, Universitätstrasse 6, CH-8092 Zürich

The essential step in producing an active, stable zeolite catalyst is the modification of the as-synthesised material. Dealumination methods such as acid leaching, complexation by oxalic acid and direct replacement of aluminium by silicon using $SiCl_4$ have been investigated extensively. Different zeolite structure types such as beta, ZSM-5 and mordenite, behave very differently towards the various dealumination methods.

Framework hydroxyl groups such as Si-OH, Al-OH and Brønsted acid sites have been observed by FTIR spectroscopy in the 3800-3400 cm^{-1} region. ^1H and ^{27}Al MAS NMR measurements of similar samples allowed the identification and the quantitative detection of the different hydroxyl groups. Combining the information from these two techniques with bulk elemental analysis allows the dealumination of the framework to be studied quantitatively.

Quantitative analysis of the ^1H MAS NMR spectra gives information about the number of Brønsted acid sites and therefore the number of framework aluminium atoms. It is possible to distinguish between two different type of Brønsted protons at chemical shifts of 3.8-4.2 ppm and 5.1-5.9 ppm. The first signal is due to the free bridging hydroxyl groups and the second signal is due to the interaction of the bridging hydroxyl groups with the zeolite framework. The ratio between the two acid sites varies in the different zeolites. In zeolite ZSM-5 only a few Brønsted protons interact with the framework whereas in zeolite beta a large number are hydrogen-bonded to the structure.

Inorganic and Coordination Chemistry **93**

Structure Determination and Rietveld Refinement of Two Copper(II) Complexes with *tamp* from a Single X-ray Powder Pattern

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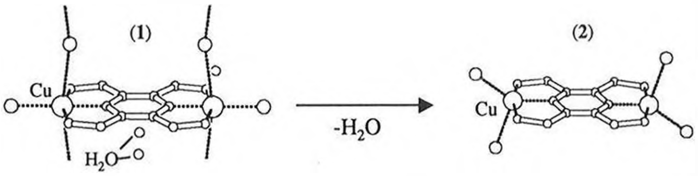
2,3,5,6-tetrakis(aminomethyl)pyrazine (*tamp*) is a bis-tridentate ligand acting as a bridging planar chelate and has been used in the formation of coordination polymers [1].
The structure of the polymeric copper(II) compound, $\{[Cu_2Cl_4(tamp)](H_2O)_{2.25}\}_n$, was first solved by single crystal methods. As the compound undergoes a slow decomposition process by the loss of water molecules, the microcrystalline product was measured after some time by X-ray powder diffraction. The powder pattern indicates, in addition to the polymeric compound, $[\{[Cu_2Cl_4(tamp)](H_2O)_{1.1}\}_n$ (**1**), the presence of an unknown second phase. The structure of this unknown compound was solved *ab initio*. A water free binuclear compound $[Cu_2Cl_4(tamp)]$ (**2**) was identified. Rietveld refinement was carried out for both structures from a single powder pattern.



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Kooordinationschemie **94**

POTENTIOMETRIC AND NMR STUDIES OF THE COMPLEXATION OF AZACROWNETHER-PHOSPHONATES

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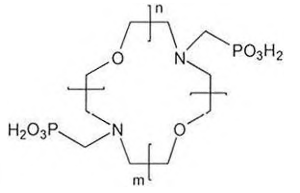
Department of Chemistry, University of Basel, Spitalstrasse 51, CH-4056 Basel

Three macrocyclic ligands of different ring size with two appended methyl phosphonate groups (**1** - **3**) have been synthesized and their complexation potential studied.



1 m = n = 1
2 m = 1, n = 2
3 m = n = 2

Their pK_H-values and complexation constants with M = Pb(II), Cd(II) and Zn(II) were determined by potentiometric titrations. The results indicate that besides mononuclear species MLH_x (x = 3, 2, 1, 0, -1) with different protonation degree, also binuclear complexes M_2LH_x (x = 1, 0, -1, -2) are formed. The stability order is Pb(II) > Cd(II) > Zn (II) for ligands **2** and **3** , but for **1** Cd(II) is more stable than Pb(II).
To study the structures in solution ^1H-, ^{13}C- and ^{31}P-NMR spectra were run as a function of pH.

Chimie Minérale et de Coordination **95**

Toward Stable and Selective Non-covalent Lanthanide Podates

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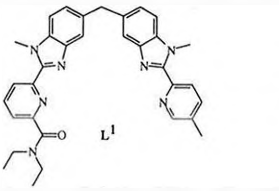
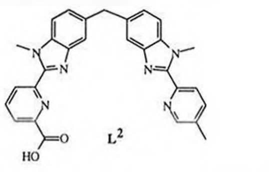
[‡] University of Geneva, Dept of Inorganic Chemistry and Laboratory for X-ray Cristallography, CH-1211 Geneva 4; [§] University of Lausanne, Chemistry Section, CH-1015 Lausanne; [†] Pharma Division, Hoffmann-La Roche, CH-4070 Basel

The recent development of new libraries of tridentate binding units for the selective complexation of lanthanide metal ions, Ln^{III}, has showed that unsymmetrical disubstituted-2,6-pyridine receptors are good candidates for the design of triple-stranded *pseudo*-tricapped trigonal prismatic building blocks $[LnL_3]^{3+}$ with predetermined structural, electronic and spectroscopic properties [1]. A close control of the facial↔meridional isomerization requires suitable tripods which organize the strands for their coordination to Ln^{III} [2]. The segmental ligands L^{1-2} are designed for this purpose and they self-assemble with equimolar mixtures of Ln^{III} and M^{II} (M=Zn, Fe, Co) to give selectively the C_3-symmetrical lanthanide podates $[LnM(L^1)_3]^{5+}$ where M^{II} occupies the facial *pseudo*-octahedral coordination site and acts as a non-covalent tripod. In $[LaCo(L^1)_3]^{5+}$, La^{III} is a templating agent which controls the formation of the stable inert podate $[LaCo(L^1)_3]^{6+}$ after oxidation. Demetallation produces quantitatively the nonadentate organized facial lanthanide receptor $[Co(L^1)_3]^{3+}$. The introduction of a terminal carboxylate group in L^2 provides a negatively charged tridentate segment adapted for the recognition and efficient coordination of Ln^{III} leading to highly stable and luminescent non-covalent podates $[LnZn(L^2\text{-}H)_3]^{2+}$.



L^1



L^2

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[2] C. Piguet, J.-C.G. Bünzli, G. Bernardinelli, G. Hopfgartner, S. Petoud, O. Schaad, *J. Am. Chem. Soc.* **1996**, 118, 6681. C. Piguet, E. Rivara-Minten, G. Bernardinelli, J.-C.G. Bünzli, G. Hopfgartner, *J. Chem. Soc., Dalton Trans.* **1997**, 421.

Chimie Minérale et de Coordination **96**

Calamitic Lanthanide Metallomesogens: Dream or Reality?

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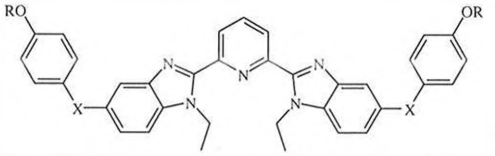
Although tridentate ligands display large chelate effects and form stable complexes with d-block and f-block metal ions, their bent structures preclude their use in metallomesogens (i.e. metal-containing liquid crystals) [1]. The recent discovery that bulky tetrahedral and octahedral complexes might give metallomesogens [2] leads us to consider rigid tridentate aromatic binding units as possible candidates for the preparation of calamitic Ln^{III}-containing thermotropic liquid crystals. As a first step toward this goal, we have synthesized the extended ligands L^i (i = 1-4) with variable spacers (X) between the coordinating unit and the axial semi-rigid lipophilic chains. X should be flexible enough to allow the structural trans-trans→cis-cis rearrangement occurring upon complexation and rigid enough to maintain the large axial anisotropy required for calamitic metallomesogens. L^1 gives only crystalline compounds, but the shorter spacers in L^i (i = 2-4) lead to rich and promising calamitic mesogenic behaviours. Upon complexation to $Lu(NO_3)_3$, the 1:1 complex $[Lu(L^2)(NO_3)_3(OH_2)]$ ($R = C_{12}H_{25}$) is formed where Lu^{III} is meridionally coordinated by the three N-atoms of L^2, the remaining sites being occupied by three bidentate nitrates and one water molecule. Thermogravimetry, DSC and polarized microscopy indicate that $[Lu(L^2)(NO_3)_3(OH_2)]$ reversibly melt at 132° to give a calamitic smectic A phase. Isotropisation occurs at 188°.



$X = CH_2\text{-}O\text{-}CO : L^1$
$X = CH_2\text{-}O : L^2$
$X = O\text{-}CO : L^3$
$X = O\text{-}CH_2 : L^4$
$R = CH_3, C_{12}H_{25}, C_{16}H_{33}$

[1] *Metallomesogens, Synthesis, Properties and Applications* J.L. Serrano Ed., VCH, Weinheim, **1996**.
[2] S. Morrone, D. Guillou, D.W. Bruce, *Inorg. Chem.* **1996**, 35, 7041. K.E. Rowe, D.W. Bruce, *J. Chem. Soc., Dalton Trans.* **1996**, 3913.

CHIMIA 51 (1997) Nr. 8/9 (August/September)

Inorganic and Coordination Chemistry **97**

An Alternative Approach to Chiral Ferrocenyl Ligands Containing P-N and P-O Bonds.

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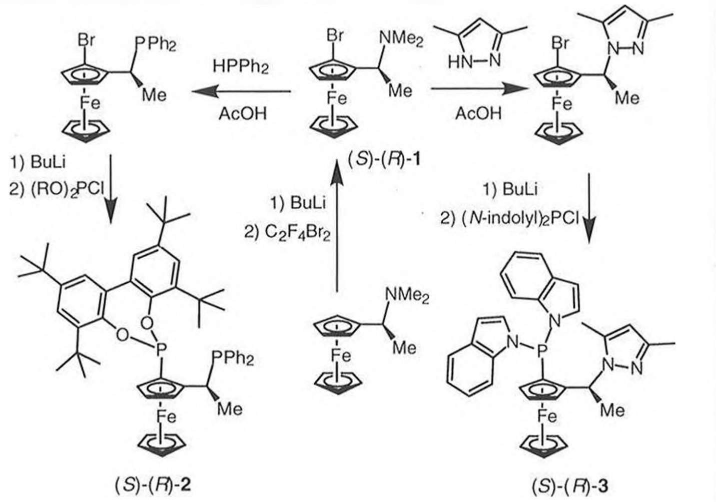
Ferrocenyl ligands of type **2** and **3**, containing π-acidic phosphorus units, were prepared by inverting the general synthetic sequence applied to *Josiphos*-derivatives [1]. Thus, via bromide **1** the ligand fragment attached to the stereogenic center is introduced *first*. The addition of the more sensitive phosphonite or bis(*N*-indolyl)phosphine moiety is achieved in the *last* step. Further examples and their applications will be presented.



[1] A. Togni et al., *J. Am. Chem. Soc.* **1994**, *116*, 4062.

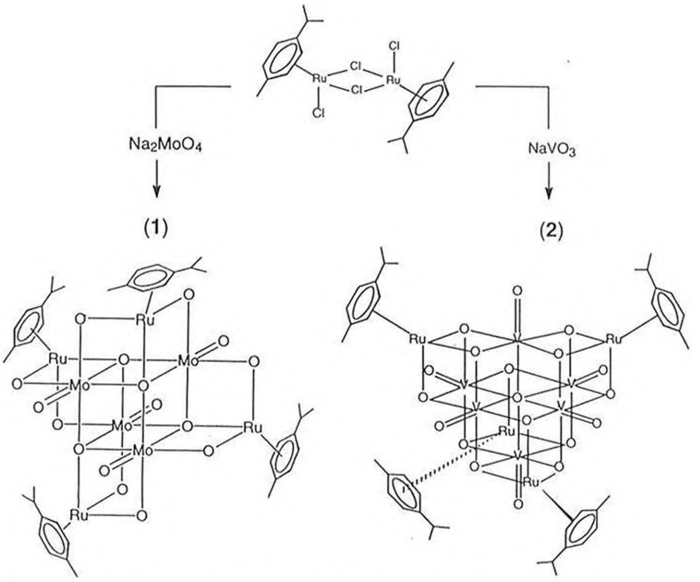
Inorganic and Coordination Chemistry **98**

Amphiphilic Organo-ruthenium Oxo-molybdenum and Oxo-vanadium Clusters

L. Plasseraud, S. Stanislas, V. Ferrand, H. Stoeckli-Evans and G. Süss-Fink*

Institut de Chimie, Université de Neuchâtel, CH-2000 Neuchâtel

Para-cymene ruthenium dichloride dimer reacts in aqueous solution with sodium molybdate or sodium vanadate to give the new amphiphilic organoruthenium clusters **1** and **2**, respectively.



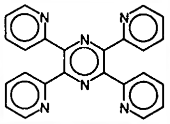
The molecular structures of **1** and **2** will be discussed.

Inorganic and Coordination Chemistry **99**

2,3,5,6-Tetra(2-PYRIDYL)PYRAZINE (TPPZ) : AN OLD LIGAND EXHIBITING A NEW COORDINATION MODE

Maciej Posel and Helen Stoeckli-Evans

Institut de Chimie, Université de Neuchâtel, Av. de Bellevaux 51
CH-2000 Neuchâtel, Switzerland



TPPZ has been shown to be a very versatile ligand and has been used in complex formation with first row transition metals. Originally TPPZ was thought to form only mononuclear complexes [1]. The bridging nature of this ligand has been established crystallographically by the study of several binuclear 3d transition metal complexes [2], an unusual macrocycle [3], and a coordination polymer. In all cases the organic ligand coordinates in a bis-tridentate manner. A new coordination mode of TPPZ has recently been observed in the formation of a "binuclear" nickel (II) complex. The reaction of TPPZ with $Ni(ClO_4)_2.6H_2O$ gave a green precipitate. This was recrystallized from a mixture of solvents containing acetylacetonate. The total content of the asymmetric unit consists of $[NiCl(acac)\text{-}tppz\text{-}NiCl_3]^- \cdot [NiCl(acac)\text{-}tppzH]^+ \cdot [NiCl(acac)\text{-}tppzH_2]^{2+} \cdot [NiCl_4]^{2-}$. In the anion $[NiCl(acac)\text{-}tppz\text{-}NiCl_3]^-$ the ligand combines two different coordination modes. Compared with the known mono-tridentate chelating coordination to nickel(II), an extra monodentate coordination is observed from a pyridine ring to a $[NiCl_3]^-$ anion.

[1] Goodwin & Lions, J.A.C.S., 81 (1959) 6415.
[2] M. Graf, B. Greaves & H. Stoeckli-Evans,
Inorganic Chimica Acta 204 (1992) 239.
M. Graf & H. Stoeckli-Evans, Inorganic Chimica Acta (1997) in press.
[3] M. Graf & H. Stoeckli-Evans, Acta Crystallogr., C50 (1994) 1461

Inorganic and Coordination Chemistry **100**

Enantiopure Double and Triple Helicates of Silver(I). The Rôle of Stacking Interactions.

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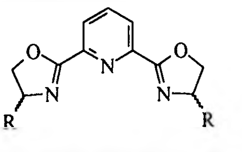
CHIAM - University of Geneva, CH-1211 Geneva 4.

Enantiopure helicates have been prepared by self-assembly around silver(I) ions. Induction of chirality has been achieved with chiral ligands of the type bis-oxazolinylpyridine.



1 : R = Benzyl (S,S-Bzpybox)
2 : R = Phenyl (R,R-Phpybox)
3 : R = 4-Ethoxyphenyl

In all cases, only one enantiomer of the helix was obtained, but depending on the ligand, the helix type is different.

The use of S,S-Bzpybox **1** led to the formation of a double helix with *P*(Δ) helicity, **1** acting as a bis-monodentate ligand. The silver(I) ions are linearly coordinated by two nitrogen atoms from the oxazoline moieties, the pyridine ring being uncoordinated. The complex has D_2 symmetry with pseudotwofold axes passing through the silver ions and through the pyridines. Different studies (ES-MS, NMR, CD) have shown that this structure is kept in solution.

The compound obtained with R,R-Phpybox **2** has a toroidal triple helix structure with *P*(Δ) helicity. The complex has crystallographic C_3 symmetry, and consists of an equilateral triangle of silver(I) ions, with the ligands bridging the sides of the triangle. Each ligand binds, via the oxazoline moieties, to one metal from below the plane of the silver atoms and to a second metal from above the plane. This structure shows strong stacking interactions between the pyridine of one ligand and the phenyls of the two others. In solution, this trimeric cation appears to be unstable leading to an equilibrium between different species. In order to stabilise the trimeric form, we have increased the stacking interactions by introducing an electrodonating group on the phenyl ring (compound **3**). The resulting complex shows nearly 90 % of trimer in solution.

Anorganische Chemie **101**

Transition Metal Complexes of Cyclic Octapeptides

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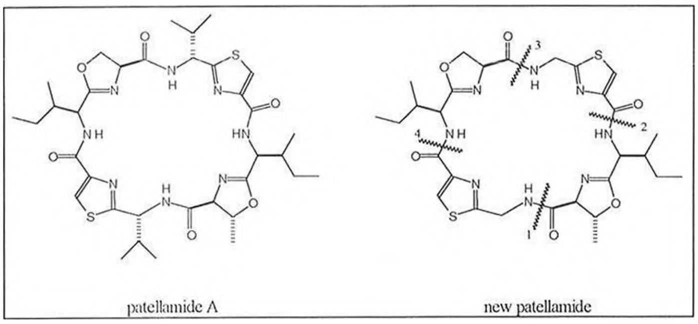
Im Neuenheimer Feld 270, 69120 Heidelberg, Germany



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 slightly simplified patellamide derivatives (see picture) and their transition metal complexes. The determination of stability constants, NMR and EPR spectra and molecular mechanics studies are used to help determine the solution structures of patellamides and their transition metal complexes. With the comparison of the solution and crystal structures of newly synthesized an known, naturally occuring patellamides, we hope to be able to predict the influence of alkyl chains and smaller rings on the conformation and stability of the patellamide complexes.

Inorganic Chemistry/Solid State Chemistry **102**

EUROPIUM COMPOUNDS CONTAINING BN$_2^{3-}$-UNITS: $Eu_7(BN_2)_5$ and Eu_2BN_2X (X=Cl,F)

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Several alkaline-earth compounds containing isolated $(BN_2)^{3-}$-units are already known [1-3]. Recently we reported on M_2BN_2X with M=Ca,Sr and X=F,Cl [5]. Trying to synthesize homologeous europium compounds we found three different new phases. The compounds were obtained from reactions of boronnitride, europium, europium nitride, and halogenides.
$Eu_7(BN_2)_5$ crystallizes in the orthorhombic spacegroup Pnma (Nr. 62) with a=12.150(2), b=17.230(1), c=6.693(2).
Eu_2BN_2Cl crystallizes in an other orthorhombic spacegroup Pnnm (Nr. 58) with a=9.455(2), b=18.473(4), c=4.068(1).
According to powder diffraction Eu_2BN_2F crystallizes isotypically to Sr_2BN_2F (Pnma: a=9.891(2), b=3.904(1), c=10.193(2)).
The novel halogenide phases can be understood as double salts and a large compound family may evolve from them. Furthermore, their existence may be taken as an indication for solubility of $(BN_2)^{3-}$ containing phases in typical salt melts which would open a large number of possible reaction and synthesis routes.

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Z. Kristallogr. 1994, **209**, 182 and 618;
Z. Kristallogr. 1995, **210**, 529; 1996, **211**, 54.
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Chimie minérale et de coordination **103**

Dissociation of Ni^{2+} Complexes with the Polymeric Amines LPEI and BPEI in Acid Solution

Urs C. Meier and Carl Wilhelm Schläpfer

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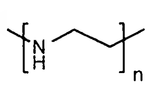
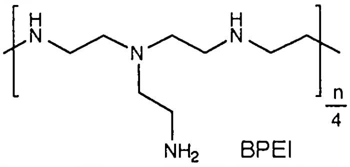


LPEI



BPEI

The polymeric amines LPEI (linear polyethyleneimine) and BPEI (branched polyethyleneimne) form at pH 8 Ni^{2+} complexes with the metal ion in a N_6 coordination sphere. The mechanism of the dissociation of these complexes (N : Ni = 10 : 1) in acid solution (0.1 M HCl and 1 M HCl) was studied by stopped flow. The evolution of the visible spectra was studied by evolving factor analysis. Two reaction steps are observed for both polymeric complexes. For NiLPEI the two observed rate determining steps are the transformation $NiN_3(H_2O)_3$ —> $NiN_2(H_2O)_4$ and $NiN_2(H_2O)_4$ —> $Ni(H_2O)_6$. The pseudo first order rate constants are 11.7 s^{-1} and 0.021 s^{-1} at 10°C. The steps leading to $NiN_3(H_2O)_3$ are to fast to be observed by our instrument. The reaction mechanism is similar to the dissociation of complexes with linear amines (1). For NiBPEI the two observed rate determining steps are NiN_6 —> $NiN_3(H_2O)_3$ and $NiN_3(H_2O)_3$ —> $Ni(H_2O)_6$, with the pseudo first order rate constants 2.25 s^{-1} and 0.057 s^{-1} at 10°C. The second step is similar to the dissociation of Ni(tren) in acid solution (2). No specific polymer effect was observed.

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Inorganic Chemistry **104**

The Many Faces of Thiophene

Sarah J. Angus-Dunne, Edwin C. Constable, Simon J. Dunne,
Catherine E. Housecroft, David Rees and Chantal X. Schmidt

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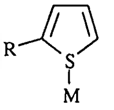
Thiophene possesses sulfur as a potential donor atom and might be expected to show a relatively simple coordination chemistry. In our studies of multidentate ligands incorporating sulfur donors, we have found that the situation is by no means so simple, and coordination modes including **1-7** are possible.



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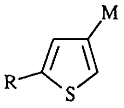

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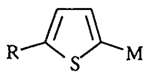

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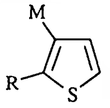

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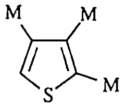

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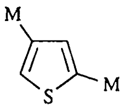

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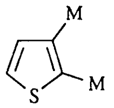

(7)

Studies on a series of pyridylthiophenes and oligothiophenes will be reported.

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Inorganic Chemistry **105**

Oligopyridines with Soft Edges

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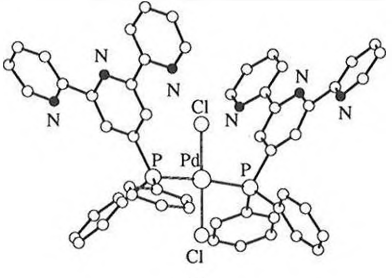
A series of oligopyridine ligands incorporating additional pendant soft donor groups has been prepared. Synthetic, structural and coordination studies on systems bearing thiophene or phosphine,[1] **1**, substituents will be reported. In addition, preliminary studies of new multinucleating ligands which possess additional soft donor atoms within the linker between the metal-binding domains, **2**, will be described.



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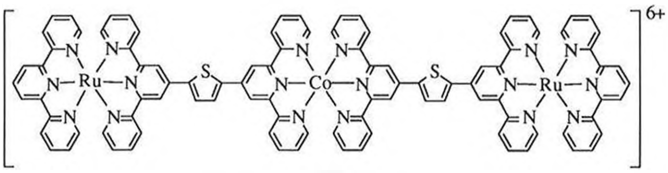

(2)

1. E.C. Constable, C.E. Housecroft, M. Neuburger, A.G. Schneider and M. Zehnder, *J. Chem. Soc., Dalton Trans.* **1997**, in press.

Inorganic and Coordination Chemistry **106**

Towards a Hydroamination Catalyst *via Ab-initio* Molecular Dynamics

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Swiss Federal Institute of Technology, CH-8092 Zürich
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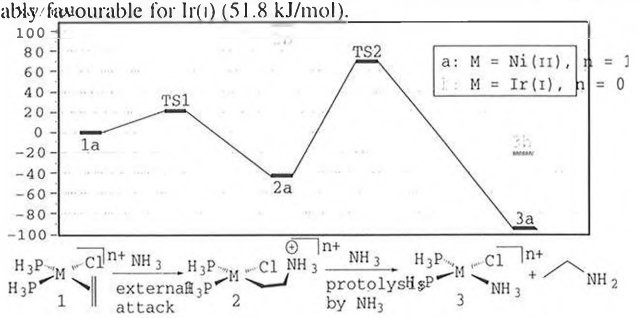
The catalytic **hydroamination of olefins**, *i.e.* the addition of N–H across a C=C double bound, is still a virtually unknown reaction [1]. Two principal mechanistic pathways are conceivable: (*A*) External nucleophilic attack onto the coordinated olefin by an amine (C=C activation) followed by protolytic cleavage of the formed M–C bond; (*B*) activation of the N–H bond by oxidative addition of the amine with subsequent olefin insertion and reductive elimination.

To establish which metal in which oxidation state may be suitable for either pathway, we investigate intermediates, transition states, and reaction paths using the **projector-augmented waves (PAW) method** [2]. Dynamics simulations are carried out by means of **Car–Parrinello** ***ab-initio*** **molecular dynamics** calculations.

For Ni(0), the aminoalkyl complex **2** formed in pathway *A* does not even correspond to a minimum on the energy hypersurface. For Ni(II), *A* appears to be feasible (Scheme), whereas the Ir(I) analogues **2b** and **3b** are considerably less favourable. On the other hand, the amido hydrido complex formed in *B* is inaccessible for Ni(II), lying 240.5 kJ/mol above the amino complex, but comparably favourable for Ir(I) (51.8 kJ/mol).



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[2] P. E. Blöchl, *Phys. Rev. B* **1994**, *50*, 17953–17979.

Inorganic Chemistry **107**

A new spin-crossover iron(II) system

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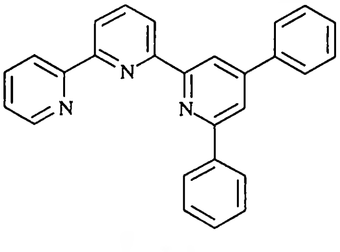
Karl Wieghardt and Margareta Zehnder

Laboratory for Supramolecular Chemistry, Institute of Inorganic
Chemistry, University of Basel, CH-4056 Basel; Institute for Inorganic
Chemistry, University of Erlangen; Max-Planck Institute for Radiation
Chemistry, Müllheim; Institute for Inorganic Chemistry, University of
Karlsruhe

The introduction of aryl substituents into the 6-position of 2,2':6',2"-terpyridine leads to the formation of spin-crossover $[FeL_2]^{2+}$ complexes. With ligand **1**, both orange (high-spin) and purple (low-spin) complexes may be isolated. Both spin states have been structurally characterized in the solid state and detailed studies of the magnetic behaviour and the interconversions of the two forms have been made. The effects of structural variation within the ligand have also been investigated.



(1)

THE COMPLEXATION OF TRANSITION METALS TO LINEAR POLY(ETHYLENIMIN): AN ELECTROCHEMICAL APPROACH

108

C.W. Schlaepfer, J. Spuck
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Fribourg, CH-1700 Fribourg

Linear Poly(ethylenimin) (LPEI) is a polymeric amine ligand, which interacts with transition metal ions such as Cd^{2+}, Cu^{2+}, Ni^{2+} and others. 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 LPEI solutions at different pH, different Cd^{2+} to Nitrogen ratios and with polymers of increasing chain length of 6, 20, 40, 100, 500 and 2000 units. Potentiometric titrations, Normal-pulse-polarography (NPP) and Chronoamperometry (CA) and gave insight into polyamine complexation behavior and the mobility of the metal ion and its complexes in solution.

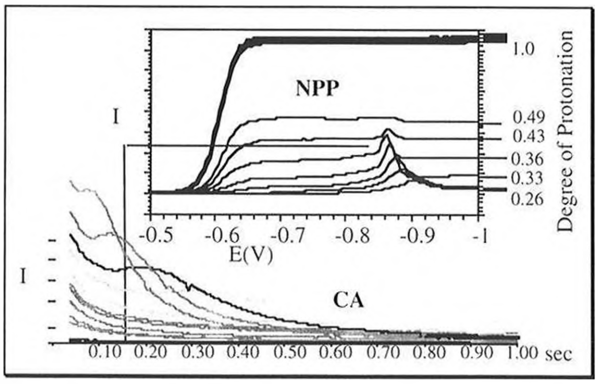

Fig.1: **NPP** of Cd^{2+}/LPEI 2000 solutions in water at increasing pH from pH2 to pH8 and **CA** at increasing Potential (pH8).

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Inorganic and Coordination Chemistry **109**

Metal-Catalyzed Asymmetric Diboration of Olefins

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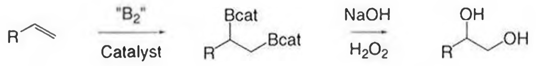
ETH Zentrum, Universitätstr. 6, CH-8092 Zürich

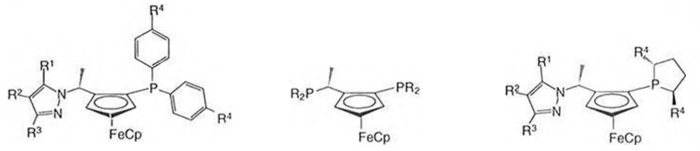
The discovery that certain transition metal complexes promote the addition of B-H [1] and B-B bonds to unsaturated organic moeties has received considerable attention for applications in organic synthesis. Recently, the catalytic diboration of alkenes (sch. 1) was discovered [2], providing a new route to a wide variety of 1,2-bifunctional organic compounds.

Scheme 1



The aim of our work is to apply this particular reaction to different prochiral substrates, such as unsaturated heterocycles or substitued alkenes and control the stereo and chemo selectivity of the bis boronate ester addition using chiral P-N or P-P ferrocenyl-type ligands shown below. Our research involves principally Rh(I), Pt(0) and Au(I) systems. Preliminary results in this field will be presented.

Scheme 2



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Inorganic Chemistry **111**

Reaction of Nitrogen Monoxide with Peroxynitrite

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Nitrogen monoxide (NO$^\bullet$) reacts with superoxide ($O_2^{\bullet -}$) to form the strong oxidant peroxynitrite ($ONOO^-$). This reaction proceeds with a rate constant that is diffusion-controlled [1] and has been proposed to contribute to the toxicity of NO$^\bullet$ *in vivo*.

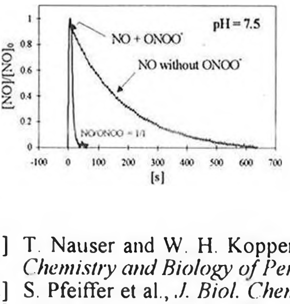
$$NO^\bullet + O_2^{\bullet -} \rightarrow ONOO^- \qquad k = 2 \times 10^{10}\ M^{-1}\ s^{-1}$$

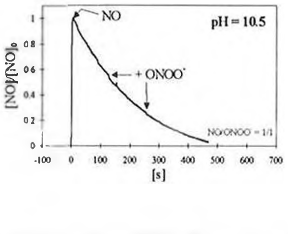
Nitrogen monoxide might react with the formed peroxynitrite and has been considered as a possible source of nitrite ions found in decomposed peroxynitrite solutions [2].

We have studied this reaction by monitoring the decrease of NO$^\bullet$ with a chemiluminescence analyzer. Stopped-flow results demonstrate that under anaerobic conditions peroxynitrous acid (ONOOH, pK_a=6.8 [3]) reacts with NO$^\bullet$:

$$k(ONOOH + NO) = 1 \times 10^4\ M^{-1}\ s^{-1}.$$

The deprotonated peroxynitrite reacts with NO$^\bullet$ only in the presence of dioxygen.





[1] T. Nauser and W. H. Koppenol, *First International Conference on the Chemistry and Biology of Peroxynitrite, Ascona, Switzerland* **1997**, 43.
[2] S. Pfeiffer et al., *J. Biol. Chem* **1996**, *272 (6)*, 3465-3470.
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Anorganische/Koordinationschemie **110**

Calorimetric Studies of the Metal Binding Properties of Cu,Zn-Superoxide Dismutase

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ETH Zentrum, Universitätsstr. 6, 8092 Zürich

Cu,Zn-Superoxide dismutase (SOD1) is an enzyme which catalyzes the dismutation of superoxide radical anion to molecular oxygen and hydrogen peroxide. It consists of two identical subunits which both contain binding sites for one Cu^{2+} and one Zn^{2+} ion [1] (Fig. 1).
In order to investigate the role of the metal ions for the altered function of mutant proteins, we plan to directly measure enthalpies of metal ion binding in native and mutant human SOD1 by isothermal titration calorimetry (ITC).

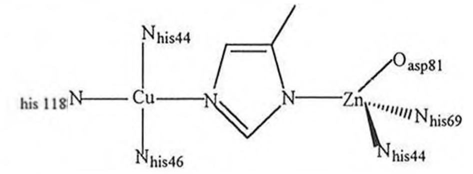

Fig. 1 Metal binding geometrys in SOD1

We present preliminary measurements of enthalpies and equilibrium constants for binding of Cu^{2+} and Zn^{2+} to apo bovine and human SOD1 (E_2E_2SOD) by ITC.

In addition, a new method for rapid and convenient preparation of apo-SOD is presented.

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Inorganic Chemistry **112**

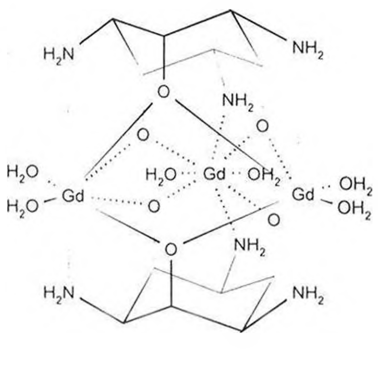
Trinuclear Lanthanide(III) Complexes : an EPR and ^{17}O NMR Study

É. Tóth[1], A. Borel[1], L. Helm[1], A. E. Merbach[1], R. Hedinger[2] and K. Hegetschweiler[2]

[1]Institut de Chimie Minérale et Analytique, BCH-Dorigny, CH-1015, Lausanne ; [2]Laboratorium für Anorganische Chemie, ETHZ, Universitätsstrasse 6, CH-8092 Zürich

Recently much attention has been given to gadolinium chelates, due to their application as contrast agents in Magnetic Resonance Imaging. Their efficiency to increase the relaxation rate of the surrounding protons depends mainly on the number and the exchange rate of water molecules coordinated to the gadolinium, on the rotational correlation time of the complex and on electronic relaxation rates.

Electronic relaxation rates and their effect on NMR relaxation rates represent the least well understood part of the whole theory. In the Gd-complex of the ligand 1,3,5-triamino-1,3,5-trideoxy-*cis*-inositol (taci) there are three lanthanide ions in very close proximity which offer the possibility to study intramolecular dipole-dipole interactions in electronic relaxation. These interactions may become important for new generation polymeric contrast agents where many Gd^{3+} ions are concentrated in space.



We present the results of a multiple field, variable temperature EPR and a multiple field, variable temperature and pressure ^{17}O NMR study of the Gd_3taci_2 complex that let us determine water exchange rate, activation volume, rotational correlation time, as well as electronic relaxation parameters.

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New insights into the dynamics and structure of Ru(II)/MeO-BIPHEP Hydrogenation catalysts via NMR methods

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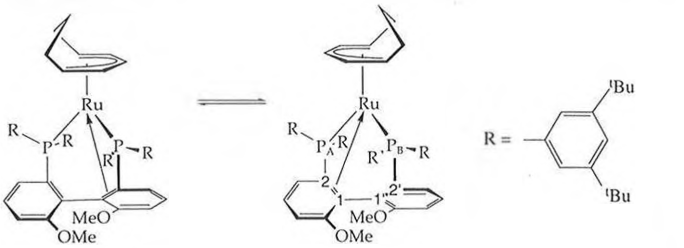
Swiss Federal Institute of Technology, ETH Zentrum,
8092-Zürich, Switzerland

NMR results on MeO-BIPHEP/Ru(II)-complexes of the following type will be presented:



MeO-BIPHEP is a well-known chiral auxiliary, which has been employed in catalytic hydrogenation [1]. For the η^5-allylic COD as shown above, an unusual interaction between a biaryl double-bond and the Ru(II) centre has been found, as shown by the following ^{13}C and ^{31}P data [2].

Labelling	1	2	versus	1'	2'		P_A	versus	P_B
^{13}C	*95.1*	*74.5*		139.7	135.4	^{31}P	*-11.2*		69.6

ROESY results are in agreement with an η^6 binding mode of MeO-BIPHEP (indicated by an arrow) together with a C_2-symmetric exchange [2]. *Moreover, four different rotation barrers* for the aryls R around the P-C^{ipso} of the R groups are found.

[1] Schmid, R.; Broger, E. A.; Cereghetti, M.; Crameri, Y.; Foricher J.; Lalonde, M.; Mueller, R.; Scalone, M.; Schoettel, G.; Zutter, U. *Pure Appl. Chem.* **1996**, *68*, 131

[2] Feiken N., Pregosin P. S., Trabesinger G., *Organometallics* **1997**, *16*, 537 - 543

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New chiral olefin complexes of Pd(0) with bisphosphine and phosphine thioether ligands

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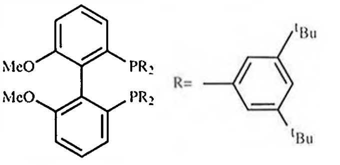
Universitätsstrasse 6, CH-8092 Zürich, Switzerland

New chiral olefin complexes of Pd(0) containing the chelating bidentate bisphosphine **1** [1] or the phosphine thioether **2** [2] have been prepared. As activated 'olefins' we used benzoquinone and cyclopenten-2,4-dione. **1** and **2** were used as ligands in asymmetric Pd catalyzed Heck and Allylic substitution reactions.



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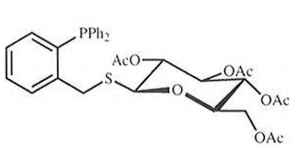
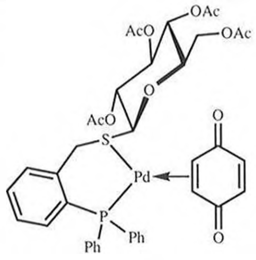


2

The solid-state structure of **3** as well as the structure and dynamics in solution are reported. The complexes show interesting dynamics depending on the size of the olefin coordinated. **3** and **4** are the first examples of Pd(0)-olefin complexes containing a P,S-chelating ligand.



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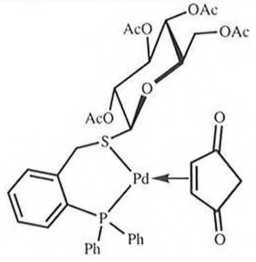

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[1] Schmid, R; Broger, E. A.; Cereghetti, M.; Crameri, Y.; Foricher, J.; Lalonde, M.; Mueller, R.K.; Scalone, M.; Schoettel, G.; Zutter, U.; *Pure & Appl. Chem.* **1996**, 68, 131

[2] Barbaro, P.; Currao, A.; Herrmann, J.; Nesper, R.; Pregosin, P. S.; Salzmann, R.; *Organometallics* **1996**, 15, 1879

Inorganic Chemistry

115

Latent Ruthenium Catalysts for the Bulk Polymerization of Cycloolefins

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CH-1723 Marly 1, Switzerland

Recently, we developed the first ruthenium based photocatalysts for ring-opening metathesis polymerization (PROMP) of dicyclopentadiene (DCPD) and other cycloolefins [1]. However, turn-over frequencies (TOF) were low (ca. 10^{-1} s^{-1}, polym. of norbornene at 60°C) and the cationic character of these complexes restricted their applicability to a polar environment.

In contrast, Ru-arene-phosphine complexes of the type $[Ru(p\text{-cymene})Cl_2(PR_3)]$ (R=Cy, **1**; *i*Pr, **2**; *n*Bu, **3**) are soluble in pure monomers (i.e. hydrocarbons) and showed TOF's of ca. 2 s^{-1} (polym. of norbornene at R.T.). Complex **1** is a very efficient initiator for the thermal, solvent-free polymerization of technical DCPD [2]. Whereas solutions of **1** in DCPD are very stable at R.T, a fast curing reaction takes place at T >80°C, leading to a crosslinked network (crosslink density: 10-20%) with excellent physical properties. Ring-opening of the cyclopentene ring seems to be the predominant crosslinking mechanism (^{13}C-CP/MAS NMR).

Due to the amazing tolerance of **1** towards impurities and water, almost any type of fillers, (*e.g.* SiO_2, $Al(OH)_3$, Al-powder, $CaCO_3$-powder, *etc.*) can be incorporated (up to 70 wt%) and it is possible to run dispersion polymerizations of DCPD and other cycloolefins in polar, protic solvents like water.

Our work to improve catalysts and polymer systems as well as novel applications in the field of electro casting, insulation and tooling will be described.

[1] T. Karlen, A. Ludi, A. Mühlebach, P. Bernhard, C. Pharisa, *J. Polym. Sci., Polym. Chem. Ed.* **1995**, *33*, 1665.

[2] A. Hafner, P. van der Schaaf, A. Mühlebach, *WO96 20235 (Ciba S.C.)*, CH-Prio: 23.12.94. A. Hafner, A. Mühlebach, P. van der Schaaf, *Angew. Chemie*, accepted for publication.

Anorganische Chemie

116

New Pendent Arm Tetraazamacrocyclic Ligands and Their Transition Metal Complexes

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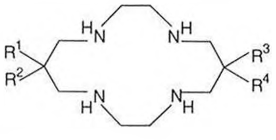
Cyclam (see chart, $R^1 = R^2 = R^3 = R^4 = H$) is one of the most versatile tetraazamacrocyles in transition metal ion chemistry[1], and trans-diammac ($R^1 = R^4 = NH_2$, $R^2 = R^3 = CH_3$) leads to very rigid and stable first transition metal row coordination compounds with exceptionally high ligand fields[2-4]. Apart from the macrocyle hole size the donor atoms are important for the selectivity towards metal ions.



a) $R^1 = H$; $R^2 = OH$; $R^3 = H$; $R^4 = OH$
b) $R^1 = H$; R^2 = 2-pyridyl; $R^3 = H$; R^4 = 2-pyridyl
c) $R^1 = NH_2$; R^2 = 2-pyridyl; $R^3 = NH_2$; R^4 = 2-pyridyl
d) $R^1 = H$; $R^2 = OH$; $R^3 = NH_2$; $R^4 = CH_3$

Hydroxy- and 2-pyridyl groups have been substituted at he C2-atom of the propyl bridge of the cyclam back bone. The structural, electrochemical and spectroscopic properties, as well as the metal ion selectivities of these ligands and the transition metal ion complexes are presented.

[1] Barefield,E.K; Wagner, F.; Herlinger, A.W.; Dahl, A.R., *Inorg. Synth.* **1976**, 16, 220

[2] Bernhardt, P.V.; Lawrance, G.A.; Hambley, T.W.; *J. Chem. Soc., Dalton Trans.* **1989**, 42, 1059

[3] Bernhardt, P.V.; Lawrance, G.A.; Hambley, T.W.; *Aust. J. Chem.* **1990**, 43,699

[4] Berhardt, P.V.; Comba, P.; Curtis N. F.; Hambley T. W.; Lawrance, G.A.; Maeder, M.; Siriwardena, A.; *Inorg. Chem.* **1990**, 29, 3208

Anorganische Chemie **117**

Construction principles of the crystal structures of Zintl compounds with planar silicon units

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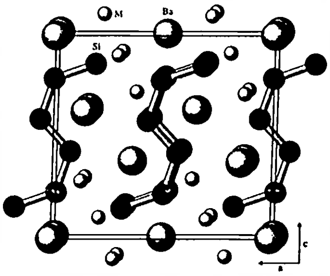
The recent structural investigations on the systems EA/Mg/Li/Si (EA = Ca, Sr, Ba) led to the discovery of a surprisingly large number of different planar polyanions of silicon [1, 2]. Often it is difficult to understand their stability with respect to the simple concepts of Zintl and Klemm, especially in cases without significant π-contributions [3].
We found that the special conformation of the planar Zintl anions is strongly influenced by the cation environment. The heavier alkaline earth metals on the one hand and lithium as well as magnesium on the other show clear structural preferences [2]. Based on the structural data and quantumchemical investigations we were able to understand the electronich structure formulate fundamental construction principles for this class of compounds. Now it seems possible to design further compounds with new planar Si-units and interesting physical properties.



Perspectivic view on the structure of $Ba_6Mg_{5.3}Li_{2.7}Si_{12}$ with ecliptically stacked planar Si_6-units [2].

[1] A. Currao, J. Curda, R. Nesper, *Z. Anorg. Allg. Chem.* **622**, 85 (1996).
[2] S. Wengert, Doktorarbeit, ETH Zürich (1997).
[3] R. Nesper, A. Currao, S. Wengert, *Organosilicon Chemistry*, Band II, From Molecules to Materials, S. 469ff, Verlag Chemie, Weinheim (1995).

Inorganic Coordination-Chemistry **118**

Partial oxidation of C_4 hydrocarbons over vanadia-silica mixed oxide catalysts

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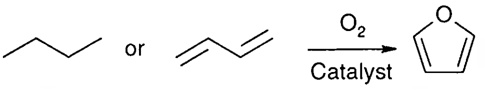
Vanadia-silica mixed oxides were prepared by a sol-gel process using i-propoxide precursors. The resulting vanadia-silica gels were dried by different methods, including conventional evaporative drying (xerogels), high temperature supercritical drying (HT aerogel), and extraction of the alcoholic solvent entrapped in the pores at low temperature with supercritical CO_2 (LT aerogel). The aerogels possessed a marked mesoporous structure whereas the conventionally dried xerogels were microporous. The proportion of V–O–Si heteroconnectivity (isolated V sites) of the sol-gel derived oxides was influenced by the drying process (LT aerogels > xerogel > HT aerogel). The catalysts were tested in the partial oxidation of *n*-butane and 1,3-butadiene to furan in order to study the dependence of morphological properties, vanadium content, vanadium dispersion in the silica matrix, and amount of acidic surface sites on furan selectivity.



The structural properties as well as the surface acidity had a major influence on the catalytic performance of the sol-gel materials. From all tested materials, the 10% V_2O_5/90% SiO_2 LT aerogel was the most selective catalyst (up to 31% furan selectivity at 13% 1,3-butadiene conversion). This aerogel possessed a high proportion of isolated V sites, a mesoporous structure and a high amount of Brønsted acidic sites. Studies involving V_2O_5 and SiO_2 as reference materials revealed, that the selectivity to furan was lowered by silica due to its intrinsic high activity for total oxidation and cracking.

Inorganic and Coordination Chemistry **119**

TlCl Adduct Formation with a Dinuclear Ruthenium(II) Complex

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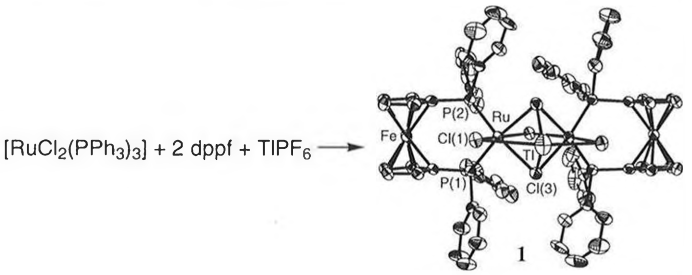
During attempts at preparing $[RuCl(dppf)_2]^+$ (dppf=1,1'-bis(diphenylphosphino)ferrocene), we have discovered that $[RuCl_2(PPh_3)_3]$ reacts non-stoichiometrically with $TlPF_6$ and dppf giving the binuclear complex **1**:



Although bimetallic compounds containing Ru-Cl-Tl bridges are known [1], the structural motif in **1** is new. Monitoring the reaction by ^{31}P NMR suggests that **1** is formed by TlCl addition to the chloro-bridged intermediate $[(dppf)(Cl)Ru(\eta^2\text{-}Cl)_2Ru(Cl)(dppf)]$ (**2**). The use of **1** and **2** as precursors for the synthesis of Ru-dppf complexes will be reported.

[1] (a) A. J. Blake, R. M. Christie, Y. V. Roberts, M. J. Sullivan, M. Schröder, L. J. Yellowlees, *J. Chem. Soc., Chem. Commun.* **1992**, 848. (b) C. Bianchini, D. Masi, K. Linn, C. Mealli, M. Peruzzini, F. Zanobini, *Inorg. Chem.* **1992**, 31, 4036.

Inorganic Chemistry **120**

On the Structure and Twinning of $PtAl_4$

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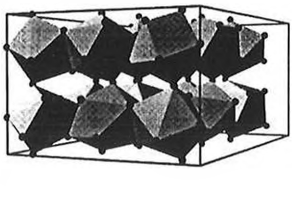
T. Chattopadhyay,
Institute Laue Langevin, Grenoble
S. Kek,
FR Kristallographie, Universität des Saarlandes, Saarbrücken

Since decagonal quasicrystals were found in the binary phase systems of the Pt-group metals and Al crystalline phases in these systems systems are of special interest in order to understand the local atomic arrangements in quasicrystals. Despite being known to exist since almost twenty years [1], the crystal structure of $PtAl_4$ was unknown up to now, mainly due to the special crystallographic problems connected with that structure.



The structure could be refined with a trigonal twin model in the space group P3c1 (No. 158) (lattice constants a=13.077(1) and c=9.6342(7)). It consists of layers of edge sharing Al_{10} polyhedra centered by Pt atoms. The polyhedra layers are stacked along c and are connected by common corners. Twinning occurs with c as the twin axis (rotation about an axis parallel to c). The crystal structure of $PtAl_4$ represents a new structure type. Interestingly $PdAl_4$, whose Al content is close to the approximant $PdAl_3$ of a decagonal phase Pd-Al, is known to have the same lattice constants and therefore probably the same or a related structure type to $PtAl_4$ [2].

[1] T. Chattopadhyay, K. Schubert, *J. Less-Common Met.* **45**, 79 (1976).
[2] M. Ellner, U. Kattner, B. Predel, *J. Appl. Cryst.* **14**, 212 (1981).

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Inorganic Chemistry **121**

CHIRAL METAL COMPLEXES WITH BIPYRIDINE AND TERPYRIDINE LIGANDS

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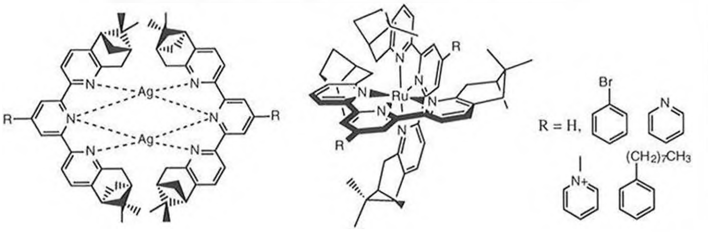
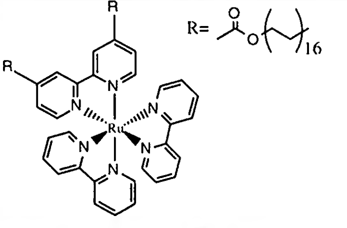
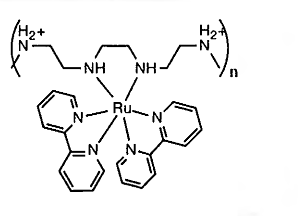
University of Fribourg, Pérolles, CH-1700 Fribourg



We have prepared a number of new chiral Ru(II) and Ag(I) complexes with [5,6]-dipineno-fused terpyridine ligands having its chiral moiety close to the coordinating metal center. These ligands proof very useful for building predetermined helical structures with Ru(II) and Ag(I). Complexing two heterochiral trpy-ligands (with R=H) leads to an achiral structure of S_4-symmetry, which is a case of 'narcissistic coupling'. Using a Chiral Building Block Strategy,[1] Λ and Δ - Ru(II) complexes useful for self-assembly on surfaces have been prepared and studied by CD-spectroscopy.



Λ-$[Ru(bpy)_2(bpy\text{-}R_2)]^{2+}$



Λ and Δ-$[Ru(bpy)_2(LPEI\text{-}n)]^{2+}$
Ru:LPEI=1:10

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[1] H. Muerner, P. Belser, A. von Zelewsky, *J. Am. Chem. Soc.* **1996**, *118*, 7989.; X. Hua, A. von Zelewsky, *Inorg. Chem.* **1995**, 34, 5791

Inorganic and Coordination Chemistry **122**

Semiconducting and Paramagnetic Charge Transfer Complexes of 1,1'-Alkylthiole-Octamethylferrocene, TCNQ and $[M(MNT)_2]^{1-}$

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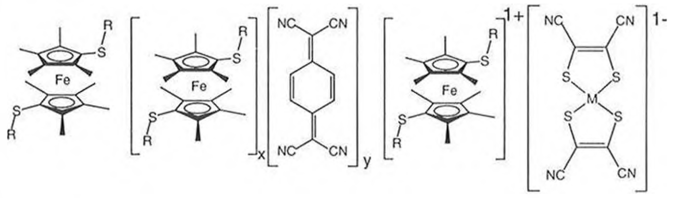
ETH-Zentrum, CH-8092 Zürich, Switzerland

Charge-Transfer complexes containing ferrocene derivatives have been shown to display interesting conducting and magnetic properties [1,2]. The new CT-Complexes **3** and **4** containing the two octamethylated ferrocene derivatives **1** and **2** and **TCNQ** were prepared and characterised by X-ray diffraction. The obtained materials are semiconducting with a room temperature conductivity up to $1.5\ mScm^{-1}$.

Several 1:1 CT-salts, **5-10**, with different $[M(mnt)_2]^{1-}$ (M=Ni, Pt, Co) were prepared and characterised by X-ray diffraction and SQUID-magnetic measurements.



1 (R=Methyl) 3 $[1]_3[TCNQ]_7$ 5-10 R=Methyl, ^{t}Butyl
2 (R=^{t}Butyl) 4 $[2]_1[TCNQ]_3$ M=Ni, Pt, Co

[1]For a review, see: Togni, A. in *Ferrocenes*, Togni A.; Hayashi, T., Eds.; VCH, Weinheim, **1995**, 433-469.
[2]Miller J. S., Calabrese J. C., Epstein A. J., Inorg. Chem. **1989**, 28, 4230-4238.

Computational Chemistry **123**

First Principles Modelling of Lithium Ions Intercalation into Mn-Oxides

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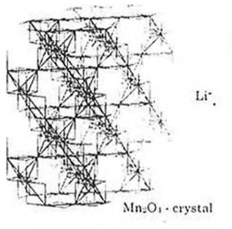
The structural behaviour of *spinel* Mn-oxide during electrochemical intercalation of Li^+ is of fundamental importance for the understanding of electrode materials in battery technology and design. Different oxidation states have been investigated considering partial Li^+ occupations.

All the calculations are done within the Density Functional Theory framework, using both Linearized Augmented Plane Waves (LAPW)[1] and LCAO[2] methods. Structural deformations during intercalation are analysed. The influence of substitution between Mn and Li is also investigated. Diffusion coefficients and hopping paths of the Li^+ within the Mn_2O_4 lattice are calculated from the electrostatic potential barrier.



Mn_2O_4 - crystal

First principles molecular dynamics[3] results are presented; these calculations are applied to compute the diffusion process within the solid and the electrochemical insertion at the interface of the solid.

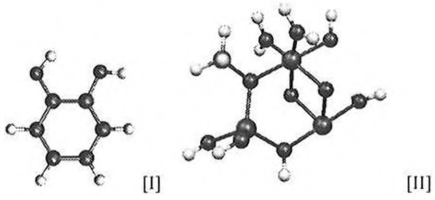
[1] P. Blaha, K. Schwarz, P. Dufek, R. Augustyn, **WIEN95**, TU Vienna, updated version of WIEN-code, P.Blaha *et. al.*, Comput. Phys. Commun. **59**, (1990) 399.
[2] R. Dovesi, V.R. Saunders, C. Roetti, M. Causà, N.M. Harrison, R. Orlando, E. Aprà, **CRYSTAL95**, University of Torino, Torino, 1996.
[3] R. Car, M. Parrinello, Phys. Rev. Lett. **55** (1985), 2471.

Computational Chemistry **124**

THEORETICAL STUDY OF THE ADSORPTION OF METHANOL ON A (110) SURFACE OF γ-ALUMINA

D.A. De Vito [1], J. Weber [1], S. Porchet [2] and A. Renken [2]

[1] Department of Physical Chemistry, University of Geneva, CH-1211 Geneva , Switzerland
[2] Institute of Chemical Engineering, Swiss Federal Institute of Technology, CH-1015 Lausanne, Switzerland



γ-alumina has recently proved to be an efficient catalyst for the gas-phase methylation of catechol [I] by methanol [1]. However the detailed reaction mechanism and the conditions leading to selectivity control are unknown.

We have therefore performed theoretical investigations using both *ab initio* and *DFT* quantum chemical methods of the various steps of this mechanism. In this work we report the first set of results obtained for the modelling of the adsorption of methanol on the (110) surface of γ-alumina. Various cluster models have been used to describe the (110) γ-alumina surface and the mechanism of adsorption of methanol. This has allowed us to rationalise the stable structures of adsorbate and the mode of bonding. The IR frequency shifts between the gas phase and the adsorbed species were also calculated and they exhibit a very good agreement with experiment.

[1] S. Porchet, S. Su, R. Doepper, A. Renken, *Chem. Eng. Technol.* **1994**, 17, pp. 108-111

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Computational chemistry **125**

A Density Functional (DF) Study on the Charge Transfer and Ligand Field Transitions of Cr^{3+} in Fluorides.

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University of Fribourg, Pérolles
CH-1700 Fribourg

Ligand-field and charge transfer (CT) transitions due to octahedral CrF_6^{3-} clusters in fluorides have been investigated with Density Functional theory. DF calculations lead to an equilibrium Cr-F distance as well as to ligand-field transitions in good agreement with experiments. Charge transfer transitions are in general much more intense than ligand-field transitions and they determine thus mainly the polarizability of a transition-metal complex and hence the Raman intensities. We have tried to assign among all the experimental bands the CT transitions. According to the present study the excitation bands of $Na_3In_2Li_3F_{12}:Cr^{3+}$ peaked at 8.0 and 8.7 eV can reasonably be assigned to CT transitions involving $t_{1u}(\alpha)\rightarrow e_g{}^*$ excitations (where $\alpha=\sigma-\pi;\sigma+\pi$) and a spin S' of the 3d subshell for the excited state equal to S'=2. Different ways to take into account the influence of the lattice (Madelung potential) are explored.

Computational chemistry **126**

MD SIMULATION ON MOLECULAR ASSEMBLIES: MONOLAYERS AND BILAYERS BUILT FROM $(BGP)_n$ PHOSPHOLIPIDS

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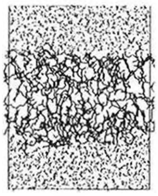
URA 422 CNRS
Institut Lebel 4, rue B. Pascal 67000 Strasbourg

Bis Geranyl Phosphate (BGP) is a small phospholipid anion capable of forming vesicles which can be viewed as mimics of primitive membranes [1]. We have undertaken a series of molecular dynamics on assemblies of BGP, in order to elucidate the stability, structural features, hydration pattern of such arrangements, and the conformation of the BGP units.

The *monolayer* $(BGP^-,Na^+)_{36}$ has been simulated at water/argon interface with (200 ps) and without (100 ps) Ewald sommation. It becomes non planar, highly distorted, with disruption of the assembly. These results are consistent with the lack of observation of monolayers [2].



The *bilayer* $(BGP)_{72}$ has been simulated in water, without counterions ant neutralized units. The BGP displays large conformational fluctuations leading to heterogenous structures of the bilayer.

[1] - G. Ourisson & Y. Nakatani, Chemistry & Biology, (1994), 1, 11-23
[2] - A. Kamino, K. Ariga, T. Kunitake, V. Birault, G. Pozzi, Y. Nakatani & G. Ourisson, Colloids & Sufaces (A), (1995), **103**, 183-194

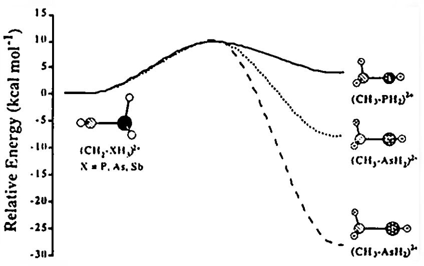
Main Group Computational Chemistry **127**

Ab Initio Study of Superelectrophilic Activation of Pnictogenocarbenium Ions $CH_2XH_2^+$ (X = P, As, Sb)

Christoph Widauer, Grace Chen and Hansjörg Grützmacher*

Laboratory of Inorganic Chemistry, Swiss Federal Institute of Technology,
ETH-Zentrum, CH-8092 Zürich, Switzerland

Superelectrophilic activation is made responsible for the greatly enhanced reactivity of carbenium ions [1]. To investigate the effects of protonation on the monocations $(CH_2\text{-}XH_2)^+$ (X = P, As, Sb), we carried out high level ab initio study of structures and potential energy surfaces of the monocations and their protonated derivatives.



Our results showed that *the dications CH_5X^{2+} are formed exothermically.* The proton affinities increase P < As < Sb for all X atoms. For the methylenephosphonium cation, the P-site protonation is favored over the C-site protonation. On the other hand, the C-site protonation is favored over the X-site protonation for the heavier analogues X = As and Sb.

[1] Recent reviews: (a) G. A. Olah, *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 767. (b) G. A. Olah, *ibid.* **1995**, *34*, 1393. (c) K. Lammertsma, P. v. R. Schleyer, H. Schwarz, *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 1321.

Physical Chemistry **128**

The adsorption of small molecules on TiO_2 anatase (101) by first principles molecular dynamics

A.Selloni[1,2], A. Vittadini[3], M. Grätzel[2]

1 University of Geneva, Switzerland
2 EPFL, Lausanne, Switzerland
3 CSSRCC-CNR, Padova, Italy

TiO_2 is an interesting material for photocatalytic applications [1]. In particular, the (101) surface of the anatase structure has been found to have a stronger activity than rutile (100) in the photoelectrolysis of water [2]. However, for this anatase surface the experimental information is still rather limited, and no theoretical first principles investigation has been so far reported. For this reason, we are carrying out a systematic theoretical study of the chemisorptive properties of anatase (101) using the Car-Parrinello first principles molecular dynamics approach. As a first step, after optimizing the structure of the clean surface, we have studied the interaction of H_2O and H_2S with a five-fold coordinated Ti^{4+} site of the undefected surface. Owing to the formation of hydrogen bonds with the surface bridging oxygens, both molecules are found to prefer non-dissociative with respect to dissociative adsorption. Calculated adsorption energies are ~ 0.8 and ~ 0.6 eV for H_2O and H_2S respectively.

[1] A.L. Linsebigler, G. Lu, J.T. Yates, Jr., Chem. Rev. 95, 735 (1995)
[2] L. Kavan, M. Grätzel, S.E. Gilbert, C. Klemenz and H.J. Scheel, J. Am. Chem. Soc. 118, 6716 (1996)

CHIMIA 51 (1997) Nr. 8/9 (August/September)

Computational Chemistry **129**

A systematic study to explore chemical accuracy in MD simulations

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As much important chemistry occurs in the liquid phase, one goal of theoretical chemists has been to achieve a more accurate description of liquid systems. Recent advances in liquid noble gas molecular dynamic simulations have focused on three key areas - the use of the best possible pair potential, the inclusion of quantum corrections and the accommodation of many body effects.

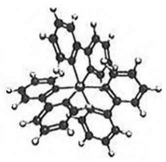
For our purposes neon has been chosen as a test system with a systematic study of the influence of basis set size on ab initio potentials and simulated properties. Quantum corrections have been included by implementing a Wigner-Kirkwood potential, which arises from an asymptotic expansion of the partition function. In addition, the influence of many body effects have been explored by combining the non-additive part of the three-body potential with different pair potentials.

The results of the simulations show that the quality of the pair potential plays a significant role for the energy and pressure and also affects the quality of other derived thermodynamical properties. On the other hand pair potential quality is less critical for determination of the pair distribution function. Deviations between experimental and calculated properties at liquid temperatures lead to the conclusion that quantum effects are always important. Inclusion of three body interactions were found to have a minor influence on the structure and the calculated thermodynamic properties. However upon decreasing the pressure and energy, especially at high densities, one might expect three body interaction of more repulsive nature to become more important.

Computational Chemistry **130**

GEOMETRY OPTIMIZATION AND EXCITED STATES OF TRIS(2,2'-BIPYRIDINE)RUTHENIUM(II) USING DENSITY FUNCTIONAL THEORY

Matthieu Buchs, Claudia Stückl and Claude Daul
Department of Inorganic Chemistry
University of Fribourg, CH-1700 Fribourg, Switzerland



Many investigations have been done for decades on molecules belonging to the family of the tris(2,2'-bipyridine)ruthenium(II). In this work a theoretical approach of the $[Ru(bpy)_3]^{2+}$ complex, using the Density Functional Theory and in particular the Amsterdam density functional (ADF) program package is presented.

The geometry of the $[Ru(bpy)_3]^{2+}$ complex has been optimized using the local density approximation (LDA). The optimization has been made within D_3 symmetry, and we found good agreement with the X-ray structure.

As the photochemical and photophysical data suggest, we see two sets of low-lying empty molecular orbitals. In a first study, we dealt with the first set of levels, which are metal-to-ligand-charge-transfer states (MLCT) and did calculate the positions of these MLCT states as well as the intensities of the transitions[1], using the Generalized Gradient Approximations (GGA). The results obtained are in good agreement with experiment[2].

In a second part, we dealt with the upper set of unoccupied orbital, which are metal centered. We did calculate the energy of the transition corresponding to the lowest Ligand Field state, which has been proposed to be responsible for the photoracemization[3], for the series $[Fe(bpy)_3]^{2+}$, $[Ru(bpy)_3]^{2+}$ and $[Os(bpy)_3]^{2+}$.

[1] : Daul, C.; Schlaepfer, C.W. *J.Chem.Soc.Dalton Trans.* **1988**, 393-400.
[2] : Felix, F.; Ferguson, J.; Güdel, H.U.; Ludi, A. *J.Am.Chem.Soc.* **1980**, 102, 4096
[3] : Van Houten, J.; Watts, R.J. *J.Am.Chem.Soc.* **1976**, 98, 4853-4858.

Computerunterstützte Chemie **131**

Theoretical Investigations of Transition-Metal NMR Chemical Shifts and Reactivities

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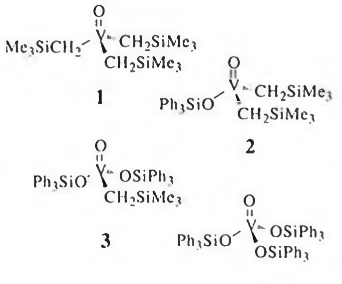
Several correlations between transition-metal NMR chemical shifts and kinetic parameters for insertion or substitution reactions are known empirically [1]. Such correlations can be reproduced and rationalized with modern tools of density-functional theory when substituent effects on the reactivities are associated with energy changes on the potential energy surfaces, for instance in the $[Rh(CO)_2(C_5H_4X)] + PH_3$ model system (X = H, Cl, NMe_2, NO_2) [2a].

A possible relation between ^{51}V chemical shifts and catalytic activities for ethylene polymerization observed with oxo-vanadium(V) species **1** - **4** [3] is investigated computationally for suitable model systems [2b].



1 2 3 4

[1] e.g. M. Koller, W. v. Philipsborn, *Organometallics* **1992**, *11*, 467.
[2] a) M. Bühl, *Organometallics* **1997**, *16*, 261. b) M. Bühl, F. A. Hamprecht, to be published.
[3] M. J. Feher, R. L. Blanski, *Organometallics* **1993**, *12*, 958.

Computational Chemistry **132**

Trans- and *cis*-reactivities in d^6 octahedral ruthenium(II) pentaaqua complexes: experimental and theoretical approaches.

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[2] Département de Chimie Physique, Université de Genève, 30, quai Ernest-Ansermet, CH-1211 Genève 4

The water exchange in the first coordination sphere of d^6 ruthenium(II) $[Ru(H_2O)_5L]^{+2}$ complexes has been studied in order to understand the *trans*- and *cis*-reactivities in dissociative substitution reactions. The effect of the ligand L (L=H_2O, CH_3CN, $(CH_3)_2SO$, CO, N_2, $H_2C{=}CH_2$, $F_2C{=}CF_2$) on the following properties has been investigated: redox potentials, the rate of exchange of the bound water molecules at the axial (or *trans*) and equatorial (*cis*) positions with respect to L by isotopic exchange, and ^{17}O NMR line broadening experiments. As expected, the redox potential, E°, increases with the π-accepting capabilities of the ligand. The increasing *cis*-effect series has been determined as follows: $F_2C{=}CF_2 \cong CO < (CH_3)_2SO < N_2 < H_2C{=}CH_2 < CH_3CN < H_2O$, and the increasing *trans*-effect series as: $N_2 << CH_3CN < H_2O < CO < (CH_3)_2SO < H_2C{=}CH_2 < F_2C{=}CF_2$. The former series can be related to E° values.

Density Functional Theory (DFT) calculations have been performed to derive structural properties, charge distribution and electronic density for the systems with L= H_2O, $H_2C{=}CH_2$, CO and N_2. Metal-ligand bond energies have been calculated, the results show that they correlate well with the experimental kinetic results. In particular, π back-bonding electron transfer to the ligand L can be related with the lability of the *trans* water molecule with respect to ligand L.

CHIMIA 51 (1997) Nr. 8/9 (August/September)

Chimie computationnelle **133**

A theoretical study of the ground-state Jahn-Teller distortion of VCl_4

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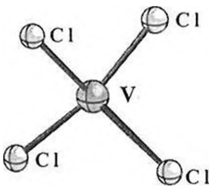
The theoretical foundation of vibronic coupling in the form of Jahn-Teller (JT) distortion as applied to transition metals is well established [1]. VCl_4 has a $3d^1$ electronic configuration with a singly occupied e orbital. Hence the molecule will distort as a consequence of first-order JT effect. Despite the large collection of experimental evidence accumulated, there is still a controversy related to the extent of the vibronic coupling in this molecule.
We propose a recipe by means of density functional calculations for deriving the JT parameters (which determine the distortion), based on a full total energy relaxation along the path of minimal energy. This method is compared with an exploration of the adiabatic energy surface along the JT active mode. The two approaches are shown to agree very well. The results thus obtained are further used to investigate some molecular properties e.g. EPR and IR spectra, so a direct correlation with experiment can be made.



[1] Bersuker, I. B. *The Jahn-Teller effect and Vibronic Interactions in Modern Chemistry*, Plenum Press, London, 1984.

Physical Chemistry **134**

Atomic and electronic structure of Cu clusters on MgO

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[1] IRRMA, CH-1015 Lausanne
[2] Department of Condensed Matter Physics, University of Geneva, CH-1211 Geneva
[3] Department of Physical Chemistry, University of Geneva, CH-1211 Geneva

The interaction of metallic clusters with supporting metal-oxide surfaces has important implications in the fields of thin film growth and catalysis. In this work, the structural and electronic properties of Cu_n ($n = 1, 13$) aggregates on defect-free MgO(100) are studied using density functional calculations. The preferred adsorption site for a single Cu atom is on top of an oxygen atom. Using the Perdew-Wang exchange correlation functional we find an adsorption energy of ~ 23 kcal/mol and an adsorption distance of about 2 Å. Well defined Cu-surface bonding states show up at the bottom of the oxygen $2p$ band. The diffusion barrier is ~ 0.45 eV, suggesting a diffusion temperature threshold of 180 ± 20 K.
The adsorption energy per Cu atom decreases with increasing the size of the cluster, while the Cu-Cu cohesive energy increases, rapidly becoming more important than the adsorption energy. For $n > 4$ three-dimensional geometries are preferred to planar ones. This is consistent with the observed Stranski-Krastanov growth mode.

Computational Chemistry **135**

Determination of the melting curves of argon and neon from pure theory

Jan Solca, Anthony Dyson, and Hanspeter Huber
Institut für Physikalische Chemie der Universität Basel

Molecular dynamics simulation provides a means by which the microscopic details of certain macroscopic processes can be investigated. We employ pair potentials constructed from accurate first principles quantum chemical calculations in our simulations [1-3], and are thus able to calculate various system properties without the use of any empirically determined data. This method has already produced good results for a number of structural and thermodynamic properties of both argon and neon [3-5]. We now report the calculation of the melting curves of these species.

Melting is simulated by application of a constant temperature gradient over the course of the MD run. Simulations performed commencing with a perfect fcc crystal structure indicate the limit of mechanical stability of the crystal, which is typically somewhat higher than the actual melting point. To determine the observed melting point, we perform simulations at constant pressure (NPH ensemble), and commence with a crystal containing a cluster of vacancy defects. The resulting melting curves are in very good agreement with experimental measurements.

[1] D. E. Woon, *Chem. Phys. Lett.* 204 (1993) 29.
[2] R. Eggenberger, S. Gerber, H. Huber, and D. Searles, *Chem. Phys.* 156 (1991) 395.
[3] R. Eggenberger, S. Gerber, H. Huber, and M. Welker, *Mol. Phys.* 82 (1994) 689.
[4] E. Ermakova, J. Solca, H. Huber, and M. Welker, *J. Chem. Phys.* 102 (1995) 4942.
[5] E. Ermakova, J. Solca, H. Huber, and D. Marx, *Chem. Phys. Lett.* 246 (1995) 204.

Computational chemistry **136**

Quantum Chemistry Based Set of Additive Contributions to Conversion Energies of All Geometric Isomers and Tautomers of the Nucleic Acid Bases Cytosyne, Isocytosyne, Uracyl, Thymine, Adenine, Xanthine and Guanine

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From quantum-chemical computations at the HF/6-31G(d,p), point-wise MP2/HF/6-31G(d,p) and MP2/6-31G(d,p) levels of all isomers of the nucleic acid bases listed in the title, a system of additive contributions to the electronic conversion energies of geometric isomers (conformers) has been derived. The contributions are perceptible directly from the structural formula as repulsive (attractive) interactions between H-atoms of OH-, NH- and NH2-substituents and H-atoms bound to adjacent ring atoms(lone pair electrons localized at N-atoms of substituents and ring system). The energy increments seem to apply rather generally to related compounds and allow to reproduce conversion energies within 0.5 kcal/mol. They may serve to estimate energies of conversion of tautomers corresponding to shifts of H-atoms bound to N-atoms of either 6- or 5-membered rings. Repulsive and attractive interactions express themselves in other properties, e.g. in electric field gradients at N nuclei of substituents and ring system, structural relaxation associated with conformer conversion and electric dipole moments [1-4].

[1] T.-K. Ha and H.H. Günthard, J. Molec. Struct. 276(1996)209.
[2] T.-K. Ha and H.H. Günthard, J. Molec. Struct. 300(1993)619.
[3] T.-K. Ha and H.H. Günthard, J. Am. Chem. Soc. 115(1993)11939.
[4] T.-K. Ha, H.-J. Keller, R. Gunde and H.H. Günthard, J. Molec. Struct. 364(1996)161; 376(1996)375.

Computational Chemistry **137**

Theoretical Parameters as Tools to Characterize Antioxidants

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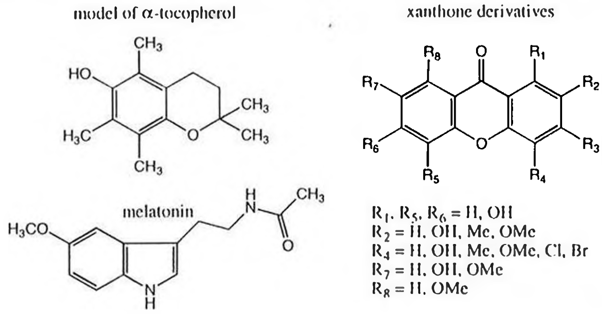
Many human diseases are associated with free radical damage. Successful antioxidant therapy requires a good understanding of the molecular mechanisms of action of antioxidants. Thus the objectives of this work were a) to evaluate quantum mechanical descriptors characterizing antioxidant activities, and b) to obtain information on the molecular mechanisms underlying the antioxidant effects of tocopherol analogs, xanthones and melatonin. In this study AM1 calculations were performed on compounds for which experimental antioxidant activities were available in the literature. The results were further validated by *ab initio* (3-21G) calculations on a subset of compounds. The quantum chemical descriptors considered here (HOMO, ΔH_{ox} and ΔH_{abs}) were fairly well correlated with experimental antioxidant activities. Moreover, these theoretical parameters suggest that vitamin E analogs could act by a dual mechanism involving single-electron transfer (SET) and direct H-atom abstraction, whereas xanthones could act by a direct H-atom abstraction and melatonin by SET.



R_1, R_5, R_6 = H, OH
R_2 = H, OH, Me, OMe
R_4 = H, OH, Me, OMe, Cl, Br
R_7 = H, OH, OMe
R_8 = H, OMe

Organic Chemistry **138**

Synthesis, characterization and mesomorphic properties of ferrocenyl dendrimers

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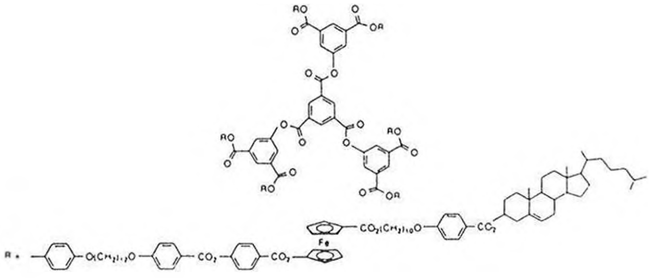
Institut de Chimie, Université de Neuchatel, avenue de Bellevaux 51
2000 Neuchatel

Ferrocenyl functionalyzed dendrimers are interesting as redox-active, thermotropic materials.

The synthesis and properties of the G1 dendrimer (shown below), composed of a phenyl-1,3,5-(carboxyphenyl) core and six ferrocene units exhibited an enantiotropic Smectic A phase and a good thermal stability.



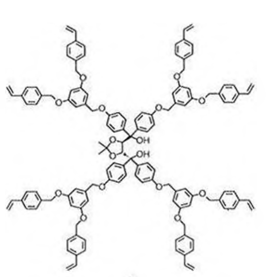
Chem. Commun., R. Deschenaux, E. Serrano and A-M. Levelut, in press.

Organic Chemistry **139**

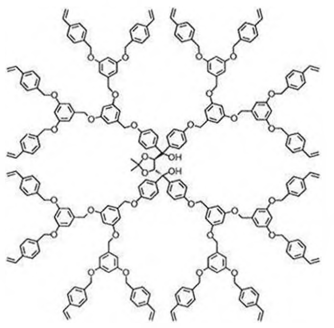
Polymer Bound Chiral Dendrimers in Heterogeneous Catalysis

Holger Sellner, P. Beat Rheiner and Dieter Seebach

Laboratorium für Organische Chemie, Eidgenössische Technische Hochschule, ETH-Zentrum, Universitätstrasse 16, CH-8092 Zürich



1
$C_{131}H_{118}O_{16}$
MG = 1948 Da



2
$C_{259}H_{230}O_{32}$
MG = 3855 Da

Polymer bound α,α,α′,α′-tetraaryl-dioxolane-dimethanols (TADDOLs) have been prepared in our group and tested as chiral *Lewis* acid catalysts [1]. In a new approach we have now synthesized chiral dendrimers **1** (of 1st generation) and **2** (of 2nd generation), which were copolymerized as crosslinkers with styrene. The dendritic spacers, which in homogeneous catalysis have virtually no influence on reaction selectivity, should make the enclosed TADDOL moieties more readily accessible in an analogous heterogeneous system.

[1] D. Seebach, R. E. Marti, T. Hintermann, *Helv. Chim. Acta* **1996**, *79*, 1710.

Organic Chemistry **140**

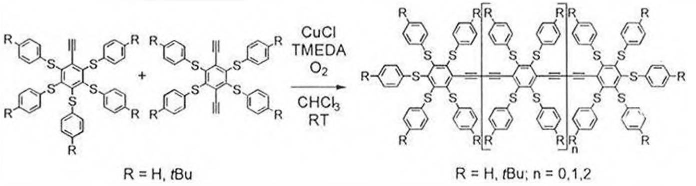
Molecular Rods Based on Diacetylene Linked Polythiophenyl Substituted Benzenes

Marcel Mayor, Jean-Marie Lehn,[a] Katharina M. Fromm and Dieter Fenske[b]

[a]Laboratoire de Chimie Supramoléculaire, Institut Le Bel, Université Louis Pasteur, 4 rue Blaise Pascal, F-67000 Strasbourg; [b]Institut für Anorganische Chemie der Universität Karlsruhe, Engerstrasse 30.45, D-76128 Karlsruhe.

Polythiophenyl substituted aromatic systems were shown to be easily reducible [1] and are therefore potential building blocks for reducible nanoscale molecular structures. In addition, they display favorable properties regarding stability, solubility and accessibility. Herein we describe the synthesis and physical properties of diacetylene-linked polythiophenyl substituted benzene derivatives as a new type of reducible molecular rods.

The building blocks were synthesized by nucleophilic aromatic substitution of halogenated benzaldehydes with sodium thiophenolates. The aldehydes were converted to dibromoolefins, and subsequently to acetylenes. *Hay* or *Glaser* coupling (Fig.) led to the desired molecular rods, which were isolated by size exclusion chromatography.



Electrochemical studies on the molecular rods display a one electron reduction per polythiophenyl substituted benzene subunit and a pronounced trend towards more positive reduction potentials with increasing molecular length.
Conformational information in the solid state was obtained by X-ray analysis of the thiophenylsubstituted dimeric compound (R=H, n=0).
Current investigations are directed towards longer rods and cyclic structures.

[1] J.H.R.Tucker, M. Gingras, H. Brand, J.-M. Lehn, *J.Chem.Soc., Perkin. Trans. 2*, in press.

Synthesis of New C_2-Symmetric Chiral Hexacoordinated Phosphates **141**

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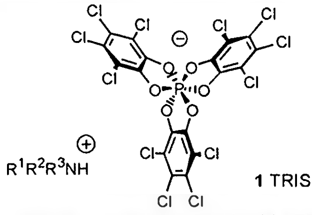
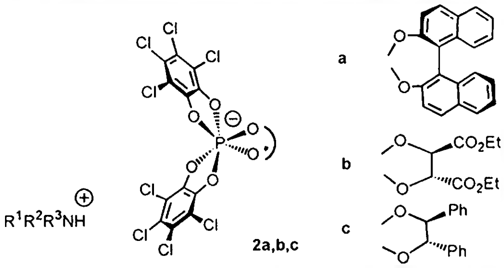
Département de Chimie Organique, Université de Genève, CH-1211 Genève

Enantiopure anions could be used in several fields of chemistry involving chiral or prochiral cationic species. Following the synthesis of enantiomerically pure tris(tetrachlorobenzenediolato)phosphate **1** (or TRISPHAT) in our laboratory, [1] we have developed a new class of chiral hexacoordinated C_2-symmetric phosphates **2a,b,c** containing one chiral ligand along with two tetrachlorocatecholates.



1 TRISPHAT

We hoped that the chirality on the ligand could control the chirality on the phosphorus and that has proven to be the case, since we obtained the desired phosphates as single diastereomers. Using enantiomerically pure chiral ligands, we were thus able to obtain enantiomerically pure phosphates.



2a,b,c

[1] J. Lacour, C. Ginglinger, C. Grivet, G. Bernardinelli, *Angew. Chem.* **1997**, *109*, 660; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 608.

Highly Diastereoselective Interactions of TRISPHAT Anion and Transition Metal Complexes. **142**

J. Lacour, S. Torche-Haldimann and C. Ginglinger

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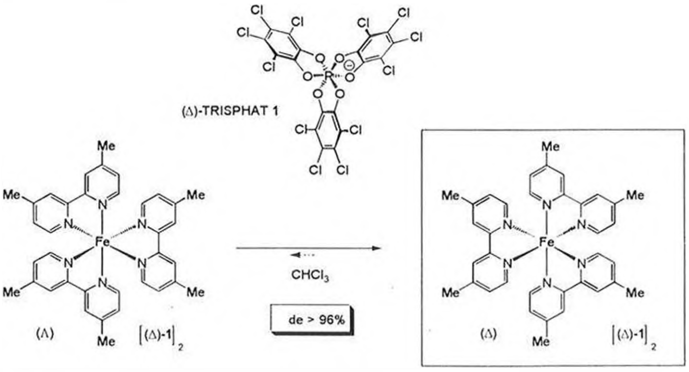
We have recently shown that easily synthesized and resolved tris(tetrachlorobenzenediolato)phosphate anion **1** (or TRISPHAT) is configurationally stable. This anion is a valuable substrate for molecular recognition studies on chiral discriminations between molecular propellers. Results of our investigations on the preferred mode of association of chiral helical cations and anion **1** (Δ^+-Δ^- *vs.* Λ^+-Δ^-), as well as the selectivity resulting from it, will be presented. For instance, the discriminating interactions that occur between enantiopure **1** and a configurationally labile tris(bisimine)-iron(II) complex lead to a highly diastereoselective transfer of chirality from the anion onto the cation (de > 96%). In this and other examples, the observed selectivity is due to a preferred homochiral Δ^+-Δ^- association between the molecular propellers, rather than a "mismatched" heterochiral (Δ^+-Λ^-) one. A model for this preferred association between the molecules will be detailed.



Organische Chemie **143**

Oligomere Viologene mit Dendrimerarchitektur

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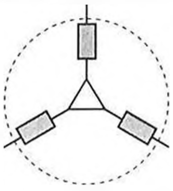
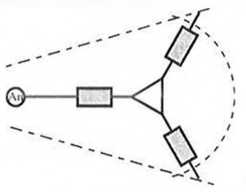
Institut für Chemie, Universität Osnabrück, D-49069 Osnabrück

Ausgehend von trifunktionellen Verzweigungskernen wie 1,3,5-Tris(brommethyl)benzol oder Trimesinsäure-trichlorid und 4,4'-Bipyridin bzw. funktionalisierten N,N'-Diaminoalkyl-4,4'-bipyridinium Salzen sind Dendrimere des allgemeinen Typs A zugänglich.



Durch Monofunktionalisierung des primären Verzweigungskerns mit -PO_3H_2 bzw. -SH lassen sich kegelförmige Arborole mit einer Elektrodenhaftgruppe (An) für Titandioxid oder Gold darstellen.



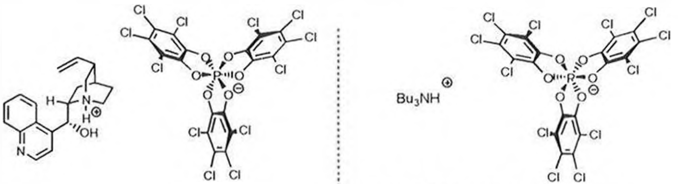
Mittels elektrochemischer, spektroelektrochemischer und EQCM-Methoden wurden entsprechend derivatisierte Elektroden untersucht.

Enhanced Resolution of Chiral TRISPHAT Anion. Application to the Purification of Organic Cations. **144**

C. Ginglinger, S. Barchéchath and J. Lacour

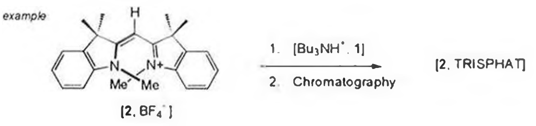
Département de Chimie Organique, Université de Genève, CH-1211 Genève

Ion pairing is an essential feature in chemistry.[1] The nature of the anion associated with a cation can dramatically accelerate a reaction or even change its course. We have, therefore, been looking for anions that would confer new properties to ion pairs (IP). Easily prepared chiral tris(tetrachlorobenzenediolato)phosphate anion **1** (or TRISPHAT) is configurationally stable.[2] Herein, we report an enhanced resolution procedure of tributylammonium TRISPHAT salt using 0.5 equiv. of cinchonidine, which leads to two enantioenriched salts **1A** and **1B** (83% ee).



1A. Cinchonidinium-*(P)*-1 (recr. > 96%) 1B. Bu_3NH^+-*(M)*-1 (ee 83 %, recr. 86%)

Common anions can be easily replaced by **1**. Simple chromatography (SiO_2, CH_2Cl_2) of organic salts with 1 equiv. of **1B** leads to the isolation of a new IP in good to excellent yieds.



[1] A. Loupy, B. Tchoubar, D. Astruc, *Chem. Rev.* **1992**, *92*, 1141.
[2] J. Lacour, C. Ginglinger, C. Grivet, G. Bernardinelli, *Angew. Chem.* **1997**, *109*, 660; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 608.

Organic Chemistry **145**

Dihydrooxepines as oxidation products of carotenoids

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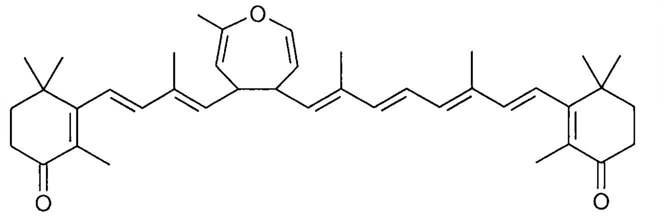
Departement für Chemie und Biochemie, Freiestrasse 3, 3012 Bern, Switzerland

A dihydrooxepine of canthaxanthin (1) was isolated from a reaction between canthaxanthin and MCPBA (m-chloroperbenzoic acid). Its structure was determined by UV/Vis, LC/MS and one and two dimensional 500 MHz NMR analysis. The same substructure was observed in thermal oxidation of β,β-carotene.

Comparing the data from literature, it must be concluded that dihydrooxepines as oxidation products have previously been isolated although a wrong structure was proposed.



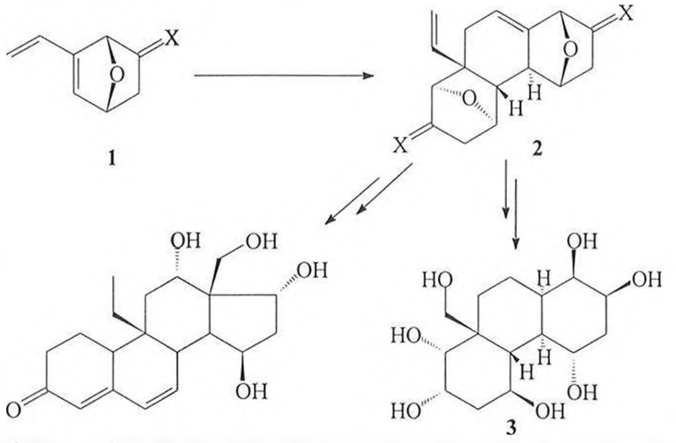
Chimie Organique **146**

Dimérisation de diènes semicycliques: étude et application à la synthèse de stéroïdes et de perhydrophénanthrènes polyhydroxylés.

Hervé Mosimann, Lieven Meerpoel, Maria-Miranda Vrahami, Pierre Vogel.

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

Une synthèse efficace de diènes semicycliques de type **1** diversement substitués en C(2) a été développée. Ces diènes subissent une dimérisation spontanée par cycloaddition selon Diels-Alder stéréospécifique pour fournir des dimères de type **2** [1]. Ceux-ci ont été utilisés pour la synthèse de polyhydroxy octahydro- et perhydrophénanthrènes (**3**) ainsi que comme point de départ d'une nouvelle voie d'accès aux stéroïdes.



[1] Meerpoel, L.; Vrahami, M.-M.; Ancerewicz, J.; Vogel, P.; *Tetrahedron Lett.* **1994**, *35*, 111-114.

[2] Mosimann, H.; Vogel, P., Pinkerton, A. A., Kirschbaum, K., *J. Org. Chem.*, *in press*.

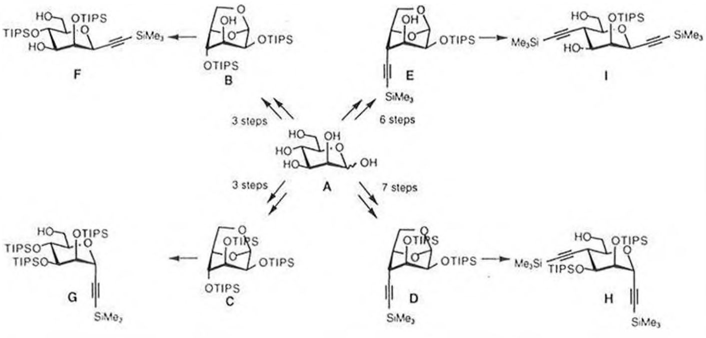
Organic Chemistry **147**

Diastereoselective Synthesis of α- and β-D-Mannopyranosyl Acetylenes

Jürgen Stichler-Bonaparte and Andrea Vasella

Laboratorium für Organische Chemie
Eidgenössische Technische Hochschule Zürich

The α- and β-configurated D-mannopyranosyl acetylenes **F**-**I** were synthesized from D-mannose **A**. Key step of the syntheses was the alkynylating cleavage of the acetals **B**-**E** by the reaction with lithium trimethylsilyl acetylide in the presence of aluminum trichloride. The diastereoselectivity depended on whether O-C(3) of the anhydroderivatives was protected or not: conversion of acetals **B** and **E** with a free hydroxyl group on C(3) yielded exclusively the β-D-anomers of **F** and **I**, respectively. When O-C(3) was protected by a triisopropyl silyl group (acetals **C** and **D**), the α-D-anomer predominated in the formation of **H** (α:β = 17:1), and was exclusively obtained in the preparation of **G**.



New cyclodextrin analogues were synthesized from the dialkyne **H**.

Organic Chemistry **148**

^{17}O-NMR Spectroscopy as a Useful Approach for Determination of the Structure of O-Containing Organosulfur Compounds

Frédéric Monnat, Elena Roversi and Pierre Vogel*

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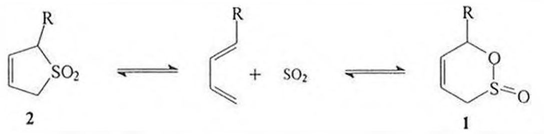
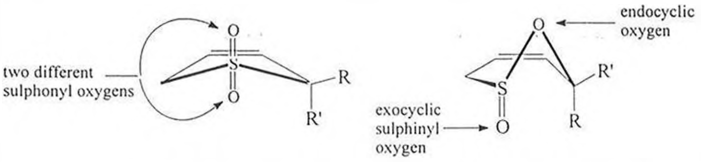
Sulfur dioxide can undergo hetero Diels-Alder or cheletropic reactions with conjugated dienes furnishing sultines **1** or sulfolenes **2**[1] respectively.



During our studies designed to explore the reactivity of conjugated dienes toward sulfur dioxide, difficulties in definitive attribution of the isolated cycloadducts were encountered. As ^{13}C and ^{1}H-NMR experiments yielded ambiguous information, ^{17}O NMR spectroscopy appeared to be a good method to distinguish between compounds containing a R(SO$_2$)R' moiety. Indeed, sulphonyl and sulphinyl oxygens are known to have different resonance frequencies.[2] Sultines **1** and sulfolenes **2** can therefore be differentiated on the basis of chemical shift data of the corresponding signals.



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Organic Chemistry **149**

ortho-Hydroxy-α-Alkylbenzylamines as Building Blocks for New Chiral Benzoxazine Ligands

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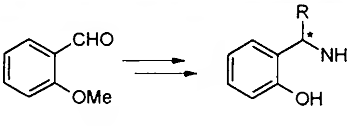
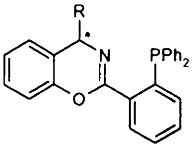
1,2-aminoalcohols are extensively used as building blocks for ligands which, in turn, are applied successfully in enantioselective catalysis [1]. In contrast, 1,3-aminoalcohol derivatives have received little attention in this field [2].



R = *i*-Pr, *t*-Bu

1a **1b**

We here report the synthesis of the new aminophenols **1**, including optical resolution and determination of the absolute configuration, and on their conversion into the chiral diphenylphosphinoaryl benzoxazine ligands **2** and the C_2-symmetric bis-benzoxazine ligands **3**. First results of applications of the two ligands in enantioselective catalysis will be presented.



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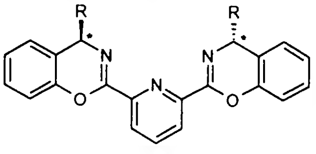

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WITHDRAWN

Organic Chemistry **151**

Radical Rearrangements of Bicyclic Ketones and Alcohols: Synthetic Applications

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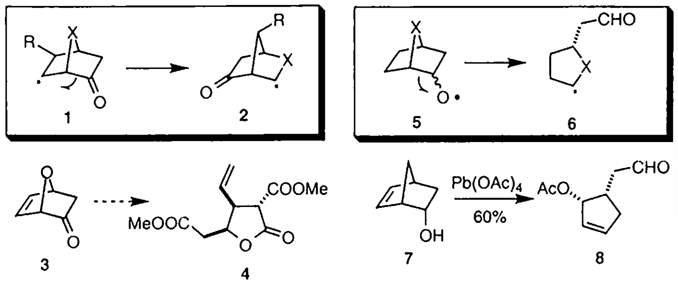
Bicyclo- and 7-oxabicyclo[2.2.1]heptane derivatives are easily obtained in optically pure form by cycloadditions reactions. Their use for the synthesis of biologically active molecules is well established. In this account, we report our efforts in finding new transformations of bicyclic systems by taking advantage of radical rearrangements. The first strategy uses a 1,2-acyl migration (**1** → **2**) [1] and it allows to prepare highly functionalized γ-butyrolactones such as **4** from 7-oxabicyclo[2.2.1]hept-5-ene-2-one **3**. The second rearrangement is the ring opening of bicyclic alcohols via oxy radicals (**5** → **6**). This is achieved by treatment of the free alcohol with lead tetraacetate, see for example the regio- and stereoselective conversion of **7** into **8**.



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Organic Chemistry **152**

Platinum Catalyzed Addition of Alkylsilane to Divinyl Compounds

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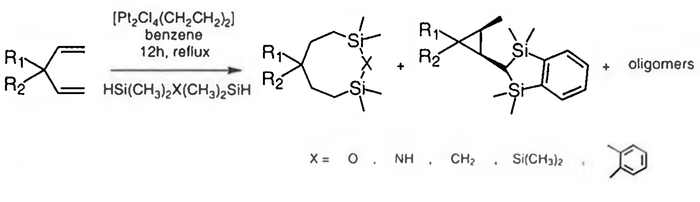
Hydrosilylation continues to be much studied and reviewed. The role of transition metal catalysts represents a key aspect of these studies[1,2]. The results of such investigations have revealed that product distributions vary considerably with the nature of the olefin, the silane structure, the catalyst and the specific reaction conditions.

Herein we report a study of the hydrosilylation reaction of divinyl compounds with various types of silanes and different transition metal complexes.

We have studied different disilanes[3] and found that selectivity depends very much on the spacer between the silicon atoms.



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Organic Chemistry **153**

SCH 21562, 6'-N-Ethyl-netilmicin
A new two step synthesis from Netilmicin

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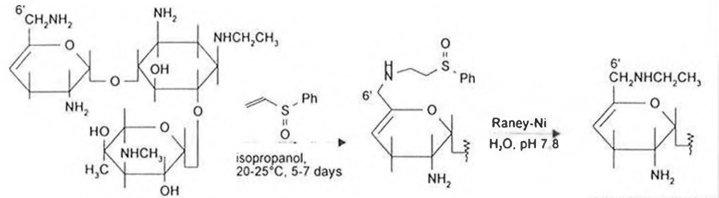
2) Schering Plough Research Institute, Union, N.J.,USA

In order to support marketing of the new antibiotic isepamicin, a test kit to determine the resistance against aminoglycoside antibiotics in bacteria was developed. To prepare these test kits - containing twelve specially selected aminoglycosides - 100 g of 6'-N-ethyl-netilmicin were needed. The existing 5 step synthesis was not applicable to prepare this amount. Therefore a new two step synthesis, applicable on multi gram scale, was developed.
Netilmicin was treated with phenyl vinyl sulfoxide in isopropanol to give 6'-N-phenylsulfinyl-netilmicin, which was converted to 6'-N-ethyl-netilmicin by Raney Nickel reduction in an overall yield of 30% on 100 g scale.



netilmicin

6'-N-ethyl-netilmicin

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Organic Chemistry **154**

Diastereoselective Propargylation/Allylation/Pauson-Khand-Cyclization of a Planar Chiral Anisol $Cr(CO)_3$ Complex

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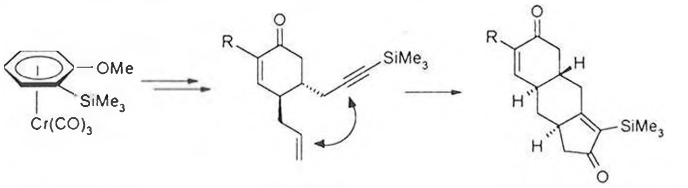
We here report on a new asymmetric transformation of arenes into highly enantioenriched *trans*-fused alicyclic molecules. Key steps are the enantioselective lithiation of [(anisol)$Cr(CO)_3$] [1], the highly diastereoselective sequential nucleophile/ electrophile addition developed previously in this laboratory[2][3], and a Pauson-Khand cyclization. Depending on the conditions, hydrolysis of the enolether can be effected with or without cleavage of the trimethylsilyl carbon bond to give either **2** or **4**. Both can be cyclized to afford the tricyclic products **3** or **5** in a highly diastereoselective process.



(+)-1 (90% ee)

2 (R=SiMe$_3$) or 4 (R=H)

(+)-3 (90% ee, R=SiMe$_3$) or (+)-5 (R=H)

Further developments and applications of this methodology will be presented.

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Organic chemistry **155**

Rh(II)-CATALYSED AZIRIDINATION WITH ((*N*-NOSYL)IMINO)PHENYLIODINANE

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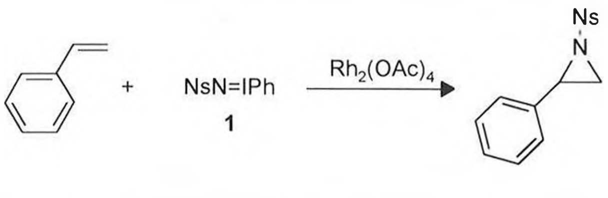
University of Geneva, CH-1211 Geneva 4, Switzerland

Olefins are aziridinated upon $[Rh_2(OAc)_4]$-catalysed decomposition of ((*N*-nosyl)imino)phenyliodinane **1**. Reaction conditions were optimized for styrene and substituted derivatives. Aziridines were isolated in yields of up to 85% [1]. The reaction is applicable to mono- and di-substituted olefins, although in some cases yields are reduced and secondary products derived from further reactions of the initially formed aziridines, may occur. 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 [2].



In presence of chiral Rh(II)-based pyrrolidone carboxylate complexes, good yields but poor enantioselectivities were observed. However, aziridination with Pirrung's bisnaphtholphosphate catalyst $[Rh_2(R\text{-bnp})_4]$ proceeded in high yields and enantioselectivities of up to 73% [2].

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Organic Chemistry **156**

Enantioselective hydrogenation of α,β–unsaturated carboxylic acids over Pd/Al_2O_3

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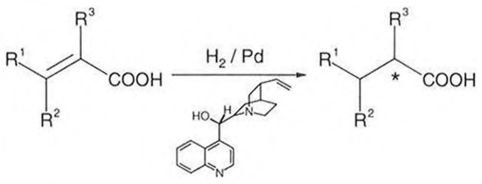
The enantioselective hydrogenation of a family of α,β–unsaturated carboxylic acids was studied over Pd/alumina modified with cinchona alkaloids and their simple derivatives.



R^1,R^2,R^3: H, methyl, ethyl, propyl or phenyl

The preliminary study of the hydrogenation of 2–methyl–2–pentenoic acid revealed that high hydrogen pressure (≥60bar), inducing high hydrogen surface concentration, favours the enantioselection [1].
We report here the synthesis and enantioselective hydrogenation of various alkyl – and aryl–substituted propenoic acids aiming at revealing the structure of the activated complex on the Pd surface.
Further information concerning the nature of the enantiodifferentiating reactant – modifier interaction are obtained by FTIR studies, molecular modelling (molecular mechanics calculations), and catalytic experiments performed with cinchona alkaloids and their simple derivatives.

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Organic Chemistry **157**

Towards the Catalytic Enantioselective Synthesis of Macrolactones

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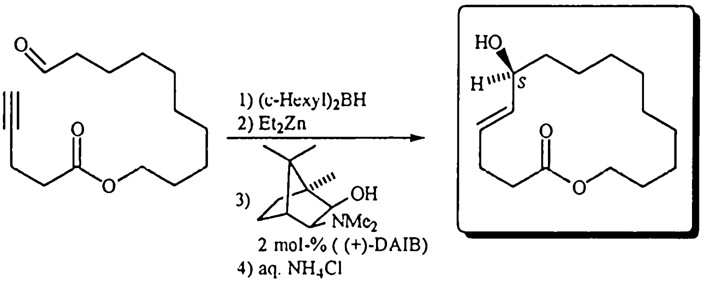
University of Geneva, CH-1211 Geneva 4, Switzerland

Macrolactones are important natural products (e.g. (-)-macrolactin A [1], scytophycin C [2], epothilone A [3], etc.). An efficient synthesis of (+)-aspicilin which made use of a (+)-DAIB catalysed enantioselctive macrocyclization protocol was reported from this laboratory [4]. In this communication we report on the extension of this methodology to a number of other macrolactones.



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† Deceased 15.03.96

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Organic Chemistry **158**

Natural Product Synthesis with Chiral Selenium Electrophiles

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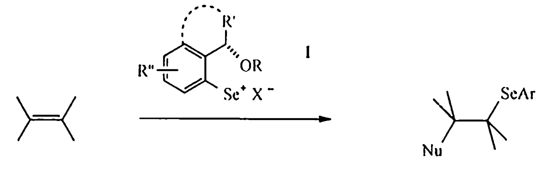
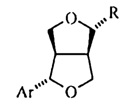
Chiral organic selenium electrophiles 1 are versatile compounds for the stereospecific functionalization of non-activated C=C double bonds. The presence of the selenium moiety in the products enables a variety of subsequent reactions.



We were able to apply this reaction in the synthesis of different natural products. Samin and membrin, two naturally occurring lignans with furofuran skeletons 2 were synthesized *via* a sequence of addition and radical cyclization. Access to isoquinoline alkaloids such as salsolidine 3, was achieved by cyclisation of ε-unsaturated carbamates.



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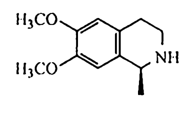

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Organische Chemie **159**

Structure and Reactivity of Chiral Dilithiocarbanions

by R. Batra, J. F. K. Müller*, M. Neuburger and M. Zehnder

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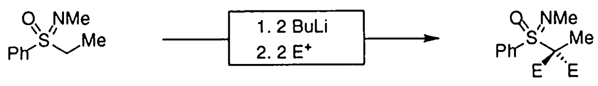
Heteroatom-stabilized dilithiocompounds are known to act as dinucleophiles in multiple C-C bond formation reactions or as supernucleophiles upon reaction with poor electrophiles [1]. The expectation that a chiral modification of such dimetallated compounds would lead to reagents which are able to undergo multiple C-C bond formations in a stereoselective manner has not yet been proven. In order to do so, we chose the sulfonimidoyl group, the chiral aza-analogue of a sulfone, as a configuratively stable chiral functional group, with the intention of preparing such a dilithio species. Another important aspect stems from the potential attenuation of chirality in the reaction of such chiral substituted dianions with prochiral biselectrophiles. We report now about the structure determination of these (di)lithiated sulfoximines [2], their reactions



with simple biselectrophiles and addition reactions with (bis)carbonyl compounds [3].

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Organic Chemistry **160**

N-Benzoylketene-*N*-cyclohexenyl-*N*,*O*-silyl acetals: Aza-Claisen rearrangement and more

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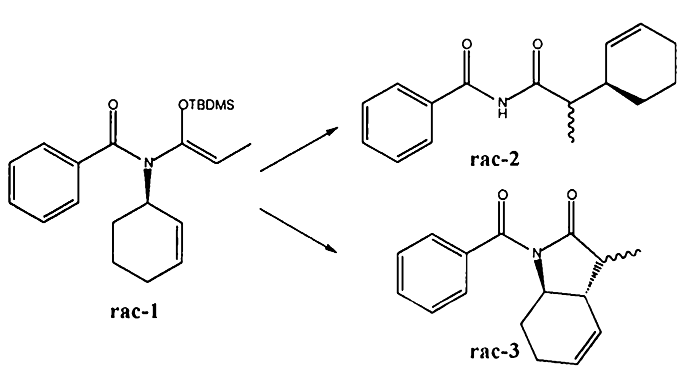
In the context of our studies of tandem reactions of N,O-silyl acetals [1] we are interested to investigate the scope and limitations of the title compound 1 to undergo an Aza-Claisen rearrangement. We intend to incorporate this reaction into a novel tandem Diels-Alder / Aza-Claisen rearrangement prozess.

Controlled by reaction conditions [2] and substituents are formed either the rearranged product 2 or with high diastereoselectivity product 3.



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Organic Chemistry **161**

Intramolecular Cyclization Reactions with Planar Chiral Arene Tricarbonylchromium Complexes

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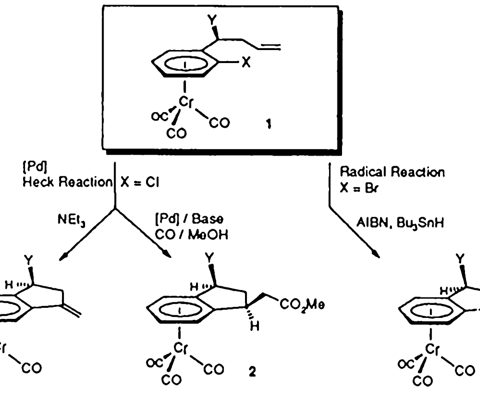
Intramolecular C-C bond forming reactions between arenes and alkenes have found widespread use in the preparation of fused aromatic compounds. We here report the results of a study of the application of the intramolecular Heck reaction [1] and of aryl radical cyclization reactions [2] with planar chiral tricarbonyl chromium complexes **1**.

First successful examples of the two cyclization reactions are shown. A rationale for the observed high diastereoselectivity (>95 % de) in the formation of **2** will be presented.



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Organic Chemistry **163**

A Simple Access to Diiron Allen Complexes

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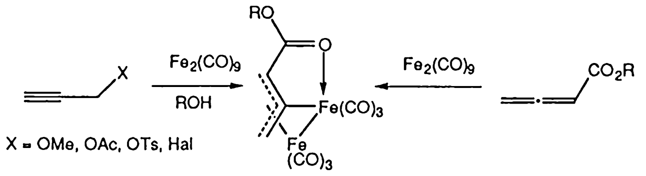
CH-1700 Fribourg

Complexation of allenes with $Fe_2(CO)_9$ leads to well known dinuclear complexes [1][2]. These complexes, however, are accompanied by mixtures of dinuclear complexes of dimerized allenes which leads to only moderate yields of the desired complexes. We found now that reaction of propargyl ethers, esters etc. with $Fe_2(CO)_9$ in alcohol solvents directly forms these complexes in good yield.



Complexation of methyl propargyl ether with $Fe_2(CO)_9$ in non-alcoholic solvents leads to the same complex ($R=CH_3$) but in reduced yield.

Interception of the intermediate derived from methyl propargyl ether by added alcohol is very efficient: a tenfold excess of menthol leads to the corresponding complexed menthyl ester exclusively.

No optical induction was observed in the latter case.

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Organic Chemistry **162**

C_2-5,7-Dimethyl-6,7-dihydro-5H-dibenzo[c,e]azepine from *o*-methoxy-phenyl-ethylamine

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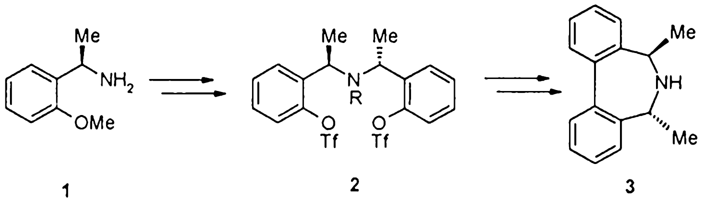
C_2-Symmetric amines play an important role in stereoselctive reactions either as auxilliaries or ligands for catalytic reactions [1]. Chiral dibenz[c,e] azepines have been synthesized with axial chirality [2] and only recently with stereogenic centers alpha to the nitrogen atom in the case of the dinaphthyl analogue [3]. We here present an asymmetric synthesis of the C_2-dibenzo[c,e]azepine **3** from the methoxy phenethylamine **1**. The key step of this synthesis is the intramolecular biaryl coupling of the bis triflate **2**.



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Organic Chemistry **164**

An Asymmetric Version of the Stork Radical Cyclization

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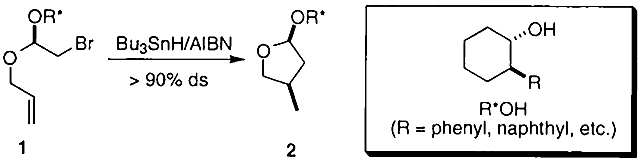
Radical cyclization is of haloacetals1 is a well established and efficient procedure for the preparation of cyclic acetals.[1] Many applications of this reaction in natural product synthesis have been reported. In this account, we describe the preparation of chiral haloacetals of type **1** and and their highly stereoselective cyclization reactions (**1** → **2**). The chiral auxilary R*OH are recoverd by simple hydrolysis of the products.



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Organic Chemistry **165**

A New Reactor for Polymer Bound TADDOL-Mediated Transformations.

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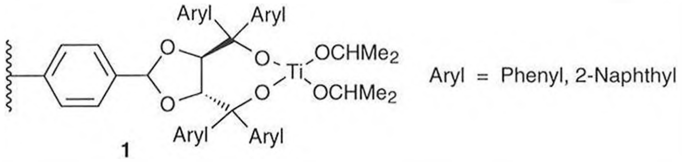
Earlier work in this group has demonstrated the preparation and application of polymer bound α,α,α',α'-tetraaryl-1,3-dioxolane-4,5-dimethanols (pb-TADDOLs, *e.g.* **1**)[1] which give reaction yields and enantiomer ratios comparable with the usual, soluble TADDOLs [2]. However, after several uses, the polymer itself is typically degraded due to the constant stirring required.

Here we describe the use of a new apparatus in which the polymer bound TADDOL is contained within a polypropylene "tea-bag". Such "tea-bags" can be successfully used many times (at least 20) with no noticeable depreciation of the polymer surface! Moreover the apparatus design allows for washing of the polymer such that the pb-TADDOL-titanate (once prepared) can be continuously used without need to quench and re-prepare the titanate between each reaction.



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[1] D. Seebach, R.E. Marti and T. Hintermann, *Helv. Chim. Acta* **1996**, *79*, 1710.

[2] For examples see: D. Seebach, D.A. Plattner, A.K. Beck, Y.-M. Wang, D. Hunziker, W. Petter, *Helv. Chim. Acta* **1992**, *75*, 2171; D. Seebach, A.K. Beck, B. Schmidt, Y.- M. Wang, *Tetrahedron* **1994**, *50*, 4363; D. Seebach, R. Dahinden, R.E. Marti, A.K. Beck, D.A. Plattner, F.N.M. Kühnle, *J. Org. Chem.* **1995**, *60*, 1788.

Organic Chemistry **166**

Selective epoxidation of *(E)*-2-hexen-1-ol over a titania-silica aerogel

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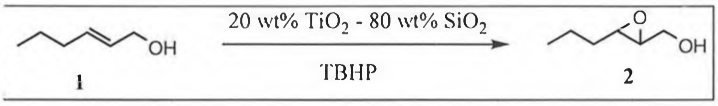
The best solid epoxidation catalysts are based on Ti and Si, including titania-on-silica, titania-silica mixed oxides and Ti-substituted molecular sieves. Most of the earlier studies described the oxidation of simple olefins, such as 1-hexene and cyclohexene. Selective epoxidation of functionalized olefins is more demanding due to competitive redox and acid-catalyzed reactions (e.g. allylic alcohols), and to the low electron density of the C=C bond (e.g. isophorone). Here we report that a titania-silica aerogel, synthesized by a sol-gel process followed by semicontinuous extraction with supercritical CO_2, can provide excellent reaction rates and epoxide selectivities in the oxidation of *(E)*-2-hexen-1-ol.



The titania-silica aerogel possessed an amorphous mesoporous structure with an average pore diameter of 9 nm and 680 m^2g^{-1} BET surface area. FTIR and UV spectroscopic analysis indicated a high dispersion of Ti in the silica matrix.

TBHP was used as oxidant for the epoxidation of hexenol. Traces of water and base greatly influenced the performance of the catalyst. The aerogel calcined at 400°C had only moderate activity and selectivity (67 % at 50 % conversion), and deactivated above ca. 60 % conversion. Dominant side reactions were the oxidation of the alcoholic function, the acid-catalyzed formation of high molecular weight by-products and epoxide ring opening by the reactant. Recalcination of the aerogel at 200°C *in situ* before use or drying by azeotropic distillation with toluene improved significantly the rate and selectivity. Simple addition to the reaction mixture of a solid base, such as $NaHCO_3$ or zeolite 4A also improved the epoxide selectivity. Zeolite 4A exerted a double effect by eliminating water formed during reaction and by acting as a base. The highest selectivities of 98 and 91 % were achieved at 50 and 96 % conversion within 5 and 60 min, respectively.

Organic Chemistry **167**

Reusable Polymer-supported Palladium Catalysts for the Suzuki Reaction. An Alternative to Terakis(triphenylphosphine)palladium.

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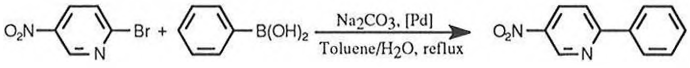
Formation of aryl-aryl bonds is an important problem for the synthesis of many biologically active compounds (*e.g.* Rosoxacin, Diflunisal). The most widely used method is the very versatile coupling reaction of an arylboronic acid (or anhydride) with a bromo- or iodo-aromatic, introduced by Suzuki's group [1]. A palladium catalyst is required : normally 10-30 mequiv. of $Pd(PPh_3)_4$ are used. This catalyst is expensive, heat- and air- sensitive and cannot be recovered after reaction.

On the contrary, our polymer-supported catalysts could be easily recovered by filtration and immediately reused [2]. They were prepared in two steps from Merrifield polymer (chloromethylated polystyrene) by phosphination (PPh_2Li), followed by introduction of palladium(0) (*ca.* 1%).

Numerous examples showed that these catalysts were very efficient for the Suzuki reaction : in typical experiments, almost identical yields were obtained when 30 mequiv. of $Pd(PPh_3)_4$ were replaced by 4 mequiv. of polymer-bound palladium. Furthermore, these catalysts were stable to air and could be used many times : they showed no decrease of activity after 5 uses.



with 2 mequiv. polymer-bound Pd, yield : 95%
with 30 mequiv. $Pd(PPh_3)_4$, yield : 94%

[1] N. Miyaura, A. Suzuki, *Chem. Rev.* **1995**, *95*, 2457.

[2] The use of polymer-bound palladium catalysts had been reported for several other reactions : *e.g.* for hydrogenation reactions, see M. Terasawa, K. Kaneda, T. Imanaka, S. Teranishi, *J. Catal.* **1978**, *51*, 406; for the Heck reaction, see C.M. Andersson, K. Karabelas, A. Hallberg, C. Andersson, *J. Org. Chem.* **1985**, *50*, 3891.

Organische Chemie **168**

Enantioselective hydrogenation of α-ketoamides

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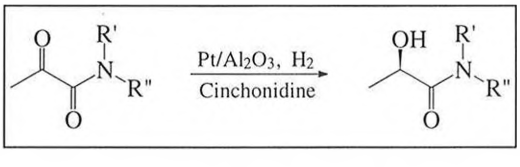
Enantioselective hydrogenation of α-ketoesters over cinchona-modified platinum, discovered by Orito in 1979 [1], has attracted much attention [2, 3]. The present work aimed at broadening the scope of the reaction and getting deeper insight into the modifier - reactant interection. A number of a-ketoamides have been synthesized and hydrogenated to the (*R*) enantiomer over Pt/alumina modified by cinchonidine, according to the sheme below.



The highest ee was achieved in the reduction of N-2,2,2-trifluoroethyl pyruvamide. Moderate hydrogen pressure (≥ 10 bar) and acetic acid as solvent favour the enantiodifferentiation. The reaction belongs to the class of ligand-accelerated asymmetric reactions. Molecular modelling indicated that good ee can be expected only when the reactant possesses a planar structure, which favours the parallel adsorption of the reactant on a flat Pt surface. The keto-group in α-ketoamides is less electron positive than in α-ketoesters, which explains the lower ee's (60 % at best, instead of 95%).

[1] Y. Orito, S. Imai, S. Niwa, *J. Chem. Soc. Japan* **1979**, 1118.

[2] H. U. Blaser, *Chem. Rev.* **1992**, 92, 935.

[3] A. Baiker, *J. Mol. Catal.* **1997**, 115, 473.

Organic Chemistry **169**

Rh(II)-catalyzed CH insertion with nitrenes

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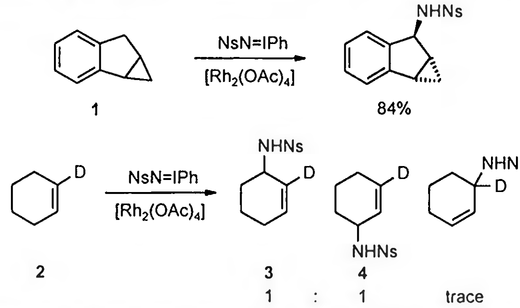
Department of Organic Chemistry
University of Geneva, CH-1211 Geneva 4, Switzerland

Hydrocarbons are transformed into nosyl-protected primary amines by a formal CH insertion *via* the decomposition of NsN=IPh with [$Rh_2(OAc)_4$] [1]. The insertion reaction gives satisfactory results when the reacting CH bond is activated by an aromatic substituent or an oxygen group in the α-position. Olefins are also aminated in the allylic position, but the insertion reaction normally competes with aziridination.



Cyclopropanes in the α-position of the reacting CH bond, for example in cycloprop[*a*]indene (**1**), do not open during the insertion reaction, which indicates that the formation of a radical intermediate is unlikely. The reaction with cyclohexene-*1-d₁* (**2**) produces a 1:1 mixture of **3** and **4** as expected for a concerted insertion mechanism.

[1] I. Nägeli, C. Baud, G. Bernardinelli, Y. Jacquier, M. Moran, P. Müller, *Helv. Chim. Acta* **1997**, in press.

Organic Chemistry **170**

Structures and Reactivity of Lithiated Chiral Bicyclic Phosphortriamides

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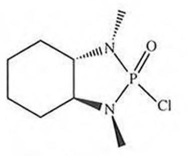
Spitalstr. 51, CH 4056 Basel

Bicyclic phosphordiamides such as **1** [1] have been used for the NMR resolution of racemic alcohols and amines.



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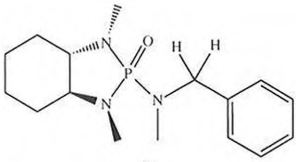

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Herein we wish to present the bicyclic phosphordiamide **1** as a new chiral auxiliary for the formation of chiral phosphortriamide derivatives such as **2**, their subsequent lithiation to chiral α-nitrogen stabilized carbanions and reaction with electrophiles [2,3].

The results of the electrophilic addition to lithiated **2** and the structures of a calculated modell system will be presented.

[1] Alexakis et al. *J. Org. Chem.* **1992**, *57*, 1224-1237.
[2] Savignac et al. *Tetrahedron* **1975**, *31*, 877-884.
[3] Müller et al., submitted.

Organic Chemistry **171**

Divinyl Disilanes: A New Class of Bidentate Ligands with Inversed Stability of its Fe(CO)₃ and Fe(CO)₄ Complexes

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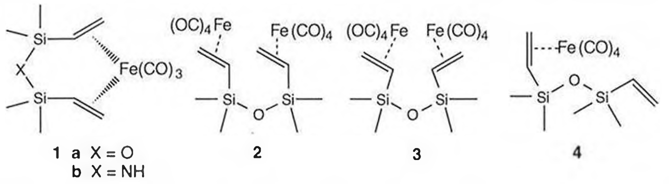
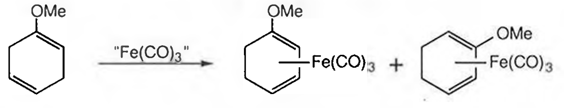
Reaction of 1,3-divinyl-1,1,3,3-tetramethyl-disiloxane with $Fe_2(CO)_9$ leads to a mixture of four labile carbonyl iron complexes. The structure of complex **1a** was established by X-ray, while the structures of the other isomers were deduced from spectroscopic evidence.
Surprisingly, the tetracarbonyl complex **4** is the most stable in the series: Heating of **1** or **2**/**3** leads to **4** whereas photolysis of the latter reverts it to **1**.



Complex **1a**, as well as its disilazane analog **1b**, are useful tricarbonyl iron transfer reagents to conveniently prepare (η^4-diene)$Fe(CO)_3$ complexes. Unlike the well known BDA-$Fe(CO)_3$ and related compounds, complex **1** transfers the $Fe(CO)_3$ unit not only to *cis*-1,3-dienes, but also to a series of other olefins, *e.g.* 2,5-dihydroanisole or verbenene, which require double bond isomerisation or ring opening prior to complexation.



Replacing the disiloxane by the analogous disilazane prevents the formation of tetracarbonyl complexes. Thus its use as transfer reagent excels the disiloxane.

Organische Chemie **172**

Diastereoselektive Synthese α-verzweigter β-Aminosäureester

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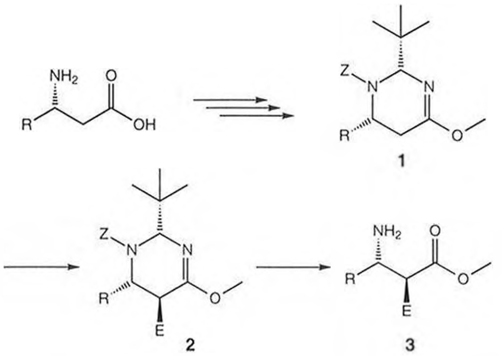
Frühere Arbeiten haben gezeigt, dass bei Umsetzungen von β-Aminosäureester-Enolaten mit Elektrophilen mässige bis gute Stereoselektivitäten erzielt werden [1], wobei sich aber die gebildeten Diastereoisomeren schlecht trennen liessen.
Analog zur Synthese nicht-proteinogener α-Aminosäureester über Oxazoline [2] wurde das Tetrahydropyrimidin **1** hergestellt, mit verschiedenen Elektrophilen umgesetzt (→ **2**) und nach Abspaltung der Z-Gruppe und Hydrolyse der Iminoestergruppe wurden in guter Ausbeute enantiomerenreine α-verzweigte β-Aminosäuremethylester des Typs **3** erhalten.



[1] H. Estermann, D. Seebach, *Helv. Chim. Acta* **1988**, *71*, 1824.
[2] M. Hoffmann, D. Seebach, *Chimia* **1997**, *51*, 90.

Chimie organique **173**

Aminocyclopropane analogues of γ-Aminobutyric Acid (GABA)

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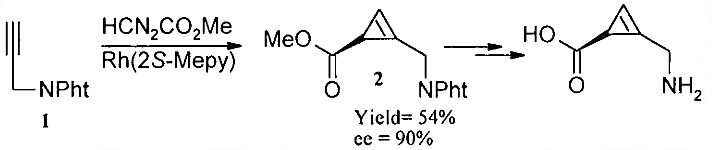
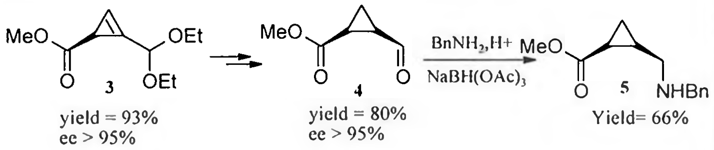
Hassan Imogaï and Paul Müller

Analogues of γ-Aminobutyric Acid(GABA), an important neurotransmitter inhibitor are compounds of high pharmacological interest, We reporte here two efficient preparation of novel γ-Aminobutyric Acids incorporating the cyclopropene or cyclopropane moiety.

The intermolecular cyclopropenation of *N*-protected propargylamine **1** with methyl diazoacetate in the presence of optically active Rh(II)-carboxamidate complexes proceeds with high enantioselectivity and allowed direct access to the Protected 2-aminomethyl cycloprop-2-ene-1-carboxylate **2**. Experiments for the deprotection of **2** will be reported.



Alternatively, diethoxypropyne may be cyclopropanated to afford **3**, which, upon catalytic hydrogenation is convertedto the *cis*-aldehyde **4**. The GABA analogue **5** is obtained *via* reductive amination.



Organic Chemistry **174**

Alkylative Decarboxylation of Amino Acids with Retention of the Optical Activity

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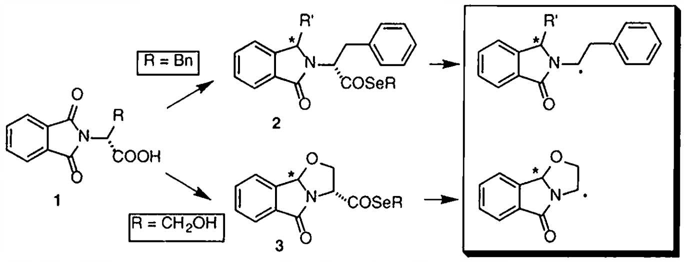
Université de Fribourg, institut de chimie organique, Pérolles, 1700 Fribourg

Very recently, we have reported an alternative method to the Barton decarboxylation procedure of N-protected amino acids based on decarbonylation of acyl radicals [1]. This process is highly efficient but leads in case of simple amino acids to racemization of the α-center. We report here our effort to avoid this epimerization. According to Seebach principle of self-regeneration of stereocenters [2], N-phthaloylamino acids **1** were converted into 3-substituted 1-isoindolinones such as **2** or **3**, the newly formed stererogenic centers is used to control the stereochemical outcome ot the radical reactions.



[1] A. Stojanovic, P. Renaud, *Synlett* **1997**, 181.

[2] D. Seebach, A. R. Sting, M. Hoffmann, *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2708.

Organic Chemistry **175**

Searching for New Secondary Structures of β-Peptides

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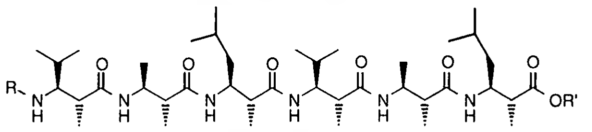
Laboratorium für Organische Chemie, Eidgenössische Technische Hochschule, ETH-Zentrum, Universitätsstrasse 16, CH-8092 Zürich

Recently the helical structure of some β-peptides has been revealed both in solution [1] and in the solid state [2]. The influence of side chains and the configuration of the two stereogenic centers upon the secondary structure is of wide interest in this rapidly growing field.



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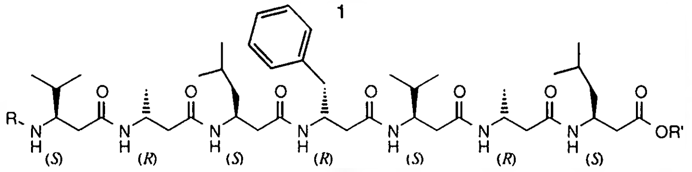

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Referring to models and to structures already elucidated, the fully substituted hexapeptide **1** and the syndiotactic β-substituted heptapeptide **2** should not be able to form stable helices. Information gained from these peptides allows further predictions about the stability of various β-peptide structures.

[1] D. Seebach *et al.*, *Helv. Chim. Acta* **1996**, *79*, 913; *ibid.*, **1996**, *79*, 2043.

[2] S. H. Gellman *et al.*, *J. Am. Chem. Soc.* **1996**, *118*, 13071.

Organic Chemistry **176**

NMR Solution Structure of an Unusual Zinc-Finger Protein

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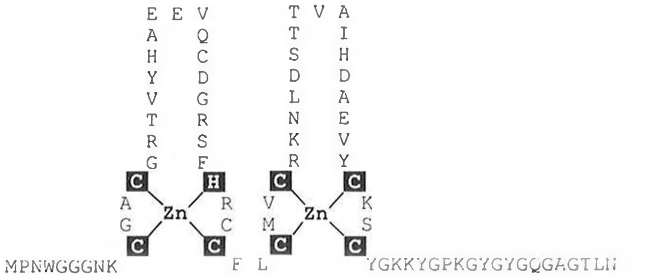
Institute of Organic Chemistry, *Institute of Biochemistry, University of Innsbruck, Austria

We have recently determined solution structure of the carboxy-terminal LIM domain (LIM2) of recombinant quail cystine-rich protein (CRP2) [1]. Here we report the structure of the N-terminal LIM Domain (LIM1, 81 residues) as determined by multidimensional NMR Spectroscopy. It comprises two zinc finger modules of the CCHC and the CCCC type. Interestingly the first zinc-finger module contains an unusual extra C in the neighbourhood of the coordinating C, whose possible function has been investigated. In addition the dynamic properties of LIM1 have been investigated by ^{15}N relaxation



This work was supported by the Austrian Science Foundation (FWF) (grant P11600).

[1] R. Konrat, R. Weiskirchen, B. Kräutler, K. Bister, *J. Biol. Chem.* **272**, 1201 (1997).

CHIMIA 51 (1997) Nr. 8/9 (August/September)

Organic Chemistry **177**

PROTEIN MIMETICS BY SEQUENTIAL CONDENSATION OF BINDING LOOPS TO TOPOLOGICAL TEMPLATES ON SOLID SUPPORTS.

Yoshihiro Yokokawa, Stéphane Peluso, Patrick Garrouste, Francesco Peri, Gabriele Tuchscherer, Pascal Dumy, Manfred Mutter *from the Institute of Organic Chemistry,* **University of Lausanne**, BCH Dorigny, CH-1015 Lausanne, Switzerland.

The introduction of chemoselective ligation procedures and orthogonal protection techniques have strongly stimulated the concept of non-native chain architectures to bypass the folding problem in protein design and mimicry. In applying these methodological innovations, we have recently proposed the replacement of the structural part of receptors by topological templates, which serve as scaffolds for the regioselective attachment of binding loops mimicking the functional part of the native molecule[1]. Here, we elaborate various strategies for the regiospecific condensation of peptide loops to topological templates in the framework of SPPS.
The methodology is illustrated by the solid phase assembly of a three-loop TASP (template assembled synthetic protein) molecule intended to mimic the complementarity-determining region of the monoclonal antibody McPC603. Critical steps of our strategy are (1) attachment of a cyclic template bearing three pairs of orthogonally protected attachment sites to the solid support, (2) condensation of the bifunctional side-chain protected peptide loops on the polymer-bound template upon sequential removal of protecting groups, (3) final deprotection and cleavage to release the target molecule. Alternatively, template assembled binding loops as protein mimetics are prepared by stepwise SPPS applying up to five orthogonal protecting groups. The various methodologies are evaluated in terms of their potential for rapid functional screening and for combinatorial approaches in drug design.

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[1] M. Mutter, P. Dumy, P. Garrouste, C. Lehmann, M. Mathieu, C. Peggion, S. Peluso, A. Razaname, G. Tuchscherer, Angewandte Chemie, Int. Ed. Engl. 35, 1482-1485, 1996.

Organic Chemistry **178**

CHIMERIC PEPTIDES AS BIOSENSORS.

Lukas C. Scheibler, Pascal Dumy and Manfred Mutter *from the Institute of Organic Chemistry,* **University of Lausanne**, BCH Dorigny, CH-1015 Lausanne and Mila Bontcheva, Horst Vogel *from the* **Swiss Federal Institute of Technology**, EPFL Ecublens, CH-1015 Lausanne, Switzerland.

Major progress in chemoselective ligation techniques has enabled the synthesis of template assembled peptides exhibiting complex structural features. Here, we present the design and synthesis of chimeric molecules based on Regioselectively Addressable Functionalized Templates (RAFT) as prototypes for molecular devices in biosensor technology. Orthogonally protected lysine side-chains pointing to opposite sites of the template backbone allow for the functionalization of topological templates with independent "effector" (e.g. thiolipids or amphipathic helices) and "receptor" (e.g. metal-binding loops or antigenic peptides for specific antibody recognition) sites (Figure). Immobilization of the chimeric molecules on gold surfaces results in self-assembled monolayers (SAM). We demonstrate, that these supramolecular assemblies show selective metal and antibody binding properties and function as surface assembled ion channels. The implications of the results for developing peptide based biosensors will be discussed.

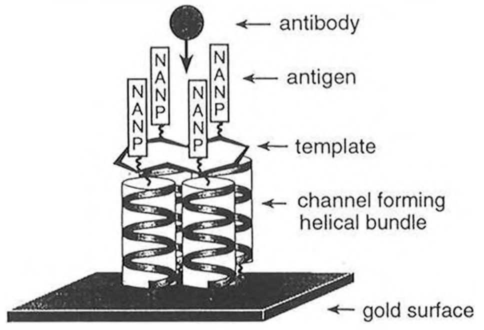

Figure: Chimeric peptides as biosensors.

Organic Chemistry **179**

NON-NATIVE ARCHITECTURES IN PROTEIN DESIGN: THE ZINC FINGER MOTIF AS LOCKED-IN TERTIARY FOLD.

Gabriele Tuchscherer, Raymond Jaquet, Irma Lang, Christian Lehmann, Marc Mathieu, Manfred Mutter, Cristina Peggion, Alain Razaname, Barbara Rohwedder *from the Institute of Organic Chemistry,* **University of Lausanne**, BCH Dorigny, CH-1015 Lausanne, Switzerland.

Despite the progress in understanding the mechanism of protein folding de novo design is still limited by the complex folding pathway of linear polypeptides. As an alternative to bypass this protein folding problem we have proposed the design of nonnative, branched chain architectures ("TASP molecules") with an increased propensity for folding. Here, we extend this concept in mimicking functional domains of proteins by assembling peptide blocks to crosslinked tertiary motifs ("locked-in folds", Figure). As an illustrative example, the ββα folding unit of a ZIF is re-assembled by covalently attaching the DNA binding helical segment to a cyclic peptide mimicking the antiparallel β-sheet part. Chemoselective ligation and orthogonal protection techniques are used for assembling the individual building blocks in solution. We show by CD, NMR and complexation studies that the resulting locked-in fold retains the major structural and functional properties and exhibits increased thermodynamic stability compared to the native molecule. In addition, a second generation of ZIF derived locked-in folds with minimal structural requirements and its assembly to multimeric ZIF mimetics is presented.

Figure: Molecular kit (α–helices, β-sheets, loops) for the construction of locked-in tertiary folds. I: Zn^{II} induced folding of a native zinc finger (Zif) unit; II: Zif derived ββα-folding unit as a locked-in fold with the appropriate geometry for Zn^{II} complexation.

Organic Chemistry **180**

A Coenzyme B_{12}-α-cyclodextrin-conjugate

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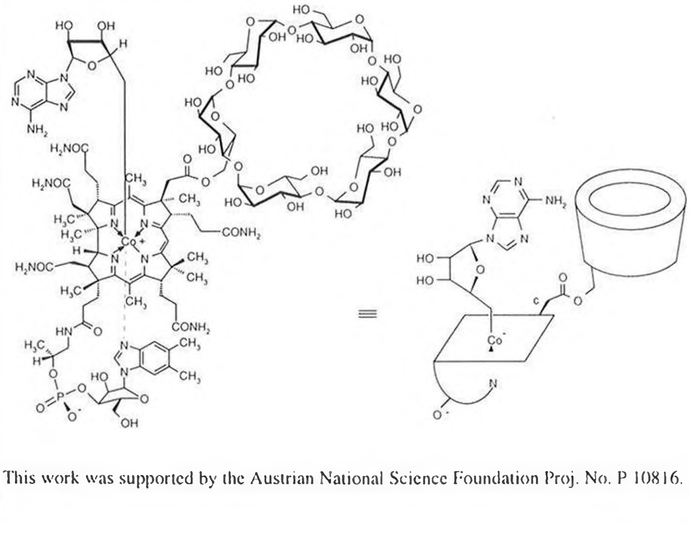
Institute of Organic Chemistry, University of Innsbruck, A-6020 Innsbruck, Austria

Coenzyme B_{12}-models are useful for studying the mechanisms of rearrangements catalyzed by coenzyme B_{12}. We synthesized the adenosylcobalamin-cyclodextrin-conjugate shown below, where the cyclodextrin is bound via one of its six primary hydroxyl groups via an ester bond to the c-side chain of the cobalamin. This side chain is located at the β-side of the corrin-ligand at which also the adenosyl group is bound to the cobalt center. On this upper side of the cobalamin the adenosyl part could interact with the cyclodextrin unit.
We report here the synthesis of the conjugate and the investigation of the structure with NMR experiments.



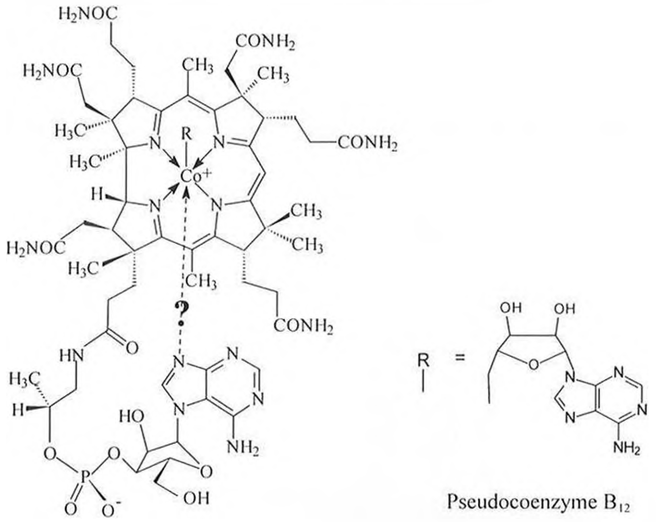
This work was supported by the Austrian National Science Foundation Proj. No. P 10816.

Organic Chemistry **181**

On a Synthesis and the Structure of Pseudocoenzyme B_{12}

W. Fieber, B. Hoffmann, R. Konrat, B. Kräutler*
Institute of Organic Chemistry, University of Innsbruck, Austria

Pseudocoenzyme B_{12} (Coβ-adenosyl-7α-adeninylcobamide) is the coenzyme B_{12} analogue, in which the cobalt coordinating 5,6-dimethylbenzimidazole base is replaced by adenine, and it appears to be the naturally occurring cofactor in *Clostridium cochlearium*. Pseudocoenzyme B_{12} was synthesized in high yield by alkylation of Co(I)-adeninylcobamide with 5'-tosyl adenosine in an electrochemical reaction. The structure of this cofactor was investigated in aqueous solution by NMR-spectroscopy.



Pseudocoenzyme B_{12}

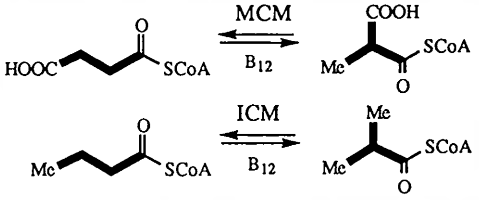
This work was supported by the Austrian Science Foundation (P 11600).

Organic Chemistry **182**

Characterisation of Isobutyryl-CoA Mutase from *Streptomyces cinnamonensis*, Producer of the Polyketide Antibiotic Monensin

Ananda Ratnatilleke, K. Burkhardt-Zerbe and John A Robinson.
Institute of Organic Chemistry, University of Zurich, Winterthurerstrasse 190, 8057 Zurich, Switzerland.

The interconversion of *n*-butyryl-CoA and isobutyryl-CoA is catalysed by an adenosylcobalamin (coenzyme B_{12}) dependent isobutyryl-CoA mutase (ICM), which is present in many polyketide-producing streptomycetes. This rearrangement closely resembles the conversion of (*R*)-methylmalonyl-CoA into succinyl-CoA catalyzed by methylmalonyl-CoA mutase (MCM) [1] :



ICM has been purified from *S. cinnamonensis* and shown to comprise two components, icmA (65 kD) and icmB (17 kD). These proteins combine with coenzyme B_{12} to form the holo ICM, which shows a cobamide-like absorbance spectrum. The *icmA* gene has been cloned [2], and shown to have a high sequence similarity to the large subunit of MCM (ca. 80 kDa) from *S. cinnamonensis*. However, the icmA protein is ca. 160 amino acids shorter than the MCM large subunit, corresponding to a truncation of the entire C-terminal B_{12}-binding domain. Work presently underway seeks to determine whether or not the icmB small subunit contains a binding site for coenzyme B_{12} that resembles that found within the complete polypeptide of the MCM large subunit.

[1] Mancia, F. et al., *Structure* **1996**, *4*, 339-350.

[2] Burkhardt-Zerbe, K. (1996), Ph.D Thesis, University of Zurich.

Organic Chemistry **183**

Potential Inhibitors of Porphobilinogen Synthase (PBGS).

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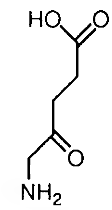
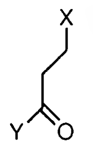
Institut de Chimie de l'Université de Neuchâtel, Av. de Bellevaux 51, CH-2000 Neuchâtel.

Biosynthesis of porphobilinogen is catalysed by PBGS which condenses asymmetrically two molecules of δ-ALA. In the context of our mechanistic study of PBGS, substrate analogues **1** were synthesised and tested on the enzyme as potential inhibitors.



δ-ALA

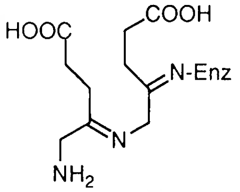


X = NO_2, COOR

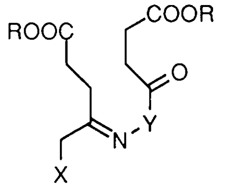
Y = CH_2NH_2, CH_2F, CH_2OH, $NHNH_2$, CF_3, ...

1

On the basis of the mechanism postulated by Jordan [1], aza- or oxa-intermediate analogues **2** were synthesised and tested on PBGS.



Jordan's intermediate



X = H, NH_2

Y = NH, O

2

[1] P.M. Jordan, J.S. Seehra, J. Chem. Soc. Chem. Comm. **1980**, 240.

Organic Chemistry **184**

Chemical and Enzymatical Deprotection of Phthalimido-Porphobilinogen-Dimethylester

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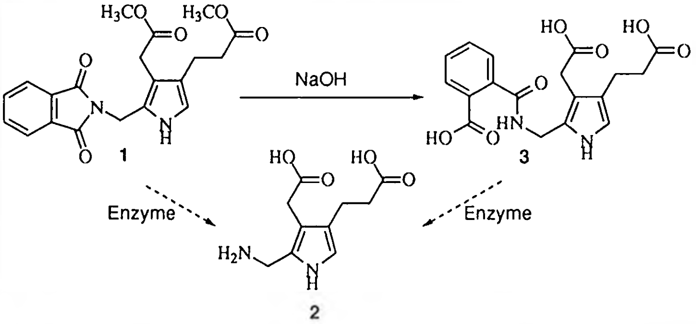
We report trials about the complete deprotection of Phthalimido-Porphobilinogen-Dimethylester **1** to Porphobilinogen (PBG) **2** by the combination of basic and enzymatic hydrolysis under mild aqueous conditions.



The classical basic hydrolysis leads to the deprotection of the estergroups and the partial cleavage of the phthalimidogroup to give the intermediate **3** [1].
In order to achieve complete deprotection we study the application of Phthalyl amidase which is known to selectivly deprotect phthalimidogroups under very mild aqueous conditions to produce the free amine [2].

[1] A. Chaperon, Dissertation Uni Neuchâtel, **1996**.
[2] C.Costello, M. Zmijewski, *Tetrahedron Lett.* **1996**, 37, 7469-7472.

Organic Chemistry **185**

Photoreactivation of Pyrimidine Dimers by Model Compounds of DNA-Photolyase

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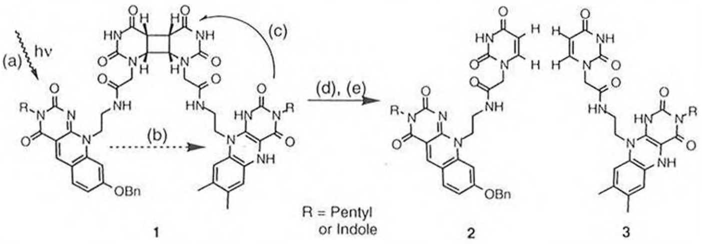
Photolyases are DNA repair enzymes which convert Pyr<>Pyr DNA-lesions into the monomers in a light driven reaction.
In order to elucidate interactions between Pyr<>Pyr and the catalytically active cofactors, which naturally occur in DNA-photolyases (FAD, 8-hydroxy-5-deazaflavin or 10-methenyltetrahydrofolate), we prepared a series of flavin [1], deazaflavin and tryptophane containing model compounds such as **1**, which are able to mimic the repair reaction.
The proposed mechanism includes energy transfer from an excited deazaflavin (a) to the reduced flavin chromophore (b), which is then able to donate an electron to the Pyr<>Pyr (c). The dimer radical anion is split into the monomers **2** and **3** (d) followed by back electron transfer of the surplus electron to the flavin (e). We investigate the reduction of the flavin using external reducing agents and/or a covalently attached indole moiety.



[1] T. Carell, R. Epple *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 620-623.

Organic Chemistry **186**

Isolation of metabolites from the culture media of *Phaeoacremonium aleophilum* and *Phaeoacremonium chlamydosporum*

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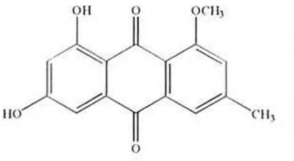
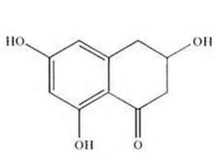
Avenue de Bellevaux, 51, CH-2000 Neuchâtel

Esca is one of the most destructive diseases of vine. It is spreading mainly in the countries in which the treatment by sodium arsenite has been forbidden. Five fungi have been reported to be responsible for this disease : *Phaeoacremonium aleophilum, Phaeoacremonium chlamydosporum, Stereum hirsutum, Eutypa lata* and *Phellinus sp.* The two fungi studied here provoke the central light-coloured soft necrosis observed in contaminated wood.[1]

In the course of the analysis of the culture media of *Phaeoacremonium aleophilum* and *Phaeoacremonium chlamydosporum*, some metabolites were isolated, among which an anthraquinone **1** and scytalone **2**.[2]



1



2

[1] P. Larignon and B. Dubos, *European Journal of Plant Pathology*, 1997, **103**, 147-157.
[2] F. Viviani, G. Michel, A. Marquet, *J. Chem. Soc. Perkin Trans. 1*, 1990, **5**, 1255-1259.

Organic Chemistry **187**

Stereoselective Preparation of the *N*-Acetylcysteamine Thioesters of Doubly ^{13}C-Labelled Crotonic, Tiglic, Sorbic, and 4-Methylsorbic Acid and Their Use to Probe the Function of a Eukaryotic Polyketide Synthase

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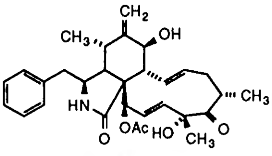
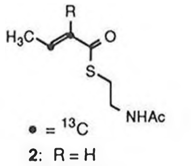
Institut für Organische Chemie der Universität Basel,
St. Johanns-Ring 19, CH-4056 Basel

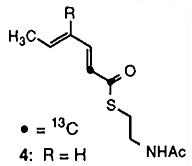
Recent insights into the mechanism of the biosynthesis of complex polyketides support the idea that acetate/malonate building blocks are assembled in a processive manner such that most of the functional groups seen in the final metabolite are individually established after each elongation step [1].



1



• = ^{13}C
2: R = H
3: R = CH_3



• = ^{13}C
4: R = H
5: R = CH_3

The polyketide synthase (PKS) systems involved in the biosynthesis of cytochalasans are of particular interest because the polyketide-derived moieties of these compounds are methylated and the functionalized product generated by the PKS seems to undergo an intramolecular Diels-Alder reaction. To probe the function of the PKS that the fungus *Zygosporium masonii* uses for the biosynthesis of cytochalasin D (**1**), the *N*-acetylcysteamine thioesters of (*E*)-[2,3-$^{13}C_2$]crotonic acid (**2**), (*E*)-[2,3-$^{13}C_2$]tiglic acid (**3**), (*E,E*)-[1,2-$^{13}C_2$]sorbic acid (**4**) and (*E,E*)-4-methyl-[1,2-$^{13}C_2$]sorbic acid (**5**), all analogues of putative early biosynthetic intermediates, were synthesized and administered to growing cultures of *Z. masonii* and their incorporation into cytochalasin D was elucidated.

[1] S. Donadio, M. J. Staver, J. B. McAlpine, S. J. Swanson, L. Katz, *Science* **1991**, *252*, 675–679.

Organic Chemistry **188**

Closing the DNA-Minor Groove by a Curtain of Alkyl Residues: What does it mean for DNA-Duplex Stability?

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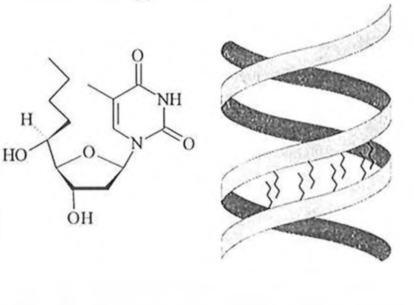
University of Berne, Freiestr.3, 3012 Bern

DNA-duplex stability is dominated by three major factors: 1) by hydrogen bonds (AT and CG base pairs), 2) π-stacking of adjacent base pairs and 3) solvation of the polyanionic duplex. For the latter, there is little known about its energetic contribution to duplex stability. Inspection of the B-DNA conformation shows, that (S)-$H_{5'}$ of the sugar residues points across the minor groove, more or less parallel to the helical axis. By replacing this hydrogen with an alkyl chain of appropriate length, it should be possible to close the minor groove with these hydrophobic residues, thereby affecting the hydration pattern in the minor groove. In suitable oligonucleotide sequences these alkyl chains can form a zipper-like curtain reminiscent of the Leucine-Zipper.



We report on the synthesis of 5'(S)-butylthymidine via a new, generally applicable synthetic route. A series of oligonucleotides containing this residue in various positions were prepared by conventional solid phase synthesis with coupling yields of > 95% / step. Binding data and structural data, as determined by UV-melting curves and CD-spectroscopy will be presented.

Organische Chemie **189**

Gas Phase Nitration of Toluene Using Solid Acid Catalysts

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Laboratory for Technical Chemistry, Swiss Federal Institute of Technology,
Universitätstrasse 6, CH-8092 Zürich

Nitrotoluenes, important intermediates in the chemical industry, are industrially produced by the liquid phase nitration of toluene using a mixture of nitric and sulfuric acids as the nitrating agent. The need for recycling huge amounts of diluted sulfuric acid or for disposing of it is a major drawback of this process, which may be overcome by using solid acid catalysts. The use of zeolites could prove to be even more beneficial because shape selectivity may allow us to shift the product composition in favour of the generally more desirable *para*-nitrotoluene.

Based on our earlier work using benzene [1], we investigated the nitration of toluene in the gas phase using nitric acid as the industrially preferred nitrating agent. A variety of solid acid catalysts, among them various zeolites, was studied. Preliminary screening studies confirmed that zeolites provide a higher *para*-to-*ortho* ratio as compared to solid acid catalysts that do not have a microporous channel system. For zeolites, such as H-mordenite, with a one-dimensional channel system, the activity dropped rapidly during short reaction periods. Zeolites, such as H-beta, with a three-dimensional channel system exhibited stable activity and selectivity over a period of 24 h time on stream. The influence of reaction parameters on activity, selectivity, and stability of solid acid catalysts for the nitration reaction will be discussed.

[1] L. Bertea, K.W. Kouwenhoven, R.Prins, *Appl. Catal. A:* **129**, 229 (1995).

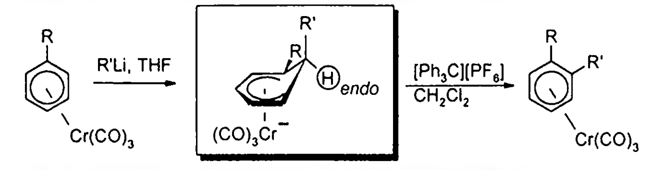
Organic Chemistry **190**

A New Route to Highly Enantionenriched Planar-Chiral Arene Complexes - Precursors in Asymmetric Synthesis

Angelika Fretzen, E. Peter Kündig

Department of Organic Chemistry
University of Geneva, CH-1211 Geneva 4, Switzerland

Oxazoline, imine and hydrazone substituted $[(\eta^6\text{-arene})Cr(CO)_3]$ complexes react with nucleophiles by addition to the *ortho*-position of the complexed aromatic ring.[1] Subsequent treatment with trityl cation yields planar chiral complexes.[2]



R = imine, oxazoline or hydrazone, R' = phenyl, methyl, vinyl ...

We here present evidence which shows that this reaction proceeds by an unprecedented *endo* hydride abstraction and report new asymmetric variants. RLi additions in the presence of chiral diethers provide an enantioselective route to the planar chiral complexes (up to 95 % ee).
Diastereoselective reactions of the enantioenriched products include benzylic alkylations and allylations as well as dearomatization reactions giving access to cyclohexadiene systems. Studies aimed at the synthesis of natural product analogues using these protocols are in progress.

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[1] Kündig, E. P.; Ripa, A.; Liu, R.; Amurrio, D.; Bernardinelli, G. *Organometallics* **1993**, *12*, 3724.

[2] For a first report see: Kündig, E. P.; Liu, R.; Ripa, A. *Helv. Chim. Acta* **1992**, *75*, 2657.

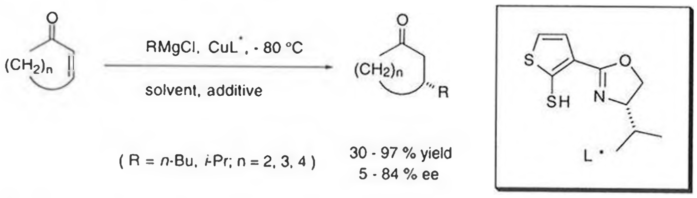
Organic Chemistry **191**

Enantioselective Copper-Catalyzed 1,4-Addition of Organometallic Reagents to Enones

Andreas K. H. Knöbel, Guy C. Lloyd-Jones, Andreas Pfaltz*

Max-Planck-Institut für Kohlenforschung
Kaiser-Wilhelm-Platz 1, 45470 Mülheim a.d. Ruhr, Germany

Copper(I) thiolate complexes derived from chiral mercaptoaryl-oxazolines have been studied as enantioselective catalysts for the conjugate addition of Grignard reagents to cyclic enones [1]. The enantiomeric excess increases in the order cyclopentenone < cyclohexenone < cycloheptenone. The selectivity as well as the yield crucially depend on the solvent, additive and the order of addition.



Conjugate addition reactions of other organometallic reagents such as R_2Mg, RMnCl and R_2Zn will also be discussed. With organozinc reagents and a new class of ligands containing an oxazoline ring and a phosphite group, promising enantioselectivities (>90% ee) have been obtained.

[1] Q.-L. Zhou, A. Pfaltz, *Tetrahedron* **1994**, *50*, 4467.

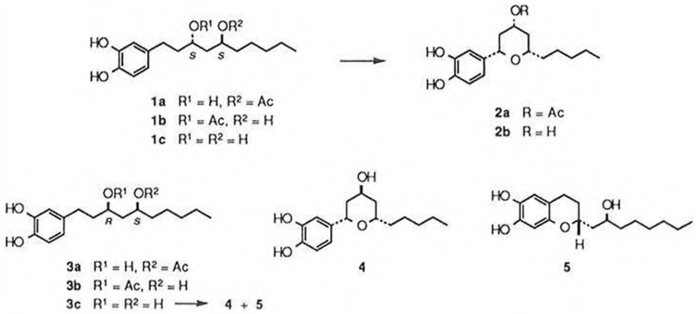
Organische Chemie **192**

Enantioselektive Synthese von n-Alkyloxycatecholen als Inhibitoren von Lipoxygenase

Mathias Juch und Peter Rüedi

Organisch-chemisches Institut der Universität, 8057 Zürich

Die aus *Plectranthus sylvestris* isolierten antioxidativ wirksamen, optisch aktiven n-Alkyloxycatechole (z.B. **1**,**2**) [1] sind Inhibitoren der Lipoxygenase (LO). Mit dem Ziel, den Einfluss der Chiralität und der Funktionalität in der Seitenkette auf die LO-Hemmung zu untersuchen, wurden neben den Naturprodukten verschiedene enantio- und diastereoisomere Verbindungen hergestellt (z.B. **3**-**5**).



Die Isomeren **1a** und **1b** stehen in Lösung *via* 1,3-Acylshift in einem langsamen Gleichgewicht (Tage), **3a**/**3b** lassen sich nicht trennen. Wegen der konformativ günstigen Anordnung der Substituenten tritt in **1** nur einer der möglichen Ringschlüsse zum 2,4,6-trisubstituierten Tetrahydropyran ein.

[1] M. Juch, P. Rüedi, *Helv. Chim. Acta* **1997**, *80*, 436.

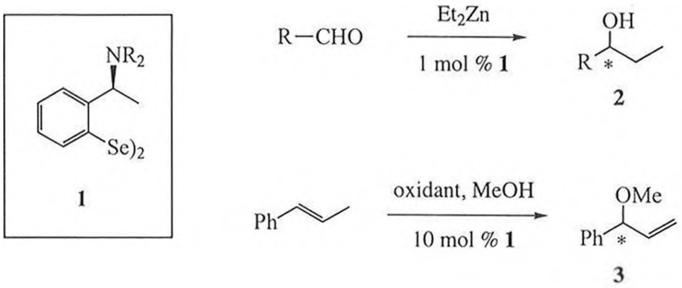
Organic Chemistry **193**

Catalytic Reactions with Chiral Selenium Compounds

Thomas Wirth

Institut für Organische Chemie der Universität Basel, St. Johanns-Ring 19,
CH-4056 Basel, Switzerland

Nitrogen containing diselenides of type **1** are easily accessible by a short synthetic sequence. These compounds are efficient pro-catalysts in the diethylzinc addition to various aldehydes. The resulting secondary alcohols **2** are obtained in high yields and optical purities. Furthermore, diselenides **1** are precursors for optically active selenium electrophiles, which are able to add to unfunctionalized alkenes. First results of a catalytic sequence of addition reaction and subsequent elimination leading to optically enriched allylic alcoholes like **3** are presented.



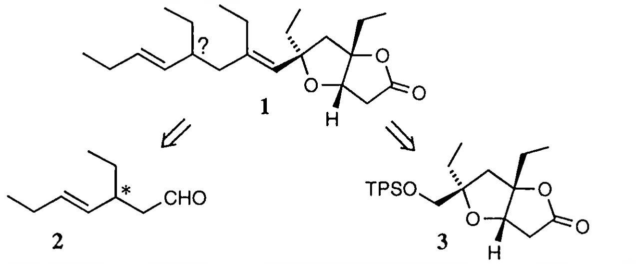
T. Wirth, *Tetrahedron Lett.* **1995**, *36*, 7849-7852.
T. Wirth, K. J. Kulicke, G. Fragale, *Helv. Chim. Acta* **1996**, *79*, 1957-1966.

Chimie organique **194**

Progrès vers la synthèse énantiosélective du plakortone A

Patrick Suter, Geneviève Fortier, Yun-Xing Cheng et John Boukouvalas*
Département de Chimie, Université Laval, Québec (Qc), Canada G1K 7P4

Le plakortone A (**1**) appartient à une famille de lactones bicycliques récemment isolées des extraits d'acétate d'éthyle de l'éponge *Plakortis halichondrioides* par des chercheurs de SmithKline Beecham [1]. La capacité de ces produits naturels à stimuler l'ATPase cardiaque pompant les ions Ca^{2+} du réticulum sarcoplasmique à des concentrations micromolaires en fait des prototypes importants dans la découverte de nouveaux médicaments pour le traitement des maladies cardiovasculaires.



Nos efforts en vue de développer une synthèse énantiosélective du plakortone A, en utilisant les composés **2** et **3** comme intermédiaires clés, seront détaillés.

[1] Patil, A. D.; Freyer, A. J.; Bean, M. F.; Carte, B. K.; Westley, J. W.; Johnson, R. K.; Lahouratate, P. *Tetrahedron* **1996**, *52*, 377-394.

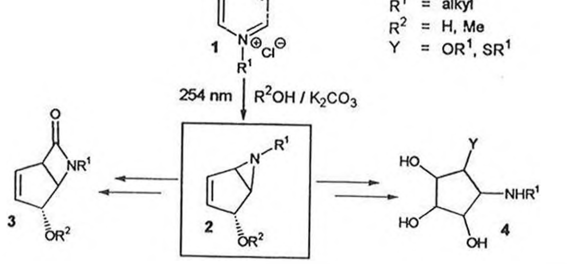
Organic Chemistry **195**

6-Azabicyclo[3.1.0]hex-3-en-2-ol Derivatives, Photochemically Generated Building Blocks for Cyclopentanoids

Fabrice Glarner, Ersin A. Acar, and Ulrich Burger

Department of Organic Chemistry, University of Geneva,
CH-1211 Geneva-4

Normally, the photolysis of pyridinium salts at 254 nm is characterized by single electron transfer processes, especially when substituents or substrats with low oxidation potential, such as carboxylates, amines, or electron-rich alkenes, are involved. However, in their absence, pyridinium salts *e.g.* **1** (R^1 = alkyl) follow an entirely different reaction course. Typically, photolysis in aqueous K_2CO_3 solution or in methanol gave the bicyclic aziridines (**2**). The reaction clearly proceeds *via* an intermediate 6-azabicyclo[3.1.0]hexenyl cation which is intercepted by the solvent. The ensuing bicyclic aziridines (**2**) posses features which make them useful building blocks for synthesis [1]. We report on their transition-metal-mediated transformation to bicyclic β-lactams (**3**), oligo-hydroxy-pentylamines (**4**), and other cyclopentanoids of biological significance.



[1] F. Glarner, S.R. Thornton, D. Schärer, G. Bernardinelli, U. Burger, *Helv. Chim. Acta* **1997**, *80*, 121-127.

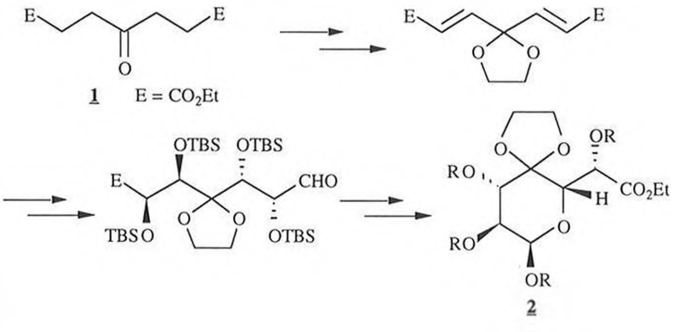
Organic Chemistry **196**

Total Synthesis of Long Chain Sugars

Sandrine Lemaire-Audoire and Pierre Vogel

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

Starting from diethyl-4-oxopimelate **1**, hepto sugars of type **2** were synthesized, using a double asymmetric dihydroxylation [1] to generate the D-*glycero* -L-*gluco* -heptopyranosid-4-ulose system.



This strategy could be applied to the synthesis of the pyranoside fragment of the very active anti-cancer drugs spongistatins [2].

[1] Kolb, H.C.; Van Nieuwenhze, M.S.; Sharpless, K.B. *Chem. Rev.* **1994**, 2483-2547.
[2] Bai, R.; Taylor, G.F.; Cichacz, Z.A.; Herald, C.L.; Kepler, J.A.; Pettit, G.R.; Hamel, E. *Biochemistry* **1995**, *34*, 9714-9721.

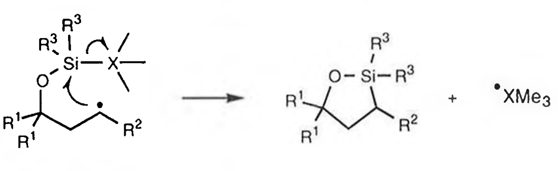
Organic Chemistry **197**

Intramolecular Homolytic Substitution Reactions at Silicon as Unimolecular Chain Transfer Steps in the Formation of 5-Membered Cyclic Silyl Ethers

Armido Studer

Laboratorium für Organische Chemie, Eidgenössische Technische Hochschule, ETH Zentrum, Universitätstrasse 16, 8092-Zürich

The fragmentation of β-stannyl radicals is the most common type of unimolecular chain transfer (UMCT) reactions. In UMCT reactions, the chain carrying species is generated in a unimolecular fashion. We report here the intramolecular homolytic substitution reaction at silicon by carbon-centered radicals with either a silyl or a stannyl radical as the leaving group. Both the silyl and the stannyl radical are capable of carrying the chain.



X = Si, Sn

The cyclic 5-membered alkoxysilanes resulting from the UMCT reactions can easily be converted to the corresponding diol derivatives by *Tamao-Fleming* oxidation [1].

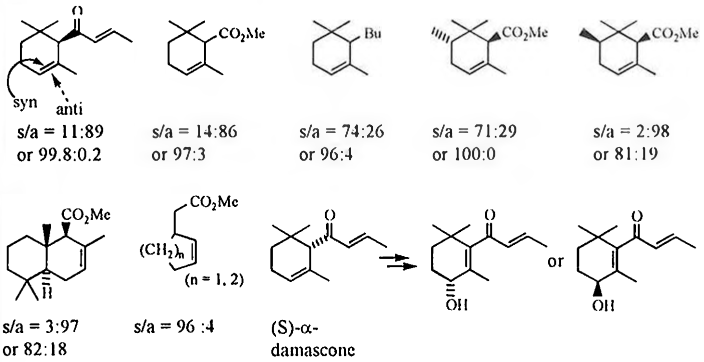
[1] G.R. Jones, Y. Landais, *Tetrahedron* **1996**, *52*, 7599.

Organic Chemistry **198**

Diastereofacial Selectivity in Epoxidations Depends on Reagent Electrophilicity

Charles Fehr

Firmenich SA, Corporate R&D Division,
P.O. Box 239, CH – 1211 Geneva 8



The π-face selectivity of epoxidations depends on steric and electrostatic (polar) interactions between reagent and substrate. By proper choice of the epoxidation reagent, the steric control can be reinforced or overridden.

As an application, a 1,3-chirality transfer sequence was developed for the transformation of (S)-α-damascone into either enantiomer of 4-hydroxy-β-damascone, a constituent of Virginia tobacco.

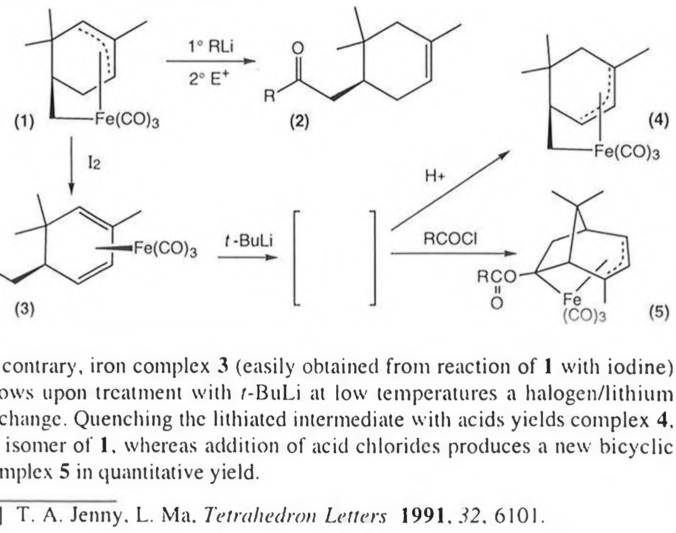
Organic Chemistry **199**

Reaction of Olefin Iron Complexes with Alkyl Lithium Reagents

Jacques RAEMY and Titus JENNY

Institute of Organic Chemistry, Fribourg University, Pérolles, 1700 Fribourg, Switzerland

Treatment of the iron complex **1** [1] with RLi (R= *n*-Bu, *t*-Bu, Me), followed by a range of electrophiles, gives a mixture of the ketones **2** via rapid intramolecular hydrid transfer.



In contrary, iron complex **3** (easily obtained from reaction of **1** with iodine) shows upon treatment with *t*-BuLi at low temperatures a halogen/lithium exchange. Quenching the lithiated intermediate with acids yields complex **4**, an isomer of **1**, whereas addition of acid chlorides produces a new bicyclic complex **5** in quantitative yield.

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[1] T. A. Jenny, L. Ma, *Tetrahedron Letters* **1991**, *32*, 6101.

Organische Chemie **200**

$ZrCp_2$-induzierte Cyclisierungen

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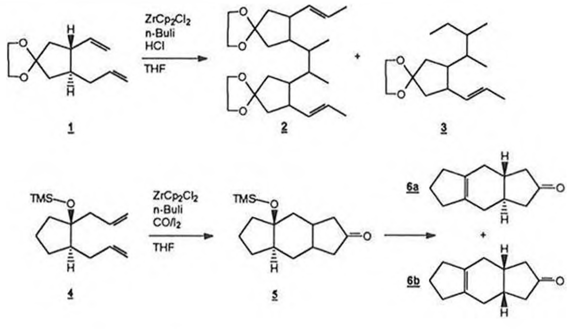
Universität Bern, Freiestrasse 3, 3012 Bern

1,6-Heptadiene lassen sich mittels $ZrCp_2$ und anschliessender Carbonylierung zu gespannten *trans*-Bicyclo[3.3.0]octanen umsetzen.[1][2]
Ausgehend von trans-3-Allyl-4-vinyl-cyclopentanon 1 versuchten wir mit demselben Konzept, Tricyclen mit zwei trans-Bicyclo[3.3.0]octan-Untereinheiten zu synthetisieren.



Die Resultate zeigen keine Cyclisierungsprodukte, sondern ergaben das Produkt der reduktiven Dimerisierung **2**, das Butyladdukt **3** sowie ein doppelbindungsisomeres Edukt. Erst bei Verwendung von trans-1,2-Diallylcyclopentanol **4** als Startmaterial gelang es, Tricyclen (**5**, **6a**, **6b**) auf dem oben genannten Weg herzustellen.

Die Synthesen von trans-3-Allyl-4-vinyl-cyclopentanon 1 und 1,2-Diallylcyclopentanol 4 werden kurz vorgestellt und auf die $ZrCp_2$-induzierte Reaktion wird näher eingegangen.

[1] C.J.Rousset, D.R.Swanson, F. Lamaty, E.Negishi Tetrahedron Lett. **1989**, *30*, 5105.
[2] V. Helbling, R. Keese, NSCG Herbstversammlung **1995** in Bern, Abstract 55.

Organic chemistry **201**

The Synthesis of Natural Acetylenic Compounds from *Stereum hirsutum*

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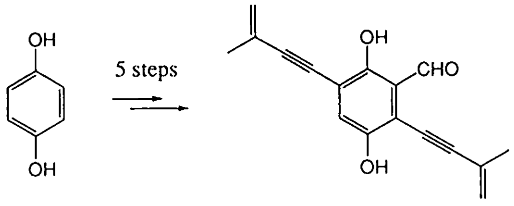
Esca is one of the most destructive disease of grapevine. This disease, increasing in Mediterranean countries, is caused by four fungii: *Phaeoacremonium aleophilum, Phaeoacremonium chlamydosporum, Phellinus sp* and *Sereum hirsutum*[1].

The study of the phytotoxicity required the isolation and structure elucidation of the active agent secreted by the fungus. From *Stereum hirsutum* culture medium, several new acetylenic compounds such as **1** were isolated.

We report here the biological activity and the regioselective synthesis of compound **1** and other derivatives.



1

[1] P. Larignon and B. Dubos, *European Journal of Plant Pathology*, (1997), **103**, 147-157.

Organic Chemistry **202**

Synthesis of (-)-Erythrodiene via a highly diastereoselective Intramolecular Palladium-Catalysed Zinc-Ene-Reaction

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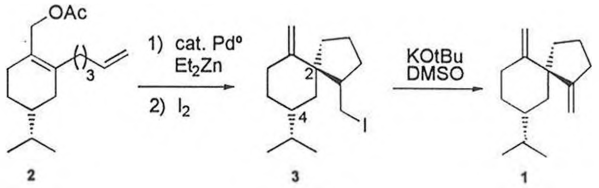
Recently we reported a novel Palladium-catalysed Zinc-ene reaction as a powerful tool for the diastereoselective construction of substituted cyclopentanes and pyrrolidines [1]. Now we present the application of this particularly mild cyclisation method in the synthesis of (-)-Erythrodiene **1**, a marine spirobicyclic sesquiterpenoid.



The key intermediate **3** was isolated in 90% yield as a 95:5 mixture of two C(2)-epimers, thus reflecting the strong directing effect of the resident stereocentre C(4) on the cyclisation topicity. The natural product was then obtained by simple dehydroiodination in 98% yield.

[1] W. Oppolzer, F. Schröder, *Tetrahedron Lett.* **1994**, *35*, 7939-7942.
[2] C. Pathirana, W. Fenical, E. Corcoran, J. Clardy, *Tetrahedron Lett.* **1993**, *34*, 3371-3372.

Organische Chemie **203**

1-Hydroxyallylsilane: Herstellung, Oxidation und Folgereaktionen

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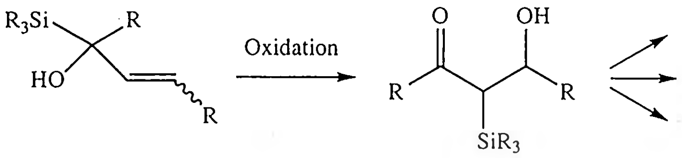
Organisch-chemisches Institut der Universität Zürich,
Winterthurerstr. 190, CH-8057 Zürich

Die Oxidation von 1-Hydroxyallylsilanen mit Persäuren oder Peroxiden führt stereoselektiv zu α-silylierten Aldolen in einer Kaskade bestehend aus Epoxidierung und Pinakol-Typ-Umlagerung [1].



Wir berichten über die Möglichkeiten und Einschränkungen dieser Transformation sowie über das Verhalten der α-silylierten Aldole in Folgereaktionen.

[1] S. Bienz, *Chimia* **1997**, *51*, 133.

Organic Chemistry **204**

A New Stereocontrolled Tandem Reaction of Butadienyl Ester Enolates

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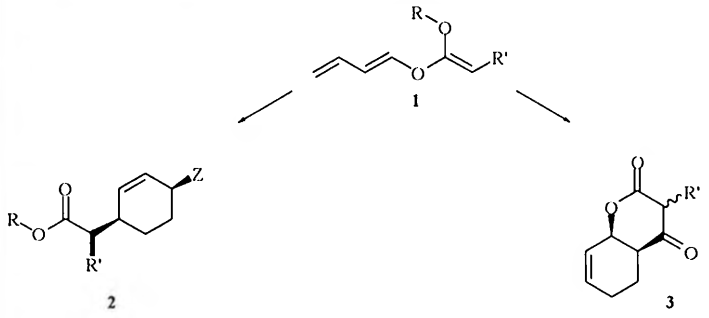
CH-2000 Neuchâtel, Switzerland

The combination of two stereoselective reactions in a tandem process may open a pathway to specifically substituted molecules [1]. Buta-1,3-dien-1-yl ester enolates **1** undergo an Ireland-Claisen like rearrangement after an initial Diels-Alder reaction. The new stereocenters formed in **2** are controlled by the endo-selectivity of the Diels-Alder reaction and by the enolate geometry. By choice of dienophile and reaction conditions the rearrangement reaction may be supressed in favour of an acylated product **3**.



Literature:
[1]: M. Baak, Y. Rubin, A. Franz, H. Stoeckli-Evans, L. Bigler, J. Nachbauer, R. Neier, *Chimia* **1993**, *47*, 233-240.

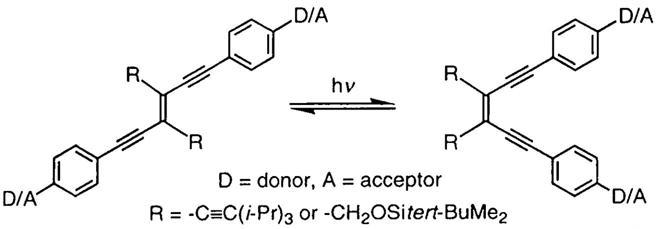
Photochemical *trans/cis* Isomerization of Functionalized Tetraethynylethenes and 1,5-Hexenediynes

205

R. E. Martin[a], J. Bartek[a], R. R. Tykwinski[a], F. Diederich[a],
E. Meister[b], A. Hilger[c] and H. P. Lüthi[c]

[a]Laboratorium für Organische Chemie, ETH-Zentrum, Universitätsstr. 16, CH-8092 Zürich, [b]Laboratorium für Physikalische Chemie, ETH-Zentrum, Universitätsstr. 22, CH-8092 Zürich, [c]Swiss Center for Scientific Computing, ETH-Zentrum, Clausiusstr. 59, CH-8092 Zürich.

The ability to control and dictate the photochemical *trans/cis* isomerization about an olefinic bond is appealing for the creation of dynamic systems for use as energy storage devices or as molcular switches. The isomerization characteristics of donor-donor, acceptor-acceptor, and donor-acceptor substituted tetraethynylethenes (TEEs) and 1,5-hexenediynes with respect to temperature, solvent, and structure have been investigated. Comparisons will be drawn to stilbenes and azobenzenes, two classes of compounds whose photochemical isomerization has been extensively explored.[1]



D = donor, A = acceptor
R = -C≡C(*i*-Pr)$_3$ or -CH$_2$OSi*tert*-BuMe$_2$

[1] R. E. Martin, J. Bartek, R. R. Tykwinski, F. Diederich, E. Meister, A. Hilger, H. P. Lüthi, *J. Chem. Soc., Perkin Trans. 2*, **1997**, submitted.

Organic Chemistry 206

Two-Point Molecular Recognition Linked to Redox Type Signal Transduction

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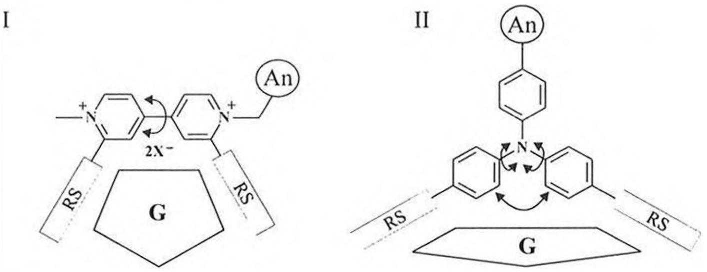
Molecular hosts consisting of a redoxactive subunit (transducer (T), e.g. 4,4'-bipyridinium salts (I) or triarylamine (II)) and two identical recognition sites (RS, e.g. anthrachinone (Q), steroids (S) or 2,6-diaminopyridine diamide (Am)) have been prepared.
Sandwich-type complexation of suitable guests (G) (e.g. intercalation into DNA for Q, hydrophobic interactions for S and H-bonding for Am) induces a shift of E° of the tranducer if its conformation changes upon complexation.
The possibility of immobilizing the electroactive host on an electrode surface via an anchoring group (An) is discussed.



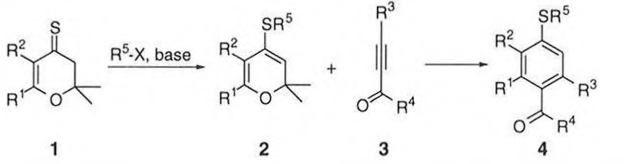
Organic Chemistry 207

Carbonyl-Alkine Exchange (CAE) Reaction of Dihydropyranthione Derivatives with Acetylenic Ketones: A Convergent Synthesis of Highly Substituted Aromatic Sulphides

Cornelia Zumbrunn, Daniel Obrecht and Klaus Müller

Pharma Research, F. Hoffmann-La Roche Ltd., CH-4070 Basel

The Carbonyl-Alkine Exchange (CAE) reaction of 2,2-dialkyl-2,3-dihydro-4*H*-pyran-4-ones with acetylenic ketones has been used previously for the synthesis of phenols [1].
We present here the use of the corresponding dihydropyran-4-thiones **1** for the synthesis of aromatic sulphides. In their S-alkylated form (**2**) they represent highly reactive, cyclic Danishefsky type dienes which undergo CAE reactions with electrondeficient acetylenic ketones **3** to give aromatic sulphides **4** in good to excellent yields and high regioselectivities. If the reactivity of the acetylene is not sufficient, Et$_2$AlCl can be used as a catalyst.



Brominated acetylenes (R^3=Br) also undergo CAE reaction. The resulting aromatic bromides are useful intermediates for further transformations.
This highly convergent approach represents a useful tool for the construction of libraries of low molecular weight compounds by combinatorial chemistry.

[1] D. Obrecht, *Helv. Chim. Acta* **1991**, *74*, 27.

Organic Chemistry 208

Pseudo-prolines : New tools in peptide mimicry

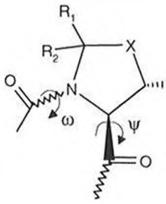
Michael Keller, Pascal Dumy, Cedric Sager, and Manfred Mutter.

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

Pseudo-Prolines are oxazolidines and thiazolidines derived from the amino acids Ser, Thr, Cys. They represent new branched proline surrogates in which variation of the substituents (R1, R2, R3, figure) results in different physicochemical and conformational properties. In particular, they can be exploited to constrain and control the peptide backbone in reverse turn motifs or to alter the imide *cis-trans* ratio [1].

We report here the relevant chemical and structural aspects of such super–prolines as potential surrogates for extending the "proline effect" in peptides. In particular, we report on the thermodynamic and kinetic features of these systems to assess the influence of ring substitution (R$_1$, R$_2$, R$_3$) upon the isomerisation of the Xaa-ΨPro bond imidic bond.

ΨPro



Most notably, the *cis* to *trans* ratio conformation can be tailored in peptides according to the nature of the substituents thus offering a wide range of applications in molecular recognition studies or protein folding as well as in drug design.

[1] P. Dumy, M. Keller, D. E. Ryan, B. Rohwedder, T. Wöhr and M. Mutter. *J. Am. Chem. Soc.* **1997**, 119, 918-925.

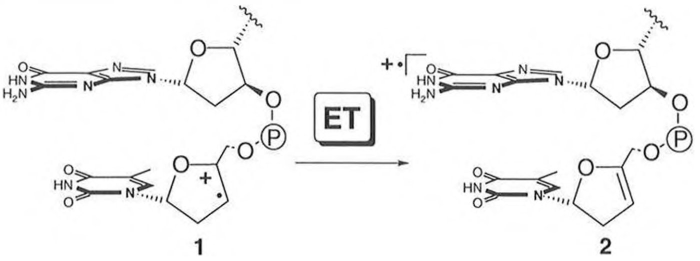
Organic Chemistry **209**

Electron Transfer in DNA from Guanine Bases to the Sugar-Phosphate Backbone during C-4' Radical Induced Strand Cleavage

Eric Meggers, Dirk Kusch and Bernd Giese
Department of Chemistry, University of Basel, CH-4056 Basel

Whether the π-stack of heterocyclic bases in DNA can serve as a molecular wire has attracted much attention during the past decade [1]. But until now only little is known about the electronic interaction between bases and the orthogonal orientated sugar moieties.

In order to study this problem, we generated a positive charge in the backbone of DNA through C-4' radical induced strand cleavage [2]. Indeed, we found that the intermediate desoxyribose radical cation **1** is reduced to enolether **2** by adjacent guanine bases. This electron transfer (ET) turned out to be very efficient (yields up to 70 %) and occurs with high selectivity only from adjacent guanine bases. Besides the theoretical interest, the ET process may be biologically relevant because it could be a possible cause of oxidative damage at guanine residues.



[1] E. K. Wilson, *C&EN* **1997**, *75(6)*, 33-39.
[2] B. Giese, X. Beyrich-Graf, P. Erdmann, M. Petretta, U. Schwitter, *Chem. Biol.* **1995**, *2*, 367-375.

Organic Chemistry **210**

Photoregulation of Cholinesterases Activities with Photolabile Cholinergic Ligands

Ling Peng and Maurice Goeldner

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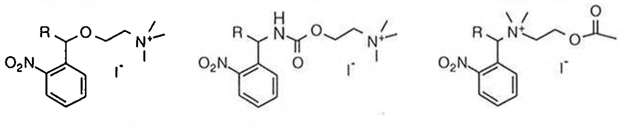
Photolabile precursors of biologically interesting molecules, or "caged" compounds can provide control of temporal and spatial release of enzyme substrate or receptor ligand by rapid photolysis, and are thus important tools in the study of fast biological processes such as substrate-enzyme catalysis or ligand-receptor binding. Acetylcholinesterase (AChE) is a particularly fast enzyme which hydrolyses the neurotransmitter acetylcholine with a turnover number approaching 20000 s^{-1}. The mechanism of its rapid hydrolysis remains unanswered despite the knowledge of the 3D structure of AChE. Time-resolved crystallography would present an ideal approach to investigate the dynamic process of enzyme catalysis at the atomic level and in real time, provided that suitable probes, which regulate the enzymatic activity by temporally and spatially controled release of enzyme substrates or product, are available. For this purpose, we synthesized and characterized different types of "caged" cholinergic ligands for their potential use in exploration of the catalytic mechanism of AChE. They are 2-nitrobenzyl derivatives of choline (the enzymatic product of AChE) [1], of carbamylcholine (a slow substrate of AChE) [2] and of nor-acetylcholine (a close analogue of acetylcholine) [3] (Figure below). They display inhibitory properties on AChE, and are able to photorelease rapidly choline, carbamylcholine and nor-acetylcholine, respectively, allowing photoregulation of AChE activity in complementary manners. Studies are presently in progress to establish the catalytic mechanism of AChE by time-resolved crystallography with these probes complexed in the AChE crystals.



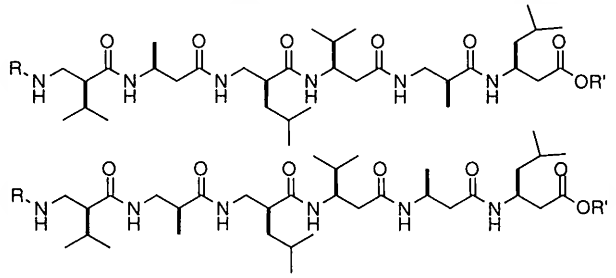
1. L. Peng, M. Goeldner, *J. Org. Chem.* **1996**, *61*, 185.
2. L. Peng et. al., *Biochemistry* **1996**, *35*, 10854.
3. L. Peng et. al., *Angew. Chem. Int. Engl. Ed.* **1997**, *36*, 398.

Organic Chemistry **211**

Delving Further into β-Peptide Chemistry

Jennifer L. Matthews, Jürg Schreiber, Tobias Hintermann
and Dieter Seebach
Laboratorium für Organische Chemie, Eidgenössische Technische Hochschule, ETH-Zentrum, Universitätstrasse 16, CH-8092 Zürich

The synthesis of β-peptides, which contain β-amino acids of differing substitution patterns, has been accomplished *via* the use of *Arndt-Eistert* and *Evans*' auxiliary methodology.



The secondary structures of these β-peptides have been investigated by NMR and CD spectroscopy and this has led to interesting comparisons with the known structures of other β-peptides [1]. Some indication as to the role of hydrophobic interactions on the stability of the secondary structures has been gained.

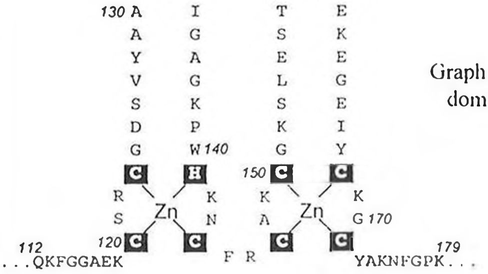
[1] D. Seebach *et al.*, *Helv. Chim. Acta* **1996**, *79*, 913; *ibid.*, **1996**, *79*, 2043.

Organic Chemistry **212**

NMR Structural Studies of the zinc-binding LIM motif

R.Konrat, G.Kontaxis, C.Eichmüller,'R.Weiskirchen,'K.Bister and B.Kräutler
Institute of Organic Chemistry, 'Institute of Biochemistry, University of Innsbruck, Austria

Tetrahedral zinc-binding domains are important structural elements in a wide variety of proteins. The four coordinating ligands are typically composed of cysteine-sulfur and histidine-imidazole nitrogen. Proteins of the cysteine-rich protein family (CRPs) are implicated in diverse processes linked to cellular differentiation and growth control. They contain so-called LIM domains, each formed by two zinc-binding modules of the CCHC and CCCC type.



Graph of the C-terminal LIM domain of quail CRP2 [1]

Based on NMR studies of wild-type CRPs as well as mutants synthesized by site-directed mutagenesis, the structural propensities of this biologically important protein family are discussed.

This work was supported by grants P 11600 and SFB-F002/211 from the Austrian Science Foundation (FWF).

[1] R.Konrat, R.Weiskirchen, B.Kräutler and K.Bister, *J.Biol.Chem.* **272**, 12001, 1997.

Organische Chemie **213**

Selektive Einführung einer Thioamid-Gruppe in Aib-haltige Peptide über eine Variation der 'Azirin/Oxazolon-Methode'

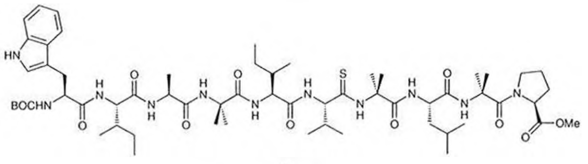
Jürg Lehmann, Anthony Linden und Heinz Heimgartner

Organisch-chemisches Institut der Universität Zürich

3-Amino-2*H*-azirine sind nützliche Bausteine zur Einführung von α-substituierten α-Aminosäuren in Peptide [1]. Wir interessieren uns seit Jahren für die konformationellen Einschränkungen in Peptiden verursacht durch solche α-substituierten α-Aminosäuren. Als weiteres Motiv für die Einschränkung der Flexibilität von Peptidketten gilt die Thioamid-Gruppe.

Wir berichten hier über eine neue Methode zur selektiven Einführung einer Thioamid-Gruppe neben dem sterisch anspruchsvollen 2-Methylalanin (α-Aminoisobuttersäure, Aib) in ein wachsendes Peptid. Dies gelingt über eine Variation der 'Azirin/Oxazolon-Methode'. Im Mittelpunkt dieser Methode steht eine neuartige Isomerisierung von **1**→**2**, welche in Ausbeuten von ca. 90% ohne Epimerisierung verläuft.

Mit dieser Methode gelang es u.a. das Decaendothiopeptid **3** herzustellen. Von **3** und anderen Modellverbindungen sollen die Synthesen und die Röntgen-Kristallstrukturen diskutiert werden.



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[1] H. Heimgartner, *Angew. Chem.* **1991**, *103*, 271.

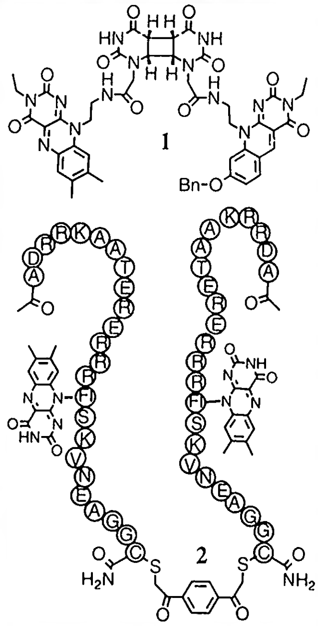
Organic Chemistry **214**

Model Compounds to Investigate DNA Repair Processes

Thomas Carell*, Robert Epple und Jens Butenandt

Laboratorium für Organische Chemie, Eidgenössische Technische Hochschule Zürich, Universitätstrasse 16, CH-8092 Zürich

In order to investigate the mechanism of the DNA repair enzyme DNA-photolyase, we have prepared **model compounds** like **1** and **2**.



Compound **1** contains a DNA-lesion building block, covalently linked to the cofactors (flavin, dezaflavins), which are essential for the repair. The results obtained from systematic studies; dealing with the solvent dependence, pH-dependence and dependence on the cyclobutane configuration and constitution, help to unravel the parameters which determine efficient lesion repair.[1]

We also report the synthesis of **chiral cofactor-aminoacids**, which were incorporated into the DNA-binding domains of transcription factors. Compounds like **2** are able to repair DNA which contains a **synthetic DNA-lesion**.

1) T. Carell *et. al, Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 620-623.
2) T. Carell *et. al, Angew. Chem. Int. Ed. Engl.* **1997**, *in press*.

Organische Chemie/ Medizinische Chemie **215**

New Photostable Fluorescent Labels for Proteins Using the Quinacridone Chromophore

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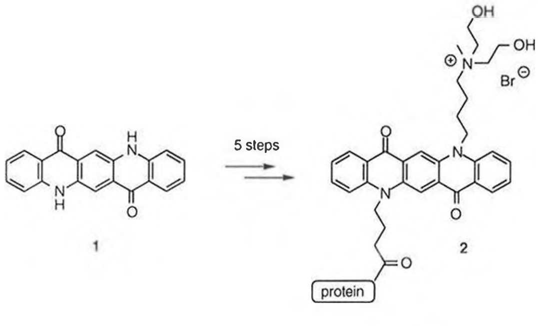
The Scripps Research Institute, 10550 North Torrey Pines Road, La Jolla, CA 92037

Fluorescence labeling of proteins gives the opportunity to monitor particular components of complex biomolecular assemblies as, for example, in living cells with high sensitivity and selectivity. A major drawback of this technique is the susceptibility of commercially available markers to photobleaching which limits the fluorescence monitoring time. Therefore we investigated the synthesis and use of soluble derivatives of quinacridone (**1**) as highly photostable fluorescence markers.



Several fluorescent labels were synthesized starting from **1** and were coupled to proteins to give conjugates such as **2**. These conjugates were found to be highly resistant to photobleaching and superior to the standard labels fluorescein and rhodamine.

Organic Chemistry **216**

Alanyl, homoalanyl and β-homoalanyl nucleo amino acids (PNA)

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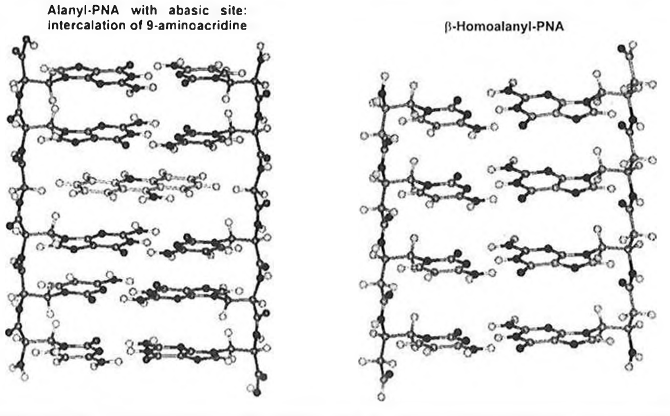
Org. Chemie & Biochemie TU München, Lichtenbergstr. 4, 85747 Garching

Peptide nucleic acids (PNAs) build of β-N9-adeninyl, β-N9-guaninyl, β-N1-thyminyl and β-N1-cytosinyl alanine are self pairing in linear complexes [1]. Pairing of G-C hexamers was observed forming a double strand with remarkable stability as well as band like structures [2]. A double strand lacking one base pair was shown to function as a host for intercalators [3].



Furthermore, we extended our studies to α- and β-homoalanyl-PNAs with interesting selectivity and tendency to stabilize in higher ordered structures.

[1] U. Diederichsen, *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 445-448.
[2] U. Diederichsen, *Angew. Chem. Int. Ed. Engl.* **1997**, in press.
[3] U. Diederichsen, *Bioorg. Med. Chem. Lett.*, submitted.

CHIMIA 51 (1997) Nr. 8/9 (August/September)

Physical Chemistry **217**

Investigation of size effects in heterogeneous catalysis using nanostructured multilayer systems

M. Schildenberger, Y. Bonetti, M. Aeschlimann, R. Prins

Catalytic reactions are referred to as *structure sensitive* or *size sensitive* if they proceed at different rates when carried out on metal particles of different crystallite sizes or different planes on a single crystal. Although investigated for many years, these size effects are not yet fully understood. Common catalyst systems used for such studies usually consist of particles having broad distribution of size and shape. Other model systems like single crystals with more defined size and structure properties, provide only small active areas. Furthermore, most of the in-situ investigation methods require high or ultrahigh vacuum conditions. We introduce a new kind of model catalysts, with which we try to bridge the usual gaps between model and more industrial oriented catalysis research.

To produce systems with a very narrow particle size distribution and an overall active area in the range of up to ten square centimetres, we use a combination of sputter deposition of up to several hundreds of metal and insulator bilayers onto a silicon wafer. After laser interference exposition of these sandwich layers they were etched by various techniques. The resulting catalytic system consists of arrays of „towers“ with lateral dimensions of less than 200 nm. The height will be about 500 nm and more. The metal layers (Pd, Pt or Ni) represent catalytically active surfaces on the side walls of each tower.

A special reactor was designed for the investigation of the catalytic properties of these new systems. The complete set-up is suitable for catalytic reactions in the gas phase at temperatures between 298K and 750K. It is possible to work at pressures from UHV (below $5*10^{-9}$mbar) up to 2000 mbar with on-line gas analysis by a quadrupole mass spectrometer at all pressures.

First tests have been made to study the oxidation of carbon monoxide. Then the hydrogenolysis of alkanes will be examined, another well suited reaction for the investigation of size effects.

Chimie physique **218**

Efficient Lateral Electron Transport Inside a Monolayer of Aromatic Amines Anchored on Nanocrystalline Metal Oxide Films

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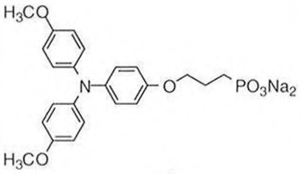
Abstract: A monolayer of a phosphonated triarylamine (**1**) adsorbed on a mesoporous nanocrystalline TiO_2 or ZrO_2 film deposited on conducting glass displays reversible electrochemical and electrochromic behavior in spite of the fact that the redox potential of the electroactive molecules (0.8 V vs NHE) lie in the forbidden band of the semiconductor. The mechanism of charge transport was found to involve hole injection from the conducting support followed by lateral electron hopping within the monolayer.

The electrochemical and electrochromic properties of the monolayers will be discussed, notably the existence of a sharp percolation threshold for electronic conductivity at a particular surface concentration of electroactive molecules. An electrochromic device exploiting the lateral electron hopping will be presented.



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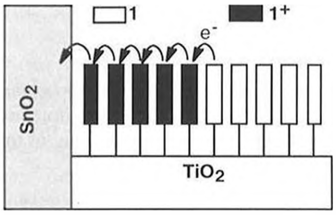

Physical Chemistry **219**

The Photochemistry of the Allyl Radical

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Hans-Jürgen Deyerl, Thomas Schultz, Thomas Gilbert, and Peter Chen

Laboratorium für Organische Chemie der ETH Zürich, 8092 Zürich

Radicals of particular importance for combustion processes or tropospheric chemistry are relatively stable ones that are converted into more reactive species upon photochemical excitation by radiation present in the particular environment. An example of such a system is the allyl radical, C_3H_5, which is excited into the UV-bands between 240 and 250 nm.

Time-resolved experiments indicate sub-100 ps lifetimes for these states, presumably due to internal conversion, forming hot allyl in its electronic ground-state, which subsequently loses hydrogen atoms. The two most important reaction channels lead to the formation of either allene or cyclopropene. The loss of hydrogen is monitored by resonant multiphoton ionization employing Lyman-α radiation. Microcanonical rate constants k(E) are obtained. From the Doppler profile of the hydrogen absorption band the translational energy release can be obtained. A statistical analysis shows that the data are in agreement with allene-formation being the dominant reaction channel.

Physikalische Chemie **220**

Reaction Rates and Yields in the Radiation Grafting Processing of Polymers : Base Polymer and Irradiation Effects

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Commodity polymer films can be transformed into membranes for separation and electrochemical applications by means of the pre-irradiation grafting method. We have developed a process shown in Figure 1, for the preparation of membranes for fuel cell applications. The grafting step in Figure 1 occurs by the grafting front mechanism shown in Figure 2.

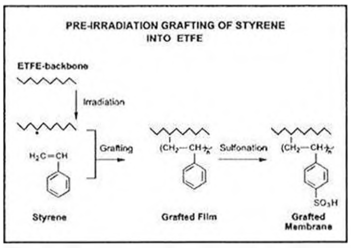

Fig 1. Pre-Irradiation Grafting Method

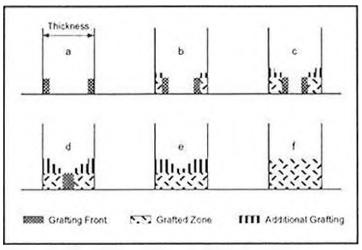

Fig. 2 Grafting Front Mechanism

In the present work the effects of such radiation processing parameters as (a) radiation source and (b) irradiation atmosphere and base polymer film properties as (1) perfluorinated versus partially fluorinated composition, (2) thickness, (3) molecular weight, and (4) orientation on the grafting reaction rate and yield are reported. Understanding these effects makes it possible to optimize our radiation-grafting processing conditions.

CHIMIA 51 (1997) Nr. 8/9 (August/September)

Physical Chemistry **221**

Nondestructive read-out of two-colour photon-gated spectral holeburning holograms at helium temperatures

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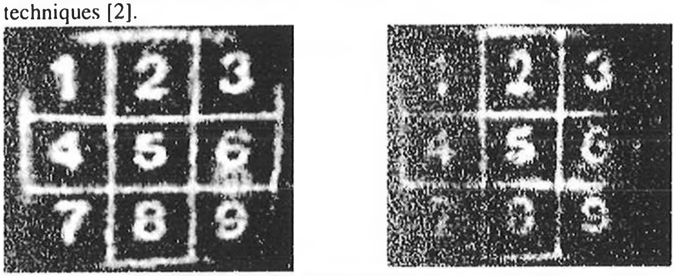
By using two-colour photon-gated persistent spectral hole burning at liquid-helium temperature we recorded picosecond photochemically accumulated stimulated photon echo (PASPE) holograms [1]. The so stored images have more than three orders of magnitude higher read-out stability compared with the one-colour process.

One can read the so stored holograms with high intensity without destroying the recorded information, i.e. after reading with about 10'000 times the writing energy the stored pattern is still visible, without using special storing techniques [2].



The image on the left shows the permanent hologram after the two-colour photon-gated persistent spectral hole burning. On the right one sees the same hologram after one colour reading of the numbers 1, 4 and 7 with 10'000 times the writing energy.

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Physical Chemistry **222**

Frequency Shifts of Single Molecules in Solids

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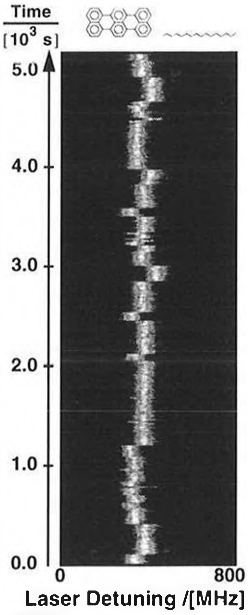
Single molecules are found to undergo spontaneous and light induced transition frequency changes at low temperatures in amorphous as well as in ordered hosts. Although "spectral diffusion" in amorphous systems is known from previous site selective techniques, it is only with the advent of single molecule spectroscopy [1] that these spectral dynamics can be studied with a great detail.

Some terrylene molecules doped in Shpol'skii systems exhibit a multistate behavior: their $S_1 \leftarrow S_0$ transition frequency is suddenly changing (jumping) to positions tens to hundreds of MHz far away in the time scale of seconds. These molecules are coupled to a few degrees of freedom of the guest/host system.

The figure shows the excitation spectra of a single terrylene molecule doped in *n*-hexadecane at 1.8 K. The spectra are recorded continuously, and plotted from bottom to top. The fluorescence intensity is proportional to the image brightness. This molecule is jumping between different frequency positions.



2000 frequency scans
256 points/scan, 10 ms/point
Excitation intensity 1 W cm^{-2}

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Chimie Physique **223**

Transfer Mechanisms of Ionizable Drugs and Solvatochromic Analysis of the Water/1,2-Dichloroethane Solvent System.

F. Reymond[1], G. Steyaert[2], P.-A. Carrupt[2], B. Testa[2] and H.H. Girault[1]

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Electrochemistry at the interface between two immiscible electrolyte solutions (ITIES) affords very promising perspectives to investigate the molecular mechanisms of organic ion distribution[1,2]. The problem, however, is that the solvents used in electrochemical measurements (mainly 1,2-dichloroethane (1,2-DCE) and nitrobenzene) are different from those traditionnally used in lipophilicity studies (*n*-octanol and alkanes).

In order to link the electrochemical results to the pharmacodynamic properties of ionizable drugs, the water/1,2-DCE solvent system has been characterised by a solvatochromic analysis[3]:

$$\log P_{DCE} = (3.7 \pm 0.6) 10^{-2} V_w - (2.44 \pm 0.72)\alpha - (4.21 \pm 2.72)\beta - (0.13 \pm 1.41);\ r^2 = 0.97$$

This analysis[4] shows no contribution of the polarizability term $\pi^{\bullet}$, and suggests that the water/1,2-DCE system may be more useful than the water/alkane system for measuring the H-bonding capacity of organic solutes (α and β terms) as a relevant parameter in structure-permeation relationships.

Otherwise, a general method to predict and interpret the transfer mechanisms of ionizable compounds at the ITIES has also been developed[5]. The approach is based on the construction of the ionic partition diagram of the solute, which consists in determining equiconcentration boundaries as a function of the Galvani potential difference and aqueous pH. The application of this method to several solutes offers a direct visualisation of all the species in both phases and demonstrates its validity and efficiency in understanding the transfer and partition mechanisms of ionizable drugs.

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Physical Chemistry **224**

Substrate optimization for hot electron induced reactions on surfaces

S. Pawlik, M. Bauer and M. Aeschlimann

One important step in many photochemical reactions between adsorbed species and a metal surface is the transfer of excited electrons from the surface into an adsorbate state. In addition to the chemical activity of the substrate, the number of electrons available for *hot electron transfer* influences the effectiveness of this process. This number will be reduced considerably by relaxation processes in the metal. Therefore a long lifetime of the electrons in the excited state is essential for an appropriate substrate.

Previous investigations have shown that the electrons in noble metals exhibit a long lifetime. However, they do not fulfill the requirement of high chemical activity. In contrast, the lifetime of electrons in the chemically more active transition metals is very short. One idea to combine both advantages is the use of a thin transition metal film on noble metal substrates.

We investigated the electron dynamics of Co on Cu as a function of cobalt coverage by using time-resolved two-photon photoemission. Our results indicate, however, that, after the deposition of only 3 ML Co, the lifetimes of the excited electrons are reduced to the typical cobalt bulk values.

The question arises as to whether a film thickness below 3ML Co will exhibit a remarkably higher activity than a clean copper surface. Recent CO hydrogenation studies have shown, however, that the chemical activity and selectivity of the Co/Cu system changes drastically with the thickness of the film. Maximum values, which are clearly enhanced compared to a thick cobalt film, are found at very low coverage.

Physical Chemistry **225**

Thermal Treatment of Glassy Carbon (GC) for Electrochemical Double Layer Capacitor (EDLC) Applications

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Department of General Energy Research, Electrochemistry Section
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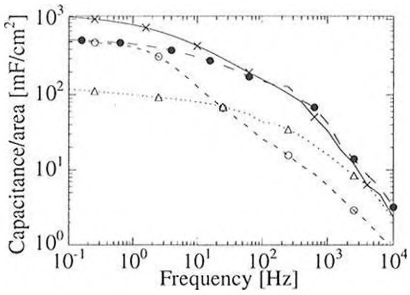
Due to its high porosity and low specific resistance [1], glassy carbon (GC) has a great potential to be used as electrochemical double layer capacitor (EDLC) electrodes for high energy and power density applications [2]. To access the internal surface, the inherently porous GC must be activated, e.g. by thermal oxidation [3]. Activation can open and enlarge closed pores and thus facilitate the penetration of electrolyte into the interior of the pores. High electrolyte transport rates into the interior of the pores are important to maintain high capacitance at high frequencies. Results are presented here on the double layer capacity and impedance of thermally activated GC. Whereas nonactivated GC has a double layer capacitance of 20 µF/cm², the activated GC samples have capacitance values up to 5 decades higher.



Capacitance vs. frequency for differently activated samples. (o): 400°C, 2 hours; (×): 450°C, 2h; (•): 500°C, 2h; (Δ): 550°C, 1h.

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Physical Chemistry **226**

Characterization of Electrolytic Manganese Dioxide using Adsorption Techniques and AFM

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Institut de Chimie de l'Université de Neuchâtel, Av. de Bellevaux 51, 2000 Neuchâtel

Electrolytic manganese dioxide (EMD) has a crystal structure of the γ type. Its superior battery performance to that of α and β types is thought to be due to differences in the surface. Therefore we decided to do a thorough surface study of EMD using various techniques.

Enthalpies of immersion were measured in solvents of varying polarity (H_2O, CH_2Cl_2, undecane). Surface areas were determined from N_2, C_6H_6, and H_2O adsorption isotherms. Contact and tapping mode AFM were used to image the surface and analyse its topography.

The data obtained from the different methods were compared with those obtained for α and β MnO_2 and provide new insight into why EMD is a better cathode component.

Physical Chemistry **227**

DEMS investigation of the electrolyte degradation in Li⁺-ion batteries

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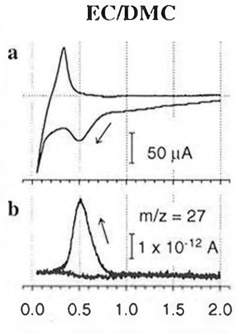
Paul Scherrer Institute, Electrochemistry, CH-5232 Villigen PSI

Li^+-ion batteries based on intercalation materials are among the most important recent improvements in battery technology. Irreversible charge losses during the first charging cycle due to electrolyte decomposition are still a major problem however. Differential electrochemical mass spectrometry (DEMS) has been used to study the reductive decomposition of cyclic and open-chain organic carbonate electrolyte solvents on composite graphite electrodes. The DEMS technique allows the detection of gaseous and volatile products formed in an electrochemical reaction cell. Cyclic voltammetry (CV) was carried out and mass signals were recorded simultaneously as a function of the potential (MSCV).

We observed that ethylene carbonate (EC) and propylene carbonate (PC) decompose to form ethylene and propylene, respectively. In the case of dimethylcarbonate (DMC) no volatile degradation product could be detected. The figure shows an experiment with EC/DMC/ 1 M $LiClO_4$ at a scan rate of 0.4 mV/s. Ethylene is represented in the MSCV by the mass m/z 27 (Fig. part b). The other detected masses of ethylene (m/z 28, 26, 25, 24) are not shown but they behave similarly. Gas evolution is restricted to a potential window between about 0.8 and 0.3 V vs. Li/Li^+. The mass signal can be correlated with a cathodic current peak in the CV (Fig. part a), which is proposed to correspond to the solvated intercalation of Li^+ ions and the formation of a solid electrolyte interphase. Ethylene and the cathodic current peak in the CV are not found in the second scan. EC/PC and EC/PC/DMC behave analogous. Similar experiments on nickel electrodes did not show ethylene/propylene evolution.



Physical Chemistry **228**

Influence of the nature of the graphite surface on protective film formation in lithium ion cells

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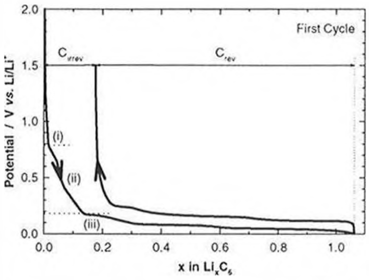
Recently, carbon electrodes achieved enormous technical importance for rechargeable lithium ion cells. Fundamental to their successful operation is the formation of a protective film due to the reductive decomposition of the electrolyte. Lithium ions are consumed for the formation of the protective film. This lithium consumption decreases the energy density of the cell, and thus it is desirable to minimize this irreversible charge loss (C_{irrev}).

We distinguish between three types of charge losses (see figure): (i) the reduction of the surface groups above ca. 0.8 V vs. Li/Li^+, (ii) the charge loss due to the film formation between ca. 0.8 V and ca. 0.2 V vs. Li/Li^+, and (iii) moderate self discharge in addition to the reversible Li^+ insertion. We have studied the influence of the nature of the graphite surface on the film formation and the intercalation properties of the graphite TIMREX SFG 6, which has a high BET specific surface area of ca. 15 m²/g, and therefore a high charge loss. If the surface groups of graphite are modified, e.g., by oxidation, reduction or vacuum treatment, a different surface film is formed, which can be seen in the shape change of the discharge curve between 3 V and 0.2 V vs. Li/Li^+ (i+ii). Discharge curves and lithium intercalation properties of modified graphites will be discussed with respect to minimizing the charge loss in the first cycle.



Physical Chemistry **229**

Gibbs Paradox of Entropy of Mixing

Shu-Kun Lin

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Gibbs paradox says that entropy of mixing *decreases* discontinuously with the increase in molecular similarity. It also implies that entropy (S) of a system *decreases* with the increase in its symmetry, or $S = -k \ln w$ (w: the symmetry number, e.g., the permutation symmetry number $N!$ of an ideal gas of N particles). It is assumed that these relations of entropy are applicable to the formation of a solid, liquid, or gaseous mixture and to the mixing of quantum states. A large number of chemical and physical observations have been presented to show that the Gibbs paradox of mixing is itself wrong [1]. It is shown here that the Gibbs paradox statement is false. We disprove it firstly through the entropy additivity principle, Secondly, from group theory, any system has a symmetry number $w \geq 1$ ($w = 1$ for the identity operation of a strictly asymmetric system). It follows that the entropy of any system is equal to, or less than, zero, following the Gibbs paradox statement. This violates the definition of entropy which is non-negative. Thirdly, Gibbs's statement of entropy and similarity obviously violates the inequality $-\sum_{i=1}^{w} p_i \ln p_i \leq \ln w$. In conclusion, $Z = S/S_{\max} = -\left(\sum_{i=1}^{w} p_i \ln p_i\right)\big/\ln w$ defines a similarity index, and entropy *increases* continuously with the property similarity of the w microstates or w subsystems. Entropy also *increases* with the symmetry [2]: $S = k \ln w_a$ (w_a: the apparent symmetry number). The theoretical consequences in chemistry will be discussed.

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Physical Chemistry **230**

Entropy of Mixing, Hydrophobic Effect and Protein Folding

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A new theory of entropy of mixing that entropy of mixing or entropy of assembling *increases continuously* with the increase in the similarity of the components, has been developed based on the abandoning of the conventional statistical mechanics theory of mixing process [1-3]. This theory has given a perfect explanation of the process spontaneity of the hydrophobic effect and the protein folding phenomena. It also provided foundation for quantitative calculation of changes of thermodynamic parameters, particularly entropy and free energy.

Acknowledgments: This work has been performed at ETH-Zürich and in Basel. The author is grateful to Professor B. Jaun (ETH-Zürich) and Dr. V. Rassetti (Ciba-Geigy AG) for their kind supports.

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Physical Chemistry **231**

Negative and Positive Temperatures of Static and Dynamic Aspects

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According to definition, total energy E and entropy S are both positive for any system. However, temperature T defined as $(\partial E/\partial S)_{N,V} = T$ may be either positive or negative [1]. Following this definition and the general criteria [1] for negative temperature, for any well-defined entropies of any systems of hierarchical structures, correspondingly temperature(s) can be defined, at least formally. We found that every system has symmetries of *static* and *dynamic* aspects [2] and the two entropies and their variations can be defined and in principle calculated according to $S = k \ln w_a$, where w_a is the apparent symmetry number or the order of the group [2].

Therefore, for a conventional thermodynamic system, because information registration involves reduced *static* symmetry ($\Delta S_s < 0$) [2] and the energy increase ($\Delta E > 0$) [3], a negative temperature T_s (s for static) can be formally defined, while the *dynamic* motion of such system has a conventionally understood positive temperature T_d (d for dynamic).

Similarly, however, for a system of electronic motion in a single atom or a molecule, the T_d of the local electronic *dynamic* motion is found to be negative with the most negative value at the electronic ground state, while its local T_s of the *static* aspect of the electronic structure, such as spin parallel orientation at excited states, is positive.

It is convenient to use these temperatures to characterize symmetry breaking phenomena at any one of many hierarchical structures in nature.

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Physical Chemistry **232**

Excitation Wavelength Dependence of Charge Separation at the Semiconductor-Dye Interface. Evidence for Adiabatic Electron Transfer

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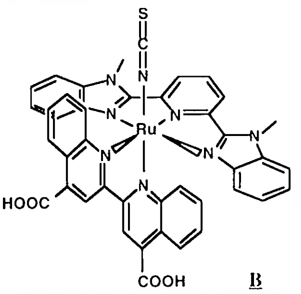
Spectral sensitization of a wide bandgap semiconductor is achieved by adsorption of dye molecules (S) or molecular aggregates on its surface which, upon optical excitation, inject an electron in the conduction band of the solid:

$$S^* \rightarrow S^+ + e^-_{cb}(SC)$$

Ultrafast spectroscopic investigations show that vibrational relaxation of the MLCT excited state of cis-Ru(II) bis (4,4'-dicarboxy-2,2'-bipyridyl) bis-thiocyanate (**A**) and Ru(II) (4,4'-dicarboxy-2,2'-biquinoline) 2,6-bis(1'-methyl-benzimidazol-2'-yl) pyridine thiocyanate (**B**) complex dyes takes place within 2-4 ps. The charge injection process has been found for such sensitizers adsorbed on the surface of TiO_2 to occur much faster, in less than 150 fs [1]. The ET reaction is thus expected to proceed adiabatically.



B

We report here on the wavelength dependence of the charge separation efficiency, measured by ns flash photolysis in **A**/Nb_2O_5 and **B**/TiO_2 systems. In these cases, the v=0 energy level of the MLCT excited state of both adsorbed dyes lies below the bottom of the conduction band of the respective semiconductors. The observed excitation energy dependence provides an evidence that interfacial charge transfer is indeed occurring prior to nuclear relaxation of the dye excited state. It also offers an easy way to determine the electron coupling matrix element that controls the rate of the ultrafast process.

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Physikalische Chemie **233**

Selective Catalytic Reduction (SCR) of NO by NH_3 over Vanadia-Based Catalyst: Parametric Sensitivity and Kinetic Modeling

B.Roduit, M.Maciejewski, R.A. Köppel, A.Wokaun and A. Baiker
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Combining non-isothermal and isothermal experiments, the kinetics of the SCR of NO with NH_3 over a vanadia-based commercial $DeNO_x$-catalyst has been studied for temperatures between 150 and 475°C and a mechanistic model has been developed. The determination of the parametric sensitivity of NH_3, NO, O_2, H_2O partial pressures and the independent calculation of the kinetic constants have been achieved by varying the temperature and concentrations of the gaseous reactants. The investigation of transport phenomena revealed a strong influence of internal mass transfer processes especially at high temperatures which has been considered in the calculations. The kinetic results are explained with the presence of different types of adsorbed species on the catalyst surface which are controlled by their immediate surface environment. The results indicate that NH_3 is adsorbed on V-OH sites as NH_4^+ and activated by an adjacent V=O site. The resulting activated ammonia can react with gaseous or weakly adsorbed nitric oxide on the catalyst surface producing N_2 and H_2O. As a side reaction adsorbed ammonia is oxidized by lattice oxygen leading to N_2 and H_2O. Lattice oxygen is involved in both reactions: SCR and direct NH_3 oxidation. On the oxide surface V=O and V-OH sites as well as oxygen vacancies are continuously created and consumed in the presence of O_2 and NO. The replenishment of the sites occurring through gaseous NO is much less significant. Consequently, the reaction proceeding between adsorbed ammonia and gaseous or adsorbed nitric oxide can be expressed by Eley-Rideal or Langmuir Hinshelwood kinetics, respectively. The direct oxidation of NH_3 proceeds between strongly adsorbed ammonia and lattice oxygen according to a Langmuir Hinshelwood mechanism. The adsorption and desorption phenomena and the reaction of the adsorbed species with lattice oxygen and nitric oxide has been confirmed by conventional thermal analysis and by novel pulse thermal analysis (PTA).

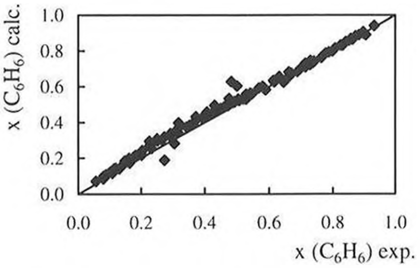
Physical Chemistry **234**

Binary Adsorption of Vapors in Active Carbons described by the combined Theories of Myers-Prausnitz and Dubinin

D. Wintgens, P. Girardin and F. Stoeckli

Institut de chimie de l'Université, Bellevaux 51, CH-2000 Neuchâtel

We have recently proposed a new method based on the combined theories of Myers-Prausnitz and Dubinin, to describe binary adsorption by microporous solids [1]. It has been applied to the adsorption of benzene + 1,2-dichloroethane vapours by a typical active carbon at 293 K. Good agreement is found between the experimental and calculated values of the adsorbed mole fraction of benzene, $x(C_6H_6)$:



Although the liquid mixture is ideal, one observes some deviation from Raoult's law in the adsorbed state, with a clear preference for benzene. This is confirmed by experiments on the liquid-solid equilibrium of the mixture, leading to similar values of activity coefficients as in the vapour-solid equilibrium. As suggested by other systems, and to be discussed in more detail, it is the result of the strong adsorption field in the micropores.

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Section Chemical Research of the NSCS

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A Selection of Papers Presented at the Fall Meeting of the New Swiss Chemical Society (NSCS) in Basel, November 21, 1996

The Section Chemical Research (SCR) of the New Swiss Chemical Society (NSCS) has decided to publish each year in CHIMIA a collection of short papers (1–2 pages each) corresponding to the most remarkable posters or oral contributions presented at the Fall Meeting of the NSCS. The main purpose of this action is to enable the authors of the awarded contributions to develop somewhat their presentation at the Fall Meeting so as the whole readership of CHIMIA may have a chance to be aware of it. The choice of the awarded contributions is made by the Committee of the SCR which takes the responsibility for the part of subjectivity inherent in such a selection. This CHIMIA issue presents a paper pertaining to the field of inorganic chemistry, whereas those related to organic chemistry, physical chemistry and computational chemistry have already been published in the CHIMIA issue 3, p. 90–99.

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The Metal Oxo [1,2]-Alkyl Shift – Towards the Aerobic Oxidation of Hydrocarbons[a])

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Abstract. The syntheses and X-ray crystal structures of novel monocyclopentadienyl tungsten(IV) and molybdenum(IV) complexes with additional 4,4'-disubstituted 2,2'-bipyridine ligands are presented. The preference for the observed μ-O bridged dimeric structure in the $[Cp^*Mo,W(\mu\text{-}O)(4,4'\text{-}R_2\text{-bipy})]_2^{2+}$ compounds rather than a monomeric structure with a terminal M=O unit is rationalized by Extended *Hückel* MO calculations. In addition, a synthetic route to C_1-, C_2- and Si-bridged *ansa*-magnesocenes is described and X-ray crystal structures of representative examples displaying an unsymmetrical cyclopentadienyl binding mode are provided. The *ansa*-magnesocenes are excellent starting materials for the syntheses of bridged dicyclopentadienyl ditungsten complexes with W,W multiple bonds. The X-ray crystal structure of the C_1-bridged tetrakis-dimethylamide compound, $Me_2C[(\eta^5\text{-}C_5H_4)W(NMe_2)_2]_2$, is presented.

Introduction and Background

Chemistry in our group is directed towards the development of new methods for the *aerobic* oxidation of organic substrates with an emphasis on alkane functionalization, *e.g.*, the oxidation of CH_4 to CH_3OH. Mechanistically, this requires quite a number of very challenging steps, such as O_2 and C–H bond cleavage, C–O bond formation *etc*. The focus of our current investigations is the development of the *thermal non-radical* oxygen transfer step shown below:

$$\overset{R}{\underset{|}{}}[M]{=}O \longrightarrow [M]{-}O{-}R$$

So far, however, still very little is known about the R–M=O [1,2]-shift [1]; it deserves special mentioning that *Sharpless* and coworkers have included this step in their mechanistic scheme for the enantioselective *cis*-hydroxylation process of olefins using OsO_4/chiral amine ligands [2].

Poster Presentations

One of our target systems, the novel mononuclear cyclopentadienyl tungsten(IV) oxo methyl complex Me–[W]=O is shown in *Fig. 1*.

The 4,4'-disubstituted 2,2'-bipyridine (bipy) ligands in these complexes cover a wide range of σ(*Hammett*) parameters and have been chosen to examine exclusively the electronic nature of the [1,2]-shift. The synthetic access to this type of W^{IV} compound was sought *via* the hitherto unknown tungsten(IV) complex, $(Cp^*WCl_3)_2$. This extremely air-sensitive paramagnetic complex was obtained by one electron Na/Hg reduction of Cp^*WCl_4; its dimeric structure was confirmed by single crystal X-ray diffraction (*Fig. 2*).

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[a]) These results were presented as posters (100–102) at the autumn meeting of the New Swiss Chemical Society (NSCS) in Basel, Switzerland, on November 21, 1996.

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The puckered arrangement of the $W_2(\mu\text{-}Cl)_2$ unit in the $(Cp^*WCl_3)_2$ *syn*-dimer enables a bonding metal-metal interaction – the observed W–W distance of 305.3(1) pm is in the range of W–W single bonds. The dimer is an excellent starting material for the synthesis of $Cp^*WCl_3(4,4'\text{-}R_2\text{-bipy})$, *i.e.*, upon addition of the 2,2'-bipyridine ligands facile cleavage of the dimer occurs and the weakly paramagnetic, pseudo-octahedral $4,4'\text{-}R_2$-bipy complexes are obtained in good to excellent yields. Weakening of the W–Cl bonds in the latter electron rich compounds is indicated through the observation of elongated W–Cl bonds (avg. 250 pm) in the X-ray crystal structure of the methyl derivative, $Cp^*WCl_3(4,4'\text{-}Me_2\text{-bipy})$. This is further corroborated by conductivity measurements in solution and through the formation of the cationic 16-electron species, $[WCl_2Cp^*(4,4'\text{-}Me_2\text{-bipy})]^+$, upon halide abstraction. The introduction of the oxygen ligand is straightforward by hydrolysis in deoxygenated H_2O, and, upon salt exchange with PF_6^- or SbF_6^- the dimeric $(\mu\text{-}O)_2$-bridged dicationic complexes are obtained in excellent yields. The X-ray crystal structure of the dark-blue, highly coloured ($\varepsilon \approx 10^4\ l{\cdot}mol^{-1}{\cdot}cm^{-1}$) methyl derivative ($Me_2$-bipy) (*Fig. 3*) confirmed the dimeric structure and based on the W–W distance of 273.2(1) pm and electron counting arguments, a W=W bond is proposed.

The formation of dimers puzzled us for a while since the analogous Mo phosphine complex with the small PMe_3 ligand, $[MoCp(PMe_3)_2(=O)]^+$, has been reported earlier by *Green et al.* to be monomeric both in solution and in the solid state [3]. Initially, we anticipated steric arguments would explain this apparent difference. However, since we could show that the analogous tungsten complex with the bulky $4,4'\text{-}(t\text{-}Bu)_2$-2,2'-bipyridine ligand is also dimeric, it was deemed that electronic factors are determining the dimer formation. To rule out that the formation of the dimers is due to a stronger metal–metal bond in the ditungsten complexes, we have also prepared and crystallographically characterized the corresponding Mo complex, $[MoCp^*(\mu\text{-}O)(4,4'\text{-}Me_2\text{-bipy})]_2^{2+}$. Its dimeric structure could unambiguously be demonstrated in the solid state by X-ray crystallography and in solution by UV/VIS- and IR-spectroscopy. This suggested that other/additional factors are operative leading to a preference for the observed μ-O-bridged complex rather than a monomeric structure with a terminal M=O unit, *i.e.*, $[Cp^*Mo,W(=O)(4,4'\text{-}Me_2\text{-bipy})]^+$.

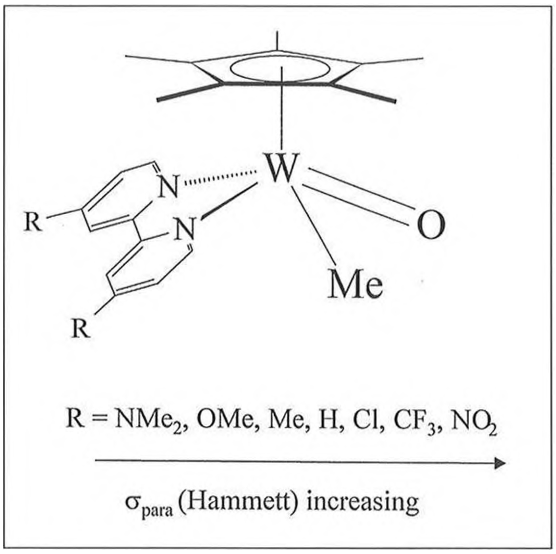

Fig. 1. *$[W(=O)Cp^*(Me)(4,4'\text{-}R_2\text{-}2,2'\text{-bipyridine})]$ system*

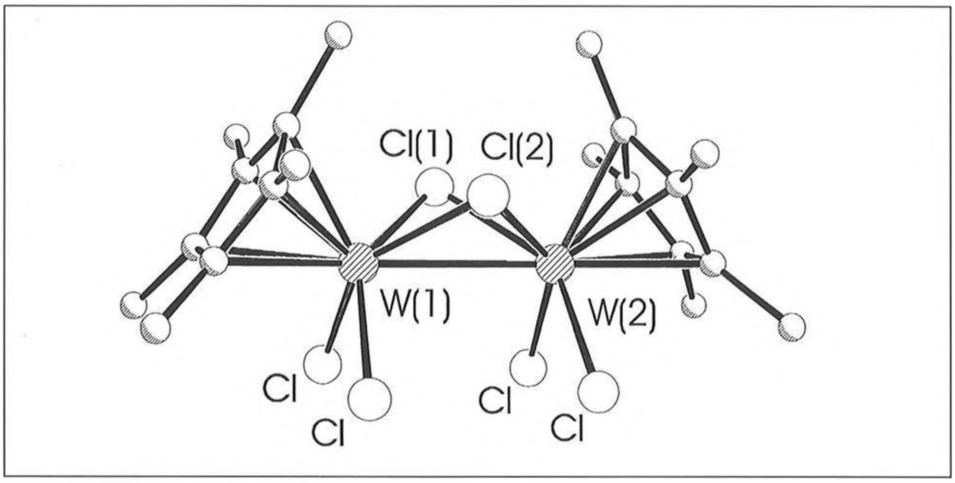

Fig. 2. *X-Ray crystal structure of dimeric $[WCp^*Cl_3]_2$*

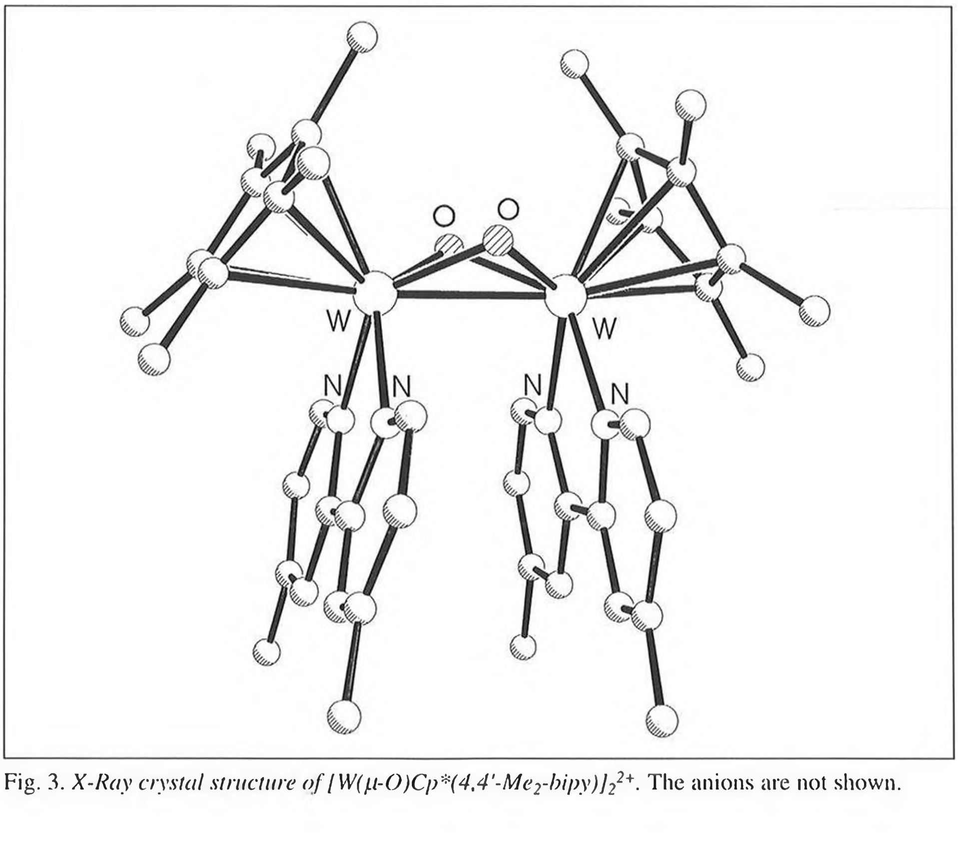

Fig. 3. *X-Ray crystal structure of $[W(\mu\text{-}O)Cp^*(4,4'\text{-}Me_2\text{-bipy})]_2^{2+}$*. The anions are not shown.

Finally, we turned to extended *Hückel* (EHT) calculations to investigate differences in the electronic structures of the phosphine and bipy compounds. These were performed for the hypothetical monomeric model complexes, $[W(=O)Cp(PH_3)_2]^+$ and $[W(=O)Cp(HN=CH–CH=NH)]^+$, in idealized C_s symmetry with the diimine (HN=CH–CH=NH) and the PH_3 ligand representing the bipy and the PMe_3 donors, respectively. The inspection of the frontier orbitals in both complexes provided a nice rationale for the observed structural difference in the N- and P-donor substituted complexes (*Fig. 4*).

Although the MOs have apparently a great resemblance in both model compounds, there is a major difference between the diimine and the PH_3 ligand substituted complexes. It can be immediately recognized from *Fig. 4* that the HOMO and LUMO are *inverted* in the N- and P-donor compounds. In the N-donor complex the LUMO is essentially a W-centered d_z^2 orbital which is perfectly suited as an *acceptor* MO for donation from the oxygen n-orbitals to form the observed dimeric complex. On the contrary, the d_z^2 orbital in the phosphine compound is *filled* (HOMO). It is, therefore, no longer available as an acceptor MO thus providing an explanation why these molecules prefer to be monomeric.

Since this unique orbital is essentially a non-bonding metal based d_z^2 orbital, its energy is (as expected) independent from the type of donor ligand (*cf. Fig. 4*). Hence, the inversion of the HOMO/LUMO in the two related systems has to be associated with the other sets of orbitals shown in *Fig. 4*. Inspection of the latter orbitals, the HOMO in the N-donor and the LUMO in the phosphine complex, reveals that they are π^*-antibonding with respect to the W=O unit in both molecules. In the diimine complex, however, π-back donation to the low lying π^* orbital of the N-donor ligand gives rise to an overall lowering of the energy. In the phosphine substituted complex on the other hand, there is no interaction of this type and therefore the d_z^2 W-centered orbital becomes the HOMO.

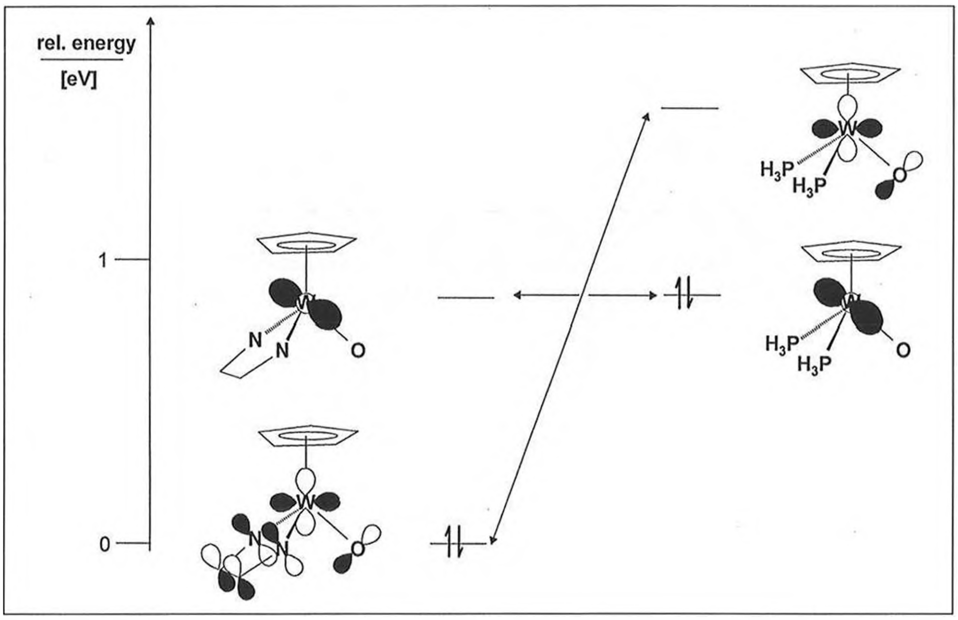

Fig. 4. *HOMO and LUMO for* L_2 = *diimine* (left) *and* $L_2 = (PH_3)_2$ (right) *for* C_s*-symmetrical* $CpWL_2(=O)^+$ *model systems*

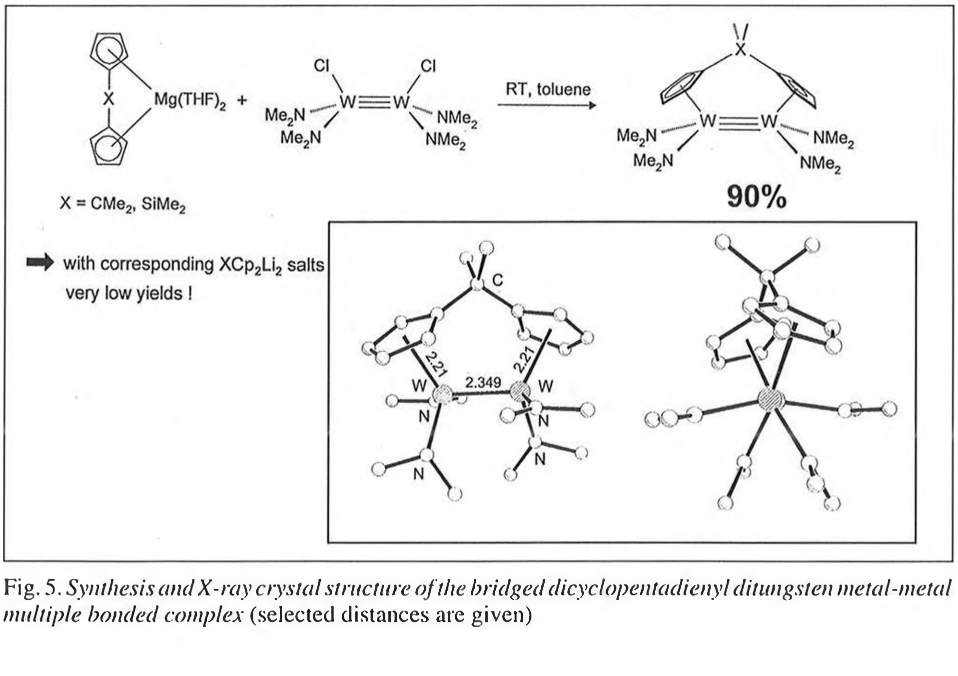

Fig. 5. *Synthesis and X-ray crystal structure of the bridged dicyclopentadienyl ditungsten metal-metal multiple bonded complex* (selected distances are given)

From this picture it becomes evident that the extent of π-back donation has a strong influence on the ordering of the frontier orbitals. This suggests that one might also be able to obtain monomeric complexes for the N-donor compounds with poor π-acceptor bipy ligands, *e.g.*, 4,4'-$(NMe_2)_2$-bipy. We are currently in the process of obtaining experimental support for this idea – the latter ligand system would also allow to perform a nice additional check: For the corresponding complex with the protonated 4,4'-$(NHMe_2^+)_2$-bipy ligand once again a dimeric structure, *i.e.* $[W(\mu\text{-}O)Cp^*(4,4'\text{-}(NHMe_2^+)_2\text{-bipy})]_2^{2+}$, would be expected due to the enhanced π-accepting power of the protonated N-donor.

In an additional poster presentation, we have described the syntheses and X-ray crystal structures of metal–metal multiple bonded dinuclear complexes, [M]≡[M]. Still within the framework of non-radical oxidations, research in this area is inspired by the idea that the metal-metal multiple bond in these compounds might serve for 'clean' O_2 activation and lead to facile formation of two [M]=O units. Shown below is the synthesis and X-ray crystal structure of one representative example, the novel C_1-bridged dicyclopentadienyl tetrakis-dimethylamide ditungsten complex (*Fig. 5*).

Although the synthesis of the related unbridged cyclopentadienyl complexes had been described earlier by *Chisholm* and coworkers [4], our initial attempts to obtain bridged W≡W bonded ditungsten complexes using the rather insoluble lithiated Cp reagents, $(Cp_2X)Li_2$ (X = CMe_2, $SiMe_2$) had only been of very limited success. Since this was attributed to the formation of cyclopentadienyl bridged oligomers, well-defined, soluble Cp transfer reagents were sought to apply the dilution principle. As shown in *Fig. 5* (top trace) use of the novel, soluble *ansa*-magnesocenes, for which a new route was

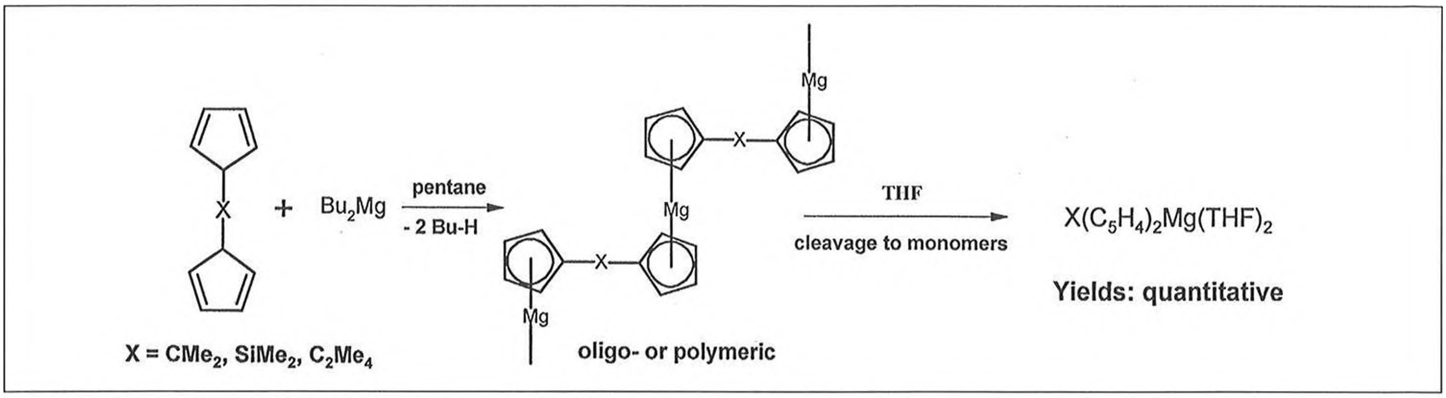

Fig. 6. *Syntheses of* ansa-*magnesocenes*

developed (*Fig. 6*) indeed gave the desired ditungsten complexes in excellent yields.

With this, a complete new research area was opened that led eventually to the discovery of the unusual cyclopentadienyl coordination mode in the bridged magnesocenes. This is best presented by the X-ray crystal structure of the C_1-bridged *ansa*-magnesocene · 2 THF shown below (*Fig. 7*).

We have now quite a number of further examples for the unsymmetrical binding of cyclopentadienyl ligands in bridged $X(Cp_2)Mg(L)_2$ complexes with X = CMe_2, C_2Me_4, $SiMe_2$ and L = σ-donor. Very recently, we even were able to isolate an exciting analogue of the Mg complex with the weak methyl isonitrile donor, for which we had expected *some* stability based on prior density functional theory (DFT) calculations. The X-ray crystal structure of this compound is shown in *Fig. 8*.

In solution, these molecules are highly fluxional and evidence for ligand dissociation processes from $XCp_2Mg(L_2)$ with concomitant formation of $XCp_2Mg(L)$ and XCp_2Mg has been provided by VT NMR-studies.

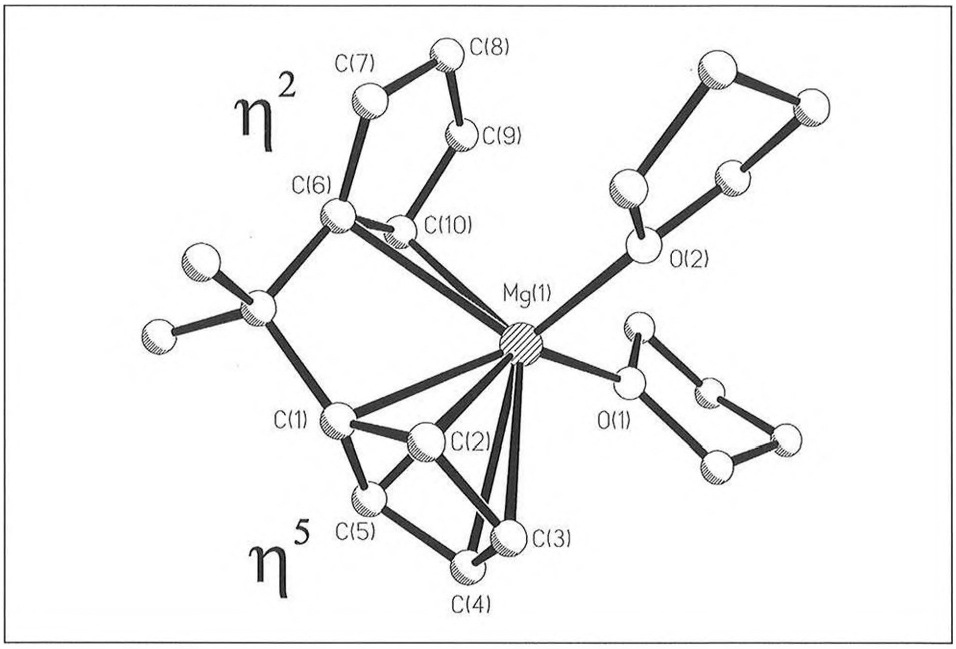

Fig. 8. *X-Ray crystal structure of the first Mg isonitrile complex, $Me_2C(C_5H_4)Mg$* (THF)(CNMe) (selected distances are given)

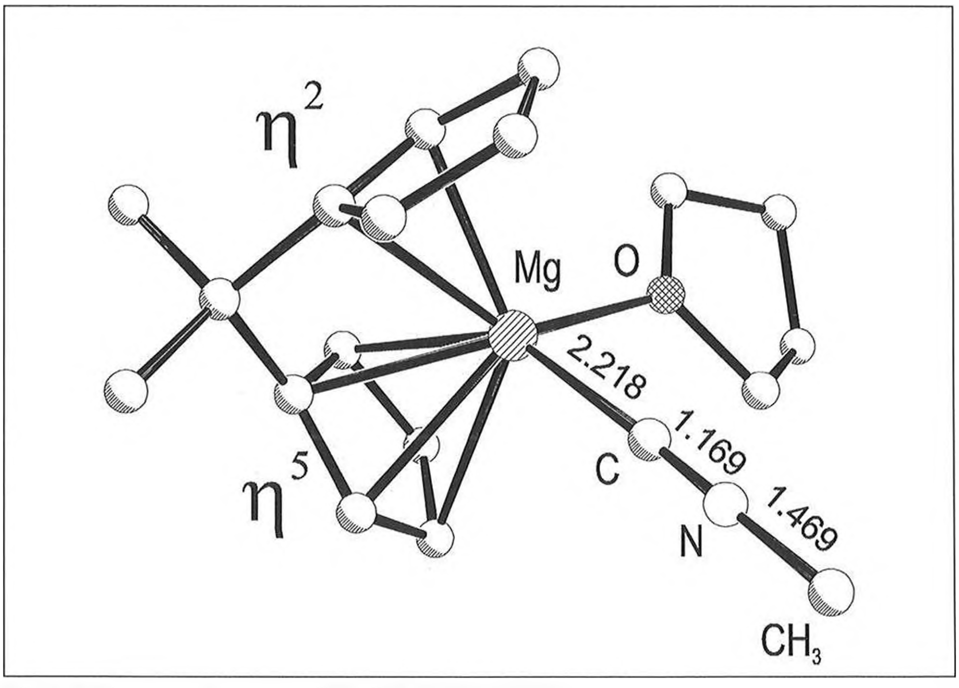

Fig. 7. *X-Ray crystal structure of $Me_2C(C_5H_4)Mg \cdot 2$ THF*

We feel very honoured for receiving this award and would like to thank the poster committee for the opportunity to present our research in some more detail in this issue of CHIMIA. We are indebted to Prof. *Heinz Berke* for his ongoing support and his interest in our research. Funding by the *Schweizerische Nationalfonds* (project 2100-047085.96) is gratefully acknowledged.

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News and Trends in Analytical Chemistry: Pittcon'97

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Abstract. In the following article on 'New Trends in Analytical Chemistry: Pittcon'97', a personal view of striking new developments in analytical chemistry is given. The overview is far from being complete. However, it may motivate colleagues to participate in a spectacle which remains to be important in order to identify general trends and capabilities of analytical chemistry.

Pittcon is not a conference about combinatorial chemistry, not is it about nuclear magnetic resonance, mass spectrometry, spectroscopy, sensor technology, process monitoring, or life sciences. What then is it? 'A gigantic performance which mirrors all trends in analytical chemistry immediately after they rose' is the answer. Pittcon'97, the 48th Pittsburgh Conference on Analytical Chemistry & Applied Spectroscopy from March 17–21, 1997, was 'performed' at Atlanta's Georgia World Congress Center. The city and its surroundings are still splendidly coined by the 16 days of the '26th Olympic Games' which opened on June 20, 1996.

Different from the Olympic Games, during Pittcon'97 only nine medals were awarded, however, to well-known scientists in chromatography, spectroscopy, general analytical chemistry, bioanalytical and pharmaceutical applications, as happens traditionally each year. 'Traditional' is not how one usually describes US life style, but analytical chemistry is not typical. 'Traditional' refers to its long history and its widespread acceptance as an important science in the USA. Even if many inventions stem from Europe, it is in the USA where new developments are 'caught', discussed, encouraged, and implemented by companies. At Pittcon, 35 000 participants (*ca.* 14 000 exhibitors and 21 000 conferees) are expected every year. The conferees have to choose between visiting the exhibition, where *ca.* 1100 booths are involved regularly, or one of the 18 parallel sessions during the five days of the conference. This creates the typical heady and tantalizing atmosphere. Some luck is needed in order to select the most informative sessions which provide a high yield in news. Otherwise, the conferee ends up misspending his valuable time.

Where in the world is it possible to listen to excellent talks by five leading analytical scientists within the same session, which went on for *ca.* 150 min. This valuable, inspiring, and visionary session was entitled

'The Future of Analytical Instrumentation'.

NMR Techniques

NMR is a method which is unrivalled in providing structural information about chemical compounds. However, the time-scale of getting a response and the resolution are insufficient for many analytical applications. Nevertheless, the first talk entitled 'NMR: Rumors of Its Demise Are ...' given by *Alexander Pines* (University of California at Berkeley) succeeded in convincing us that the demise of NMR for analytical use was a long way off. *Pines* described evolving techniques in solid-state NMR, magic angle spinning [1], and multiple quantum spectroscopy. Magic angle spinning of solids results in spectra comparable to liquids and allows monitoring of highly resolved two- and three-dimensional spectra including those of isotopes with quadrupolar effects and negative magnetogyric ratio such as ^{15}N [2–4]. In another part of his talk, he showed the influence of spin polarization and visioned NMR imaging of the air space in the lung based on ^{17}O-NMR. A nearly 100% spin-polarization effect is exerted on ^{17}O by spin-polarized ^{3}He or ^{129}Xe nuclei, which are polarized by circularly polarized laser light. In this way, ^{17}O and the air space can be imaged as in a condensed phase. The patient inhales the nobel gas and refrains from exhaling and breathing for 25 s. The polarized state can be maintained for hours and even days and can serve to enhance the effects of injected compounds [5][6].

The trend to develop smaller instruments with high resolution was illustrated in *Yannoni*'s (*IBM* Almaden Research Center, San Jose, CA) session of MRFM (Magnetic Resonance Force Microscopy) [7]. The MRFM tip is magnetic and generates a magnetic field gradient relative to a magnetic field gradient source. Simultaneously, the tip selects a volume of resonant spins, permitting magnetic resonance imaging (MRI).

The benefits of coupling a NMR-radio-frequency microcoil to a polyimide-coated HPLC microbore column (76.5 μm ID, 357 μm OD) have been known since 1994 [8]. At that time, the technique was not thought particularly attractive since the signals were lost in the noise, and the line widths of 11 Hz prevented the observation of proton scalar coupling. A 100-fold increase in the mass sensitivity (signal-to-noise ratio) compared to conventional H NMR was obtained when: the coil region of the 5-nl capillary detection cell was surrounded with a magnetic suscepti-

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bility matching fluid, a perfluorinated organic liquid, using a 5-mm spinning tube for comparisons and a 300-MHz (7.05 T) spectrometer [9].

Mass Spectrometry

The development of instruments in mass spectrometry has been specially influenced by the requirements of both parallel and combinatorial chemistry, and molecular biology. The latter requires the analysis of biological species such as peptides, proteins, and nucleotides, whereas in parallel and combinatorial chemistry, it is desirable to have instruments that are: small (bench-top instruments) and fast coupled to high throughput, that consume little sample and that allow continuous monitoring. In trying to meet these requirements, standard instruments with relatively low mass resolution (m/z 1000–1500) have been linked to the sample flow between reactor/UV detector and fraction collector (*D. Kassel*, *CombiChem*, UK). The sample is splitted, but only 1–5% of the relatively large sample volume is consumed by the ESI/triple-Q mass spectrometer (*e.g.*, *PE SCIEX API 165 LC/MS* and *API 365 LC/MS/MS*). *Hewlett-Packard* showed up with an open titer-plate collector coupled to the MS detector. Recently, however, direct sampling from the titer plate by MALDI-TOF has been proposed by *G. Siuzdak*, La Jolla, CA, at the 1st ComTech conference in Freiburg, Germany, in February 1997.

The type and arrangement of the inlet system, the ionization source, and the mass analyzer determine the features of the mass spectrometer involved in the analytical process. Hyphenation to other techniques determines the capability and features of the analytical system. Since the mass spectrometer is primarily used as a detector, hyphenated techniques have been extensively investigated and discussed. The TOF analyzer offers exciting possibilities with respect to speed, especially when it is used with an ESI source and a quadrupole analyzer (TOF, time-of-flight; ESI, electrospray ionization). The TOF spectrometer allows inlet frequencies of up to 20 kHz (*Analytica of Branford Inc.*) and, therefore, quasi-continuous operation. Leading companies in the field are *Finnigan*, *Fisons*, *Micromass*, *PerSeptive Biosystems*. The Nanobore HPLC – Nanoflow^{TM} probe allows flow rates of 5 nl up to 1 ml to be introduced into the ion source at atmospheric pressure (*Micromass Ltd.*, UK). For single shot analysis, a borosilicate capillary enables the injection of 3 nl, so that the final amount of substance in the analyzer is 10^{-12}–10^{-15} moles. A paper presented by *Berry Karger et al.* dealt with how to introduce the sample from a multichannel capillary electrophoresis chip by interfacing the microchip to a triple-Q electrospray mass spectrometer (*TSQ-700*, *Finnigan Instruments*, CA) and with the characteristics of the hyphenated technique. The mass of, *e.g.*, human growth hormone (22 124 Da), was resolved with a relative inaccuracy of 0.02% [10][11]. Remarkably, the chip was supposed to be disposable to render a washing step unnecessary.

The highest resolution of routine systems is yielded by the reflectron TOF mass spectrometer, which provides mass resolution ($m/\Delta m$ at FWHM, fraction of peak width at half height of mass peak) of 5000 and screening of a mass range m/z up to 7000 (*Micromass Ltd.*, UK) even with $5 \cdot 10^{-16}$ moles amounts of substance in the detector. This means resolving a m/z ratio of 20 at the peak mass of m/z equal to 10^5. This is especially attractive for molecular biology, where multiply charged ions should be resolved with high resolution. The reflectron TOF mass spectrometer makes use of an electric field applied to one end of the flight tube. The latter acts as a mirror and reflects the ions elastically according to their kinetic energy. This principle results in the ion beam being focused and the resolution enhanced. The same effect arises from the time-lagged focusing by a delayed inlet system, where a species with a mass < 5000 (*e.g.*, peptides) can be fragmented within the source. If the mass detector is hyphenated with a MALDI-source (matrix-assisted laser desorption ionization), a continuous sampling is not feasible. Nevertheless, the molecule peaks of species with masses as high as 600 000 are displayed, albeit with a resolution of only FWHM 500. Fisons offers a 2D-gel-plate reader to be combined with a MALDI-TOF spectrometer. A considerably enhanced resolution of FWHM 3000 for a mass range up to 10^5 is yielded if an rf-guide for the ion beam is connected to the ion source. In addition, the MALDI sampling plate can be inspected by a videocamera in order to observe the crystal structure of the matrix, and to check and visualize the local desorption process. These features suggest that it may be possible to identify biological molecules without separation. This would speed up the analytical process as separation is the most time-consuming step.

A challenging approach, which only just belongs to the field of mass spectrometry, was presented by *Marshall et al.* on FT-ICR mass spectrometry (*Fourier*-Transform Ion Cyclotron Resonance MS). In this approach, the ions are forced into a cyclotron course by applying a magnetic field and by overlaying a pulsed differential electric field. This enhances the FWHM resolution up to 10^6, which allows the isotope ratios of nuclei to be resolved in a mass peak. When combined with MALDI, even masses $>10^5$ can be resolved with $m/z < 1$. In addition, compounds containing, *e.g.* sulfur nuclei, are distinguished from sulfur-free compounds. This is relevant for the analysis of peptide structures in that it answers questions about the amino-acid sequence [12–15]. There are clear analogies with the gain in resolution obtained not only through the data acquisition process, but also through *Fourier*-Transform data processing in NMR as *Richard Ernst*'s investigations have unambiguously demonstrated.

This year, the sessions dedicated to mass spectrometry were among the most attractive since new applications in combinatorial and parallel chemistry, in molecular biology and bioanalysis have led to various innovations. In addition, a generally stronger representation of the field of mass spectrometry was noticed. On a more philosophical note, the question was raised whether 'MS can compete in the DNA world?' [16].

Alternative Separation Techniques

The three limiting characteristics of separation techniques, namely high resolution, high capacity, and high flow rate span the 'triangle' determining the ultimate goal of separation techniques.

The currently discussed leading techniques are electrokinetic chromatography, separation with porous columns involving functionalized polymers, micellar separation techniques, pervaporation replacing head-space sampling, and membrane inlet techniques. In those fields, pharmaceutical science and food technology is much stronger involved than ever before.

In capillary electrokinetic chromatography (CEC), the electroosmotic flow, which controls the separation of ions in capillary electrophoresis, is prevented using filled columns. Filled columns (*e.g.*, 400 length, 0.1 mm OD, 1.3 µm beads), closed with a frit of sintered silica, are used to solve specific problems, such as the separation of lipids with high resolution and faster separation as compared to LC [17]. In [17], a setup is described using an electric field of 20 kV applied along the column, and, simultaneously, a pressure of 10 bar. The mobile phase is acetonitrile/Tris-buffer buffered to pH 8.

In capillary perfusion chromatography, porous silica beads (10–50 μm diameter) with 0.5–0.7 μm pores are used in short columns (10–20 cm length). This enables fast separation, but the high resolution is sacrified. Precolumns of 4 cm length, functionalized with enzymes such as trypsin, allow enzymatic digestion prior to LC (*PerSeptive Biosystems*). On the other hand, fast separation and high resolution can both be achieved if certain steps are taken: avoid band broadening by *Eddy* diffusion, inhibit low mass transfer efficiency at the walls of columns, and avoid beads that contribute with nonuniformity to minor resolution. In particular, the separation of peptides can be improved by using a continuous bed matrix from 'in-column' polymerized material. This material provides excellent resolution and reproducibility as well as fast separation for anionic and cationic species such as peptides, proteins, and nucleic acids (*Bio-Rad*). The mass transfer efficiency is enhanced by functionalizing the polymer with specific ligands.

In order to obtain improved resolution of neutral and hydrophobic compounds, micellar techniques are gaining importance in capillary electrophoresis (MCE, micellar capillary electrophoresis) and electrokinetic chromatography (MEKC, micellar electrokinetic chromatography; MEEKC, micro-emulsion electrokinetic chromatography). Separation of such compounds in open tubes or capillaries relies on partitioning between the polar solvent and the apolar phase of microemulsions or micelles. The partitioning can be supported by functionalizing the micellar phase with ligands, such as *e.g.* cyclodextrins. Reversed micellar electrokinetic chromatography (RevMEKC) is the logical consequence of these developments. In this technique, the outer solvent phase constitutes the apolar phase, whereas the reversed micelle contains the polar components. With SDS (sodium dodecyl sulfate), stable micelles are prepared. This results in a higher peak capacity and a high resolution, especially for acids and basic compounds.

Portable Instruments

Given the deplorable statistics about the concentration of land mines in war-torn areas, improved land mine detectors are urgently required. According to the statistics, there are 152 land mines per square mile in Bosnia/Herzegovina, which is equal to 0.68–1.36 mines per inhabitant. It is estimated that there are, in total, 3–6 Mio. mines distributed all over the area. 11 Detectors based on various principles, including the canine nose, chemical and sensors and biosensors, have been compared, but without establishing one as the best [18]. On the other hand, 13 suppliers of portable instruments based on GC and GC/MS technology were cited in [19], neglecting mobility spectrometers in this review. Portable instruments and speedy sample preparation techniques are other goals of the conference and exhibition which are rather application-oriented. Developing portable instruments is a growing field which shares the market where chemical sensors and biosensors are in. Chemical sensors and biosensors are more and more used to monitor pollution indicators. In both cases, the sensors and detectors should, ideally, be used on-site, and allow immediate and continuous monitoring.

Advances in Sensor Technology

After a cleaning process in the sensor market, many chemical sensors have reached 'maturity'. The current trend is to market individual sensors for specific applications, hence biosensors for, *e.g.*, lactate, glucose, glutamate, *etc.*, are commercialized by *YSI*, and fiber optical sensors for, *e.g.*, determinations of pH and oxygen partial pressure by *Ocean Optics*. The development of sensing arrays shows its most relevant impact in the design of 'electronic noses'. Some companies such as *AlphaMOS*, *Neotronics*, and *AromaScan* start to show up at Pittcon regularly with still small booths but respectable presentations on improved applications.

However, one of the most challenging new development in sensor technology is the GeneChip probe array of *Affymetrix Inc.* (Santa Clara, CA, [20]), which is covered by at least five patents involving some 100 typed pages issued since 1995. The last one being issued on January 14, 1997. The chip consists of two ports for introducing and removing fluids, a hybridization chamber, and alignment features for the optical reader. The inside of the hybridization chamber contains the 'chemistry' involving 96 fields where combinations of DNA oligomers are attached to the microfabricated polymer support. The patterning of the molecular recognition area of 20 μm is programmed in a highly systematic way in order to avoid false positive or false negative results. Each GeneChip probe array is specifically designed to perform DNA analysis in a typical sample. The HIV PRT probe array contains over 15000 different DNA oligomers. The chip works by contacting the luminescence-labelled DNA in a sample to be analyzed after the sample has undergone, *e.g.*, DNA amplification by PCR (polymerase chain reaction). The luminescence pattern of hybridized 3-μm areas is excited by an argon-ion laser and the pattern is read from the chip by an electronic scanner. The laser-optical GeneArray scanner was provided by *Hewlett-Packard* (*HP G2500A*). It is able to read a 20000-cell probe array within 15 min. In terms of size, however, the liquid handling system and the scanner dominate the bench.

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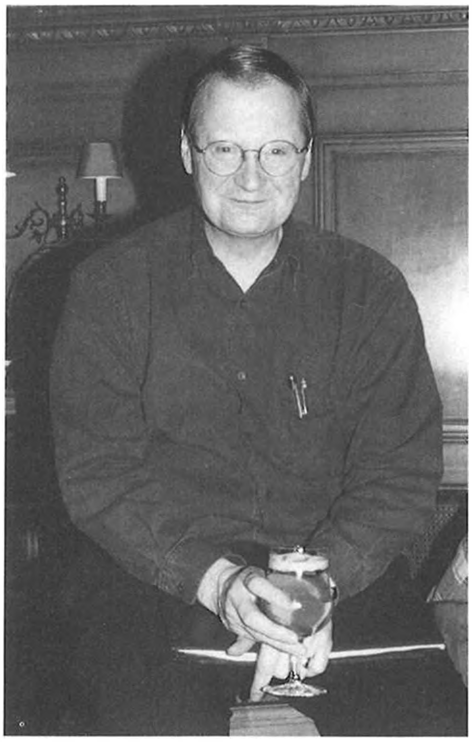
32nd Euchem Stereochemistry Conference Bürgenstock, April 27–May 3, 1997

On Saturday morning, May 3rd 1997, the participants of the 32nd Euchem Stereochemistry Conference were leaving the beautiful Bürgenstock resort in the Swiss Alps, going back home to 23 different countries around the world. After a week of brilliant lectures, ranging from quasicrystals, biosynthetic studies, enzyme mechanism elucidation, structural biology and structural organic chemistry to asymmetric catalysis and natural product synthesis, none of the 115 participants from industry and academia could have left unsatisfied.

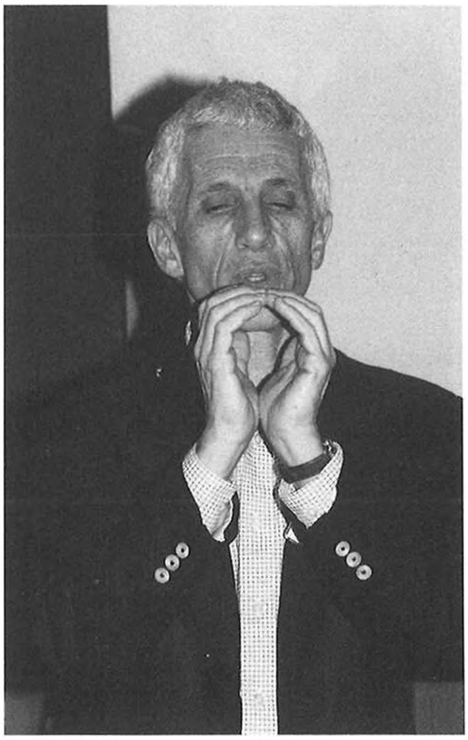
It all started 32 years ago when *A. Dreiding* organized the first Bürgenstock-Stereochemistry Conference. Many people showed potential interest in the conference but first wanted to know the exact program. Because *A. Dreiding* had given the lecturers the freedom to change the titles of their contributions up until the first day of the Conference – in an attempt to have the Conference deal with the most recent thoughts and results – they were unable to provide the program in advance. This has, since then, set the precedent for all Bürgenstock Conferences keeping the program a mystery until the opening day. The result of this policy has been to prevent the Conference from becoming a 'consumer activity', *i.e.*, one which attracts listeners rather than participants. This year's event was not an exception to the rule and people could only lay eyes on the program after arriving at the Conference site; for some of them *via* a breathtaking scenic boat trip and funicular ride. This years outstanding program was arranged by the Conference President, *Steven V. Ley* (Cambridge, UK), reflecting his broad scientific interests. In his Sunday night speech the President introduced this year's guest of honor, Sir *Alan Battersby*, also from Cambridge and former President of the 12th Bürgenstock conference in 1976. Vice President *Manfred T. Reetz* (Max-Planck Institut, Mülheim, Germany) was nominated the man in charge of the weather.

Thanks to the generous support of the *European Science Foundation* (Strasbourg, France) and the *Swiss National Science Foundation*, 24 young European chemists were able to experience the unique atmosphere at one of the most mythic and prestigious chemistry conferences in the world.

The first day was devoted to a large range of subjects. The opening lecture by *D.L.D. Caspar* (Florida State University, Tallahassee, USA) introduced us to the world of five-fold symmetry in quasicrystal, fullerene and virus structures. He demonstrated that crystallographic methods can be applied to index and interpret diffraction patterns from well-ordered quasicrystals that display non-crystallographic five-fold symmetry. Shifting gears, *G. Pattenden* (University of Nottingham, UK) focused on 'Macro- and polycycle constructions 'organized' by radical and metal templating'. He presented beautiful examples of radical-mediated cascade cyclisations and macrocyclisation-transannulation reactions leading to complex molecules, such as steroid and taxane derivatives. Much of the following discussion focused on whether preorganisation of the substrate was occurring prior to the cyclisation reactions and if so, on the degree of it.


S. Ley *(the President)*


T. Richmond

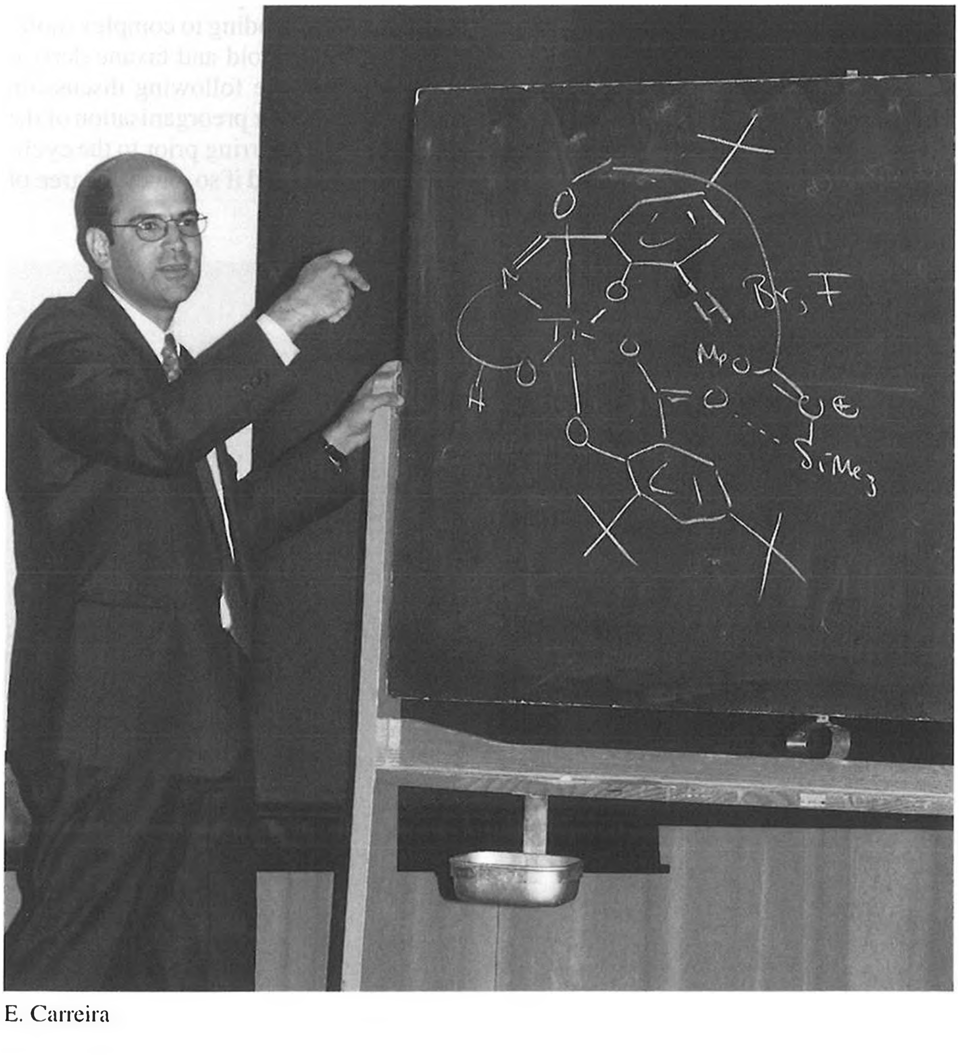

S. Harrison

Monday, Tuesday, Thursday and Friday afternoons were dedicated to a two part poster session. Twelve posters, six each on Monday and Thursday, were selected for oral presentation of three minutes each. This not only motivated the participants to attend the poster sessions, but also reflected the special emphasis that Conference President *S. Ley* and the Committee *H.B. Bürgi*, *F. Diederich*, *E.P. Kündig* and *K. Müller* gave to allow younger participants to present their work. The high number and quality of the posters presented reflected the brilliance of this conference.

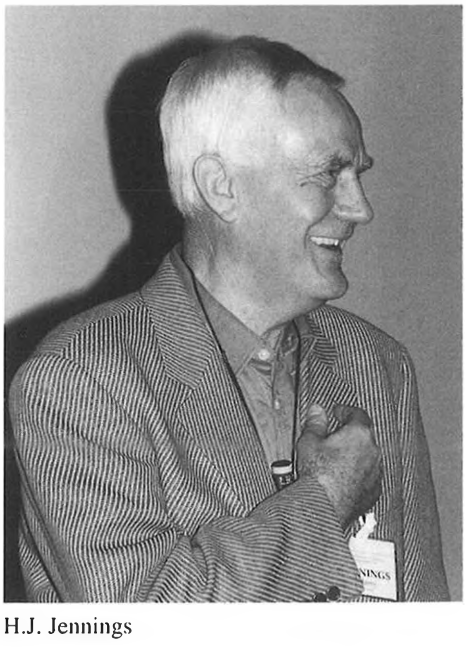
The evening lecture on the opening day was given by *I.K. Ugi* (Technische Universität München, Garching, Germany) and titled: 'Fast and permanent changes in organic chemistry through multicomponent reactions and their libraries'. He not only presented his famous three and four component reactions, but also focused on the extension to seven and more component reactions as an efficient way to construct complex molecules. This, of course, is a very valuable tool for the construction of complex libraries and the session inevitably ended with a discussion about legal and patent problems associated with such libraries; do you have to identify every compound in the library and do you make the compound if it has not been identified and characterized?

The second day lectures were devoted to one of the major themes of the conference, structural biology. All lectures showed, in exciting presentations, the exquisite level of structural details that can today be obtained in this field. *W.A. Hendrickson* (Columbia University, New York) spoke on the HIT family of proteins. Their activity is not yet well understood and he discussed their possible involvement in phosphotransfer catalysis. He described the structural information he has obtained on the histidine triade active site and on a tungsten-based transition state analog using, as a powerful technique, intense synchrotron X-ray radiation on proteins crystallized with selenium methionine instead of methionine. The second lecture of the day was an impressive report by *T. Richmond* (ETH-Zürich) on the structure of a nucleosome of chromatin assembled from 146 bp DNA fragments and a histone octamer complex prepared from expression of the four core histones in bacteria. 24 crystals (!) of nucleosome as well as two months of acquisition at E.S.R.F. (Grenoble) were needed to solve the structure. He discussed in great detail the nature of the interactions of the proteins between themselves and with DNA. In the evening, *S. Harrison* (Harvard University, Cambridge) presented a lecture on not just one, but two subjects dealing with protein assemblies interacting with DNA. First, he discussed the importance of DNA recognition by proteins and showed for NFAT that, although there are significant regularities, no clear recognition code could be determined. He then focused on DNA translocation and proposed a mode of action for DNA topoisomerase II based on an X-ray crystallographic study.

The third day of the meeting began with *H.J. Jennings* (Institute for Biological Sciences, Ottawa, Canada), who presented his work on the chemical and structural characterization of carbohydrate antigens and on the development of novel synthetic and conjugate vaccines against bacterial infections. Using NMR studies and molecular modeling, he provided the participants with valuable insights into the structural basis of polysaccharide epitopes and showed how they could be of use for formulating glycoconjugate vaccines against bacteria causing meningitis. The Wednesday session was closed by *K. Suzuki* (Tokyo Institute of Technology, Tokyo, Japan) on a subject entitled: 'Stereochemical issues met in the synthesis of sugar-aromatic and isoprenoid-aromatic hybrid natural products'. During the first part of his presentation, *Suzuki* described the *Lewis* acid catalyzed rearrangement of the glycosyl moiety in aryl glycosides to



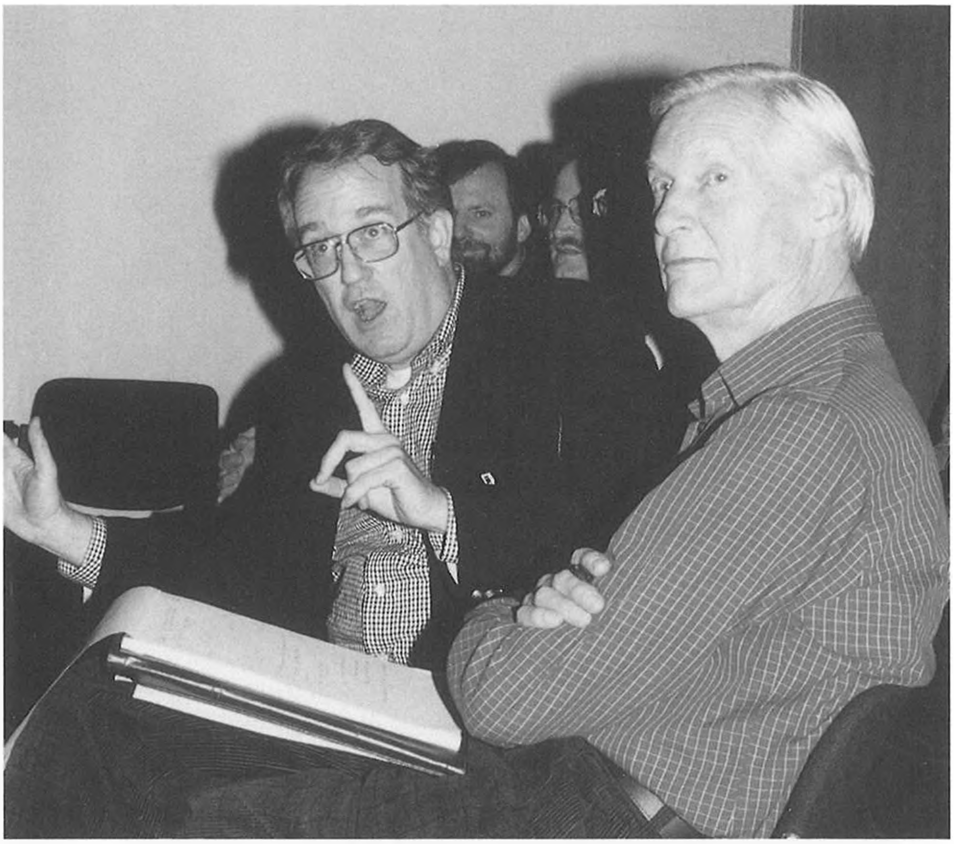
E. Carreira


H.J. Jennings

obtain *ortho*-glycosyl substituted phenolic compounds as intermediates for the synthesis of sugar-aromatic hybrid compounds. The best catalyst turned out to be a cationic Hafnium compex which led *E. Carreira* (CalTech, California) to ask 'What's special about Hafnium?'. For the synthesis of the aromatic-isoprenoid hybrid natural products, *K. Suzuki* was facing the problem of the poor migrating ability of alkynyl groups in the *Lewis* acid catalyzed rearangement of α-alkoxy alkynols. Transforming the triple bond into its dicobalt hexacarbonyl complex proved to be the best solution, making it one of the best migrating groups. The origin of this effect resides in the ability of the cobalt complex to stabilize the intermediate carbocation *via* both α and β-participation.

After a rather gray afternoon (as usual), a wonderful concert organized by the president *S. Ley* featured an 'all-scientist' but very talented quartet led by *A. Miller* (Imperial College, London). This Ensemble masterfully interpreted two quartets for oboe and three strings (violion, viola and violoncello) from *W.A. Mozart* and *Gordon Jacob*.

On the next day, again a large variety of topics was presented. The first morning lecture by *U.B. Sleytr* (Zentrum für Ultrastrukturforschung, Vienna) was devoted to two-dimensional protein crystals (or S-layers). S-Layers are the most commonly observed cell surface structures of eubacteria and archaeobacteria, composed of a single protein or glycoprotein species. He presented their stunning ability to assemble into two-dimensional arrays either in suspension, on solid supports, at the air/water interface, on lipid films or liposomes. He confronted us with their use for numerous applications: as membranes for ultracentrifugation, as matrices for controlled immobilization of functional molecules for diagnostic systems, for the design of conjugated vaccines, for liposome technology, and for the functionalization of surfaces in the fields of molecular nanotechnology, micro- and nano-lithography. The morning session was closed by *P.F. Leadlay* (University of Cambridge, Cambridge, UK) on stereochemical aspects of complex polyketide biosynthesis. Polyketides are one of the richest sources of promising molecules which are made by bacteria and fungi in an assembly-line process involving *ca.* 30 enzymes in which each enzyme hands off its product to the next. Understanding the aspects of this complex biosynthetic process might lead to the development of new versions of old wonder drugs, as ever more strains of bacteria develop resistance to conventional antibiotics. One way to generate new polyketide variants involves tinkering with the genes for the enzymes that are the 'workers' in the assembly-line process.



A.B. Smith III Sir A. Battersby

K. Suzuki

S. Kobayashi

The final lecture of the day, presented by *G. Newkome* (University of South Florida, Tampa, USA), was devoted to dendritic macromolecules. He gave an overview of the development of these molecules, and addressed the essential question of the purity of dendrimers. He showed that by using reactive fluorescent markers, one can detect the presence of unreacted internal carboxylic acid moieties in amide-based dendrimers and apply this simple

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A. Miller H. McCann T. Addenbrooke J. Ogilvie

method to qualitatively analyze the dendritic homogeneous and heterogeneous structural integrity. The construction of ligand functionalized branched building blocks to afford entrance to a series of dendrimers possessing multiple, internally incorporated piperazine moieties, which readily form Pd^{II} and Cu^{II} complexes was presented.

The morning session of the last day of the Conference was devoted to asymmetric catalysis and its use in stereoselective organic reactions. The first lecture was given by *S. Kobayashi* (Science University of Tokyo, Tokyo, Japan), one of the leading young scientists who was an Assistant Professor before obtaining his Ph.D. with Professor *T. Mukayama*. He presented the use of stable lanthanide *Lewis* acids as catalysts for *Mukayama*-type aldol reactions and 3 component *Mannich* reactions in aqueous solvent mixtures. After extending the scope of these lanthanide *Lewis* acids as catalysts for the allylation of aldehydes and aldimines, he discussed the lanthanide catalyzed construction of quinoline libraries from a three component imino hetero *Diels-Alder* reaction for which he also prepared polymer supported catalysts. The final part of his presentation was reserved to the design of chiral *Lewis* acids as catalysts for asymmetric (hetero) *Diels-Alder* and *Mannich* type reactions.

The morning session was closed by another brilliant young scientist, *E. Carreira* (California Institute of Technology, Pasadena, USA), who has become a few years after starting his independent career one of the leaders in the field of asymmetric catalysis. The first part of his presentation 'Asymmetric synthesis with transition-metal reagents and catalysts' dealt with the design of titanium-based chiral *Lewis* acids for *Mukayama*-type acetate aldol reactions and allylations for the synthesis of β-hydroxy carbonyl compounds and homoallyl alcohols with exceptionally high enantiomeric excesses for this type of reactions. Switching to nitrogen transfer reactions required the design of new nitrido molybdenum complexes which are very useful for the diastereoselective β-amination of glycals. Finally, the design of homochiral nitrogen transfer reagents allows for the first time asymmetric nitrogen transfer reactions to achiral alkenes; however, not yet in a catalytic way.

As the last lecturer of the conference, *A.B. Smith III* (University of Pennsylvania, Philadelphia, USA) presented the heroic efforts of his group towards the synthesis of spongistatin. This extremely complex macrocyclic lactone of marine origin inhibits the formation of microtubulin and is one of the most active anti-cancer agents ever screened by the National Cancer Institute of the USA. A carefully planned strategy not only resulted in an almost completed total synthesis, but also in the development of new methodologies such as a new and elegant way for the heterocoupling of different epoxides with lithiated 1,3-dithianes. Since the world supply of the spongistatins is only a few milligrams, synthetic endeavors of this type are of extreme importance for further evaluation of this remarkable class of compounds.

The Bürgenstock Conference ended with *K. Müller*'s (*F. Hoffmann-La Roche AG*, Basel) skillful summary of the week's proceedings with humour and talent. He also introduced *Manfred T. Reetz* as the president for the 33rd Euchem Conference on Stereochemistry, which will take place at the Bürgenstock resort from April 26 to May 2, 1998.

Dr. Jef de Brabander
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International Chemistry Olympiad 1997: A Silver Medal for Switzerland

Thanks to *Dominik Langer*, an 18-year-old student from the Kantonsschule Limmattal, our country has got a silver medal in the 29th International Chemistry Olympiad.

This competition took place from July 13th to 22nd 1997 in Montréal, Canada. Forty-seven countries sent their best four students from a pre-university level. After theoretical and practical examinations both lasting five hours, the best students were rewarded by gold, silver, and bronze medals. The first 10% got gold medals, 20% got silver, and 30% bronze.

The theoretical tasks are given with full details in annex, with their solutions. Try to solve them in less than five hours, as did *Dominik Langer*!

The best result went to a Turkish student (82 points out of a maximum of 100 points), and *Dominik Langer* obtained 66 points. As a whole the best nation was Germany with three gold medallists, before Hungary, Korea, Poland, and Taipei.

National teams are usually formed of four students and two mentors. The four Swiss competitors were selected at Easter 1997 at the Gymnase de Chamblandes, Pully, Lausanne, at the end of a training week. They are:

- *Luca Castiglioni*, 6313 Menzingen
- *Dustin Hofstetter*, 6340 Baar
- *Dominik Langer*, 8912 Obfelden
- *Massimo Lunati*, 6952 Canobbio.

Two years ago two candidates were coming from the same city: Sion (VS). A similar phenomenon happened this year as two candidates were coming from the Kantonsschule Zug.

The mentors were Dr. *Maurice Cosandey* and Dr. *Blenda Weibel*, both from the canton of Vaud.

It may be worth mentioning also that our 1996 Swiss gold medallist, *Thomas Braschler*, did not take part of the 1997 Chemistry Olympiad, but of the 1997 Physics Olympiad, also in Canada, where he got a silver medal. So our country has for the first time a double medallist gold + silver.

The next Chemistry Olympiad will happen in Australia 1998, then Bangkok 1999, and Copenhagen 2000. Switzerland has been approached for hosting an Olympiad in 2004. A dynamic committee has recently been formed in the NSCG for boosting this idea in our country.

Maurice Cosandey

Problem 1

Compound **X** is a trisaccharide which occurs principally in cottonseed. Compound **X** does not react with *Benedict*'s or *Fehling*'s solutions nor does it mutarotate. Acid-catalyzed hydrolysis gives three different D-hexoses: **A**, **B**, and **C**. Compounds **A** and **B** give the same osazone upon reaction with excess acidic phenylhydrazine. Compound **C** reacts with nitric acid to give an optically inactive compound **D**. The *Kiliani-Fischer* approach is used to establish the configurational relationship between D-glyceraldehyde and **C**. The intermediate aldotetrose which leads to **C** does not give a *meso*-compound when oxidized by nitric acid. When **A** is treated with nitric acid, the dicarbonic acid produced (aldaric acid) is optically active. Both **A** and **B** reacts with 5 moles of HIO_4. One mole of **A** gives 5 moles of formic acid and 1 mole of formaldehyde. One mole of **B** gives 3 moles of formic acid and 2 moles of formaldehyde and 1 mole of CO_2. Both **A** and **B** are related to the same aldotetrose which is the diastereoisomer of the one to which **C** is related. Methylation of **X** followed by hydrolysis gives a 2,3,4,6-tri-*O*-methyl-D-hexose (**E**, derived from **A**), a 1,3,4,6-tetra-*O*-methyl-D-hexose (**F**, derived from **C**), and a 2,3,4,6-tetra-*O*-methyl-D-hexose (**G**, derived from **C**).

i) Draw the *Fischer* projection formulas of **A**, **B**, **C**, and **D**.

ii) Draw the *Haworth* projection formulas to clearly show the absolute stereochemistry of **E**, **F**, and **G**.

iii) Underline the correct representation of the connectivity sequence of the three monosaccharides present in trisaccharide **X**. Note that A_5, B_5, C_5 represent the furanose (5-membered ring) form of carbohydrate **A**, and that A_6, B_6, C_6 represent the pyranose (6-membered ring) form of the same carbohydrates.

A_6, B_6, C_5	A_6, B_5, C_6	A_5, B_6, C_6
B_6, C_6, A_5	B_6, C_5, A_6	B_5, C_6, A_6
C_6, B_6, A_5	C_6, B_5, A_6	C_5, B_6, A_6

Problem 2

Professor *Molina*, from MIT, won the *Nobel* Prize in 1995 for his work on acid rain and atmospheric chemistry. He proposed two possible reactions A and B for the production of H_2SO_4 in the atmosphere:

A: $H_2O(g) + SO_3(g) \rightarrow H_2SO_4(g)$
B: $2\,H_2O(g) + SO_3(g) \rightarrow H_2SO_4(g) + H_2O(g)$

i) Using simple collision theory, what reaction orders would be expected for proposals *A* and *B*?
Proposal *B* is thought to proceed by the following two-step process

$$SO_3 + 2\,H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} SO_3 \cdot 2\,H_2O \text{ (fast)}$$

$SO_3 + 2\,H_2O \rightarrow H_2SO_4 + H_2O$ (slow, with a rate constant $k_2 << k_1$ or k_{-1})

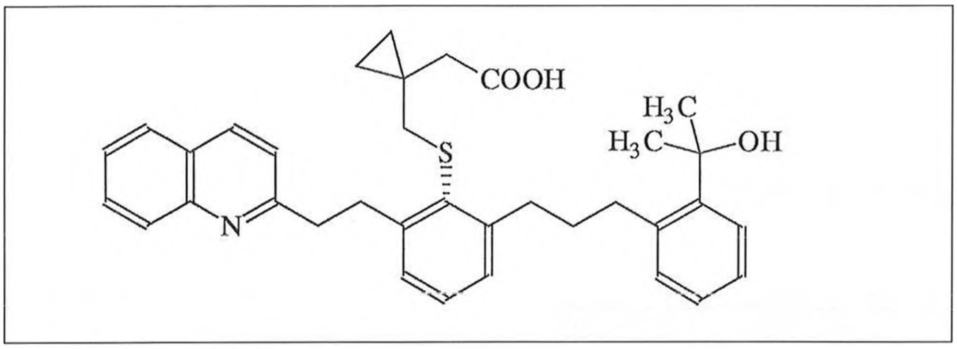
ii) By applying the principle of stationary (steady) states, derive the rate law and hence the reaction order of the two-step mechanism for proposal *B*.

iii) Quantum chemical calculations have shown that the overall activation energies for the two proposals are + 80 kJ/mol for *A*, and –20 kJ/mol for *B*. State the relationship between the rate constant and the temperature (*Arrhenius* relationship) for *A* and *B*, and predict the temperature dependance of the rate constants for *A* and *B*.

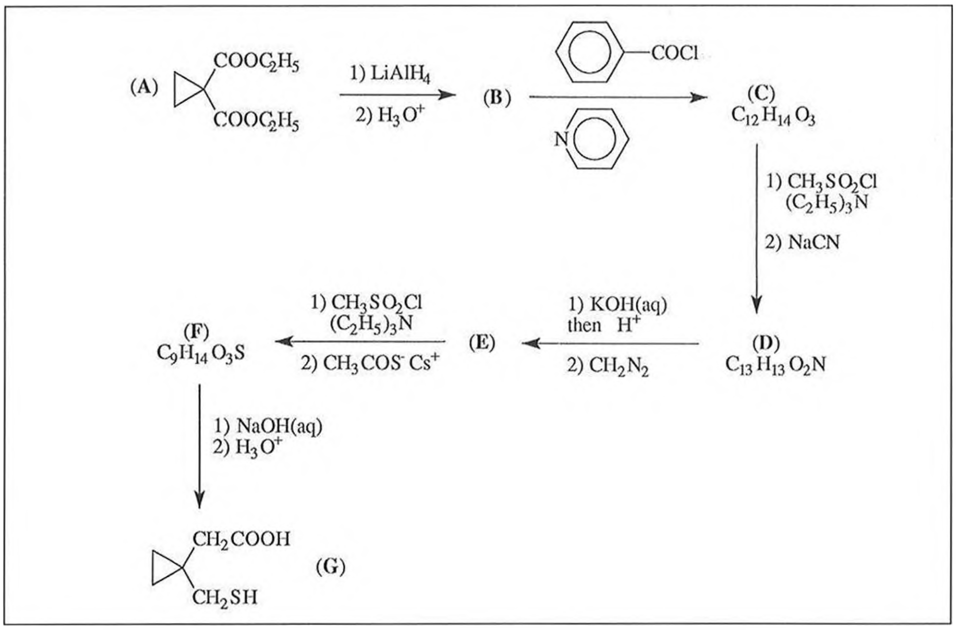
iv) The formation of H_2SO_4 is faster in the upper atmosphere ($T = 175$ K) than at the earth's surface ($T = 300$ K). Which proposed pathway dominates in the upper atmosphere?

Problem 3

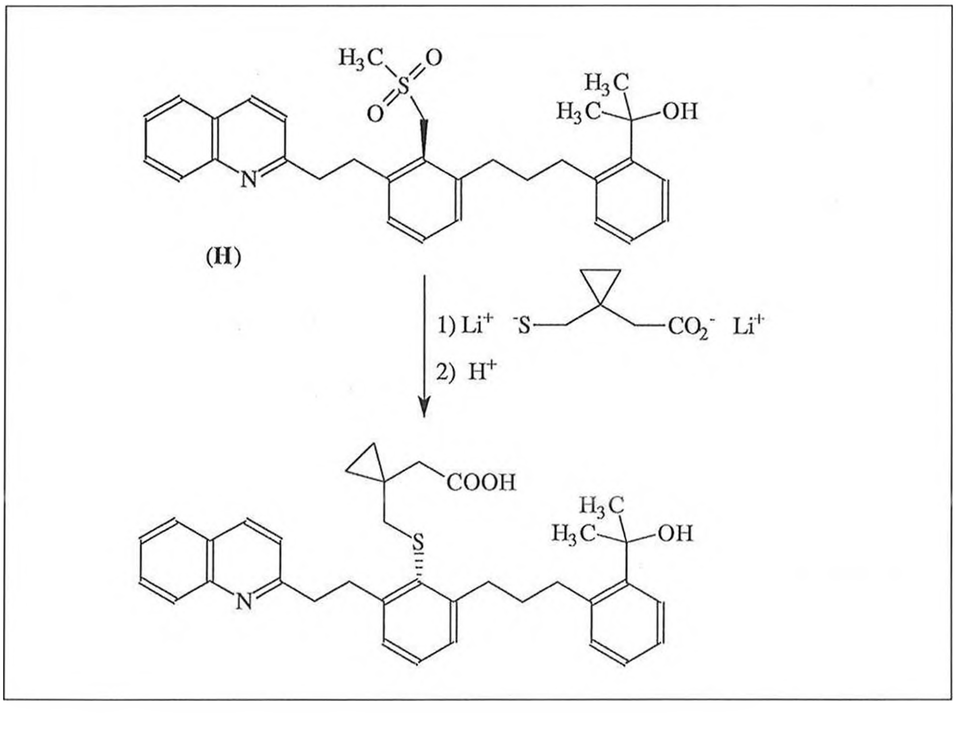
The following substance MK-0476, synthetized at *Merck Frosst*, is a useful drug against asthma.



The thiolate part of this molecule is obtained by the following way:



In one of the last steps of the synthesis of MK-0476, the dilithium salt of **G** was coupled with the side chain of the rest of the molecule as shown below



ii) What is the mechanistic designation of this coupling process?

iii) What change would occur to the overall reaction rate if the concentration of both the thiolate salt and the substrate **H** were simultaneously tripled?

iv) For the nucleophilic substitution reaction, model studies were carried out using bromoethane as the substrate to perfect the above coupling. Draw the major product of the reaction of one molar equiv. of bromoethane with

a) **G** plus two molar equiv. of base,

b) **G** plus one molar equiv. of base.

v) A side reaction of **G** is its oxidative dimerization. Draw the dimeric product, showing all non-bonded electrons.

Problem 4

HIn is a weakly acidic indicator

$$\mathrm{HIn} + \mathrm{Na^+OH^-} \rightleftharpoons \mathrm{Na^+In^-} + \mathrm{H_2O}$$

also written as

$$\mathrm{HIn} \rightleftharpoons \mathrm{H^+} + \mathrm{In^-}$$

At normal temperature, the acid dissociation constant for the indicator is $K_a = 2.93 \cdot 10^{-5}$. The absorbance data in 1.00 cm cells for $5.00 \cdot 10^{-4}$ M solns. of this indicator in strongly acidic and strongly alcaline solutions are given in the following table.

λ(nm)	400	470	485	490	535	555	570	585	615	625	650
A(ac)	0.401	0.447	0.453	0.452	0.390	0.342	0.303	0.263	0.195	0.176	0.137
A(bas)	0.067	0.050	0.052	0.054	0.170	0.342	0.515	0.648	0.816	0.823	0.763

i) Predict the observed colour of the acidic and basic forms of the indicator

ii) A filter is located between the light source and the sample. What colour filter would be most suitable for the photometric analysis of the indicator in a strongly acidic medium?

iii) Same question for a basic soln.

iv) What would be the absorbance of a $1.00 \cdot 10^{-4}$ M soln. of the indicator in alcaline form if measured at 545 nm in a 2.5 cm cell?

v) Solutions of the indicators were prepared at pH 1 and pH 13. Perfectly linear relationship between absorbance and concentration were observed at 490 nm and 625 nm. The molar absorbitivities ε in $M^{-1}cm^{-1}$ at these two wavelengths are:

λ	490 nm	625 nm
ε(HIn)	904 $M^{-1}cm^{-1}$	352 $M^{-1}cm^{-1}$
ε(In)	108 $M^{-1}cm^{-1}$	165 $M^{-1}cm^{-1}$

Calculate the absorbance in a 1.00 cm at the two wavelengths for an aq. 1.80 10^{-3} M soln. of this indicator.

Problem 5

Iron metal has a density of 7.874 g cm^{-3} at 293 K and melts at 1811 K. Between r.t. and 1811 K, iron can exist in different allotropic or crystalline forms. Up to 1185 K, the crystal structure is a body-centered cubic (bcc) lattice known as α-iron. From 1185 K to 1667 K, the structure becomes face-centered cubic (fcc) and is called γ-iron. Above 1667 K and up to its melting point, iron reverts to a bcc structure. The phase is called δ-iron.

a) *i*) Calculate the atomic radius r of iron (in cm).

ii) Calculate its density (in g cm^{-3}) at 1250 K, neglecting the thermal expansion.

Steel is an alloy of carbon and iron in which the interstitial spaces ('holes') of the iron crystal lattice are occupied by carbon atoms. If a hot liquid mixture containing 4.3% of carbon in mass is cooled rapidly, the carbon atoms remain dispersed within the α-iron phase. The new solid, called martensite, is hard and brittle. But the size of the unit cell is the same as that of α-iron (bcc).

b) Asuming that the carbon atoms are evenly distributed in the iron structure,

i) Calculate the average number of carbon atoms per unit cell of α-iron in martensite.

ii) Calculate the density of this material.

Problem 6

a) *i*) Draw the geometric shapes of the $PtCl_6^{2-}$ and the $PtCl_4^{2-}$ anions.

ii) Draw and label all possible stereoisomeric structures of monomeric $Pd(NH_3)_2Cl_2$.

iii) Write the equation of the reduction of $HAuCl_4$ into Au using $FeSO_4$.

iv) Write the equation of the combustion of $Pd(NH_3)_2Cl_2$ in air to give Pd metal.

b) Reaction of a main group chloride (24.71 g) with ammonia (10.90 g) gave a mixture of products consisting of NH_4Cl (25.68 g), a solid element A (2.57 g), and a yellow crystalline nitride of A (7.37 g) according to the following equation:

$$n\ A_wCl_x + m\ NH_3 \rightarrow p\ NH_4Cl + q\ A + r\ A_yN_z$$

where m, n, p, q, r, w, x, y, and z are to be determined. A sample of the nitride undergoes controlled polymerization on heating to give a bronze-colored fibrous solid that exhibits metallic conductivity. Element A also undergoes polymerization to a high molecular weight linear polymer upon heating.

i) Identify element A.

ii) Write the complete balanced equation

iii) Write the balanced redox half-reaction equations.

Problem 7

i) Draw the complete MO energy diagram of Cl_2. Predict the bond order, and whether this molecule is dia-, para-, or ferromagnetic.

One mole of Cl_2(g), which may be assumed to obey the ideal gas law, initially at 300 K and 100.0 atm, is expanded against a constant external pressure of 1.000 atm to a final pressure of 1.000 atm. As a result of this expansion the gas cooled to a temperature of 239 K (which is the normal boiling point of Cl_2), and 0.100 mol Cl_2 is condensed.

The following properties of Cl_2 are given:

- Enthalpy of vaporization: 20.42 kJ/mol at 239 K
- Molar heat capacity C_V: 28.66 J/K
- Density of liquid Cl_2: 1.56 g cm^{-3}.

ii) Calculate the changes of internal energy and of entropy of the system for the changes described above.

Problem 8

An aq. soln. of $H_2SO_4 + CuSO_4$ has a volume of 100.0 cm^3 and the following concentrations: $[H^+]$ = 1.000 M, $[Cu^{2+}]$ = 0.1000 M. Two cubic platinum electrodes having a volume of 1.00 cm^3 are immersed in the liquid. Both of the electrodes are single crystals with only one face (100) exposed to the electrode; the other five faces are covered by an insulator. A total charge of 2.000 C is passed between the anode and the cathode. At the anode, O_2 is generated. At the cathode, two simultaneous processes are occuring : deposition of an epitaxial (layer-by-layer) Cu layer, and H_2 generation. If the pressure is 0.1000 atm, and T = 273.15 K, the volume of H_2 is equal to 2.000 cm^3.

i) Write the equations of the processes taking place at the electrodes.

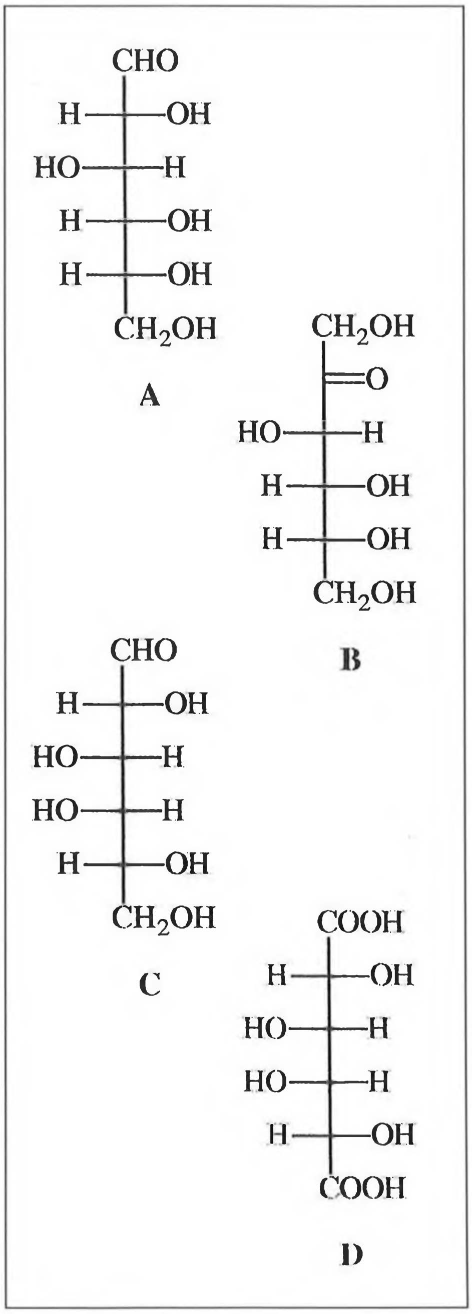
ii) Calculate the number of moles of H_2 and Cu produced

iii) Calculate the number of Cu monolayers formed on the Pt (100) cathode, if the crystallographic structure of Pt and Cu is face centered cubic (fcc), and if the lattice constant of Pt is equal to: a(Pt) = $3.9236 \cdot 10^{-8}$ cm.

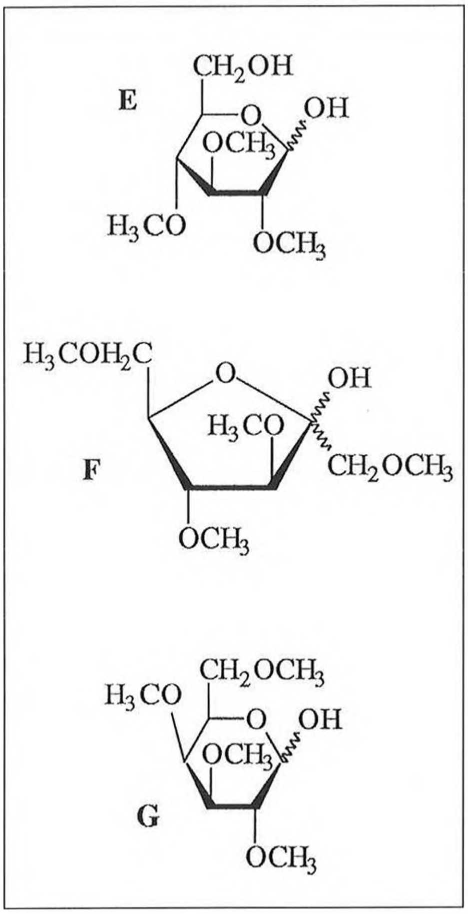
Answers

Problem 1

i)



ii)



iii) $\mathbf{C_6, A_6, B_5}$

Problem 2

i) *A* 2nd order, *B* 3rd order

ii) 3rd order

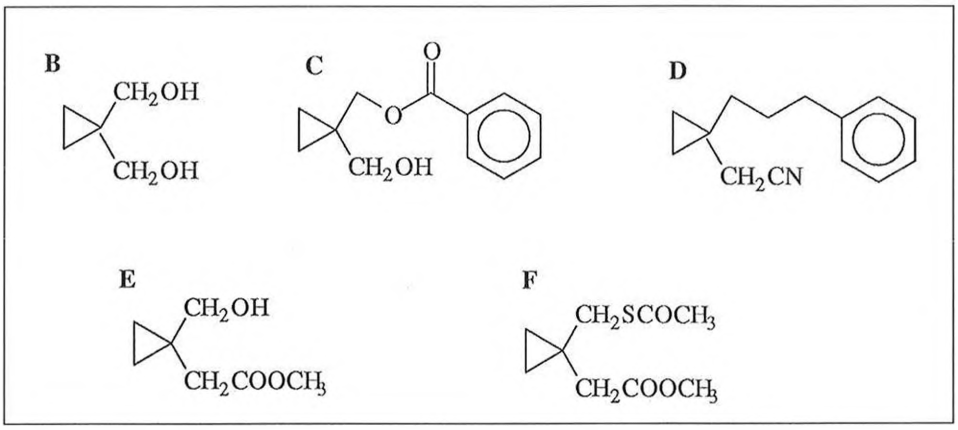
$$\frac{d[H_2SO_4]}{dt} = K_{eq}\, k_2[SO_2][H_2O]^2$$

iii) For *A*: $k(A) = A \cdot e^{-80000/RT}$ increases with increasing *T*
For *B*: $k(B) = A \cdot e^{+20000/RT}$ decreases with increasing *T*

iv) *B*

Problem 3

i)



ii) S_N2
iii) Factor 9
iv) cyclopropane substituted 1,1
  a) by $CH_3SC_2H_5$ and CH_2COOH
  b) by CH_2SH and $CH_2COOC_2H_5$

Problem 4

i) acid yellow-orange; basic blue
ii) blue
iii) yellow-orange
iv) 0.128
v) $A(490\,nm) = 1.45; A(625\,nm) = 0.911$.

Problem 5

a) *i*) $r = 1.241 \cdot 10^{-8}$ cm;
  ii) 8.572 $g \cdot cm^{-3}$.
b) *i*) 0.42 C atoms;
  ii) 8.228 $g \cdot cm^{-3}$.

Problem 6

a) *i*) $PtCl_6^{2-}$: octahedral ; $PdCl_4^{2-}$: square planar
  ii) Two structures: *cis* and *trans*
  iii) $HAuCl_4 + 3\, FeSO_4 \rightarrow Au + HCl + FeCl_3 + Fe_2(SO_4)_3$
  iv) $Pd(NH_3)_6Cl_2 + O_2 \rightarrow Pd + N_2 + 2\, H_2O + 2\, HCl$

N is oxidized, O and Pd are reduced.

b) *i*) Element Sulfur S.
  ii) $3\, SCl_2 + 8\, NH_3 \rightarrow 6\, NH_4Cl + S + S_2N_2$
  ii) Disproportionation: S(II) is oxidized to S(III) and reduced to S(0)

Problem 7

i) $1\sigma^2 1\sigma^{*2} 2\sigma^2 2\sigma^{*2} 3\sigma^2 1\pi^4 1\pi^{*4} 3\sigma^{*2} 4\sigma^2 4\sigma^{*2} 5\sigma^2 2\pi^4 2\pi^{*4}$.
Bond order: 1. Diamagnetic
ii) DE = –3591.8 kJ, DS(sys) = 21.35 J/K.

Problem 8

i) $2\, H_2O \rightarrow 4\, H^+ + O_2 + 4\, e$
Cathode: $2\, H + 2\, e \rightarrow H_2$, and $Cu^{2+} + 2\, e \rightarrow Cu$
ii) $n(H_2) = 8.923 \cdot 10^{-6}$ mol, $n(Cu) = 1.441 \cdot 10^{-6}$ mol
iii) 668 monolayers

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Biotechnologie an der Zürcher Fachhochschule Winterthur

Bernhard Sonnleitner*, **Ursula Graf** und **Heinz Winzeler**

Biotechnologie ist gemeinsam mit der Elektronik und Neuen Materialien eine Schlüsseltechnologie des nächsten Jahrhunderts. Für ein 'High-Tech-Land' wie die Schweiz ist die Biotechnologie daher für das Bestehen im internationalen Wettbewerb äusserst wichtig.

Im europäischen Verständnis bedeutet Biotechnologie *die Integration von Natur- und Ingenieurwissenschaften. Ziel ist die Anwendung von biologischen Systemen und Agenzien für Produkte und Dienstleistungen.*

Unter biologischen Systemen werden Viren, Mikroben und höhere Zellen sowie Teile davon, etwa Enzyme, verstanden. Im Nachsatz zu dieser Definition der Europäischen Föderation für Biotechnologie (EFB) stehen zwei wichtige Präzisierungen:

1) *zum Wohle der Menschheit* und
2) *unter Befolgung biologischer Prinzipien.*

Kulturelle Unterschiede

Im Gegensatz zu Europa und Japan wird im amerikanischen Raum Biotechnologie mit Gentechnik gleichgesetzt. Diese Anschauung steht im Widerspruch zur europäischen Realität. Molekularbiologie und Gentechnologie machen gemäss europäischer Definition eben noch nicht die 'Biotechnologie' aus. Es fehlt darin die essentielle Komponente 'Technologie'.

Japan ist aufgrund seiner Insellage zur gezielten Nutzung biotechnologischer Produktions- und Entsorgungsmethoden faktisch gezwungen. Die Wettbewerbsfähigkeit wird dort durch Kompetenzverbunde insbesondere im Bereich 'Biochemical Engineering' (deutsch: Bioverfahrenstechnik) zwischen Hochschulen und Industrie in ausgedehnten Bereichen präkompetitiver Entwicklungen enorm gesteigert.

Die Bioverfahrenstechnik ist ein unverzichtbares Instrument zur Bereitstellung von Produkten und Dienstleistungen! Diese klare Zielsetzung ist Voraussetzung für die Akzeptanz der Biotechnologie, insbesondere in den deutschsprachigen Ländern Europas. Umsomehr ist die Pflege der Bioverfahrenstechnik von entscheidender Bedeutung auch für den High-Tech-Ausbildungs-, Entwicklungs- und Produktionsstandort Schweiz.

Industrieller Wandel

Die chemische Industrie wandelt sich stark und entwickelt sich klar in Richtung biologischer Verfahren und Produkte. Das belegen unter anderem die jüngsten Firmenzusammenschlüsse (*Novartis*, *Hoffmann-La Roche* und *Boehringer*). Neue, bisher unzugängliche oder unbezahlbare Produkte werden dadurch erschlossen. Neben ökologischer Nachhaltigkeit bieten viele biotechnologische Verfahren auch handfeste ökonomische Vorteile [1].

Fast alle grossen Pharmaunternehmen gliedern gegenwärtig weniger rentable Zweige aus und setzen massive Mittel für den Ausbau biotechnologischer Verfahren ein. Allein mit fünf modernen, biotechnologisch hergestellten Pharmaprodukten wie Humaninsulin, Erythropoetin (EPO), Interferon, colony stimulating factor (CSF) und Somatotropin (STH) wurden 1995 weltweit über 2 Mrd. USD umgesetzt; die Wachstumsraten des europäischen Marktes lagen 1996 und liegen 1997 bei 10–12%.

Anpassung an die neuen Marktbedürfnisse

Die Entwicklung zuverlässiger Technologien ist ein grundlegendes gesellschaftliches Bedürfnis. Es geht dringlich darum, die Biotechnologie vom Image eines mystischen Kunsthandwerkes zu lösen und zu einer sicheren, fehlertoleranten Technologie zu machen, welche das Vertrauen der Allgemeinheit geniesst.

Am TWI wurde dieser Entwicklung schon frühzeitig Rechnung getragen: Einem erfolgreichen Nachdiplomstudium in Biotechnologie folgte die Integration dieser Inhalte in den normalen Chemiestudiengang. Für die Fachhochschule ist ein eigener Biotechnologie-Zweig geplant und genehmigt.

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Postfach 805
CH-8401 Winterthur

Der Schwerpunkt Bioverfahrenstechnik an der Zürcher Fachhochschule Winterthur (ZFW) umfasst folgende aF&E-Gebiete:

- Mikrobiologische, zellbiologische, kinetische und physiologische Analyse von technisch bedeutsamen Biosystemen (Bakterien, Pilze, Hefen, animalische Zellen)
- Bioreaktionstechnik (Prozessanalyse, -auslegung und -führung, Steriltechnik, Stoff- und Energietransport)
- Bioprozesskontrolle (on-line-Messtechnik, Datenmanagement und Steuerung/Regelung)
- Aufarbeitungstechnik und Prozessintegration (*in-situ* product removal, insbes. Membrantechniken)
- Modellbildung und Simulation als Mittel für obengenannte Zwecke

Definitionen für 'Biotechnology' (Biotechnologie)

- European Federation of Biotechnology (EFB), 1981:
  The integrated use of biochemistry, microbiology and engineering sciences in order to achieve technological (industrial) application of the capabilities of microorganisms, cultured tissue cells and parts thereof.
- Organization for Economic Cooperation and Development (OECD), 1982:
  The application of scientific and engineering principles to the processing of materials by biological agents to provide goods and services.
- EFB, 1989:
  The integration of natural sciences and engineering sciences in order to achieve the application of organisms, cells, parts thereof and molecular analogues for products and services.

- The aims of EFB are:
  - to advance biotechnology for the public benefit
  - to promote awareness, communication and collaboration in all fields of biotechnology
  - to provide governmental and supranational bodies with information and informed opinions on biotechnology
  - to promote public understanding of biotechnology

Definition für 'Biochemical Engineering Science' (Bioverfahrenstechnik)

- European Section of Biochemical Engineering Science (ESBES), 1996, Dublin (by MD Lilly):
  Biochemical Engineering Science represents the fundamental research into all aspects of the interactions between engineering and other disciplines necessary to underpin the development of industrial scale biologically based processes.

Die EFB hat ebenfalls strategische Zeichen gesetzt und 1996 eine 'Section of Biochemical Engineering Science' gegründet, deren Schwergewicht beim Engineering liegt. Biochemical Engineering wird wohl am besten mit Bioverfahrenstechnik übersetzt. Die EFB-Arbeitsausschüsse für Bioreaktoren, Mess- und Regeltechnik sowie Produktaufarbeitung haben mit diesem gemeinsamen Schritt klar gemacht, wie bedeutend robuste und zuverlässige biotechnologische Verfahren zur Produktherstellung, zur Nutzung erneuerbarer Rohstoffe und zur Beseitigung oder Vermeidung von Abfallstoffen sind. Es sind die erfolgreichen Stoffumwandlungen und nicht bloss die neuen Ideen von denen die Firmen leben und die Menschen profitieren.

Schwerpunktbildung

Die universitären Hochschulen streben vermehrt in Richtung der reinen Grundlagenwissenschaften. Die kommenden Fachhochschulen sind dazu aufgerufen, insbesondere angewandte Forschung und Entwicklung (aF&E) voranzutreiben und zu fördern.

Zwischen reiner wissenschaftlicher Forschung an universitären Hochschulen und Industrieforschung liegen Bereiche, die von keiner dieser Institutionen wahrgenommen werden wollen oder können. Beispiele dafür sind anwendungsorientierte, präkompetitive Entwicklungen auf der Basis von Forschungsresultaten, die noch nicht reif für die Industrieentwicklung oder Vermarktung sind, aber eindeutig in diese Richtung weisen. Dazu gehören etwa neue, potentielle Stoffe für die Therapie, messtechnische Methoden und Geräte oder ökologisch nachhaltige Verfahren.

Mögliche Märkte drohen brach zu liegen, wenn der Einstieg für kleine Unternehmungen zu riskant und für grosse zu wenig lukrativ ist.

Kompetenzverbund für Bioverfahrenstechnik

Um diese Lücke zu schliessen, also um sowohl die Industrie als auch kleine und mittlere Unternehmen (KMU) anziehen zu können, müssen neben hochkarätiger Ausbildung in allen Biotechnologie-Bereichen effiziente Möglichkeiten für aF&E aber auch Service geboten werden. Dies wird vor allem in der Verantwortlichkeit der zukünftigen Zürcher Fachhochschule Winterthur liegen.

Heutige Spitzenleistungen in der Bioverfahrentechnik sprengen allerdings den Rahmen üblicher (Hochschul-)Institute in logistischer, finanzieller und personeller Hinsicht. Das belegen auch die Erfahrungen mit Grossforschungsinstituten und Regionalverbunden, etwa in Deutschland oder Japan. 'Einzelkämpfer' können auch die kritische Masse an Personal mit dem erforderlichen Know-how sowie an modernen Geräten und Infrastrukturen nicht erreichen. Zusammenschlüsse wie Verbunde oder Zentren müssen geschaffen werden. Menschen und Mittel müssen effizient, d.h. gemeinsam und gut koordiniert genutzt werden.

Ein Kompetenzverbund für Bioverfahrenstechnik ist ein taugliches Mittel zur Realisierung des Technologietransfers im Bereich Biochemical Engineering. Er soll einzelne, bereits bestehende Aus- und Weiterbildungsaktivitäten an den universitären Hochschulen und Fachhochschulen komplementieren und dringliches Aufholen gegenüber Dritten ermöglichen. Dazu braucht es:

- Transfer von Know-how, Methoden, Spezialfertigkeiten, zu erreichen über Forschung, Entwicklung und Lehre: nachträgliche und vorsorgliche Erarbeitung von Grundlagen für Entwicklungen von industriellem Interesse. Dies ist besonders wichtig für KMU, die diesen Beitrag nicht selbst zu leisten vermögen, zum Teil aber auch für grosse Betriebe, wenn etwa Interessenkonflikte bestehen oder Out-sourcing nötig ist.
- Bereitstellung und Betrieb von High-Tech- und Pilotgeräten und -anlagen für angewandte Forschung und Entwicklung mit folgenden Detailzielen:
  - Know-how im Inland mehren, verteilen und halten,
  - Abdecken fehlender Grundlagen für Entwicklungen und Beurteilungen
  - High-Tech Anlagen für Spezialfälle in aF&E mit dem nötigen Know-how,
  - Anreiz für internationale Spezialisten, Erfindungen und Know-how frühzeitig ins Land zu bringen, hier zu testen und weiter zu entwickeln.
- Bereitstellung von Probierplätzen (User-labs) für vernetzte Forschungs- und Entwicklungsgruppen sowie besonders für KMU.
- Beratung von Kunden für Planung, Ausrüstung, Nachrüstung, Ersatz.

In diesem Sinn kommt dem Kompetenzverbund eine Integrationsfunktion zu, wobei die ZFW eine zentrale Rolle auf dem Gebiet der Bioverfahrenstechnik übernimmt. Die Hochtechnologie-Hardware sollte nicht x-mal angeschafft, betreut und gewartet werden müssen, aber trotzdem durch viele 'Kunden' genutzt werden können. Einheiten von Methoden, Verfahren und Prozessen sind dabei zu fördern und die ökologische Nachhaltigkeit ist gleichzeitig zu verbessern.

Aussprachen im Zusammenhang mit der letzten Schwerpunktprogramm-Ausschreibung haben den Bedarf an gut ausgerüsteten und zuverlässig funktionierenden Bioreaktionssystemen ausgewiesen. Ausbildungsbedarf für Praktiker sowie aF&E-Projekte (Prototyp-Herstellung von Stoffen und Geräten für Testzwecke, Engineering) sind sowohl aus der etablierten Grossindustrie als auch insbesondere von KMU genügend vorhanden. Speziell KMU sind auf ein Benutzer- und Beraterzentrum kritischer Grösse mit entsprechender Ausrüstung, Flexibilität, Infrastruktur und fachlicher Kompetenz angewiesen.

Stellung der Zürcher Fachhochschule Winterthur

Am TWI hat die Biotechnologie eine etablierte Tradition.

aF&E wird eindeutig prozess- und engineering-orientiert betrieben. Damit wird den Bedürfnissen von über 50 in der Region angesiedelten KMU entsprochen, welche am Biotechnologie-Markt beteiligt sind. Dies ist in Winterthur aufgrund der soliden Grundausbildung in Chemie, Biologie und Verfahrenstechnik, der engen Vernetzung mit anderen Ingenieurabteilungen am TWI, einer vertraglich festgeschriebenen Zusammenarbeit mit der ETH-Zürich sowie der etablierten Kooperation mit der chemischen Industrie möglich. Die ISW könnte diesen Schwerpunkt mit ihrer eher gewerblichen Ausrichtung und ihrer Vernetzung mit Agro- und Lebensmitteltechnologie sehr gut komplementieren.

Der Stärken der Zürcher Fachhochschule Winterthur werden eingesetzt für den Wissens- und Technologietransfer sowie für den Ausbau bestehender Kompetenzen und internationaler Kooperationen in den folgenden Bereichen:

- Bioprozess- und -verfahrenstechnik,
- Stoffumwandlung, -aufarbeitung und -reinigung,
- Prozess- und Umweltanalytik,
- Modellbildung und Prognostik,
- Automatik und Informatik.

Der Studiengang und das geplante berufsbegleitende Nachdiplomstudium werden, wie schon das frühere Nachdiplomstudium, international validiert. Der Studiengang wird auch national durch den Schweizerischen Koordinationsausschuss für Biotechnologie (SKB) im Auftrag der Schweizerischen Hochschulkonferenz koordiniert.

Eingegangen am 11. Juli 1997

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[1] E. Berger, E. Heinzle, K. Hungerbühler, 'Biotechnologische Produktion von Chemikalien – Vorteile für die Umwelt', *Neue Zürcher Zeitung*, 5.3.1997, S. 67.

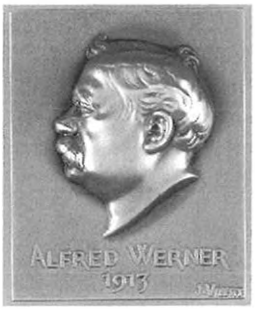
CHIMIA 51 (1997) Nr. 8/9 (August/September)

Wissenschaftliche Auszeichnungen der NEUEN SCHWEIZERISCHEN CHEMISCHEN GESELLSCHAFT

Ausschreibung für die Verleihung 1998

Distinctions scientifiques de la NOUVELLE SOCIÉTÉ SUISSE DE CHIMIE

Mise au concours pour 1998



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 1998 statt.
Einreichefrist: 31. Oktober 1997.

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 1998.
Délai de présentation: 31 octobre 1997.

Sandmeyer-Preis

Der *Sandmeyer*-Preis wird für hervorragende Arbeiten auf einem Gebiet der industriellen oder angewandten Chemie an ein Arbeitsteam oder einen Einzelnen verliehen. Die Arbeit soll in der Regel in der Schweiz oder im Ausland von einem Arbeitsteam mit Beteiligung von Schweizer Bürgern und Bürgerinnen ausgeführt worden sein.
Die Preisverleihung findet im Frühjahr 1998 statt.
Einreichefrist: 31. Oktober 1997.

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 1998.
Délai de présentation: 31 octobre 1997.

Dr.-_Max-Lüthi_-Preis

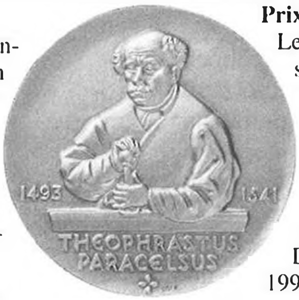
Die Dr.-*Max-Lüthi*-Auszeichnung wird für ausgezeichnete Diplomarbeiten verliehen, die an Chemieabteilungen von höheren technischen Lehranstalten der Schweiz ausgeführt werden.
Anträge der Abteilungsvorsteher der Chemieabteilungen müssen bis Ende Dezember 1997 an den Geschäftsführer der NSCG eingereicht werden.
Die Preisverleihung findet im Frühjahr 1998 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 1997.
La remise du prix aura lieu au printemps 1998.

Paracelsus-Preis

Der *Paracelsus*-Preis kann Wissenschaftern, die im internationalen Vergleich Hervorragendes in der wissenschaftlichen Forschung auf dem Gebiet der Chemie geleistet haben, zuerkannt werden.
Der *Paracelsus*-Preis wird das nächste Mal im Herbst 1999 verliehen.
Einreichefrist: 31. Oktober 1998.



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 la prochaine fois en automne 1999.
Délai de présentation: 31 octobre 1998.

Vorschläge und Bewerbungen sind mit den notwendigen Unterlagen an den Geschäftsführer der NSCG 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

Adresse: c/o Ciba, K-25.1.47
CH–4002 Basel

CHIMIA 51 (1997) Nr. 8/9 (August/September)

NEUE SCHWEIZERISCHE CHEMISCHE GESELLSCHAFT
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The LIC provides:
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- a document delivery service
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- book and journal loans
- services of visiting researchers
- historical chemistry information service.

All members of the New Swiss Chemical Society are entitled to use the services of the LIC at a specially low price. The centre can be contacted at:

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INFORMATION

International Union of Pure and Applied Chemistry

President's Report on the State of the Union

It has been a very busy presidency up to now and I am convinced that it will remain so until the end of the year. In these days of rapid globalization, we can readily perceive the effect that the high-speed changes taking place around us are having on IUPAC. Yet globalization is not new to IUPAC: looking back over the union's history, we see that globalization was an important topic as early as 1919 and that it was the driving force behind the creation of IUPAC just after the First World War. Globally accepted standards, codices and nomenclature for chemicals had the same prime importance for academia and industry then as they have now. This being said, however, I have to add that IUPAC's objectives, as set out in our Statutes, give the union a much broader mandate.

Today, the rapid pace of growth and change in the basic experimental sciences of biology, chemistry, and physics is apparent to all. Looking at the information explosion in these areas, our attention is frequently drawn to the crossover between the sciences and to the fact that Nature is (alas) not organized like our universities. Adaptation and flexibility are needed in academia as well as industry.

Moreover, it is our responsibility as scientists to ensure that both government and the public at large are made aware of scientific progress at an early stage. In particular, our task as chemists is to put over the message that chemistry is already very important today and that it will go on to be a key science in the world of tomorrow, with a tremendous out-

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reach into sister sciences, the environment, industry and the economy as well as into our everyday lives.

Achievements

Administration and Finances

As you are aware, Dr. *Mo Williams*, who was head of the IUPAC Secretariat from 1968, retired this year at the end of April. You will also be aware that our new Executive Director, Dr. *John W. Jost*, took up his post at Research Triangle Park (RTP), NC, USA at the beginning of April. The transitional period, during which there will be two Secretariats, will last until September 1997. In October our Oxford office will ship documents to RTP and then close down.

At this point in my report I feel privileged to have the opportunity to express my sincere thanks to *Mo Williams* for his long and outstanding service, and for his loyalty during his time with IUPAC. He personified stability for a substantial part of IUPAC's existence and was also the leading authority on all matters relating to IUPAC. At the same time I also want to extend my very best wishes to our new Executive Director, who is building up our new USA Secretariat into a globally active Secretariat, devoting special care to emphasizing activities which will ultimately enhance IUPAC's visibility.

As part of this process, our web site (current home page address http://chemistry.rsc.org/rsc/iupac.htm) will be further enlarged and made more accessible by setting up a main site at RTP with the domain name of iupac.org. The current site, hosted by the Royal Society of Chemistry, will become our European mirror site. We expect soon thereafter to also have an Asia/Pacific mirror site. It is intended that the site should become the chief channel of communication with the community and especially with those engage on IUPAC projects.

Our finances are now in good shape, thanks to the work of our Treasurer, as well as to the Finance Committee and the new US banker taking care of our securities. These have been supplemented by windfall money from Barings Bank. The Executive Committee decided that the Treasurer should set up a new endowment fund to harbor our surprise resources.

Congresses

I would like to pick out just three of the many IUPAC-sponsored conferences that have taken place or are still to take place this biennium.

This year, for the first time since 1967, the IUPAC Congress and General Assembly (GA) have been scheduled to take place in the same city in two successive weeks – 'back to back', so to speak. The venue is Geneva, Switzerland, and the two events will be taking place in the last two weeks of August; the Congress first, then the GA. The same pattern will be repeated in 1999 in Berlin, Germany, after which IUPAC will be able to take proper stock of the new combined event. Holding the two events in successive weeks obviously increases the organizing committees' workload substantially, and I would like to express my thanks to the two organizing bodies in Switzerland and Germany who have taken up the challenge.

In fall 1996 the CHEMRAWN IX Conference took place in Seoul, Republic of Korea, under the heading 'The Role of Advanced Materials in Sustainable Development: Use, Disposal and Recycling of Materials'. Thanks above all to a magnificent effort by the South Korean industry, the event was a great success. Incidentally, this was the third time that IUPAC has had the pleasure of holding a CHEMRAWN Conference in the Asian/West Pacific Rim region: the other two were 'Chemistry and World Food Supplies' in Manila in 1982 and 'Advanced Materials' in Tokyo in 1987.

A third IUPAC workshop on Safety in Chemical Production was organized in April 1997 by our industrial wing COCI, the Committee on Chemistry and Industry. The workshop was held in San Francisco, CA, in conjunction with the American Chemical Society, the Chemical Manufacturers Association and the United States Environmental Protection Agency. The attendance of two 1995 chemistry *Nobel* laureates generated keen interest. After the first workshop, which was held in Basle, Switzerland (1990), and the second, which was held in Yokohama, Japan (1993), there is still continued interest in holding workshops in other parts of the world.

Nomenclature

I am happy that IUPAC is now able to submit a final list of names and symbols for elements 101 to 109 to the Council for approval in Geneva in August this year. As you are aware, the naming of the transfermium elements was a lengthy, controversy-ridden process. The three laboratories in Germany, Russia, and the USA which were involved in the discovery of the elements have been consulted at length and their comments solicited. Their input was most important, given that one of IUPAC's responsibilities is to formulate widely accepted recommendations capable of forming a basis for international communication in chemistry. A press release was issued in February 1997 and the final say rests with the Council. I should also mention that activities have been started to enable IUPAC to put forward proposals for the nomenclature of elements 110 to 112. The process will be conducted in accordance with our Bylaws and in close collaboration with the discoverers. Once these activities have concluded the final decision will once again be made by the IUPAC Council.

Collaboration with UN and ICSU Bodies

Collaborative efforts with UNESCO, UNIDO, and WHO have been substantially intensified during the biennium.

CHEMRAWN IX was organized jointly by our CHEMRAWN committee and UNESCO, while COCI continued its three-way collaboration with UNIDO and UNESCO. This gives safety experts from the third world the opportunity to spend a period of approximately one month with IUPAC Company Associates and discuss existing safety measures in a direct hands-on fashion. The visiting safety experts, a substantial number of whom were government specialists, subsequently returned to their home countries. We are thus constructing a progressively expanding network of safety experts in chemical production and also bringing IUPAC into closer contact with the developing world.

All the programs which IUPAC is undertaking in conjunction with UNESCO are supervised by the International Chemistry Council (ICC), a body comprising four chemistry *Nobel* laureates from Canada, France, UK, and USA, one Japanese industrialist and three developing world representatives from Africa, Asia/Pacific, and Latin America. The inaugural meeting took place in Paris in January 1997. The executive part of the programs is in the hands of IUPAC and UNESCO Officers. The ICC will convene every second year to make a critical assessment of all joint IUPAC/UNESCO activities. We will also be inviting representatives of our Committee on Teaching for Chemistry (CTC) to take part in IUPAC's annual meetings with UNESCO. This is because CTC has been collaborating with UNESCO for quite some time in areas of key interest to the ICC. Furthermore, some of our Commissions have been enlisting UNESCO's help to have larger-scale programs followed up. Such joint activity also presents an opportunity for us to strengthen our links with the International Organization for Chemical Sciences in Development (IOCD) and the Third World Academy of Sciences (TWAS).

The President of our Division on Chemistry and the Environment is acting as WHO liaison. He is representing our interests at the WHO-led International Forum for Chemical Safety (IFCS) and International Programme for Chemical Safety (IPCS). In the course of his duties, he will be maintaining very close contact with the President of our Division on Chemistry and Human Health. IUPAC together with IUPHAR, IUTOX and the International Life Science Institute (ILSI), constitute the scientific ICSU-NGOs in these UN bodies. IUPAC is currently acting as the group's spokesman.

Collaboration with ICSU executive bodies, a large number of sister unions, ILSI and the ICSU Scientific Committee on Problems of the Environment (SCOPE) has improved substantially in 1996–97.

Chemistry and Society

In October 1996 COCI published its first White Book as a contribution from science to the debate on the effects of chlorine and chlorine-containing compounds on the environment. This 'White Book on Chlorine', published as a special issue of the IUPAC journal *Pure and Applied Chemistry*, is an independent and unbiased collection of original articles written by renowned scientists from all over the world, which critically evaluates various aspects of the subject. It has proven to be a success and of interest not only to academic institutions, industry, governmental agencies, and environmental organizations, but also to the general public.

The White Book is the first publication of this type and more are set to follow. IUPAC is thus able to use its special position as a science-based, non-governmental, non-industry foundation with a worldwide network of experts from various fields of chemistry and sister disciplines to offer a platform for publications.

State of the Union

Countries and Companies

A glance at the world map of National Adhering Organizations (NAOs) and Observer Countries (OCs) shows that while IUPAC is represented in all but a few areas of the Americas, the West Pacific Rim, and Europe, it has as yet failed to

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enlist broad participation from either the strip of countries stretching from Syria to Kazakhstan or the countries of Africa (with the exception of Egypt, the Republic of South Africa, and Tunisia). Egypt and South Africa have both been affiliated to IUPAC for quite some time now. This year the Executive Committee will have the pleasure of submitting to the Council in Geneva the membership application of the Union of Yugoslav Chemical Societies as well as requests for upgrading from Pakistan and the Philippines, two of our Observer Countries. Let me add at this juncture that our well accepted voting system is special in that it reflects the countries' actual chemical turnover figures as published by the UN. As a rule, while NAOs with stronger chemical and pharmaceutical industries have a somewhat larger voting share in the Council, they also make a greater financial contribution to IUPAC.

The participation of single companies (IUPAC is the only scientific union with direct industry participation) is remarkable, and membership of the Company Associate scheme remains astonishingly stable given the conditions which industry has to contend with today. Top of the participating companies table in 1996 was Japan with 46 companies, followed by USA with 23 and Germany with 12. The EU15 have 44 altogether. Comparing financial contributions for 1996, the USA is on first place, followed by Japan and Germany. The EU15 are on second place behind the USA.

Adapting Mission, Goals, and Structures

My predecessors' state of the union reports discussed the critical remarks voiced against some of IUPAC's activities in considerable depth. Incidentally, some of these criticisms are still the subject of discussion. I would like here to inform you about the actions taken in 1996–97 in response to valuable constructive criticism. I believe that the steps we have taken will result in goals and structures which reflect the tasks facing IUPAC in the next millennium.

Several brainstorming sessions took place during the biennium at which IUPAC Officers, all of whom were very much involved in the organization of the meetings, were able to discuss thoroughly IUPAC's current situation, mission, objectives, and future. These always involved well-known chemists from academia and industry, plus representatives from inside and outside IUPAC. An initial meeting was held in Belmont, USA, during June 1996. A subsequent European one-day meeting was organized in London for February 1997 and a third brainstorming workshop for the Asia/Pacific region took place in Singapore during June 1997. All were very fruitful in clarifying IUPAC's mission and goals as it heads into the next millennium as well as in promoting an intensive and rewarding exchange of opinions about the strengths and weaknesses of the Union. The meetings reinforced the need for the changes being discussed in IUPAC. All were extremely valuable, instrumental even, in the formulation of new objectives and activities, and to increasing IUPAC's visibility.

The IUPAC Officers also held an extraordinary meeting with the Divisional Presidents/Vice-Presidents and Section Presidents in Frankfurt, Germany, on March this year. This meeting was an opportunity to go through each division's restructuring plans. While the creation of the Divisions on Chemistry and the Environment, and on Chemistry and Human Health at the last General Assembly represent a major step there are still some desiderata. We need to find ways of integrating both the area of materials and the major scientific activities taking place at the interface between chemistry and biology into IUPAC. With the Divisional Presidentsí input, the Frankfurt meeting yielded proposals for solutions which should result in structural changes to eliminate overlap and provide IUPAC with the missing activities and structures. The meeting was also used for a thorough discussion of the Vice-President's Critical Assessment and to some extent for discussion of further proposals for structural change.

These proposals and the Vice-President's Critical Assessment were taken up again at the Executive Committee (EC) meeting at Jerusalem in April 1997. After detailed discussions the EC decided to establish a Strategy Development and Implementation Committee (SDIC) to define the science policy of the union and to examine the feasibility of converting the bulk of IUPAC's scientific work to a project-driven/ project-financed system with time-limited Commissions, as described in the concept endorsed by the EC. The eleven members of the SDIC were appointed by myself following consultations. The Committee was placed under the chairmanship of Vice-President *Joshua Jortner* and it met for the first time in June.

Scientific Work

I am delighted at the large number of committed volunteers who devote their time and scientific expertise to furthering the IUPAC cause. More than 1000 scientists are actively involved in IUPAC, an achievement which I strongly believe to be cause for congratulation. That this is an enormous strength goes without saying, and we have to safeguard its continuity under the best possible circumstances. It also goes without saying that the limited financial resources available to IUPAC and the small time window available for new scientific endeavors are forcing us to choose our projects carefully.

Future Perspectives

As the only purely scientific global chemical organization mandated to undertake this kind of work, it is essential that IUPAC continues with its codification, nomenclature and standardization activities. It has to do so at a much faster pace than in the past and in close association with the professional bodies which are also involved in these activities. They are working rapidly using their excellent skills, and IUPAC should try to find a collaborative basis with them which is not only acceptable to all stakeholders, but which will also enable all parties to benefit from the special advantage which IUPAC derives from being a global, strictly scientific, non-governmental organization.

It is also my belief that collaboration with UN and ICSU bodies has to be intensified and focused. Here IUPAC has a special responsibility, arising from the immense outreach of chemistry into the other sciences and the remarkably close relationship which has existed for quite a long time between chemistry in academia and the now giant chemical and pharmaceutical industry. This relationship has no parallel in physics and has started to emerge in biology only relatively recently with the advent of small biotechnological companies, the first of which was set up in California in 1976. Chemistry is a pervasive part of our every day lives and one that accompanies us throughout our lives.

For these reasons, IUPAC should also increase its activities in the field of 'Chemistry and Society'. Here again the Union occupies a very special position, maintaining as it does close contact with all the major stakeholders in innovation, *i.e.*, academia, industry, government, and society. We have been successful in strengthening our links with society, and through society with governments as well, nevertheless, I think, there is still a lot of room for improvement.

As always, there are still some issues to be resolved. One is that all of us in IUPAC have to make greater efforts to recruit the best scientists for our activities. This is extremely important to IUPAC since all our collaborators are volunteers. One of the advisors whom I had the pleasure of consulting during my period as Vice-President summed it up by saying that serving IUPAC comes under the heading of *noblesse oblige*.

A second unresolved issue is that we have to be very careful in selecting the activities in which we wish to get involved. We have to make sure that we are resolute in the pursuit of our goals once they are defined and that we come up with the desired result quickly. Let me also add that we have to remain true to our scientific base, unswayed by any pressure of a non-scientific nature, irrespective of whether it comes from academia, industry, governments or society.

Conclusions

Significant progress has been made, but a lot still remains to be done.

I have enjoyed having responsibility for a large number of teams, and I feel privileged to have been able to work with such colleagues as my IUPAC Officers and the members of the Secretariat, Executive Committee and Bureau as well as to have interacted with the Council, IUPAC's highest body. I am also very pleased to have been given the opportunity to establish contacts with our Divisional Presidents as well as with the Chairmen of CHEMRAWN, COCI, CTC, the Committee for Printed and Electronic Publications (CPEP) and the Committee on Affiliate Membership (CAM). If we look at CAM, it becomes apparent that although progress has been made, there is still a need for further action. Additionally, CPEP is in need of a new policy on the submission of papers for publication in *Pure and Applied Chemistry*.

Let me close by thanking all members of IUPAC bodies for their efforts and the dedication with which they have worked for our Union over the last biennium in particular, even though I am aware that most of them have been working on IUPAC's behalf for substantially longer. It is due to them, their commitment, flexibility and creativity, that we can look with confidence to the future of IUPAC.

Albert E. Fischli
IUPAC President

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SATW Schweizerische Akademie der Technischen Wissenschaften

Warum braucht es die SATW?

Warum braucht es die Schweizerische Akademie der Technischen Wissenschaften (SATW)?

Die SATW vereinigt unter ihrem Namen Spitzenpersönlichkeiten aus dem Gebiet der Ingenieurwissenschaften aus der Schweiz. Als Einzelmitglieder tragen sie die Verantwortung für die Vertretung der technischen Wissenschaften in der Gesellschaft. Ungefähr 60 Gesellschaften, die total *ca.* 65 000 Ingenieure vertreten, unterstützen als Kollektivmitglieder die Bestrebungen der SATW. Seit 1989 ist die SATW Mitglied des Council of Academies of Engineering and Technological Sciences (CAETS), Washington, D.C.

Mitglieder und Organe

Die Akademie hat heute 150 Einzelmitglieder (darunter 4 Schweizer *Nobel*-Preisträger) und 22 korrespondierende Mitglieder. Diese Einzel- und korrespondierenden Mitglieder stammen sowohl aus der Industrie wie auch aus Forschung und Lehre.

Der Akademie angeschlossen sind *ca.* 60 Mitgliedsgesellschaften; sie vertritt damit ungefähr 65 000 Ingenieure und Wissenschafter aller denkbaren technischen Fachrichtungen. Die Delegierten dieser Mitgliedsgesellschaften nehmen mit Stimmrecht an der jährlichen Mitgliederversammlung teil, sie wählen sowohl neue Einzel- als auch Vorstands- und WBR-Mitglieder. Im Jahre 1996 zum Beispiel wurden die Mitgliedsgesellschaften eingeladen, an der alljährlich stattfindenden gemeinsamen Tagung zwischen Vorstand WBR teilzunehmen. Diese Zuammenkunft stand unter dem Thema 'Realität des Technologietransfers in die industrielle Produktion – Vom Forschungslabor zu Produktionsstätte – Wozu dient die Forschung?'. Dieses Jahr beteiligen sich die drei grössten Mitgliedsgesellschaften aktiv an der Vorbereitung und der Durchführung der im September stattfindenden Jahrestagung. Es ist wünschbar und für die Akademie notwendig, dass sich die Mitgliedsgesellschaften und ihre Delegierten aktiv am Leben der Akademie beteiligen. Mit ihren Mitgliederbeiträgen unterstützen sie die SATW auch finanziell.

Ein rund 20köpfiger Vorstand, in ausgewogener Zusammensetzung (Hochschulen, Industrie), legt Jahresziele und Budget fest, bereinigt und verabschiedet Stellungnahmen der Akademie. Der Vorstand hat sich in den letzen Jahren zu einem überaus wertvollen Think tank entwickelt, welcher über die Interessen der einzelnen Fachdisziplinen hinaus den Gedankenaustausch pflegt. Das Ergebnis dieser Beratungen fliesst ein in die Tätigkeit des Wissenschaftlichen Beirates und in weitere, ausserhalb der Akademie stehende wissenschaftspolitische Gremien.

Der rund 20köpfige Wissenschaftliche Beirat (WBR) strukturiert das Detailarbeitsprogramm der Akademie. Aus der Tätigkeit der Kommissionen und Arbeitsgruppen der WBR resultieren einerseits interessante Publikationen, welche ohne Akademiearbeit wohl kaum angegangen worden wären. Insbesondere fördert der WBR Aktivitäten zur Studienmotivation in technischer Richtung, welche sich an Mittelschülerinnen und Mittelschüler richtet. Seine Priorität sieht er in der Förderung des Nachwuchses in den Ingenieurberufen. Zu seiner Arbeit gehören aber auch Überlegungen in Richtung Zukunftsbewältigung, Energie, Ethik, nachhaltige Entwicklung, Förderung der Umsetzung von technisch/wissenschaftlichen Erkenntnissen. Dabei zieht er – gleich wie auch der Vorstand – Nutzen aus dem Umstand, dass seine Mitlglieder, Damen und Herren, ohne Ausnahme in ihren jeweiligen Fachbereichen durchwegs eine hohe Reputation geniessen. Selbstverständlich wird dabei dem Aspekt der Öffentlichkeitsarbeit die nötige Aufmerksamkeit zuteil, damit die Erkenntnisse aus der Akademiearbeit auch in ein weiteres Publikum hinausgetragen werden.

Ein Generalsekretariat mit einem vollamtlichen Generalsekretär und zwei Mitarbeiterinnen dient der Bewältigung der täglichen Arbeit und ein separates Stipendiensekretariat verwaltet die Stipendienmittel des SATW/Branco Weiss-Fonds und weiterer Quellen.

Aktivitäten

In den 16 Jahren ihrer Existenz hat sich die SATW einen beachtlichen Leistungsausweis erarbeitet: Dank des grossartigen Einsatzes der ersten Präsidenten und ihrer Vizepräsidenten sowie der Mitarbeit unzähliger freiwillig im Milizsystem Mitwirkenden sind die Aktivitäten vielfältig. Sie schlagen sich – besonders erwähnenswert – nieder in der Veranstaltung von Jahrestagungen mit bereichsübergreifender Thematik, aber auch in weiteren Aussprachen und Vortragsangeboten. Sie spannt die Brücke zwischen den einzelnen Mitgliedsgesellschaften und vertritt deren Interessen nach aussen. Wichtig ist die Unabhängigkeit des Dachverbandes auch bei der Publikation von Schriften, vorab zu Fragen der Zukunftsbewältigung und der Fortentwicklung der Technik, oder in der Veröffentlichung von Stellungnahmen im Vorfeld von wichtigen Entscheidungen oder Abstimmungen zuhanden der Öffentlichkeit oder der Bundesbehörden. Nicht zuletzt deshalb wird die SATW im heutigen Forschungsgesetz als eine der vier durch den Bund zu fördernden wissenschaftlichen Akademien anerkannt. Die Akademie selber ist zudem eine Institution der Forschungsförderung und verteilt die ihr vom Bund zugesprochenen Mittel im Rahmen ihrer Möglichkeiten für verschiedene Projekte ihrer Mitgliedsgesellschaften. Dieser Auftrag wird von den Verantwortlichen der SATW mit grösstmöglicher Umsicht und Fairness erfüllt.

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Präsident: Prof. *Dr. J.-C. Badoux*
Generalsekretär: Dr. *B. Rouvé*

Tagungen, Veranstaltungen, Weiterbildung

New Phase of Strategic Development within *Alusuisse-Lonza*

The *Alusuisse-Lonza Group* remains a diversified industrial, albeit managed along different lines, strictly market and performance driven. It will focus its activities in 6 sectors offering substantial growth potential and platforms for achieving global leadership positions.
They are:

1. Fine Chemicals and Specialties, which comprise our exclusive synthesis and bio-technology propositions to the Life Science industry both in Europe and in the United States, as well as our selective biocidal chemical business headquartered in the US.
2. Chemical Intermediates and Additives, a technology driven set of businesses with strong proprietary know-how and strong market positions, headquartered in Italy, but trading in Europe, the US, and the Far East.
3. Food and Tobacco Packaging. The first segment focuses on flexible packaging for the food markets, currently active in Europe and in North America, whereas the second is a market leader in the production of flip-top cartons for the major tobacco producers.
4. Pharmaceutical and Cosmetics Packaging, comprises a wide range of product offerings to these industries and is already the biggest globally.
5. Upstream Aluminium Businesses, which comprise our bauxite/alumina operations in Australia, our anode plant in Holland, and our smelter positions in Iceland and Norway; and
6. Downstream Activities, which serve, through a system approach, the Automotive, Mass Transportation, Industrial and Building markets, not only through aluminium conversion, but increasingly more with other materials and composites offerings.

These sectors will continue to be managed by the Executive Committee. Effective August 1, 1997, it will be extended with the inclusion of two new members, Mr. *Hans Noetzli* and Mr. *Andrea De Virgiliis*.

Mr. *Hans Noetzli* currently head of our US chemical activities, will assume responsibility for our newly created Pharmaceutical and Cosmetic Packaging sector, which will trade under the name of Lawson Mardon Wheaton, and includes the other related activities of previous Packaging organization. This sector will be headquartered in the United States.

Mr. *Henk van de Meent* will retain responsibility for the Lawson Mardon Packaging, which now as a sector will focus on Food Flexibles and Tobacco.

Mr. *Andrea De Virgiliis*, currently head of our Polymers and Additives businesses, will assume responsibility as sector head of our newly formed Intermediates and Additives business, which will include in Polymers and Additives business in Italy, the US, and Singapore.

Mr. *Leander Tenud* will retain

responsibility for the Fine Chemicals, including Biotechnology and Specialties.

Given the interrelated nature of our Aluminium based activities, Mr. *Kurt Wolfensberger* will retain responsibility for both the Upstream and the Downstream activities of *Alusuisse*.

The flatter organisation is designed to more effectively support the management of the businesses and be more responsive to market dynamics.

Alusuisse-Lonza has also established a set of ambitious financial goals. A continuous earnings improvement profile of 10% per annum on the average over the next 5 years and a growth goal in sales to the 15 bn CHF mark by the end of 2002.

Some businesses from the current portfolio, totalling some CHF 800 Mio. in sales, will be divested. They are mostly Packaging.

Neue Bücher

Bei der Redaktion eingetroffene Bücher

N. Kläntschi, P. Lienemann, P. Richner, H. Vonmont
'Elementanalytik'
Spektrum Akademischer Verlag, Heidelberg – Berlin – Oxford, 1996

M. Bochmann
'Metallorganische Chemie der Übergangsmetalle'
Basistexte Chemie, Band 13/14
VCH, Weinheim – New York – Basel – Cambridge – Tokyo, 1997

S. Lee, G. Robinson
'Organische Synthese – vom Labor zum Technikum'
Basistexte Chemie, Band 15
VCH, Weinheim – New York – Basel – Cambridge – Tokyo, 1997

C.L. Willis, M. Wills
'Syntheseplanung in der Organischen Chemie'
Basistexte Chemie, Band 16
VCH, Weinheim – New York – Basel – Cambridge – Tokyo, 1997

Vorträge

Département de Chimie Organique, Université de Genève

Auditoire A-100, Sciences II
30, quai Ernest-Ansermet, Genève

Jeudy 2.10.1997 16.30 h	Prof. *D.P. Curran* University of Pittsburgh, USA titre à communiquer
Vendredi 10.10.1997	Prof. *A.I. Meyers*, Fort Collins, USA Prof. *M.T. Reetz*, Max-Planck-Institut, Mühlheim, Deutschland '*Oppolzer* Memorial Lecture'
Jeudi 16.10.1997 Vendredi 17.10.1997 16.30 h	Prof. *H. Kessler* Technische Universität München, Deutschland 'High-Resolution NMR Investigations of Peptides and Proteins Bound to Membranes'
Jeudi 30.10.1997 Vendredi 31.10.1997 16.30 h	Prof. *A. Holmes* University of Cambridge, UK 'Adventures in the Synthesis of Medium Ring Heterocycles' and 'Polymer Light Emitting Diodes'

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Chimia-Report (Talon 3 Monate gültig)
Ich bitte um Unterlagen zu den angekreuzten Kennziffern:

1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
11	**12**	**13**	**14**	**15**	**16**	**17**	**18**	**19**	**20**
21	**22**	**23**	**24**	**25**	**26**	**27**	**28**	**29**	**30**
31	**32**	**33**	**34**	**35**	**36**	**37**	**38**	**39**	**40**
41	**42**	**43**	**44**	**45**	**46**	**47**	**48**	**49**	**50**
51	**52**	**53**	**54**	**55**	**56**	**57**	**58**	**59**	**60**
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71	**72**	**73**	**74**	**75**	**76**	**77**	**78**	**79**	**80**

Name ____________________

Firma ____________________

Strasse ____________________

PLZ/Ort ____________________

Datum ____________ Unterschrift ____________

CHIMIA 51 (1997) Nr. 8/9 (August/September)

CHIMIA-REPORT

Bitte an die Inserenten

Richten Sie Ihre Beiträge für die Rubrik CHIMIA-REPORT nicht an die Redaktion, sondern ausschliesslich an: Kretz AG, Postfach, CH–8706 Feldmeilen Besten Dank!

Bühler AG, ANATEC lädt ein zur 7. NIR-Tagung am 9. Oktober 1997

Zum 7. Mal werden sich in Uzwil/ Schweiz die NIR-Interessierten treffen.

Lassen Sie sich einen kleinen Vorgeschmack auf das Programm geben, das Sie dort erwartet.

- **Online NIR-Spektroskopie**
  Das Ziel aller Online-Aktivitäten soll eine Optimierung der Produktionsabläufe sein. An ausgewählten Beispielen wird Ihnen ein Einblick in die Anwendungsbreite der NIR-Online-Anwendungen ermöglicht.
- **NIR-Transmissionsmessungen an Tabletten**
  Die spektrale Information dient zur begleitenden Überwachung Ihrer klinischen Muster. Die Technologie, die ohne aufwendige Probenvorbereitung zerstörungsfrei eine qualitative Beurteilung Ihrer Prüfmuster zulässt.
- Überzeugen Sie sich von den Vorteilen der revolutionären chemometrischen **Software NIRCAL Version 2.0 unter Windows NT**. Sie besteht aus qualitativen und quantitativen Kalibrationsmodulen, einer BASIC Makrosprache und Tutorials.

Innovation, Information, Kommunikation und Kontakte, das sind die vier Eckpfeiler der 7. Bühler-NIR-Tagung. Information und Kommunikation sind entscheidend dafür, wie Innovationen erfolgreich zum Einsatz kommen und wie die richtigen Kontakte geschlossen werden. Anerkannte Experten berichten über praxisorientierte Anwendungsbeispiele.

Alle Referenten der 7. Bühler-NIR-Tagung und die Mitarbeiter der Bühler ANATEC würden sich freuen, Sie am 9. Oktober 1997 in Uzwil begrüssen zu dürfen.

Anmeldung oder weitere Informationen erhalten Sie bei:

- Bühler AG, ANATEC
  CH–9240 Uzwil
  Telefon 071 955 24 96
  Telefax 071 955 33 56
  E-Mail nircal@buhler-ag.com

Leserdienst Nr. 34

Die nützliche Internet-Adresse für alle, die mit Analytik zu tun haben

Jetzt ist sekundenschnell klar, wie IG Instrumenten-Gesellschaft AG, Zürich, das analytische Leben erleichtert. http://www.igz.ch stellt das Lieferprogramm an Geräten, Systemen, Einwegartikeln und Reagenzien für das chemische, biologische, medizinische Labor sowie den Betrieb vor.

Mit 5 Buttons lässt sich von der Homepage aus bequem zu den gewünschten Informationen navigieren. Unter 'Produkte' führt das alphabetische Stichwortverzeichnis zum Ziel. Der Begriff 'Vertretungen' ordnet das breite Angebot nach diesem Suchkriterium. 'Top News' – laufend aktualisiert – präsentiert Neuheiten, aktuelle IG-Seminare und -Ausstellungen. Das 'Portrait' ist wohltuend kurz gehalten, auf der Seite 'Adressen' finden sich der IG-Hauptsitz sowie die Niederlassungen Basel, Bern, Genève.

Produkteverzeichnis von A bis Z

So erhalten Sie umgehend Ihre Unterlagen:

- Interessen markieren
- Adresse am Schluss der Liste eintragen

☐ Abzugsleisten
☐ Abwasserprobenehmer
☐ Agar-Fertignährböden
☐ Anaerobenkammern
☐ Analysenwaagen
☐ Arbeitsunterlage (saugfähig)
☐ Aufschluss (Schwefel/Halogen)
☐ Aufschluss-Systeme
☐ Autoklavensäcke

☐ Bad/Umwälzthermostate

- IG Instrumenten-Gesellschaft AG
  Räffelstrasse 32
  CH–8045 Zürich
  Telefon 01 456 33 33
  Telefax 01 456 33 30
  Internet http://www.igz.ch
  E-Mail igz@igz.ch

Leserdienst Nr. 35

Seminar: Analytische Mikromethoden

Am 15. Oktober 1997 findet im Biozentrum Basel ein Seminar mit dem Thema 'Analytische Mikromethoden für Proteinchemie und Kombinatorische Chemie' statt. Das Seminar mit Referenten aus Wissenschaft und Technik behandelt Themen wie:

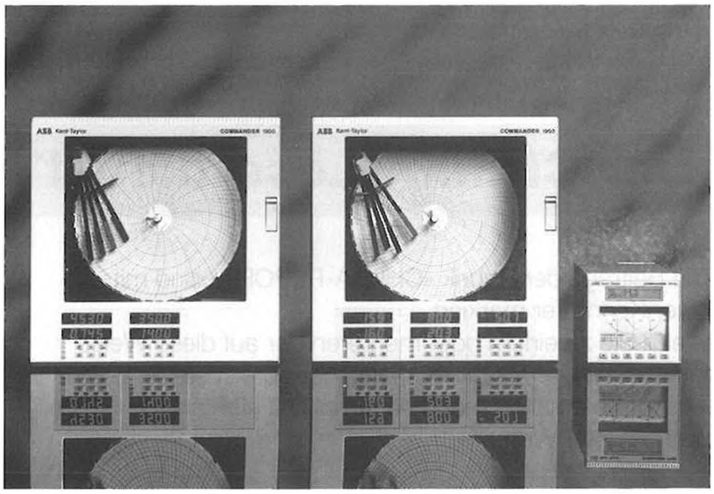
- Single Bead Analysis for Combinatorial Studies
- Strategies for Proteome Analysis
- The Use of Capillary Chromatography/Tandem MS for the Structure Elucidation of Phosphorylation Sites in Proteins
- Microtechniques for Sample Handling and Analysis

Dieses Seminar richtet sich vor allem an Benutzer mit Schwerpunkt Proteinchemie, aber auch für zukünftige Anwender der Mikro-HPLC, die das Seminar zum Erfahrungsaustausch nutzen können.

- OmniLab Biosystems AG
  Untere Bahnhofstrasse 14
  CH–8932 Mettmenstetten
  Telefon 01 768 22 11
  Telefax 01 768 23 21
  E-Mail omnilab@omnilab.ch
  Internet http://www.omnilab.ch

Leserdienst Nr. 36

Optimale Prozessüberwachung



Der Name Commander steht für eine Baureihe von Schreibern, Reglern und Anzeigegeräten, die sich alle durch eine robuste, industrietaugliche, formschöne Ausführung und ein breites, branchenkompatibles Einsatzspektrum auszeichnen.

Das Commander-Programm bietet gleichermassen eine bequeme Bedienung über die handliche Tastatur direkt am Gerät oder alle Kommunikationsmöglichkeiten moderner Automationssysteme über die RS 485-Schnittstelle mit dem Modbus-Protokoll.

Das Sortiment reicht von einfachen Ausführungen, die eine einfache Aufgabe zuverlässig und dauerhaft erfüllen, bis hin zu komplexen Geräten, die Schreiber und Regler in einem sind und zudem noch über eine gut ablesbare LCD-Anzeige verfügen. Dabei ist eine robuste Ausführung (bis IP 66) ebenso selbstverständlich wie eine kompakte Ausführung in den Standardmassen für Einbaugeräte. Die geringe Einbautiefe erlaubt Installationen auch bei sehr beengten Raumverhältnissen.

- ABB Normelec AG
  VH-G4/Instrumentierung
  Badenerstrasse 790
  CH–8048 Zürich
  Telefon 01 435 66 68
  Telefax 01 435 66 07

Leserdienst Nr. 37

Sitechdata – Infosystem für sicherheitstechnische Kenngrössen von Flüssigkeiten und Gasen

Möchten Sie wichtige Kenngrössen von Flüssigkeiten und Gasen, die in Industrie und Gewerbe gebräuchlich sind, rasch abrufen können? Damit Sie Gefahren beim Umgang und Lagern dieser Stoffe einfach beurteilen können?

Die Diskette SITECHDATA ermöglicht Ihnen den problemlosen Zugriff auf die Daten von 250 Stoffen. Das Programm erlaubt zudem das Erfassen neuer oder Mutieren bestehender Daten. Neuere Erkenntnisse – vor allem bei den Explosionsgrenzen – wurden berücksichtigt.

Neben den allgemeinen Stoffdaten wie Dichte, Schmelz- und Siedepunkt, Dampfdruck, Dichte dampfgesättigter Luft und relative Verdunstungszahl stehen Ihnen auch die für den Explosionsschutz relevanten Kenngrössen zur Verfügung: Flammpunkt, Explosionsbereich, untere und obere Explosionsgrenze, Zündtemperatur und Dampfkonzentration gesättigter Luft.

Die deutsche und französische Version befinden sich auf derselben Diskette und laufen unter DOS sowie OS/2. Sie kann im Format $3^{1}/_{2}$ oder $5^{1}/_{4}$ Zoll zum Preise von CHF 100.– bestellt werden bei:

- SUVA
  Kundendienst
  Postfach
  CH–6002 Luzern
  Telefon 0041 41 419 58 51
  Telefax 0041 41 419 59 17

Leserdienst Nr. 38

Pilot Scale Simulated Moving Bed Chromatography System

The **Simulated Moving Bed (SMB) Chromatography** range has been designed for the purification of optically pure products from racemates or for final polishing of products prepared by conventional processes and for binary separations of any kind. The **SMB** systems permit a continuous separation (raised productivity) and the reduction in solvent use for reduced costs.

PROCHROM SMB systems are based upon its unmatched experience in Preparative and Production Scale Chromatography.

A new system adapted to Pilot Scale high efficiency separations has been introduced to the range of **PROCHROM SMB** systems.

The **SMB 8-50** system details are:

- Productivity up to 200 g/day
- Flow rates up to 200 ml/min,
- 8 Dynamic Axial Compression (DAC) columns, 50 mm I.D., up to 30 cm long
- Flexible configuration
- Any packing material can be used
- Continuous monitoring, display and recording of parameters: pressure, flow, detector signals, alarms.

- PROCHROM S.A.
  B.P. 9 – 5, Rue Jacques Monod
  F–54250 Champigneulles
  Phone (33) 383 312 244
  Fax (33) 383 312 051
  E-Mail
  prochrom@millipore.com

Leserdienst Nr. 39

Preiswerte Motorkolbenbürette für die Laborroutine

Die neue Motorkolbenbürette 'Titronic 96' von Schott, Mainz, ist aufgrund ihrer Einfachheit ein ideales Umsteigemodell von der klassischen Glasbürette in die schnelle, genaue und sichere Titration. Das manuelle Titrieren erfolgt bequem per Knopfdruck über den Handtaster. Die Rührfunktion übernimmt ein Magnetrührer, der kabellos an die Bürette angeschlossen wird.

Eine präzise Dosiertechnologie ermöglicht eine Dosiergenauigkeit von 0,15% bezogen auf 20 ml Nennvolumen. Das minimale Dosiervolumen beträgt 0,01 ml. Die grosse Dialoganzeige und die RS-232-C-Schnittstelle für Drucker oder PC ermöglichen eine umfassende Dokumentation.

Die Motorkolbenbürette 'Titronic 96' ist die moderne und preiswerte Alternative zu den herkömmlichen Glas- und Digitalbüretten.

- Schott Schleiffer AG
  Chemie-Technik
  CH–4132 Muttenz
  Telefon 061 467 90 32
  Telefax 061 467 90 40

Leserdienst Nr. 40

Das Herz Ihrer HPLC ...

Bei der Untersuchung komplexer Stoffgemische entscheiden Genauigkeit und Reproduzierbarkeit von Fluss und Gradienten, ob Komponenten richtig identifiziert und präzise quantifiziert werden. Dies gilt umso mehr, als der Trend zu kleinen Flüssen die Anforderungen an die Güte der Gradientenmischung beachtlich gesteigert hat. Oft wird auch übersehen, dass neben Genauigkeit und Reproduzierbarkeit die Pulsationsfreiheit das wichtigste Qualitätsmerkmal einer modernen HPLC-Pumpe darstellt. Denn die Nachweisgrenze einer Substanz hängt mitunter stärker von der Restpulsation als vom Detektorrauschen ab.

Pulsationsfreie Förderung: Die P580 ist eine serielle Doppelkolbenpumpe, sie kommt ohne Pulsdämpfer aus! Denn das von Gynkotek patentierte Prinzip der isokinetischen Vorkompression erlaubt die Regelung der Vorkompression für jeden Eluenten. Dadurch ist trotz minimalem Verzögerungsvolumen die Restpulsation kaum noch messbar. Typisch: 0,5 bar bei 250 bar.

Genauigkeit und Präzision: Der überdimensionierte, ultragenau tachogeregelte Gleichstrommotor erreicht eine Volumenauflösung von 0.01 ul (10 nl) – und fast völlig geräuschlos! Sie fahren auch bei 100 ul Gesamtfluss präzise Gradienten mit einer Auflösung von 0,5%! Micro-HPLC: Kein Problem!

Niedrige Kosten: Die P580 ist komplett ausgestattet. Was sonst als Option angeboten wird, hat die P580 serienmässig: Die Niederdruckgradientenversion einen eingebauten 4-Kanal-Degasser, die Hochdruckversion zwei komplette Pumpwerke und einen Solvent Selector '2 aus 4'. Beide Versionen haben eine dynamische Mischkammer! Die P580 ist für den Dauerbetrieb ausgelegt: 24 h, 7 Tage die Woche! Wartungsintervall-Anzeige ist selbstverständlich.

Wir kaufen Ihre alte Pumpe zurück! Erkundigen Sie sich über unsere Eintauschaktion!

- Gynkotek AG
  Trockenloostrasse 1
  CH–8105 Regensdorf
  Telefon 01 870 12 12
  Telefax 01 870 12 14

Leserdienst Nr. 41

Dionex-Roadshows Herbst 1997 Ionenchromatographie/HPLC/Extraktion

Die Seminar-Teilnahme an einem zentralen Ort ist für den Besucher mit einem entsprechenden Zeitaufwand für die Hin- und Rückreise verbunden. Dionex (Switzerland) AG führt deshalb im Herbst 97 in der gesamten Schweiz an 10 Orten sog. 'Roadshows' durch. Bei diesen Veranstaltungen können die Besucher in lockerer Atmosphäre Informationen in kurzen Seminarvorträgen erhalten, die ausgestellten Geräte besichtigen oder mit den Dionex-Mitarbeitern über ihre analytischen Problemstellungen diskutieren, und natürlich wird auch für das leibliche Wohl gesorgt.

Themen der Veranstaltungen sind Chromatographie und Probenvorbereitung. Mit dem kompakten Ionenchromatographen DX-120 gibt es seit 1996 High-Tech im Low-Cost-Bereich. Und für die Beschleunigte Lösemittelextraktion (ASE^{TM}) bietet der Extraktor ASE200 in Kombination mit dem Solvent-Controller für 4 verschiedene Extraktionsmittel, oder Mischungen aus ihnen, enorme Flexibilität für Methodenentwicklung oder Routine-Betrieb.

Folgende Termine und Orte sind vorgesehen: 21.10. Monthey und Bellinzona, 22.10. Genève, 24.10. Neuchâtel, 28.10. Bern und St. Gallen, 29.10. Zürich, 30.10. Luzern und Schaffhausen, 5.11. Basel.

Detaillierte Informationen und Anmeldeunterlagen erhalten Sie bei:

- Dionex (Switzerland) AG
  Solothurnerstrasse 259
  Postfach, CH–4603 Olten
  Telefon 062 205 99 66
  Telefax 062 205 99 60

Leserdienst Nr. 42

Neue Firmendokumentation: ENVIRO-CHEMIE AG Wasser- und Abwassertechnik

Die auf Wasser- und Abwassertechnik spezialisierte ENVIRO-CHEMIE AG hat ihre Dokumentationsunterlagen aktualisiert und gleichzeitig die erweiterten Technologie-Schwerpunkte Oxidations-/Membrantechnik miteinbezogen.

Diese neuen Dokumentationen: Firmenbroschüre, Produktgruppeninfos ULTRASYSTEMS – Oxidationstechnik, URT – Membrantechnik, SPLIT-O-MAT$^{®}$-Standardanlagen, spezifische Brancheninfos, sind zu beziehen bei:

- ENVIRO-CHEMIE AG
  Wasser- und Abwassertechnik
  CH–8733 Eschenbach
  Telefon 055 286 18 18
  Telefax 055 286 18 00

Leserdienst Nr. 43

in Abzugsvorrichtungen ermöglicht. Ergänzt werden diese Kompaktsysteme durch anwenderspezifische Ausbaustufen, z.B. die Oberflächenbeschichtung aus PTFE zum Schutz vor aggressiven Medien oder durch einen Medienfühler zum Kontrollieren der Probentemperatur.

- STERICO AG
  Binzstrasse 5
  Postfach 167
  CH–8953 Dietikon 1
  Telefon 01 740 13 70
  Telefax 01 740 72 37

Leserdienst Nr. 46

Schnelle Lösung für Trocknungsprobleme

Der plattenbeheizte Vakuum-Trockenschrank VT 6060 P kann aufgrund seiner veränderten elektrischen Ausrüstung mit bis zu 300° beziehungsweise 400° Nenntemperatur betrieben werden. Durch ihren speziellen Aufbau erhitzen sich die Einlagen sehr schnell und gleichmässig und geben ihre Wärme direkt auf das Probengefäss ab. Jede Einlage ist mit einem eigenen Temperatursensor ausgerüstet. Entsprechend des Wärmebedarfs des Trockengutes kann die Temperatur auf dem gewünschten Wert konstant gehalten werden. Der entscheidende Vorteil der Plattenbeheizung besteht im kurzen Energie-Transportweg. Dies ermöglicht schnelle Aufheiz- und Prozesszeiten.

Beim mantelbeheizten Gerät VT 6060 M erfolgt die gleichmässige Wärmeübertragung von den äusseren Heizelementen auf die Einlagen zum Trockengut. Die Nenntemperatur des Gerätes beträgt bis zu 200°.

Beide Ausführungen der vacutherm-Serie sind in den Baugrössen von 53 und 128 l Innenraumvolumen erhältlich. Zusätzlich bietet Heraeus ein Kompaktgerät mit 25 l Innenraumvolumen in mantelbeheizter Ausführung an – den VT 6025. Die Geräte sind GS-geprüft und haben eine 2jährige Garantie.

- Heraeus AG
  Räffelstrasse 32
  CH–8045 Zürich
  Telefon 01 454 12 12
  Telefax 01 454 12 99

Leserdienst Nr. 44

AspenTech gibt Batch Plus für die Modellierung von Batchverfahren auf Rezepturbasis frei

Die Aspen Technology, Inc. (NASDAQ: AZPN), hat die Freigabe von Batch Plus bekanntgegeben. Es handelt sich um ein neues Softwaresystem für die Modellierung und Simulation von komplexen pharmazeutischen und chemischen Batchverfahren auf der Grundlage von Rezepturen.

Batch Plus ist das erste im Handel erhältliche System, das die auf Rezepturbasis erfolgende Prozessmodellierung über den gesamten Lebenszyklus hinweg unterstützt, von Forschung und Entwicklung über die technische Gestaltung bis hin zur Produktion. Batch Plus ist eines der ersten Software-Systeme zum Modellieren von chemischen Verfahren auf Rezepturbasis; es ist erhältlich für Windows 95 und Windows NT.

- AspenTechn Europe S.A./N.V.
  Rue Colonel Bourg 127–129
  B–1140 Brussels
  Telefon ++32-2/724 01 00
  Telefay ++32-2/726 97 64

Leserdienst Nr. 45

Vielfach-Magnetrührer mit Heizung

Aus dem Konzept der kompakten Vielstellenrührer und den zentral beheizbaren Rühr-Blockthermostaten sind nun die flachen Rührheizplatten MULTITHERM mit 6 oder 15 Rührstellen entstanden. Jetzt endlich ist es möglich, sogar unterschiedlichste Probengefässe gleichzeitig zu rühren und zu erwärmen. Somit spart man wertvollen Laborplatz und teure Heizenergie.

Diese Magnetrührsysteme eignen sich z.B. hervorragend für zu reproduzierende Reihenuntersuchungen, insbesondere für Materialprüfungen, zum Aufkonzentrieren sowie zum gefahrensicheren Abdampfen von Lösungsmitteln.

Dabei garantieren das motorlose Antriebsprinzip und die hermetisch dichte Kapselung Verschleissfreiheit, auch bei höchsten Temperaturen über Jahre hinweg.

Der Rührantrieb wird über ein Steuergerät fernbedient, das digitale Drehzahl- und Temperaturanzeige, Dauer- oder Intervallbetrieb und die Aufstellung des Rührantriebs direkt

Aktuelles von der Planarchromatographie: Validierte HPTLC-Methode zur Bestimmung von Ornidazol in Plasma

Ornidazol (α-Chloromethyl-2-methyl-5-nitroimidazol-1-ethanol) ist ein Chemotherapeutikum gegen Amöben und Bakterien. Es wird zur Vorbeugung bzw. Behandlung einer Infektion mit anaeroben Keimen eingesetzt. Analysen von Ornidazol in Blutplasma fallen in den gefährdeten Gebieten in grosser Zahl an. Die validierte HPTLC-Methode ist geeignet für die Bestimmung der Bioverfügbarkeit bzw. Bioäquivalenz. Die typische Konzentration von Ornidazol im Blutplasma therapierter Patienten liegt bei 40 µg/ml.

Die Analysenvorschrift kann kostenlos bezogen werden.

Ein Methodenvergleich hinsichtlich Kosten, Zeit und Validierung zwischen HPTLC und HPLC ist beschrieben.

- CAMAG
  Chemie-Erzeugnisse und
  Adsorptionstechnik AG
  Sonnenmattstrasse 11
  CH–4132 Muttenz 1
  Telefon 061 467 34 34
  Telefax 061 461 07 02

Leserdienst Nr. 47

Chemometrisches Softwarepaket Nircal Version 2.0 – 120 Tage kostenloses Testen der Vollversion unter WindowsNT

Bühler hat eine Evaluations-CD zur neuen Version ihres chemometrischen Softwarepaketes Nircal 2.0 zusammengestellt. Die kostenlose 120-Tage-Lizenz ermöglicht Ihnen ein intensives Kennenlernen des Nircal-Programmpaketes bestehend aus qualitativen und quantitativen Kalibrationsmodulen, einer BASIC-Makrosprache und Tutorials, um sich selbst von den vielen Vorteilen dieser revolutionären chemometrischen Software überzeugen zu können. Weitere Highlights auf dieser Evaluations-CD sind das Microsoft WindowsNT Server 4.0, die Internetseiten mit Produktbeschreibungen zu anderen Bühler NIR-Produkten und der Microsoft Internet Explorer Version 3.01 und 3.02.

Die verschiedenen Import- und Export-Routinen erlauben es dem Anwender, beliebige XY-Daten mit diesem stand-alone Programm zu bearbeiten. Die Anzahl Datensätze (z.B. Spektren), der Datenpunkte (z.B. Wellenzahlen) pro Datensatz und der Eigenschaften, die mit Nircal bearbeitet werden können, wird nur noch durch die Speicherkapazität des Rechners begrenzt.

Optional sind zu diesem Nircal-Programm verschiedene Gerätetreiber für NIR-Spektrometer und Applikationsprogramme erhältlich.

Der Preis für eine Einzelplatzlizenz beträgt CHF 7000.–. Eine Mengenstaffelung bei gleichzeitiger Bestellung von mehreren Paketen sowie hohe Hochschulrabatte machen das Programm auch für wissenschaftliche Institutionen attraktiv. Studenten erhalten gegen Vorlage einer entsprechenden Bescheinigung das Nircal-Programmpaket für CHF 500.–.

- Bühler AG, ANATEC
  CHF–9240 Uzwil
  Telefon 071 955 11 11
  Telefax 071 955 33 56
  Nircal-Hotline 071 955 12 55
  E-Mail nircal@buhler-ag.com

Leserdienst Nr. 48

Vollständig automatisierbares Analysensystem für die kombinatorische Chemie

Hewlett-Packard hat ein voll automatisierbares Analysensystem der Serie HP 1100 für die kombinatorische Chemie eingeführt, mit dem die Analyse von pharmazeutischen und biopharmazeutischen Produkten beschleunigt werden kann. Kombinatorische Chemie ist eine Technik, die die Synthese, das Screening und die Analyse vieler verschiedener Verbindungen mit vielfältigen Molekulargewichten ermöglicht. Damit wird der Zeitraum, um ein pharmazeutisches Produkt zur Marktreife zu entwickeln, erheblich verkürzt.

Das System verbindet die Module des Flüssigkeitschromatographen der Serie HP 1100 mit einem Probeninjektor 233 Gilson XL (Gilson Middleton, Wis.), einer HP ChemStation für LC-Systeme und einer Software, um die Steuerung der Probenanalyse, der Fraktionierung und der Datenverwaltung aus einer Hand zu bieten. Der Anwender hat die Wahl zwischen den sehr zuverlässigen Modulen der Serie HP 1100 sowie zwischen vielseitigen Detektoren wie z.B. einem variablen Wellenlängendetektor, einem Dioden-Array-Detektor und dem vor kurzem eingeführten massenselektiven Detektor (LC/MSD-System der Serie HP 1100).

Die Software hat zwei Betriebsweisen. In dem Probennahmemodus können Proben von jeder der 6 Mikrotiterplatten injiziert und analysiert werden. In dem Modus Probennahme/Fraktionensammlung kann der Probennehmer Proben von jeder der Mikrotiterplatten entnehmen und Fraktionen auf weiteren Mikrotiterplatten sammeln. Der Probennahmemodus ist speziell für Analysen mit hohem Durchsatz entwickelt worden.

- Hewlett-Packard (Schweiz) AG
  In der Luberzen 29
  CH–8902 Urdorf
  Telefon 155 35 60
  Telefax 01 735 77 44

Leserdienst Nr. 49

Pulverdosiergerät im Laborbereich

In unzähligen Fällen wird immer noch die Zugabe kleinster Pulvermengen in Reaktionsgefässe wie z.B. 3-Halskolben mühsam und zeitaufwendig von Hand vorgenommen.

Der in Zusammenarbeit mit einem Chemieunternehmen entwickelte Mikrodosierer Typ GMD von Gericke gestattet die genaue Zugabe auch kleinster Pulvermengen im mg- oder g-Bereich.

Das nach dem Prinzip einer Ringnut arbeitende Gerät erlaubt sehr geringe Dosierleistungen ab ca. 10 ml/h bis ca. 10 l/h im gleichmässigen Dosierstrom, soweit dies von der Kornstruktur her möglich ist. Für die Reinigung ist das Gerät in wenigen Sekunden vollständig zerlegbar. Zudem können aufsetzbare Dosierteile für die verschiedenen Produkte verwendet werden.

Bei der Konstruktion wurde berücksichtigt, dass der Aufbau auf einen Reaktionskolben bei gleichzeitig aufgebautem Rührwerk möglich ist. Der Einsatz verschiedener Ringnuten sowie der weite Drehzahlbereich mit Schrittmotor ermöglichen den grossen Verstellbereich der Dosierleistung, mit Ansteuerung durch Zeitschaltung oder Gewichtssignal. Das preisgünstige und handliche Gerät dient der Automation des Betriebes von Laborreaktoren, zum Bilanzieren, zur Mengenaufbereitung und Zugabe von Additiven in Labor und Produktion sowie zur Abfüllung von Kleinstmengen.

- Gericke AG, Postfach
  CH–8105 Regensdorf-Zürich
  Telefon 01 871 36 36
  Telefax 01 871 36 00

Leserdienst Nr. 50

Carbohydrate Membrane Desalter (CMD)

Die von Dionex in den achtziger Jahren eingeführte Kohlenhydrat-Analytik mittels hochauflösender Anionenaustausch-Chromatographie und gepulster amperometrischer Detektion ermöglicht Trennungen von Mono- über Oligo- bis zu kleineren Polysacchariden. Bei der Untersuchung von Glycoproteinen können hiermit Oligosaccharide aufgetrennt werden, die sich nur geringfügig in ihren Bindungspositionen unterscheiden, so dass sich diese Methode speziell als Vorbereitung weiterer Untersuchungsmethoden, wie z.B. Massenspektrometrie, eignet. Aufgrund der alkalischen Elutionsbedingungen mit Natronlauge/Natriumacetat kann das Eluat jedoch nicht direkt eingesetzt werden. Für LC/MS-Kopplungen oder generell zur Fraktionierung ist von Dionex anlässlich der PittCon 97 der sog. 'Carbohydrate Membrane Desalter' eingeführt worden.

Der 'Carbohydrate Membrane Desalter' basiert auf dem gleichen Funktionsprinzip wie die in der Ionenchromatographie zur Unterdrückung der Hintergrundleitfähigkeit eingesetzten selbstregenerierenden Suppressoren. Auf diese Weise werden nach Chromatographie und Detektion Natronlauge in Wasser und Natriumacetat in Essigsäure überführt, letztere kann durch Lyophilisation leicht entfernt werden. Im Lieferumfang des 'Carbohydrate Membrane Desalters' sind alle für Installation und Betrieb notwendigen Komponenten enthalten.

Jim Thayer (R&D Dept., Dionex Corp.) präsentierte den praktischen Einsatz des 'Carbohydrate Membrane Desalters' anlässlich der 'Conference on Well-Characterized Biotechnology Pharmaceuticals' 1997. Ein Abdruck des Posters und Unterlagen über den 'Carbohydrate Membrane Desalter' sind auf Anfrage erhältlich.

- Dionex (Switzerland) AG
  Solothurnerstrasse 259
  Postfach
  CH–4603 Olten
  Telefon 062 205 99 66
  Telefax 062 205 99 60

Leserdienst Nr. 51

Pufferlösungen von RADIOMETER mit GLP-Qualitätszertifikat

RADIOMETER-pH-Puffer unterliegen strengen Produktionsbedingungen und einer unnachsichtigen Qualitätskontrolle. Zur Herstellung der Pufferlösungen werden nur Chemikalien und Wasser höchster Reinheit verwendet. Die zur Produktionskontrolle benutzten Standards entsprechen den IUPAC/NIST-Referenzstandards. Zusätzlich dazu verfügt RADIOMETER über einen weiteren, unüberbietbaren Referenzstandard: eine Normal-Wasserstoff-Elektrode. RADIOMETER ist eines der wenigen Unternehmen, das über eine solche apparative Ausstattung verfügt und autorisiert ist, pH-Werte gemäss IUPAC/NIST zu zertifizieren. RADIOMETER-Pufferlösungen werden mit GLP-Qualitätszertifikat geliefert.

Um die Pufferlösungen vor dem Einfluss mikrobiologischer Kontamination zu schützen, Licht und Kohlendioxideinwirkung auszuschliessen, werden die Puffer mit Spuren von Germiziden versetzt, in dickwandigen, milchigen Flaschen aufbewahrt, die wiederum in luftdicht abgeschlossenen Dosen aufbewahrt werden. So bleibt der nominale pH-Wert des Puffers bis zum Moment der Kalibration erhalten. RADIOMETER garantiert den pH-Wert seiner Pufferlösungen bei verschlossener Dose für vier Jahre ab Produktionsdatum.

- IG Instrumenten-Gesellschaft AG
  Räffelstrasse 32
  CH–8045 Zürich
  Telefon 01 456 33 33
  Telefax 01 456 33 30
  Internet http://www.igz.ch
  E-Mail igz@igz.ch

Leserdienst Nr. 52

Neues Ventil für Anwendungen in der Lebensmittel- und Pharmaindustrie

Der Mucon-Manschettenverschluss Typ K, der für die Pharma-Industrie entwickelt wurde, hat sich jetzt auch in der Lebensmittelindustrie als geeignet erwiesen, z.B. bei der Säntis Milchpulver AG Sulgen, wo dieser Ventiltyp montiert ist. Säntis ist ein Hersteller verschiedener Produkte wie Milchpulver, Babynahrung, Pflanzenextrakte, Vitamine und pharmazeutische Produkte. Gesucht wurde eine Ventil für

regelbaren Durchfluss der Endprodukte vom Trockenturm direkt in Säcke. Hygienische Bedingungen und leichtes Reinigen waren wichtige Forderungen, ebenso auch das schnelle Demontieren, da das Ventil an zwei verschiedenen Orten zum Einsatz kommt.

Der Mucon-Manschettenverschluss Typ K wurde anstelle einer Drosselklappe eingebaut, und er gibt für Säntis eine genau regulierbare Durchfluss-Strömung des Produktes.

'Dieses Ventil ist jetzt seit Anfang 1996 in Betrieb und wird ca. 50mal pro Tag betätigt, und eine Reinigung erfolgt je nach Anwendungsfall etwa dreimal pro Woche. Es erfüllt alle unsere Dosier-, Handhabungs-, Reinigungs- und Hygienevorschriften, und ausserdem können wir jetzt sehr schnell Materialproben entnehmen, ohne sterile Werkzeuge einzusetzen', erklärte uns Herr Krüsi, Prozessingenieur R&D der Säntis Milchpulver AG.

Der Mucon-Manschettenverschluss gehört zur Familie der Mucon-Irismanschettenventile, die durch Kemutec England hergestellt werden. Diese sind für viele Anwendungen erstklassig geeignet, in sehr vielen Industrien und seit über 50 Jahren. In dieser ganzen Zeit wurde das gleiche Konzept beibehalten. Der Mucon-Verschluss gilt immer noch als hervorragendes Regulierventil für den Durchfluss von Schüttgütern. In der Praxis hat es sich erwiesen, dass diese Ventile präzise arbeiten, sehr robust sind, leicht zu reinigen und ideal für Hand- oder Automatikantrieb.

- Paliwoda AG
  Oetlisbergstrasse 16
  CH–8053 Zürich
  Telefon 01 381 01 92
  Telefax 01 381 01 77

Leserdienst Nr. 53

Stereomikroskope von Leica passen sich an ihre Benutzer an und nicht umgekehrt!

Das Arbeiten mit dem Stereomikroskop erfordert eine millimetergenaue Positionierung der Augen vor dem Gerät. Die damit verbundene starre Körperhaltung ist dann besonders ermüdend und körperlich belastend, wenn die Einblickhöhe nicht mit der individuellen Grösse der Menschen korrespondiert. In der Folge muss der Beobachter seine Kopfhaltung nach der Einblickhöhe des Instruments richten – eine sehr ermüdende Situation und in vielen Fällen die Ursache von Leistungsabfall und Arbeitsunfähigkeit.

Wie kein anderer Stereomikroskop-Hersteller hat sich Leica zum Ziel gesetzt, die Beanspruchung des Benutzers durch die vorwiegend statische Körperhaltung am Stereomikroskop auf ein Mindestmass zu beschränken. Mit dem grössten Sortiment unterschiedlicher Binokulartuben auf dem Markt kann der Benutzer von Leica Stereomikroskopen Einblickhöhe und -winkel an seine individuelle Körpergrösse anpassen. Ausser dem ErgoTubus™ mit variablem Einblickwinkel 10–50° stehen jetzt weitere optimale Lösungen für den ermüdungsfreien Dauereinsatz zur Verfügung: Der variable ErgoKeil™ 5–25°, das ErgoModul™ 50 mm und das variable ErgoModul™ 25–80 mm. Die neuen Ergo-Module sind an das Design der Stereomikroskope Leica MS5, MZ6, MZ8, MZ12 und MZAPO angepasst. Benutzer von Modellen, die nicht mehr im Programm sind, können ebenfalls die neuen Ergonomie-Vorteile nutzen.

- Leica Mikroskopie Systeme AG
  Verkaufsgesellschaft
  Kanalstrasse 21
  CH–8152 Glattbrugg
  Telefon 01 809 33 33
  Telefax 01 810 79 37

Leserdienst Nr. 54

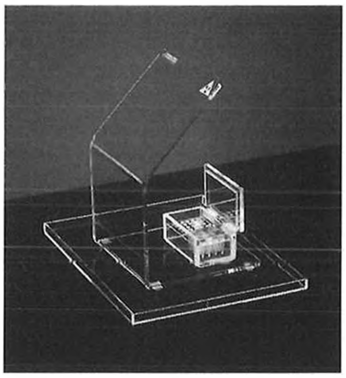
Validat für Windows™

Kontron Instruments hat ein neues Softwarepaket – Validat für Windows™ – herausgegeben, welches den Analytiker in seiner sehr vielfältigen Arbeit der analytischen Methodenentwicklung im gesamten Spektrum von der Validierung von Wägemethoden bis hin zur Massenspektrometrie unterstützt. Validat kann so konfiguriert werden, dass bestehende Arbeitsvorschriften – von der Planung über die Datenberechnung bis hin zur Datenausgabe übernommen werden können. Einzigartig erfüllt diese Software FDA-, DIN- und ISO-Vorschriften. Verfügbar ist Validat in deutscher oder englischer Sprache.

- Kontron Instruments AG
  Postfach
  CH–8010 Zürich
  Telefon 01 733 57 33
  Telefax 01 733 57 34

Leserdienst Nr. 55

Schutz vor Beta- und Gamma-Strahlen



Die neue Produktepalette von UVP für den Schutz vor Beta- und Gamma-Strahlen beinhaltet Schutzschilder, Behälter verschiedenster Formen und Grössen. Alle diese Artikel sind aus speziellen Materialien gefertigt, um die Strahlung der gängigen Betaisotope wie ^{32}P, ^{35}S, ^{3}H, ^{14}C und Gamma ^{125}I effektiv zu blockieren.

Das Beta- und Gamma-Cabinet wurde konzipiert als völlig geschlossene Arbeitsstation mit grossen Türen, um eine gute Zugänglichkeit zu ermöglichen. Bei geschlossenen Türen sind die radioaktiven Proben effektiv isoliert.

Zum Programm gehören ebenfalls Schutzschilder in verschiedenen Grössen und Formen, um die verschiedensten Bedürfnisse optimal abzudecken.

Sehr praktisch sind die Aufbewahrungsboxen für verschiedene Gefässe wie Eppendorf-, Zentrifugen-, Falcon-Röhrchen, Scintillation-Vials und Cryoröhrchen.

Weitere Informationen erhalten Sie über:

- OmniLab Biosystems AG
  Untere Bahnhofstrasse 14
  CH–8932 Mettmenstetten
  Telefon 01 768 22 11
  Telefax 01 768 23 21
  E-Mail omnilab@omnilab.ch
  Internet http://www.omnilab.ch

Leserdienst Nr. 56

Neue Analysatoren-Baureihe bietet höchsten Sicherheitsstandard

Die neuen Sauerstoff- und Ozon-Analysatoren von Orbisphere wurden für einen grossen Kreis von Messgerätenutzern entwickelt. Sie liefern effizient präzise Messwerte mit einer Nachweisgenauigkeit von 0,1 ppb, auch unter rauhen und gefährlichen Umgebungsbedingungen. Das Modell 3650EX ist tragbar, das Modell 3660EX ist für die Wandmontage vorgesehen.

Die Analysatoren sind nach den CENELEC-Normen EN 50020/50014 ausgelegt. Sie erfüllen die Sicherheitsanforderungen für Zone 0 und haben damit die höchste Schutzstufe. Erhältlich sind sie entweder zur Messung von Sauerstoff in flüssigen oder gasförmigen Proben oder zum Nachweis von Ozon in flüssigen Proben.

Diese Analysatoren speichern bis zu 500 Zeit-Messwert-Paare zum späteren Abruf. Die Messwerterfassung kann automatisch in zuvor festzulegenden Intervallen erfolgen. Software unter Windows® vereinfacht das Datenhandling und ist kompatibel mit eventuell vorhandener Datenbank- oder Tabellenkalkulationssoftware.

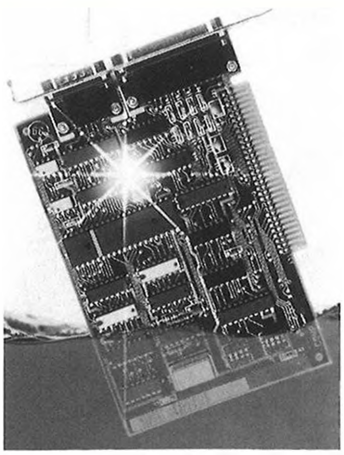
- Orbisphere Laboratories
  20, rue du Puits-Godet
  CH–2000 Neuchâtel
  Telefon 032 721 41 95
  Telefax 032 725 34 33
  E-Mail salesinfo@orbisphere.ch

Leserdienst Nr. 57

Ersatz für ozonschädigende Substanzen in speziellen Anwendungsbereichen

3M HFE (Hydrofluorether) Flüssigkeiten sind neue Substanzen, die in der Industrie als Ersatz für Fluor-Chlor-Kohlenwasserstoffe (FCKWs) und andere ozonschädigende Stoffe zukünftig in speziellen Anwendungen eingesetzt werden. Sie wurden entwickelt, um den industriellen Bedarf nach einem hochleistungsfähigen Produkt zu erfüllen, welches die uns schützende Ozonschicht nicht beeinträchtigt.

Die HFE Produkte von 3M besitzen kein ozonschädigendes Potential. Wei-



tere umweltrelevante Vorteile sind eine kürzere Lebensdauer in der Atmosphäre und daher ein niedrigeres Treibhauspotential als bei FCKWs. HFE-7100 ist nicht brennbar und praktisch nicht toxisch, was besonders wichtig für die Sicherheit und Handhabung am Arbeitsplatz ist. Die nichtkorrosiven Flüssigkeiten sind verträglich mit den üblichen Werkstoffen wie z.B. Kunststoffen, Metallen und Elastomeren und zeichnen sich durch eine niedrige Viskosität und Oberflächenspannung aus. Eines der wichtigsten Einsatzgebiete ist die Präzisionsreinigung von hochwertigen komplexen Komponenten in Elektronikgeräten, Computern, Flugzeugen, medizinischen Geräten und im Fahrzeugbau. Auch als Wärmeübertragungsflüssigkeiten in Kühlsystemen sind HFEs bestens geeignet. Sie können ausserdem als Trägerflüssigkeit für den Auftrag spezieller Schmiermittel, z.B. auf Computerfestplatten, und als wichtige Komponente in Sprays zur Reinigung von Kontaktflächen bei der Wartung und Reparatur im Elektronikbereich verwendet werden.

Die Firma Prochimac SA in Neuchâtel ist der 3M Handelspartner für die neuen HFE Produkte in der Schweiz. Neben dem Vertrieb und dem technischen Kundendienst kümmert sich Prochimac auch um das Füllen und Einstellen der Anlagen sowie um das Testen des neuen Produktes in den Geräten des Kunden.

- Prochimac SA
  Rue du Château 10
  Case postale
  CH–2004 Neuchâtel
  Telefon 032 724 45 75
  Telefax 032 724 45 78

Leserdienst Nr. 58

Waldbronner Themen

Zwei Jahre nach den 'Waldbronner Themen 1995' in Nürnberg findet diese erfolgreiche Vortragsveranstaltung ihre Fortsetzung.

Das Hotel Esplanade in Jena ist vom 1.–3. Dezember 1997 Treffpunkt der Teilnehmer an den Waldbronner Themen 1997. Das Veranstaltungskonzept mit Plenarvorträgen und zwei parallelen Vortragsreihen mit den Themen Pharma- und Bioanalytik sowie Lebensmittel- und Umweltanalytik wird beibehalten.

Neu ist die Zusammenarbeit von Hewlett-Packard mit der Deutschen Lebensmittelchemischen Gesellschaft zur Erstellung des wissenschaftlichen Programmes im Thema Lebensmittel- und Umweltanalytik. Es freut uns besonders, mit dem Vorsitzenden der Gesellschaft Herrn Prof. *Steinhart*, Hamburg, und den Herren Prof. *Ludwig*, Dresden, und Prof. *Mosandl*, Frankfurt, als wissenschaftlichem Beirat zusammenzuarbeiten.

Die Plenarvorträge werden allgemeine Fragestellungen der Themen aufgreifen. In den einzelnen Vortragsreihen werden viele interessante und detaillierte Aspekte angesprochen und diskutiert. Ausserdem besteht am Abend die Möglichkeit zur Diskussion mit den Vortragenden. Der Informationsaustausch und die fruchtbare Diskussion zwischen den Teilnehmern ist das Ziel der Waldbronner Themen.

- Hewlett-Packard (Schweiz) AG
  Chemische Analysen Systeme
  In der Luberzen 29
  CH–8902 Urdorf
  Telefon 155 35 60
  Telefax 01 735 77 44

Leserdienst Nr. 59

Umfassender Schutz und perfekte Hygiene am Arbeitsplatz

Kimberly-Clark, weltweit anerkannt als Spezialist für Hygiene und Schutz am Arbeitsplatz und Marktführer in den meisten Produktsegmenten, bietet Unternehmen der chemischen Industrie jetzt ein massgeschneidertes, umfassendes Produktprogramm an hochleistungsfähigen Wischtüchern, Arbeitsschutzkleidung, Handreinigungsprodukten sowie Produkten zur Leck- und Auslaufkontrolle.

Kimberly-Clark hat sein neues 'Produktprogramm Arbeitsplatz' auf die spezifischen Bedürfnisse der verschiedenen Industriezweige abgestimmt, ein Produktprogramm wurde speziell für die Unternehmen der chemischen Industrie entwickelt. So sind selbstverständlich alle Wischtücher auch im Nasszustand extrem fusselarm; sie sind lösemittelbeständig, auch gegen aggressive Lösemittel. Wo Keimfreiheit bzw. Sterilität Voraussetzung ist, können Nonwoven-Wischtücher aus dem Hause Kimberly-Clark vor dem Einsatz sterilisiert werden. Schutzkleidung hat ihre Einsatzbereiche überall dort, wo entweder der Mensch beim Umgang mit Gefahrstoffen geschützt werden muss, oder aber, wo Produkte bzw. Arbeitsvorgänge hygienisch vom Menschen abgeschirmt werden müssen.

- Kimberly-Clark GmbH
  Postfach 157
  A–5021 Salzburg
  Telefon/Telefax (0662) 87 22 76

Leserdienst Nr. 60

μ-Fraktionierung mittels Probenroboter 'PROBOT'

Der Probenroboter übernimmt für Sie vielfältige Aufgaben im Bereich der Probenvorbereitung und Weiterverarbeitung, so z.B. das Online-Auftragen der Fraktionen einer HPLC- oder CZE-Analyse auf die Probenträger von MALDI-Massenspektrometern, oder PVDF-Membranen zur anschliessenden Sequenzierung. Ebenso kann es in Mikrotiterplatten oder andere Gefässhalter fraktionieren.

- Autragen auf MALDI-Targets oder PVDF-Membranen
- Auftragen auf PVDF-Membranen und MALDI-Targets im gleichen Arbeitsgang
- Sammeln in Mikrotiterplatten
- Pipettieren auch kleinster Mengen
- Steuerprogramm unter Windowsoberfläche, Anzeige der Abläufe auf dem Bildschirm graphisch und digital
- Ein Dosiermodul kann automatisch Reagenzien oder Lösungsmittel zumischen.

- OmniLab Biosystems AG
  Untere Bahnhofstrasse 14
  CH–8932 Mettmenstetten
  Telefon 01 768 22 11
  Telefax 01 768 23 21
  E-Mail omnilab@omnilab.ch
  Internet http://www.omnilab.ch

Leserdienst Nr. 61

Lovibond®-Labor-Trübungsmessgerät ET860

Ein neues Labor-Trübungsmessgerät stellt die Tintometer GmbH (D–44287 Dortmund) in Anlehnung an die Forderungen der DIN 38 404 sowie der ISO 7027 vor.

Die Messung der Trübung von flüssigen Medien erfolgt im Infrarotbereich bei 860 nm und ist somit unabhängig vom Einfluss gefärbter Lösungen. Als Probenbehälter werden Präzisions-Rechteckküvetten mit 40 mm Schichttiefe und maximal 50 ml Probenvolumen eingesetzt. Drei Messbereiche erfassen insgesamt 0–200 TE/F- bzw. FNU-Einheiten.

Selbstverständlich erfolgt die Nullpunkteinstellung automatisch. Die Lichtquelle schaltet sich in Messpausen selbsttätig aus. Bedient wird das Trübungsmessgerät über eine Folientastatur mit nur fünf Funktionstasten.

- Tintometer AG
  Hauserstrasse 53
  CH–5210 Windisch
  Telefon 056 442 28 29
  Telefax 056 442 41 21

Leserdienst Nr. 62

Computer-Etiketten für feuchte Oberflächen – CILS Etiketten nun mit neuem Aqua-Klebstoff!

CILS hat ihr Sortiment von dauerhaften computerbedruckbaren Labor-Etiketten erweitert und stellt nun ihr neues Sortiment von Aqua-Klebstoff-Etiketten vor. Die neue Produktserie dient dem wachsenden Bedarf im Labor für Etiketten, die permanent auf feuchten Oberflächen kleben sollen.

CILS Aqua-Klebstoff-Etiketten sind aus dauerhaften computerbedruckbaren Materialien hergestellt, die den härtesten Labor-Anwendungen widerstehen, u.a. Tiefkühllagerung (–40° und niedriger), hohen Temperaturen (+155°), Chemikalien, Säuren, Luftfeuchtigkeit etc.

CILS Etiketten sind ideal für Anwendungen auf Röhrchen, Flaschen und Behältern, deren feuchte Oberflächen nach Kühlschrank/Tiefkühllagerung dauerhaft markiert werden müssen.

CILS Aqua-Klebstoff-Etiketten werden in allen Grössen, Formen und Farben, blanko oder mit Aufdruck wie Firmenname und Logo, Symbole, Text geliefert. CILS Etiketten haben einzigartige toner-aufsaugbare, laserbedruckbare Oberflächen – fügen Sie variable Informationen (Barcode, Seriennummern, Probenbeschriftung, Datum, Symbole usw.) dauerhaft mit Ihrem eigenen PC und Drucker (Laser, Thermo Transfer, Nadel oder Tintenstrahl) hinzu.

Für spezifische Anwendungsberatung und Musteretiketten wenden Sie sich bitte an:

- Computer Imprintable
  Label Systems Ltd.
  'CILS Label Technology Centre'
  3 Home Farm Business Park
  Home Farm Road
  Brighton
  East Sussex
  BN1 9HU, England
  Telefon ++44 (0) 1273 681000
  Telefax ++44 (0) 1273 681144

Leserdienst Nr. 63

Neu – Analytische Bestleistungen über das gesamte Periodensystem der Elemente

Spectroquant ist der Name des neuesten Produkts aus dem Hause Spectro. Mit Spectroquant lassen sich erstmals analytische Bestleistungen quer über das Periodensystem hinweg erzielen.

Alle mit der ICP-OES-Methode bestimmbaren Elemente – von den Alkalien bis zu den Halogenen – können jetzt gemessen werden. Das Besondere des Spectroquant ist die Kombination von drei optischen Systemen, bestehend aus einem Monochromator und zwei Polychromatoren, die in ein platzsparendes Tischgerät integriert sind. Mit dem neuen Spectroquant setzt Spectro die auf Qualität, Schnelligkeit und Flexibilität ausgerichtete Bauweise der Spectroflame-Familie fort.

Die Anwendungsgebiete des Analysegerätes sind vielfältig: Es wird in der Geologie, Umwelt, Medizin, Landwirtschaft und in der Nahrungsmittelindustrie ebenso eingesetzt wie in der Halbleitertechnik und Mineralölproduktion.

Sein Alleinstellungsmerkmal, die Halogenbestimmung in organischen Materialien, bekommt beispielsweise bei der Verbrennung von Altölen eine besondere Wichtigkeit. Denn Spectroquant analysiert das Element Chlor, das bestimmend ist für die Grenzwertüberwachung bei der Dioxinbildung.

Neben all diesen Leistungsmerkmalen erfüllt das Spectroquant ausserdem die europäischen DIN- und ISO- sowie die amerikanischen EPA-Normen.

- Spectro
  Analytical Instruments GmbH
  Boschstrasse 10
  D–47533 Kleve
  Telefon 02821-892 119
  Telefax 02821-892 167

Leserdienst Nr. 64

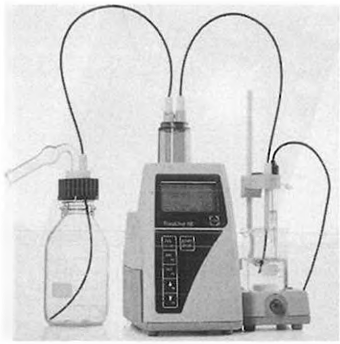
TitroLine 96 – intelligenter Titrator für die Säure-Basen-Titration

Mit dem neuen Titrator 'TitroLine 96' von Schott, Mainz, können Titrationen mit genauem Analysenergebnis per Tastendruck durchgeführt werden.

'TitroLine 96' erkennt automatisch ohne Parametrierung das Analysenende. Der pH-Wert für Endpunkttitrationen ist leicht einstellbar. Dabei erscheinen die auf der pH-Skala hinterlegten Indikatoren automatisch in der 2. Zeile. Ist dieser Wert nicht bekannt, kann eine Equivalenzpunkt-Titration durchgeführt werden. Der Titrator findet in diesem Arbeitsmodus das Titrationsende automatisch.

Voraussetzung für genaues Titrieren ist eine zuverlässige und exakte Dosiertechnologie.

Der Präzisionsglaszylinder aus dem Borosilikatglas 'Duran', mit automatisch arbeitendem Ventil, stellt diese Voraussetzung sicher. Die Forderungen der deutschen und internationalen Normen für Kolbenbüretten werden in der Genauigkeit um Faktor 2 übertroffen.



Die Dokumentation der Ergebnisse wird erleichtert durch das grosse Display mit ml-Verbrauch, Titrationsart und Indikatorangabe. Die RS-232-C-Schnittstelle ermöglicht den Anschluss von PC oder Drucker zur Datensicherung.

- Schott Schleiffer AG
  Chemie-Technik
  CH–4132 Muttenz
  Telefon 061 467 90 32
  Telefax 061 467 90 40

Leserdienst Nr. 65

HPLC-Serie 300 jetzt noch besser

Die bekannte und äusserst erfolgreiche HPLC-Serie 300 bietet jetzt noch mehr Leistung zu noch günstigeren Preisen. Die Pumpensysteme 322 und 325, für Hochdruck- und Niederdruckgradientenbetrieb, zeichnen sich durch aussergewöhnliche Druckstabilität aus. Sie gewährleisten dadurch auch bei kritischen Applikationen eine hervorragende Basislinienstabilität.

Darüber hinaus präsentiert Kontron Instruments mit dem variablen 2-Kanal-UV-VIS-Detektor 335 eine neue Detektorgeneration mit gesteigerter Nachweisempfindlichkeit. Diese Neuheiten addieren sich zu den bereits vielfach geschätzten Eigenschaften der HPLC-Serie 300: z.B. Stapelbarkeit der Module mit Platzersparnis, Erweiterungsfähigkeit und Systemkontrolle im stand-alone-Betrieb. Selbstverständlich ist eine Steuerung, Datenaufnahme und Integration über die Softwareprodukte der Datensystem-450-Familie und dem Labordatensystem Kroma-System 2000 gewährleistet.

Die HPLC-Serie 300 eignet sich zum Einsatz in Qualitätslaboratorien, im universitären Lehrbetrieb und im klinischen Anwendungsbereich (z.B. Hämoglobinanalytik).

- Kontron Instruments AG
  Postfach
  CH–8010 Zürich
  Telefon 01 733 57 33
  Telefax 01 733 57 34

Leserdienst Nr. 66

Jahrbuch 'Chemische Rundschau' 1997, 46. Auflage

Das Jahrbuch 1997 der Chemischen Rundschau gibt einen Überblick über die wirtschaftliche Entwicklung der Schweizer Grosschemie und das Geschehen auf der internationalen Bühne der Branche des an Mergers und Akquisitionen reichen letzten Jahres. Das bewährte Artikel- und Lieferantenverzeichnis für Entscheidungsträger in Forschung, Labor und Produktion wurde auf den neusten Stand gebracht und repräsentiert das Angebot von 1997.

Das Jahrbuch kann zum Preis von CHF 25.– plus Porto bezogen werden bei:

- Vogt-Schild AG
  Abonnenten- und Leserdienst
  Zuchwilerstrasse 21
  Postfach 748
  Ch–4501 Solothurn
  Telefon 032 624 71 11
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Leserdienst Nr. 67

Neu: Pervaporationssysteme von Sulzer Chemtech

Um ihre Position auf dem Gebiet der Trennverfahren zu festigen, hat die Sulzer Chemtech AG das GFT-Membransystemgeschäft von der zur Carbone-Lorraine-Gruppe gehörenden Deutschen Carbone übernommen. GFT ist weltweit führend in der Entwicklung, Fertigung und Vermarktung von Pervaporationssystemen.

Diese Systeme werden vorwiegend zur Trennung von azeotropen Gemischen und zur Entwässerung von Alkoholen und Estern verwendet. Der Markt weist derzeit hohe Wachstumsraten auf, da Feinchemikalien- und Pharmaunternehmen das Recycling der verbrauchten Lösungsmittel anstreben.

Sulzer Chemtech ist ein führender weltweiter Anbieter von Trennsystemen für die pharmazeutische, die chemische und die petrochemische Industrie. Durch die Aufnahme der Pervaporationssysteme in ihr Angebot kann Sulzer Chemtech ihren Kunden ein noch breiteres Spektrum an Lösungen bieten. Synergien werden insbesondere bei der Destillation erwartet, wo Kombinationen mit beiden Technologien nun aus einer Hand angeboten werden können.

Sitz für das GFT-Geschäft ist weiterhin Neunkirchen (bei Saarbrücken), Deutschland. Es erhält jedoch den neuen Namen 'Sulzer Chemtech – Membrane Systems'.

Wie funktioniert die Pervaporation?

Das zu trennende Gemisch wird über ein Modul geführt, das ein Paket nichtporöser Membranen enthält und in einem Vakuumbehälter installiert ist. Bei der Pervaporation erlaubt ein Lösungs-Diffusions-Mechanismus den selektiven Transport einer Komponente durch die Membran, gesteuert durch eine Partialdruckdifferenz zwischen Vorder- und Rückseite der Membran. Diese Komponente verdampft auf der anderen Seite der Membran, wird danach kondensiert und ausgetragen. Eine Vakuumpumpe entfernt die nichtkondensierbaren Komponenten und sorgt für die Aufrechterhaltung des erforderlichen Vakuums.

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Leserdienst Nr. 68

LSC™: Die grösste Innovation in der Zytometrie seit drei Jahrzehnten

Das LSC™ ist ein scannendes Laser-Zytometer, welches dieselben Daten liefert wie ein klassisches Flow Zytometer. Zusätzlich hat es den grossen Vorteil, dass die Zellen auf dem Objektträger eines Mikroskopes gemessen werden. Dadurch bietet das LSC™ eine bisher unerreichte Sensitivität und Flexibilität. Mit dem LSC™ besteht nicht die Qual der Wahl zwischen Mehrfarbenfluoreszenzanalyse und morphologischer Information, oder zwischen Zellsuspensionen und Gewebeschnitten, denn das LSC™ deckt all diese Möglichkeiten ab.

Das LSC™ misst in jedem Durchgang 4-Farbenfluoreszenz und Lichtstreuung und merkt sich den Messzeitpunkt und die Position einer jeden Zelle. Dadurch können die Zellen mehrmals mit verschiedenen Farbstoffen oder Farbstoffkombinationen gefärbt, immer wieder relokalisiert, re-analysiert und photographiert werden. Typische LSC™-Anwendungen sind FISH, DNA Bestimmung, Immunfluoreszenz, Immunophenotyping, Zellzyklusanalyse, Apoptose etc.

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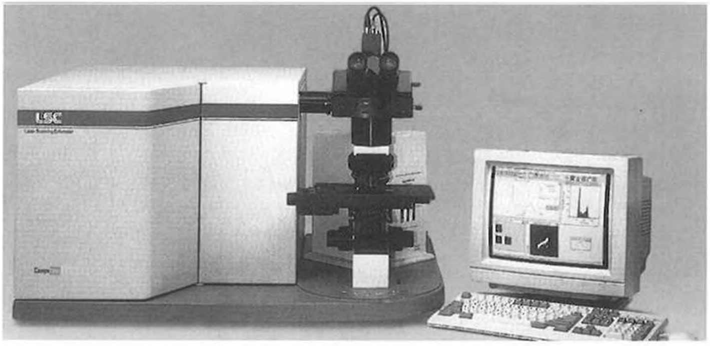
Leserdienst Nr. 69



STELLENMARKT

Fluka Prize

Reagent of the Year 1997

62279	Lipase, immobilized in Sol-Gel-AK from Pseudomonas cepacia, ~ 60 U/g, 1 g / 5 g
62281	Lipase, immobilized in Sol-Gel-AK from Aspergillus niger,~ 2.7 U/g, 1 g / 5 g
62277	Lipase, immobilized in Sol-Gel-AK from Candida antarctica,~ 1.6 U/g, 1 g / 5 g
62278	Lipase, immobilized in Sol-Gel-AK from Candida cylindracea,~ 16 U/g, 1 g / 5 g
62324	Lipase, immobilized in Sol-Gel-AK from hog pancreas, ~ 65 U/g, 100 mg / 500 mg
62282	Lipase, immobilized in Sol-Gel-AK from Mucor miehei, ~7 U/g, 1 g / 5 g
62283	Lipase, immobilized in Sol-Gel-AK from Pseudomonas fluorescens, ~ 55 U/g, 1 g / 5 g

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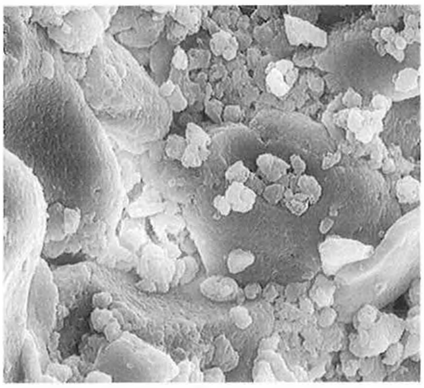
The Prize Winner 1997:

Manfred T. Reetz received his PhD from the University of Göttingen in 1969. After postdoctoral studies with Prof. R. W. Hoffmann he qualified as university lecturer at the University of Marburg in 1974. In 1978 he became C3-Professor at the University of Bonn and only 2 years later, in 1980, obtained a full professorship in organic chemistry at the University of Marburg. In 1993 he was appointed director of the «Max-Planck-Institut für Kohlenforschung» at Mülheim an der Ruhr. For his work in the field of organic chemistry he was awarded a «Dozentenstipendium des Fonds der Chemischen Industrie» (1976), the «Otto-Bayer-Preis» (1986) and the «Leibniz-Preis der Deutschen Forschungsgemeinschaft» (1989).

The Reagent:



Scanning electron-micrograph of a sol-gel immobilisate with Aspergillus niger lipase, Fluka No. 62281

The development of immobilized lipases produced by inclusion of the enzyme in sol-gel materials has been awarded the 1997 Fluka prize. In organic synthesis lipases play an important role. Two major problems, however, are the decreased enzyme activity in organic solvents and difficult recovery. These problems can be solved with a new immobilization procedure in which lipases are incorporated in hydrophobic organic-inorganic hybrid materials with the help of a sol-gel process [1-3]. This new class of heterogeneous biocatalysts has several advantages:

- increased enzyme activity (up to a factor of 100) with esterifications in organic solvents [1-3].
- conservation and increase of enantioselectivity in acylation reactions [1-5].
- remarkably high long-term stability [1-3].
- increased temperature stability [2].
- convenient recovery [1-3].

The porous and lipophilic character of the lipase-containing gels [6] (see scanning electron-micrograph) results in unexpectedly high activity. The new gels can be coated on to glass beads (e.g. SIRAN®) and used as heterogeneous biocatalysts in fluidized bed reactors [7]. Preliminary experiments show that catalytic reactions are also possible in water [8]. A review article will be published soon [9].

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The Fluka Prize:

The winner will be awarded the sum of sFr. 10 000.–. Nominations for the Fluka Prize «Reagent of the Year» should be submitted to the Fluka Prize Commitee c/o Fluka Chemie AG, CH-9471 Buchs/Switzerland no later than September 30th. Full details regarding the Fluka Prize are available upon request.

Fluka

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