7·8/99

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CHIMIA

Herbstversammlung 1999
Assemblée d'automne 1999
Fall Meeting 1999

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

VERLAG HELVETICA CHIMICA ACTA

Novartis Chemistry Lectureship

Novartis Pharma AG and Novartis Crop Protection AG are pleased to announce the following Novartis Chemistry lecturers of 1999–2000

Horst Kunz
(University of Mainz, FRG)
September 29, 1999

Varinder Aggarwal
(University of Sheffield, UK)
November 3, 1999

Stephen L. Buchwald
(MIT, Cambridge, USA)
December 1, 1999

Sue Gibson
(King's College London, UK)
January 12, 2000

Scott Miller
(Boston College, Boston, USA)
February 2, 2000

William R. Roush
(Univ. of Michigan, Ann Arbor, USA)
March 6, 2000

Uli Kazmaier
(University of Heidelberg, FRG)
April 5, 2000

Shu Kobayashi
(University of Tokyo, Japan)
May 3, 2000

Location: Müllheimerstrasse 195, WKL-430.3.20, CH-4057 Basel
Time: 10.30 am (get together: 10.00 am)

The Novartis Chemistry Lectureship is set up to recognize the outstanding contributions of academics in natural product synthesis and the development of synthetic methodology.

NOVARTIS

New Skills in the Science of Life

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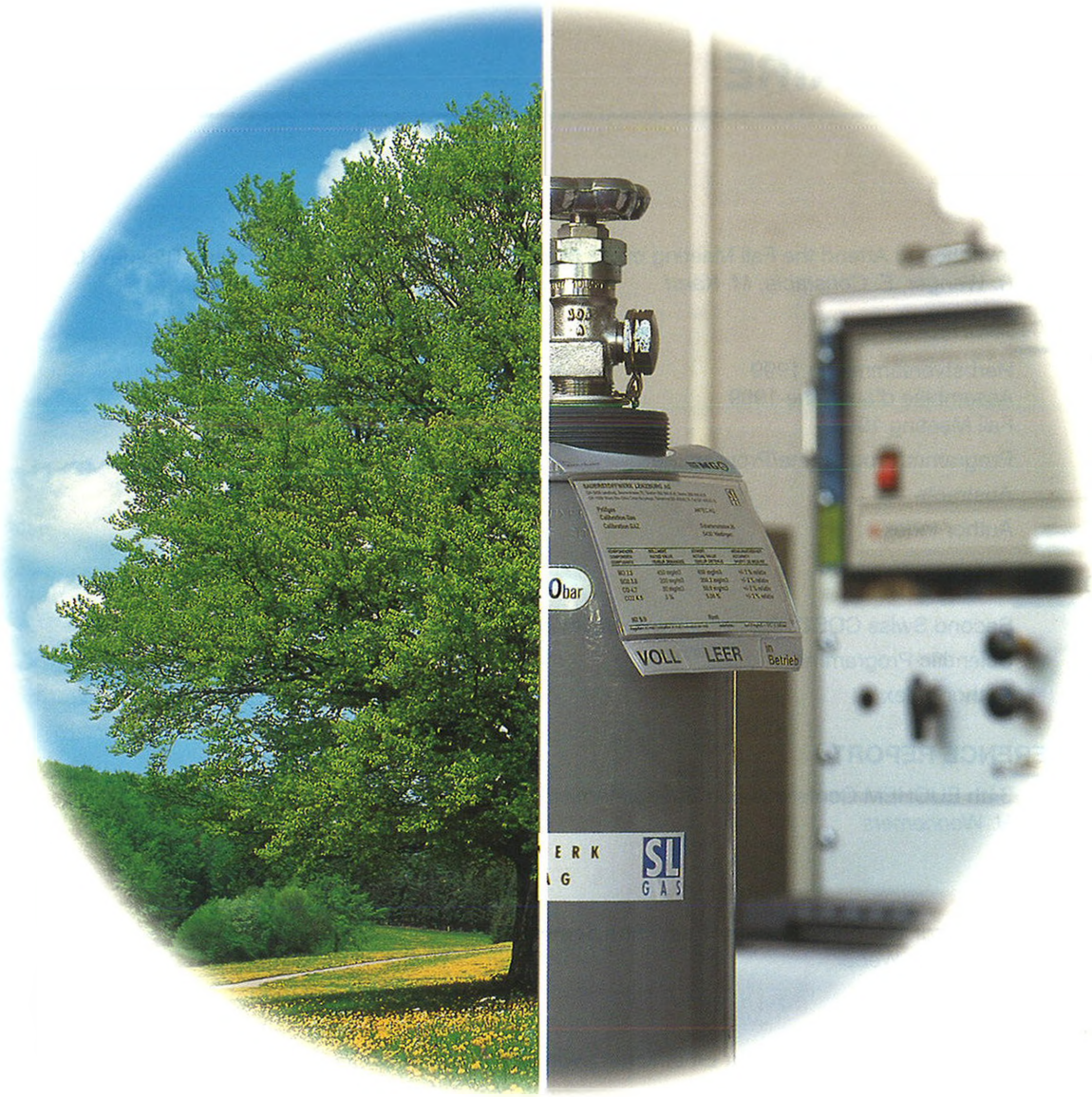

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Alle Gase aus Lenzburg

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CHIMIA 1999, 53, No. 7/8

EDITORIAL

Invitation to Attend the Fall Meeting of the New Swiss Chemical Society in Basel, Tuesday, October 12, 1999

On behalf of the New Swiss Chemical Society (NSCS) and the local Organizing Committee, it is our pleasure to invite you to attend the 1999 Fall Meeting of the NSCS. This is the first of the Fall Meetings in the new cycle involving a biennial rotation between the major linguistic regions of Switzerland and the first in the biennial cycle in which the meeting is linked with ILMAC in Basel.

The venue of ILMAC in Basel offers unparalleled opportunities to combine our scientific meeting with an internationally renowned scientific trade fair. In addition to the Fall meeting itself, there are a number of satellite meetings during the four days of ILMAC in which the NSCS is directly or indirectly involved. On Tuesday, October 12, a meeting entitled 'Process Simulation in Industrial Chemistry, Biotechnology, and Chemical Technology' will take place, organized by the Section of Industrial Chemistry of the NSCS. Under the patronage of the Section of Chemical Research of the NSCS, a one-day symposium on 'Supramolecular Chemistry and Molecular Recognition' will be held on Wednesday, October 13. Also on Wednesday, October 13, a meeting on 'Trace Determinations of Emerging Water Pollutants: Endocrine Disruptors, Pharmaceuticals, and Specialty Chemicals' will be held under the auspices of the Section of Analytical Chemistry of the NSCS, which has furthermore organized meetings entitled 'Trends in Clinical Chemistry' and 'Quality Assurance of Analytical Data', both taking place on Thursday, October 14. Moreover, under the patronage of the Section of Medicinal Chemistry of the NSCS, symposia on 'Molecular Modelling for Drug Design' and 'HTP-Purification, Analysis, and Quantification of Combinatorial Libraries of Single Compounds' will be held on Thursday, October 14. Other meetings cover topics such as 'Genomics' and 'Molecular Diagnostics', and on Friday, October 15, the Second Swiss COST Chemistry Symposium will be launched.

As you can see, a highly stimulating scientific programme awaits you. We are looking forward to welcoming you in Basel and hope that you will enjoy the Fall Meeting 1999.

Dr. Roland Wenger
Chairman of the Section of
Chemical Research of the NSCS

Professor Edwin Constable
Chairman of the local
Organizing Committee

Dr. Martin Karpf
Co-chairman of the local
Organizing Committee

Ruzicka-Preis 1999

Aus dem Fonds für den *Ruzicka*-Preis wird in der Regel alljährlich einer jungen Forscherin oder einem jungen Forscher für eine hervorragende veröffentlichte Arbeit auf dem Gebiet der allgemeinen Chemie, die in der Schweiz oder von einer Schweizerin bzw. einem Schweizer im Ausland durchgeführt worden ist, ein Preis verliehen.

Vorschläge für Kandidatinnen und Kandidaten, die das 40. Altersjahr nicht überschritten haben, können bis spätestens **30. September 1999** (Eingangsdatum) beim Vizepräsidenten für den Bereich Forschung der Eidgenössischen Technischen Hochschule Zürich, ETH Zentrum, CH–8092 Zürich eingereicht werden.

Folgende Unterlagen müssen mit dem Empfehlungsschreiben eingereicht werden: auszuzeichnende Publikation (und evtl. weitere wichtige Publikationen), Publikationsliste, CV.

Ruzicka-Prize 1999

The *Ruzicka*-Prize is awarded each year to a young scientist for his/her outstanding, published contribution in the field of general chemistry, achieved either in Switzerland or by a Swiss citizen abroad.

Proposals for candidates (age limit: 40 years) may be submitted until **September 30, 1999** (date of arrival) to the Vice-President for Research at the Swiss Federal Institute of Technology, ETH Zentrum, CH–8092 Zürich.

The proposal shall include reprints of the most important publication(s), publication list and CV.

SensLab ´99 Conference, 5th Anniversary of the Center for Chemical Sensors (CCS)

(September 17–18, 1999)

The Center for Chemical Sensors /Biosensors and bioAnalytical Chemistry (CCS) at ETH-Technopark in Zurich celebrates its 5th Anniversary with the Conference SensLab '99. Parallel to invited lectures of leading scientists in the field of sensor research, an exhibition presented by companies that collaborate with CCS will illustrate the link between research, development and real applications. A poster session allows scientists and industrials to present their latest progress under the headings:

- Molecular recognition
- Functional indicator dyes
- Optical, potentiometric and amperometric sensors
- Nano- and microtechnology
- Gas sensors
- Biosensors and bioarrays

Open-Day on Saturday, September 18th
CCS staff will present the current state of research with short presentations. Visitors will have the opportunity to visit the laboratories with optical, potentiometric and amperometric sensors running.

For more information, please contact:
Gerhard J. Mohr, Center for Chemical Sensors, Technoparkstr. 1
CH–8005 Zurich, phone: ++41 1 445 13 50, fax: ++41 1 445 12 33
gerhard@chemsens.pharma.ethz.ch
http://www.chemsens.ethz.ch/html/events.html

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NEUE SCHWEIZERISCHE CHEMISCHE GESELLSCHAFT

NOUVELLE SOCIETE SUISSE DE CHIMIE

NEW SWISS CHEMICAL SOCIETY

SEKTION ANALYTISCHE CHEMIE
SEKTION MEDIZINISCHE CHEMIE
SEKTION CHEMISCHE FORSCHUNG

SECTION CHIMIE ANALYTIQUE
SECTION CHIMIE THERAPEUTIQUE
SECTION RECHERCHE CHIMIQUE

Herbstversammlung 1999
Assemblée d'automne 1999
Fall Meeting 1999

Dienstag, 12. Oktober 1999
Mardi, 12 octobre 1999
Tuesday, October 12, 1999

Basel/Bâle
ILMAC 99

Kongresszentrum Messe Basel
Centre de Congrès de la Foire de Bâle
Messe Basel

Messeplatz 21, 2. Stock/2ème étage/2nd Floor

Neu: Die besten Vorträge und Posters werden prämiert.
Nouveau: Les meilleures conférences et posters seront récompensés par un prix.
New: The best communications and posters will be rewarded with a prize.

Jury: Session Chairpersons

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Organizing Committee:

Prof. E.C. Constable, University of Basel (chair)
Dr. H.-R. Dettwiler, *LONZA AG*, Visp
Prof. C.E. Housecroft, University of Basel
Prof. A. Pfaltz, University of Basel
Prof. M. Quack, ETH Zürich
Prof. J. Robinson, University of Zürich
Prof. H.-J. Wirz, University of Basel
Prof. C. Daul, University of Fribourg
Dr. R. Giger, *Novartis Pharma AG*, Basel
Dr. M. Karpf, *Hoffmann-La Roche AG* (co-chair)
Prof. P. Pregosin, ETH Zürich
Dr. P. Radvila, Gais
Dr. R. Wenger, *Wenger Chemtech*

Secretary: Ingrid Falk, Sekretariat des Instituts für Anorganische Chemie, Universität Basel, Spitalstrasse 51, CH–4056 Basel, Tel. 061/267 10 22, Fax 061/267 10 05, E-Mail: nscg@ubaclu.unibas.ch

Informationen:

Keine Anmeldung erforderlich, der Eintritt ist frei.

Eintritt: Eingang Kongresszentrum neben Hotel *Le Plaza* (Swissôtel). ILMAC 99 Eintritts-Billette werden am Eingang von der NSCG verteilt. Der Zutritt zum '*Paracelsus* Vortrag' ist ab 16.30 Uhr frei.

Studierende, die Mitglied der NSCG sind, erhalten folgende Reisekosten zurückstattet: Bahnbillet nach Basel, 2. Kl. 1/2-Tax (Anreise aus dem Ausland: Rückerstattung der Reisekosten ab Schweizer Grenze). Das Bahnbillet ist dem Rückerstattungssantrag beizulegen. Der Rückerstattungssantrag ist unter Angabe der Arbeits- und Privatadresse, des Bank- oder PC-Kontos sowie – wenn möglich – unter Beilage eines Einzahlungscheines beim Sekretariat der NSCG, Frau *L. Etter*, c/o Novartis, K-25.1.45, CH–4002 Basel, einzureichen.

Lunch: Sandwiches, Café u.s.w. werden in der Nähe der Posters zur Verfügung stehen. Es hat auch Verpflegungsmöglichkeiten an der ILMAC oder in nahegelegenen Restaurants.

Informations:

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

Entrée: L'entrée est à côté de l'Hôtel *Le Plaza* (Swissôtel). A l'entrée des billets donnant accès à l'ILMAC 99 seront distribués par la NSSC. L'entrée à la Conférence du Lauréat du prix *Paracelse* est libre à partir de 16.30.

Les étudiants membres de la NSSC peuvent demander le remboursement des frais de voyage sur la base du billet de train Bâle et retour, 2e classe, 1/2 prix (pour les membres qui viennent de l'étranger, seulement 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 NSCC – Madame *L. Etter*, c/o Novartis K-25.1.45, CH–4002 Bâle.

Lunch: Des sandwiches, boissons et cafés seront offerts près des posters. On trouve des restaurants à l'ILMAC ou dans les alentours du centre de congrès.

Location:

The Fall Meeting 1999 takes place at the Messe Basel.

Transportation:

Morning:			**Evening**:		
Train from	Departure	Arrival Basel	Departure Basel	Arrival	Train to:
BE	07.49	08.56	18.22	20.04	BE
FR	07.16	08.56	19.04	20.43	FR
GE	06.47	09.38	18.22	21.13	GE
Lausanne	07.10	09.38	18.22	20.49	Lausanne
NE	08.00	09.38	18.22	19.59	NE
ZH	08.37	09.38	18.20	19.22	ZH

From the main station, take tram No. 2 directly to ILMAC 99 (Tram Stop 'Mustermesse')

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Programm der Herbstversammlung 1999
Programme de l'assemblée d'automne 1999
Programme of the Fall Meeting 1999

10.00–10.40 Opening Ceremony
Auditorium: Montreal
Dr. *H.L. Senti*

Presentation of the *Werner* Prize 1999

Lecture of the *Werner* Prize Winner 1999
Prof. ***Frédéric Merkt***
Laboratorium für Physikalische Chemie
ETH Zürich
'High *Rydberg* States in Technology and Chemistry'
Abstract *1*, see page 326

11.00–16.30 Analytical Chemistry
General assembly of members:
Auditorium: Kleiner Festsaal
Lectures: *Auditorium: Kleiner Festsaal*
Poster Session: *2nd Floor Foyer*
Programme, see page 321
Abstracts, see page 326

11.00–16.00 Medicinal Chemistry
General assembly of members
Auditorium: Rio
Lectures: *Auditorium: Rio*
Poster Session: *2nd Floor Foyer*
Programme, see page 321
Abstracts, see page 331

10.45–10.55 Chemical Research
General assembly of members:
Auditorium: Montreal

11.00–16.30 Inorganic and Coordination Chemistry
Lectures: *Auditorium: San Francisco*
Poster Session: *2nd Floor Foyer*
Programme, see page 322
Abstracts, see page 334

11.00–16.30 Organic Chemistry
Lectures: *Auditorium: Singapore, Sydney, Montreal*
Poster Session: *2nd Floor Foyer*
Programme, see page 322
Abstracts, see page 357

11.30–16.30 Physical and Computational Chemistry
Lectures: *Auditorium: Osaka, Samarkand*
Poster Session: *2nd Floor Foyer*
Programme, see page 324
Abstracts, see page 383

16.40–16.45 Presentation of the Prizes for the Best Communications and Posters
Auditorium: Montreal

16.45–18.00 Presentation of the *Paracelsus* Prize 1999
Auditorium: Montreal

Lecture of the *Paracelsus* Prize Winner 1999
Auditorium: Montreal
Prof. ***Albert Eschenmoser***
Laboratorium für Organische Chemie
ETH Zürich
'Über die Lust zu forschen: Von der biogenetischen Isoprenregel zur Aetiologie der Nukleinsäurestruktur'

Analytical Chemistry

11.00–11.20 **General Assembly of Members**
Auditorium: Kleiner Festsaal

Lecture and Panel Discussion: *Auditorium: Kleiner Festsaal*
Abstract 2, see page 326
Chairperson: *P.R. Radvila (SACh)*

11.20–11.45 ***P.R. Radvila***
SACh/NSCG
Chemische Analytik – Zukünftige Anforderungen an Technik und Ausbildung
Abstract 2

11.45–12.30 Panel Discussion
R. Battaglia, R. Etter, M. Oehme, P.R. Radvila

14.00–15.15 **Poster Session A**
2nd Floor Foyer
Chairperson: *U. Spichiger (ETH)*
Abstracts 3–12, see page 326–329

15.15–16.30 **Poster Session B**
2nd Floor Foyer
Chairperson: *U. Spichiger (ETH)*
Abstracts 13–23, 243, see page 329–331, 386

One Prize for the Best Poster (*P. Radvila, U. Spichiger*)

Medicinal Chemistry

11.00–11.20 **General Assembly of Members**
Auditorium: Rio

Lectures: *Auditorium: Rio*
Abstracts 24 and 25, see page 331, 332
Chairperson: *R. Giger*

11.20–11.40 ***D. Obrecht***, *C. Abrecht, B. Dhanapal, P. Ermert, J.-P. Obrecht, K. Sekanina*
Polyphor AG, Winterthurerstrasse 190, CH–8057 Zürich
Efficient Strategies towards High-Quality Compound Libraries and their Impact in Lead Discovery and Optimization
Abstract 24

11.40–12.00 ***F. Gasparini,*** *K. Lingenhoehl, P.J. Flor, N. Stoehr, C.I. Vranesic, H. Allgeier, M. Schmutz, W. Spooren, M. Varney, E. Johnson, S.D. Hess, A. Sakaan, E. Santori, G. Velicelebi, R. Kuhn,*
Nervous System Research, Novartis Pharma AG, CH–4002 Basel, Switzerland/SIBIA Neuroscience Inc., La Jolla, CA 92037, USA
Discovery of 2-Methyl-6-(phenylethynyl)pyridine (MPEP): A Highly Potent and Selective MGLUR5 Antagonist
Abstract 25

12.00–12.30 **Poster Session**
2nd Floor Foyer
Abstracts 26, 27, see page 332

Lectures: *Auditorium: Rio*
Abstracts 28–32, see page 332, 333
Chairperson: *W. Froestl*

14.00–14.20 ***S. Roggo,*** *S. Hintermann, V. Rasetti, M. Tintelnot-Blomley, U. von Krosigk*
Nervous System Research, Novartis Pharma AG, CH–4002 Basel
Synthetic Aspects and SAR of Non-Peptidic, Irreversible Caspase Inhibitors
Abstract 28

14.20–14.40 ***E. Altmann***
Oncology, Novartis Pharma AG, CH-4070 Basel
7-Pyrrolidinyl- and 7-piperidinyl-5-aryl-pyrrolo[2,3-*d*]pyrimidines – Highly Potent Inhibitors of the Protein Tyrosine Kinase c-Src
Abstract 29

14.40–15.00 ***Y.P. Auberson,*** *P. Acklin, H. Allgeier, S. Bischoff, S. Ofner, M. Schmutz, S. Veenstra*
Nervous System, Novartis Pharma AG, CH–4002 Basel
The Structure-Activity Relationship of AMPA and NMDA(gly) Antagonists Derived from 5-Aminomethylquinoxaline-2,3-dione
Abstract 30

15.00–15.20 ***G. Bold,*** *J. Frei, P. Manley, P. Furet, M. Sills, F. Hofmann, S. Ferrari, J. Mestan, R. Cozens, J. Brüggen, J. Wood*
Oncology and Core Technology, Novartis Pharma AG, CH–4002 Basel
Potent and Orally Active Inhibitors of VEGF Receptor Tyrosine Kinases as Inhibitors of Tumor-Driven Angiogenesis
Abstract 31

15.20–15.40 ***C. Papageorgiou,*** *R. Albert, P. Floersheim, E. Andersen, V. Hungerford, M. Zurini, H.-P. Weber, M.H. Schreier*
Novartis Pharma AG, WSJ-350.3.14, CH–4002 Basel
Bioisosteres of Leflunomide as Antibody production Inhibitors. A Medicinal-Chemistry-Based Discovery of a Novel Biochemical Mechanims for B-Cell Inhibition
Abstract 32

15.40–16.00 *P. Angehrn, I. Heinze-Krauss, M. Page,* ***H.G.F. Richter***
F. Hoffmann-La Roche Ltd., Basel, Switzerland
Cephalosporin-Carbapenem Combinations: Antibiotics with Ultra-Broad Spectrum
Abstract 211

One Prize for the Best Presentation or Poster (*R. Giger, W. Froestl*)

Chemical Research

10.45–10.55 **General Assembly of Members**
Auditorium :Montreal

Inorganic and Coordination Chemistry

Minisymposium: *Auditorium: San Francisco*
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Chairperson: *P. Pregosin*

11.00–11.35 ***U. Röthlisberger***
Laboratorium für Anorganische Chemie, ETH Zürich
Computational Inorganic Chemistry: Today and Tomorrow
Abstract 33

11.40–12.15 ***D. Nocera***
Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts, USA
Characterization and Utility in Multielectron Photocatalysis
Abstract 34

12.20–12.55 ***P. Hoffmann***
Organisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg, Germany
From Theory and Organometallic Model Chemistry to Catalysis
Abstract 35

14.00–15.15 ***Poster Session A***
2nd Floor Foyer
Abstracts 36–80, see page 334–345
Chairperson: *C.E. Housecroft*

15.15–16.30 ***Poster Session B***
2nd Floor Foyer
Abstracts 81–124, 210, see page 346–356, 378
Chairperson: *E.C. Constable*

Four Prizes for the Best Posters (*E. Constable, C. Housecroft*)

Organic Chemistry

11.00–12.00 **Poster – Short Presentations**
Auditorium: Singapore, Sydney, Montreal: The results described in each poster will be presented

by the main author; 2 slides/3 min. max. each presentation.

Singapore: Chairman: *P. Strazewski,* University of Basel
M. Fasching, B. Hoffmann, E. Leroy, W. Mühlecker, L. Nezbedová, J.V. Schreiber, M. Tharin, E. Vockelmann, J. Valverde, Q. Wang, T. Netscher, J. Ferrari, G. Klein, P. Folly, T. Damiano, E. Gonzalès, K.A. Brun, I. Chevalley, N. Bensel, R.R. French.
Abstracts 125–144, see page 357–361

Sydney: Chairman: *J. A. Robinson,* University of Zürich
A. Gebert, M. Rueping, E. Couché, M. Raemy, G. Jenzer, C.M. Saudan/F. Viton, F. Robvieux, H. Jacobsen, S. Pache, L. Quaranta, E.F. Murphy, N. Soldermann, S. Gillet/S. Thibeaut, A. Tomassini, V.P. Bulugahapitiya, C. Allemann, M. Blagoev, C. Botuha, R. Cannas/S. Tchertchian, J. Hoffner.
Abstracts 145–164, see page 362–366

Montreal: Chairman: *H. Heimgartner,* University of Zürich
C. Gaul, C. Poliart, C.G. Bochet, L. Gobbi, R.T.N. Luykx, I.S. Marcos, D.G. Monchaud, C. Ollivier, A. Pichota, G. Rapenne, D. Renneberg, J.-M. Simone, F. Mazé, C. Benhaïm, M. von Arx, M. Dusi, S. Amrein, R. Chuard, R. Chuard, C. Ollivier, F. Stauffer
Abstracts 165–185, see page 367–372

12.00–13.40 **Poster Sessions**
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Lectures: *Auditorium: Singapore*
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13.50–14.10 ***R. Schütz**, C. Leumann*
University of Bern, Department of Chemistry and Biochemistry
OPA: the Olefinic Peptide Nucleic Acid Analogue
Abstract 186

14.10–14.30 ***D. Weicherding**, U. Diederichsen*
Organische Chemie und Biochemie, Technische Universität München, Garching
Electron Transfer in Alanyl Peptide Nucleic Acids
Abstract 187

14.30–14.50 ***P.A. Lorenzetto**, A. Strehler, P. Rüedi*
Organisch-chemisches Institut, Universität Zürich
Synthese von optisch aktiven Acetylcholin-Mimetika
Abstract 188

14.50–15.10 ***S. Wessely**, M. Spormann, U. Lindemann, E. Meggers, B. Giese*
Department of Chemistry, University of Basel
On the Mechanism of Long-Range Charge Migration in DNA
Abstract 189

15.10–15.30 *E. Biala, O. Botta,* ***P. Strazewski***
Institute of Organic Chemistry, University of Basel
3'-Aminoacyl- and 3'-Peptidyl-RNA
Abstract 190

15.30–15.50 *B. Muckensturm,* ***S.M. Farahi,*** *J.P. Reduron*
Université de Haute Alsace, Ecole Nationale Supérieure de Chimie de Mulhouse/Conservatoire Botanique de la Ville de Mulhouse
A New Norsesquiterpene from *Eryngium giganteum*
Abstract 191

15.50–16.10 ***A. Wittelsberger**, M. Keller, L. Scarpellino, L. Patiny, H. Acha-Orbea, M. Mutter*
Institute of Organic Chemistry, University of Lausanne/Institute of Biochemistry and Ludwig Institute, University of Lausanne, ISREC
The Pseudo-Proline Concept as Tool in Structure-Activity Studies of Bioactive Peptides
Abstract 192

16.10–16.30 *G. Renevret,* ***D. Lefebvre**, C. Le Drian*
Ecole Nationale Supérieure de Chimie de Mulhouse
A New Reagent for the *Koenigs-Knorr* Reaction: Bromotetraisobutyrylglucose
Abstract 193

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Abstracts 194–201, see page 374–376
Chairperson: *R. Neier (University of Neuchâtel)*

13.50–14.10 ***F. Villar**, P. Renaud*
Université de Fribourg, Institut de Chimie Organique
Radical Cyclization of Chiral Haloacetals: Synthesis of (–)-Eldanolide and Other Natural Products
Abstract 194

14.10–14.30 *E. P. Kündig,* ***H. Ratni***
Département de Chimie Organique, Université de Genève
Asymmetric Synthesis *via* Arene Chromium Complexes: Methodology and Application to Natural Product Synthesis
Abstract 195

14.30–14.50 ***C. Geyer**, A. Baiker*
Laboratorium für Technische Chemie, ETH Zürich
Solvent-Free Synthesis of Vinyl Carbamates from Alkyne, Amine and Carbon Dioxide
Abstract 196

14.50–15.10 ***J. J. Jodry**, J. Lacour*
Département de Chimie Organique, Université de Genève
Asymmetric Induction of TRISPHAT Anions onto Chiral Transition-Metal Complexes
Abstract 197

15.10–15.30 ***S. Tohill**, P. Müller*
Département de Chimie Organique, Université de Genève

Intermolecular Cyclopropanation *vs.* CH Insertion in Rh(II)-Catalyzed Carbenoid Reactions
Abstract 198

15.30–15.50 ***V. Huber***, *J. Raemy, T.A. Jenny*
University of Fribourg, Institute of Organic Chemistry
New Reactions of Pinene-Derived Iron Carbonyl Complexes
Abstract 199

15.50–16.10 *R. Batra,* ***J.F.K. Müller***, *M. Neuburger, B. Spingler*
University of Basel, Institute of Inorganic Chemistry
Chiral Dilithiomethane-Derivatives: Structure Determination and Application in Asymmetric Reactions
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16.10–16.30 ***C. Fehr***, *J. Galindo, O. Etter, E. Ohleyer*
Firmenich SA, Corporate R&D Division, Geneva
A New Variant of the *Claisen* Rearrangement from Malonate-Derived Allylic Silyl Ketene Acetals. Efficient, Highly Enantio- and Diastereoselective Syntheses of (+)-Methyl Dihydroepijasmonate and (+)-Methyl Epijasmonate
Abstract 201

Lectures: *Auditorium: Montreal*
Abstracts 202–209, see page 376–378
Chairperson: *W. Woggon (University of Basel)*

13.50–14.10 ***P. Weyermann***, *F. Diederich*
Laboratorium für Organische Chemie, ETH Zürich
Dendritic Iron Porphyrins with Tethered Axial Ligands as Model Compounds for Cytochromes
Abstract 202

14.10–14.30 ***K.N. Koch***, *A. Linden, H. Heimgartner*
Organisch-chemisches Institut, Universität Zürich
Synthesis of Cyclic Depsipeptides *via* Direct Amide Cyclization
Abstract 203

14.30–14.50 ***A. Specht***, *L. Peng, M. Goeldner*
Laboratoire de Chimie Bio-organique, UMR 7514 CNRS, Strasbourg
Calixarene Complexes with Photolabile Cholinergic Ligands: Models of Artificial Cholinergic Receptors
Abstract 204

14.50–15.10 ***C. Brändli, T.R. Ward***
Department of Chemistry and Biochemistry, University of Berne
Solution-Phase Combinatorial Synthesis of Substituted Pyridines
Abstract 205

15.10–15.30 ***J. Schlögl***, *B. Kräutler*
Institute of Organic Chemistry, University of Innsbruck
Calixporphyrins, Porphyrinoid Container Molecules
Abstract 206

15.30–15.50 ***M. Mayor***, *J.-M. Lehn*
Institut für Nanotechnologie, Forschungszentrum Karlsruhe GmbH, Karlsruhe; Laboratoire du Chimie Supramoléculaire, ISIS, Université Louis Pasteur, Strasbourg
Polythiophenyl-Substituted Benzenes as Reducible Subunits in Nanoscale Structures
Abstract 207

15.50–16.10 ***U.H. Hirt***, *O.G. Wiest, T. Wirth*
Institut für Organische Chemie, Universität Basel; Department of Chemistry and Biochemistry, University of Notre Dame, USA
Computer-Supported Design of Chiral Hypervalent Iodine Compounds: Comparison of Experimental Data and Calculations
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16.10–16.30 ***A. Studer***
Laboratorium für Organische Chemie, ETH Zürich
New Tin Free-Radical Cyclization Reactions Using the Persistent Radical Effect (PRE)
Abstract 209

Six Prizes for the Best Presentations or Posters (*P. Strazewski, J. A. Robinson, H. Heimgartner, J. Hunziker, R. Neier, W. Woggon)*

Physical and Computational Chemistry

Lectures: *Auditorium: Osaka*
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Chairperson: *M. Quack (ETH Zürich)*

11.30–11.50 ***P.-A. Muller***, *E. Haselbach, P. Jacques, X. Allonas, D. Burget, A.-C. Sergenton, H. Galliker*
Institute of Physical Chemistry, University of Fribourg/Département de Photochimie Générale, Université de Mulhouse/ Chemistry Department, Stans Gymnasium,
Intramolecular Multiple *Rehm-Weller* Plots in Photoinduced Electron-Transfer Processes: Competition between π- and n-Type Donor Sites in Benzylamine
Abstract 230

11.50–12.10 ***M. Willeke***, *J. Pochert, M. Quack*
Laboratorium für Physikalische Chemie, ETH Zürich
Intramolecular Vibrational Redistribution in the Chiral Molecule CF_3CHFI: Experiment and *Ab Initio* Theory
Abstract 231

12.10–12.30 ***S. Megelski***, *M. Pfenninger, H. Maas, G. Calzaferri*
Department of Chemistry and Biochemistry, University of Bern
Very Fast Energy Migration and Trapping by Su-

pramolecular Organisation of Dyes in Zeolite L Nanocrystals
Abstract 232

12.30–13.30 Lunch

Chairperson: *D. Stahl (EPFL)*

13.30–13.50 ***D. Brühweiler***, *R. Seifert, G. Calzaferri*
Department of Chemistry and Biochemistry, University of Bern
Quantum-Sized Silver-Sulfide Clusters in Zeolite A
Abstract 233

13.50–14.10 ***I. Gassiot***, *N. Brand, A. Arlt, M. Frank, A.M. Braun*
Lehrstuhl für Umweltmesstechnik, Engler-Bunte-Institut, Universität Karlsruhe
Efficiency of VUV-Induced Gas-Phase Oxidation of VOC. Influence of Water and Reactor Geometry.
Abstract 234

14.10–14.30 ***M. Brynda***, *T. Berclaz, M. Geoffroy, G. Bernardinelli, University of Geneva*
Barrière à la Rotation autour d'une Liaison C–P: Variation en Fonction de la Température du Spectre RPE du Radical Dibenzobarrellène phosphinyl en Phase Monocristalline
Abstract 235

14.30–14.50 ***N. Brand***, *P. Mazellier, G. Mailhot, M. Bolte*
Laboratoire de Photochimie Moléculaire et Macromoléculaire, UMR CNRS Université Blaise Pascal No 6505, Aubiere
Les Complexes Aqueux de Fer(III) en Solution Diluée: Caractérisation et Comportement Photochimique
Abstract 236

14.50–15.10 ***S. Göb***, *E. Oliveros, A.M. Braun, C.A.O. do Nascimento*
Lehrstuhl für Umweltmesstechnik, Engler-Bunte-Institut, Universität Karlsruhe, D–76128 Karlsruhe/ Escola Politécnica, Universidade de Sao Paulo, Sao Paulo
Modeling of the Photochemically Enhanced *Fenton* Reaction Using Artificial Neural Networks
Abstract 237

Lectures: *Auditorium: Samarkand*
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Chairperson: *J. Weber (University of Geneva)*

13.30–13.50 ***A. Magistrato***, *U. Röthlisberger*
Inorganic Chemistry, ETH Zentrum
Ab Initio Molecular Dynamics Simulation of Electron-Transfer-Induced Carbon-Sulfur Bond Cleavage in Rhenium and Technetium Thioether Complexes
Abstract 238

13.50–14.10 ***K. Doclo***, *U. Röthlisberger, P. Carloni*
Inorganic Chemistry, ETH Zentrum; International School of Advanced Studies, Trieste
Hybrid *Car-Parinello* Simulations as a Tool for the Rational Design of Biomimetics
Abstract 239

14.10–14.30 ***J.V. Vondele***, *U. Röthlisberger*
Inorganic Chemistry, ETH Zentrum
Overcoming the Time-Scale Barrier in *Ab Initio* Molecular Dynamics
Abstract 240

14.30–14.50 ***B. Kirchner***, *S. Searles, A.J. Dyson, P. Vogt, H. Huber*
Universität Basel, Inst. für Phys. Chemie/MPI für Festkörperforschung, Stuttgart/University of Queensland, Dept. of Chemistry, Brisbane
Disproving the Iceberg Effect? The Deuterium Quadrupole-Coupling Constant of Water in DMSO
Abstract 241

14.50–15.10 ***I. Ciofini***, *C.A. Daul, S. Daul*
Institut de Chimie Inorganique, Université de Fribourg/ Institut de Physique Théorique, Université de Fribourg
Density Matrix Renormalization Group (DMRG) as a Tool for Magnetic Properties Calculations
Abstract 242

15.30–16.00 ***Poster Session A***
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Abstracts 221–229, see page 381–383
Chairperson: *J. Wirz*

Two Prizes for the Best Presentations or Posters (*M. Quack, D. Stahl, J. Weber, J. Wirz)*

Physikalische Chemie **1**

High Rydberg states in technology and chemistry

F. Merkt,
Laboratorium für Physikalische Chemie, ETH Zürich, CH-8092 Zürich, Switzerland.

The properties of atomic and molecular Rydberg states vary rapidly with the principal quantum number n. Their lifetime scales as n^3, their polarizability as n^7, the dimension of the Rydberg electron orbit as n^2, the binding energy of the Rydberg electron as n^{-2} and the energy spacing between adjacent states of a given Rydberg series as n^{-3}. Atomic and molecular Rydberg states of high principal quantum number ($n \geq 100$) thus possess very unusual properties that can be exploited in chemistry and technology [1].
Using a new experimental method, based on double-resonance excitation using a home-built broadly tunable (tunable range 10-20 eV) high resolution (bandwidth 0.1 cm^{-1}) vacuum ultraviolet laser system and millimeter waves [2], spectroscopic measurements can be carried out on high Rydberg states at a resolution of $2 \cdot 10^{-6}$ cm^{-1}. By analysing the dependence of the line shapes and line positions in the spectra of high Rydberg states on intentionally applied electric fields, very precise measurements of ion concentrations and of stray electric fields can be made [3]. By monitoring the field ionization of high Rydberg states located just below successive molecular ionization thresholds, high resolution spectroscopic measurements can be carried out on important and as yet only poorly characterized molecular ions, such as for example CH_4^+ [4].

[1] F. Merkt, *Ann. Rev. Phys. Chem.* **48**, 675 - 709 (1997)
[2] F. Merkt and H. Schmutz, *J. Chem. Phys.* **108**, 10033 - 10045 (1998)
[3] A. Osterwalder and F. Merkt, *Phys. Rev. Lett.*, **82**, 1831 - 1834 (1999)
[4] R. Signorell and F. Merkt, *J. Chem. Phys.*, **110**, 2309 - 2311 (1999)

Analytische Chemie **2**

Chemische Analytik – Zukünftige Anforderungen an Technik und Ausbildung

P.R. Radvila

Sektion Analytische Chemie der NSCG

Die Erfolge der Naturwissenschaften und der Technik haben vergessen lassen, dass sie nur dank einer immer ausgefeilteren und effizienteren Analysen- und Messtechnik zustande kamen. Die Analytik ist Messlatte und Triebfeder im Innovationsprozess – von der Forschung und Entwicklung bis zur Produktionssteuerung und Qualitätskontrolle. Fortschritt ist messbar.

Die Bedeutung der Analytik ist immens – sowohl für die Wissenschaft selbst als auch für die Öffentlichkeit (Gesundheitswesen, Umweltschutz) und Wirtschaft. Alle sind auf zuverlässige und reproduzierbare Resultate sowie eindeutige und klare Daten-Interpretation angewiesen.

Die Analytische Chemie ist heute ein Disziplin überschreitender Wissenschaftsbereich. Jede Disziplin ist auf Analytik angewiesen und mag ihre Eigenheiten haben – die Analytik basiert aber stets auf gemeinsamem Wissen und Grundsätzen.

Ein grosser Teil der Naturwissenschafter ist ausschliesslich oder teilweise mit Analytik beschäftigt, ein beträchtlicher Teil ist auf Analysendaten angewiesen. Aber alle sind auf eine fundierte Analytik-Ausbildung angewiesen.

Trotz Erfolgen dank Analytik, Effizienzsteigerungen und Proliferation der Messtechnik deutet Verschiedenes auf Mängel: Datenflut mit Schwierigkeit bei der Dateninterpretation, unzureichende Datenqualität und ungesicherte Wiederholbarkeit von Resultaten, Infragestellung der Glaubwürdigkeit, Erfahrungen bei der Qualitätssicherung und Ausbildung weisen auf Lücken bei der Basisausbildung hin. Analoge Mängel sind in andern Ländern festgestellt worden.

Analytical Chemistry **3**

Ion trap MS/MS detection, a sensitive and selective alternative to NICI-MS and EI-HRMS

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The trace analysis of polychlorinated environmental contaminants has gained an increased interest in recent years. Environmental regulations restrict or ban the use of certain compound classes, for example polychlorinated bornanes (toxaphene) and chlorinated paraffins (CPs). Besides a sufficiently low detection limit, a high selectivity is needed to detect these components in real samples since interferences caused by other chlorinated compounds or by sample matrix might occur.

Electron capture detection (ECD) and negative ion chemical ionization (NICI) mass spectrometry (MS) coupled to capillary gas chromatography are most frequently used for quantification. Common problems are very different response factors for different congeners and interferences from other organochlorines [1,2]. Electron ionization MS (EI-MS) provides another possibility. However, due to extensive fragmentation a lower sensitivity and selectivity compared to NICI-MS is obtained for low resolution techniques (LRMS). High resolution EI-MS (EI-HRMS) overcomes this drawback [3], but its high costs make it less attractive for routine analysis. A recent publication [4] indicated that ion trap MS/MS could be an alternative. This presentation shows that this technique has a comparable sensitivity but better selectivity as NICI-LRMS and a better sensitivity but comparable selectivity as EI-HRMS for the compound classes mentioned above.

[1] Lau B. Et al.; *Chemosphere* **1996**, 32, 1021.
[2] Gjøs N. et al.; *Anal. Chem.* **1982**, 54, 1316.
[3] Santos E.J. et al.; *Rapid Comm. Mass. Spectrom.* **1997**, 11, 341.
[4] Chan H.M., Zhu J., Yeboah F.; *Chemosphere* **1998**, 36, 2135.

Analytical Chemistry **4**

Analysis of tannins extract by ESI-MS/MS^n

Camille Perret, Roger Pezet and Raffaele Tabacchi

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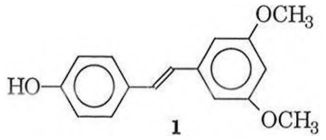
Botrytis cinerea produces an hydroxystilbene-degrading enzyme when grown on a pectin-containing medium, identified as a laccase. This stilbene oxidase oxidizes both pterostilbene **1** and resveratrol to produce non-toxic compounds [1].
Polyphenolic fractions of the healthy grape berries of Gamaret cause a rapid inhibition of this laccase at low concentration. The pure tannins extract contains condensed and hydrolysable tannins. These polar compounds are very difficult to purify and to identify. Electospray-mass spectrometry combined with sequential tandem MS (ESI-MS/MS^n) is a powerful analytical tool providing molecular mass and structural information on this polyphenol mixture. Sensitive detection is obtained in negative ion mode without any buffer addition, generating intense deprotonated molecular ion. The mass range of these polymers is between 290 (catechin) and 3100 uma (decamers of proanthocyanidins). A quasimolecular ion at m/z 255 $[M-H]^-$ corresponding to the molecular weight of pterostilbene **1**, is present in these active extracts. This information suggests the possibility of tannin-complex formation or ester linkage to prevent stilbene degradation by the laccase.



1

[1] R. Pezet, V. Pont and K. Hoang-Van, *Physiological and Molecular Plant Pathology*, **1991**, *39*, 441-450.

5

TIME-RESOLVED IDENTIFICATION OF AEROSOL EMISSION SOURCES USING ORGANIC TRACERS

Olivier P. Haefliger, Thomas D. Bucheli, and Renato Zenobi

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The dynamic behavior of aerosol-bound polycyclic aromatic hydrocarbons in urban air was studied over the course of several whole days, both next to a street with heavy traffic and in a city park. Two-step laser mass spectrometry (L2MS), a highly sensitive and selective technique, allowed measurements with 15 minutes time resolution. Large variations in particle concentration and chemical composition were observed, reflecting the contributions from Diesel trucks, gasoline-powered cars, and house heatings to urban aerosols. These sources were clearly distinguished using specific mass spectral patterns. Rapid speciation of aerosol-bound organic carbon is now possible to complement conventional monitoring of atmospheric pollutants.

On a much longer timescale, analyses were also performed on aerosols collected during the course of a whole year at four different locations selected to be representative of Switzerland. These were part of a joint project between several research groups using various analytical techniques to achieve a complete characterization of the most important aerosol emission sources. L2MS was especially suitable for this study as this method allows the speciated organic analysis of a large number of samples at a low cost. Considerable seasonal variation was observed, the extent of which was more pronounced at certain sites than at others.

Analytische Chemie 6

Ageing of Triterpene Varnishes studied by Graphite-Assisted Laser Desorption/Ionization Mass Spectrometry

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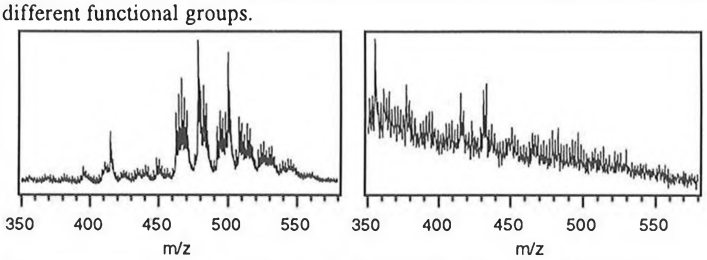
ETH Zürich, Laboratorium für Organische Chemie, Universitätstrasse 16, 8092 Zürich

As part of a collaboration with the Berner Fachhochschule für Gestaltung and the Schweizerisches Institut für Kunstwissenschaft, the natural and artificial ageing of triterpene varnishes was studied by means of graphite-assisted laser desorption/ionization mass spectrometry. Films of dammar and mastic resins were aged artificially by light, heat, or both. Pure reference triterpenes were also aged under the same conditions. The artificially aged samples were compared with naturally aged triterpene varnishes from old master paintings. The triterpenes in the aged resins showed different stages of breakdown as characterized by the degree of oxidation, polymerization and fragmentation. The samples of naturally aged varnishes from paintings yielded mass spectra that were very similar to those of the artificially aged resins. This suggests that the artificial ageing methods are representative of the natural processes. The reference triterpenes showed the same behavior as the resins, but more details are visible. Above all, there are substantial differences between triterpenes with different functional groups.



Mass spectra of fresh mastic resin (left) and a 48 year old naturally aged mastic varnish from a Rembrandt painting (right).

Analytical Chemistry 7

LC/ES-MS methods for the qualitative and quantitative analysis of ginseng phytopharmaceuticals

K. Ndjoko, J.-L. Wolfender and K. Hostettmann

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

In recent years, *Panax* ginseng C. A. Meyer. (Araliaceae) has become one of the most popular medicinal plants. Phytopharmaceuticals containing P. ginseng extracts are best selling drugs in many countries. The plant is principally used as tonic[1]. The quality of the phytopreparations rely on their saponin content. Usually these constituents are quantified by HPLC/UV methods which require derivatization, long gradients and present a rather poor sensitivity. In order to improve the control of ginseng preparation, a rapid and sensitive method based on liquid chromatography and electrospray mass spectrometry has been developed. The selectivity of the LC/MS detection avoids LC-resolution of non isomeric saponins and the separation time can be shorten drastically. The method presented here allowed the quantification of the eight main ginsenosides in less than 15 min by direct injection of the crude phytophamaceutical extracts on to a short C_{18} reversed phase column (70 x 2 mm i.d.) and rapid acetonitrile-water gradient elution. The ionisation was improved by adding ammonia post-column and quantification was made with an internal standard. Multiple stage mass spectrometry (MS^n) experiments performed on the molecular ions of the saponins gave additional structural information on-line and other ginsenosides present in the extract were also identified.

[1] KH. Han et al., *Am. J. Chin. Med.* **1998**, *26*, 199.

Analytical Chemistry 8

Pharmaceutical applications of nonaqueous capillary electrophoresis

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Laboratory of Pharmaceutical Analytical Chemistry, 20 Bd. D'Yvoy, University of Geneva 1211 Geneva 4

Recently, widening the application range of capillary electrophoresis (CE) by using non aqueous buffers has encountered a growing interest. The different chemical and physical properties of organic solvents (viscosity, dielectric constant, polarity, auto-protolysis constant, electrical conductivity, etc.), compared to water, result in the improvement of selectivity which is a challenging task in the science of separation. The use of organic solvents proved to be useful in analyzing hydrophobic compounds as well as drugs and metabolites which are difficult to separate in aqueous buffers. Very high efficiency and resolution, short analysis time and the possibility to increase the analyte solubility are the main reasons for this success. In addition, non aqueous media are suitable for on-line coupling to mass spectrometry.

In this presentation, the potential of nonaqueous CE for the analysis of a large number of pharmaceuticals, including basic and acidic compounds will be discussed. The usefulness of nonaqueous media for achieving rapid separations is also highlighted. Finally, the quantitative aspect of nonaqueous CE, including validation and robustness testing, is presented.

Analytische Chemie **9**

Experiences in Analysing Pyrethroid Insecticides in Food

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Kantonales Labor Basel-Stadt, Kannenfeldstr. 2, Postfach, CH-4012 Basel

The insecticidal power of chrysantheme flowers due to pyrethrin constituents is well known for a long time. At the end of the forties the first pyrethroids, analogs to the pyrethrins were synthesized. Today over 1000 pyrethroids are known, but only 100 compounds are of commercial interest. About 20 pyrethroids are used as insecticides in agriculture, against ectoparasites in pharmaceuticals, as conservatives in wood and against moths in textiles. The main indoor use against insects is in electric evaporators, where main exposure to people may occur. Also Pyrethroids are very toxic for fish and other aquatic organisms (e.g. in 1993 permethrin killed the whole fish population of the River Goldach). Pyrethroids are accumulated in fat tissues but metabolised and eliminated rapidly after intake. Severe intoxications are known from workers exposed to pyrethroids at work. In Swiss legislation tolerance values in food exist for several pyrethroids, Fenvalerate, Bifenthrin, Cyfluthrin, Permethrin etc.
Plant materials (salad, fruits) were mixed and extracted with ethylacetate by use of a mixer, then the organic layer separated by centrifugation. The extracts injected into the GC splitless [1] onto a laminar cup liner without further clean-up. Fat containing food needed a further clean-up after the extraction with acetone/petrolether. The extract was reextracted with acetonitrile to remove the fat, then cleaned on a florisil column. The pyrethroids were separated on two columns of different polarity and detected with electron capture detection (ECD).
Mean recoveries of all matrices (vegetables, strawberries, fish, milk) range from 74 to 92 %.

[1] Konrad Grob et.al.: Determination of organophosphorous insecticides in edible oils and fats by splitless injection of the oil into GC. Z. Lebensm Unters Forsch 198 (1994), 335.

Analytic Chemistry **10**

The new Revision of the EURACHEM/CITAC Guide on "Efficient Methodology for the Evaluation of Uncertainty in Analytical Chemistry"

M. Rösslein

Swiss Federal Laboratories for Materials Testing and Research, Department of Chemistry, Lerchenfeldstrasse 5, 9014 St. Gallen

The comparability of analytical results is the basis of mutual acceptance of decisions, which have been taken by e.g. estimating yields in the drug production, checking environmental samples against legal limits. To achieve this comparability of analytical results one needs additional quantitative information about the reliability of the measurement, which is the measurement uncertainty.
The author will first introduce the concept of the evaluation of the measurement uncertainty [1]. This evaluation is based on the ISO guide to the expression of uncertainty in measurement and has to be apply nowadays in all fields of measurement science. Special aspects of the evaluation process for analytical chemistry are highlighted in the second part with the aim of improving the efficiency of the task. It includes:

- The use of a cause and effect diagram to identify uncertainty sources.
- The utilisation of validation data to evaluate the uncertainty.

[1] A. Williams, S. Ellison, M. Berglund, W. Hässelbarth, R. Kaarls, M. Månsson, M. Rösslein, R. Stephany, W. Wegscheider, R. Wood, A. van der Veen, H. van de Wiel, D. Galsworthy, K. Yasuda, M. Salit, A. Squirrell, P. X. Rong, R. Johnson, J.-K. Lee, D. Mowrey, P. De Regge, K. Hedegaard, *Efficient Methodology for the Evaluation of Uncertainty in Analytical Chemistry*, EURACHEM, CITAC, AOAC & IAEA - Guide, to be published.

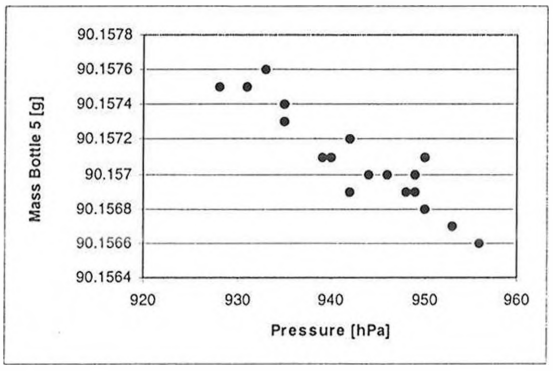
Analytical Chemistry **11**

The Influence of Variations in Atmospheric Pressure on the Uncertainty of Weighing Results

K. Kehl, S. Wunderli and V.R. Meyer

EMPA St. Gallen, Abteilung Chemie, Postfach 9014, St. Gallen

The mean atmospheric pressure at an elevation of 640 m (EMPA St. Gallen) is approx. 940 hPa (mbar) with a span from 925 to 955 hPa. This gives a pressure standard uncertainty u(p) of $(15/\sqrt{3})$ hPa = 9 hPa if the model of a rectangular distribution is used. It is necessary to consider this uncertainty in the standard uncertainty calculation of weighing operations.
Weighing experiments over 6 months with 5 empty Pyrex glass bottles with m = 90 g gave a correlation $\Delta m/\Delta p$ of $-3 \cdot 10^{-5}$ g/hPa or a mass uncertainty, related to u(p) = 9 hPa, of u(m) = 0.3 mg. Theoretical calculations by using the air buoyancy equations give the same result.



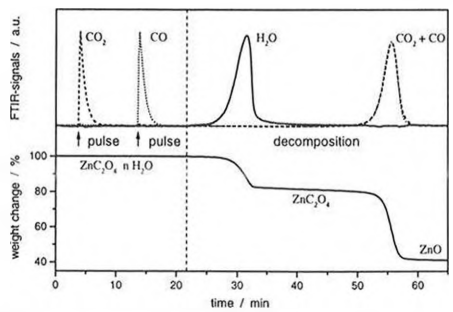
Analytical Chemistry **12**

Application of Pulse Thermal Analysis (PTA) Method for Quantifying FTIR Signals

F. Eigenmann, M. Maciejewski and A. Baiker

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

Pulse thermal analysis (PTA) method based on the injection of gaseous reactants into a carrier gas stream and monitoring the changes in the mass, enthalpy and gas composition was successfully applied for quantitative calibration of mass spectrometric signals [1]. Here we report the results of investigation of PTA for quantifying FTIR spectra.
The influence of several experimental parameters such as concentration of the analyzed species, temperature and flow rate of the carrier gas on the FTIR signals has been investigated. The correctness of quantifying FTIR signals was checked by determination of CO and CO_2 evolved during decomposition of ZnC_2O_4. The sample was decomposed under helium with a heating rate of 10 K/min; in order to quantify the FTIR signals, 1 ml pulses of CO and CO_2 were injected before the beginning of the decomposition. Detected amounts of CO and CO_2 agree well with the stoichiometric values.



[1] M. Maciejewski, C.A. Müller, R. Tschan, W.D. Emmerich and A. Baiker, *Thermochim. Acta*, **1997**, 295, 167

Analytical Chemistry **13**

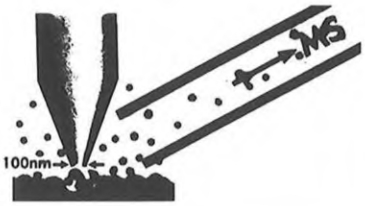
Subwavelength Laser Ablation Mass Analysis

Raoul M. Stöckle, Patrick Setz, Volker Deckert, Yung Doug Suh
Christian Fokas, and Renato Zenobi

Swiss Federal Institute of Technology Zürich,
Laboratoy for Organic Chemistry, Universitätstrasse 16, 8092 Zürich

Scanning near-field optical microscopy (SNOM) has become increasingly important for molecular analysis in the nanometer scale regime. Until recently chemical nano-analysis mostly centered on vibrational or fluorescence spectroscopy using SNOM probes while the combination with other analytical techniques remained poorly studied.

Improved SNOM probes [1] withstanding high power laser pulses allow for subwavelength laser ablation.[2] The most obvious application of laser induced ablation of materials with near-field optical resolution is patterning of surfaces. More challenging is to collect the desorbed material for further analysis, e.g. by mass spectroscopy. An interface between the desorption SNOM and a mass spectrometer allowing for analytical nano-sampling will be shown. It consists of a tapered metal nozzle through which the ablated material is directly sucked into a vacuum chamber for subsequent ionization and detection by a quadrupole mass spectrometer.



Schematic of the experimental setup

Besides the high lateral resolution, one of the main advantages of the system is the possibility to spectroscopically image (Raman, Fluorescence) the sample non-invasivly using the same probe. Futhermore, all chemical analysis is taking place under ambient conditions.

[1] R. Stöckle, N. Schaller, V. Deckert, C. Fokas, and R. Zenobi, J. Microsc. **1998**, accepted..
[2] B. Dutoit, D. Zeisel, V. Deckert, and R. Zenobi, J. Phys. Chem. B **1997**, 101, 6955.

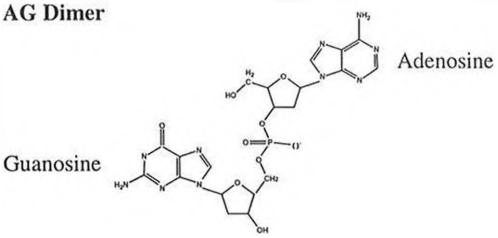
Analytical Chemistry **14**

Characterizing MALDI Plume Dynamics in a Fourier Transform Ion Cyclotron Resonance Mass Spectrometer

E. Stevenson, K. Breuker, and R. Zenobi
ETH Zentrum, Universitätstr. 16, CH-8092 Zürich, Switzerland

Several theories have been proposed to describe fundamental matrix-assisted laser desorption ionization (MALDI) processes [1]. A transfer of energy into the internal modes of the matrix and analyte molecules will occur during both desorption and ionization. Therefore, it is possible to gain information about the mechanisms of ion formation by investigating energy distributions and the time at which ions are formed, i.e. plume dynamics. In the work undertaken here a simple method was designed to monitor the relative internal energies of ions as a function of the speed at which the ions are traveling after the application of laser light to the sample. All data were collected on a Fourier transform ion cyclotron resonance (FTICR) mass spectrometer because it offers the unique advantage over other mass spectrometers of being able to trap a collection of ions and subsequently induce dissociation. Collision-induced dissociation (CID) studies were conducted to measure the internal energy of the MALDI ions.
Oligonucleotide dimers (see below) were selected as analytes due to their interesting chemistry and ease of fragmentation. In order to compare the influence of different sublimation temperatures and gas-phase basicities, various matrix compounds were used to generate the MALDI spectra.

AG Dimer



[1] R. Zenobi and R. Knochenmuss, Mass Spectrom. Rev. **1998**, 17, 337.

Analytical Chemistry **15**

Electrospray LC-MS-MS Determination of Trimethoprim in Muscle of Swine

D. Guggisberg and H.Koch, Swiss Veterinary Office Schwarzenburgstr. 161
CH-3003 Berne

In human and veterinary medicine TRIMETHOPRIM [Fig 1] is therapeutically used in combination with sulfonamides as an antibiotic agent [eg Farmavet ...]. Residues of trimethoprim can have unpleasant effect on humans, especially those who are chronically ill, pregnant or elderly. In recent years, numerous efforts have been made to develop analytical methods to detect and quantify trimethoprim at the tolerance level of 50 ppb. Many methods are using ion-pair chromatography and UV-detection at 225nm. The aim of this study was to develop a method for the quantitative screening and confirmatory analysis of trimethoprim in pigmuscle samples by electrospray-LC-MS-MS at the 50 ppb level.

Extraction and Clean-up

Muscles of swine (5 g) are brought to about pH=2 with trichloroacidic acid-buffer. After centrifugation, the pH is adjusted to 4.4 and the solution is filtered. The solution is further cleaned on a SCX cation-exchange column. Trimethoprim is eluted with basic methanol and dried under nitrogen. 1 µl is injected to a Nucleosil 100-5 C_{18}AB (125mm x 3mm x 5µm) column connected to a Quattro-LC-MS. The quantification is performed by external standard (5, 25, 50, 100 ppb).

Fig 1 Trimethoprim

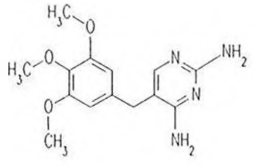
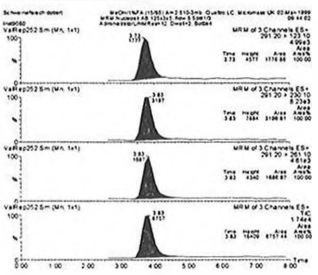


Fig 2 Trimethoprim spiked in pig muscle at 25 ppb



Analytical Chemistry **16**

LC/MS^n, a powerful method for in depth on-line structural investigation of plant constituents

J.-L. Wolfender, K. Ndjoko and K. Hostettmann

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

LC/MS has been routinely used for screening plant metabolites since several years in our laboratory [1]. This technique should ideally provide molecular weight and fragment information on the constituents on-line. However most of the LC/MS ionisation techniques provide mainly molecular weight information and often only few fragments are generated. Thus, complementary technique such as MS/MS or multiple stage MS/MS (MS^n) have to be used to generate additional structural information.
In this respect, we have evaluated the potential of an LC/IT-MS instrument (ion trap) equipped with APCI (atmospheric pressure chemical ionisation) and ES (electrospray) interfaces for screening crude plant extracts. The combined use of ES and APCI ionisation has demonstrated that the analysis of a very broad range of plant metabolites has been made possible. Molecular ions of simple small phenols as well as large labile constituents such as saponins were efficiently recorded. With the LC/IT-MS, structural information on each LC-peak was generated either within the source (up-front CID) or in the ion trap by selective multiple stages MS/MS (MS^n). These different MS experiments were performed sequentially during a single LC/MS analysis of a crude plant extract, generating an important amount of structural information on-line. In particular LC/ES-MS^n has been applied successfully for the determination of the sugar sequences of numerous saponins. As reproducible LC/MS/MS spectra can be obtained with this method, the build up of LC/MS/MS databases allowing an efficient matching of MS/MS spectra is underway for a rapid and rational dereplication of crude plant extracts.

[1] J.-L. Wolfender, S. Rodriguez, K. Hostettmann, *J. Chromatogr.* A **1998**, *794*, 299.

Analytische Chemie **17**

Strategies in Pesticide Screening Analysis of Vegetables and Fruits

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Kantonales Labor Basel-Stadt, Kannenfeldstr. 2, Postfach, CH-4012 Basel

The palette of the typically applied pesticides in agriculture has changed over the last years. The classical persistent, organochlorine pesticides are partly banned or substituted more and more with degradable pesticides. While organochlorine pesticides can be detected with electron capture detection (ECD) the new structures require more universal detectors such as mass spectrometry. The latter enables also the identification of unknown compounds (pesticides/metabolites).
The experiences of the last two years resulted in new strategies in screening analysis:

1. Analyse for a palette of specific contaminants (often used in agriculture, structures with poor mass spectra for identification or often detected in food) with common detectors (ECD, NPD, FPD).
2. Extract sample with solvent and analyse with GC/MS without clean up.
3. Search thoroughly through chromatogramme for possible pesticides (identification with libraries, typical mass fragments etc.). Identify and estimate amounts. Identification is possible down to 100 μg/kg.
4. Calibration: spike extracts with different amounts of the identified contaminants. Calculation includes recoveries of each substance. Quantification is possible down to 10 μg/kg.
5. For concentrations less than 10 μg/kg sample extracts and spiked extracts are concentrated. Identification is possible down to 10 μg/kg, quantifications down to 1 μg/kg.

Our strategies are shown with a sample of minced pear spiked with several pesticides.

Analytical Chemistry **18**

On-line capillary electrophoresis-electrospray mass spectrometry for the analysis of pharmaceuticals

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Because of its high efficiency, flexibility, accuracy and resolution, capillary electrophoresis (CE) has revealed an enormous potential for the analysis of pharmaceutical compounds. However, one of the limitations of CE with on-column UV detection is its relatively low sensitivity because of the short optical path-length afforded by the small internal diameters of the capillaries. Additionally, many interesting pharmaceuticals do not possess a chromophore agent and therefore their UV detection requires a derivatization procedure.
The on-line coupling of CE with electrospray mass spectrometry (ESI-MS) is a promising combination of two analytical techniques : while CE provides high separation efficiency per unit of time, MS affords high sensitivity and selectivity, as well as molecular structural information.
This contribution presents the potential of CE-ESI-MS to solve complex analytical problems. The applicability of this technique for the analysis of Ecstasy and derivatives in urine samples will be demonstrated. Furthermore, the usefulness of the on-line information obtained both by CE-ESI-MS and CE-UV is emphasized in the analysis of natural compounds in plant extract. The use of in-source collision induced dissociation (CID) to differentiate between compounds possessing the same molecular mass, such as positional isomers, is also highlighted. Finally, the potential of CE-ESI-MS combined with the partial-filling technique is discussed for the stereoselective analysis of chiral drugs.

Analytical Chemistry **19**

Isolation and identification of phytotoxic metabolites from the culture medium of *Ceratocystis ulmi*

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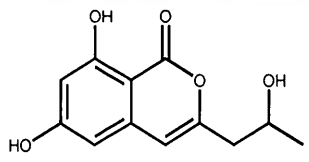
Avenue de Bellevaux 51, CH-2000 Neuchâtel

The Dutch elm disease was discovered in 1920. The bark beetles (*Scolytus scolytus*) and the mankind (forester, roadman) carry the fungus *Ceratocystis ulmi*[1] responsible for the elm canker disease. The spread of this disease is an important problem in urban environment.

The chemical composition of the culture medium of *Ceratocystis ulmi* have been investigated. From the phytotoxic fractions obtained from the ethyl acetate extract, we isolated and identified naphtalenones and isocoumarines.

Compounds **1** and **2**, showed the strongest phytotoxic activity [2].



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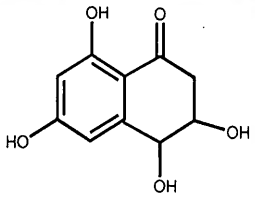

2

Several other metabolites have been charaterized and biotests are in progress to determine their activity.

[1] C.A. Salemink, H. Rebel, L.C.P. Kerling, V. Tchernoff, Science 149, 202-203, 1965
[2] N. Burki, Ph. D. Thesis, University of Neuchâtel, Neuchâtel, 1996

Analytic Chemistry **20**

Application of "Electronic noses" to Swiss Emmental cheese

Emmanuelle Schaller[a], Jacques O. Bosset[a] and Felix Escher[b]

[a] Federal Dairy Research Station of Liebefeld, Department of Chemistry, Schwarzenburgstrasse 161, CH-3003 Berne
[b] Swiss Federal Institute of Technology (ETH), Institute of Food Science, CH-8092 Zürich

Swiss Emmental cheese samples of different ripening stages were measured using four "electronic nose" systems and five sensor technologies. Up to now, the metal oxide semiconductors (MOS) technology allowed the best discrimination between the measured samples. However, this type of sensors suffers from unexplained poisoning effects. Organic conducting polymer (CP) sensors showed a poor sensitivity to volatile components of cheese, the main problem being a rapid drift of the sensors. The response of quartz microbalance (QMB) sensors was too weak to detect any difference between cheese samples. Discrimination using a newly designed mass spectrometry system was difficult due to the low sensitivity of this instrument for volatile compounds of cheese. Metal oxide semiconductor field effect transistor (MOSFET) sensors did not give good discrimination between the samples. However, their combination with MOS sensors could be a promising system for application in cheese quality evaluation.

Analytical Chemistry **21**

Zinc and Tin as Primary Materials to Achieve Traceability of Calibration Standards to the SI*

G. Fortunato[1], V. Leepipatpiboon[1], Ch. Bissig[2], Ch. Moor[2] and S. Wunderli[1]

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[2] EMPA Dübendorf, Überlandstr.129, CH-8600 Dübendorf

Traceability and reliability of analytical results can be guaranteed by use of calibration solutions, which are traced to completely characterised pure metals or metal salts. Hereby, these metals serve as primary reference materials providing the link between the content of a calibration standard and the SI.

Many commercially available metals have a high degree of purity with respect to metallic impurities, but their certification reports are often incomplete. However, the use of metals as primary standards requires the measurement of all metallic and non-metallic impurities.

This project has been started to evaluate the suitability of the "high vacuum distillation" as a purification method, followed by the full characterisation of the product metals.

The distillation apparatus consists of a high vacuum chamber (austenitic steel) which is equipped with a resistively heated crucible, a metal collector, a pyrometer, pressure gauges and a quadrupole mass spectrometer for the analysis of the residual gas composition.

As starting materials mainly 6N zinc and 5N8 tin were chosen. The necessary metal vapour pressure was achieved by increasing the temperature step by step, until a deposition and growth of the distilled metal at the collector begins.

Metallic and non-metallic trace impurity contents as well as purification degrees were determined by ICP-MS, AAS and Inert Gas Fusion. Morphological and surface properties were studied with SEM.

*Système International

Analytical Chemistry **23**

A selective and reversible NO_2 gas sensor

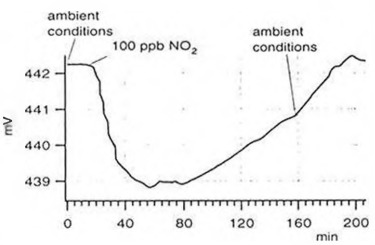
T. Nezel [1], G. Zhylyak [1], T. Roth [1], G. J. Mohr [1], A. Hensel [2], U. E. Spichiger [1]

[1] Centre for Chemical Sensors, ETH Technopark, CH-8005 Zürich.
[2] Bosch Telecom GmbH, Ludwig Bölkow-Allee, D-85521 Ottobrunn

We have recently introduced a NO_x-sensitive polymeric optode membrane, based on the cobalt(III)-cobyrinate derivative Pefa 10105 and the Nile Blue derivative ETH 5418. The detection limit was at 50 ppb or 100 $\mu g \cdot m^{-3}$ and the response was reversible. [1]

A large variety of NO_2-sensitive polymer membranes was investigated in order to achieve resistance to high temperature and humidity, and to improve the lifetime of the sensor. The resulting optimized NO_2-sensitive optodes exhibit stability at 60 °C and no cross-sensitivity to humidity. Polymeric membranes of this type also show a high selectivity for NO_2 over NO, CO and SO_2.

The membrane was casted onto a photodiode with an area of 9 mm^2 and a red LED was used as a light source. When exposing the membrane to 100 ppb NO_2 under ambient conditions a voltage change of ΔV = 3 mV was obtained after 24 minutes ($t_{90\%}$).



The fire detector based on this technology is called Magic-Sens™ and Bosch Telecom GmbH is going to commercialize it. It includes this NO_2 optode as well as a NH_3 optode, both developed at the CCS.

[1] A. Hensel, C. Demuth, T. Nezel, U. E. Spichiger, Chimia 1998, 7-8, 383.

Analytische Chemie **22**

Transmission electron microscopy study of vanadium oxide nanotubes

F. Krumeich, H.-J. Muhr, M. Niederberger, F. Bieri, and R. Nesper

Laboratory of Inorganic Chemistry, ETH Zürich, 8092 Zürich

Tubular materials like the carbon nanotubes have caught world-wide interest because this strongly anisotropic structure is associated with interesting physical and chemical properties. Such a tubular morphology has been recently discovered in modified vanadium oxides [1,2].

Vanadium oxide nanotubes are prepared in a template-assisted sol-gel reaction followed by a hydrothermal treatment starting with a vanadium(V) alkoxide precursor and an amine or a α,ω-diamine, respectively. TEM images show that the product exclusively consists of tubes. Their lengths are up to 15 μm; their outer diameters range from 15 to 150 nm, the inner ones from 5 to 50 nm. The tube walls consist of 2-30 crystalline layers. The structure within the layers gives rise to a set of reflections in electron diffraction patterns which can be indexed on the basis of a square lattice with a=0.62 nm. A second set of reflections is caused by the regular distance between the layers. These inter-layer distances (1.7-3.8 nm) increase with the chain length of the amine.

The layers consist of vanadium oxide while the template molecules are located in between. This has been confirmed by electron spectroscopic imaging: cross-sectional vanadium maps show that V is present inside these layers; carbon maps that C is in between. Furthermore, cross-sectional TEM images reveal that the majority of the VO_x-NTs are serpentine-like, single or double layer scrolls. Arrangements of concentric layers are scarcely present (< 1%) and occur only if the tube walls comprise five or fewer layers.

[1] M.E. Spahr, P. Bitterli, R. Nesper, M. Müller, F. Krumeich, and H-U. Nissen, *Angew. Chem. Int. Ed.* **37**, 1263-1265 (1998).
[2] R. Nesper and H.-J. Muhr, *Chimia* **52**, 571-578 (1998).

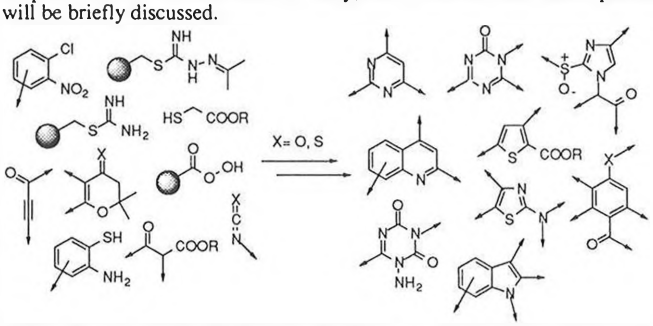
Medicinal Chemistry **24**

Efficient Strategies towards High Quality Compound Libraries and their Impact in Lead Discovery- and Optimization

D. Obrecht, C. Abrecht, B. Dhanapal, P. Ermert, J.-P.Obrecht, K. Sekanina

Polyphor AG, Winterthurerstrasse 190, CH-8057 Zurich

In recent years *Combinatorial and Parallel Chemistry* have emerged as powerful tools to create large numbers of compound libraries for general screening embracing many different classes of compounds such as peptides, peptoides, oligonucleotides and small-molecular-weight carbocyclic and heterocyclic molecules [1]. Originally the combinatorial synthesis of large libraries started with mixtures of compounds whereas today a gradual shift towards the parallel synthesis of well characterized single compound libraries can be observed. Polyphor has developed a series of novel strategies for the synthesis of high quality/purity libraries for lead finding and lead optimization. Using highly functionalized novel reactive building blocks, solid-supported assembly and cleavage strategies, solid-supported reagents and parallel purification techniques, a wide variety of diverse heterocyclic scaffolds amenable for parallel synthesis of high purity single compound libraries has been developed. A selection of examples will be presented. Furthermore the impact of quality and purity of the compounds on parameters such as chemical stability, validated hit rate and false positive hits will be briefly discussed.



[1] D. Obrecht, J.-M. Villalgordo, *Solid-Supported Combinatorial and Parallel Synthesis of Small-Molecular-Weight Compound Libraries*, Tetrahedron Organic Chemistry Series, Vol. *17*, Pergamon, **1998**.

CHIMIA 1999, 53, No. 7/8

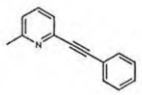
Medicinal Chemistry **25**

DISCOVERY OF 2-METHYL-6-(PHENYLETHYNYL)-PYRIDINE (MPEP): A HIGHLY POTENT AND SELECTIVE MGLUR5 ANTAGONIST.

F. Gasparini[1], K. Lingenhoehl[1], P.J. Flor[1], N. Stoehr[1], C., I. Vranesic[1], H. Allgeier[1], M. Schmutz[1], W. Spooren[1], M. Varney[2], E. Johnson[2], S. D. Hess[2], A. Sakaan[2], E. Santori[2], G. Velicelebi[2] & R. Kuhn[1].

[1]Nervous System Research, Novartis Pharma AG, CH-4002 Basle, Switzerland. [2]SIBIA Neurosciences Inc., La Jolla, CA 92037, USA

In the nervous system the neurotransmitter L-glutamate stimulates PI hydrolysis by activating group I metabotropic glutamate receptors (mGluR1 and mGluR5). To understand the role of these receptors in normal brain function and NS disorders, subtype-selective compounds are needed. We report here the discovery of 2-methyl-6-(phenylethynyl)-pyridine (MPEP), a novel potent mGluR5-selective antagonist.



MPEP

MPEP is related to SIB-1893, a mGluR5-selective antagonist recently discovered by [Ca^{2+}]-based functional screening. Chemical derivatization revealed that replacement of the CC double bond with a triple bond largely increased not only potency but also selectivity for the hmGluR5 subtype.

At hmGluR5a stably expressed in mammalian cells, MPEP completely inhibited quisqualate- and glutamate-stimulated phosphoinositide hydrolysis with IC_{50} values of 36 nM and 39 nM, respectively, while having no agonist or antagonist activities up to 100 uM at the human mGlu1b, -2, -3, -4a, -7b and -8a receptors. Furthermore, MPEP showed no agonist or antagonist effect at the ionotropic glutamate receptors $hNMDA_{1A\,2A}$, $hNMDA_{1A\,2B}$, rat AMPA (GluR3) or human kainate (GluR6) receptors. In rat neonatal brain slices, MPEP inhibited DHPG-stimulated PI hydrolysis with a potency and selectivity similar to that observed on human mGlu5 receptors. Intravenous application of MPEP in rats demonstrated that MPEP selectively inhibits neuronal firing induced by microiontophoretic application of DHPG but not AMPA.

Systemic administration of MPEP may lead to new insights into the potential therapeutic use of mGluR5 antagonists.

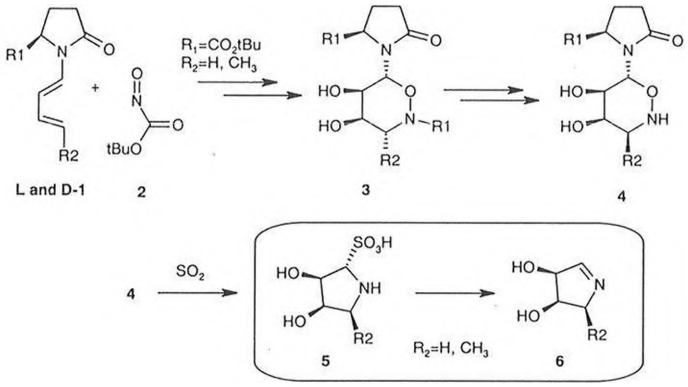
Therapeutic Chemistry **26**

4-Amino-4-Deoxytetroses : Synthesis and Inhibition of α-L-Fucosidase

M. Joubert, A. Defoin, C. Tarnus, and J. Streith

Université de Haute Alsace, ENSCMu, LSOCM, 3, rue A. Werner, 68093 Mulhouse Cedex

Potent α-L-fucosidase inhibitors are precursors to α-fucosyltransferase inhibitors. Sulfitic derivatives **5**, analogs of L-fucose, its corresponding imines **6**, and some other isomers were synthesised and then tested as inhibitors of α-L-fucosidase. Our synthetic strategy is based on a regiospecific and stereoselective hetero-Diels-Alder reaction between an asymmetric diene **1** and the nitroso compound **2**.



Therapeutic Chemistry **27**

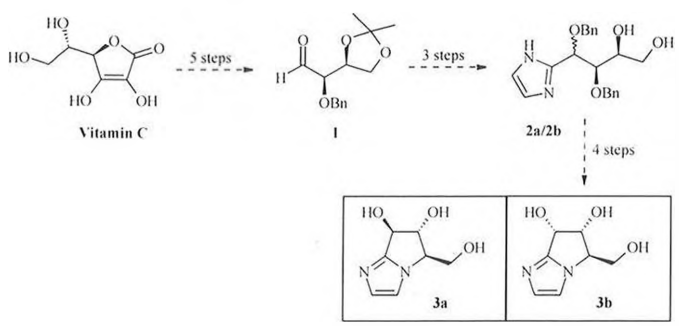
From Vitamin C to glycosidase inhibitors

F. Gessier, T. Tschamber and J. Streith

Université de Haute-Alsace, ENSCMu, LSOCM, 3, rue Alfred Werner 68093 Mulhouse

In recent years, many studies were focused on imidazole sugars since a number of them appeared to be glycosidase inhibitors. On account of this, we report the synthesis of the D-arabino **3a** and the D-ribo **3b** imidazole sugar, two potential glycosidase inhibitors from a natural product, Vitamin C.

The Vitamin C was converted into the L-threose derivative **1** in 5 steps, involving an oxydative degradation reaction. The aldehyde thus obtained was immediately treated with a 2-lithiated-N-protected imidazole to give the two diastereoisomers **2a** and **2b** in three steps. Cyclisation of these intermediates, followed by deprotection, gave the desired cyclic compounds in four steps.



Medicinal Chemistry **28**

SAR and Chemistry of Non-Peptidic, Irreversible Caspase Inhibitors

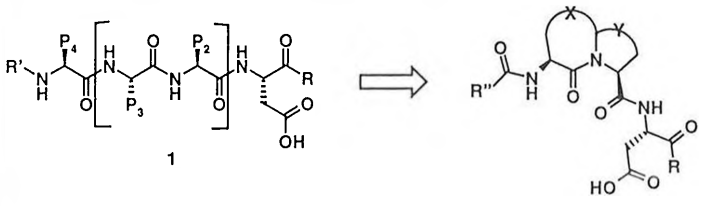
S. Roggo, S. Hintermann, V. Rasetti, M. Tintelnot-Blomley, U. von Krosigk

Pharmaceutical Research, Nervous System, Novartis Pharma AG, CH-4002 Basel

Cysteine Aspartyl Proteases are a new family of intracellular enzymes involved in inflammatory and apoptotic processes. Inhibitors of these enzymes might offer new treatments of inflammatory and neurodegenerative diseases.

Starting from peptidic substrate mimics (**1**) such as Ac-DEVD-aldehyde or z-VAD-fluoromethyl ketone, a new generation of potent irreversible caspase inhibitors were designed. Lipophylic P_2 and P_3 mimics were introduced to reduce the peptidic character of the compounds. The optimal selection of the active principle R allowed to fine tune enzyme specificity and *in vivo* activity.

Synthetic strategies and structure activity relationships will be presented.



Medicinal Chemistry **29**

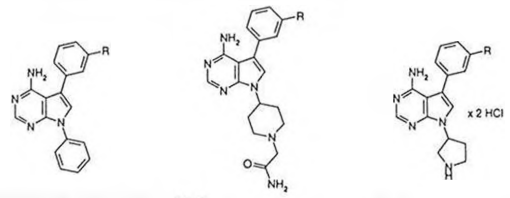
7-Pyrrolidinyl- and 7-piperidinyl-5-aryl-pyrrolo[2,3-d]pyrimidines - Highly potent inhibitors of the protein tyrosine kinase c-Src

Eva Altmann, Novartis Pharma AG, 4002 Basel

The non-receptor tyrosine kinase p60c-src (c-Src) plays a unique and essential role for the proper function of osteoclasts, the cells responsible for bone resorption. c-Src inhibitors should thus reduce excessive osteoclast activity and be useful in the treatment of diseases characterized by extensive bone loss, such as osteoporosis.

We have discovered a new class of c-Src-inhibitors and report on one of our optimization strategies for our lead compound CGP62464 (Fig.1), involving replacement of the N^7-phenyl moiety by different heterocycles.

Figure 1: Selected examples of c-src inhibitors (IC50's).



R = H	**CGP62464** (100 nM)	N.D.	N. D.
R = OH	**CGP68245** (0.3 nM)	**CGP80137** (1 nM)	**CGP76403A** (6 nM)
R = OCH_3	**CGP63160** (20 nM)	**CGP79713** (22 nM)	**CGP76625A** (53 nM)

As CGP62464 inhibits c-Src in an ATP-competitive fashion, it is assumed that binding occurs to the ATP binding site of the enzyme. According to this model, the N^7-phenyl ring is located within the pocket that is usually occupied by the ribose moiety of ATP. Substitution of polar heterocyclic moieties for the N^7-phenyl substituent in CGP62464 should thus allow for additional interactions with polar amino acids within this sugar pocket that are not utilized by CGP62464. This strategy has led to the identification of potent and selective c-Src inhibitors (Fig.1) which will be discussed in the presentation.

Medicinal Chemistry **30**

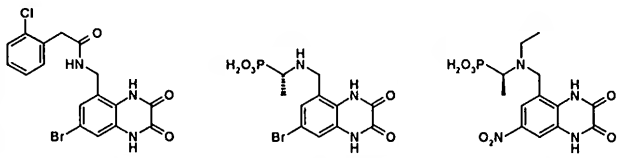
The structure-activity relationship of AMPA and NMDA(gly) antagonists derived from 5-aminomethylquinoxaline-2,3-dione.

Y. P. Auberson, P. Acklin, H. Allgeier, S. Bischoff, S. Ofner, M. Schmutz, S. Veenstra.

Novartis Pharma AG, 4002 Basel, Switzerland.

5-Aminomethylquinoxaline-2,3-diones have been shown to bind to AMPA receptors, as well as to the glycine modulatory site of the NMDA receptor complex. As such, they are potential candidates for new therapies of e.g. epilepsy, pain or neurodegenerative diseases.

After identifying N-acyl (e.g. **1**) derivatives as potent and selective antagonists of the strychnine-insensitive glycine-binding site, we discovered a series of water-soluble N-phosphonoalkyl-5-aminomethylquinoxaline-2,3-diones with improved pharmacological properties (e.g. **2**, **3**). These N-phosphonoalkyl derivatives, in contrast to the first series which was only active *in vitro*, display good *in vivo* anticonvulsant properties, and can be optimized to block either AMPA or NMDA(gly) receptors. In the mouse electroshock test, the ED_{50} value of **2** and **3** after i.p. administration and 30 minutes pretreatment time are 12 and 7 mg/kg respectively. We discuss here the *in vitro* and *in vivo* structure-activity relationship of these novel compounds.



	1	**2**	**3**
$NMDA_{gly}$:	IC_{50} = 7 nM	IC_{50} = 7 nM	IC_{50} > 10 μM
AMPA:	IC_{50} > 10 μM	IC_{50} = 3 μM	IC_{50} = 56 nM

Medicinal Chemistry **31**

Potent and Orally Active Inhibitors of VEGF Receptor Tyrosine Kinases as Inhibitors of Tumor Driven Angiogenesis

G. Bold, J. Frei, P. Manley, P. Furet, M. Sills, F. Hofmann, Stefano Ferrari, J. Mestan, R. Cozens, Josef Brüggen, and J. Wood

Oncology Research and Core Technology, Novartis Pharma AG, 4002 Basel

In order to grow large enough to cause life-threatening disease, a solid tumor requires a blood supply. The growth of blood vessels, known as angiogenesis, also facilitates tumor metastasis by providing an avenue of transmission of the cancer cells to other sites. The growth factor VEGF (Vascular Endothelial Growth Factor) is secreted by many tumors and induces angiogenesis by interaction with receptors located on the epithelial cells on the surface of blood vessels, leading to activation of VEGF receptor tyrosine kinases, which *via* autophosphorylation, stimulate the sprouting of new blood vessels towards the tumor tissue.

CGP 79787 is a representative of a series of potent and selective inhibitors of Flt-1 and KDR, the two VEGF receptor tyrosine kinases, which inhibits the autophosphorylation of the receptor in cellular systems. Administered as its dihydrochloride salt, CGP 79787 is well absorbed after oral administration and inhibits the sprouting of blood vessels in a VEGF-driven angiogenesis model in mice. It also reduces the growth of primary tumors and metastasis in a rodent model. Since CGP 79787 is well tolerated in animals, this novel compound demonstrates the therapeutic potential of VEGF kinase inhibitors for the treatment of solid tumors and other diseases where angiogenesis plays an important role. The synthesis and the *in vitro* and *in vivo* biological data for CGP 79787 and some other related compounds will be discussed.

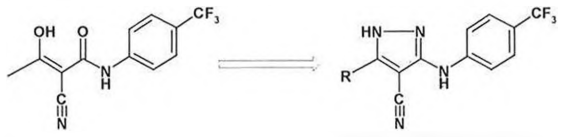
Medicinal Chemistry **32**

Bioisosteres of Leflunomide as Antibody Production Inhibitors. A Medicinal Chemistry Based Discovery of a Novel Biochemical Mechanism for B Cell Inhibition

Ch. Papageorgiou, R. Albert, Ph. Floersheim, E. Andersen, V. Hungerford, M. Zurini, H-P. Weber and M.H. Schreier

NOVARTIS Pharma AG, WSJ-350.314, CH-4002 Basel, Switzerland

T-cell immunosuppressant based therapies efficiently control early graft rejection in allotransplantation settings. They fail, however, to prevent those rejection events which are mediated by transplant-induced antibody (Ab) responses such as those involved in xenograft rejection. As yet, the control of these Ab responses has only been achieved by cytostatic agents like leflunomide and mycophenolic acid derivatives that mediate their effects via the inhibition of the de novo nucleotide biosynthesis. In search for non-cytostatic Ab production inhibitors, pyrazoles were designed as constrained analogues of leflunomide and were shown to have similar biological profile. Interestingly, variation of the substituent R in the pyrazole series led to the discovery of compounds that inhibited Ab production by a biochemical mechanism independent of the de novo nucleotide biosynthesis [1]. Such compounds represent a valuable tool for the identification of new B cell



BIOACTIVE LEFLUNOMIDE BIOISOSTERIC PYRAZOLES

targets for Ab production inhibition lacking cytostatic character.

[1] Ch. Papageorgiou, R. Albert, Ph. Floersheim, M. Lemaire, F. Bitsch, H-P. Weber, E. Andersen, V. Hungerford, M.H. Schreier. J. Med. Chem. 1999, 41, 3530.

CHIMIA 1999, 53, No. 7/8

Coordination Chemistry **33**

Computational Inorganic Chemistry: Today and Tomorrow

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Laboratorium für Anorganische Chemie, ETHZ, 8092 Zürich

During the last decade the field of computational chemistry has experienced enormous progress. Due to the large increase in computer power and the development of new computational methods, it has now become possible to treat many complex problems on an accurate and realistic level. Two of the most promising recently developed computational tools are ab initio molecular mechanics and mixed QM/MM calculations based on density functional theory.

In this lecture the current situation in computational inorganic chemistry will be illustrated with applications to organometallic transition metal, and bioinorganic systems. In particular, examples of the computer simulation of catalytic reactions and the application of computational tools for a rational design of biomimetic will be given. Finally, the outlook for anticipated developments in the field of computational inorganic chemistry will be presented.

Coordination Chemistry **34**

Characterization and Utility in Multielectron Photocatalysis

Daniel G. Nocera

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

The overlap of two orbitals, each containing an electron, defines the simplest chemical interaction between atoms. The electron population of the resulting bonding and antibonding orbitals gives rise to four electronic states. Although recognized at the inception of valence and molecular orbital bonding theories, the manifold comprising these four states had escaped experimental verification. We will provide the first complete spectroscopic characterization of the four-state manifold in a single molecule. The discussion will then demonstrate how the reactivity of selected states within this manifold can be exploited to engender the first discrete multielectron transformations (two and four) of a molecule in an excited state. Based on this reactivity, work from current investigations will be presented that targets the photocatalytic splitting of HX to H2 and X2.

Coordination Chemistry **35**

From Theory and Organometallic Model Chemistry to Catalysis

Peter Hoffmann

Organisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg

Theoretical work (EH, ab initio, DFT calculations) on ruthenium based olefin metathesis catalysts of the Grubbs type and interesting mechanistic findings will be presented. These have led us to synthesize new classes of neutral and cationic Ru carbene complexes with tailor-made chelating bisphosphine ligands. They show unprecedented activity especially in ROMP reactions. En route to these novel catalyst systems, we have found various unusual Ru hydride and dihydrogen complexes. Their molecular and electronic structures will be discussed. If time permits, recent work on catalytic CO_2 hydrogenation will be reported as well.

Anorganische Chemie **36**

Organically Modified Titania-Silica Aerogels for Epoxidation of Olefins and Allylic Alcohols

C.A. Müller, A. Gisler, M. Maciejewski, T. Mallat, and A. Baiker
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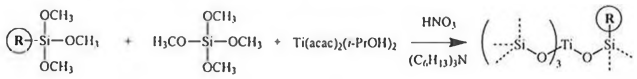
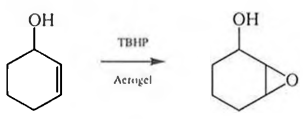
ETH Zentrum, CH-8092 Zürich

Mesoporous titania-silica mixed oxides with covalently bound organic groups were prepared by a sol-gel process and ensuing low temperature supercritical extraction with CO_2.



The modifiying group R was varied in order to study its influence on the aerogel structure and on the catalytic behavior in liquid phase oxidation reactions. For each modifier, the sol-gel process had to be adjusted to ensure the desired properties. Alkyls, aromatic, chloroalkyl, hydroxyalkyl, and aminoalkyl groups were chosen as modifying functions R.
The materials were tested in the epoxidation of various olefins and allylic alcohols (e.g. cyclohexenol, see below) with t-butylhydroperoxide. The epoxidation activity and selectivity varied strongly depending on the structure of the modifying group. The influence of organic modification on the surface of titania-silica could be interpreted by considering the interaction of the functional group with the reactant and the titanium active site. Also, adsorption effects influencing the mass transport might play an important role. High substrate selectivities to cyclohexenol oxide up to 93% were obtained with R = $CH_2CH_2CH_2N(CH_3)_2$.



CHIMIA 1999, 53, No. 7/8

Inorganic Chemistry **37**

Synthesis of alkaline earth metal halide clusters and their theoretical studies

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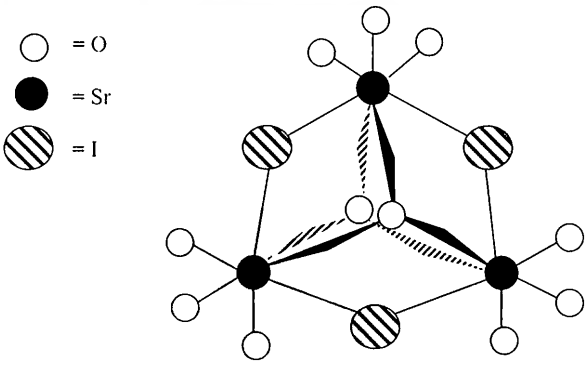
Aiming to tranfer the principles of transition metal cluster synthesis to alkaline earth metals, we developed a new synthetic approach yielding mixed ligand alkaline earth metal clusters. Thus, a Ca_{14}- and a Sr_3-compound were isolated and structurally characterised. The synthesis and structure of $\{[Sr_3I_3(\mu_3\text{-}OH)_2(thf)_9]I\}$ will be presented in detail. Based on this cluster compound, theoretical calculations were performed on the systems $[M_3X_3(\mu_3\text{-}OH)_2(OH_2)_9]^+$ (M = Ca, Sr, Ba, X = Cl, Br, I) in order to study the bonding situation and charge distribution.



Inorganic Chemistry **38**

Approaches to new alkali and alkaline earth metal clusters

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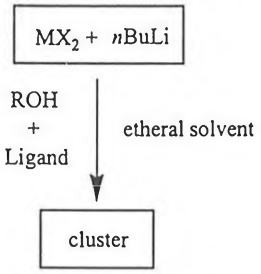
In the course of our studies on novel types of alkali and alkaline earth metal clusters, the synthesis of a new type of mixed ligand cluster compound, Li $[\{Ca_7(\mu_3\text{-}OH)_8I_6(thf)_{12}\}_2(\mu_2\text{-}I)].3THF$ where two Ca_7-cluster units form dimers by hydrogen bonds through a μ_2-bridging iodide, was achieved recently [1] :

$$CaI_2 + n\text{BuLi} \xrightarrow{\text{THF/LiOH}} \text{Li}\,[\{Ca_7(\mu_3\text{-}OH)_8I_6(thf)_{12}\}_2\ (\mu_2\text{-}I)\,].\,3THF$$

Based on this result, we wish to develop synthetic routes using excess of metal halide in etheral solution to react with organoalkali compound, in the presence of various polydentates O- and N-donor ligands.



[1] K.M. Fromm, submitted.

Inorganic Chemistry **39**

Double Salts of Zintl Phases and Halides

Steffen Wengert, Reinhard Nesper

Laboratorium für Anorganische Chemie, ETH Zürich

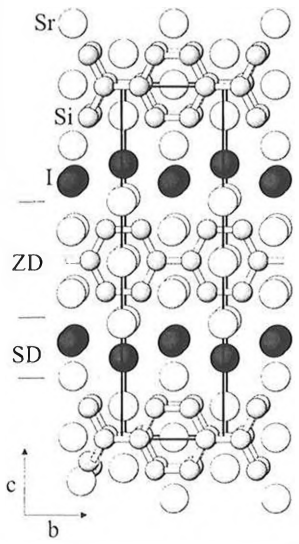


Fig. 1: Crystal structure of $Sr_5Si_6I_2$.

By exploring the reactivity of Zintl phases, M_xE_n (M = alkaline- or alkaline earth metals, E = semimetals of group 14 and 15), in melts of typical salt like compounds, M_xX_n (M = alkaline- or alkaline earth metals, X = nonmetals of groups 16 and 17, e.g. halides or chalcogenides) interesting novel solid compounds built of halide and *Zintl anions* were found and characterized by X-ray diffraction on single crystals.

Thus, in addition to theoretical and bondlength considerations, one has now a chemical argument to speak of *Zintl anions* in the sense of a chemical species. Most structures of this *Double Salts* show a clear separation in *Zintl phase-like* (ZD) and *salt-like* (SD) domains (cf. Fig. 1). From the combination of typical physical properties of isolators with semimetallic or in some cases metallic properties of Zintl phases interesting anisotropic physical properties are expected for this new class of compounds.

Inorganic Chemistry **40**

Amorphous FeO_x-SiO_2 Aerogels for the Selective Catalytic Oxidation of Ammonia

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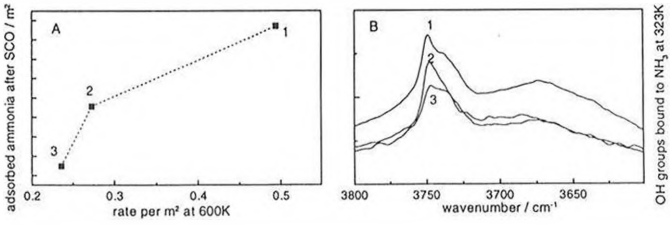
Laboratorium für Technische Chemie, ETH-Zentrum, 8092 Zürich

The emission of ammonia gives rise to acidification of the environment. Beside agriculture, an important source is the ammonia slip in the selective catalytic reduction of NO_x by NH_3 applied as NO_x control technique. Selective catalytic oxidation of ammonia (SCO) to nitrogen and water is an efficient method for NH_3-removal from stack gases.

Among the catalysts developed for SCO, only little attention has been given to the iron oxide - silica system so far [1]. Here we report amorphous FeO_x-SiO_2 aerogels, which exhibit very high selectivity to N_2 (96 - 98%) between 300 and 500°C. The sol-gel method followed by extraction of the solvent with supercritical CO_2 allowed to prepare highly dispersed mixed oxides with high surface area. Variation of the sol-gel parameters (hydrolysis, base) influenced the morphology and acidic properties of the aerogels. The latter were investigated by ammonia adsorption (A) and DRIFTS studies (B, NH_3 adsorption on aerogels prepared using different bases 1: N,N-diethylaniline, 2: trihexylamine, 3: ammonium carbonate). The catalytic activity in SCO was found to be correlated with the acidic properties (Brönsted sites).



[1] F. Janssen, F. van den Kerkhof, *KEMA Scientific & Technical Reports* **1985**, 3, 71.

Inorganic Chemistry **41**

Potential and Limitations of Ir Catalysts in the Selective Catalytic Reduction of NO_x with Hydrocarbons

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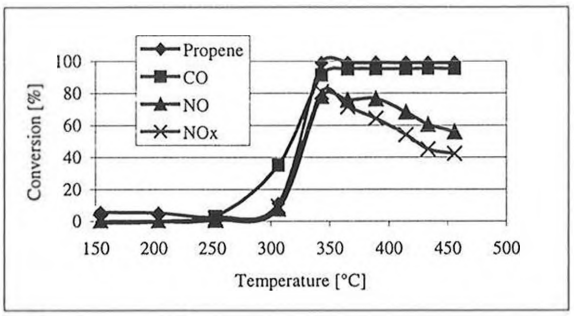
In exhaust gas catalysis one of the most challenging targets is the design of catalytic systems for lean and diesel engines, i.e. which are capable of removing NO_x under lean gas conditions (air/fuel ratio > 1). Contrary to reports in literature [1] Ir has been found capable of catalysing the reduction of NO to N_2 with remarkably high conversions of almost 80 % (see figure below). The catalyst is active in a temperature window ranging from just above 325 to 450 °C in a synthetic lean engine exhaust gas containing propene as main reducing agent (10 % H_2O, 10.7 % CO_2, 8 % O_2, 270 ppm NO, 1650 ppm propene, 350 ppm CO, rest N_2). The catalytic tests were performed with 5 % Ir on H-ZSM5 and were carried out between 150 and 450 °C. Special attention was paid to harmful by-products and possible side reactions which could hamper the overall efficiency of the NO_x reduction process.



[1] P. Bourges, S. Lunati and G. Mabilon, *Studies in Surface Science and Catalysis*, **1998**, 116, 213.

Inorganic Chemistry **42**

Influence of the Support on the Catalytic Activity in the Low Temperature CO Oxidation on Gold Catalysts

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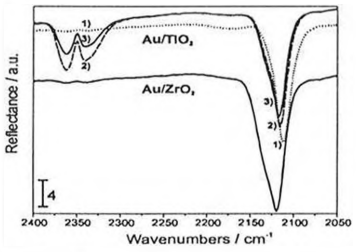
Laboratorium für Technische Chemie, ETH-Zentrum, 8092 Zürich

* Haldor Topsøe A/S, Nymøllevej 55, DK- 2800 Lyngby, Denmark

Finely dispersed gold on metal oxides catalyses the oxidation of CO at low temperatures, whereas gold as metal is quite inert. In order to study the interplay between gold and the support, Au/TiO_2 and Au/ZrO_2 catalysts were prepared by fixation of gold colloids on the support in aqueous solution. The colloids of 2 nm size adsorbed onto the supports without significant change in particle size, as evidenced by HRTEM [1].

Au/TiO_2 catalysts were catalytically active in CO oxidation at 300 K, both in the as prepared and in the calcined (673 K) state. Au/ZrO_2 catalysts showed activity at room temperature only after calcination, with significantly lower conversion. From the detailed investigation with DRIFTS, in addition to structural analysis with HRTEM, we concluded that the number of low-coordinated gold sites is different on the two supports due to different support interaction resulting in different shape of the gold particles.



The figure shows in situ DRIFTS studies of Au/TiO_2 and Au/ZrO_2 catalysts in CO oxidation at 300K. Transient evolution of CO_2 was recorded on the Au/TiO_2 sample during change from CO atmosphere (trace 1) to $CO/O_2 = 1$ (traces 2, 3).

[1] J.-D. Grunwaldt, C. Kiener, C. Wögerbauer, A. Baiker, *J.Catal.* **1999**, *181*, 223.
[2] J.-D. Grunwaldt, M. Maciejewski, O. Becker, P. Fabrizioli, A. Baiker, *J.Catal.*, in press.

Inorganic and Coordination Chemistry **43**

Topological Phase Transitions on Hyperbolic Manifolds

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The recognition of the topological relevance of the information coded in the permutations and extinction rules of the first structure factors (SF), near the origin of reciprocal space, is the starting point of the definition of Periodic Nodal Surfaces (PNS), which are hyperbolic manifolds [1]. PNS have proved their effectiveness in the topological characterisation of space group symmetry, as they separate Euclidean space in two non-intersecting labyrinths. The topologies of the labyrinths may help in describing chemical networks and in relating different topologies to each other. This approach can be used in the approach to first order phase transitions, where structural changes and distance between the space groups of the involved phases can be important [2]. Chemical networks, which are supported by the space group symmetry of a hyperbolic surface, can further be generated. This is possible, as the intersection of two PNS, each one carrying a different symmetry information results in a hyperbolic tessellation: its lines and points serve in building a network. In this way, many different networks can be generated, corresponding to known chemical structures or representing new, hypothetical frameworks[2].

Networks developing on surfaces can be made to transform into each other, by transforming the PNS supporting them. The flat point of the gyroide (Y**) surface are related to the flat points on the D* surface, through a Bonnet transformation. This for example provides a model for the martensitic transition[3].

With this method relationships between networks can be easily discovered. Great advantage derives from its application to phase transitions, where the involved phase may be very distant with respect to their symmetry, and no structural path connecting them are known.

[1] H.G.v.Schnering, R.Nesper, Z.Phys. **B83**, 407(1991)
[2] S.Leoni, Ph.D. Thesis No. 12783, ETH Zurich, 1998
[3] S.T.Hyde, S.Andersson, Z.Kristallogr., (1986) **174**, 255-236

Inorganic Chemistry **44**

The Wall-Structure of Vanadium Oxide Nanotubes

M. Wörle, J. de Onate, H.-J. Muhr, F. Bieri, R. Nesper,

Laboratorium für Anorganische Chemie, ETH Zürich,

Hydrothermal synthesis of vanadium oxides lead to a huge variety of different structures [1]. The use of templates (various amines) during the synthesis leads under special conditions to the formation of vanadium oxide nanotubes [2]. The X-ray powder diffraction patterns could be indexed with tetragonal unit cells with a = 6.11Å and with the c-axis between 13 and 35 Å, depending on the type of amines used. The size of the nanotubes is large enough to give well resolved diffraction patterns, which allowed the determination of the structure type. All vanadium oxide nanotubes observed so far are build with one type of vanadium oxide sheets, first found in $BaV_7O_7 \cdot nH_2O$ [3]. The sheets consist of bilayers formed of quadratic VO_5-pyramids and VO_4-tetrahedra. A view along the V_7O_{16} layers which build the nanotubes is shown in Fig. 1. The arrangement of the organic amines (e.g. dodecylamine) cannot be directly determined from the diffraction experiment and are shown in one of the possible arrangements (Fig. 1).

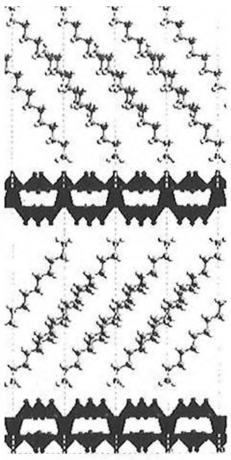

Fig. 1

[1] T. Chirayil, P. Y. Zavalij, M. S. Whittingham, *Chem. Mater.* **1998**, *10*, 2629.
[2] M. E. Spahr, P. Bitterli, R. Nesper, M. Müller, F. Krumeich, H. U. Nissen, *Angew. Chem. Int. Ed. Engl.* **1998**, *37*, 1263.
[3] X. Wang, L. Liu, R. Bontchev, A. J. Jacobson, *J. Chem. Soc., Chem. Commun.* **1998**, 1009.

Inorganic Chemistry **45**

Novel Cathode Materials for Lithium-Ion Batteries

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[b]*Swiss Federal Institute of Technology, Laboratory of Inorganic Chemistry, ETH-Zentrum, CH-8092 Zurich, Switzerland*

Transition metal oxides, particularly the oxides of 3*d* elements, are promising candidate active materials for positive electrodes in high-energy lithium-ion batteries. In our present work we set ourselves the goal of preparing stable, preferably layered manganese oxides leading to better specific charge, cycling stability, and Li^+ mobility than the spinel-type oxides investigated in the past. For the reaction:

$$y\ LiAl + (1\text{-}y)\ LiMnO_4 \rightarrow LiAl_yMn_{1-y}O_2 + (1\text{-}2y)\ O_2$$

a starting temperature of 200°C is sufficient. The stoichiometries explored range from y = 0.1 to y = 0.5 and the time of thermal treatment from 12 to 96 hours. Electrochemical investigations of this material showed that its initial specific charge, of up to 250 Ah/kg, is high but its cycling stability is not competitive. After a small number of cycles the specific charge drops to values in the range from 150 to 100 Ah/kg.

An additional stabilization was attempted by introducing further stabilizing cations:

$$x\ LiAl + x\ CaNi_2 + (1\text{-}3x)\ LiMnO_4 \rightarrow Li_{1-2x}Ca_xAl_xMn_{1-3x}Ni_{2x}O_2 + (1\text{-}6x)\ O_2$$

Ca^{2+} is expected to be an interlayer stabilizer. For synthesis of these materials, reaction times of 24 and 48 hours and temperatures of 300°C, 500°C, 700°C, and 900°C have been applied. The electrochemical experiments showed that the low-crystallinity samples produced at 300°C and 500°C initially exhibit high specific charge (>200 Ah/kg) but degrade within a few cycles, while the well crystallized ones produced at 700°C and 900°C exhibit low specific charge (~100 Ah/kg) but retains it during the first 15 to 20 cycles.

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

Anorganische Chemie **47**

Template-Directed Synthesis of Inorganic Materials: Novel Micro- and Nanostructured Vanadium-, Molybdenum-, and Iron Oxides

M. Niederberger, H.-J. Muhr, F. Krumeich, R. Nesper

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In the synthesis of nanostructured materials, the control over particle size, size distribution, shape, and composition is of great interest with regard to specific applications. The recent advances in sol-gel processing combined with the application of supramolecular long-range ordered aggregates of surfactant molecules provides a highly appropiate method for the preparation of mesostructured transition metal oxides [1].

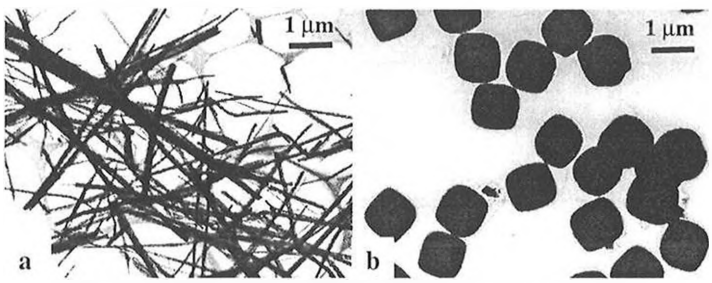

Figure 1. TEM images of (a) Molybdenum oxide fibers and (b) Iron oxide particles

Here we report our latest progress in the template-directed synthesis of vanadium-, molybdenum-, and iron oxides. After the hydrolysis of different metal oxide precursors in the presence of neutral template molecules, the hydrothermal treatment resulted in the formation of micro- and nanostructured transition metal oxide particles with different morphologies (Figure 1).

[1] P. Behrens, Angew. Chem. Int. Ed. Engl. **1996**, *35*, 515

46

Functionalization and Microstructuring of Vanadium Oxide Nanotubes

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[1]Laboratory of Inorganic Chemistry, ETH Zürich, 8092 Zürich
[2]Nonmetallic Inorganic Materials, ETH Zürich, 8092 Zürich

Multi-walled vanadium oxide nanotubes (VO_x-NTs) are obtained as the main product in a sol-gel reaction followed by hydrothermal treatment from vanadium(V)alkoxide precursors and primary amines ($C_nH_{2n+1}NH_2$ with $4 \leq n \leq 22$). The alkylamines act as structure-directing templates and are intercalated in between the vanadium oxide layers in protonated form [1,2].

TEM investigations of cross-sections of VO_x-NTs revealed that the major fraction of the tubes has a chrysotile-like morphology, i.e. in most cases, they are single- or double layer scrolls. This scroll-like structure is highly flexible and permits numerous exchange reactions: The cationic organic template can be substituted by metal cations (Na^+, K^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Fe^{2+}, Co^{2+}) without destruction of the tubular morphology. Furthermore, the tubes show a pronounced intercalation selectivity towards potassium and withstand several metal/alkylamine exchange cycles.

VO_x-NTs can be oriented into lines of subsequent, aligned nanotubes on glass substrates by micromoulding in capillaries using micropatterned PDMS moulds [3]. The width of these lines, which are several µm long, is dependent on the volume fraction of the applied suspension of nanotubes in octanol and can be varied from 1 to 5 µm with a mould of 5 µm wide capillaries. This method allows for a controlled manipulation and ordering of such anisotropic nanoparticles with respect to the investigation of the physical properties (e.g. electrical conductivity) and may be used as a powerful tool for generation of functional nanodevices.

[1] M.E. Spahr, P. Bitterli, R. Nesper, M. Müller, F. Krumeich, and H-U. Nissen, *Angew. Chem. Int. Ed.* **37**, 1263-1265 (1998).
[2] R. Nesper and H.-J. Muhr, *Chimia* **52**, 571-578 (1998).
[3] E. Kim, Y. Xia, G.M. Whitesides, *Nature* **376**, 581-584 (1995).

Inorganic Coordination Chemistry **48**

A new Polyoxo-Polyolato Complex of Tantalum(V) with a Double Adamantane-Like $[Ta_7O_{12}]^{11+}$ Core

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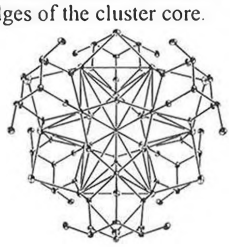
The coordination chemistry of *cis*-inositol (cyclohexane-1,2,3,4,5,6-hexol = ino) was investigated for a variety of highly charged metal cations. The complexation was identified by significant shifts and line splitting in the ^{1}H- and ^{13}C-NMR spectra. With Ta(V), suitable crystals for X-ray structure analysis containing the anion $[Ta_7K_6O_{12}ino_6(H_2O)_{14}]^+$ **(1)** could be obtained. Ta, as an early transition metal, has a pronounced tendency in its highest oxidation state to form polynuclear, oxo-bridged aggregates in aqueous solution. It was found, that the Ta_7O_{30} structure is virtually the same as in the previously described heptanuclear complex with the 1,3,5-tridcoxy-1,3,5-tris(dimethylamino)-*cis*-inositol ligand [1]. In addition, the structure of this polyoxo anion is completed by six potassium ions which are coordinated to the hydroxy and alkoxo groups of the deprotonated inositol ligands and to the oxo bridges of the cluster core.



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Inorganic and Coordination Chemistry **49**

Anionic Vanadium Oxo and Peroxo Complexes as Catalysts in the Oxidative Functionalisation of Methane

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We recently discovered that sodium vanadate, in the presence of pyrazine-2-carboxylic acid (pcaH), efficiently catalyses the reaction of methane with molecular oxygen (from air) and hydrogen peroxide to give methyl hydroperoxide under very mild conditions (H_2O, 50°, 85 bar, TON 480) [1].

$$CH_4 + 1/2\ O_2 + H_2O_2 \longrightarrow CH_3\text{-}OOH + H_2O$$

In order to get a mechanistic understanding of this remarkable reaction, we studied the reaction of vanadate (catalyst) with pcaH (co-catalyst) and with related compounds such as anthranilic acid (anaH) without and in the presence of hydrogen peroxide.

$$[VO_3]^- + 2\ pcaH \longrightarrow [VO_2(pca)_2]^- + H_2O$$

$$[VO_2(pca)_2]^- + H_2O_2 \longrightarrow [VO(O_2)(pca)_2]^- + H_2O$$

These vanadate anions have been isolated as the tretrabutylammonium salts and unambiguously characterised by X-ray crystallography, which revealed the pca ligands (derived from the most efficient co-catalyst) to be *N,O*-co-ordinated to vanadium, whereas in the analogous ana derivative $[VO_2(ana)_2]^-$ the ana ligands (derived from the least efficient co-catalyst) are *O,O*-co-ordinated to vanadium.

[1] G. V. Nizova, G. Süss-Fink and G. B. Shul'pin, *J. Chem. Soc., Chem. Commun.*, **1997**, 397; G. Süss-Fink, Hong Yan, G. V. Nizova, S. Stanislas and G. B. Shul'pin, *Russ. Chem. Bull.*, **1997**, *46*, 1801.

Chimie minérale et de coordination **50**

Novel ways to carbon dioxide/limestone utilisation ?

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The huge amount of CO_2, present in the atmosphere, hydrosphere and emitted as waste from the combustion of fossil raw materials, suggests that it could be an interesting basic C1-unit in a future carbon based synthetic chemistry. The same applies for carbonate rocks, dolomite and limestone. Although numerous chemical, technical, and economic questions have to be solved beforehand - such as the production of the hydrogen needed - this is a great challenge for chemists, given that the most important reaction in volume on the Earth is photosynthetic carbon dioxide reduction.

Several attempts have been made to reduce CO_2: in the presence of amines, platinum group metal complexes have been found active to produce formic acid, formate esters or formamides (in organic phase, in biphasic systems or in supercritical CO_2)[1-4].

In this contribution we present our results on the reduction of aqueous carbon dioxide/limestone/dolomite systems using water soluble Ru-phosphine catalysts. For these reactions we ***do not*** use any amine as a thermodynamic sink for the reduction. The reactions were followed *in situ* by medium and high pressure UV-vis and NMR spectroscopy under various H_2 and CO_2 pressures. We have investigated the initial rate of the reduction and propose a mechanism for these homogenous catalytic reactions.

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[3] G. Jessop, T. Ikariya, R. Noyori, *Chem. Rev.*, **1995**, *181*, 27
[4] W. Leitner, E. Dinjus, F. Gassner, in *Aqueous-Phase Organometallic Catalysis* (B. Cornils, W. A. Herrmann, eds.), Wiley-VCH, Weinheim, **1998**, p. 486

This work was supported by the Office Fédéral de l'Education et de la Science, Suisse (OFES C98.0011). N. L. is grateful for an OFES fellowship. This research is part of the collaboration within the COST Action D10/0001 Working Group.

Organic Chemistry **51**

Regioselective Synthesis of *trans*-1 Fullerene Bis-Adducts Directed by Crown Ether and Tetraphenyl Porphyrin Type Tether

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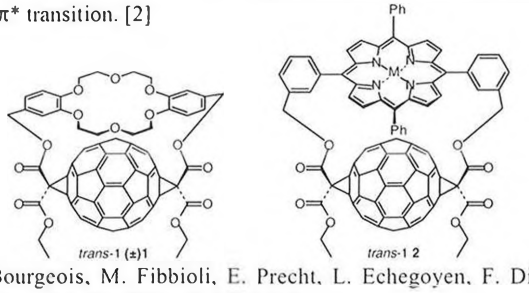
We present here the first regioselective Bingel macrocyclisation of C_{60} with a bis-malonate containing a novel dibenzo[18]crown-6 tether which yields up to 50 % of the planar-chiral *trans*-1 bis-adduct (±)**1** as well as the C_{60} macrocyclisation with a bis malonate teraphenyl porphyrin wich yield up to 17 % of the C_{2v} *trans*-1 cyclophane-type molecular dyad **2**. [1, 2] In these macrocycles the doubly bridged chromophore (crown ether, porphyrin) adopts a close, tangential orientation relative to the surface of the carbon sphere wich provides some particular properties: Electrochemical investigation of (±)**1** revealed for the first time a substantial effect of cation complexation on the redox properties of the carbon sphere. [1] Photochemical investigation of **2** showed a very strong quenching of the porphyrin fluorescence as well as a hypsochromical shift of the *Soret* band and the ππ* transition. [2]



1. J.-P. Bourgeois, M. Fibbioli, E. Precht, L. Echegoyen, F. Diederich, *Angew. Chem. Int. Ed.* **1998**, *37*, 2118-2121.
2. J.-P. Bourgeois, L. Echegoyen, J.-F. Nierengarten, F. Diederich, *Helv. Chim. Acta*, **1998**, *81*, 1835-1844.

Inorganic and Coordination Chemistry **52**

Binuclear Transition Metal Complexes With a New Double Macrocyclic Ligand Based on Pyrazine

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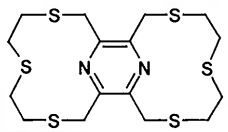
The new bis-macrocyclic ligand ***L1*** has been synthesised and used in the formation of some first row transition metal complexes.



L1

A binuclear complex which contains the metal ion in a trigonal bipyramidal coordination sphere was form by the reaction of copper(II) bromide with ***L1***. The three-dimensional structure could be determined by single crystal structure analysis. The reaction of ***L1*** with nickel(II) nitrate resulted in the formation of an insoluble micro-crystalline product. The structure of this binuclear nickel(II) complex containing 21 atoms per asymmetric unit was determined from laboratory X-ray powder diffraction data. The nickel shows a slightly distorted octahedral coordination. Magnetic measurements for both metal complexes are discussed.

A surprising result was obtained when investigating the reaction of ***L1*** with Zinc(II)iodide. A rearrangement of the macrocycles attached to the pyrazine ring was found to occur.

Inorganic and Coordination Chemistry **53**

Specific Hydrolysis of a Phosphate Diester by a Binuclear Bismacrocyclic Zn(II) Complex

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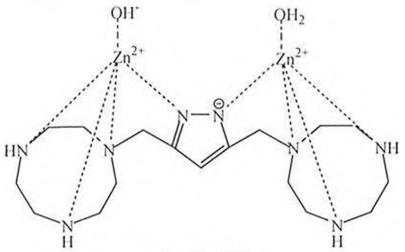
The hydrolysis of phosphate esters by metal complexes can be used to model metal ions in metalloenzymes such as alkaline phosphatase. Therefore, the hydrolysis of bis(4-nitrophenyl)phosphate (BNP) in the presence of **1** was investigated. From the pH dependance of the apparent rate constants, the active species was identified as Zn_2LH_{-2}, a monohydoxo species. The hydrolysis of BNP specifically gives 4-nitrophenylphosphate (NPP), which is an inhibitor of the reaction.



1 = Zn_2LH_{-2}

The reaction proceeds *via* a phosphate ester-coordinated intermediate as indicated by the Michaelis-Menten kinetics and ^{31}P-NMR studies.

The second order rate constant k ($M^{-1} \cdot s^{-1}$) = $1.87(5) \cdot 10^{-4}$ at 35°C is similar to values obtained with other dinuclear Zn(II) complexes [1] and distincly larger than that with mononuclear Zn(II) species [2].

[1] C. Bazzicalupi, A. Bencini, A. Bianchi, V. Fusi, C. Giorgi, P. Paoletti, B. Valtancoli, D. Zanchi, *Inorganic Chemistry*, **1997**, *36*, 2784

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Inorganic and Coordination Chemistry **54**

Arylcyclam-Metal-Compexes: Syntheses und Interactions with Carboxylic Acids studied by ^{1}H-NMR- and VIS-Spectroscopy

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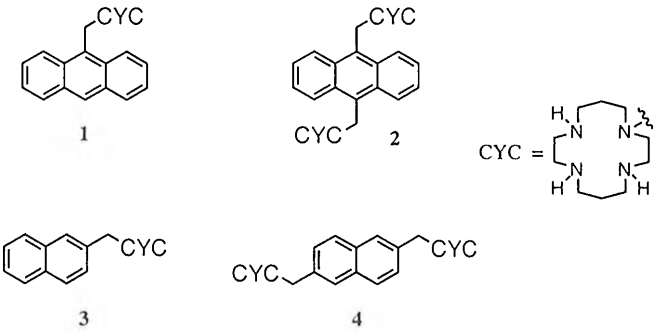
Zn(II) and Ni(II) complexes of **1-4** were synthesized in three steps[1]. The interaction of these complexes with carboxylates carrying an aliphatic or aromatic side chain was studied by VIS-spectroscopy for Ni^{2+} and by ^{1}H-NMR for Zn^{2+} [2].



The changes in the VIS-spectra of the Ni^{2+} complexes show that the carboxylic acids axially bind to the metal ion. In the case of Zn^{2+} chemical shifts of the aromatic signals are observed for p-(methoxyphenyl)propionic acid. This seems to indicate that beside coordination to the metal ion π-π-interactions between the side chain of the acid and the pendant group of the macrocycle take place.

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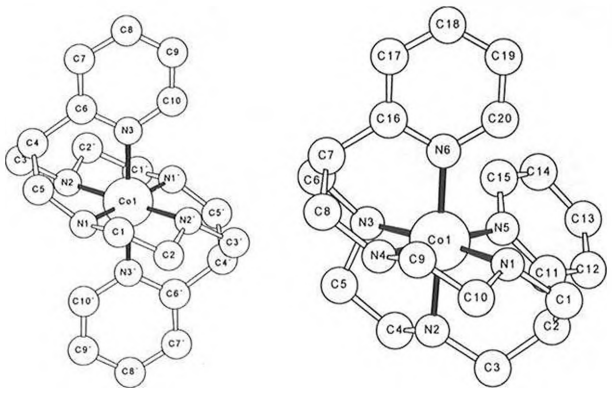
55

Template synthesis and properties of a new tetraazamacrocyclic ligand with two pendent pyridinyl groups

Peter Comba, Stephan Luther, Oliver Maas, Hans Pritzkow and Annette Vielfort

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

The syn- and anti-isomer of the bis-2-pyridyl-substituted cyclam derivative pypymac is obtained in a copper(II) directed template synthesis in the ratio 1:9. Single crystal X-ray and solution (NMR) structures of the metal-free ligand and their transition metal compounds (copper(II), nickel(II), cobalt(III), zinc(II)) are reported together with spectroscopic and redox properties and with experimentally determined stability constants.



Inorganic Coordination Chemistry **56**

Cobalt(III)-Complexes with *cis*-3,5-Diaminopiperidine as a Template of the Synthesis of Macrocyclic Compounds

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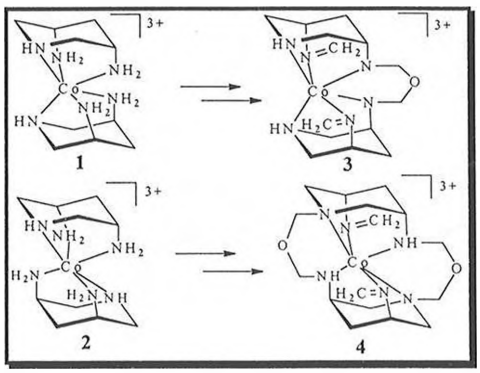
Tridentate cyclic polyamines which are restricted to facial coordination are versatile building blocks for tailored multidentate ligands. Due to the presence of endocyclic and exocyclic nitrogen donors, *cis*-3,5-Diaminopiperidine (**dapi**) is a particularly interesting representive of this class. Its coordination chemistry has been, however, only scarcely investigated [1]. We report here the synthesis of the cobalt(III)-cage-complexes **3** and **4** where two dapi fragments are fused to a macrocyclic ligand system. The separation of the cis-trans-isomeres of $[Co(dapi)_2]^{3+}$ **1** and **2** was achieved by chromatography on Sephadex™. The subsequent synthesis of the macrocyclic compounds **3** and **4** was performed by a template method using formaldehyde and triethylamine in acetonitrile as solvent.



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57

The formation of new stable $Cu_2^{(II)}$ -O_2-species with binucleating preorganized open-chained ligands

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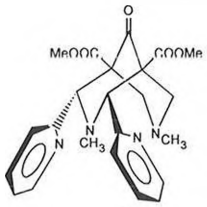
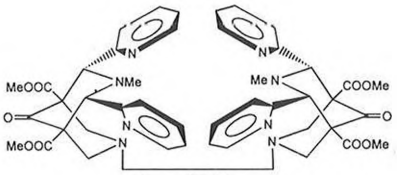
b.Chemistry Department, Emory University, 1515 Pierce Dr., Atlanta, GA 30322
email: boerzel@akcomba.oci.uni-heidelberg.de



L_1



L_2 = -$(CH_2)_2$-
L_3 = -$(CH_2)_3$-
L_4 = m-xylyl

The complexation of $[Cu(CH_3CN)_4]X$ (X= BF_4^-, OTf) with the bispidone ligand L_1 in CH_3CN leads to the formation of two isomers (a 4- and a 5-coordinate compound) of $[Cu(L_1)]X$, characterized by x-ray crystallography. Oxygenation of $[Cu(L_1)]BF_4$ compound at –20°C leads to the formation of the purple μ-1,2-peroxo-dicopper(II) species $[Cu_2(L_1)_2(O_2)](BF_4)_2$ (**I**), characterized by UV-Vis and Raman spectroscopy.

Complexation of the corresponding binucleating ligands L_2 to L_4 with $[Cu(CH_3CN)_4]BF_4$ leads to dinuclear complexes of the composition $[Cu_2L_{(2,3,4)}](BF_4)_2$. Upon oxygenation, all these compounds form μ-1,2-peroxo-dicopper(II) complexes, characterized by UV-Vis and Raman spectroscopy; their stability is strongly dependent of the nature of the spacer group, with $[Cu_2L_2(O_2)](BF_4)_2$ and $[Cu_2L_4(O_2)](BF_4)_2$ being stable at room temperature and $[Cu_2L_3(O_2)](BF_4)_2$ being comparable in its decomposition behavior to $[Cu_2(L_1)_2(O_2)](BF_4)_2$.

Increasing the steric bulk at the pyridine donors decreases the reactivity of the compounds with O_2; this is explained by changes in the redox potential of the Cu^I/Cu^{II} couple.

Molecular Mechanics calculations are used to design the optimum geometry of the spacer group.

Inorganic Coordination Chemistry 58

Coordination properties of 1,3,5-Tris(2'-pyridylmethylamino)-1,3,5-tridcoxy-*cis*-inosit (pmaci)

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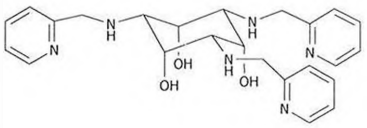
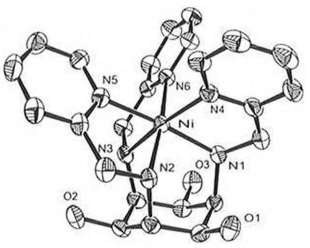
[c]Universität Potsdam, Anorganische Chemie, D-14467 Potsdam, Germany

Polyaminopolyalcohols have been established to be versatile ligands for the complexation of a large variety of metal ions. The coordination properties of 1,3,5-triamino-1,3,5-trideoxy-*cis*-inosit (**taci**) has already been studied extensively in our group [1]. Our aim was now to expand the coordination modi of taci by adding further donor atoms to the ligand. The reaction of the primary amines of taci with pyridine-2-carbaldehyde and reduction of the resulting Schiff base with sodium hydridoborate was an easy route to synthesize the title compound **pmaci** (**1**). The pk_s values of pmaci and stability constants with $Cu^{2+}$and Zn^{2+} were determined by potentiometric titration and crystal structures of the complexes with Cu^{II}, Ni^{II} and Zn^{II} could be obtained and will be presented.



(1)



[1] Hegetschweiler, K.; Weber, M.; Huch, V.; Geue, R. J.; Rae, D.; Willis, A., C.; Sargeson, A., M.; *Inorg. Chem.* **1998**, *37*, 6136 – 6146.

Inorganic Coordination Chemistry 59

1,3,5-Trideoxy-1,3,5-tris-(dimethylamino)-*cis*-inositol, Determination of the Stability Constants and the Crystal Structures of Cu^{II} complexes

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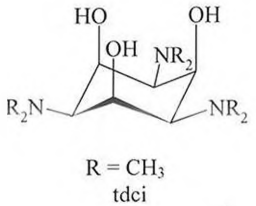
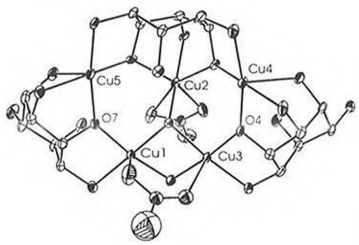
Polyamino-polyalcohol-compounds offer different binding types (O-and/or N-donors) for interaction with metal-ions. An interesting representative of this group is 1,3,5-Trideoxy-1,3,5-tris-(dimethyl-amino)-*cis*-inositol (**tdci**). Its bulky $N(CH_3)_2$ groups force a rigid structure with three axial oxygen-donors. The presence of intramolecular bases enable the deprotonation of the hydroxyl-groups. Therefore tdci is well known as an effective ligand for highly charged, hard metal ions [1]. But its coordinating properties with softer transition metals are less investigated. Now we report on the variety of **Cu^{II} complexes** formed by **tdci**. The species distribution in aqueous solution was investigated by potentiometric measurements and in solid state by X-ray diffraction studies. The structure of $[Cu(tdci)_2](NO_3)_2$ and of a polynuclear species $[Cu_5(H_{-1}tdci)_2tdci(OH)_2(NO_3)_2]^{4+}$ containing a Cu to ligand ratio of 5:3 could be determined.



R = CH_3
tdci



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Inorganic Coordination Chemistry 60

Linear Primary Polyamines as Building Blocks for Coordination Polymers

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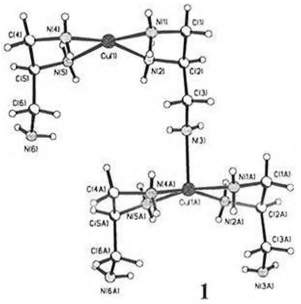
A series of linear primary polyamines $H_2N\text{-}CH_2\text{-}(CH\text{-}NH_2)_n\text{-}CH_2\text{-}NH_2$ ($1 \leq n \leq 3$) was prepared from the corresponding polyalcohols [1]. The crystal structure of Cu^{II} with the 1,2,3-triaminopropane exhibited a chain structure **1** whereas with 1,2*S*,3*S*,4-tetraaminobutane and Cu^{II} a two dimensional honeycomb like network **2** was formed. The acidity constants of the amines in aqueous solution were determined and the pH-dependent formation of a variety of species $M_xL_yH_z$ with M = Ni^{II}, Cu^{II} was established by potentiometric titrations.



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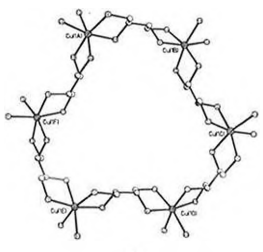

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[1] A. Zimmer, I. Müller, G. J. Reiß, A. Caneschi, D. Gatteschi, K. Hegetschweiler, *Eur. J. Inorg. Chem.* **1998**, 2079.

Inorganic Coordination Chemistry **61**

An Improved Synthesis of *cis*-3,4-Diaminopyrrolidine and its Coordination Properties Towards Metal Ions

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[b]Universität Kaiserslautern, Fachbereich Chemie, D-67663 Kaiserslautern
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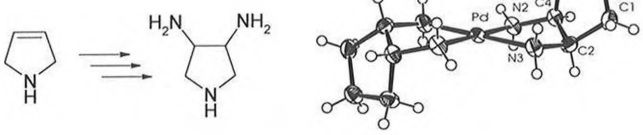
[d]Universität Potsdam, Anorganische Chemie, D-14467 Potsdam

Cyclic polyamines have been the subjects of intense and broad investigations in coordination chemistry. Nevertheless up to now nothing was kown about the coordination properties between metal ions and *cis*-3,4-Diaminopyrrolidine (**dap**) **1** in aqueous solution. Due to its structure as a cyclopentane derivative *cis*-3,4-Diaminopyrrolidine has the possibility to coordinate metal ions establishing three five-membered chelate rings. To investigate the coordination chemistry of dap a new and efficient synthesis [1] was developed yielding the ligand in multigram amounts. The pK_a-values and the stabiltiy constants with the divalent metal ions **Ni^{II}**, **Cu^{II}**, **Zn^{II}** and **Cd^{II}** were examined by the use of potentiometric titrations. The available X-ray structures of $[Pd^{II}(Hdap)_2](ClO_4)_4$ **2** and $[Pt^{IV}(Hdap)Cl_4]Cl$ indicate the preference of the ligand for coordination with the primary amino groups.



1 **2**

[1] Wormser, H.C. *J. Pharm. Sci.* **1969**, *58*, 1038.

Inorganic Coordination Chemistry **62**

3,5-Bis-(2-hydroxyphenyl)-1,2,4-triazoles – New Effective Ironchelators

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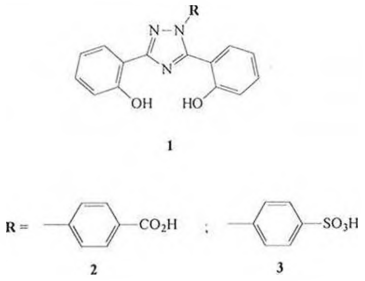
[b] Novartis AG, Schwarzwaldallee 215, CH-4058 Basel, Switzerland

N-substituted 3,5-bis-(2-hydroxyphenyl)-1,2,4-triazoles **1** are easily to prepare by a ring formation reaction from 2-(2-Hydroxyphenyl)-benzo[e]-1,3-oxazin-4-one with the suitable phenylhydrazines [1]. These ligands are potential pharmaceuticals for the treatment of β-thalassemia. To verify the selectivity of the ligands for Fe^{III} in contrast to biologically relevant metals (Ca^{II}, Mg^{II}, Cu^{II}, Zn^{II}), extensive spectrometric and potentiometric determinations were performed. Due to the insolubility below pH 7.4 the investigations of the p-benzoic acid derivative **2** were made in a partially non aqueous solvent (mole fraction of DMSO = 0.2). The water soluble benzosulphonic acid derivative **3** facilitates the comparison between the measured stability constants of the metal complexes in a partially non aqueous solvent and in pure water.



1 **2** **3**

[1] Yu. I. Ryabukhin, L. N. Faleeva, V. G. Korobkova, *Chem. Heterocycl. Compd.* 19, 3, **1983**, 332 – 336.

Inorganic Chemistry **63**

Complex Synthesis via Activated N-ligands using Alkali-Enamides

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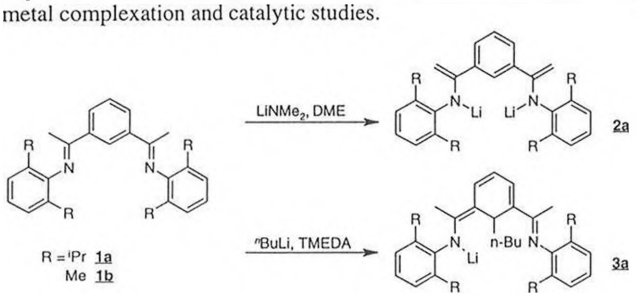
University of Zürich, Institute of Inorganic Chemistry
8057 Zürich, Switzerland

Very recently, Brookhart and independently Gibson et al. [1a,b] reported on excellent Fe(II) and Co(II) olefin polymerization catalysts, which are based on sterically demanding tridentate pyridine diimine ligands. In the search for complexes of the related carbo-analogues of these nitrogen donors, we have prepared the novel ligands **la,b** presented below. However, in sharp contrast to the results reported in [1a,b], we have not been able to obtain the corresponding cobalt and rhodium complexes of ligands **la,b** directly even under very forcing conditions. We attributed this apparent difference to difficulties with the prerequisite for a C-H activation step. We have therefore attempted to activate our ligands for metal complexation through deprotonation. These experiments will be presented along with transition metal complexation and catalytic studies.



[1] a) M. Brookhart et al. *J. Am. Chem. Soc.* **1998**, 120, 4049;
b) V.C.Gibson et al. *Chem. Commun.* **1998**, 849.

Inorganic and Coordination Chemistry **64**

Complexes of a chiral, facially coordinating tridentate ligand

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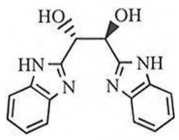
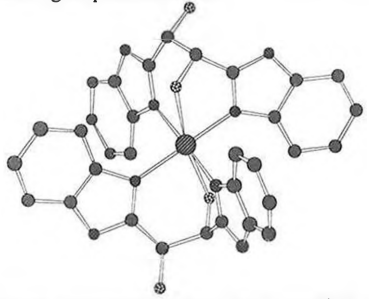
Département de Chimie Minérale, Analytique et Appliquée, Université de Genève, Sciences II, CH 1211 Genève 4.

The chiral ligand (SS)-1,2-bis(1H-benzimidazol-2-yl)ethane-1,2-diol (bzimed) is readily synthesized from (R,R)-tartaric acid and 1,2-diamino benzene.

(S,S)- bzimed :



The ligand forms 1 : 2 complexes with Fe, Co, Ni, Cu and Zn. The crystal structure of $[Cu(bzimed)_2]^{2+}$ shows the ligand to act as a tridentate (NNO) ligand with the alcohol group coordinated.



The stabilities of the complexes have been studied by potentiometric titrations, which also show the complexed alcohol to be deprotonated at quite low pH.

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Inorganic and Coordination Chemistry **65**

Structural studies of chiral pybox cobalt(II) complexes in solution and solid state

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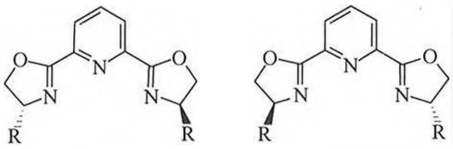
University of Geneva, CH-1211 Geneva 4, Switzerland.
christophe.provent@chiam.unige.ch

Chiral bis-oxazolinylpyridine compounds, also called « pybox » [1], are interesting tridentate ligands to prepare ML_2 complexes with an octahedral metal such as cobalt(II).

Phpybox : R = C_6H_5

Mepybox : R = CH_3

Bzpybox : R = CH_2-C_6H_5



RR SS

The stoechiometry of all the complexes prepared with these ligands is CoL_2. They have been studied by X-ray diffraction, ^{1}H NMR, ES-MS, UV-visible, NIR spectrophotometry and CD spectroscopy. Cyclic voltametry showed that they all have a relatively high redox potentials (between 1 and 1.2 V/NHE). The diastereoselectivity of complex formation has been studied. Equimolar mixtures of RR and SS Mepybox and Bzpybox show mixtures of homochiral and heterochiral complexes, but Phpybox shows exclusive formation of the heterochiral species. This selectivity is correlated with structural and electronic properties of the complex.

[1] H. Nishiyama, M. Kondo, T. Nakamura, K. Itoh, *Organometallics* **1991**, *10*, 500.

Inorganic and Coordination Chemistry **66**

Fine Tuning of Fe^{II} Spin Crossover Properties in Heterodimetallic d-f Complexes

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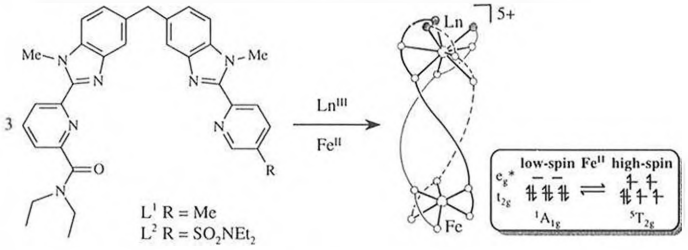
The segmential ligand L^1 has been designed for the synthesis of d-f heterodimetallic complexes $[LnM(L^1)_3]^{5+}$. Depending of the choice of the 3d and 4f ions, these complexes display different electronic and spectroscopic properties; $[LnZn(L^1)_3]^{5+}$ work as UV-Vis light–converting devices [1], while $[LnFe(L^1)_3]^{5+}$ display tunable spin-crossover properties [2]. The introduction of a sulfonamide group in the 5-position of the pyridine provides a new ligand L^2. While the photophysical properties of the $[EuZn(L^2)_3]^{5+}$ are not strongly affected by this substituent, the spin-state equilibrium properties of the $[LnFe(L^2)_3]^{5+}$ are significantly modified. Detailed magnetic and photophysical studies together with theoretical calculations bring us information about the origin of this effect.



[1] Piguet, C.; Bünzli, J.-C. G.; Bernardinelli, G.; Hopfgartner, G.; Petoud, S.; Schaad, O. *J. Am. Chem. Soc.* **1996**, *118*, 6681.

[2] Piguet, C.; Rivara-Minten, E.; Bernardinelli, G.; Bünzli, J.-C. G.; Hopfgartner, G. *J. Chem. Soc., Dalton Trans.* **1997**, 421.

Coordination Chemistry **67**

BENT TRIDENTATE RECEPTORS FOR NEW LUMINESCENT LANTHANIDE-CONTAINING MATERIALS

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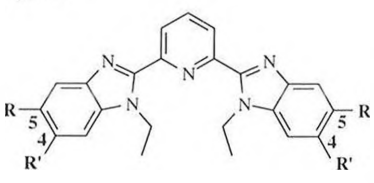
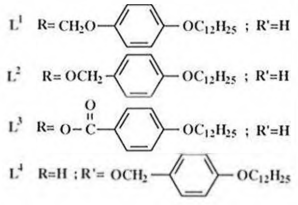
[‡] Institute of Inorganic and Analytical Chemistry, BCH 1402, CH-1015 Lausanne-Dorigny

[⊥] Institute of Chemistry, University of Neuchâtel, 51 Av. de Bellevaux, CH-2000 Neuchâtel

A new synthetic strategy has been developed to introduce bent and rigid tridentate 2,6-bis(benzimidazole-2'-yl)pyridine cores into rod-like and U-shaped ligands L^{1-4}. [1] The *trans-trans* conformation of the tridentate receptor in L^{1-3} provides a linear arrangement of the semi-rigid lipophilic side chains compatible with the formation of mesophases below 200 °C. Substitution at the 4 position affects the geometry arrangement in L^4 and removes the liquid crystalline behaviour. The nature of the spacers between the benzimidazole side arms and the connected semi-rigid lipophilic chains allows a fine tuning of the electronic and thermal properties. Complexation to Ln^{III} produces 1:1 complexes $[Ln(L^i)(NO_3)_3]$ (i=1-4) whose shape, structure and photophysical properties depend on the structural design of the ligand.





[1] Nozary, H.; Piguet, C.; Tissot, P.; Bernardinelli, G.; Bünzli, J.-C.G.; Deschenaux, R.; Guillon, D. *J. Am. Chem. Soc.* **1998**, *120*, 12274-12288.

Inorganic and Coordination Chemistry. **68**

A new imine-type ligand for the formation of supramolecular triple-helicates.

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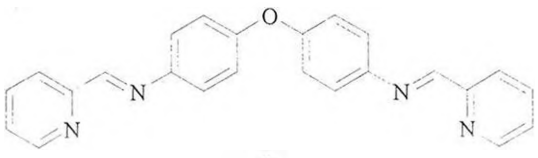
Université de Neuchâtel, Institut de Chimie, Avenue de Bellevaux 51, 2000 Neuchâtel

Supramolecular chemistry, and in particular, self-assembling processes in which metals and ligands spontaneously form 3D architectures, are themes of intense current interest.

We will present the X-ray structure of a new bis(bidentate) Schiff base (**L**) and some of its coordination supramolecular chemistry.

The ligand was easily prepared by mixing, 2 equivalents of pyridine-2-carbaldehyde and 1 equivalent of 4,4'-diaminodiphenylether giving a very high yield (95%).

We will also present the X-ray structures of some first row transition metal triple helicates.



L

Structural scheme of the ligand, **L**.

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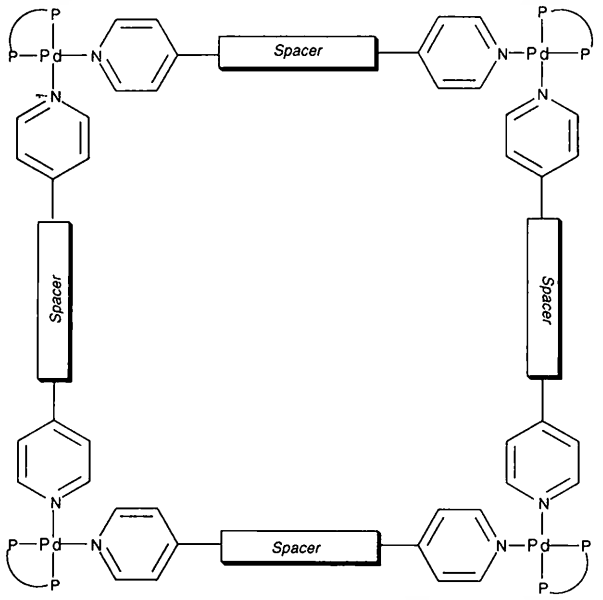
Inorganic Chemistry **69**

Molecular polygons with functional spacers

Edwin C. Constable, Catherine E. Housecroft and Chantal Schmitt

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

The introduction of functional spacers between the vertices of molecular polygons represented by structures such as **1** will be presented.



(1)

Inorganic and Coordination Chemistry **70**

Metal complexes of a terpyridine-like nitronyl nitroxide biradical

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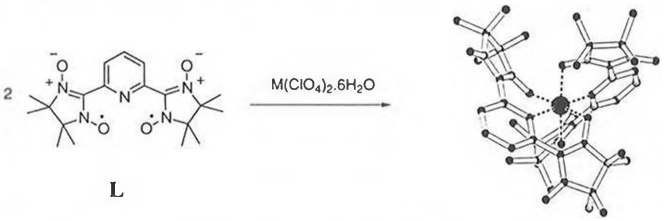
[a]Departement für Chemie und Biochemie
Universität Bern, CH-3012 Bern, Switzerland
[b]Institut de Chimie Université de Neuchâtel
CH-2000 Neuchâtel, Switzerland

The synthesis of metal complexes incorporating organic free radicals directly bound to their coordination sphere has deserved much attention during the last decade. These complexes provide very good models for the study of metal-radical exchange interactions and are also the basis of some extended systems with cooperative magnetic properties.

The nitronyl nitroxide biradical **L** behaves as a terdentate ligand and forms stable complexes with transition metal ions. In our contribution we will report on the synthesis, crystal structures and magnetic properties of compounds $L_2M(ClO_4)_2$ (M = Mn, Co, Ni, Cu, Zn).



L

Strong antiferromagnetic metal-radical interactions are generally the rule in these systems and this has indeed been observed for most of the metal complexes studied. Interestingly, in the copper (II) complex, two nitroxide radicals bind in axial positions and couple ferromagnetically to the metal centre. The other two radicals are antiferromagnetically coupled and bind in equatorial positions, giving rise to a S = 1/2 ground state.

Anorganische-Koordinationschemie **71**

Bis- and Tris-Oligopyridinamines, Oligopyridines Containing Diazepinones: Properties and Metal Complexes

Reza-Ali Fallahpour

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Novel functional groups such as azides, nitro and bromo have been inserted to Oligopyridines, especially to 2,2':6',2"-terpyridines [1-2].

Starting from azido compounds new oligopyridines containing diazepinones (Fig. 1) were obtained. Dendrimers based on nitrogen (Fig. 2) are of interest and the preparation as well as their metal complexes are reported.

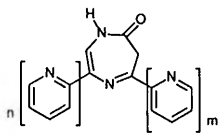


Fig. 1

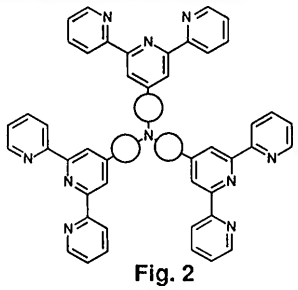


Fig. 2

[1] R.-A. Fallahpour, M. Neuburger and M. Zehnder, *New J. Chem.*, 1999, **23**, 53.

[2] R.-A. Fallahpour, M. Neuburger and M. Zehnder, *Synthesis*, 1999, in the press.

Inorganic and Coordination Chemistry **72**

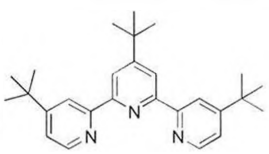
LMCT Deactivation Pathways of Eu(III) Luminescence : Influence of Bulky Substituents

Hans-Ruedi Mürner[a], Domique Suhr[b], Randolph P. Thummel[c] and Jean-Claude G. Bünzli[a]

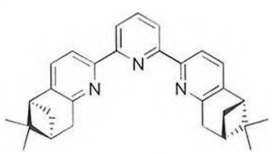
a) Insitut de Chimie Minérale et Analytique, Université de Lausanne, BCH, 1015 Lausanne; b) Institute de Chimie Minérale et Analytique, Université de Fribourg, Pérolles, 1700 Fribourg; c) Department of Chemistry, University of Houston, Houston, TX 77204.

The excitation of lanthanide compounds relies on an efficient energy transfer from the ligand sphere (antenna effect) and numerous research efforts have been devoted to the synthesis of efficient sensitizing ligands. On the other hand, various deactivation pathways also determine the overall quantum yield of lanthanide luminescence. Detailed results on the importance of deactivating LMCT processes for Eu^{III} complexes of several ligands with terpyridine and bis(benzimidazole)pyridine core, respectively have recently been published.[1] These studies are now being extended to two other derivatives of terpyridine, namely ligands **I** and **II**. Upon complexation, the bulky *t*-butyl groups in **I** are expected to point away from the metal center whereas the pinene moieties in **II** are expected to lead to a sterically demanding environment. The measured stability constants with representative lanthanide ions (La^{III}, Eu^{III} and Lu^{III}) corroborate these assumptions. These results as well as photophysical properties of Eu^{III} and Tb^{III} complexes with **I** and **II** will be discussed.

I



II



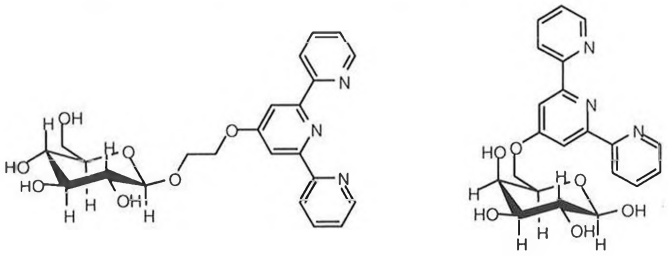
[1] Petoud, S.; Bünzli, J-C.G; Glanzmann, T.; Piguet, C.; Xiang,Q.; Thummel, R.P. *J.Lumin.* **82**, 69, (1999).

Inorganic and Coordination Chemistry **73**

Sweet Ligands, Bitter Complexes: Sugar-functionalized 2,2':6',2"-Terpyridines

Edwin C. Constable, Catherine E. Housecroft and Stefan Mundwiler

Institut für Anorganische Chemie, Spitalstrasse 51, 4056 Basel



We are interested in the influence of metal complexes on the recognition abilities of biomolecules. Therefore, glucose- and galactose-derivatives, covalently linked to 2,2':6',2"-terpyridine, and their iron(II) and ruthenium(II)-complexes were synthezised.
Their properties were tested by enzymatic reactions characteristic of the sugar substituents: β-glucosidase was used for the glucose-derivatives, galactose dehydrogenase for the galactose-derivatives.
The metal complexes do not undergo enzymatic reactions, although the free ligands do. The metal complex of the galactose-derivative inhibits galactose dehydrogenase.

Inorganic Chemistry **74**

Thermally Induced Spin State Transition in Cationic 16e⁻ Tungsten(IV) Complexes

Christian Cremer and Peter Burger*

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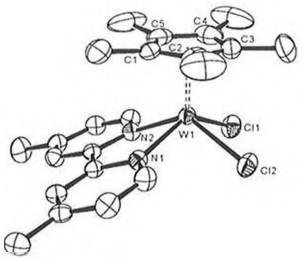
8057 Zürich, Switzerland

The synthesis and magnetic behavior of the novel 16e⁻ tungsten(IV) complexes $[Cp^*W(R_2bipy)Cl_2]^+(BPh_4^-)$, where R_2bipy is a 4,4'-disubstituted bipyridine donor, will be reported.[1] The cationic complexes have a pseudo square pyramidal structure with an open coordination site trans to the Cp* ligand (see below for R=Me). Both complexes are paramagnetic, displaying a strong deviation of the temperature dependence of their magnetic moment from the Curie law. The magnetic behavior is attributed to a thermally induced high-spin low-spin crossover with a singlet ground state. The energy gap between the two spin states was determined in solution from the temperature dependence of the ^{1}H NMR shifts using the van Vleck equation. The results indicate a strong influence of the bipyridyl substituent R on the high-spin low-spin energy gap, which is supported by DFT calculations.



[1] C. Cremer, P. Burger, *J. Chem. Soc., Dalton Trans.* in press.

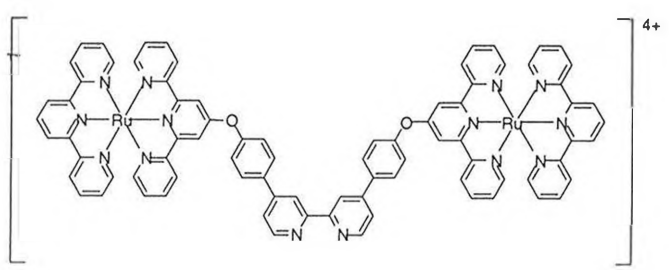
Inorganic Chemistry **75**

Heptanuclear metallostars

Edwin C. Constable, Catherine E. Housecroft and Ingo Poleschak

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

Metal-directed self-assembly has been used in a convergent approach to generate heptanuclear metallostars. The synthesis of ligand **1** and the formation and characterization of $[Ru(\mathbf{1})_3]^{14+}$ will be discussed.



(1)

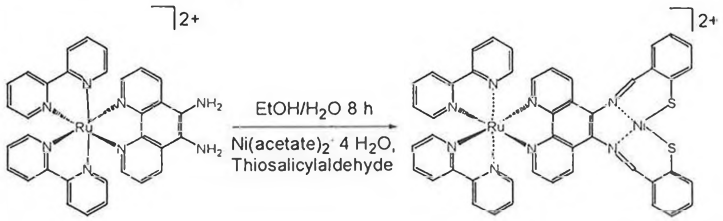
Anorganische Chemie und Koordinationschemie **76**

Synthesis and Properties of a Heterodinuclear Coordination Compounds

Peter Comba, Kyaw Naing, Alexander Peters

Universität Heidelberg, Anorganisch-ChemischesInstitut,
Im Neuenheimer Feld 270, 69120 Heidelberg

Synthesis, structures and electronic properties of heterodinuclear transition metal compounds with a ruthenium bis-bipy (phen) and a tightly linked second chromophor, such as the phen-5,6-linked $Ni^{II}N_2S_2$ center shown in the figure below.



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Inorganic and Coordination Chemistry **77**

Stereoselective Synthesis of Chiral Building Blocks for Nanoscale Polynuclear Coordination Species

Liam M. Gilby and Alex von Zelewsky

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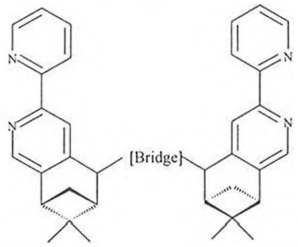
New ligands of the tetradentate chiragen group have been synthesised and characterised. They are predisposed to coordinate to Ru(II) metal centres with a predetermined absolute helical configuration.

These ligands form the basis of chiral building blocks, of the form $Ru[CG(bridge)]X_2$, X = monodentate ligand), which are suitable for forming stereochemically defined polynuclear coordination species. The physical properties of the oligomers can then be investigated, in particular,

i) effects of the chirality on photoinduced intramolecular energy and electron transfer within the supramolecular arrays,
ii) interactions with biological substrates,
iii) the properties of nanometer arrays containing luminescent and paramagnetic centres.

By judicious choice of bridging moiety we can control the steric demands of the metal centre and ultimately the formation of nanometer-sized, configurationally-defined oligonuclear metal complexes.



Inorganic and Coordination Chemistry **78**

Metal Complexes with New Chiragens Type Ligands

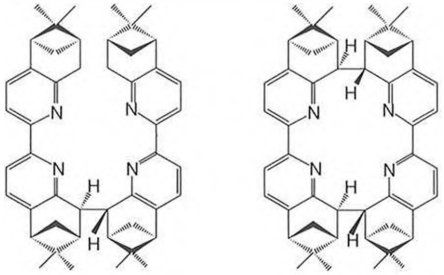
Danut Bilc, Olimpia Mamula, Alex von Zelewsky
Institute of Inorganic and Analytical Chemistry, University of Fribourg, Pérolles; Fribourg,
CH-1700, Switzerland

The chiralized bipyridine ligands have found widespread interest in coordination chemistry. It has been shown that the bis-bipyridine pinene ligands (Chiragens) connected through a bridge:

(i) predetermine the chirality of complexes containing metal centers with various coordination geometry.[1]

(ii) form, via self-assembly processes, multinuclear highly organized species.[2,3]

We present here new members of the Chiragen family containing the two bis-pinenebipy moieties directly connected. These ligands are very interesting for the control of the chirality at tetrahedral metal centers [**I**] but also as potential macrocyclic coordinating units [**II**] with various metal ions.



I **II**

[1] Hayoz, P.; von Zelewsky, A; Stoeckli-Evans, H.; *J. Am. Chem. Soc.* **1993**, *115*, 5111.
[2] Mürner, H.; Belser, P.; von Zelewsky, A.; *J. Am. Chem. Soc.* **1996**, *118*, 7989.
[3] Mamula, O.; von Zelewsky, A; Bernardinelli, G.; *Angew. Chem Int. Ed.* **1998**, *37*, 290.

Inorganic and Coordination Chemistry **79**

Chiral Polynuclear Architecture with Palladium(II) and Platinum(II) Bipyridine Complexes

Dominique Suhr and Alex von Zelewsky

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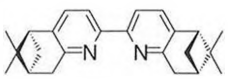
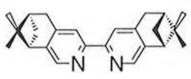
Starting with different chiral bipyridine type ligands, attemps to obtain chiral squares have been investigated following the model of Fujita [1]. The corners are Platinum or Palladium complexes with the following pineno-fused bypiridines.

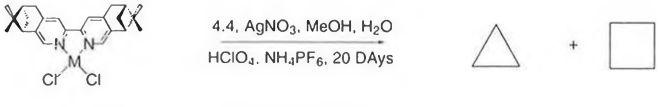


b(5,6)pinenebipy



b(4,5)pinenebipy

Leading to the same proposition made by Fujita, and according to the mass spectra, the reaction medium yields to a mixture of squares and triangles.



M= Pt, Pd

The resulting mixtures have been analyzed by ^{1}H-NMR (Cosy-2D, Spectra at different temperature) and ^{13}C-NMR (Hetcor), mass spectrometry (ESI). All attemps to get crystals suitable for X-Ray structure determination. were for the moment unsuccessful

[1] M. Fujita et al., Chem. Comm., (1996), 1535-1536.

Inorganic and Coordination Chemistry **80**

η^3-Allyl Palladium(II) Complexes with Chiral Bipyridine Ligands : Synthesis and Characterization

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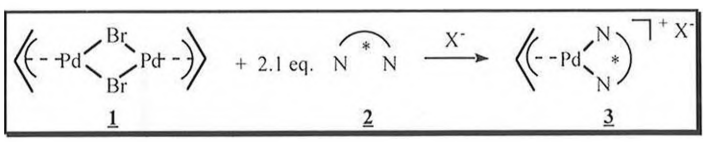
Allyl palladium complexes with chiral bipyridine ligands have been prepared. The natural products α-pinene and myrtenal have been used as source of chirality. A variety of counterions (X^- = Br^-, PF_6^-, $CF_3SO_3^-$), leading to different solubility, could influence the activity of the complexes (**3**).

Starting with bromide derivatives, prepared at low temperature in tetrahydrofuran by treatment of di-μ-bromobis[η^3-2-propenyl]-dipalladium(II) (**1**) with 2.1 equivalents of ligand (**2**), we have synthesized hexafluorophosphate complexes by adding at room temperature an aqueous solution of NH_4PF_6. Triflate salts have been obtained in excellent yield by reaction of $[Pd(\eta^3\text{-}C_3H_5)Br]_2$ with 2 equivalents of ligand and silver triflate in dichloromethane at room temperature.



1 **2** **3**

The complexes have been characterized by ^{1}H- and ^{13}C-NMR, mass spectrometry, elemental analysis and some of them by X-ray diffraction.

CHIMIA 1999, 53, No. 7/8

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Protonation of Chiral Bipyridin Ligands

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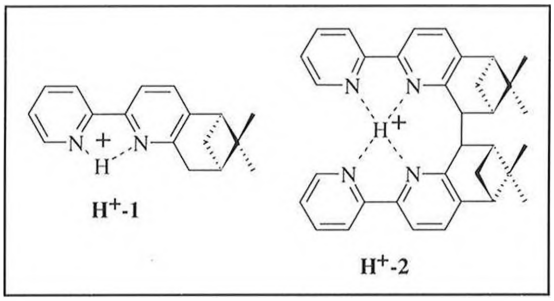
We are interested in the protonated forms of chiral Pinenbipyridine-Derivatives such as 5,6 Pinenbipyridine (**1**) or 5,6-Chiragen[0] (**2**).
Both of these two ligands show a large shift of the peaks in the UV-Spectrum following protonation with a strong acid (hydrochloric acid, trifluoracetic acid).
The CD-Signal of the 5,6-Chiragen[0] (**2**) shows an increase of intensity upon protonation, due to a change of the conformation.
The 5,6-Chiragen[0] (**2**), which has most probably a chirally "chelated" proton will be tested in enantioselective protonation reactions [1].

[1] C. Fehr, *Angew.Chem. Int. Ed. Engl.*,**1996**, *35*, 2566-87.



Inorganic and Coordination Chemistry Chemistry **82**

Asymmetric Ruthenium- and Molybdenum catalyzed Epoxidations

D. Lötscher and A. von Zelewsky

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Balavoine et al. [1] showed that it is possible to carry out stereospecific epoxidations in a two-phase system (H_2O/CH_2Cl_2) catalyzed by Ruthenium and bipyridine as the ligand. We are interested in realizing asymmetric epoxidations using chiral bipyridines such as **1**. (Fig. 1)

According to Thiel's procedure [2] we synthesized a hepta-coordinated Oxobisperoxo-Mo-complex **2** with bis-4,5-pinenebipyridine as the ligand. This complex is now tested in the catalytic epoxidation of cyclooctene and in asymmetric catalysis. (Fig. 2)

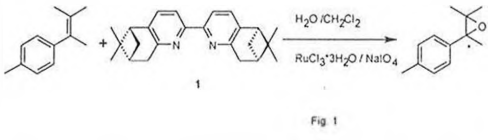

Fig. 1

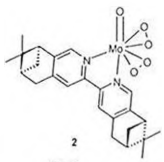

Fig. 2

[1] G. Balavoine, C. Eskenazi, F. Meunier, H. Rivière, *Tetrahedron Lett.*, **1984**, *25*, 3187
[2] W.R.Thiel, J. Eppinger, *Chem.Eur.J.*, **1997**, *3*, 696

Coordination Chemistry **83**

A strong π-acceptor ligand for energy and electron transfer studies in Ru and Os diads

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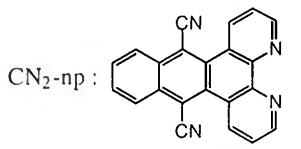
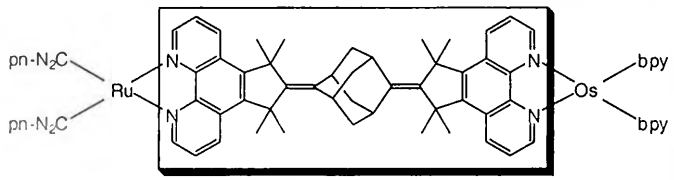
The novel CN_2-np ligand has a very low energy lying ^{3}IL state intrinsic of the dicyanoanthracene unit, which gives rise to a strong π-acceptor character of the ligand and to peculiar properties of the corresponding Ru(II) complexes [1]. For such properties, CN_2-np can be used for investigation of energy and electron transfer processes occuring between Ru(II) and Os(II/III) metal centers linked by the PAP [2] bridging ligand.





PAP

[1] G. Albano, P. Belser, L. De Cola, *Chem. Comm.* **1999**, in press.
[2] S. Bernhard, P. Belser, *Synthesis* **1996**, 192.

Coordination Chemistry **84**

Intra and Intermolecular Energy and/or Electron Transfer in Ruthenium(II) Complexes

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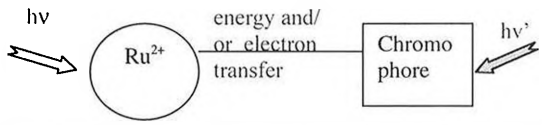
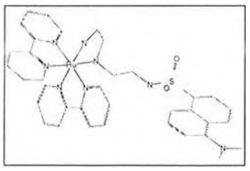
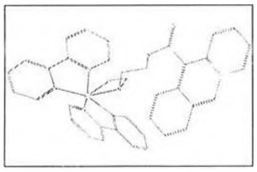
There is a great interest in Ruthenium(II)-bis-bipyridyl complexes as models for the study of photophysical and photochemical processes.[1]



We report the synthesis and characterization of new Ruthenium(II)-bis-bipyridyl complexes, which are covalently linked to the organic chromophores, 5-dimethyl-amino-1-naphtalene sulfonyl (dansyl) and anthracene. Preliminary results on the energy and/or electron transfer processes in these systems will be given and compared with the corresponding intermolecular processes.





[1] Luisa De Cola, Vincenzo Balzani, Peter Belser, Roland Dux and Marcel Baak, ***Supramolecular Chemistry***, vol.5, **1995**, 297-299.

Inorganic and Coordination Chemistry **85**

The Synthesis and Coordination Chemistry of 1,10-phenanthroline-5,6-diolate, a Versatile Bis-Bidentate Ligand for the Synthesis of Three-Dimensional Polynuclear Systems

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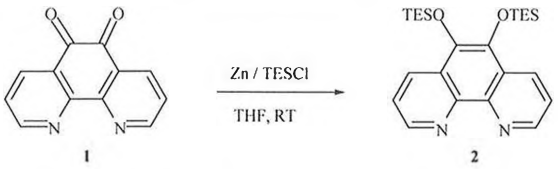
Universität Bern, CH-3012 Bern, Switzerland

There is currently a great interest in the study of electron- and energy-transfer in polynuclear complexes bridged by rigid spacers. Molecular building blocks consisting of fused aromatic rings with two available coordinating sites, are promising building blocks for the assembly of π-conjugated three-dimensional multinuclear systems. One example of such a ligand is 1,10-phenanthroline-5,6-dione (phendione) **1**. Phendione, also possesses an interesting redox chemistry which can be further exploited, since it can be readily converted by one electron reduction to the semiquinone, or by two electron reduction to the catechol. The catechol donor site of phendione can be temporarily rendered inert by protection with a TES (triethylsilyl) group. The synthesis of the protected ligand **2** together with a preliminary investigation of its coordination chemistry will be discussed. Deprotection of the catechol binding site provides us with a new versatile building block that has a dual coordinating ability. The use of this ligand as a rigid spacer in the controlled design of polymetallic supramolecular structures will also be presented.



1 2

TESCl = triethylsilyl chloride

Inorganic and Coordination Chemistry **86**

The Introduction of a 1,10-Phenanthroline-5,6-Diimine Bridge into the Chemistry of Oligomeric Tris Diimine Ruthenium(II) Complexes

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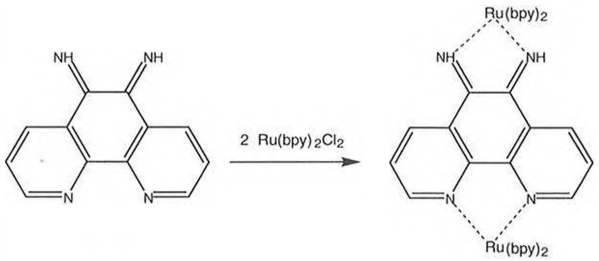
Universität Bern, CH-3012 Bern, Switzerland

Oligonuclear polypyridyl Ru(II) complexes are currently under intense study because their rich electrochemical and photochemical properties render them attractive systems for several applicative purposes. Planar rigid polyaromatic bridges are very convenient as building blocks for the construction of polynuclear metal complexes since they behave as connectors for long-range energy- and/or electron-transfer processes in an optimised and known geometry. This work introduces a new bis-coordinate bridging ligand which allows us to exploit for the first time metal-ligand interactions via 5,6-diimine bridges. The synthesis and coordination chemistry of **1** will be reported, together with a preliminary investigation of the electrochemical and photophysical consequences of introducing this novel metal-diimine linkage **2** into supramolecular polymetallic systems.



1 2

Inorganic Chemistry **87**

Metal ion catalyzed hydroxylation with carboxylates as ligands

Wim Buijs[1], Peter Comba[2], Danny Corneli[2]

[1] DSM Research, P.O. Box 18, 6160 MD Geleen, Netherlands,

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

Selective oxidations of hydrocarbons in the liquid phase are a major challenge in fundamental and applied research. Generally free radical chain mechanisms dominate and only in specific cases (xylenes, toluenes) a high selectivity is obtained A lot of approaches have been proposed to overcome these problems, with limited success. We try to avoid free radical chain oxidations using two or more metal ions to oxygenate hydrocarbons. Starting point for our studies is the Dow Phenol process.

We studied the influence of apical ligands in paddle-wheel structures (see Figure1) containing N-donors. When the compounds are heated in a closed silica tube the normal decomposition of the complex was not disturbed by the presence of substituted pyridine donors. Interestingly, the use of 2-bromopyridine as apical donor leads to the complete reduction to pyridine (HPLC analysis).

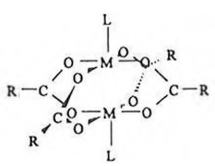


Figure1. Metal carboxylate (paddle-wheel structure); M=Cu, L = N-donor ligand

Inorganic Chemistry **88**

Spectroscopic and redox properties of amicyanin mutants with modified C-terminal loops

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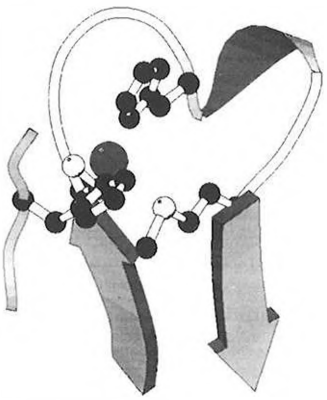
a) Leiden Institute of Chemistry, Gorlaeus Laboratiories, 2300 RA Leiden, The Netherlands

b) Anorganisch-Chemisches Institut, Universitaet Heidelberg, D-69120 Heidelberg



C-terminal loop of rusticyanin

Blue copper proteins (Cupredoxines) are redox proteins which are involved in the electron transfer in the respiratory chain of several organisms. A new loop mutant based on the amicyanin of paracoccus versutus with a C-terminal loop based on rusticyanin from thiobacillus ferroxidans has been expressed. Dynamic and structural characteristics of the new mutant have been studied by UV-Vis, EPR, NMR and cyclic voltammetry. These data are compared with those of the wt proteins and other amicyanin loop mutants. These include loop lengths from 5 to 13 amino acids between the coordinating cysteine and methionine ligands.

Anorganische Chemie und Koordinationschemie **89**

Intramolecular Equilibria in Metal Ion Complexes of Adenosine 5'-Diphosphate (ADP^{3-}) and Adenosine 5'-Triphosphate (ATP^{4-})

Emanuela M. Bianchi, S. Ali A. Sajadi, Bin Song, and Helmut Sigel

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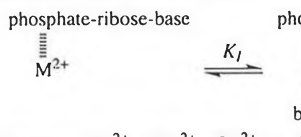
Adenine (and guanine) nucleotides are at the crossroad of many biological events, which in general also involve metal ions [1]. While the metal ion-binding properties of nucleoside mono- and triphosphates are relatively well studied [2], the corresponding knowledge on nucleoside diphosphates is scarce. Our recent achievement [3] in establishing log K^{M}_{ML} *versus* pK^{H}_{HL} plots for simple diphosphate monoesters (L), R-O-P(O)$_2^-$-O-PO_3^{2-}, where R represents a non-coordinating residue, allowed us now to study the extent of macrochelate formation of the complexes formed in aqueous solution (25°C; I = 0.1 M, $NaNO_3$) between Mg^{2+}, Mn^{2+}, Cu^{2+} or Zn^{2+} (M^{2+}) and adenosine 5'-diphosphate (ADP^{3-}) as well as Mg^{2+} or Zn^{2+} and guanosine 5'-diphosphate (GDP^{3-}). The macrochelates form by the interaction of the phosphate-coordinated metal ion with N7 of the purine residue; their formation degree reaches 13±9%, 22±8%, 51±6% and 26±7% for the $M(ADP)^-$ complexes of Mg^{2+}, Mn^{2+}, Cu^{2+} and Zn^{2+}, respectively. The corresponding values for the $M(ATP)^{2-}$ species (in the same order) are 11±6%, 17±10%, 67±2% and 28±7% [4]. Hence, the extent of nucleobase-backbinding of a phosphate coordinated metal ion is significant in both series of adenine nucleotides and comparable to results obtained for the Mg^{2+} and Zn^{2+} complexes of GDP^{3-} which are 21±10% and 63±4%, respectively.



Supported by the Swiss National Science Foundation.

[1] A. Sigel and H. Sigel (Eds.), "Interactions of Metal Ions with Nucleotides, Nucleic Acids, and Their Constituents", *Volume 32* of *Metal Ions in Biological Systems*; Dekker, New York, 1996, pp. 1-814.
[2] H. Sigel and B. Song, *Met. Ions Biol. Syst. 32* (1996) 135-205.
[3] S. A. A. Sajadi, B. Song, F. Gregáň, and H. Sigel, *Inorg. Chem. 38* (1999) 439-448.
[4] H. Sigel, *Eur. J. Biochem. 165* (1987) 65-72; *Chem. Soc. Reviews 22* (1993) 255-267.

Anorganische Chemie und Koordinationschemie **90**

Cisplatin Coordinated to N1 or N7 of 9-Methyladenine (9MeA). Its Acidifying Properties on the $(N7)H^+$ or $(N1)H^+$ Sites

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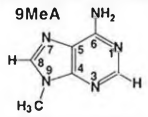
[a] *Inst. Inorg. Chem., University, Spitalstr. 51, CH-4056 Basel, Switzerland*
[b] *Dept. of Chem., University, Otto-Hahn-Str. 6, D-44227 Dortmund, FRG*

Cisplatin, *cis*-$(NH_3)_2PtCl_2$, a powerful antitumor agent, coordinates as *cis*-$(NH_3)_2Pt^{2+}$ to nucleobases of DNA and this fact has fostered considerable interest in nucleobase-metal ion interactions [1]. We report now on the acid-base properties of the complexes resulting from the coordination of *cis*-$(NH_3)_2Pt(1\text{-MeC})^{2+}$, where 1-MeC = 1-methylcytosine, to the N1 or N7 sites of 9MeA. The corresponding acidity constants were calculated from ^{1}H-NMR shift data [2] and those of $H_2(9MeA)^{2+}$ from UV spectrophotometric and potentiometric pH titrations (25°C; I = 0.1 M, $NaNO_3$). From the results (Table) it is evident that Pt^{2+} coordinated at N7 acidifies the $(N1)H^+$ site, as one would expect (Δ p$K_{a/N1}$ = 2.17). This contrasts with the apparent basicity enhancement of the N7 site if Pt^{2+} is at N1. However, the latter comparison rests on the pK_a values of $H_2(9MeA)^{2+}$; i.e., on the deprotonation of $(N7)H^+$ in a situation where N1 is also protonated. The valid comparison has to be made with the H·9MeA$^+$ tautomer in which the proton is at N7 and N1 remains free; we have now estimated this micro acidity constant based on data published earlier [3] for adenosine: $pk^{N7\text{-}N1}_{H\cdot N7\text{-}N1(9MeA)}$ = 2.43±0.30. Application of this value in the comparison gives Δ p$K_{a/N7}$ = (2.43±0.30) – (0.45±0.09) = 2.0±0.3; a value identical to the one given above for the $(N1)H^+$ deprotonation. Hence, the acidifying effect of Pt^{2+} coordinated at N1 on the $(N7)H^+$ site equals that of N7-coordinated Pt^{2+} on $(N1)H^+$.



Acid	pK_a of $(N7)H^+$	pK_a of $(N1)H^+$	Δ pK_a
$H_2(9MeA)^{2+}$	–0.37±0.06	4.10±0.01	
cis-$(NH_3)_2Pt(1\text{-MeC})(H;9MeA\text{-}N7)^{3+}$		1.93±0.08	2.17±0.08
cis-$(NH_3)_2Pt(1\text{-MeC})(H;9MeA\text{-}N1)^{3+}$	0.45±0.09		–0.82±0.11

Supported by the Swiss National Science Foundation, the Swiss Fed. Office for Education & Science (COST D8), the Novartis Foundation (formerly Ciba-Geigy-Jubilee Found.), and the 'Deutsche Forschungsgemeinschaft'.

[1] H. Sigel and B. Lippert, *Pure Appl. Chem. 70* (1998) 845-854.
[2] R. Beyerle-Pfnür, B. Lippert, et al., *Inorg. Chem. 24* (1985) 4001-4009.
[3] R. B. Martin, *Met. Ions Biol. Syst. 32* (1996) 61-89.

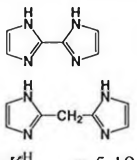
Anorganische Chemie und Koordinationschemie **91**

Comparison of the Metal Ion-Binding Properties of 2,2'-Biimidazole (BiIm) and Bis(imidazol-2-yl)methane (BiImM)

Rolf Griesser,[a] Larisa E. Kapinos,[a] Arati Saha,[b] Nityananda Saha,[c] and Helmut Sigel[a]

[a] *Inst. Inorg. Chem., University, Spitalstr. 51, CH-4056 Basel, Switzerland*
[b] *Basanti Devi College, Dept. of Chemistry, Calcutta 700 029, India*
[c] *University of Calcutta, Dept. of Chemistry, Calcutta 700 009, India*

The imidazole residue is an abundant metal ion-binding site in biological systems. Therefore, we considered it interesting to learn if the formation of 5-membered chelates, as with BiIm [1], or of 6-membered ones, as with BiImM [2], is favored. The recently established log K^{M}_{ML} *versus* pK^{H}_{HL} straight-line plots [3], which hold for simple imidazole-type ligands like 1-methylimidazole, allow an evaluation of published stability constants (exptl) [1,2] towards the indicated goal. Application of the acidity constants $pK^{H}_{H(BiIm)}$= 5.19 [1] and $pK^{H}_{H(BiImM)}$ = 6.93 [2] to the straight-line equations [3] allows to calculate (calcd) the stability of the $M(BiIm)_{op}$ and $M(BiImM)_{op}$ species in which the ligands are coordinated in a monodentate fashion (op = open form). The difference log Δ_{ML} = log K_{exptl} – log K_{calcd} is a reflection of the increased complex stability due to chelate formation. The results in the Table show that the formation of the 6-membered chelates is favored over the 5-membered ones; this contrasts with the complexes of 2,2'-bipyridine and bis(2-pyridyl)methane, where the 5-membered chelates are more stable. However, it needs also to be noted, that the formation degree of the chelates for all the systems given in the Table exceeds 97%.



M^{2+}/L	log K^{M}_{ML} exptl	log K^{M}_{ML} calcd	log Δ_{ML}
Cu^{2+}/BiIM	6.27±0.12	3.39±0.03	2.88±0.12
Zn^{2+}/BiIm	3.48±0.09	1.88±0.07	1.60±0.11
Cu^{2+}/BiImM	9.64±0.03	4.05±0.03	5.59±0.04
Zn^{2+}/BiImM	5.53±0.03	2.39±0.07	3.14±0.08

Supported by the Swiss National Science Foundation, the Swiss Federal Office for Education & Science (COST D8), and the Novartis Foundation (formerly Ciba-Geigy-Jubilee Foundation).

[1] I. Török, P. Surdy, T. Gajda, et al., *J. Inorg. Biochem. 71* (1998) 7–14.
[2] K. Várnagy, I. Sóvágó, et al., *J. C. S. Dalton Trans.* (1994) 2939-2945.
[3] L. E. Kapinos, B. Song, H. Sigel, *Inorg. Chim. Acta 280* (1998) 50-56.

Anorganische Chemie und Koordinationschemie **92**

Chelate Effect in the Gas Phase

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Table 1 lists thermodynamic data for the addition of bidentate ligands L–L to $Ni(tmhd)_2$ (reaction (1)) in the gas phase and in toluene.

$$Ni(tmhd)_2 + L\text{–}L \rightarrow Ni(tmhd)_2(L\text{–}L) \qquad (1)$$

tmhd: 2,2,6,6-tetramethyl-3,5-heptanedionate.
L–L: BPY = 2,2'-bipyridine; TEMED = 1,2,-bis(dimethylamino)-ethane (tetramethyletylenediamine); TEMPD = 1,2,-bis(dimethylamino)-propane (tetramethylpropylenediamine); DMAO = dimethylamino-methoxyethyl.

L–L	ΔH_f(550K) kJmol^{-1} (g)	ΔS_f(550K) Jmol^{-1}K^{-1} (g)	ΔG_f(550K) kJmol^{-1} (g)	ΔG_f(298K) kJmol^{-1} calcul. (g)	ΔG_f(298K) kJmol^{-1} measured (l)
BPY	-110	-133	-37	-70	-48
TEMED	-136	-169	-43	-85	-57
TEMPD	-58	-66	-22	-38	-43
DMAO	-114	-167	-22	-64	-42

In the gas phase the entropies of the complex formation with the flexible ligands TEMED and DMAO are the same but the TMED complex is more stable because of the larger bond energy of Ni–N than Ni–O.
In the gas phase as well as in solution the complexes with TEMPD and DMAO have similar stabilities, i.e. the smaller chelate effect of the six membred chelate ring of the TEMPD complex is compensated by the increase in stability of a Ni-N- as compared to a Ni-O-bond in the five membred chelate ring.
ΔG_f(g) extrapolated to 298 K are more negative than ΔG_f(l) measured in toluene (except for TEMPD). This indicates that the solvation energies of the reactants are more negative than the solvation energies of the products.

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FORMATION AND DECOMPOSITION OF $[N(C_2H_5)_4]_3[Co(CN)_5(OONO)]$

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Nitrogen monoxide ($NO^{\bullet}$) reacts at a diffusion-controlled rate with superoxide ($O_2^{\bullet-}$) to yield peroxynitrite ($ONOO^-$). As shown recently, $NO^{\bullet}$ reacts with the coordinated dioxygen of haeme in oxyhaemoglobin, which has a superoxide-like character. The spectroscopic and kinetic data suggest that the intermediate species in the reaction to methaemoglobin and nitrate is a haemoglobin-peroxynitrite complex [1].

Our complex of interest is tris(tetraethylammonium) pentacyanosuperoxocobaltate(III). The coordination of the dioxygen in the anion $[Co(CN)_5O_2]^{3-}$ is „end-on". The dimerisation to the dinuclear complex ion $[(CN)_5CoOOCo(CN)_5]^{6-}$ is suppressed by the bulkiness of the cations [2]. The red solution of $[Co(CN)_5O_2]^{3-}$ in acetonitrile absorbs one equivalent of $NO^{\bullet}$, while the colour changes from red to yellow at the end of the reaction. The UV/VIS-spectrum shows a shoulder at 279 nm, which can be assigned to coordinated peroxynitrite. The absorption shoulder is disappears in one hour. The rate constant is in the range of (3.5-4.0) x 10^{-3} s^{-1}.

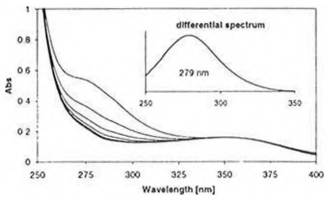

Figure 1: The spectra show the decrease of the shoulder at 279 nm after 0 min, 3.5 min, 7 min, 10.5 min, 15.5 min and 45.5 min.

[1] Herold, S., FEBS Letters, **1999**, *443*, 81-84
[2] White, D.A. et al., Inorg. Chem., **1972**, *11*, 2160-2167

94

REACTION OF PEROXYNITRITE WITH CARBON DIOXIDE

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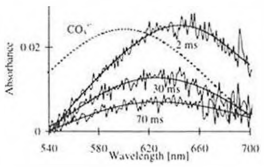
At alkaline pH, peroxynitrite reacts with carbon dioxide [1]. We detected a transient absorption with a broad maximum at 640 nm within 2 ms upon mixing peroxynitrite with excess carbon dioxide [2]. The absorption at 640 nm cannot be due to carbon dioxide hydrogencarbonate(1-), carbonate or even nitrogen monoxide, nitrogen dioxide, dininitrogen trioxide or dinitrogen tetraoxide. We therefore assign the 640 nm absorption to the adduct, 1-carboxylato-2-nitrosodioxidane.

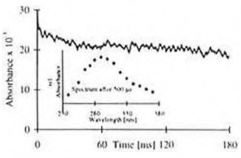


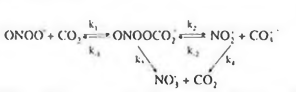
This absorption decreases while the maximum shows a blue-shift. The shift to lower wavelength suggests formation of trioxocarbonate(1-) radicals (dashed line of Fig. 1). This conclusion is strengthened by the observation of a weak ESR signal at g = 2.013.

In the presence of nitrogen monoxide, which scavenges trioxocarbonate(1-) as well as nitrogen dioxide radicals, the absorption at 640 nm was still detected, but without a shift to lower wavelenths.

The decay of the absorption at 640 nm, takes place in about 100 ms and therefore, its lifetime is much longer than it has been estimated before.

Trioxocarbonate(1-) and nitrogen dioxide radicals are conveniently produced by pulse radiolysis of dinitrogen saturated solutions of nitrite and carbonate. Our experiments revealed the formation of a species that absorbs at 300 nm (Fig. 2, Inset). During the experimentally accessible window of 400 ms, this absorption remained fairly stable. This absorption may be due to peroxynitrite, the yield of which is on the order of 25%, relative to the trioxocarbonate(1-) radical.





Our results indicate that the reactions of peroxynitrite and carbon dioxide can be described by two consecutive equilibria, see Scheme.

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[2] Meli, R. et al., *Helv. Chim. Acta.* **1999**, *82*, 722.

Anorganische Chemie

95

Kinetic and Mechanistic Studies of the Reaction between Oxymyoglobin and Peroxynitrite

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It has been shown that peroxynitrite can diffuse through the erythrocyte membrane and react with oxyhemoglobin ($HbFeO_2$) to yield methemoglobin ($HbFe^{III}$)[1]. As the rate constant for this reaction is large, it represents one of the major pathways of peroxynitrite degradation *in vivo*. Interestingly, $HbFe^{III}$ does not seem to react with peroxynitrite.

We have studied the reaction between oxymyoglobin and peroxynitrite by stopped-flow spectroscopy. The presence of more than one isosbestic point in the time resolved absorption spectra indicates that the reaction proceeds via an intermediate. Detailed kinetic studies suggested that the intermediate species is ferryl myoglobin ($MbFe^{IV}$=O). In a second step $MbFe^{IV}$=O reacts with a further equivalent of peroxynitrite to yield $MbFe^{III}$. To verify this mechanism we studied the reaction of $MbFe^{IV}$=O with peroxynitrite and obtained the same rate constant as for the second step of the reaction between $MbFeO_2$ and peroxynitrite. The observed rate constants for the two steps are both linearly dependent on the peroxynitrite concentration and increase with decreasing pH, which indicates that the protonated form (HOONO) is the reactive species.

Oxymyoglobin is in equilibrium with its deoxygenated form ($MbFe^{II}$; $K_{eq} = 0.92\times10^6\ M^{-1}$)[2]. Preliminary results show that the rate constant for the reaction between $MbFeO_2$ and HOONO increases with decreasing oxygen concentration suggesting that $MbFe^{II}$ is the reactive species. Indeed, we found that also $MbFe^{II}$ reacts with HOONO to $MbFe^{III}$ via the $MbFe^{IV}$=O intermediate.

[1] Denicola, A. et al. *Proc. Natl. Acad. Sci. USA*, **1998**, *95*, 3566-3571
[2] Wan, L. et al. *Proc. Natl. Acad. Sci. USA*, **1998**, *95*, 12825-12831

Anorganische Chemie

96

Voltammetry experiments with peroxynitrous acid

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Reductive linear sweep voltammograms of *in situ* formed peroxynitrous acid and dinitrogen tetraoxide were recorded in a flow/stopped flow electrochemical cell with a gold electrode.

Irreversible reduction currents from peroxynitrous acid were obtained. This signal was used to estimate $E^{\circ\prime}$ for the one-electron reduction of peroxynitrous acid. The signal shifted little between pH = 5.6 and pH = 3.2, which means the reaction must be written as:

$$ONOOH + e^- \longrightarrow OH^- + NO_2^{\bullet}$$

rather than $ONOOH + e^- + H^+ \longrightarrow H_2O + NO_2^{\bullet}$.

The signal was assigned to the reduction of peroxynitrous acid, because the decay rate constant of the wave was 1 s^{-1} at 22-23°C. $NO_2^{\bullet}$ is the most probable reduction product. It rapidly forms N_2O_4 which is reduced again by the electrode and contributes to the total current. N_2O_4 hydrolyzes ($k \approx 10^3\ s^{-1}$), but below pH ≈ 4 it is partially recovered from its hydrolysis product HNO_2 which yields $NO_2^{\bullet}$ again. The current for N_2O_4 reduction sets on at 0.93 V. The calculated value [1] of E° for $N_2O_4 + 2e^- + 2H^+ \longrightarrow 2HNO_2$ is 1.07 V, which implies an overvoltage of 0.14 V for the electrode process. The current onset for ONOOH was at 1.10 V, which leads to an estimate of $E^{\circ\prime}$ = 1.24 V. Extrapolation of the peak shift depending on the sweep rate [2] and Feldberg simulation [2] of the signal suggest $E^{\circ\prime} \approx 1.1 - 1.2$ V. A conservative estimate of the upper limit is $E^{\circ\prime} \approx 1.3$ V, a value compatible with the observed redox chemistry of peroxynitrous acid.

[1] Pourbaix, M., Atlas of Electrochemical Equilibria in Solution, Natl. Assoc. Corrosion Eng. / Centre Belge d'Etude de la Corrosion, 1974.
[2] Bard, A. J. and Faulkner, L. R., Electrochemical Methods, Wiley and Sons, 1980.

Anorganische Chemie **97**

The odd stochiometry of iodide oxidation by peroxynitrous acid

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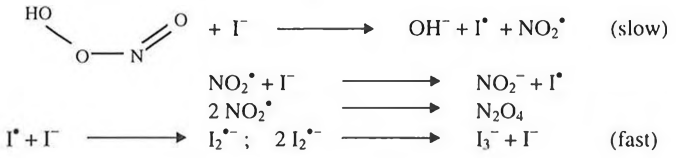
Peroxynitrous acid, a powerful oxidant generated in living organisms by the rapid recombination of nitrogen monoxide with the superoxide ion, has been tested with many biological reductants. The redox mechanism remains a puzzle because of the strange stochiometries.

Iodide oxidation produced equally inconsistent results [1]. Below an iodide concentration of 10 mM only 0.5 equivalents of I^- appeared to be oxidized to I_2. Above 10 mM I^-, about 1.5 equivalents were converted. The authors concluded [2] that radical chain reactions must take place. This is in stark contrast to other peroxides which are determined by iodometry because of their neat 2-electron oxidations of iodide. For comparison, we studied a range of 0.5 to 50 mM [I^-]. We found 0.82 to 0.93 equivalents oxidized at I^- concentrations below 10 mM and 1.4 to 1.5 equivalents above 10 mM [I^-], and always the same rate constant. Since peroxynitrous acid also isomerizes at acidic pH, the results suggests a 1:1 stochiometry in the rate-determining step which is followed by a faster second oxidation caused by a product of the first step. This product is eliminated by a concurrent reaction when the iodide concentration is low. We propose



[1] S. Goldstein, G. Czapski, *Inorg. Chem.* **34**, 4041 (1995)

[2] S. Goldstein, G.L. Squadrito, W.A. Pryor, G. Czapski, *Free Rad. Biol. Med.* **21**, 965 (1996)

Inorganic Chemistry **98**

Intermediate Peroxynitrito- and Nitrito-Metmyoglobin Complexes

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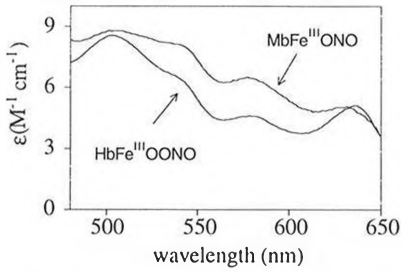
One of the most significant aspects of the NO•–chemistry is its ability to react with the heme centers of a variety of different proteins[1]. A relevant example is the NO•–mediated oxidation of oxy- to methemoglobin, a reaction which is considered to be the major pathway for NO• depletion in the blood vessels. It has been shown that, in analogy to the formation of peroxynitrite by reaction of NO• with $O_2^{\bullet-}$, this oxidation proceeds via an intermediate peroxynitrito–methemoglobin complex ($HbFe^{III}OONO$) which then decays to methemoglobin ($MbFe^{III}$) and nitrate [2]. Another noteworthy example is the NO•–mediated reduction of ferrylmyoglobin ($MbFe^{IV}=O$) to $MbFe^{III}$, which may represent a protective reaction against $MbFe^{IV}=O$ mediated oxidations [3].

We have studied by stopped-flow spectroscopy the reactions of NO• with oxymyoglobin ($MbFeO_2$) and $MbFe^{IV}=O$ in the pH range 5–9.5. In both cases an intermediate species was identified, which corresponds to the peroxynitrito- and the nitrito-metmyoglobin complexes, respectively.

The UV-vis spectra of the two intermediates, obtained at pH 9.5, are similar to that reported for HbFeOONO [2]. In particular, all the spectra display an absorption band around 630 nm which seems to be characteristic for methemoglobin or metmyoglobin complexes with anionic oxygen donor ligands. MbFeOONO decays at a much faster rate than the corresponding hemoglobin intermediate. It can be observed only at pH ≥ 8.5 and even at pH 9.5 it was not possible to obtain a spectrum of the pure intermediate. The nitrito–metmyoglobin complex is significantly more stable.



[1] Radi, R. *Chem. Res. Toxicol.* **1996**, *9*, 828-835. [2] Herold, S. *FEBS Letters* **1999**, *443*, 81-84. [3] Gorbunov, N.V. et al. *Biochemistry* **1995**, *34*, 6689-6699.

Inorganic Chemistry **99**

Investigations on the hydridic behaviour of $WH(NO)(CO)(PMe_3)_3$

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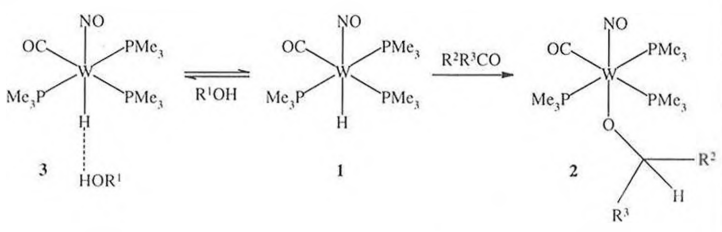
$WH(NO)(CO)(PMe_3)_3$ **1** is synthesized from $W(NO)(CO)(PMe_3)_3(HBH_3)$ in good yield. Its reactivity towards unsaturated compounds was investigated in reactions with various aldehydes and ketones, giving insertion products **2**. $Re_2(CO)_{10}$ can be inserted, as well. However, this reaction turned out to be an equilibrium, for which the thermodynamic data could be determined. In further experiments the hydridic character of the H ligand of **1** was established by its capability to undergo hydrogen bonding interactions. The strength of the H···H interactions in **3** was investigated over a wide range of pK_A values of the alcohols by NMR T_1(min) experiments. In addition H···H interactions with certain chiral alcohols and their NMR effects are reported. These results are compared to those of earlier work carried out in our group [1,2].



[1] Van der Zeijden, A. A. H.; Veghini, D.; Berke, H. *Inorg. Chem.* **1992**, *11*, 5106.

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Inorganic Chemistry **100**

Synthesis and Reactivity of a New Type of Tungsten Hydride Complex

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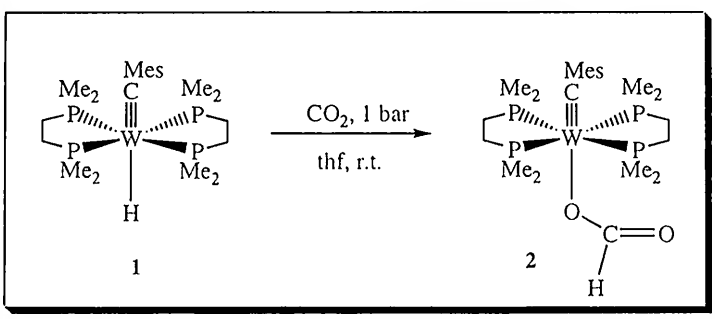
The synthesis of the novel tungsten carbyne hydride complex, $W(CMes)(dmpe)_2H$ (**1**), is reported and the reactivity of its W-H moiety towards small molecules containing unsaturated bonds such as CO, CO_2, propionaldehyde, benzaldehyde and acetone (*e.g* see equation below) is presented [1]. In addition, the hydride complex has been characterized in detail by multinuclear NMR spectroscopy.

In order to compare the trans-influence/effect of the 3-electron donors NO and the carbyne ligand, it is sought to evaluate the chemistry of the analogous nitrosyl hydride.



[1] Ph.D. Thesis, E. Bannwart, University of Zürich, 1997.

Inorganic and Coordination Chemistry **101**

Dioxygen Activation by Five-Coordinate Osmium(II) Complexes

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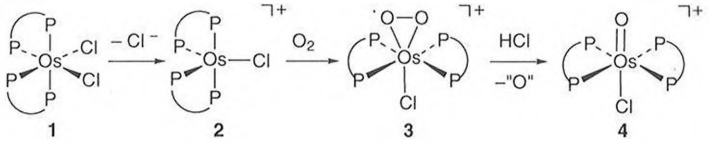
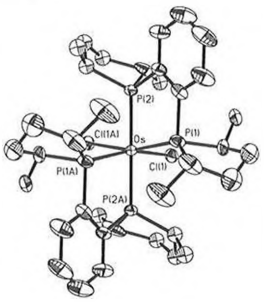
We have recently shown that the dioxygen complex $[OsCl(\eta^2\text{-}O_2)(dcpe)_2]^+$ (**3**) (dcpe=1,2-bis(dicyclohexylphosphino)ethane), formed by reaction of O_2 with the 16-electron species $[OsCl(dcpe)_2]^+$ (**2**) [1], gives the stable oxo complex $[OsCl(O)(dcpe)_2]^+$ (**4**) in the presence of HCl gas [2].



Although a high reactivity is expected for d^4 oxo complexes such as **4**, so far we did not observe oxene transfer from **4** to a number of substrates, including PMe_3. Suspecting that steric factors account for the lack of reactivity, we have studied osmium complexes with other ligands, including 1,2-bis(diethylphosphino)ethane (depe) and the chiral diphosphine duphos. The chemistry of the analogues of **1**-**4** with these ligands will be reported, as well as an X-ray study of *cis*-$[OsCl_2(duphos)_2]$ (**1**), the precursor of five-coordinate $[OsCl(duphos)]^+$ (Figure 1).

Figure 1



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Inorganic Chemistry **102**

Silica Xerogels Containing Bidentate Phosphine Ruthenium Complexes. Textural Properties and Catalytic Behaviour in the Synthesis of *N,N*-Dimethylformamide from Carbon Dioxide

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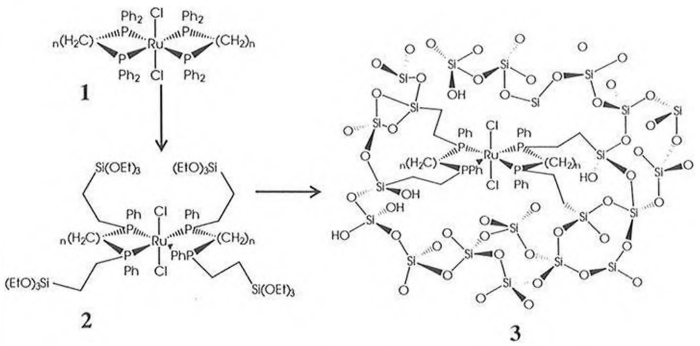
Ruthenium complexes having bidentate phosphine ligands (**1**) were incorporated into an amorphous silica matrix via chemical anchoring using a silylether bridge (**2** → **3**). The integrity of the complexes after immobilization was confirmed by CP/MAS ^{31}P NMR. Amorphous hybrid gels with pores smaller than 4 nm exhibited outstanding catalytic activity in the synthesis of *N,N*-dimethylformamide from supercritical carbon dioxide, hydrogen and dimethylamine. At 100 °C a turnover frequency of 970 h^{-1} was achieved with 100 % selectivity to dimethylformamide [1]. This is the highest activity reported to date for a heterogeneous catalyst. The incorporated ruthenium complexes are stable in air, making them particularly suitable for technical applications.



[1] L. Schmid, O. Kröcher, R.A. Köppel, A. Baiker, *Micropor. Mesopor. Mat.*, in press.

Inorganic Chemistry **103**

Diffusion measurements as a tool for determining the nuclearity of organometallic complexes

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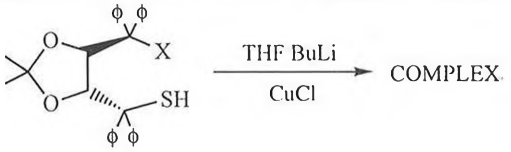
In the identification and characterisation of organometallic compounds one of the first problems concerns the determination of the nuclearity of the complex. A direct, easy and fast technique,[1] which can be used in most cases, involves the diffusion measurements by NMR spectroscopy.
We applied this method to a set of TADDOL ligands and complexes.



X=OMe, OH, NMe_2

We demonstrate that the OH compound exists as a dimer and the other two derivates as monomers. In addition we also show that the copper-complexes are all tetramers.
Other useful applications concern ion pairs in solution, intimate or separated, as well as problems of equilibria between monomers and dimers.

1. P. Stilbs, *Progress in NMR Spectroscopy*, 1987, **19**, 1.

Inorganic and Coordination Chemistry **104**

Ruthenium(II)–Catalyzed Asymmetric Epoxidation with H_2O_2

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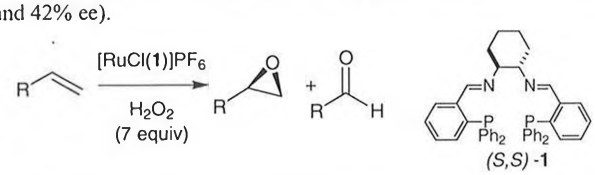
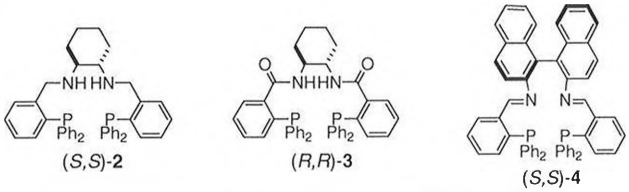
We have recently discovered that cationic ruthenium complexes of the type $[RuCl(PNNP)]^+$ (PNNP = tetradentate P_2N_2 ligand) catalyze the asymmetric epoxidation of olefines with H_2O_2 as oxidant [1]. We find now that the catalytic system formed *in situ* from $[RuCl_2(1)]$ and $TlPF_6$ improves the enantioselectivity and activity (35% styrene conversion after 2 h and 42% ee).



In order to investigate systematically the electronic effects of different N-donors, as well as the steric effects of the chelate bridge, we have prepared the six-coordinate complexes $[RuCl_2(PNNP)]$ with the ligands **2**, **3** [2], and **4** shown below, and are testing them in the asymmetric epoxidation of unfunctionalized olefins. The coordination chemistry and the catalytic properties of the ruthenium derivatives of **2**–**4** will be reported.



[1] R. M. Stoop, A. Mezzetti, *Green Chemistry* **1999**, *1*, 39.

[2] J. X. Gao, T. Ikariya, R. Noyori, *Organometallics* **1996**, *15*, 1087.

Inorganic Chemistry **105**

Ir - Catalyzed Asymmetric Intramolecular Hydroamination

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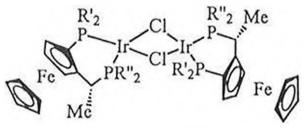
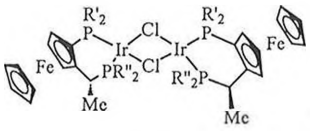
We have previously shown that dinuclear Ir(I) complexes of type **1** are suited catalysts for the addition of aniline to norbornene in the presence of cocatalytic amounts of fluoride.[1]

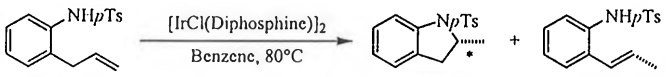


cis - **1**



trans - **1**

We now extended this reaction to substrates capable of intramolecular hydroamination, such as **2**. The corresponding cyclisation product is obtained with enantioselectivities up to 58% ee. However, competing olefin isomerisation remains a major reaction pathway.



2 **3** *cis*, *trans* **4**

The different conditions favoring the hydroamination product will be presented including ligand, solvent and catalyst variations.

[1] a) Bieler, N. H.; Egli, P.; Dorta, R.; Togni, A.; Eyer, M. **1999**, EP 0 909 762 A2. b) Dorta, R.; Egli, P.; Zürcher, F.; Togni, A. *J. Am. Chem. Soc*, **1997**, *119*, 10857

Inorganic and Coordination Chemistry **106**

[IrCl(PIGIPHOS)]: Structure and Reactivity Studies on a Chiral Iridium(I) Complex

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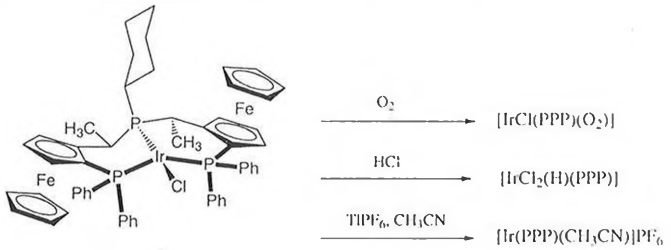
Eidgenössische Technische Hochschule, CH-8092 Zürich

Using the ligand PIGIPHOS [1] we have prepared the chiral iridium(I)-complex **1**. An X-ray study revealed the coordination sphere around Ir to deviate strongly from the ideal square-planar geometry. The *trans*-angles P-Ir-P and P-Ir-Cl amount to 154° and 167°, respectively.



1

In view of current interest in iridium(I) chemistry directed towards catalytic applications, we untertook general reactivity studies of **1**. We found that **1** forms a peroxo complex with air and easily adds acidic H–X-bonds.

We will also report on our continuing studies concerning O–H-bond activation (ROH, H_2O) [2], using **1** as a mononuclear model system.

[1] P. Barbaro, A. Togni, *Organometallics* **1995**, *14*, 3570 – 3573

[2] R. Dorta, A. Togni, *Organometallics* **1998**, *17*, 3423 – 3428. See also: K. Tani, A. Iseki, T. Yamagata, *Angew. Chem.* **1998**, *110*, 3590 – 3593

Inorganic and Coordination Chemistry **107**

Characterization of Catalytically Active Ferrocenyl Dendrimers

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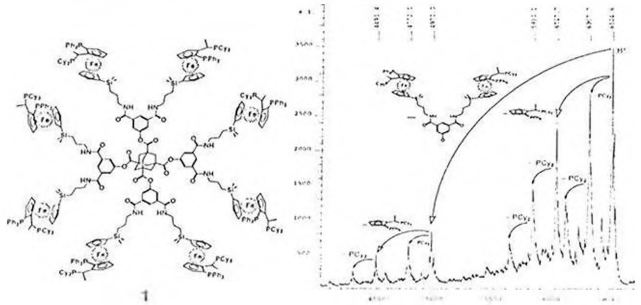
Laboratorium für Anorganische Chemie, ETH-Zürich, CH-8092 Zürich,

Dendrimers containing peripheral catalyst units are of interest in terms of recovering expensive catalysts.[1] As an interface between heterogeneous and homogeneous catalysis, these catalysts react in homogeneous solution and may be recycled by virtue of their molecular size (membrane reactor) and their altered solubility.

We report on the characterization of dendrimers such as **1**[2] with up to 16 diphosphine or phosphine pyrazol units. These organometallic dendrimers were investigated with methods such as two-dimensional NMR techniques, FAB- and MALDI-TOF mass spectroscopy. Unusual fragmentations were found in the MALDI-TOF mass spectra but in most cases the molecular peak could be detected. Combination of MALDI and NMR data leads to an unequivocal characterization of our dendrimers.



1

MALDI-TOF Mass spectra of **1**
calculated mass: 6502.95

[1] a) Knapen, J.W.J.; van der Made, A.W.; de Wilde, J.C.; van Leeuwen, P.W.N.M.; Wijkens, P.; Grove, D.M.; G.van Koten, G. *Nature* **1994**, 372, 659. b) Davies, P.J.; Grove, D.M.; van Koten, G. *Organometallics* **1997**, 16, 802. c) Seebach, D.; Herrmann, G. F.; Lengweiler, U. D.; Amrein, W. *Helv. Chim. Acta* **1997**, 80, 989.

[2] Köllner, C; Pugin, B.; Togni, A. *J.Am.Chem.Soc.* **1998**, *129*, 10274.

Inorganic and Coordination Chemistry **108**

Fluorinated chiral ferrocenyl ligands for Palladium-catalyzed CO/Propene copolymerisation

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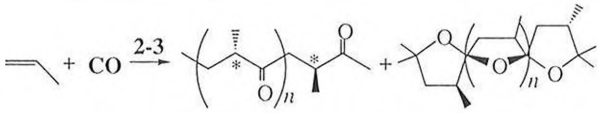
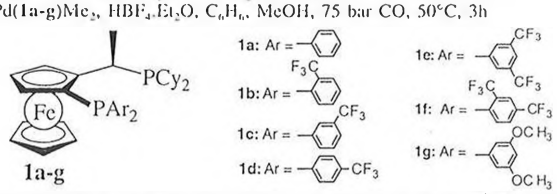
[b] *Laboratorium für Anorganische Chemie, ETH-Zürich, CH-8092 Zürich*

Carbon monoxide/olefin co- and ter-polymerisation reactions yielding alternating copolymers represent a very attractive field of research [1].



2: $Pd(OAc)_2$, **1a-g**, $BF_3.Et_2O$, CH_2Cl_2, MeOH, 75 bar CO, 50°C, 3h
3: Pd(**1a-g**)Me_2, $HBF_4.Et_2O$, C_6H_6, MeOH, 75 bar CO, 50°C, 3h



1a-g

High activities and productivities up to 1050 $g.gPd^{-1}.h^{-1}$ were obtained using ferrocenyl ligands containing peripheral CF_3 groups [2]. Better π-accepting ligands at the Pd centre may cause a lower binding energy with the monomers and render the metal centre more electrophilic [3].

References

[1] a) Drent, E.; Budzelaar, P. H. M., *Chem. Rev.*, **1996**, *96*, 663
b) Bronco, S.; Consiglio, G.; Di Benedetto, S.; Spindler, F.; Togni, A. *Helv. Chim. Acta* **1995**, *78*, 883

[2] a) Schnyder, A.; Togni, A.; Wiesli, U. *Organometallics* **1997**, *8*, 155
b) Pioda, G.; Togni, A. *Tetrahedron : Asymmetry* **1998**, *9*, 3903

[3] Drent, E.; Budzelaar, P. H. M.; van Broekhoven, J. A. M. *Recl. Trav. Pays-Bas* **1996**, *115*, 263

109

Diphosphines with Stereogenic Phosphorus Atoms in the Rhodium-Catalyzed Asymmetric Hydrogenation

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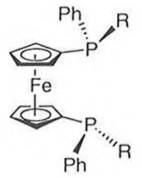
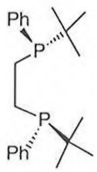
[b] *Novartis Services Ltd, CH-4002 Basel*

The rhodium(I) derivatives of diphosphines **1** and **2** bearing stereogenic P atoms are excellent catalysts for the asymmetric hydrogenation of *N*-alkylated acetamidocinnamates (> 97% ee) [1].

In order to enlarge the scope of these ligands, we are investigating the effects of the variation of the diphosphine bridge and of the substituents at the P atoms. With the aim of introducing alkyl and aryl groups that are symmetric with respect to the rotation about the P–C bond, we extended the procedure described by Jugé [2] to the synthesis of ligands **3** and **4**. These have been already prepared by a different procedure [3,4], but have not been tested in catalysis yet. The asymmetric hydrogenation of olefins with rhodium(I) derivatives of **3** and **4** will be reported.



R= *o*-anisyl (**1**) or 1-naphthyl (**2**)



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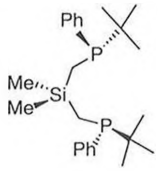

4

[1] F. Maienza, M. Wörle, P. Steffanut, A. Mezzetti, F. Spindler, *Organometallics* **1999**, *18*, 1048.
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Inorganic chemistry

110

Chiral aryl-phosphine complexes of Pd(II). a non-square planar d^8

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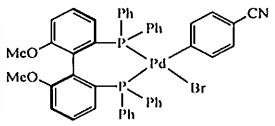
The chiral aryl complexes PdBr(p-NCC_6H_4)(LL) LL=MeO-BIPHEP and p-tol-BINAP have been prepared. The solid state structures of both compounds have been solved by X-ray diffraction.
Complex **1** shows a strong distortion so that its structure can no longer be considered to be square-planar. Complex **2** shows the longest Pd-P bond known so far. These and other structural results will be presented



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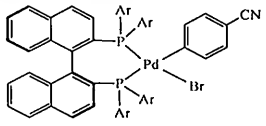
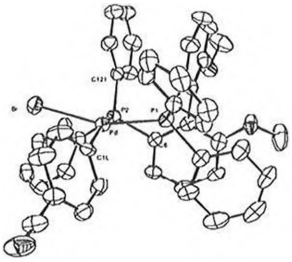


Ar= C_6H_4-4-Me **2**



1

Inorganic Chemistry

111

P-C Bond Splitting in Chiral Ru-Complexes

Carolien den Reijer and P.S. Pregosin

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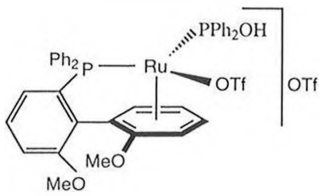
The reactions of $Ru(OAc)_2$(MeO-Biphep) and $Ru(OAc)_2$(BINAP) with CF_3SO_3H in 1,2-dichloroethane at 90°C gave the products **1** and **2** respectively as their triflate (OTf) anions. The new products arise from P-C bond splitting and subsequent arene complexes. Intermediates involving novel mono-dentate phosphinites and the crystal structures of the final products will be described. 2D-NMR (^{31}P-^1H HMQC) spectroscopy was used to identify the PPh_2OH ligand and showed that the 'OH'-group remained on the phosphorus atom.



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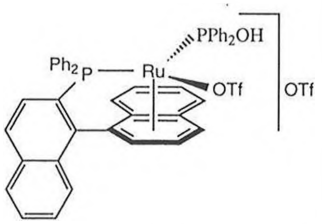

2

Chimie minérale et de coordination

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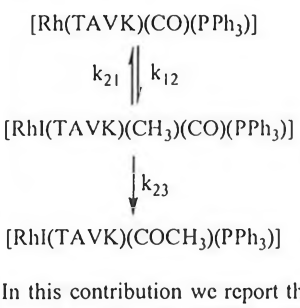
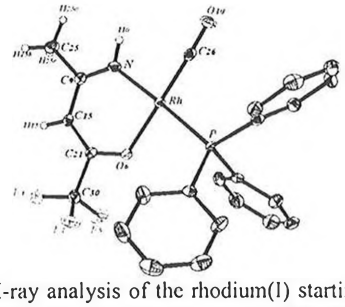
Variable Temperature and Pressure Studies of Oxidative Addition of Methyl Iodide to Aminovinylketonato Carbonyl Phosphine Complexes of Rhodium(I)

S. Detti[1], G. Laurenczy[1], K. Schenk[2], R. Roulet[1], L. Damoense[3], A. Roodt[3]

[1]Institut de Chimie Minérale et Analytique, BCH-Dorigny
[2]Institut de Cristallographie, BSP-Dorigny
Université de Lausanne, CH-1015
[3]Departement of Chemistry, University of the Free Orange State
P. O. Box 339, Bloemfontein 9300, South Africa

Several important industrial processes use rhodium catalysts in oxidative addition reactions. Oxidative addition of methyl iodide to the complexes of the type [Rh(LL')(PR_3)(CO)] where LL' is a mono-anionic bidentate ligand with N, O donor atoms [1], gives Rh(III)-methyl complexes which further rearrange to give the final Rh(III)-acetyl complexes.





In this contribution we report the X-ray analysis of the rhodium(I) starting complex with LL' = TAVK = 1,1,1-trifluoro-4-aminopent-3-en-2-onato (see figure) and a kinetic study of the reaction using variable temperature and pressure FT-infrared spectroscopy.

[1] M. R. Galding, T. G. Varshavasky, S. Yu, L. V. Osetrova, A. Roodt, *Rhodium Express*, 1995, **9**, 36-43.

Inorganic Chemistry **113**

Organometallic metallodendrimers and metallostars

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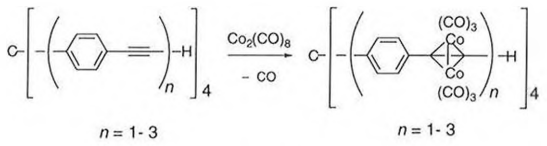
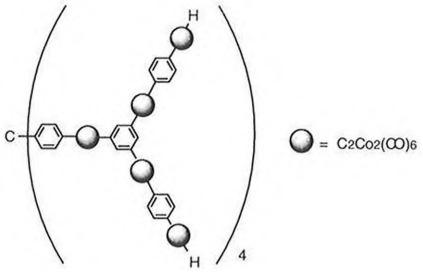
Laboratory for Supramolecular Chemistry, Institute of Inorganic Chemistry, University of Basel, CH-4056 Basel

Polyalkynes with tetrahedral C- or planar aromatic C_6-cores have been synthesized and converted through reactions with $Co_2(CO)_8$ into organometallic metallostars and metallodendrimers.

Examples to be discussed include the metallostar synthesis in Scheme 1, and the metallodendrimer **1**.



Scheme 1



1

Inorganic Chemistry **114**

Reactions of [(MeCp)$_2$Mn(dmpe or tmeda)] with Alkynes: New 17- and 16-Electron Half-Sandwich Manganese Complexes

S. Kheradmandan, H. Schmalle and H. Berke*

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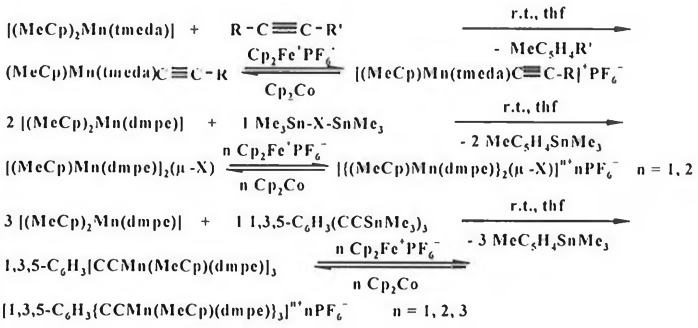
Based on reactions of the manganocene-adduct-complexes [(MeCp)$_2$Mn(dmpe or tmeda)][1, 2] with alkynes, we have prepared new alkynyl Mn(II) complexes. Treatment of either [(MeCp)$_2$Mn(tmeda)] with RC≡CR' (R = C_6H_5-, TMS-C≡C-, TMS-, 'Bu-; R' = H, $SnMe_3$) or [(MeCp)$_2$Mn(dmpe)] with Me_3Sn-X-$SnMe_3$ (X = 1,3- and 1,4-C≡C-C_6H_4-C≡C-) and 1,3,5-C_6H_3(C≡C-$SnMe_3$)$_3$ in thf gave the desired manganese compounds with d^5 configuration in good yields (60-80 %)[3]. The paramagnetic Mn(II) complexes can be reversibly oxidized to Mn(III) species.



[1] Wilkinson et al., *J. Am. Chem. Soc.* **1984**, *106*, 2033-2040.
[2] Berke et al., *Organometallics* **1999**, *18*, 1525-1542.
[3] cf. Berke et al., *Angew. Chem.* **1999**, in press.

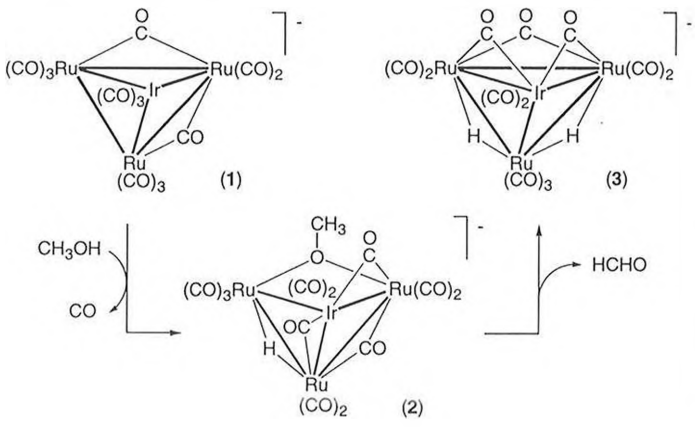
Inorganic and Coordination Chemistry **115**

Fixation and Oxidation of Methanol on a Cluster Framework: The Cluster Anions [HRu$_3$Ir(CO)$_{12}$(OCH$_3$)]$^-$ and [H$_2$Ru$_3$Ir(CO)$_{12}$]$^-$

G. Süss-Fink, S. Haak, C. M. Thomas, A. Neels and H. Stœckli-Evans

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

The anionic mixed-metal cluster [Ru$_3$Ir(CO)$_{13}$]$^-$ (**1**), catalytically active in the carbonylation of methanol [1], reacts with methanol at 70°C to give the cluster anion [HRu$_3$Ir(CO)$_{12}$(OCH$_3$)]$^-$ (**2**), which upon prolonged reaction looses formaldehyde to give the cluster anion [H$_2$Ru$_3$Ir(CO)$_{12}$]$^-$ (**3**).



Both anions **2** and **3** crystallise together as the double-salt [N(PPh$_3$)$_2$]$_2$–[HRu$_3$Ir(CO)$_{12}$(OCH$_3$)][H$_2$Ru$_3$Ir(CO)$_{12}$], the X-ray structure analysis of which reveals a butterfly Ru$_3$Ir skeleton for **2** and a Ru$_3$Ir tetrahedron for **3**.

[1] G. Süss-Fink, S. Haak, V. Ferrand and H. Stœckli-Evans, *J. Chem. Soc., Dalton Trans.* **1997**, 3861; *J. Mol.Catal., A* **(1999)**, in the press.

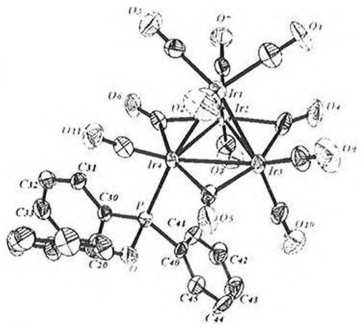
Chimie minérale et de coordination **116**

Solution Dynamics of Phosphite, Phosphinite and Phosphonite Derivatives of Ir$_4$(CO)$_{12}$

S. Detti[1], F. Fiorito[1], G. Laurenczy[1], R. Roulet[1], K. Schenk[2]

[1]Institut de Chimie Minérale et Analytique, BCH-Dorigny
[2]Institut de Cristallographie, BSP-Dorigny
Université de Lausanne, CH-1015

The dynamic behaviour of mono- and di-substituted phosphite P(OR)$_3$ (R = Me, Ph) and P(OCH2)$_3$CEt [1], phosphinite (PPh$_2$OR, R = Me, Ph) and phosphonite PPh(OMe)$_2$ derivatives of Ir$_4$(CO)$_{12}$ have been studied by variable temperature ^{13}C– and ^{31}P–NMR spectroscopy. For the mono-substituted derivatives three isomers are present in solution, one with all terminal CO ligands and two with 3 edge-bridging CO's and with the phosphorous ligand in axial (see figure) or radial position. Thermodynamic and kinetic parameters of isomerisation have been calculated from variable temperature ^{31}P-NMR spectra in two different solvents. For the di-substituted derivatives a major isomer is present in solution with 3 edge-bridging CO's and one phosphorous ligand in axial and the other one in radial position.



[1] a) K. Besançon, G. Laurenczy,. T. Lumini, R. Roulet, G. Gervasio, *Helv. Chim. Acta*, 1993, **76**, 2926; b) R. Roulet, Ed. L. J. Farrugia; NATO ASI Series vol. **465**, Kluwer Academic Publ. 1995, pp.159-174.

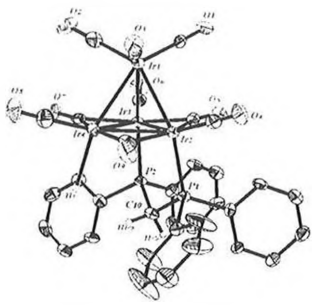
Chimie minérale et de coordination **117**

Synthesis, Characterisation and Dynamic Behaviour of $[PPN][Ir_4(CO)_9(H)(Ph_2P(CH_2)_nPPh_2)]$, n = 1, 2, 3

S. Detti[1], T. Lumini[1], G. Laurenczy[1], R. Roulet[1], K. Schenk[2], R. Ros[3], A. Tassan[1]

[1]Institut de Chimie Minérale et Analytique, BCH–Dorigny
[2]Institut de Cristallographie, BSP–Dorigny
Université de Lausanne, CH–1015
[3]Dipartimento dei Processi Chimici dell'Ingegneria, Università di Padova, Via Marzolo 9, 35131 Padova, Italy

The reactivity of mono-, di- and tri-substituted phosphine and arsine derivatives of $Ir_4(CO)_{12}$ with several inorganic and organic bases has been investigated. Numerous anionic derivatives have been obtained and characterised by IR, ^{1}H-, ^{13}C-, ^{31}P-NMR and X-Ray diffraction.
The formation of the hydride derivatives with bidentate phosphine ligands $[PPN][Ir_4(CO)_9(H)(Ph_2P(CH_2)_nPPh_2)]$ with n = 1, 2, 3 (PPN^+ = bis(triphenyl-phosphoranylidene) ammonium) will be presented in detail. In each derivative the hydride ligand is coordinated in axial position replacing (see figure) the unique axial CO ligand in $Ir_4(CO)_{10}(Ph_2P(CH_2)_nPPh_2)$, n = 1, 2, 3 [1].
Their dynamic behaviour has been studied by variable temperature ^{13}C-NMR and some activation parameters have been determined.



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Inorganic Chemistry **118**

ORGANOMETALLIC COMPOUNDS AS PRECURSORS FOR NEW MATERIALS

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Advanced synthetic procedures in organometallic chemistry allow the controlled design of compounds of a given stoichiometry. Fe, Te ratios of 3:2 and 4:2 occur in $Fe_3Te_2(CO)_9$ (**1**) and the recently synthesized $Fe_4Te_2(CO)_{11}$ (**2**) [1], in contrast to known binary Fe-Te phases. The thermal decomposition of (**1**) leads to the formation of a new metastable phase "Fe_3Te_2" [2].

Recently we determined the Fe K-edge EXAFS properties of "Fe_3Te_2" and its organometallic precursor (**1**) [3]. In continuation of our work we have now measured the Te K-edge EXAFS (*SNBL* at the *ESRF*, Grenoble) of (**1**) and its decompostion product "Fe_3Te_2" as well as $Fe_{1.1}Te$ and elemental Te.

The results for (**1**) and $Fe_{1.1}Te$ from the latest measurements are not only in accordance with known crystallographic data, but also agree with the previous results from the Fe K-edge measurements. The latter is very important, because in this case information from both data sets can be combined. This is extremely valuable when spectra of an unknown compound, i.e "Fe_3Te_2", must be interpreted.

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Inorganic Chemistry **119**

Theoretical studies of nonclassical carbonyl complexes.

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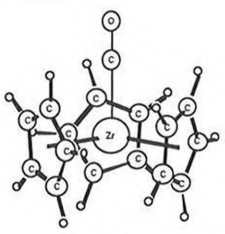
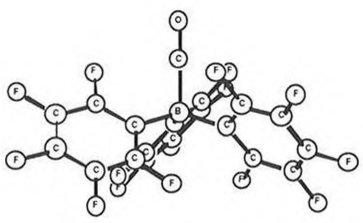
A growing class of metal carbonyl compounds is known with unusually high ν(CO) stretching values [1], indicating that π back donation does not represent the dominant bonding interaction. The A theoretical study has proposed that electrostatic effects are responsible for this nonclassical behavior [2]. We quantify this effect in calculations for cationic d^0-transition metal complexes like $[ZrCp_3\text{-}CO]^+$ **1**$^+$, and evaluate the contribution of substituent based π backbonding. Comparisons are made with main group adducts like $(C_6F_5)_3B\text{-}CO$ **2**, and the question of the stability of main group metal carbonyl complexes is addressed. The discussion is extended to other π-donors like isonitriles, and to solvate molecules.



1$^+$



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Inorganic Chemistry **120**

Phase Width of $BaMg_xGa_{4-x}$

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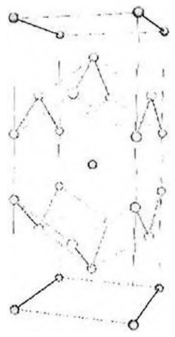
Up to now 17 binary phases in the Ba-Mg-Ga system are known. They show a wide structural diversity, four of the binary Ga-Mg-phases have their own structure type [1].
The quasi binary section between Ba_6Mg_{23} ($Fm\bar{3}m$) and $BaGa_4$ (I4/mmm) was examinated. A ternary phase width of the $BaAl_4$ structure type was found, two samples, $BaMg_xGa_{4-x}$ (x=1.0, 1.4), were characterized by X-ray diffraction on single crystals. One of the Ga positions has a mixed occupation with Mg.
Further samples of $BaMg_xGa_{4-x}$ indexed based on X-ray powder diffraction patterns show an enlargement of the c-axis with increasing at. % of Mg.
The measurements revealed a relationship between the axis length and the amount of Mg. The results are interpreted towards the understanding of chemical bonding of mixed occupation sites in intermetallics and subsequent partitioning of the gallium framework.



Structure of $Ba_2Mg_xGa_{8-x}$

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Inorganic & Coordination Chemistry **121**

The Structure and Dynamics of Interlayer Water and Hydrated Cations in Montmorillonite Clays: Neutron Scattering Studies

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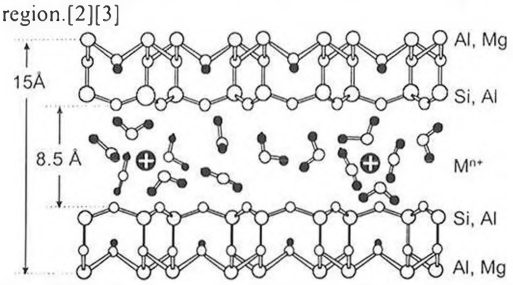
Montmorillonite clay consists of regular stacks of negatively charged aluminosilicate layers separated by charge-balancing interlayer cations. Exposure to humidity leads to hydration of the interlayer cations and the internal clay surfaces (see cross-section of a clay hydrate below). The behaviour of the interlayer water and cations is related to the use of clays in catalytic applications, in environmental remediation, and in the disposal of toxic or radioactive wastes.[1] We present the results of neutron diffraction and quasielastic incoherent neutron scattering (QINS) spectroscopy studies that probe the detailed molecular-level structure and dynamics of the interlayer region.[2][3]



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Inorganic & Coordination Chemistry **122**

Water Dynamics in Gd^{3+}-doped Zeolite Y: an ^{17}O and ^{1}H NMR Study of a Potential MRI Contrast Agent

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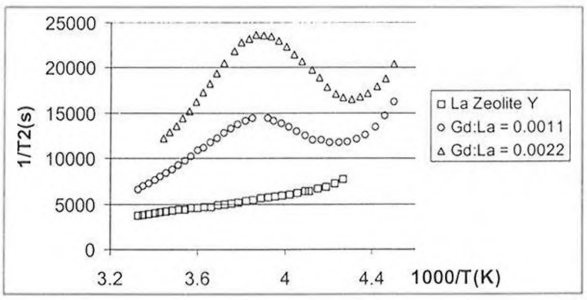
Gadolite® is a potential contrast agent for magnetic resonance imaging (MRI) of the gastro-intestinal tract based on a Gd^{3+} doped zeolite NaY.[1] The proton relaxivity, a measure of the efficiency of the contrast agent, will depend on the electronic relaxation of Gd^{3+}, the rotational correlation time for the Gd^{3+} aquo ions and the residence time of water in the first hydration shell. In order to address these problems we are performing a multiple magnetic field, variable temperature, ^{1}H and ^{17}O NMR study of a hydrated zeolite Y, where the exchangeable sodium ions have been replaced by La^{3+} and different concentrations of Gd^{3+}. The increase of proton relaxation rates with increasing concentration of Gd^{3+} (Fig) show a typical changeover from fast-exchange to exchange-controlled to outer sphere relaxation regimes with decreasing temperature and so allow an accurate determination of the water exchange rate on the Gd^{3+} aquo ion.



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Inorganic Chemistry **123**

A New Platinum Complex with a Nucleobase Derivative of Biological Importance

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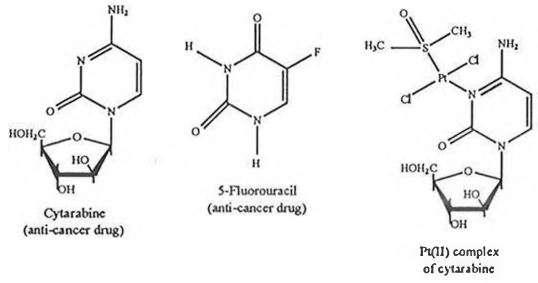
Many reports have appeared claiming that metal complexes of some drug molecules exhibit greater biological activity than does the free ligand. Our target molecules are mixed-ligand complexes with established antitumor drug molecules like 5-fluorouracil or cytarabine (1-ß-D-arabinofuranosyl cytosine) which, when bound to platinum, may act *in vivo* in the form of a coordination complex or as a biologically active "leaving group". The characterization of such complexes represents a contribution to the basic coordination chemistry of pharmacologically important molecules. Here, we report on the complex trans-dichloro(dimethylsulfoxide)(cytarabine) platinum(II) monohydrate and related complexes.



Anorganische-Koordinationschemie **124**

$Li_xSrAl_{(1-x)}Si$: a New Intermetallic Phase at the Zintl Border

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Lab. für anorg. Chemie, ETH Zürich, Universitätstrasse 6, 8092 Zürich

The structure of the new phase $Li_xSrAl_{(1-x)}Si$ (x = 0.45) was solved: this compound crystallize in the tetragonal space group P 4/nmm with a=443.7(1) pm, c = 724.2(2) pm. Conductivity measurements show metallic behavior. This new phase is both isostructural and isoelectronic with NaAlSi. Assuming a formal charge transfer from the electropositive to the electronegative atoms, the exchange of the Na- by the Sr-atoms increases the number of valence electrons per formula unit in the Al-Si-layer by one. This is compensated by substitution of about 50% of aluminum with lithium. It is interesting to note that despite the typical intermetallic character the structure clearly tends to be "electron precise". The bonds between the apical silicon and the four basical aluminum can be described as 6e-5c bonds like in the similar $BaAl_4$ phase, the silicon apical atoms have then a non bonding electron pair.

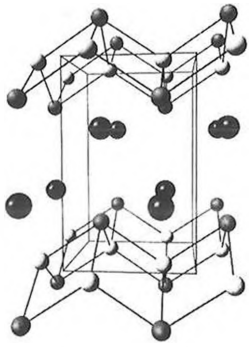

Fig.1: Sr black, Si dark grey, M bright grey (M = 55 % Al, 45 % Li)

Organic Chemistry **125**

Alkyl-Bridged B_{12}-Dimers with Rotaxane-like Structures

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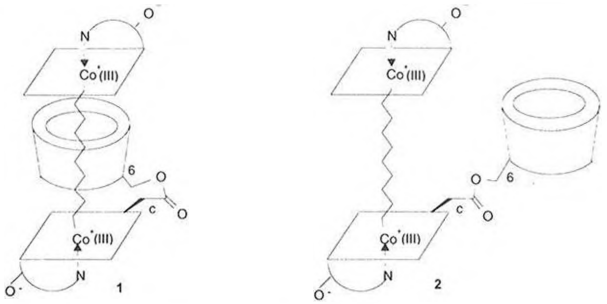
As an approach to organometallic B_{12} enzyme models [1,2], alkyl-bridged B_{12}-dimers were prepared, with a cyclodextrin moiety covalently bound to one of the B_{12} parts. Cyanocobalamin-c-acid-α-cyclodextrin-6-ylester [2] was alkylated electrochemically with ω-bromoalkyl-cob(III)alamins, the number of the methylene groups varying from 10 to12. Two isomeric forms were obtained, one with the alkyl chain threaded through the cyclodextrin cavity (e.g. **1**), the other one with the alkyl chain outside the cyclodextrin moiety (e.g. **2**), as was shown by NMR spectroscopy. The ratio of the two isomers obtained depended on the length of the alkyl chain. In exploratory thermolyses experiments the presumed induced strain in the isomers of type **1** was examined.



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Organic Chemistry **126**

Refined Solution Structure of the B_{12}-binding Subunit of Glutamate Mutase

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Glutamate mutase (Glm) is a member of the coenzyme B_{12}-dependent enzyme family that catalyzes the reversible rearrangement of (*2S*)-glutamate to (*2S,3S*)-3-methylaspartate. The interconversion of substrate and product is achieved by a radical mechanism for which no analogue exists in organic chemistry. Glm consists of two subunits (of 54 and 15 kDa) that in its active form is an $\alpha_2\beta_2$ tetramer containing two B_{12} molecules. The smaller subunit of the Glm components, MutS (*from C. tetanomorphum*) or GlmS (from *C. cochlearium*), respectively, have been identified as the B_{12}-binding subunit. Recently, the solution structures and the backbone dynamical properties of B_{12}-free ^{15}N-labelled MutS [1] and GlmS [2] have been determined. By NMR-spectroscopy we have now refined the solution structure of ^{13}C-,^{15}N-labelled MutS. While the major part of MutS is well structured with a tertiary structure strikingly similar to the GlmS crystal structure [3], the B_{12}-binding site itself is only partially formed in solution. One segment of MutS, which in the GlmS crystal structure lines the B_{12}-binding cleft in form of an α-helix, is dynamically disordered and undergoes interconversions between random coil and α-helical conformations. However, the doubly labelled MutS sample provided additional NMR-derived dihedral angle constraints which are consistent with a temporary presence of a complete α-helix in this process of conformational exchange. Thus the B_{12}-binding cleft of MutS, which accommodates the nucleotide 'tail' of the cofactor in the protein bound state, appears to be temporarily preformed even in the absence of coenzyme B_{12}.

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127

A New β-selective Glycosidase Inhibitor

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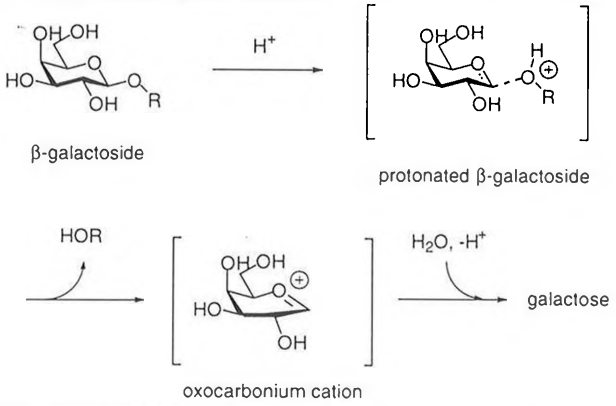
We are interested in developing glycosidase catalytic antibodies.[1] We recently reported a new inhibitor of α-L-fucosidase.[2] We have now extended this concept to prepare an inhibitor of β-galactosidase. The inhibition patterns observed with this and other structurally related inhibitors suggests that these are mimic of the protonated glycosides with the departing group (HOR) still attached, rather than of the intermediate oxocarbonium cation, as illustrated here for β-galactoside cleavage. Such inhibitors are optimally suited as haptens to generate catalytic antibodies.



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Organic Chemistry **128**

Constitution of a Fluorescing Chlorophyll Catabolite from Sweet Pepper (*Capsicum annum*). Indications for Species-dependent Stereoselectivity in Chlorophyll Breakdown.

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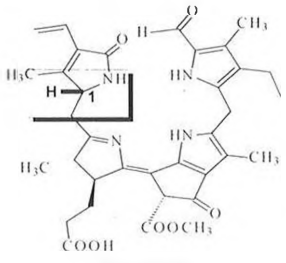
[1] Institute of Organic Chemistry, University of Innsbruck, Innrain 52a A-6020 Innsbruck, Austria
[2] Department of Plant Biology, University of Zurich, Zollikerstrasse 107, CH-8008 Zurich, Switzerland

The key steps in the breakdown of chlorophyll to its colorless catabolites are the oxygenolytic cleavage of the tetrapyrrolic macrocycle and the subsequent formation of a primary fluorescent catabolite (pFCC). The first such pFCC to be structurally characterized (*Bn*-FCC-2) was found in canola (*Brassica napus*) [2]. A pFCC with similar but not identical chromatographic behavior was recently isolated from sweet pepper (*Capsicum annum*). Spectroscopic investigations revealed a structure similar to that of *Bn*-FCC-2 except for the configuration on the stereogenic center C1.



Bn-FCC-2

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Organic Chemistry **129**

Enzymatic Phenol Oxidation is the Key Step in the Biosynthesis of the Spermine Alkaloid Aphelandrine

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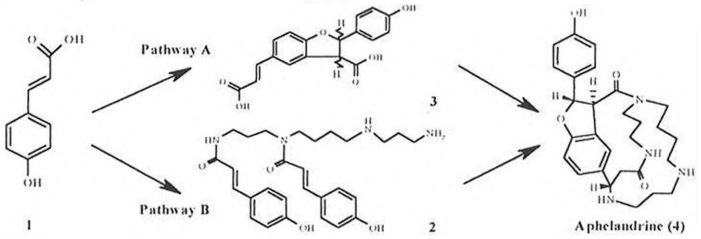
Organisch-chemisches Institut der Universität Zürich, Winterthurerstrasse 190, CH-8057 Zürich

The oxidation of phenols by one-electron transfer affords phenolic radicals which, by radical pairing, form new C-C or C-O bonds either intra- or intermolecular. Recently it has been shown that P-450 enzymes are the biocatalysts responsible for these phenol-coupling reactions. An example of a natural product which is presumably synthesized via a phenol-coupling is the macrocyclic spermine alkaloid aphelandrine (**4**).

The experiments with the microsomal fraction of *Aphelandra squarrosa* roots show that cinnamic acid is transformed by P-450 into *p*-coumaric acid (**1**). Two possibilities now exist for the further steps of aphelandrine pathway.

Pathway A: *p*-coumaric acid is first phenol coupled to form the dimer of *p*-coumaric acid **3**, a building block of the apheladrine macrocycle. Our studies confirmed that peroxidase catalyzed the transformation of **1** to **3**.

Pathway B: spermine is first acylated by *p*-coumaric acid and then coupled to yield the benzofuran fragment of aphelandrine. Since bis (*p*-coumaroyl)-spermine **2** has been shown to occur in *Aphelandra* plants the latter possibility seems to be more likely [1].



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Organic Chemistry **130**

Dependence of the Secondary Structure of β-Peptides on Terminal Protecting Groups and Their Influence on α-Peptidic Structures

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Laboratorium für Organische Chemie der Eidgenössischen Technischen Hochschule, ETH-Zentrum, Universitätstrasse 16, CH-8092 Zürich.

A novel class of peptide analogues, the β-peptides with proteinogenic side chains, has been found to form surprisingly stable helices and other secondary structures [1-3]. Two different types of helices have been discovered so far [4]. Hydrophobic interactions of and hindered solvent accessibility by the side chains, as well as a resulting macro-dipole moment are regarded as important factors influencing the relative stability of the two types of helices [2]. We have, now, systematically investigated the dependence of the two typical helix CD pattern from protecting groups and chain lenghts. We also studied the influence of the (M)-3_{14}-helical structure of β^3-peptides on the (M)-3.6_{13}-helical structure of D-α-peptides (see Fig. 1). Various peptides consisting of β^3- and α-peptidic fragments have been synthesised and their secondary structures investigated by CD measurement.

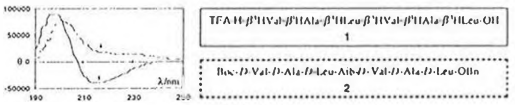

Fig. 1. *Typical CD pattern of an* (M)-3_{14}- *and of an* (M)-3.6_{13}-*helical structure exhibited by the* β^3-*peptide 1 and the* D-α-*peptide 2.*

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Organic Chemistry **131**

Synthesis of Permethylated β-Cyclodextrin as Substituent of a 14-C-4 Crown Ether

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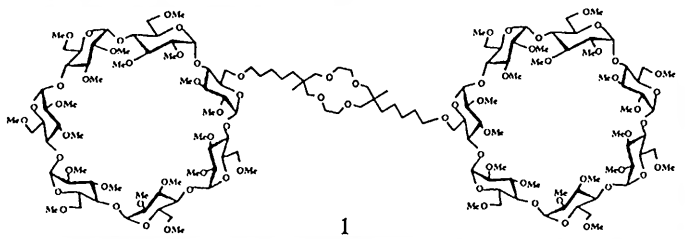
Institut de Chimie de l'Université de Neuchâtel,
Avenue de Bellevaux 51, CH-2000 Neuchâtel

In the course of our studies of new macromolecules we synthesised the following compound:



1

The ability of modified cyclodextrins to form inclusion complexes causes unusual selectivity when used in enantiomeric separation processes [1]. Crown ethers, owing to the cavity structure and the strong electronegative effect of heteroatoms on the ring, show unique selectivity for metal cations, aromatic and polar compounds [2]. All these features led us to think that **1** could be used as new versatile stationary phase for GC and capillary electrophoresis.

Here, we report the total synthesis of compound **1**. The production of the crown ether required high dilution techniques. Monohydroxy permethylated cyclodextrin was obtained by selective protection with TBDMSCl.

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Organic Chemistry **132**

Norvalinyl and Methoxyalanyl Peptide Nucleic Acids

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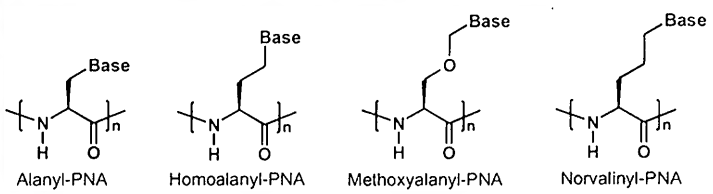
Homology was shown to be a valuable tool to design nucleobase stacks in linear alanyl- and homoalanyl peptide nucleic acids (PNAs) [1]. The orientation [2] and the stacking distance [3] of base pairs can be defined. In this context, three atom linkers should be promising. The prefered nucleobase orientation and selectivity is expected to be as known from alanyl-PNA but backbone spacing, conformational flexibility of the side chains and solubility should be enhanced. Therefore, the synthesis and pairing properties of norvalinyl- and methoxyalanyl PNA are presented.



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[2] U. Diederichsen, H. W. Schmitt, *Tetrahedron Lett.* **1996**, *37*, 475.
[3] a) U. Diederichsen, H. W. Schmitt, *Angew. Chem. Int. Ed. Engl.* **1998**, *37*, 302. b) U. Diederichsen, *Bioorg. Med. Chem. Lett.* **1997**, *7*, 1743.

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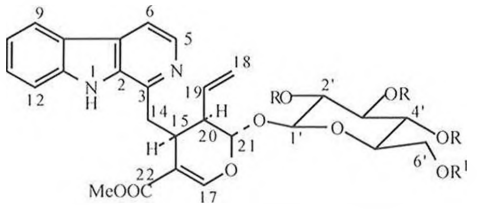
Organic Chemistry **133**

Indole Alkaloids with β-Carboline Chromophore and Monoterpenoid Origin from the Rubiaceae *Palicourea adusta* Standley.[1,2]

J. Valverde[1], G.Tamayo-Castillo[2] and M. Hesse[1]

[1]Organisch-chemisches Institut der Universität Zürich, Winterthurerstr. 190, 8057 Zürich, Switzerland. [2]Instituto Nacional de Biodiversidad (INBio), Santo Domingo de Heredia, Costa Rica

Lyaloside (**1**), a monoterpenoid glycoside alkaloid [1], was isolated from the leaves of *Palicourea adusta* together with its hydroxycinnamic acid derivatives, (*E*)-*O*-(6')-cinnamoyl-4"-hydroxy-3"-methoxy-lyaloside (**2**) and (*E*)-*O*-(6')-cinnamoyl-4"-hydroxy-3", 5"-dimethoxy-lyaloside (**3**), which have been separated for the first time by high pressure liquid chromatography (HPLC). Their molecular weights were determined by HPLC electrospray ionization mass spectrometry (ESI-MS) and further identification of the structures was carried out by spectroscopic methods. This is the first phytochemical study for discovering of alkaloids in *P.adusta*.



1, R = R[1] = H, Lyaloside
2, R = H, R[1] = (*E*)-*O*-(6')-cinnamoyl-4"-hydroxy-3"-methoxyl
3, R = H, R[1] = (*E*)-*O*-(6')-cinnamoyl-4"-hydroxy-3", 5"-dimethoxyl

[1] J. Levesque, J. L., Pousset, A. Cavé, *C. R. Hebd. Seances Acad. Sci., Ser. C* **1975**, *280*, 593.

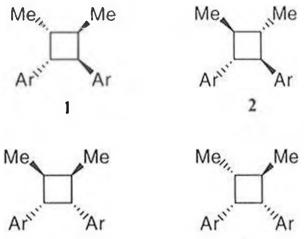
Organic Chemistry **134**

New cyclobutane-type lignans from *Mosla scabra*

Q. Wang, C. Terreaux, A. Marston and K. Hostettmann

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

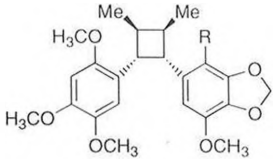
Cyclobutane-type lignans, in which no oxygen is incorporated in the coupling of phenylpropanoid units, are rare natural products. Only 3 symmetric natural stereoisomers of 1,2-dimethyl-3,4-bis-(2,4,5-trimethoxy-phenyl)-cyclobutane (**1-3**) are known to this date, as well as an asymmetric synthetic one (**4**) [1]. Two new lignans of such type, **5** and **6**, together with the known derivatives **1** and **2**, were isolated from the whole plant dichloromethane extract of Mosla scabra (Lamiaceae), a plant used for the treatment of heatstroke, common cold, fever and chronic bronchitis in Chinese traditional medicine. These compounds represent the first examples of naturally-occurring cyclobutane-type lignans with asymmetric substitutions in the phenyl groups.



1 **2**

3 **4**

Ar = 2,4,5-trimethoxyphenyl-



5 R = H
6 R = OMe

[1] S. Kadota, K. Tsubono, K. Makino, M. Takeshita, T. Kikuchi, *Tetrahedron Lett.* **1987**, *28*, 2857.

Organic Chemistry **135**

Dehydrotocopherols – New Vitamin E Components

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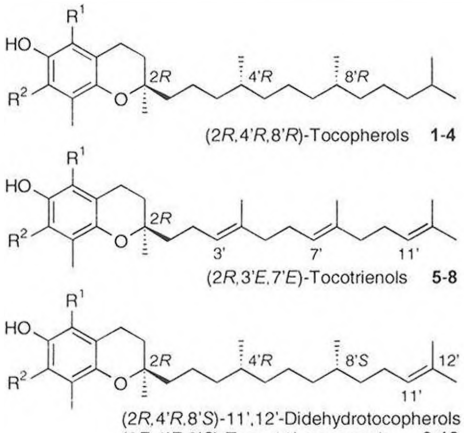
Vitamin Research and Technology Development, F. Hoffmann-La Roche Ltd, CH-4070 Basel, Switzerland

Tocopherols **1-4** and tocotrienols **5-8** are well-known naturally occurring compounds of the vitamin E group [1]. On the contrary, structurally related dehydrotocopherols like **9-12** have been scarcely characterized so far [2,3]. We wish to report on selected examples of isolation, structure elucidation including full stereochemical analysis, and total synthesis of individual tocoenols which have been shown to be associated with tocopherols and tocotrienols in various commercial vitamin E concentrates of natural origin.



(2*R*,4'*R*,8'*R*)-Tocopherols **1-4**

(2*R*,3'*E*,7'*E*)-Tocotrienols **5-8**

(2*R*,4'*R*,8'*S*)-11',12'-Didehydrotocopherols
(2*R*,4'*R*,8'*S*)-Toco-11'-monoenols **9-12**

	R^1	R^2
1 5 9	CH_3	CH_3
2 6 10	CH_3	H
3 7 11	H	CH_3
4 8 12	H	H

[1] Th. Netscher, *Chimia* **1996**, *50*, 563-567, and references cited therein.
[2] A. Matsumoto, S. Takahashi, K. Nakano, S. Kijima, *Yukagaku* **1995**, *44*, 593-597; *Chem. Abstr.* **123**, 226445.
[3] C.G. Rammell, J.J.L. Hoogenboom, *J. Liquid Chromatogr.* **1985**, *8*, 707-717, and cit. lit.

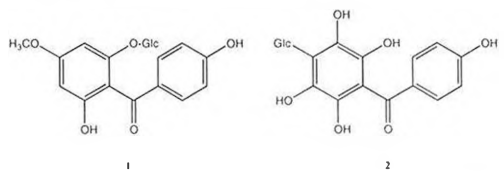
Organic Chemistry **136**

Novel benzophenone glucosides from *Gnidia involucrata* (Thymelaeaceae)

J. Ferrari[a], C. Terreaux[a], J.D. Msonthi[b] and K. Hostettmann[a]

[a] Institut de Pharmacognosie et Phytochimie, Université de Lausanne, BEP, CH-1015 Lausanne, Switzerland
[b] Dept. of Chemistry, University of Swaziland, Kwaluseni, Swaziland

As most of the studies on the Thymelaeaceae concern their lipophilic extracts, rich in irritant diterpenes [1], it was decided to focus on the polar constituents of this family. Consequently, *Gnidia involucrata* Rich., a yet unstudied African plant from Malawi, was investigated. Fractionation of its aerial parts methanolic extract, monitored by HPLC/UV analysis, was achieved by a combination of silica gel column chromatography, gel filtration on Sephadex LH-20 and reversed-phase LPLC.
By this means two flavonoids, yuankanin and kaempferol-3-O-glucoside, two new benzophenones (**1**, **2**) and a xanthone, mangiferin, were isolated. The structures were established by spectroscopic methods, including 2D-NMR heteronuclear correlation experiments.



1 **2**

Furthermore, a chemotaxonomic study of the methanol extracts of other *Gnidia* species using LC/UV/ESI-MS will be presented.

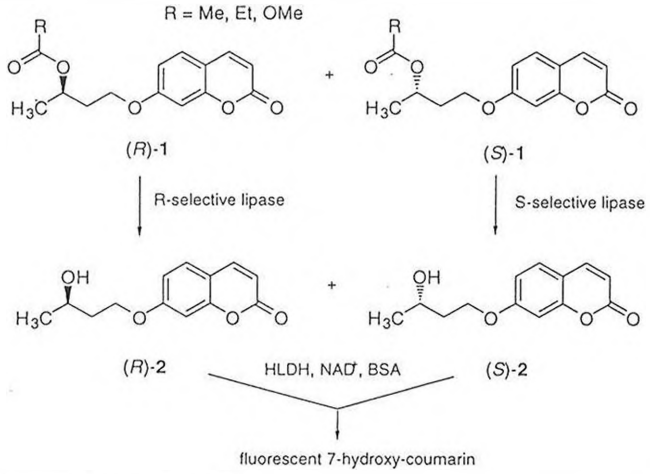
[1] F.J. Evans, S.E. Taylor, *Prog. Chem. Org. Nat. Prod.* **1983**, *44*, 1.

137

Enantioselective Fluorogenic HTS-Assay for Lipases

Gérard Klein and Jean-Louis Reymond*
Universität Bern, Dept. für Chemie & Biochemie, Freiestr. 3, 3012 Bern

We report a novel high throughput screening (HTS) assay for lipases that is applicable to chiral acetates, propionates and methyl-carbonates, which very important class of chiral substrates that are resolved in practice using lipases. Lipase mediated hydrolysis of chiral esters and carbonates related to (*R*)-**1** or (*S*)-**1** forms the corresponding alcohols of type (*R*)-**2** or (*S*)-**2**, which undergo a fluorogenic oxidation in the presence of horse liver alcohol dehydrogenase (HLDH), NAD^+, and BSA.[1]



[1] a) G. Klein, J.-L. Reymond, *Bioorg. Med. Chem. Lett.* **1998**, *8*, 1113; b) G. Klein, J.-L. Reymond, *Helv. Chim. Acta* **1999**, *82*, 400.

Organic Chemistry

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Chlorophyll *b* Catabolism in *Hordeum vulgare*

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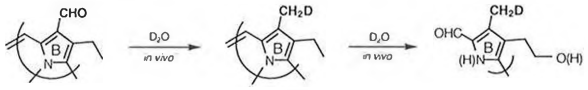
University Fribourg • Institute of Organic Chemistry • CH-1700 Fribourg

In 1991, the first chlorophyll catabolites were isolated and characterized from the Chlorophyte *Chlorella protothecoides*[1] and the Spermatophyte *Hordeum vulgare*[2]. Both, chlorophyll (Chl) *a* and *b* catabolites, are excreted by the former whereas only Chl *a* catabolites can be isolated from diverse higher plants.

Chl *b* occurs as an accessory pigment of the light harvesting systems in higher plants and green algae and comprises up to 30% of the total Chls[3]. With the discovery of the Chl *b*(*a*) inter-conversion cycle[4] it has been occasionally speculated that in higher plants Chl *b* is converted to Chl *a* prior to degradation.

In our present work we have evidenced by high resolution ^1H-, ^2H-NMR and MS-ICR spectroscopic methods that a significant fraction of the key methyl group of the Chl *a* catabolite becomes mono-deuterium labeled when green barley leaves (*H. v.*) are de-greened by permanent darkness in heavy water[5]. Our results show that Chl *b* is indeed converted to Chl *a* prior to degradation *i.e.* the Chl *a* catabolite isolated has emerged from both, Chl *a* and Chl *b*.



Partial structures of Chl *b*, labeled Chl *a*, and of the emerging apparent Chl *a* catabolite

[1] Engel, N., Jenny, T. A., Mooser, V., and Gossauer, A. (1991) *FEBS Lett.* **293**, 131. [2] Kräutler, B., Jaun, B., Bortlik, K., Schellenberg, M., and Matile, P. (1991) *Angew. Chem. Int. Ed. Engl.* **30**, 1315. [3] Scheer, H., The Chlorophylls, (1991) CRC Press, Boca Raton. [4] Ito, H., Ohtsuka, T., and Tanaka, A. (1996) *J. Biol. Chem.* **271**, 1475. [5] Folly, P., and Engel, N., (1999) *J. Biol. Chem.* **274**, in print. We wish to thank the SNSF for financial support of the project.

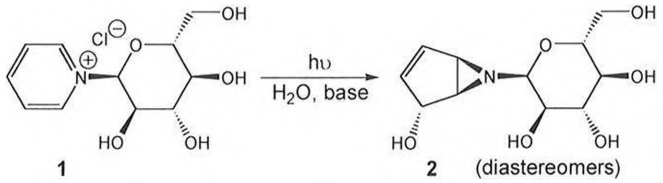
Organic Chemistry

139

6-Azabicyclo[3.1.0]hex-3-en-2-ol Derivatives, Photochemically Generated Building Blocks for Aminocyclopentitols

T. Damiano, B. Acar, F. Glarner, and U. Burger*
University of Geneva, Department of Organic Chemistry, 1211-Geneva-4

The photohydration of N-substituted pyridinium salts in alkaline medium has been shown to proceed smoothly to give the azabicylic title compounds in good preparative yield [1][2]. By applying this reaction to N-glycosyl pyridinium salts (*e.g.* **1**), diastereomers of the corresponding bridged aziridines (*e.g.* **2**) were obtained. The diastereomers can readily be separated and thereby provide valuable intermediates for further elaboration into aminocylopentitol glycosidase inhibitors [3]. We report on selective aziridine opening and face specific oxidation.



[1] F. Glarner, S.R. Thornton, D. Schärer, G. Bernardinelli, and U. Burger, *Helv. Chim. Acta* **1997**, *80*, 121-127.

[2] E.A. Acar, F. Glarner, and U. Burger, *Helv. Chim. Acta* **1998**, *81*, 1095-1104.

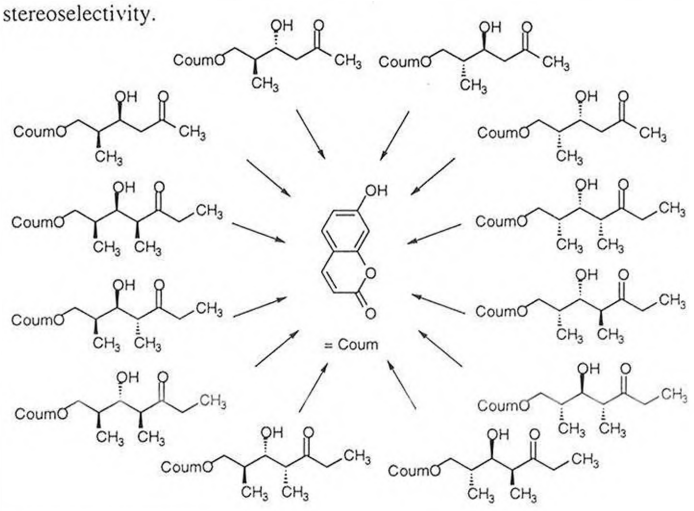
[3] A. Berecibar, C. Grandjean, and A. Siriwardena, *Chem. Rev.* **1999**, *99*, 779-844.

140

Fluorescence HTS-assay for double-stereoselective aldolization

Raquel Pérez Carlón, Eva Gonzalès and Jean-Louis Reymond*
Universität Bern, Dept. für Chemie & Biochemie, Freiestr. 3, 3012 Bern

We report the synthesis, separation, structure determination and fluorogenic properties of 12 new stereoisomeric aldols. These aldols represent prototypical polypropionate fragments. Since the aldol reaction is reversible and its stereoselection can be measured in retroaldolization mode,[1] these substrates can be used to assay aldolase biocatalysts for activity and stereoselectivity.



[1] a) Reymond, J.-L. *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2285; b) N. Jourdain, R. Pérez Carlón, J.-L. Reymond, *Tetrahedron Lett.* **1998**, *39*, 9415.

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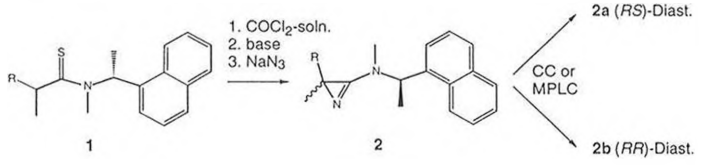
Organic Chemistry **141**

New Optically Active 3-Amino-2*H*-azirines as Synthons for α,α-Disubstituted α-Amino Acids in Peptide Synthesis

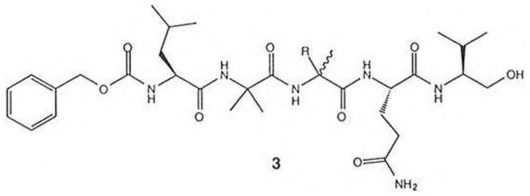
K. A. Brun, A. Linden, H. Heimgartner

Organisch-chemisches Institut der Universität Zürich

α,α-Disubstituted α-amino acids can easily be introduced into peptides by using 3-amino-2*H*-azirines as amino acid synthons [1].
New 3-amino-2*H*-azirines with a chiral 3-amino group are described in this poster. Due to the presence of the chiral auxiliary 3-amino group, diastereoisomers were obtained during the synthesis, which could be separated by chromatography.



The enantiomerically pure synthons **2a** and **2b** were incorporated into model peptides of type **3**.



[1] H. Heimgartner, *Angew. Chem.* **1991**, *103*, 271.

Organic Chemistry **142**

New phenolic radical scavengers from *Saxifraga cuneifolia* (Saxifragaceae)

I. Chevalley, A. Marston and K. Hostettmann

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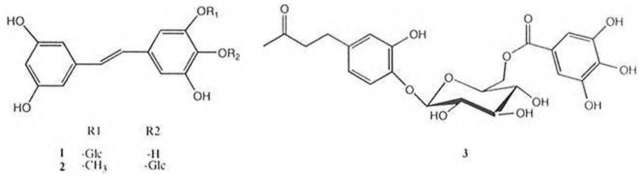
Saxifraga cuneifolia L is a small plant that can be found in all the montainous regions of Europe. Although flavonoids have been described from *Saxifraga* species, little is known about constituents of the genus. Fractionation of the methanol extract of the whole plant was guided by a TLC assay for radical scavenging activity using the DPPH (2,2-diphenyl-1-picrylhydrazyl) radical as a spray reagent [1].
By this means 4-(3',4'.dihydroxyphenyl)-butan-2-one-4'-glucoside, (*R*)-rhododendrin, 1-*O*-galloyl-β-glucose, catechin, 3-*O*-galloyl-epigallocatechin, gallocatechin, clitorin, rutin and five new compounds, (*E*)-5-*O*- β -D-glucopyranosyl-stilbene-3,3',4,5'-tetraol (**1**), (*E*)-4-*O*-β-D-glucopyranosyl-5-methoxy-stilbene-3,3',5'-triol (**2**), 4-[4'-*O*-(6"-*O*-galloyl-β-D-glucopyranosyl)-3'-hydroxyphenyl]butan-2-one (**3**), 3-*O*-(6''-*O*-galloyl-β-D-glucopyranosyl)-epigallocatechin and 3-*O*-β-D-glucopyranosyl-epigallo-catechin, were isolated.



Radical scavenging properties of all thirteen isolated compounds were evaluated against the DPPH radical in a spectrophotometric assay.

[1] M. Cuendet, K. Hostettmann, O. Potterat, *Helv. Chim. Acta* **1997**, *80*, 1144.

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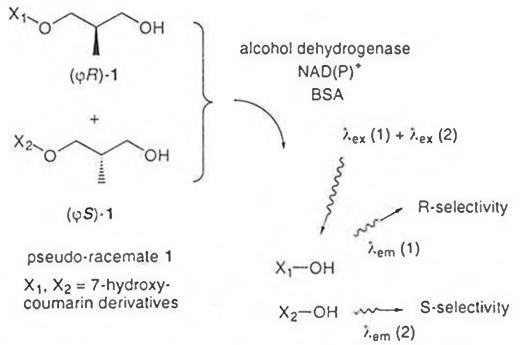
Orthogonal fluorophores for HTS-assays of kinetic resolution

Nicolas Bensel, G. Klein and J.-L. Reymond*
Universität Bern, Dept. für Chemie & Biochemie, Freiestr. 3, 3012 Bern

High throughput screening (HTS) is an essential component in the discovery of novel catalyst using library appraoches such as catalytic antibodies, enzyme discovery or evolution, and combinatorial catalyst synthesis. We have recently reported a series of enantioselective fluorogenic assays for carbonyl-forming reactions suitable for HTS, based on the fluorophore 7-hydroxy-coumarin.[1] Ideally a selective reaction on stereoisomers of the same substrates, in the sense of a kinetic resolution, should be assayed using a racemic mixture directly. Herein we report on new HTS for kinetic resolution using a pair of coumarin-type fluorophores that are structurally very similar but orthogonal in their fluorescence properties. These fluorophore can be used to prepare pseudo-enantiomeric mixtures that allow to test kinetic resolution in HTS.



[1] a) G. Klein, J.-L. Reymond, *Bioorg. Med. Chem. Lett.* **1998**, *8*, 1113; b) N. Jourdain, R. Pérez Carlón, J.-L. Reymond, *Tetrahedron Lett.* **1998**, *39*, 9415.

Organic Chemistry **144**

Regioselective Double Bond Cleavage of β,β-Carotene: An Enzyme Mimic for β,β-Carotene 15,15' Dioxygenase

Richard R. French, Philipp Holzer and Wolf-Dietrich Woggon.

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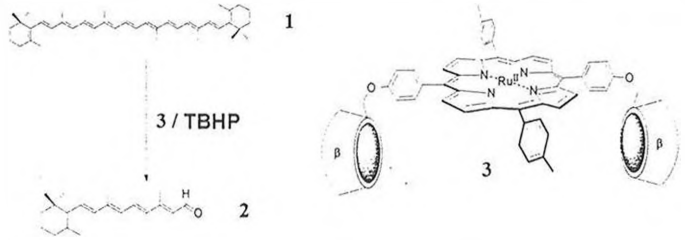
St. Johanns-Ring 19, 4056 Basel.

The enzymes which cleave β,β-carotene **(1)** to provide retinal **(2)**, the precursor for retinol (vitamin A), are of significance to animal and human nutrition. Two modes of cleavage of β,β-carotene have been proposed: i) excentric cleavage which yields apocarotenals, and ii) central cleavage which gives retinal directly. Porphyrinato Ruthenium complexes are known to cleave (*E*)-double bonds to aldehydes in the presence of TBHP.[1] We report here on the reactivity of a water soluble bis-cyclodextrin porphyrinato Ruthenium complex **3** towards β,β-carotene. In order to investigate the cleavage of the central double bond of **1**, a mixture of **1** in 9:1 / hexane:$CHCl_3$ and **3** in H_2O were stirred vigorously in the presence of TBHP. Aliquots were subjected to HPLC conditions which had been developed for the analysis of carotene dioxygenase enzyme assays.[2] Retinal could be characterised by its retention time and UV-spectrum and quantified by comparison with an external standard.



[1] Holzer, P., French, R.R., Woggon, W.-D., *In preparation.*
[2] Wirtz, G., Bornemann, C., Woggon, W.-D., Autumn meeting of the Society for Biochemistry and Molecularbiology, Jena, Germany, 1998.

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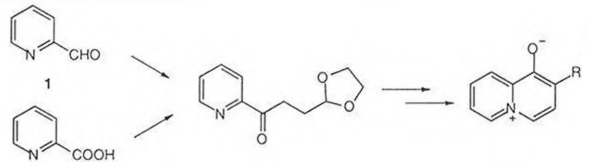
Organic Chemistry **145**

Synthesis of 2-Alkylquinolizinium-1-olate Heterobetaines and their 1,3-Dipolar Cycloaddition with Acetylenes

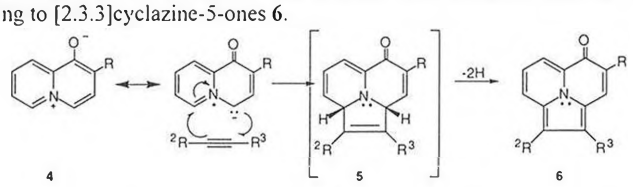
A. Gebert[1], M. Barth[1], U. Widmer[2], A. Linden[1] and H. Heimgartner[1]

[1]Organisch-chemisches Institut der Universität Zürich
[2]F. Hoffmann-La Roche Ltd., CH-4070 Basel

Like the mesoionic oxazolones, discovered by *Huisgen et al.* [1], quinolizinium-1-olate heterobetaines **4** are mesoionic compounds of the azomethine-ylide type. Several heterocycles of type **4** were prepared *via* a new route [2] from ketone **3**.



These heterobetaines have *a priori* the potential to undergo different cycloaddition reactions with double or triple bonds, namely 1,3-dipolar- or Diels-Alder reactions. We report on the scope and limitations of the reactivity of **4** in cycloadditions with electron poor acetylene derivatives leading to [2.3.3]cyclazine-5-ones **6**.



[1] R. Huisgen, H. Gotthardt, H.O. Bayer, F.C. Schaefer, *Angew. Chem.* **1964**, *76*, 185.
[2] M. Bös, U. Widmer, Eur.Pat. 0657'462, **1998**.

Organic Chemistry **146**

Synthesis of Specifically Labelled Oligo[(*R*)-3-hydroxybutanoic acid] Derivatives for Structure Determination in Solution

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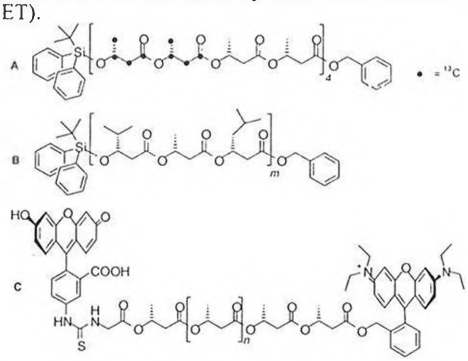
Laboratorium für Organische Chemie
der Eidgenössischen Technischen Hochschule Zürich
Universitätstrasse 16, CH-8092 Zürich, Switzerland

PHB has not only been found accumulated in inclusion bodies of several procaryotic cells but also in cell membrane fractions of procaryots and eucaryots. This membrane component has been shown to act as a non-proteinogenic transmembrane ion-channel [1-3]. For the characterization of the membrane-associated *PHB* the determination of the solution structure of this biopolymer is of great importance. Therefore specifically labelled HB-oligomer derivatives (**A**: ^{13}C, **B**: side chains, **C**: chromophores), suitable for studying the structure in solution, have been prepared. While the specifically ^{13}C-labelled HB-oligomer **A** and the HB-analog **B** of a β-peptide will be determined by NMR-spectroscopy, the double-fluorescence-labelled oligomer **C** will be examined by Fluorescence-Resonance-Energy-Transfer (FRET).



[1] S. Das, U.D. Lengweiler, D. Seebach, R.N. Reusch, *Proc. Natl. Acad. Sci.*, **1997**, *94*, 9075-9079.
[2] M. G. Fritz, P. Walde, D. Seebach, *Macromolecules*, **1999**, *32*, 574-580.
[3] D. Seebach, M.G. Fritz, *Int. J. Biol. Macromol.*, **1999**, in press.

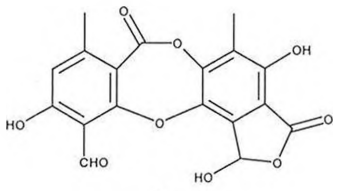
Organic Chemistry **147**

Synthesis of Natural Depsidones Containing an Hydroxyphtalid Ring

*E.Couché, A.Fkyerat, M.Rama, N.Droux and R. Tabacchi**

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

Recently, in the course of phytochemical studies in our laboratory on the lichen *Bryoria Fuscescens* [1], we have isolated several depsidones with an hydroxyphtalid ring such as norstictic acid **1** :



1

The structure of this compound was elucidated by spectroscopic methods.

The depsidone **1** and 19 analogous have been previously isolated [2] but never been synthesized. Here, we report the total synthesis of **1** in 16 steps, including the regioselectivity of photobromination on methyl groups to generate the phtalid ring with a good yield.

[1] M.Rama, Thèse de l'Université de Neuchâtel, **1997**.
[2] C.F. Culberson, Chemical & botanical guide to lichen product, University North Carolina, Chapell Hill, **1969**.

Organic Chemistry **148**

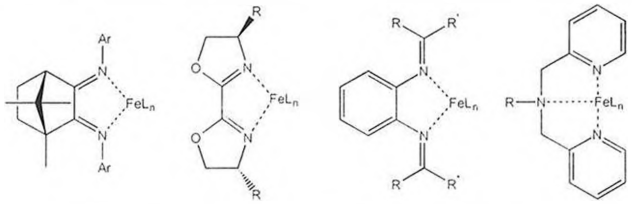
HOMOGENEOUS IRON HYDROGENATION CATALYST

Titus A. Jenny, Manuel Raemy and Thomas P. Sieber

Institute of Organic Chemistry, University of Fribourg, Pérolles, Fribourg

Homogeneous hydrogenation is a very important tool in modern synthetic chemistry, but only very few iron hydrogenation catalysts for selected substrates are reported so far[1].

We devised now a new homogeneous iron hydrogenation catalyst which allows the hydrogenation of olefins with different substitution patterns.



Conjugated diimines contained in 1,4-diazadiene or 2,5-diazatriene systems as well as non-conjugated, tridentate bis(2-pyridyl)ethylamines are appropriate ligands for iron in this case.

[1] Porta F.; Cenini S.; Giordano S.; Pizzotti M. . *J. Organomet. Chem.* **1978**, *150*, 261. Bianchini C.; Meli A.; Peruzzi M.; Frediani P.; Bohanna C.; Estruelas M. A. and Oro L. A., *Organometallics* **1992**, *11*, 138.

CHIMIA 1999, 53, No. 7/8

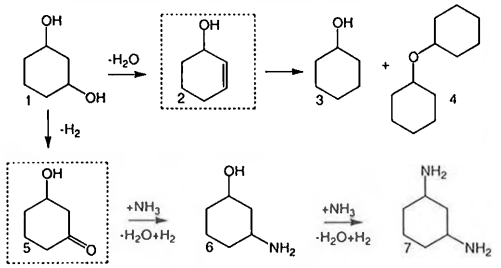
Organic Chemistry **149**

Cobalt-Catalyzed Amination of Bifunctional Alcohols in Supercritical Ammonia

G. Jenzer, A. Fischer, T. Mallat and A. Baiker

ETHZ, Laboratorium für Technische Chemie, 8092 Zürich

The one-step procedure of amination of bifunctional alcohols to diamines has been investigated in a continuous fixed bed reactor. Application of supercritical NH_3 as solvent and reactant suppressed catalyst deactivation. Amination yields increase remarkably in the narrow pressure range of subcritical-supercritical transition of the medium [1]. However, yields are strongly dependent on the diol structure [2,3]. Diamine (**7**) selectivity of 1,3-dihydroxy compounds (**1**) is poor due to water elimination leading to undesired monofunctional products (**3**, **4**) via allylic alcohol intermediates (**2**). This side reaction does not occur with 1,4-dihydroxy compounds which afford high aminol and diamine selectivities under similar conditions. Amination of bifunctional secondary alcohols with ammonia was found to be faster, but not more selective than that of primary diols.



[1] A. Fischer, T. Mallat, A. Baiker, *J. Mol. Catal.* in press.
[2] A. Fischer, T. Mallat, A. Baiker, *Angew. Chem., Int. Ed. Eng.* **1999**, 38, 351.
[3] G. Jenzer, T. Mallat, A. Baiker, *Catal. Lett.* submitted.

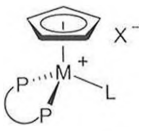
Organic Chemistry **150**

Iron and Ruthenium Lewis Acids with Chiral CO Emulating Ligands in Asymmetric Catalysis

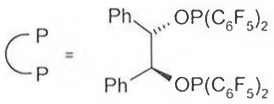
E. P. Kündig, C. Massardier, C. M. Saudan and F. Viton

Université de Genève, Département de Chimie Organique, 1211 Genève 4

We have recently shown that the rate of asymmetric Diels-Alder reactions catalyzed by the chiral complex [CpRu(BIPHOP-F)][X] is very dependent on the nature of the anion X^- with activity increasing in the order $OTf^- < BF_4^- < PF_6^- < SbF_6^- <$ TFPB [1]. We have now found that an analogous trend exists in the corresponding iron catalysts [2]. Moreover, the Fe-catalysts, while less stable than the Ru-catalysts, are more reactive. The poster will detail these studies and also report on ongoing work on new ligand design and catalyst modification.



M = Fe, Ru



BIPHOP-F

[1] E. P. Kündig, C. M. Saudan, G. Bernardinelli, *Angew. Chem. Int. Ed.* **1999**, *38*, 1220.
[2] M. E. Bruin, E. P. Kündig, *Chem. Commun.* **1998**, 2635.

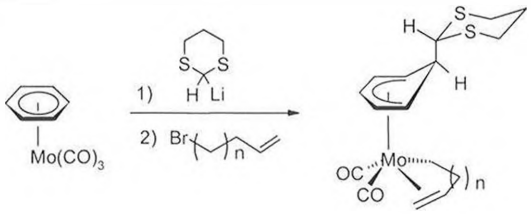
Organic Chemistry **151**

Recent Advances in the Chemistry of |(Arene)Mo(CO)$_3$| Complexes

G. Grossheimann, E. P. Kündig, F. Robvieux, P. Romanens

Département de Chimie Organique. Université de Genève, 1211 Genève 4

Complexation of an arene to the electrophilic $Cr(CO)_3$ moiety dramatically changes the reactivity of the arene and this has led to many applications in organic synthesis[1]. Surprisingly, analoguous reactions with the corresponding [(arene)$Mo(CO)_3$] complexes have not received attention to this date. Based on the differences between Mo and Cr, notably the higher kinetic lability of the Mo-arene bond and the the differences in M-H and M-C bond energies, new chemistry and applications may emerge from the Mo complexes. We have started to look at the fundamental steps in activation of arenes by a $Mo(CO)_3$ fragment: arene complexation, reactivity, and product cleavage. For example, the sequential nucleophile/electrophile addition has allowed the isolation of intermediates **1** on the pathway to the dearomatized diene products:



1 (n=1, 2, 3)

[1] Semmelhack, M. F. in *Comprehensive Organometallic Chemistry II*, Abel, E. W.; Stone, F. G. A.; Wilkinson, G. Ed.; Pergamon, Oxford, **1995**; Vol 12, p.979.

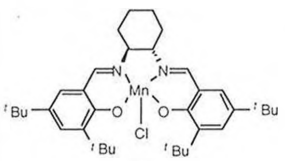
Organic Chemistry **152**

Computational studies of epoxidation reactions catalyzed by (salen)Mn(III)-complexes.

Heiko Jacobsen[a] and Luigi Cavallo[b]

[a]Anorganisch-chemisches Institut der Universität Zürich, Winterthurerstr. 190, CH-8057, Zürich; [b]Dipartimento di Chimica, Università degli Studi di Napoli "Federico II", Via Mezzocannone 4, I-80134 Napoli.

Epoxidation reactions have been established as an effective method for the formation of carbon-oxygen bonds. In particular, the catalytic protocol developed by Jacobsen [2] and coworkers, which utilizes optically active (salen)manganese(III) complexes **1**, yields products in high enantiomeric excess. Although the factors controlling the enatioselectivity are well understood, the mechanism of oxygen transfer to the double bond is still a matter of some controversy [2]. The *cis-trans* isomerisation observed in the transformation of conjugated alkenes gave rise to several mechanistic proposals, including concerted reactions, and pathways proceeding via radical intermediates and manganaoxetanes. We have examined the different proposals using density functional theory combined with force field calculations. Our calculations support the notion that the epoxidation reaction proceeds via radical intermediates. Implications on the diastereoselectivity of the reaction are discussed.



1

[1] E. N. Jacobsen et al., *J. Am. Chem. Soc.* **1991**, *113*, 7063.
[2] T. Linker, *Angew. Chem. Int. Ed. Engl.* **1997**,*36*, 2060.

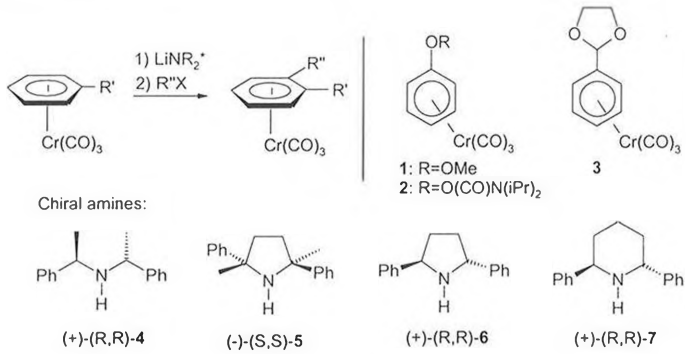
Organic Chemistry **153**

Use of Chiral Lithium Amide Bases for the Synthesis of Planar Chiral Arene Chromium Complexes

S. Pache, A. Quattropani and E. P. Kündig

Département de Chimie Organique, Université de Genève, 1211 Genève 4

Chiral [(η^6-arene)Cr(CO)$_3$] complexes are useful building blocks in organic synthesis and ligands for asymmetric catalytic reactions. Enantioenriched complexes have been obtained by either resolution or by asymmetric synthesis. We here report on ongoing studies of an enantioselective method involving *ortho*-lithiation followed by electrophile addition.[1]



The study was carried out with arene complexes **1-3** and the amide bases **4-7** [2]. The enantioselectivities observed were found to be highly dependent on the structure of the amide and the complex.

[1] A. Quattropani, G. Bernardinelli, E.P. Kündig, *Helv. Chim. Acta* **1999**, *82*, 90 and ref cit.

[2]We thank Dr. J. Einhorn, Université Joseph Fourier, Grenoble, for a sample of enantiopure **5**.

Organic Chemistry **154**

Chiral Relay Effect in Lewis Acids Promoted Enantioselective Reactions

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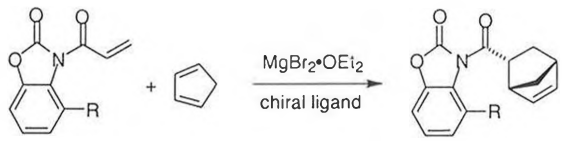
CH-1700 Fribourg, Switzerland

The choice of the achiral template for Lewis acid promoted enantioselective transformations is crucial. Excellent results have been obtained with simple 1,3-oxazolidinones, however, Lewis acids bearing sophisticated chiral ligands are necessary to reach high enantioselectivitie. In order to use more simple chiral Lewis acids, we are developing new achiral templates which can act as chiral relay between the Lewis acid and the reaction center.

Various 4-substituted *3H*-benzooxazol-2-one [1] have been tested for Diels-Alder reactions of acrylamides with cyclopentadiene (see equation). The substituent at position 4 plays a major role in the stereochemical control. This chiral relay effect will be discussed in detail.



[1] The use *N*-crotonyl-*3H*-benzooxazol-2-one has already been reported: E. J. Corey and I. N. Houpis, *Tetrahedron Lett.*, **1993**, 2421-2424.

Organic Chemistry **155**

Catalytic Gas Phase Oxidation of Isophorone to Ketoisophorone

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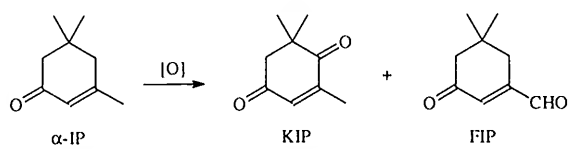
[a] Laboratorium für Technische Chemie, ETH-Zentrum, 8092 Zürich

[b] F. Hoffmann-La Roche Ltd., Vitamins and Fine Chemicals Division, 4070 Basel

Ketoisophorone (KIP) is a key intermediate in the synthesis of various carotenoid and flavoring substances [1]. Current synthetic routes to KIP involve catalytic liquid phase oxidation of α- and β-isophorone (α- and β-IP). Technical and environmental advantages of the gas phase oxidation of IP to KIP have not until now been exploited. In this contribution we present our results concerning the gas phase oxidation of α- and β-IP to KIP over selected metal oxide catalysts. Excellent combined selectivities to KIP and FIP (> 90 %) are found at low conversions of IP at ca. 200 °C. The oxidation of IP is presented in context with competing isomerization and rearrangement reactions.



[1] O. Isler, Carotenoids; Birkhauser-Verlag, Basel, 1971.

Organic Chemistry **156**

Synthetics applications and mechanistics studies of the Diels-Alder / Ireland-Claisen rearrangement tandem reaction

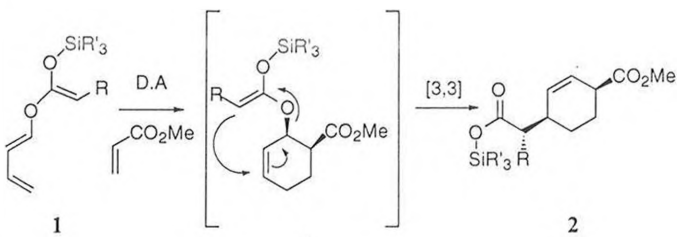
N. Soldermann, J. Velker, O. Vallat, R. Neier*

Université de Neuchâtel, Institut de chimie, Bellevaux, CH-2000 Neuchâtel

The use of tandems reactions in organic synthesis opens pathways to unconventional products. In our group a new tandem reaction Diels-Alder / Ireland-Claisen rearrangement starting from O-butadienyl-ketene-acetals **1** has been developed.

In order to apply this reaction we need a high stereocontrol in the tandem process. In this way, the Diels-Alder reactions are well known in the literature but the control of the Ireland-Claisen rearrangement is less developed and explained.

In this work we report some new informations about this rearrangement. The influence of the R group and the protecting group of the enolate on the tandem reaction has been studied.



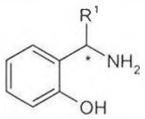
Organic Chemistry **157**

o-Hydroxy-α-alkylbenzylamines : Chiral Ligands and Auxiliaries.

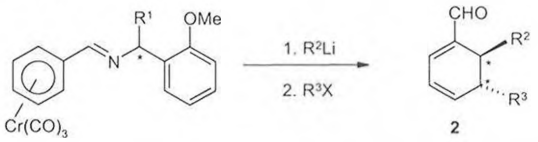
S Gillet, E. P. Kündig and S. Thibault.

Département de Chimie Organique, Université de Genève, 1211 Genève 4

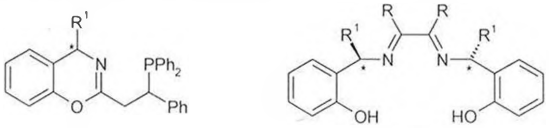
Chiral 1,3-aminophenols **1** are readily accessible by resolution or asymmetric synthesis. We here report on the use of **1** in the synthesis of chiral ligands and auxiliaries.



Chiral auxiliary: The chiral amine finds application in the transformation of $Cr(CO)_3$ complexed benzaldehydes. Imine formation followed by a diastereoselective dearomatization sequence affords enantioenriched cyclohexadienes **2** [1].



Chiral ligands: Following our first report on new chiral oxazine P/N-ligands [2], recent synthetic work has focused on bidentate chiral oxazine ligands **3** and tetradentate N/O ligands **4**.



[1] Kündig, E.P; Amurrio, D.; Anderson, G.; Beruben, D.; Khan, K.; Ripa, A; Liu, R. *Pure Appl. Chem.* **1997**, 69, 543.

[2] Kündig, E. P.; Meier, P. *Helv. Chim. Acta.* **1999**, in press.

Organic Chemistry **158**

Enantiospecific synthesis of (*R,R*)-2,2'-Bipyrrolidine

Tomassini A., Chouillet C., Roland S., Alexakis A

Université de Genève, Département de chimie organique
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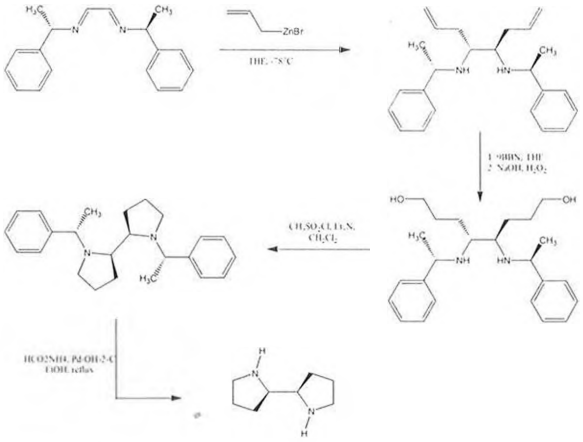
An enantiomeric (*R,R*)-2,2'-Bipyrrolidine has been prepared from enantiomeric N,N'-Bis [(*S*)-1-phenylethyl]ethanediimine. We used for this synthesis an enantioselective allylation of diimine with allylzinc chloride, prepared from allylchloride and zinc powder, at –78°C in tetrahydrofuranne to give N,N'-Bis-[(*S*)]-1-phenyl]-(*R,R*)-4,5-diamino-1,7-octadiene which was transformed to diol by hydroboration with 9-BBN. This diol was cyclised in presence of Mesylchloride and Triethylamine to give N,N'-[(*S*)-1-phenylethyl]-(*R,R*)-2,2'-bipyrrolidine. Then the (*R,R*)-2,2'-Bipyrrolidine was obtained by hydrogenation with ammonium formate on Pearlmann catalysts.

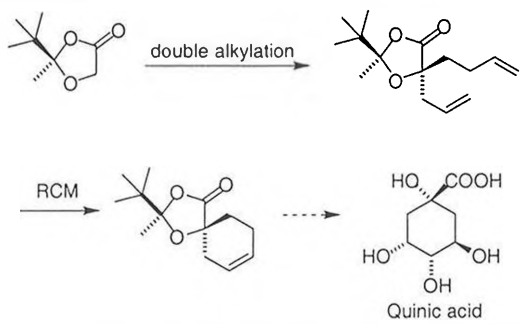


Organic Chemistry **159**

Chiral Cyclic α -Hydroxyacids from a Chiral Equivalent of Glycolic Acid

Vajira P. Bulugahapitiya, Liliana Parra-Rapado, Philippe Renaud

We report the preparation cyclic α-hydroxyacids from (*R*)- and (*S*)-2-*tert*-butyl-2-methyl-1,3-dioxolanone [1]. The key reactions are a double enolate alkylation followed by a ring-closing metathesis (RCM) [2]. This procedure is complementary to the radical annulation approach we have recently published [3].



To illustrate this approach, the synthesis of quinic acid was achieved according to the above scheme.

[1] P. Renaud, S. Abazi, *Helv. Chim. Acta* **1996**, 79, 1696.

[2] S. K. Armstrong, *J. Chem. Soc. Perkin. Trans. 1*, **1998**, 371. R. H. Grubbs, S. Chang, *Tetrahedron* **1998**, 54, 4413.

[3] S. Abazi, L. Parra Rapado, K. Schenk, P. Renaud, *Eur. J. Org. Chem.* **1999**, 477.

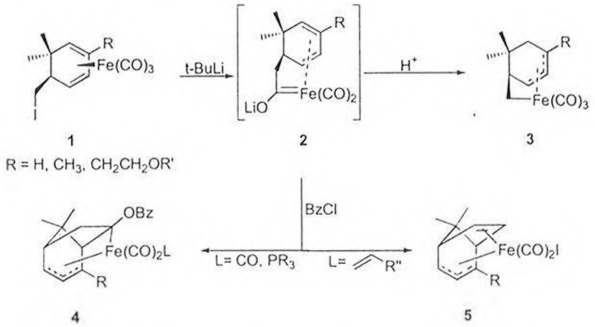
Organic Chemistry **160**

Intramolecular carbonyl alkylation as key step in the synthesis of a novel chiral Fp analog

C. Allemann, J. Raemy, T. A. Jenny*

*Université de Fribourg, Institut de chimie organique, Pérolles, 1700 Fribourg

Optically active iodo complexes **1** are readily accessible from apopinene (R=H), pinene ($R=CH_3$), and nopol derivatives ($R=CH_2CH_2OR'$) *via* ring opening complexation with $Fe(CO)_5$[1] followed by reaction with iodine. Lithiation of **1** with t-BuLi affords at low temperatures carbene complex **2** (spectroscopically detected, not isolated) which quantitatively yields either one of the three different products (**3**, **4**, or **5**) depending on the reaction conditions. Quenching carbene complex **2** with a weak proton source (*e.g.* acetophenone) furnishes σ-alkyl, π-allyl complex **3**, whereas reaction with strong electrophiles devoid of acid protons (*e.g.* benzoyl chloride) blocks the carbenoid structure of **2** by acylation. Warming of the latter product in presence of CO or phosphanes results in an intramolecular carbene addition yielding **4**, but in presence of an olefine (*e.g.* isoprene) produces complex **5** containing a novel chiral ligand which finds applications as stereoinducing and electronically chiral Cp analog. Preliminary studies on the reactivity of complex **5** point to promising stoichiometric and catalytic applications of this new chiral Fp analog.



1 R = H, CH_3, CH_2CH_2OR' 2 3 4 5

[1] T. A. Jenny, L. Ma, Tetrahedron Lett. **1991**, 32, 6101

CHIMIA 1999, 53, No. 7/8

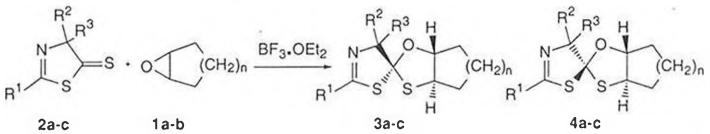
Organic Chemistry **161**

Scope and Limitations of the Reaction between Thiocarbonyl Compounds and Bicyclic Epoxides

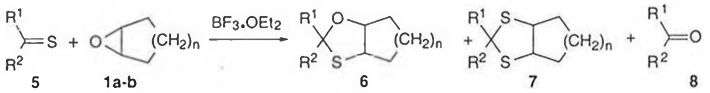
M. Blagoev, A. Linden, H. Heimgartner

Organisch-chemisches Institut der Universität Zürich
Winterthurerstr.190, 8057 Zürich

The synthesis of 1,3-oxathiolanes can be achieved in different ways. One of them, resulting in the formation of spirocyclic compounds *via* the reaction of oxiranes and cyclic thiocarbonyl compounds in the presence of a *Lewis*-acid, has already been described [1]. In order to investigate the scope and limitations of this reaction, bicyclic epoxides **1a-b** were reacted with different types of thiocarbonyl compounds.
With various thiazolethiones **2a-c** the reaction proceeded smoothly, giving two diastereoisomeric 1:1 adducts **3a-c** and **4a-c**.



In the reaction with thioketones **5**, 1,3-oxathiolanes **6**, 1,3-dithiolanes **7**, and the corresponding carbonyl compounds **8** were formed.



[1] P. C. Tromm, H. Heimgartner, *Helv. Chim. Acta* **1990**, *73*, 2287; V. Oremus, A. Linden, H. Heimgartner, *ibid.* **1991**, *74*, 1500.

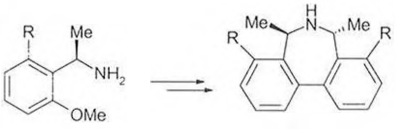
Organic Chemistry **162**

C_2-Symmetric Dibenzo [c,e] Azepine Derivatives Synthesis and First Applications

C. Botuha, E. P. Kündig, L. Saudan

Département de Chimie Organique, Université de Genève, 1211 Genève 4

C_2-chiral amines have found widespread use as auxiliaries and as chiral bases in asymmetric synthesis and as ligands in asymmetric catalysis. We here report on synthetic and conformational studies of new C_2-symmetric dibenzo [c,e] azepine derivatives **2**.



Enantioenriched *o*-methoxyphenethylamines **1** were used as chiral building blocks with an intramolecular Stille coupling as key-step in the azepine ring formation. Theoretical and NMR-studies of the conformational preference of **2a** indicate that the preferred conformer has the Me groups in pseudoequatorial positions. Synthetic studies underway aim at the synthesis of **2b** where $A_{1,3}$-strain may lead to a different conformational preference.
The lithium amide of the azepine **2a** has been tested in enantioselective deprotonation reactions [1] (see also poster S. Pache). Azepine **2a** was also converted to phosphoramidate ligands and first tests in their use in enantioselective catalytic conjugate addition reactions [2] have been carried out in collaboration with the group of A. Alexakis.

[1] Shirai, R.; Sato, D.; Tanaka, H.; Koga, K. *Tetrahedron.* **1997**, 17, 5963.
[2] Alexakis, A.; Vastra, J.; Burton, J.; Benhaim, C.; Mangeney, P. *Tetrahedron Lett.* **1998**, *39*, 7869.

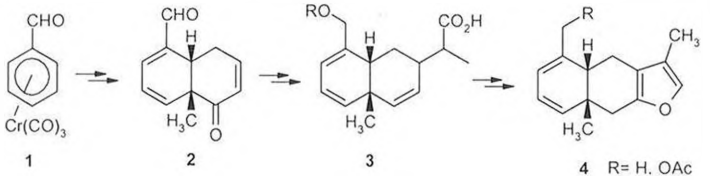
Organic Chemistry **163**

Aspects of a New Asymmetric Synthesis of Tubipofurans

R. Cannas, E. P. Kündig, R. Liu and S. Tchertchian

Département de Chimie Organique, Université de Genève, 1211-Genève 4

The tubipofurans **4** are biologically active furanoterpenoids isolated from marine organisms [1]. Our retrosynthetic analysis of **4** concluded that these products should be accessible from benzaldehyde. Containing all essential functions required for the synthesis of **4**, the key intermediates are the *cis*-fused carbocyclic ring compounds **2** and **3**. Complex **1** was converted into **2** via methodology previously developed in this laboratory. Three pathways for the conversion of **2**→**3** were investigated and will be discussed: conjugate addition, Pd-catalyzed allylic substitution and Ireland Claisen rearrangement.



In parallel, work on an asymmetric version of the transformation **1**→**2** has advanced. Our approach centers on a chiral ligand mediated enantioselective addition of a nucleophile to a cyclohexyl imine derivative of **1** [3].

[1] Iguchi, K.; Mori, K.; Suzuki, M.; Takahashi, H.; Yamada, Y. *Chem. Lett.* **1986**, 1789.
[3] Amurrio, D.; Khan, K.; Kündig, E.P. *J. Org. Chem.* **1996**, *61*, 2258

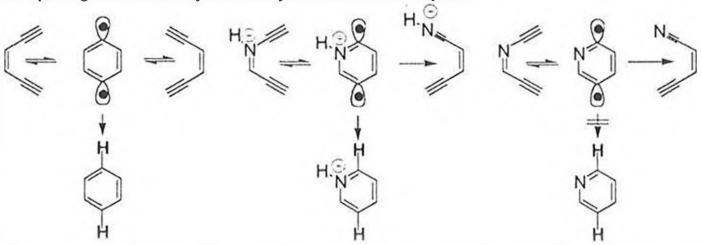
Organic Chemistry **164**

Azaenediynes Behave Differently from Enediynes

Johannes Hoffner, Peter Chen
Laboratorium für Organische Chemie, Eidgenössische Technische Hochschule, CH 8092 Zürich

Enediynes are an intensively studied group of potent cytotoxines. They undergo Bergman cyclization to form intermediate *p*-benzyne biradicals, which are able to abstract two hydrogen atoms from DNA, leading to double strand breakages and finally cell death. Due to their extreme cytotoxicity the enediyne family was hoped to be a real breakthrough in cancer treatment, but the selectivity against tumor cells is too small.

Less is known about their nitrogen analogues: the azaenediynes.[1,2] They undergo Bergman cyclization [2] as well and form *p*-pyridyne biradicals, whose reactivity can be altered by protonation.[1] In model experiments protonated *p*-pyridyne biradicals abstract hydrogen more readily than unprotonated *p*-pyridyne biradicals. We therefore expect the azaenediynes to damage selectively acidified cells (e.g. solid tumor cells) rather than ordinary cells. In this poster we are comparing the reactivity of enediynes and azaenediynes.



Bergmann cyclization of an enediyne Bergman cyclization of an azaenediyne

[1] Hoffner, J.; Schottelius, M. J.; Feichtinger, D.; Chen, P.; *J. Am. Chem. Soc. 120* (1998) 376-385.
[2] David, W. M.; Kerwin, S. M.; *J. Am. Chem. Soc. 119* (1997) 1464-1465.

Organic Chemistry **165**

A Novel Chiral d^1 Reagent: Stereoselective Addition to Aldehydes

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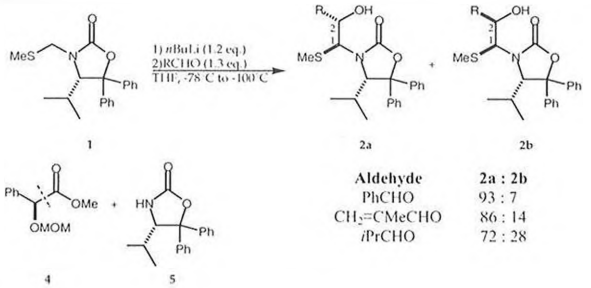
Laboratorium für Organische Chemie, ETHZ, 8092 Zürich

Chiral d^1 reagents [1], especially nucleophilic formylating reagents [2], provide efficient methods for the enantioselective synthesis of α-hydroxy carbonyl compounds from aldehydes. We have found recently [3] that the carbonyl group of the *gem*-diphenyl-substituted oxazolidinone moiety [4] is sterically well protected from nucleophilic attack, even by BuLi. This property has now been exploited by the use of 3-methylsulfanylmethyl-oxazolidin-2-one **1** as a synthetic equivalent of a chiral methoxy carbonyl anion. Thus, compound **1** is treated with BuLi in THF, followed by addition of an aldehyde to give a mixture of two diastereoisomers **2a** and **2b** in high yields and with good to excellent stereoselectivities. Products **2a** and **2b** have a single identical configuration at C-1 and are epimeric at C-2. The benzaldehyde adduct **2a** (R = Ph) has been converted to the enantiopure α-hydroxy methyl ester **4**, and the chiral auxilary **5** [3] is easily recovered by filtration.



Aldehyde	2a : 2b
PhCHO	93 : 7
CH_2=CMeCHO	86 : 14
*i*PrCHO	72 : 28

[1] D. Seebach, *Angew. Chem.*, **1979**, *91*, 259.
[2] A. Dondoni, L. Colombo, *Advances in the Use of Synthons in Organic Chemistry*, JAI Press, London, **1993**, 1.
[3] T. Hintermann, D. Seebach, *Helv. Chim. Acta*, **1998**, *81*, 2093.
[4] D.A. Evans, H. Bartroli, T.L. Shih, *J. Am. Chem. Soc.*, **1981**, *103*, 2127.

Organic Chemistry **166**

Isolation and synthesis of 4-hydroxy-3-(3-methyl-but-2-enyloxy)-benzoic acid, a new natural product from *Phaeoacremonium chlamydosporum*

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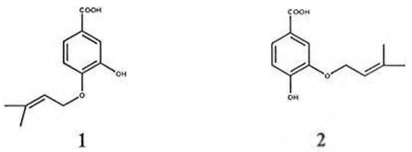
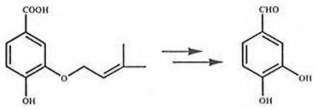
Phaeoacremonium chlamydosporum is a fungus implied in a vine disease: ESCA [1]. From the culture medium of this hyphomycetes, several compounds have been isolated and identified. The spectroscopic data of one of them led to the proposal of two structures (**1**, **2**), both corresponding to new natural products.



In order to etablish the structure of the natural compound, the regioselective syntheses of those two products were realized starting from 3,4-dihydroxy-benzaldehyde. We could conclude that *Phaeoacremonium chlamydosporum* was producing 4-hydroxy-3-(3-methyl-but-2-enyloxy)-benzoic acid.



[1] P. Larignon and B. Dubos, *European Journal of Plant Pathology*, **103**, 147-157, 1997.

Organic Chemistry **167**

Monochromatic Light as a Selective Reagent

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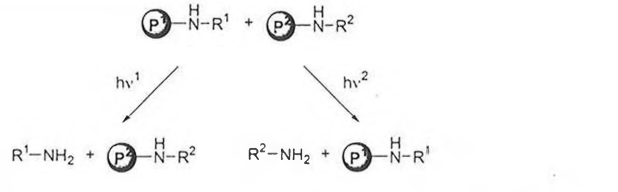
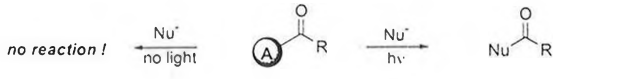
Light is a very cheap and clean reagent for chemical reactions, and its use in organic synthesis has been known for several decades. It is however not very selective, and such reactions were until now limited to systems with only one photoreactive center. In this work, we will show that selectivity can be obtained by using monochromatic light.



Scheme 1

P = protecting group

For example, the selective and complementary deprotection of carbamates was carried out at two different wavelengths (*Scheme 1*). This concept is not limited to simple cleavage, and bonds could also be formed by light activation (*Scheme 2*).



Scheme 2

A = photoactivable leaving group

Organic Chemistry **168**

Tetraethynylethenes as a Novel Class of Reversible Molecular Photoswitches

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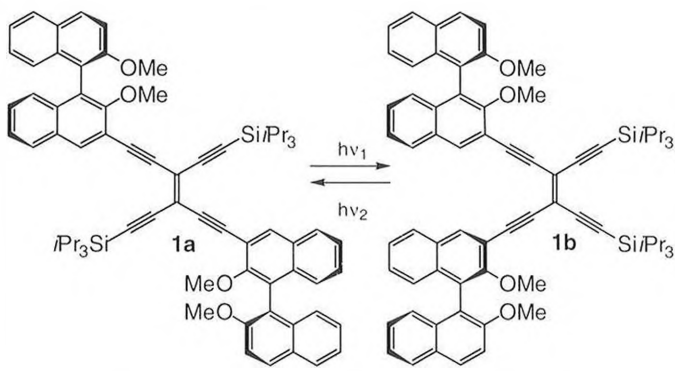
Universitätstrasse 16, 8092 Zürich

The tetraethynylethene (TEE) moiety provides a scaffold for a novel class of molecular photoswitches, as demonstrated in our previous work [1]. In order to better understand the properties of molecular switches based on a TEE group and to investigate possible applications, we are synthesizing derivatives like **1a**. The use of the chiral compound **1** to switch between liquid crystalline phases is under investigation.



[1] L. Gobbi, P. Seiler, F. Diederich, *Angew. Chem. Int. Ed.* **1999**, *38*, 674-678.

Organic Chemistry **169**

Synthesis of the Antibiotic Trichovirin I using the Azirine/Oxazolone Method

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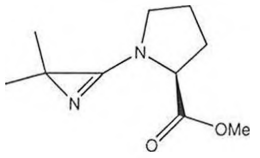
Universität Zürich, Organisch-chemisches Institut, Winterthurerstrasse 190, 8057 Zürich

The peptaibol trichovirin I (TV I) is a mixture of seven 14-residue peptides which shows antibiotic activity. It was isolated from the fungus *Trichoderma viride* NRRL 5243 [1]. We synthesized the TV I 1B with the sequence Ac-Aib-Asn-Leu-Aib-Pro-Ser-Val-Aib-Pro-Aib-Leu-Aib-Pro-Leuol using the Azirine/Oxazolone method. The Aib-Pro sequence appears three times in the peptaibol; therefore, we prepared the methyl *N*-(2,2-dimethyl-2*H*-azirin-3-yl)-L-prolinate (**1**) as building block of the dipeptide unit [2].



1

The structure of the C-terminal 6 – 14 segment and the N-terminal 1-6 segment was established by single-crystal X-ray crystallography.

[1] H. Brückner, T. Kripp, M. Kiess, 'Sequencing of new Aib-Peptides by tandem mass spectrometry and automated Edman degradation', in Peptides, Eds. E. Giralt and D. Andreu, ESCOM, Leiden, 1991, S. 347-9.
[2] R. Luykx, C. B. Bucher, A. Linden, H. Heimgartner, *Helv. Chim. Acta* **1996**, *79*, 527-9.

Organic Chemistry **170**

Synthesis of *ent*-halimanolide from *ent*-halimic acid

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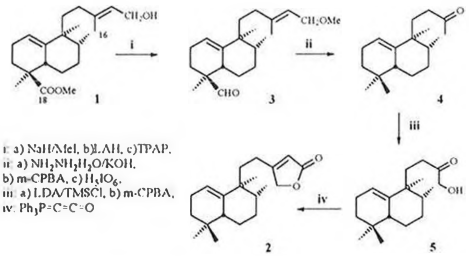
Using *ent*-halimic acid methyl ester[1] **1**, the major component of *Halimium viscosum* (Villarino de los Aires), natural *ent*-halimanolide **2**, originally isolated from *Polyalthia longifolia* [2] (Annonaceae), has been synthesised. The first step in the synthesis is the reduction of C_{18}. The subsequent functionalization at C_{16} to obtain lactones is achieved from the intermediate methyl ketone **4**, the product of side-chain degradation. The lactone ring is achieved following the Bestmann[3] methodology. The spectroscopic properties of **2** are identical to those of the natural product, allowing confirmation of chemical structure and absolute configuration.



[1] J.G. Urones, J. de Pascual Teresa, I.S. Marcos, D. Diez, N.M. Garrido, R. Alfayate, *Phytochemystry*, **1987**, *26*, 1077.
[2] N. Hara, H. Asaki, Y. Fujimoto, Y.K. Gupta, A.K. Singh, M.Sahai *Phytochemistry* **1995**, *38*, 189.
[3] H.J. Bestmann, *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 349.

Organic Chemistry **171**

Synthesis of Chiral Hexacoordinated Phosphorus Anions Conformationnal and Configurational Studies by ^{31}P-NMR Spectroscopy.

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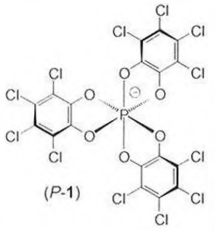
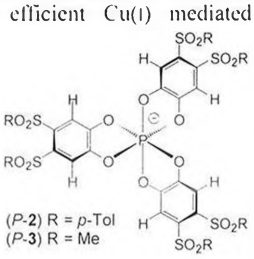


Our laboratory is engaged in the synthesis and resolution of stable enantiopure hexacoordinated phosphate anions, such as TRISPHAT (**1**), and in their use as chiral auxiliaries. The configurational sensitivity of this anion towards strong acidic conditions is a limitation for its broad use in asymmetric chemistry.[1] Herein, we report the synthesis of two novel derivatives, the 4,5-*ST*-TRISPHAT (**2**) and 4,5-*SM*-TRISPHAT (**3**), more stable in acidic media due to the presence of stronger electron withdrawing substituents (-SO_2R) on the catechol rings. Short syntheses of the required catechols have been developed using the efficient Cu(I) mediated sulphonylation of aryl iodides.[2] The slow conformational isomerism of the two sulphonyle groups on each of the three catechol ligands induces the presence of four isomeric products for each enantiomer of the anion. They can be observed in ^{31}P-NMR spectroscopy. Asymmetric induction studies onto Fe(II)tris(diimine) complexes are currently under way.



[1] Lacour, J.; Ginglinger, C.; Grivet, C.; Bernardinelli, G. *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 608-610.
[2] Suzuki, H.; Abe, H. *Tetrahedron Lett.* **1995**, *36*, 6239-6242.

Organic Chemistry **172**

Generation of Alkyl Radicals from *B*-Alkylcatecholboranes via Photolysis of *N*-Methoxycarbonyloxypyridine-2-thione

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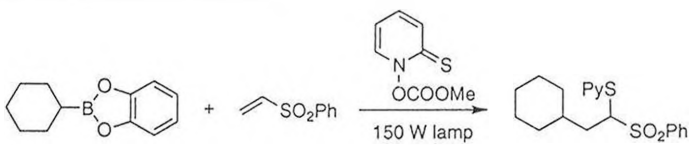
The use of organoboranes as radical precursors has been reported in the early seventies by Brown [1]. Recently, we have shown that *B*-alkylcatecholboranes are efficient radical precursors which can be applied for conjugate addition to α,β-unsaturated ketones and aldehydes, or trapped by 2,2,6,6-tetramethylpiperidine-*N*-oxyl (TEMPO) [2].

We report here that *B*-alkylcatecholboranes react efficiently with *N*-methoxycarbonyloxypyridine-2-thione [3] under irradiation to give the corresponding alkyl 2-pyridylsulfides in good yield. When a radical trap such as phenyl vinyl sulfone is added to the reaction mixture, the product of conjugate addition is isolated.



[1] H. C. Brown, G. W. Kabalka *J. Am. Chem. Soc.* 1970, *92*, 714.
[2] C. Ollivier, P. Renaud *Chem. Eur. J.* 1999, 5, 1460 ; C. Ollivier, R. Chuard, P. Renaud *Synlett* 1999, in press.
[3] M. Newcomb, M. Udaya Kumar, J. Boivin, E. Crépon, S. Z. Zard *Tetrahedron Lett.* 1991, *32*, 45.

Organic Chemistry **173**

Synthesis of Thio-TADDOL-Derivatives, their Application in Copper(I)-Catalyzed Conjugate Addition of *Grignard* Reagents to Enones and Enoates, and Mechanistic Investigations

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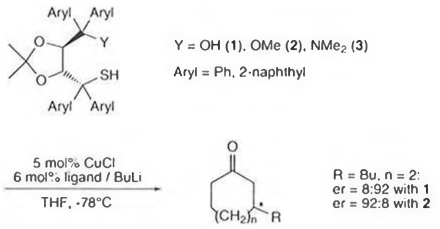
Laboratorium für Organische Chemie[a] and Laboratorium für Anorganische Chemie[b], ETH Zürich Universitätstrasse 16 and 6, CH-8092 Zürich

Recently, we have synthesized TADDOL-derivatives with sulfur atoms as coordinating units and these thio-TADDOL-analogs have been used successfully as ligands for the catalytic copper(I)-catalyzed conjugate addition of *Grignard* reagents to cyclic enones [1].
We have discovered that the second chelating group in the ligands (**1** and **2**) has an extraordinary effect, in that it leads to a reversal of the stereochemical course of the reaction (formation of either enantiomer). Here we present mechanistic studies (NMR, NLE) concerning this intriguing reversal of asymmetric induction in catalysis, as well as new results obtained by varying the structure of the ligands, the substrates and the nucleophiles. An X-ray crystal structure of a tetranuclear copper(I)-complex will be presented.



[1] D. Seebach, G. Jaeschke, A. Pichota, L. Audergon, *Helv. Chim. Acta* **1997**, *80*, 2515.

Organic Chemistry **174**

Regioselective One-Step Synthesis of *trans*-3,*trans*-3,*trans*-3 and *e,e,e* [60]Fullerene Tris-Adducts Directed by a C_3-Cyclotriveratrylene Tether

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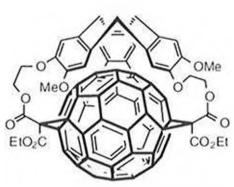
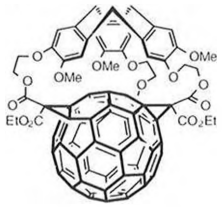
[a] *ETH-Zentrum, Universitätstrasse 16, CH-8092 Zürich, Switzerland.*
[b] *ENS Lyon, 46 Allée d'Italie, 69364 Lyon Cedex 07, France.*
[c] *University of Miami, Coral Gables, FL 33124, USA.*

Many functionalization reactions of C_{60} leading to a variety of mono- and bis-adducts have been reported but only few examples of tris-adducts have been described.[1] We present here the regioselective synthesis of two new highly symmetrical C_3-tris-adducts having (*trans*-3,*trans*-3,*trans*-3) and (*e,e,e*) structures, in one step from C_{60}. Our strategy involves the use of a C_3-symmetrical tris-malonate derivative of cyclotriveratrylene which acts as a template for the reaction thanks to its ability to form inclusion compounds with C_{60}.[2]



(±)-**3** : *trans*-3,*trans*-3,*trans*-3
11%



(±)-**4** : *e,e,e*
9%

1. F. Diederich, R. Kessinger, *Acc. Chem. Res.* **1999**, in press.
2. J.W. Steed, P.C. Junk, J.L. Atwood, M.J. Barnes, C.L. Raston and R.S. Burkhalter, *J. Am. Chem. Soc.* **1994**, *116*, 10346.

Organic Chemistry **175**

Towards the Total Synthesis of Xenicanes

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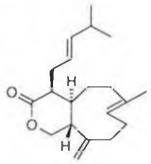
Xenicanes are a class of diterpenes and norditerpenes isolated from marine organisms from all parts of the world. They exhibit interesting biological properties like the antiinflammatory activity [1]. The core structure contains a nine-membered ring with an *E*-double bond as e.g. in coraxeniolide A.



Coraxeniolide A

We report here the synthesis of the bicyclic Enon **1**, which represents a useful intermediate in the total synthesis of optically active xenicanes. Compound **1** was synthesized in 20 steps using the *Grob*-fragmentation as keystep for the elaboration of the nine-membered ring containing the *E*-double bond.

No Z-isomer could be isolated and product **1** was obtained in optically pure form. The structure of **1** was confirmed by X-ray structure analysis.

[1] G.J. Hooper, M.T. Davies-Coleman, M. Schleyer, *J.Nat.Prod.* **1997**, *60*, 889-893.

Organic Chemistry **176**

Synthesis of a Hydrophobic Analogue of Nonactic Acid

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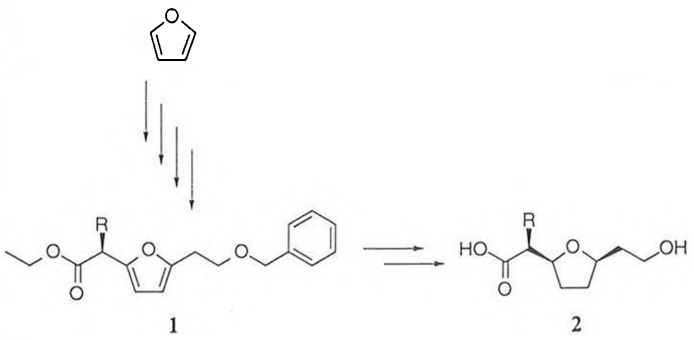
Université de Neuchâtel, Institut de Chimie, Bellevaux 51, 2000 Neuchâtel

For applications of nonactine in sensors, it is important to obtain more hydrophobic derivatives of this ionophore. We decided to study a *de novo* synthesis of analogues of nonactic acid. To be able to vary the proprieties of these analogues, the synthesis has to be cheap, easy to vary and if possible high yielding. We report our studies of the synthesis of compounds like **2** starting from furane in 6 steps.



1 **2**

CHIMIA 1999, 53, No. 7/8

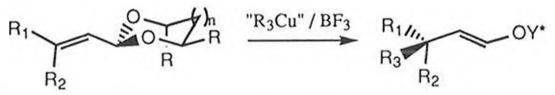
Organic Chemistry **177**

Stereochemistry of allylic substitution using organocopper reagent

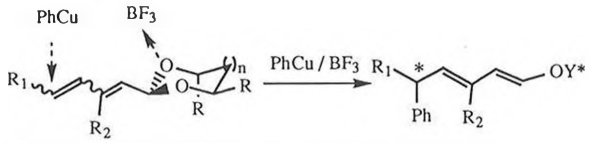
A. Alexakis, P. Mangeney, F. Mazé

Université de Genève, 30, Quai Ernest Ansermet, 1211 Genève 4

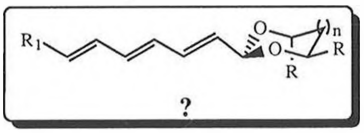
It has been previously shown [1] that α,β ethylenic acetals were opened regio and diastereoselectively by aryl copper reagent in the presence of BF_3 following an anti S_N2' process.



The same reaction on dienic acetal afforded S_N2'' products with stereochemical inversion when compared to S_N2'. It led to syn process.



What about reactions with trienic acetals?



[1] H. Rakotoarisoa, R. Guttierez Perez, P. Mangeney, A. Alexakis *Organometallics*, **1996**, 15, 1957

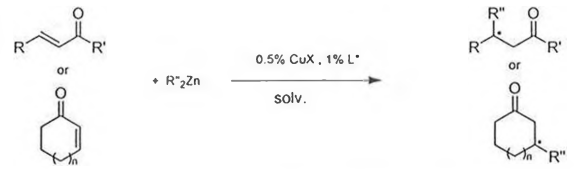
Organic Chemistry **178**

New Developments in Asymmetric Conjugate Addition

C.Benhaïm, C. Malan, X. Fournioux, J.M. Lévêque, A. Van Den Heuwel, S. Rosset, A. Alexakis.

***Université de Genève,** Département de Chimie Organique,30 quai Ernest-Ansermet 1211 Genève*

The conjugate addition reaction, one of the most important synthetic transformation, was usually best achieved using organocopper reagents, i.e. with a stoechiometric quantity of respectively organocopper and chiral auxiliar to induce a chirality. Nowadays, the catalytic version is the most interesting. Thus, we introduced the use of R_2Zn[1] as primary organometallic reagent and found that copper triflate is the most adequate copper source[2]. The asymmetric induction is brought by a catalytic quantity of chiral phosphorus compounds[2-5].



We shall discuss the design and the synthesis of the chiral phosphorus ligand, the reaction conditions and the different type of substrates.

[1] Alexakis, A.; Frutos, J.; Mangeney, P. *Tetrahedron: Asymmetry* **1993**, *4*, 2427-2430.
[2] Alexakis, A.; Vastra, J.; Burton, J.; Mangeney, P. *Tetrahedron: Asymmetry* **1997**, *8*, 3193-3196.
[3] Alexakis, A.; Burton, J.; Vastra, J.; Mangeney, P. *Tetrahedron: Asymmetry* **1997**, *8*, 3987-3990.
[4] Alexakis, A.; Vastra, J.; Mangeney, P. *Tetrahedron Lett.* **1997**, *38*, 7745-7748.
[5] Alexakis, A.; Vastra, J.; Burton, J.; Benhaim, C.; Mangeney, P. *Tetrahedron Lett.* **1998**, *39*, 7869-7872.

Organic Chemistry **179**

First Selective Heterogeneous Catalytic Reduction of an α,β-Unsaturated Ketone to Allylic Alcohol by Dihydrogen

M. von Arx, T. Mallat, A. Baiker

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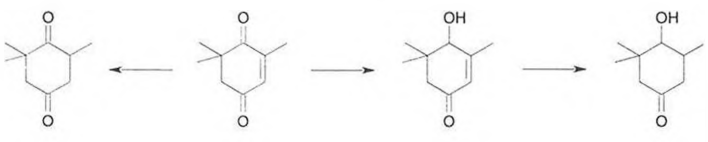
Allylic alcohols can be prepared from α,β-unsaturated ketones by the use of stoichiometric amounts of hydridic reagents, enzymes, homogeneous catalysts or by hydrogen transfer reactions over basic oxides, but only poor yields were obtained with (supported) metal catalysts and molecular hydrogen so far [1]. Here we report the first selective heterogeneous catalytic reduction of an α,β-unsaturated ketone to the corresponding allylic alcohol using dihydrogen as a reductant.

2,2,6-trimethyl-cyclohex-2-en-1,4-dione **1** was hydrogenated over a 5 wt % Pd/Al_2O_3 catalyst affording the allylic alcohol **2** with a selectivity of 93%. The reaction must be stopped after the consumption of about 1 equivalent of H_2, otherwise the ketoalcohol **3** is the main product. The competing hydrogenation of the C=C double bond can be suppressed by the use of a methanol/acetic acid mixture as solvent and low hydrogen pressure. Addition of acid favours the formation of **2** through partial protonation of the carbonyl oxygen atom (acid catalysis), and accelerates the reaction. Other noble metals (e.g. Pt/Al_2O_3) favoured the formation of **4**.



4 1 2 3

[1] M. Soukup, T. Lukac, R. Zell, F. Rössler, K. Steiner, W. Widmer, Helv. Chim. Acta 72 (1989) 365; P. Claus, Topics in Catal. 5 (1998) 51; R. L. Augustine, Catalysis Today 37 (1997) 419.

Organic Chemistry **180**

Selective Epoxidation of Allylic Alcohols with Amine-Modified Titania-Silica Aerogels

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Amorphous titania-silica aerogels active for the epoxidation of olefins can be synthesized by the solution sol-gel process followed by semicontinuous extraction with supercritical CO_2 [1, 2]. Their outstanding performance in the epoxidation of cycloalkenes with TBHP was attributed to the high surface area, mesoporous structure and high Ti-dispersion in the silica matrix [3].

Epoxidation of allylic alcohols was much less successful, affording often low epoxide yields. We have found recently [4] that the acidity of titania-silica can be tuned and the epoxide selectivity improved with amine additives. Various aliphatic, cycloaliphatic and aromatic amines were employed in the aerogel catalyzed epoxidation of cyclohexenol, alkyl-substituted cyclohexenols and other cyclic and linear allylic alcohols.

Small amount of amines suppressed the non-oxidative consumption of the substrate (isomerization, dehydration, oligomerization), and the epoxide ring opening by the reactant allylic alcohol. Formation of byproducts was catalyzed by the acidic sites on the aerogel. Suppression of side reactions is obviously due to partial neutralization of the major acidic sites: the surface silanol groups and $Ti(OSi)_4$ (responsible for the epoxidation activity).

[1] H. Kochkar and F. Figueras, *J. Catal.*, **1997**, *171*, 420.
[2] D. C. M. Dutoit, M. Schneider and A. Baiker, *J. Catal.*, **1995**, *153*, 165.
[3] R. Hutter, T. Mallat and A. Baiker, *J. Catal.*, **1995**, *153*, 177.
[4] M. Dusi, T. Mallat and A. Baiker, *Chem. Commun.*, **1999**, 197.

Organic Chemistry **181**

Stereoselective Radical Aryl Migration from Silicon to Carbon

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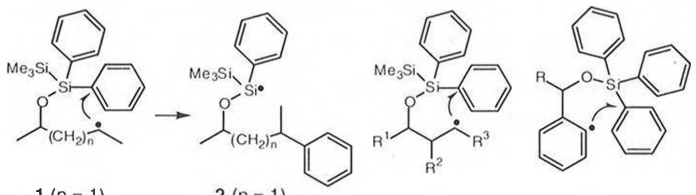
We have recently shown that the intramolecular *ipso* substitution in diphenyl(trimethylsilyl)silyl ethers is an efficient method for the stereoselective C(sp^3)–phenyl bond formation (**1** → **2**).[1]



1 (n = 1) **4** (n = 0, 2) **2** (n = 1) **5** (n = 0, 2) **3** **6**

We now report the scope and limitations of this reaction. The effect of the substituents R^1, R^2, and R^3 on the selectivity will be discussed (see **3**). Functionalized aryl groups can also be transferred. Stereoselective 1,4- as well as 1,6-phenyl migrations will be presented (**4** → **5**). In addition, a novel biphenyl synthesis starting from readily available triphenyl silyl ethers will be discussed (see **6**).

[1] A. Studer, M. Bossart, H. Steen, *Tetrahedron Lett.* **1998**, *39*, 8829.

Organic Chemistry **182**

Radical Fragmentation of Bicyclic Alkoxy Radicals

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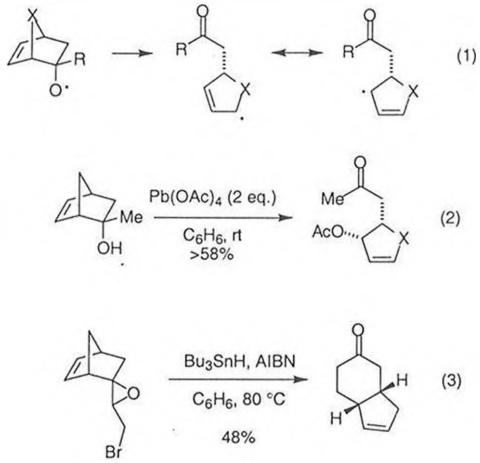
Norbornenone and 7-oxanorbornenone are useful chiral building blocks for the synthesis of products of biological interest. In this account, we report the fragmentation of such bicyclic systems via alkoxy radicals leading to intermediate allyl radicals (eq 1). The generation of alkoxy radicals is achieved either by lead tetraacetate oxidation of the corresponding alcohol (eq. 2) or fragmention of an oxiranyl methyl radical (eq. 3). Preliminary results concerning the application of this approach to natural products synthesis will be reported.



Organic Chemistry **183**

The Evans-Mislow Rearrangement: a New Approach for the Generation of Alkoxy Radicals

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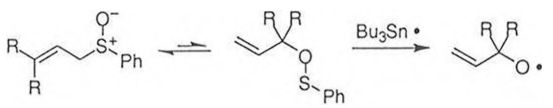
Université de Fribourg, Institut de Chimie Organique, Pérolles CH-1700 Fribourg, Switzerland

Despite the number of existing methods for the generation of oxygen centered radicals from alcohol, their generation from hindered secondary and tertiary alcohols is still problematic and challenging. For instance, sulfenates are excellent precursors of alkoxy radicals, however, their preparation is limited to primary and non-hindered secondary alcohols.

In this account, we report a solution to this problem for allylic substrates. This method takes advantage of the well-known [2,3]-sigmatropic rearrangement of allyl sulfoxides to allyl sulfenates (Evans-Mislow rearrangement).[1,2]



A one-pot procedure for the conversion of allyl sulfoxides to alkoxy radicals followed by radical rearrangements has been developed.

[1] E. G. Miller, D. R. Rayner, K. Mislow, *J. Am.. Chem. Soc.* **1966**, 3139.
[2] D. A. Evans, G. C. Andrew, *Acc. Chem. Res.* **1974**, *7*,, 147.

Organic Chemistry **184**

Efficient Radical Amination of Alkyliodides

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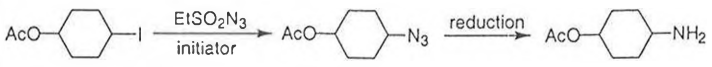
Université de Fribourg, Institut de Chimie Organique, Pérolles CH-1700 Fribourg, Switzerland

Nucleophilic and electrophilic azidation are classical procedure to introduce amino functional groups. The radical version of this reaction has never been reported [1]. Moreover, other methods for radical amination were studied in the past [2], but no efficient and simple procedure has been developed.

We present here the azidation of radicals using ethanesulfonyl azide ($EtSO_2N_3$). The reaction is based on a iodine atom transfer process similar to the one developed by Zard for the radical allylation of alkyliodides [3]. Subsequent reduction under mild conditions affords the corresponding amine [4]. Scope and limitations of this approach will be discussed.



[1] For intramolecular reactions of azide with radicals, see: S. Kim, G. H. Joe, J. Y. Do *J. Am. Chem. Soc.* **1993**, *115*, 3328-3329.
[2] D. H. R. Barton, J. Cs. Jaszberenyi, E. A. Theodorakis, J. H. Reibenspies *J. Am. Chem. Soc.* **1993**, *115*, 8050-8059.
[3] F. Le Guyader, B. Quiclet-Sire, S. Seguin, and S. Z. Zard *J. Am. Chem. Soc.* **1997**, *119*, 7410-7411.
[4] G. Vidyasagar Reddy, G. Venkat Rao, and D. S. Iyengar *Tetrahedron Lett.* **1999**, *40*, 3937-3938.

Organic Chemistry **185**

Synthesis of Inhibitors for a Mechanistic Investigation on Porphobilinogen Synthase (PBGS).

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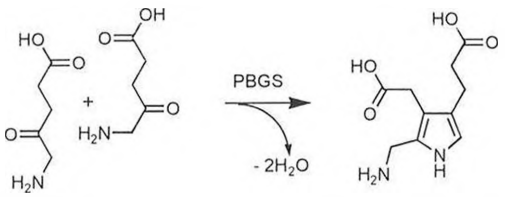
Université de Neuchâtel, Institut de Chimie, Av. Bellevaux 51, 2000 Neuchâtel, Switzerland

Despite the fact that its structure is known[1], the mechanism used by PBGS to condense asymmetrically two 5-aminolevulinic acid is still not fully elucidated



We are pursuing the concept of mechanistic investigation by kinetics studies of inhibitors that are analogues of the substrate, of postulated intermediates or of the product as initiated in our group[2]. Now we are able to discriminate the two recognition sites as far as inhibition is concerned and we have strong indications to favour one of the bond forming sequences. An other aspect of this important enzyme, the use of unnatural substrates, will be discussed.

[1] P.M. Shoolingin-Jordan et al., *Nature Structural Biology*, **1997**, *4*, 1025.
[2] R.M. Lüönd, J. Walker, R. Neier, *J. Org. Chem.*, **1992**, *57*, 5005.

Organic Chemistry **186**

OPA: the olefinic peptide nucleic acid analogue

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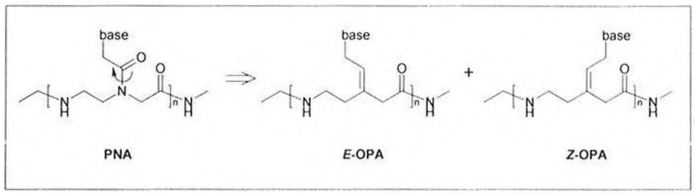
University of Berne, Department of Chemistry and Biochemistry, Freiestrasse 3, CH-3012 Berne

Peptide nucleic acid (PNA)[1] has attracted considerable attention for different biological applications due to its unique binding properties to nucleic acids. Uncomplexed single stranded PNA exists as a mixure of tertiary amide bond rotamers, whereas in PNA-nucleic acid complexes the carbonyl groups point towards the C-terminus[2]. In order to eliminate this structural ambiguity the amide function was replaced by a Z- or E-configured double bond. From these preorganized olefinic PNA analogues (OPA) information on the structural and electrostatic role of the tertiary amide function on affinity and selectivity in PNA/DNA (RNA) recognition can be obtained.



The synthesis of the monomeric building blocks[3], the solid-phase synthesis and the binding properties of E-and Z-OPA are described.

[1] P. E. Nielsen, M. Egholm, R. Berg, O. Buchardt, *Science* **1991**, *254*, 1497-1500
[2] M. Eriksson, *Nucleosides & Nucleotides* **1997**, *16*, 617-621
[3] M. Cantin, R. Schütz, C. Leumann, *Tetrahedron Letters* **1997**, *38*, 4211-4214

Organic Chemistry **187**

Electron Transfer in Alanyl Peptide Nucleic Acids

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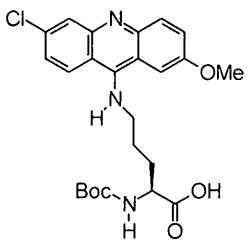
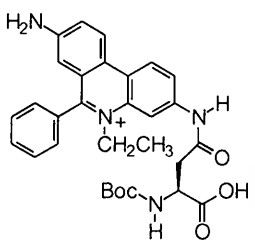
Pairing complexes of alanyl peptide nucleic acids (PNAs) form linear and rigid double strands [1]. They can be used as a well defined nucleobase stack model of DNA. Furthermore, the substitution of nucleobases by aromatic residues mostly stabilize the base stack. Amino acids **1** and **2** with covalently linked 2-methoxy-6-chloroaminoacridine and ethidium dyes were prepared and incorporated in alanyl-PNA [2].



1



2

First indications of photoinduced electron transfer in alanyl-PNA containing the chromophors are presented. For the first time, electron transfer is shown in a base stack with a backbone different from nucleic acids.

[1] U. Diederichsen, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1886.
[2] a) U. Diederichsen, D. Weicherding, *Synlett*, in press. b) K. Fukui, K. Iwane, T. Shimidzu, K. Tanaka, *Tetrahedron Lett.* **1996**, *37*, 4983. c) S. O. Kelly, R. E. Holmlin, E. D. A. Stemp, J. K. Barton, *J. Am. Chem. Soc.* **1997**, *119*, 9861.

Organische Chemie **188**

Synthese von optisch aktiven Acetylcholin-Mimetika

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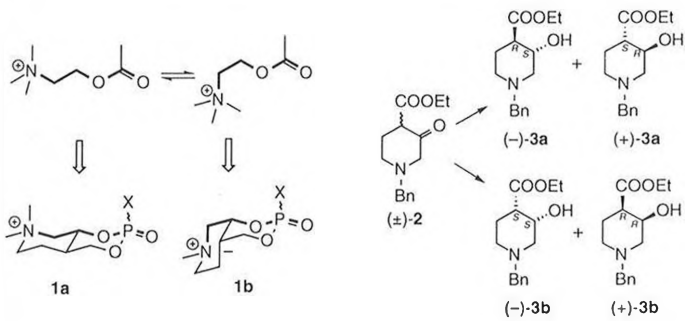
Organisch chemisches Institut, Universität Zürich Winterthurerstrasse 190, CH-8057 Zürich, Schweiz

Im Rahmen unserer Arbeiten zur Untersuchung der Regio- und Stereochemie der Inhibition von Serin-Hydrolasen mit Organophosphaten [1] werden optisch aktive Acetylcholin-Analoga hergestellt. Enantioselektive Reduktion von **2** ergab die Piperidine (+)- und (–)-**3a** und **3b** als Vorläufer der *cis*- und *trans*-Azaphosphadecaline **1** mit fixierter Konfiguration und Konformation (X = F, Cl, 4-Nitrophenoxy, 2,4-Dinitrophenoxy, axial/equatorial).



Dabei verläuft die biologische Reduktion zu den *trans*-Verbindungen mit einer anderen Stereoselektivität als die Ru-katalysierte Hydrierung. Der Grund scheint in der verschiedenartigen Koordination der reduzierenden Agenzien mit **2** zu liegen. Modellvorstellungen und die Herleitung der absoluten Konfiguration werden im Vortrag erläutert.

[1] W. Ganci, E.J.M. Meier, F.A. Merckling, G. Przibille, U. Ringeisen, P. Rüedi, *Helv. Chim. Acta* **1997**, *80*, 421; S. Furegati, W. Ganci, G. Przibille, P. Rüedi, *ibid.* **1998**, *81*, 1127.

Organic Chemistry **189**

On the Mechanism of Long-Range Charge Migration in DNA

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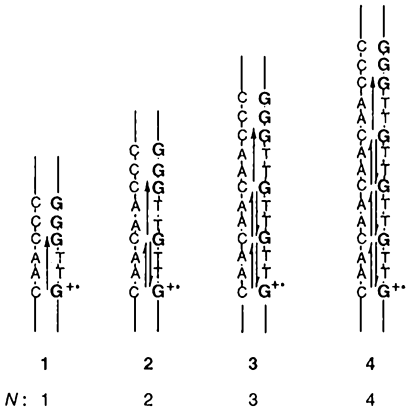
Department of Chemistry, University of Basel,
St. Johanns-Ring 19, CH-4056 Basel

Charge transport through DNA occurs via a multistep hopping process. Relay stations for the charge are bases of similar redox potential. Since guanine (G) is the base of lowest oxidation potential in DNA, migration of positive charge takes place by tunneling between nearest G bases.
Rate measurements performed with DNA strands **1-4** show that the overall charge transport rate k_{rel} is weakly dependent on the number of hopping steps N [1]:

$$\ln k_{rel} \propto -1.7 \ln N$$



[1] B. Giese, S. Wessely, M. Spormann, U. Lindemann, E. Meggers, M. E. Michel-Beyerle *Angew.Chem.Int.Ed.* **1999**, *38*, 996

Organic Chemistry **190**

3'-AMINOACYL- AND 3'-PEPTIDYL-RNA

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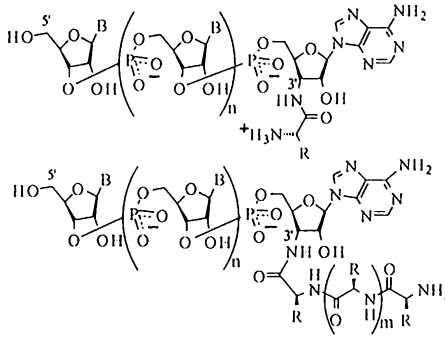
Institute of Organic Chemistry, University of Basel,
St. Johanns-Ring 19, CH – 4056 Basel

We are interested in the synthesis and evaluation of the structure and thermodynamics of RNA strands that are covalently linked to amino acids or peptides at their 3' terminus. We developed a synthetic procedure that allows us to synthesise a peptide and an RNA strand both in a stepwise fashion on the same solid support.



Our technique of synthesising 3'-terminal peptidyl-RNA without interlinking spacer or phosphate is dictated by the parental, charged transfer RNA molecule. In a first test series we synthesised 3'-alanyl-RNA 22mers, as well as 3'-Ala_4- and 3'-Ala_8-RNA oligomers. We characterised the products using MALDI-ToF MS and enzymic digestion/HPLC, and analysed the folding of the conjugates by UV abd CD spectroscopy.

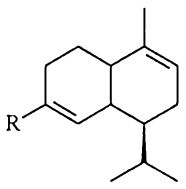
Organic Chemistry **191**

A new Norsesquiterpene from *Eryngium giganteum*.

B. Muckensturm, S.M. Farahi, J.P. Reduron

Université de Haute Alsace, Ecole Nationale Supérieure de Chimie de Mulhouse, 3, rue A. Werner, F-68093 Mulhouse CEDEX, Conservatoire Botanique de la Ville de Mulhouse, 2, rue Pierre Curie, F-68200 Mulhouse.

A new norsesquiterpene and six known sesquiterpenoids were identified from the seeds of *Eryngium giganteum*, representing 95% of the total peak area of the gas chromatogram. 14-oxy-α-muurolene, 14-nor-α-muurolene, 14-hydroxy-α-muurolene, ledol, and spatuledol are reported from a member of Umbelliferae for the first time. Their structures were elucidated by spectroscopic analysis.



R= H 14-nor-α-muurolene
R= CHO 14-oxy-α-muurolene
R= CH_2OH 14-hydroxy-α-muurolene

B. Muckensturm, S.M. Farahi, J.P. Reduron, *Phytochem.*, awaiting publication for 1999.

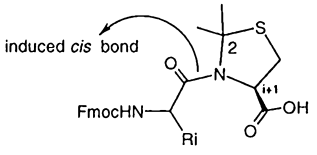
Organic Chemistry **192**

The Pseudo-Proline Concept as Tool in Structure-Activity Studies of Bioactive Peptides

Angela Wittelsberger[1], Michael Keller[1], Leo Scarpellino[2], Luc Patiny[1], Hans Acha-Orbea[2] and Manfred Mutter[1]
[1]*Institute of Organic Chemistry, University of Lausanne, BCH-Dorigny, CH-1015 Lausanne.* [2]*Institute of Biochemistry and Ludwig Institute, University of Lausanne, ISREC, Ch. des Boveresses 155, CH-1066 Epalinges.*

Pseudo-prolines (Ψ-Pro) are synthetic proline analogues readily obtained by cyclocondensation of the amino acids serine, threonine or cysteine with aldehydes or ketones. Variation of their C(2)-substituents allows to modulate physico-chemical, pharmakokinetical and biological properties of peptides and proteins [1,2]. For example, the *cis*-inducing effect of Ψ-prolines upon the Xaa_i-ΨPro_{i+1} peptide bond can be increased to 100 % when C(2)-dimethylated [2]. Consequently, this class of pseudo-prolines can serve as mimics of biologically relevant *cis*-prolyl conformations.

Fmoc-Xaa_i-Cys($\Psi^{Me,Me}$pro)



As a representative example, a mimetic of the HIV-1 gp120 V3 loop will be presented. The recently proposed infection-active loop tip conformation involving a Xaa-Pro *cis*-peptide bond has been induced by introduction of a dimethylated thiazolidine derivative (Figure). Experimental data obtained with antibodies raised against the *cis*-conformation demonstrates the pseudo-proline concept to be a versatile tool for investigating conformational effects during the infection process [3].

[1] Wöhr, T.; Wahl, F.; Nefzi, A.; Rohwedder, B.; Sato, T.; Sun, X.; Mutter, M. *J. Am. Chem. Soc.* **1996**, *118*, 9218-9227.
[2] Dumy, P.; Keller, M.; Ryan, D. E.; Rohwedder, B.; Wöhr, T.; Mutter, M. *J. Am. Chem. Soc.* **1997**, *119*, 918-925.
[3] Wittelsberger, A; Keller, M; Scarpellino, L; Patiny, L; Acha-Orbea, H; Mutter, M. *J. Am. Chem. Soc.*, submitted for publication.

Organic Chemistry **193**

A new reagent for the Koenigs-Knorr reaction : Bromotetraisobutyrylglucose

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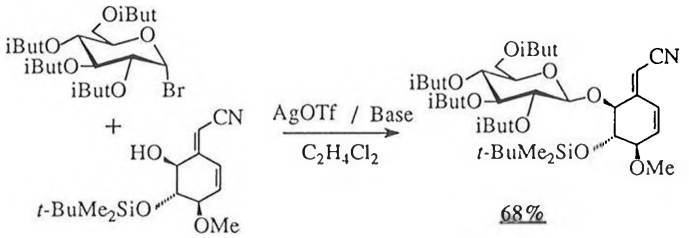
Ecole Nationale Supérieure de Chimie de Mulhouse,
3, rue Alfred Werner F-68093 MULHOUSE Cedex.

Despite numerous methods in literature, the formation, in acceptable yields, of ß-glucosides of hindered secondary alcohols remains a challenge. One of the best methods is the Koenigs-Knorr procedure using acetobromoglucose. However, orthoester formation is usual and is at least partly responsible for the modest yields of ß-glucosides often obtained. This side-reaction can be avoided by the use of bromotetrapivaloylglucose [1], but, unfortunately, its reactivity is weak. During the total synthesis of Bauhinin, we proposed [2] the use of bromotetraisobutyrylglucose in acidic medium. We describe herein the use of this reagent in almost neutral conditions where even the presence of a silyl ether can be tolerated. The glycosidations of several terpenic alcohols : borneol, fenchol, isopulegol, citronellol, is shown here as additional examples.



(2 equiv. AgOTf, 2 equiv. Bromosugar, $C_2H_4Cl_2$, 1,36 equiv. Base; progressive addition of 0,64 equiv. Base during 20 minutes at rt. then, 2 h at rt.)

[1] H. Kunz, A.Harreus, *Liebigs. Ann. Chem.* **1982**, 41

[2] G. Desmares, C. Le Drian, *Chimia* **1996**, *50*, 354

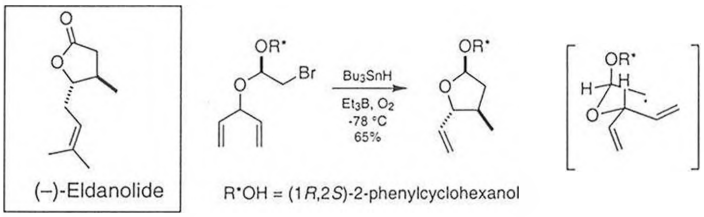
Organic Chemistry **194**

Radical Cyclization of Chiral Haloacetals: Synthesis of (–)-Eldanolide and Other Natural Products

Félix Villar and Philippe Renaud

Université de Fribourg, Institut de Chimie Organique, Pérolles
CH-1700 Fribourg, Switzerland

Recently, we demonstrated that the stereochemistry of the Ueno-Stork [1] radical cyclization of haloacetals can be controlled by the acetal center [2]. This approach was used for the synthesis of (–)-botryodiplodin [3]. An easy and highly stereoselective synthesis of (–)-eldanolide was also achieved. The key reaction is the cyclization of a bromoacetal derived from 1,4-pentadien-3-ol. The chiral auxiliary (1*R*,2*S*)-2-phenylcyclohexanol was efficiently recovered after hydrolysis of the chiral acetal.



The stereochemical outcome of the haloacetalization and of the radical cyclization will be discussed

[1] Ueno, Y.; Chino, K.; Watanabe, M.; *J. Am. Chem.Soc.* **1982**, *104*, 5564. Stork, G.; Mook, R.; Scott, A. B.; *J. Am. Chem.Soc.* **1983**, *105*, 3741.

[2] Renaud, P.; Villar, F.; *Tetrahedron Lett.*, **1998**, *39*, 8655.

[3] Villar, F.; Andrey, O.; Renaud, P. *Tetrahedron Lett.* **1999**, *40*, 3375

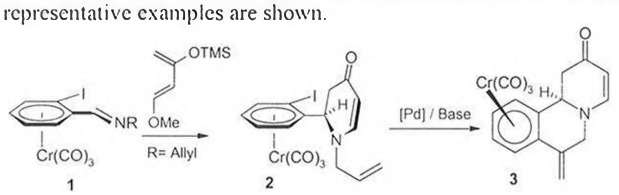
Organic Chemistry **195**

Asymmetric Synthesis *via* Arene Chromium Complexes: Methodology and Application to Natural Product Synthesis

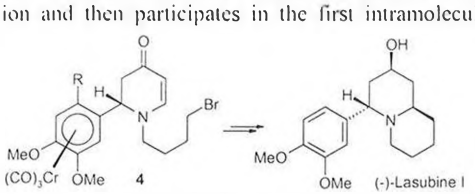
E. P. Kündig, H. Ratni

Département de Chimie Organique, Université de Genève, 1211 Genève 4

Enantiopure aryl hydropyridinone complexes (e.g. **2** and **4**) are readily accessible *via* aza-Diels-Alder reaction between enantiopure *o*-substituted arylaldehyde imine complexes and Danishefsky's diene.[1] The $Cr(CO)_3$ group serves both as steric control element and as activating group. In this communication we report on ongoing studies of the application of this methodology. Two representative examples are shown.



The *o*-halo-substituent in **1** directs the faciality of the aza- Diels-Alder reaction and then participates in the first intramolecular Heck reaction of an arene complex to yield the enantiopure hydroisoquinoline complex **3**. [2] The second example centers on the use of the planar chiral complex **4** in the asymmetric synthesis of (-)-lasubine(I) and (+)-subcosine(I), members of quinolizidine alkaloïds of the Lythraceae family.



[1] E.P. Kündig, L.H. Xu, P. Romanens, G. Bernardinelli, *Synlett*, **1996**, 270.

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Organic Chemistry **196**

Solvent-free Synthesis of Vinyl Carbamates from Alkyne, Amine and Carbon Dioxide

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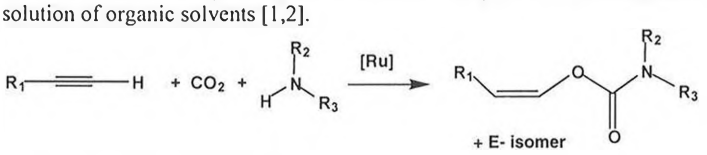
Laboratorium für Technische Chemie, ETH-Zentrum, CH-8092 Zürich,

Vinyl carbamates (VC's) are used as intermediates for the production of agricultural and pharmaceutical products as well as polymers. The different pathways for the synthesis of VC's all procede via the toxic phosgene. An interesting alternative route is the use of carbon dioxide instead of phosgene. In this one step process a secondary amine, a terminal alkyne and CO_2 are transformed to the vinyl carbamate (E- and Z- isomers) (scheme). The reaction is catalysed by various metal complexes in homogenous solution of organic solvents [1,2].



Here we show, that with certain simple air stable ruthenium complexes the reaction can also be carried out in supercritical CO_2 as solvent. We used phenyl acetylene (R_1 = Ph) and diethylamine (R_2 = R_3 = Et) as cosubstrates. The reaction represents a new example for the simultaneous use of carbon dioxide as solvent and reactant. However, the reaction also occurs without solvent under an atmosphere of gaseous CO_2. A comparison of the conversions and selectivities of the reactions in the different media, especially in supercritical carbon dioxide and in conventional organic solvents is presented. Advantages and disadvantages of the application of supercritical carbon dioxide will be discussed.

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Organic Chemistry **197**

Asymmetric Induction of TRISPHAT Anions onto Chiral Transition Metal Complexes.

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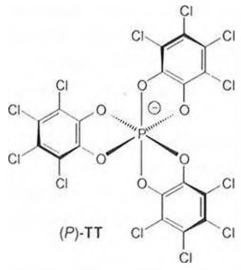
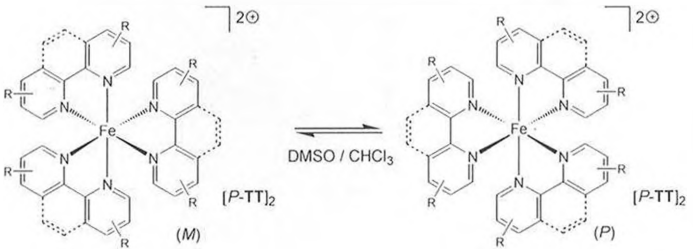
Département de Chimie Organique, Université de Genève, 1211 Genève 4



Induction of optical activity by chiral hosts onto configurationally labile guest molecules is an essential phenomenon (Pfeiffer effect). Recently, we have shown that TRISPHAT anions (**TT**) efficiently control the configuration of a labile $[Fe(diimine)_3]^{2+}$ cationic guest complex (d.e. > 96%).[1] Herein, we report that the homochiral or heterochiral nature of the association between the molecular propellers, as well as its diastereoselectivity, strongly depend upon the structure of the diimine ligands. Extension of this work to $[Co(diimine)_3]^{2+}$ derivatives, $[Cu(diimine)_2]^{+}$ derivatives and binuclear cationic supramolecular structures will be presented.



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Organic Chemistry **198**

Intermolecular Cyclopropanation *vs* CH Insertion in Rh(II)-catalyzed Carbenoid Reactions

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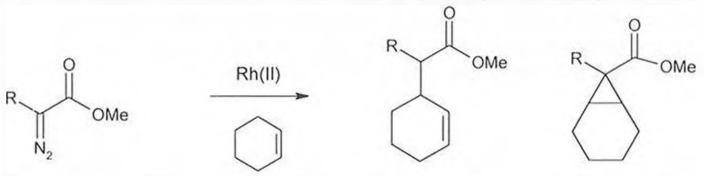
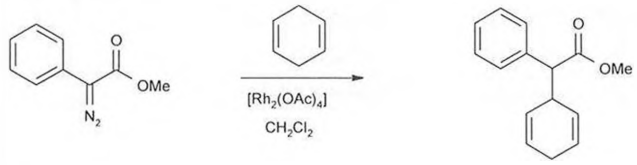
The decomposition of diazo compounds by transition metal catalysts of Cu(I) or Rh(II) affords products derived from cyclopropanation of double bonds, or from insertion into carbon-hydrogen bonds. We have investigated the carbene selectivity for insertion *vs* cyclopropanation in function of the carbene, the catalyst and the substrate. With cyclohexene, disubstituted carbenes exhibit a pronounced preference for insertion with Rh(II) catalysts.



Exceptionally high selectivity for insertion was observed in the case of $[Rh_2(OAc)_4]$-catalysed reaction of 1,4-cyclohexadiene with 1.0 equivalent of methyl phenyldiazoacetate to afford the insertion product in 70% yield and up to 75% ee.



Organic Chemistry **199**

New Reactions of Pinene Derived Iron Carbonyl Complexes

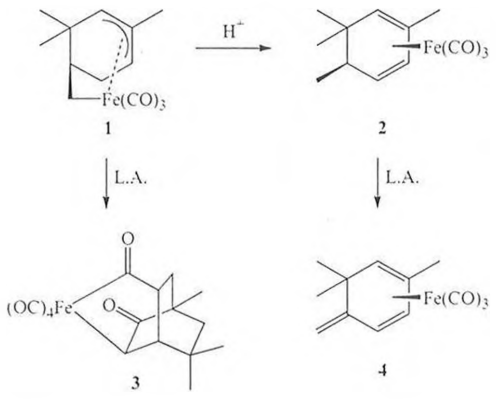
Vroni Huber, Jacques Raemy and Titus A. Jenny

University of Fribourg, Institute of Organic Chemistry, Pérolles, Fribourg

Iron carbonyl complex **1** is obtained from (−)-β-pinene by complexation with iron pentacarbonyl.

Strong protic acids (e.g. trifluoroacetic acid) isomerize **1** to the diene complex **2** whereas Lewis acids (e.g. aluminium chloride) yield a mixture of products containing the bicylic complex **3** as a major product.

Treatment of the diene complex **2** with aluminium chloride leads to complex **4**, in an unprecedented dehydrogenation reaction.



Organic Chemistry **200**

Chiral Dilithiomethanederivatives: Structure Determination and Application in Asymmetric Reactions

by R. Batra, J. F. K. Müller, M. Neuburger, and B. Spingler

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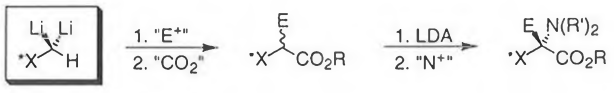
Our goal is the formation of chiral geminal dilithiated compounds. We studied its structures in the solid state by X-ray analyses as well in the gas phase by quantum chemical methods.[1] We could show that sulfoximine-stabilized dilithiosalts are truly dilithio compounds, which are highly aggregated in coordinating solvents, and do not form QUADAC's.[2,3] Derived from our structural studies we used such reagents for the synthesis of quarternary amino acids in a one pot alkylation-electrophilic-amination sequence.



*X = PhS(O)(NSiMe3)

References:

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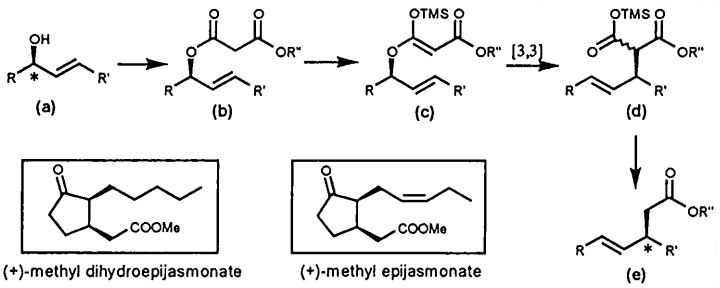
Organic Chemistry **201**

A New Variant of the Claisen Rearrangement from Malonate-Derived Allylic Silyl Ketene Acetals. Efficient, Highly Enantio- and Diastereoselective Syntheses of (+)-Methyl Dihydroepijasmonate and (+)-Methyl Epijasmonate

Charles Fehr, José Galindo, Olivier Etter and Eric Ohleyer

Firmenich SA, Corporate R&D Division, CH-1211 Geneva 8

The new Claisen rearrangement herein reported shows several advantages when compared to the Johnson orthoester Claisen rearrangement, in which the unavailability and low reactivity of orthoesters are often problematic. In addition, the new version allows a perfect chirality transfer from **(a)** to **(e)**. We have also developed a method for the preparation of a single enantiomer of malonates of type **(b)** starting from racemic alcohols of type **(a)** via kinetic resolution and racemization of the recovered alcohol enantiomer. This rearrangement represents one key-step in the efficient syntheses of (+)-methyl dihydroepijasmonate and (+)-methyl epijasmonate.



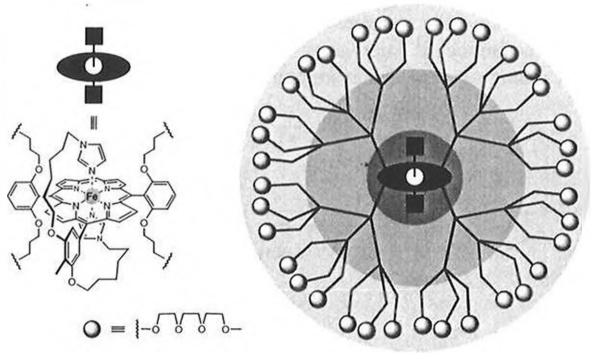
Organic Chemistry **202**

Dendritic Iron Porphyrins With Tethered Axial Ligands as Model Compounds for Cytochromes

Philipp Weyermann and François Diederich

Laboratorium für Organische Chemie, ETH-Zentrum, Universitätstrasse 16, CH-8092 Zürich (Switzerland)

Following the interesting electrochemical behaviour of our earlier dendritic iron porphyrins [1], new iron porphyrin dendrimers, that include defined axial ligation have been designed to more closely mimic natural systems. A family of iron(III)porphyrins with tether-linked imidazoles as axial ligands bearing modified *Newkome*-type dendrons as mimic of a nonpolar protein shell is presented. These novel cytochrome models closely resemble small electron transfer proteins like cytochrome c in both size and shape. The electrochemical properties of the compounds have been investigated and significantly, the dendritic shell has been found to impose a remarkable effect on the redox properties of the core.



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Organic Chemistry **203**

Synthesis of Cyclic Depsipeptides *via* Direct Amide Cyclization

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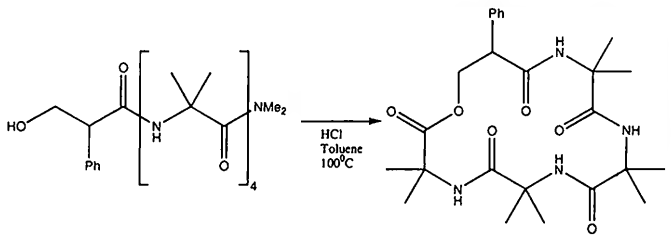
Organisch-chemisches Institut der Universität Zürich, Winterthurerstrasse 190, CH-8057 Zürich

Since several years, we are interested in the development of new methods for the synthesis of cyclic depsipeptides *via* ester-bond formation. Details of the successful preparation of a number of cyclic depsipeptides using the so-called direct amide cyclization [1] will be presented. The ring closure to the cyclic depsipeptides was performed *via* ester-bond formation.

The linear peptide precursors were designed to contain one β-hydroxy carboxylic acid and several α,α-disubstituted α-amino acids. These precursors were synthesised *via* the so-called azirine/oxazolone method [2].



The cyclic depsipeptides were characterized by 2-D NMR and X-ray Crystallography.

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Organic Chemistry **204**

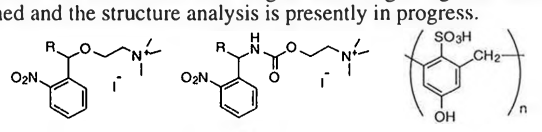
Calixarenes Complex with Photolabile Cholinergic Ligands: Model of Artificial Cholinergic Receptors

Alexandre Specht, Ling Peng, and Maurice Goeldner

Laboratoire de Chimie Bio-organique, UMR 7514 CNRS, U.L.P Strasbourg

Both acetylcholine receptors and acetylchcholinesterases are important macromolecules in the regulation of neurotransmission at the cholinergic synapses. Since several years, we were interested particularly in synthesizing and characterizing a series of "caged" cholinergic ligands, photolabile precursors of cholinergic ligands (Figure **A** and **B**), in order to photoregulate acetylcholinesterase's activities as well as to explore the catalytic mechanism of cholinesterases by time-resolved crystallography [1]. At the same time, we would like to use supramolecules as artificial cholinesterases and cholinergic receptors as simplified biomimic models. Since calixarenes have been demonstrated to bind cholinergic ligands [2], we would like to probe their ability to bind our caged cholinergic ligands and to undertake time-resolved crystallographic studies on the corresponding guest-host complex.

p-Sulfonatecalixarenes (Figure **C**) display affinities for both caged choline (**A**) and caged carbamylcholine (**B**) with binding constants varying from 20 μM to 100 μM. Photoirradiation of complex of calixarenes and caged cholinergic ligands triggers the release of the corresponding cholinergic ligands [3]. This could allow us to undertake the biomimic studies of cholinergic receptors on one hand, and to envisage detailed mechanistic studies on the photochemical reaction process by time-resolved crystallography on the other hand. Crystals of complexes of calixarenes and caged cholinergic ligands have been obtained and the structure analysis is presently in progress.



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205

Solution-Phase Combinatorial Synthesis of Substituted Pyridines

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Heterocycles are found in nature and in drugs as one of the most biologically relevant and active class of compounds. Pyridine derivatives are among the most common heterocyclic compounds:[1] The pyridine motif is found in various therapeutic agents, including numerous antihistamines, antiseptic, antiarrythmic, antirheumatic and other pharmaceutical compounds.[2] Herein we present the combinatorial synthesis of substituted pyridines.

To date, the combinatorial generation of pyridines was achieved primarily via the synthesis of dihydropyridines (Hantzsch condensation), followed by an oxidation.[3] However, this route limits the substitution pattern of the pyridines.

We use a transition-metal catalyzed reaction for the one-pot generation of a solution-phase library of substituted pyridines. In order to apply this methodology to the 96-well plate format, we developed a new mild catalyst as well as a Teflon coated 96-well plate. This allows us to carry out the reaction on a bench top and is thus ideally suited for solution-phase combinatorial synthesis of substituted pyridines.

With this methodology at hand and with commercially available starting materials, we have access to > 2 10^9 compounds.

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Organic Chemistry **206**

Calixporphyrins, Porphyrinoid Container Molecules

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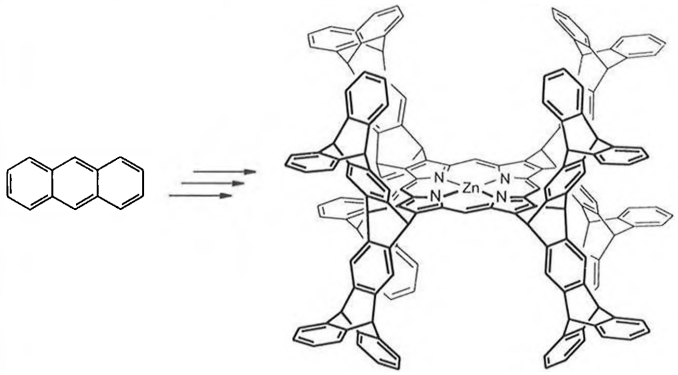
Institute of Organic Chemistry, University of Innsbruck, Innrain 52a, A-6020 Innsbruck, AUSTRIA

By opening the third dimension to porphyrinoid ligands, tetrapyrrolic compounds with unprecedented reactivities may result. Jim Collman's "picket-fence" [1] porphyrin represents a pioneering example for this. Porphyrinoid metal complexes, structured according to similar concepts, have been used successfully as shape-selective [2] and enantio-selective [3] catalysts. We delineate here the efficient assembly of calixporphyrins [4] starting from anthracene derivatives. These new three dimensional structured porphyrins with defined size and shape act as hosts for a variety of organic guest molecules



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[4] J. Schlögl, B. Kräutler, *Synlett* **1999**, in press.

Organic Chemistry **207**

Polythiophenyl-Substituted Benzenes as Reducible Subunits in Nanoscale Structures

M. Mayor and J.-M. Lehn

Institut für Nanotechnologie, Forschungszentrum Karlsruhe GmbH, Postfach 3640, D-76021 Karlsruhe; Laboratoire du Chimie Supramoléculaire, ISIS, Université Louis Pasteur, 4 rue Blaise Pascal, F-67000 Strasbourg

Polythiophenyl substituted aromatic systems have been shown to be easily reducible[1] and to have favorable properties regarding stability, solubility, accessibility and variety. The potential of this structural motif as a reducible subunit in electroactive molecular systems is presented with several examples.

A perthiophenyl benzene unit combined with a potassium binding site constitutes a reducible potassium cryptate. The interdependence between redox state and potassium binding properties imparts ion sensor capabilities[2].

The mobility of electrons through various bridging groups with structures bearing reducible perthiophenyl benzene subunits at each terminus is described.

As very promising π-conjugation connectors, diacetylene bridged perthiophenyl benzene subunits are also explored. Linkage *via* diacetylene-bridges in the *para*-position provides access to linear reducible rods,[3] while the connection in *meta*-position allows the construction of molecular cycles of variable size. These morphologically rigid structures display interesting optical and electrochemical properties which make them promising candidates for the design of nanoscale molecular devices.

[1] J.H.R. Tucker, M. Gingras, H. Brand, J.-M. Lehn, *J. Chem. Soc., Perkin. Trans. 2* **1997**, 1303. [2] M. Mayor, J.-M. Lehn, *Helv. Chim. Acta* **1997**, *80*, 2277. [3] M. Mayor, J.-M. Lehn, K.M. Fromm, D. Fenske, *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2370.

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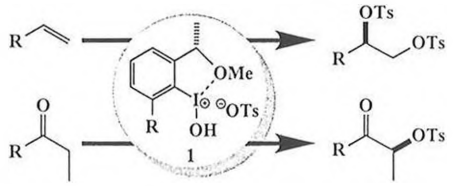
Computer Supported Design of Chiral Hypervalent Iodine Compounds: Comparison of Experimental Data and Calculations

Urs H. Hirt, Olaf G. Wiest †, Thomas Wirth*

* *Inst. f. Org. Chemie, Uni Basel, St. Johanns-Ring 19, CH-4056 Basel, Switzerland*
† *Dept. of Chemistry and Biochemistry, University of Notre Dame, Notre Dame IN46556-5670,USA*

The increasing number of applications of hypervalent iodine compounds in organic synthesis indicates a growing interest in this class of reagents. The oxidative as well as the electrophilic properties of these compounds allow for a wide range of different reactions. In some of these reactions new stereogenic centers are generated. This suggests that chiral hypervalent iodine compounds **1** could be used to induce chirality in prochiral substrates.[1] Only a few chiral hypervalent iodine compounds have been synthesized to date, their application in asymmetric synthesis has not been well explored. The use of experimental data as an entrance into computational chemistry has been well documented. The comparison of X-ray data of known chiral hypervalent iodine reagents and the optimized structures generated by *ab-initio* calculations shows the suitability of computational chemistry in supporting this experimental work. The highest level of theory used in our study was the B3LYP hybrid functional with the Hay/Wadt LANL2DZ effective core potential using G94 and G98. A number of new compounds were designed computationally, synthesized and evaluated experimentally.



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U. H. Hirt, B. Spingler, T. Wirth *J. Org. Chem.* **1998**, *63*, 7674 - 7679.

Organic Chemistry **209**

New Tin Free Radical Cyclization Reactions Using the Persistent Radical Effect (PRE)

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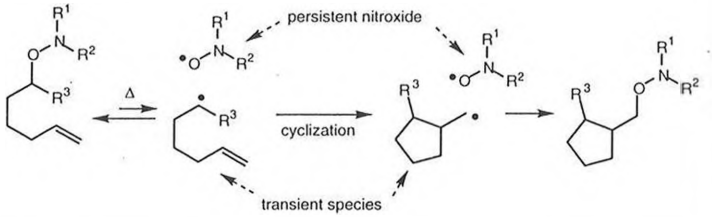
Laboratorium für Organische Chemie, Eidgenössische Technische Hochschule, ETH Zentrum, Universitätstrasse 16, 8092-Zürich

The PRE is a general principle to explain the highly specific formation of the cross-reaction product (R_1-R_2) between two radicals R_1 and R_2 if one species is rather persistent (R_1), the other transient (R_2), and the two radicals are formed at equal rates.[1] The initial buildup of the persistent species caused by the self-termination of the transient radicals ($\rightarrow R_2$-R_2) steers the reaction to follow a single pathway, the cross-reaction.

In the talk, the concept of the persistent radical effect will be discussed. Applications of the PRE for the conduction of tin free radical cyclization reactions will be presented.



The effect of the substituents R^1, R^2, and R^3 on the reaction outcome will be discussed. Simulations of the dynamic processes will also be presented.

[1] H. Fischer, *J. Am. Chem. Soc.* **1986**, *108*, 3925.

Chimie Minérale et de Coordination **210**

Classical NMR kinetic methods associated to high pressure NMR techniques for a comparative cyanide exchange study on square planar complexes

Monlien F. J., Abou-Hamdan A., Helm L. and Merbach A. E.

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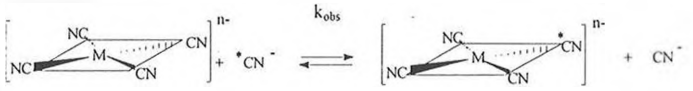
Université de Lausanne BCH ; CH-1015 Lausanne, Suisse.

Previous studies of cyanide exchange on square planar tetracyanometalate complexes $[M(CN)_4]^{n-}$ where M= Au(III), Pd(II), Pt(II) and Ni(III) have been undertaken only at a high pH[1]. For a more complete fundamental understanding of these systems involved in important industrial applications, we extended the investigations of these exchanges over a large pH range.



NMR kinetics methods (line broadening, magnetisation transfer, isotopic exchange) proved to be very useful for obtaining quantitative rate data on the cyanide exchange on these complexes. In fact it is quite significant that the reactivity of these metal centers span a *ca.* 11-order of magnitude rang as a function of pH.

Variable temperature and variable pressure[2] studies were undertaken and the activation parameters in acidic and basic conditions obtained thereof. The reactivities of the metal centers were thus compared and important mechanistic conclusions will be presented.

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Medicinal Chemistry **211**

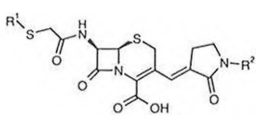
Cephalosporin-Carbapenem Combinations: Antibiotics with Ultra-broad Spectrum

P. Angehrn, I. Heinze-Krauss, M. Page and H.G.F. Richter

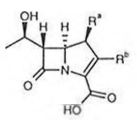
F. Hoffmann-La Roche Ltd., Basel, Switzerland

β-Lactam antibiotics are the most frequently prescribed antibiotics worldwide due to their excellent safety and tolerability. However, the intensive usage of antibiotics has resulted in development of resistance. Especially for multi-resistant Gram-positive pathogens, e.g. Methicillin-resistant staphylococci (MRSA), an urgent medical need for new antibiotics exists. In many organisms resistance to β-lactam antibiotics emerges through the expression of β-lactamases. In addition, in staphylococci, high-level resistance is due to the expression of a single additional transpeptidase (PBP 2') that has very low affinity for marketed β-lactams.

Vinyl-pyrrolidinone cephalosporins discovered at Roche are able to overcome resistance to established β-lactams in Gram-positive bacteria (especially multi-resistant staphylococci) due to their potent inhibition of the resistant transpeptidases. However, compounds with a 7-thioacetyl side chain have impaired β-lactamase stability and only weakly inhibit the Gram-negative transpeptidases. We found that combination with a suitable carbapenem is an effective way to overcome these liabilities. The combination acts synergistically against MRSA and provides an extremely broad coverage of important Gram-positive and -negative pathogens that now pose a severe clinical problem. An account on the synthesis and the structure-activity as well as structure-property relationships for the cephalosporin will be given in the presentation.



Vinyl-pyrrolidinone thioacetyl cephalosporins



Carbapenems

Physikalische Chemie **212**

Optimizing experimental conditions with the help of XUV–millimeter wave double resonance spectroscopy on high Rydberg states

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Laboratorium für physikalische Chemie, ETH Zürich
8092 Zürich

The quest for the ultimate resolution in the spectra of high Rydberg states consists to an important part in finding out about the experimental conditions, in particular about stray electric and magnetic fields. The high sensitivity of Rydberg states towards electric fields makes them ideal field sensors. We will show that XUV–millimeter wave double-resonance spectroscopy allows the determination of homogenous electric fields with very high accurracy and enables the measurment of inhomogenous electric field distributions and ion concentrations. Under conditions where stray fields are minimized to less than 20 μV/cm we are able to record spectra of high Rydberg states (principal quantum number n >100) at 60 kHz resolution and PFI–ZEKE spectra at 0.2 cm^{-1} resolution.

This work is financially supported by the ETH Zürich.

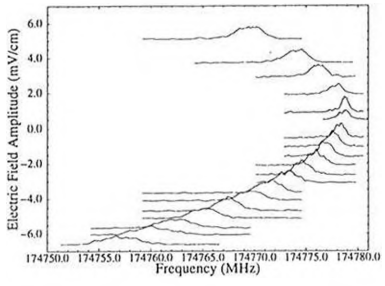

Figure 1: The $91f[5/2](J = 2) \leftarrow 76d[3/2](J = 1)$ transition at different external electric fields. The apex of the parabola corresponds to zero effective field.

Physikalische Chemie **213**

The determination of the H_2^+–Hyperfine structure through the investigation of high Rydberg states

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The unusual properties of high Rydberg states, in particular their high spectral density and their sensitivity towards experimental perturbations, render their experimental study a real challenge. However, these properties are precisely those that are responsible for the success of new spectroscopic methods such as PFI–ZEKE photoelectron spectroscopy or MATI spectroscopy.

Using XUV–millimeter wave double–resonance excitation followed by delayed selective field ionization, we are now able to investigate high Rydberg states of atoms and molecules at a resolution of better than 1 MHz. We show that it is possible to almost completely resolve the hyperfine structure in high Rydberg states of H_2 at n values beyond 50. Such measurments can be used to determine, by extrapolation, the hyperfine structure of the H_2^+ ion.

This work is financially supported by the ETH Zürich.

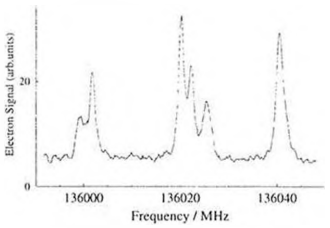

Figure 1: Detail of a high resolution spectrum of H_2 showing the $54f \leftarrow 52d$–transition in ortho-H_2 below the lowest ionization limit (Rotational quantum number of the ionic core $N^+ = 1$).

Physikalische Chemie **214**

High resolution PFI-ZEKE photoelectron spectroscopy of Kr_2: Accessing the Franck-Condon forbidden states of Kr_2^+.

R. Signorell, U. Hollenstein, and F. Merkt.
Laboratorium für Physikalische Chemie. ETH Zürich. CH-8092 Zürich. Switzerland.

The first electronic states of Kr_2^+ have been investigated by high resolution pulsed-field-ionization zero-kinetic-energy (PFI-ZEKE) photoelectron spectroscopy. The spectra, which were recorded in the range between 103500 cm^{-1} and 118200 cm^{-1} (12.83-14.65 eV) using a broadly tunable XUV laser source, reveal extensive vibrational progressions associated with the ground $A\,^2\Sigma^+_{1/2u}$ ionic state of the most abundant isotopomers of Kr_2.
From the spectra accurate adiabatic ionization potentials and potential energy functions are extracted for the ground and several electronically excited states of Kr_2^+.

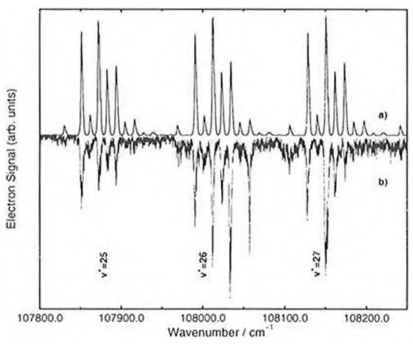

Figure: PFI-ZEKE photoelectron spectrum of the $A\,^2\Sigma^+_{1/2u}$ (v^+=25-27) $\leftarrow$ $X\,0^+_g$ transitions of Kr_2^+. At each value of v^+ several lines are observed that correspond to the 14 most abundent isotopomers of Kr_2^+ (in order of increasing energy 86-86, 86-84, 86-83, 84-84, 86-82, 84-83, 84-82, 83-83, 86-80, 83-82, 84-80, 82-82, 83-80 and 82-80). a) Calculated spectrum, b) experimental spectrum.

Physikalische Chemie **215**

VUV spectroscopy between 10-17eV at a resolution of 0.01cm^{-1}.

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Laboratorium für Physikalische Chemie, ETH Zürich, CH-8092 Zürich, Switzerland.

A new broadly tunable (12-17 eV) high resolution VUV laser system is presented. This system enables the recording of photoabsorption, photoionisation, and photoelectron spectra at high resolution. The bandwidth of 0.01 cm^{-1} opens new prospect for VUV photochemistry and photophysics.

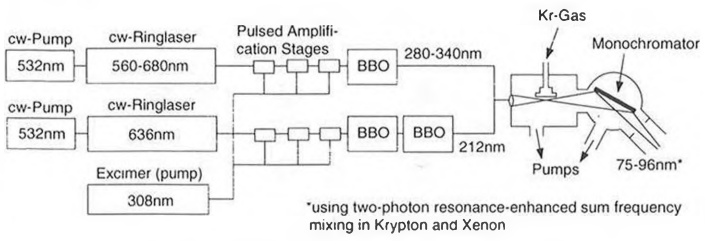

Figure 1: Schematic set-up of our new light source.

Physikalische Chemie **216**

Jahn–Teller Distortion in CH_4^+ and its Isotopomers

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Laboratorium für Physikalische Chemie, ETH-Zürich, CH-8092 Zürich

The high resolution pulsed-field-ionization (PFI) zero-kinetic-energy (ZEKE) photoelectron spectra of CH_4, CH_3D, CH_2D_2 and CD_4 have been recorded between 101000 cm^{-1} and 103000 cm^{-1}. These spectra show an extensive progression of rotationally resolved transitions. The isotope shift of the adiabatic ionization potential and the vibrational structure of the Jahn-Teller distorted ions at low energies have been analyzed in terms of a one-dimensional model for the pseudorotational motion of the ions. The analysis of the rotational structure confirms a fluxional behavior for CH_4^+, whereas $CH_2D_2^+$ in its electronic ground state can be treated as a rigid rotor.

Reference: R. Signorell and F. Merkt, J. Chem. Phys., **110**, 2309 (1999)

This work is supported financially by the ETH-Zürich and the Robert Gnehm-Stiftung.

Physical Chemistry **217**

Mode Selective Stereomutation in Hydrogen Peroxide: 6D Tunnelling and Wavepacket Dynamics

Benjamin Fehrensen, David Luckhaus, and Martin Quack

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As the first in the series of the dihydrogendichalcogenides H_2X_2 and related compounds, which show chirality by C_2 symmetry in their equilibrium geometry, H_2O_2 is among the simplest prototypes for stereomutation, albeit in the low barrier limit [1,2]. The full quantum dynamics for the interconversion of left and right handed enantiomers of hydrogen peroxide isotopomers is studied both from the spectroscopic point of view and by using explicitly time dependent wavepacket dynamics. The six dimensional tunnelling dynamics of H_2O_2, HOOD, and D_2O_2 are investigated on a recently developed analytical global potential energy hypersurface for the electronic ground state of hydrogen peroxide [3]. A new formulation of the harmonic reaction path hamiltonian approximation gives good agreement with the results of a new fully coupled six dimensional adiabatic channel approach [4]. The experimentally observed pure torsional spectrum and mode specific tunnelling are well reproduced, as are the few known isotope shifts. 6D time dependent wavepacket dynamics confirm the adiabaticity of the stereomutation. Predictions are made for the torsional tunnelling spectrum of HOOD and D_2O_2 as well as for the stereomutation dynamics of H_2O_2 at very high excitations.

[1] M. Quack, *Angew. Chem. Int. Ed.* (Engl.), **28**, 571 (1989).
[2] A. Bakasov, T.-K. Ha, and M. Quack, *J. Chem. Phys.*, **109**, 7263 (1998).
[3] B. Kuhn, T. R. Rizzo, D. Luckhaus, M. Quack, and M. A. Suhm, *J. Chem. Phys.*, **110**, xxx (1999).
[4] B. Fehrensen, D. Luckhaus, and M. Quack, *Z. Physik. Chem.*, **209**, 1 (1999); *Chem. Phys. Lett.*, **300**, 312 (1999).

218

Photodissociation of carbonyl cyanide $CO(CN)_2$: From single molecules to clusters and cryogenic matrices

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We present a comparative study of the photodissociation of carbonyl cyanide $CO(CN)_2$ photolyzed at 193 nm, as it occurs (a) in isolated gas-phase molecules, (b) in jet-cooled clusters $[CO(CN)_2]_n$ and $[CO(CN)_2]_mAr_n$, and (c) isolated molecules in cryogenic Ar and Xe matrices. The gas phase results were obtained using photofragment translational energy spectroscopy, while those in the matrix were monitored infrared spectroscopy.

According to a comprehensive analysis of the $CO(CN)_2$ monomer results in the gas phase, a major fraction of ≈94% of the excited molecules decay to OCCN + CN (radical channel). Besides this a molecular decay to CO+NCCN with a yield of ≈6 % was observed. The average kinetic energy of the fragment pairs was determined to be 37 and 190 kJ/mol for the radical and molecular decay channel, respectively, corresponding to 18% and 30% of the available energy. A minor fraction of the OCCN fragments (≈18 %) undergo spontaneous secondary dissociation to CO+CN.

The cluster photoproducts were also analyzed by photofragment translational spectroscopy. The fragments CO, CN, OCCN, NCCN and $CO(CN)_2$ were identified. The ratio of the products OCCN and NCCN, is larger or equal to the ratio found for isolated $CO(CN)_2$ molecules. We observed a large fraction of OCCN and NCCN fragments with very low kinetic energies. ($\langle E_T \rangle \approx 3$-4 kJ/mol). Since these slow species possess less than 10% of the kinetic energy found for isolated molecules, they must originate from the cluster interior.

The major fragment species of gas phase monomers and clusters, CN+OCCN, were not detected in the matrix environment. This is attributed to complete caging and recombination of the nascent species in the matrix. Three new IR appear with an initial increase followed by a decrease upon prolonged irradiation. Based on the kinetic behaviour and a comparison with calculated ab initio frequencies, these IR bands are attributed to the compound CO(CN)(NC) formed by photoisomerization of the parent molecule. The final products found after prolonged irradiation are CO, NCCN and a small amount of CNCN. A reaction scheme is presented which accounts for the various photoproduct species of $CO(CN)_2$ in caged environment.

Physical and Computational Chemistry **219**

Molecular Interaction Between Cinchonidine and Acetic Acid Studied by NMR, FTIR and *ab initio* Methods

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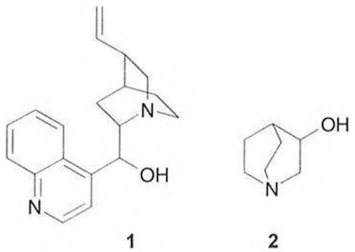
Laboratorium für Technische Chemie, ETH Zentrum, 8092 Zürich

Nitta [1] and Borszeky [2] postulated the formation of acid-modifier adducts as intermediates in the enantioselective hydrogenation of α,β-unsaturated carboxylic acids by cinchonidine (**1**) modified Pd catalysts. In our study acetic acid was chosen as reference for the investigation of its interaction mode with (**1**). The changes in the IR spectra of (**1**)-acetic acid solutions at different acid concentrations have been followed leading to the identification of 1:1 and 1:2 cyclic (**1**)-acetic acid ion-pairs. The latter appears to be the major species present in excess acetic acid. The experimental OH and CO frequencies correlate well with *ab initio* Hartree Fock calculated frequencies and relative energies. Calculations assumed that (**1**) mainly adopts an open conformation as previously shown [3]. The interaction results from hydrogen bonds between the protonated quinuclidine-N and OH sites of (**1**) and the acetate ions. For comparison, (**2**) formed only open complexes. These findings emphasize the relevance of the OH group of (**1**) in the hydrogenation of α,β-unsaturated carboxylic acids.



1 2

[1] Y. Nitta, A. Shibata, *Chem. Lett.* **1998**, 161.
[2] K. Borszeky, T. Mallat and A. Baiker, *Tetrahedron: Asymmetry* **1997**, *8*(22), 3745.
[3] T. Bürgi, A. Baiker, *J. Amer. Chem. Soc.* **1998**, *120*, 12920.

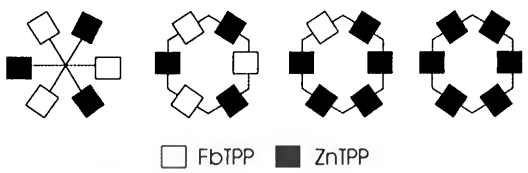
Chimie Physique **220**

INVESTIGATION OF EET PROCESSES IN HEXAPORPHYRIN ARRAYS

Ana Morandeira[1], Eric Vauthey[1], Nicolas Hogler[2], Anne Schuney[2], Olivier Mongin[2], Albert Gossauer[2]

[1]Institut de Chimie-Physique de l'Université de Fribourg
[2]Institut für Organische Chemie der Universität Freiburg
Pérolles, CH-1700 Fribourg

The dynamics of intramolecular electronic energy transfer (EET) within hexaporphyrin arrays has been investigated using various picosecond techniques. These arrays contain Zn-tetraphenylporphine (ZnTPP) and free base tetraphenylporphine (FbTPP) moieties arranged as follows:



Two types of EET take place:

- Energy hopping between ZnTPP moieties
- Irreversible EET from ZnTPP to FbTPP, which acts as an energy trap

These arrays can be considered as synthetic analogues of light harvesting antenna systems which transfer the absorbed energy to the reaction center of photosynthesis in higher plants and photosynthetic bacteria.

The dynamics of the individual energy transfer steps as well as the overall energy trapping efficiency of these arrays will be discussed in detail.

Chimie Physique **221**

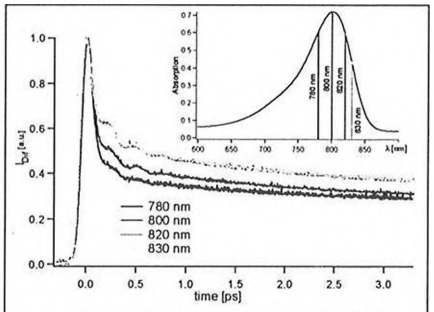
SOLVATION DYNAMICS OF A DYE IN ALCOHOLS AND NITRILES USING FEMTOSECOND THIRD ORDER NONLINEAR SPECTROSCOPIES

Jean-Claude Gumy, Olivier Nicolet, Eric Vauthey

Institut de chimie physique, Université de Fribourg, CH-1700 Fribourg

Recent investigations of solvation dynamics have revealed that two types of solvent motion are involved: diffusional motion whose dynamics depends on viscosity and inertial motion, which is independent on viscosity and takes place in the 100 fs timescale. The most used method for these studies is the dynamics Stokes shift spectroscopy that probes the solvation dynamics of the excited state.

We have investigated the solvation dynamics of an organic dye (IR140) in the ground state in series of nitriles and alcohols by performing spectral hole-burning spectroscopy. The refilling dynamics of the holes at different wavelengths was monitored using two different four-wave-mixing methods: the heterodyne transient dichroism and the transient grating techniques.



Time profile of the diffracted intensity with IR 140 in methanol excited at different wavelength. Insert: absorption spectrum of IR 140.

The two above mentioned contributions to solvation were indeed observed in all solvents. Interestingly, the relative magnitude of these contributions was found to be both solvent and wavelength dependent. A model allowing this finding to be rationalised will be presented.

Chimie Physique **222**

Free Ion Formation after Excitation of Aromatic Ketones in Polar Solvents: What Does Happen?

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[a] Institut de Chimie Physique, Université de Fribourg, 1700 Fribourg

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The kinetics of free ion formation upon excitation of several aromatic ketones in acetonitrile has been investigated using the transient photoconductivity (TP) technique. Two mechanisms seem to operate depending on the incident excitation energy:

1. bimolecular triplet-triplet annihilation via electron transfer

$$^3M^* + {}^3M^* \longrightarrow M^{\cdot-} + M^{\cdot+}$$

2. monomolecular photoionisation of the triplet state

$$^3M^* + h\nu \longrightarrow M^{\cdot+} + e^-$$

As shown in Figure A, the first mechanism results in a slow photocurrent rise, which becomes faster as the concentration of $^3M^*$ is increased. On the other hand, the photocurrent rise due to ions formed via mechanism 2 is instantaneous (Fig. B).
The efficiency of mechanism 2 strongly depends on the excitation frequency. The threshold frequency, above which this mechanism occurs, has been determined by performing photoconductivity measurements with a tunable laser.
It will be shown how they lead to an estimate of solvation energy of $M^{\cdot+}$ and the oxidation potential of **M**.

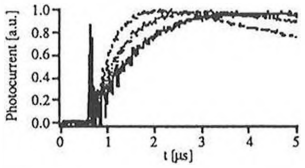

Fig. A Normalised TP kinetics of benzophenone (BP) in MeCN excited at 355 nm with various concentrations of triplet.

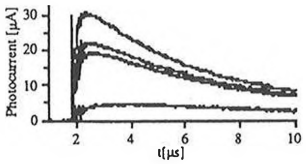

Fig. B TP kinetics of BP in MeCN excited at 266 nm with various concentrations of triplet.

Physical Chemistry **223**

Orientation dependence of the flatband potential of anatase TiO_2

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Laboratoire de Photonique et Interfaces, Dept. Chimie, EPFL Lausanne

The performance of charge separation/injection devices based on nanocrystalline TiO_2 films like dye sensitized solar cells depends strongly on the interfacial energetics and therefore on the flatband potential of the semiconductor. We report here on the influence of the surface type of TiO_2 exposed to the solution interface on the flatband potential. Single crystals of the metastable but better performing *anatase* polymorph of TiO_2 have been grown at low temperatures (~700°C) by a chemical transport reaction ($TiO_2+TeCl_4 \rightarrow TiCl_4+TeO_2$). Impedance measurements on anatase single crystal electrodes with different crystal orientations ((101) and (001)) have then been performed in aqueous electrolytes. The Mott-Schottky plots showed a 60 mV more negative flatband potential for the (001) than for the (101) surface. This is attributed to the different adsorption of water on the anatase surfaces [1]. On the (101) surface water is adsorbed molecularly, saturating the Ti-atoms coordinatively. In contrast to this, on the (001) surface water is adsorbed dissociatively, which leads to surface OH-groups on still five-fold coordinated Ti-atoms with an accompaning negative shift of the conduction band edge. Voltammetric experiments under illumination and in the dark confirmed these findings, which could show the way to possibly higher efficiencies of dye sensitzed solar cells as already indicated by an increase of the open circuit voltage of these solar cells of the same order of magnitude after chemisorption of water on the TiO_2 films [2].

[1] A.Vittadini, A.Selloni, F.Rotzinger, M.Grätzel Phys. Rev. Let. 81 (1998) 2954

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Physical Chemistry **224**

Pressure Swing Adsorption on active carbon beds combined with Quadrupole Mass Spectrometry: A comparison of experiments with theoretical models

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Université de Neuchâtel, Inst. de Chimie, Av. Bellevaux 51, 2000 Neuchâtel

Pressure Swing Adsorption (PSA) is a process, which has been routinely used to separate vapours and gases. We have combined PSA and Quadrupole Mass Spectrometer (QMS) techniques to obtain the experimental results, which are compared with theoretical results based on the Dubinin-Ashtakov (DA) equation[1] and the recent Myers-Preusnitz-Dubinin (MPD) approch[2].

We introduce compressed air with organic vapours into the PSA system, where the organic vapours are adsorbed and desorbed in alternating adsorption and regeneration cycles. The process is stopped when the active carbon is completely saturated. We control the concentrations (input, output) by QMS.

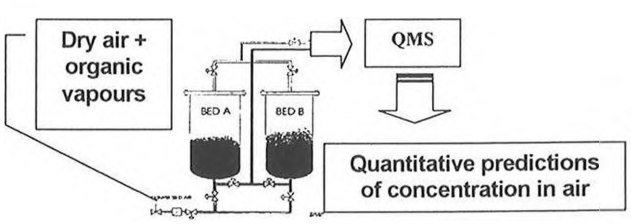

Fig. 1. Schematic view of the system used for the experiment

[1] A. Lavanchy, P. Rebstein, F. Stoeckli, *Pure&Applied Chem.* **1993**, 65, 2175

[2] A. Lavanchy, F. Stoeckli, *Carbon* **1999**, 37, 315

Chimie physique et computationelle. **225**

HyperHelper - front-end for HyperChem force filed optimization.

P.Goetzen and H.Stoeckli-Evans

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It is necessary to perform calculations on a huge number of compounds to add and verify the force field parameters. One then has to compare the calculated models with the starting structures obtained form the Cambridge Structural Database. This includes the comparison of bond lengths, angles, torsion angles etc. The process of comparison consists of nine steps:

1. Initial geometry calculation of CSD crystal model (choosing the atoms)
2. Sending the data and the picture of the molecule to MS Excel worksheet
3. Geometry optimization with original MM+ force field
4. Recalculation of geometry
5. Sending the data of the molecule to MS Excel worksheet
6. Geometry optimization using new, MM* force field parameters
7. Recalculation of new geometry
8. Sending the data and the picture of the molecule to MS Excel sheet
9. Post-calculation treatment in MS Excel sheets

HyperHelper automatically does all the above steps on a subset of the data. The program is a front-end for HyperChem, Babel and MS Excel 8.0. It has been written in Visual Basic 5.0 and uses HyperChem Command Language through Dynamic Data Exchange interface. Visual Basic is chosen because it provides a very fast way of building extensions to HyperChem.
With the help of the program some new parameters have been added to an existing MM+ force field (HyperChem) to improve geometry optimization calculations for compounds containing pyridine, pyrazine and their transition metal complexes.

Computational Chemistry **226**

Excitation energies in DFT using response theory and ΔSCF for different types of molecule

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DFT has provided an extremely successful description of ground-state properties of atoms, molecules and solids. Current best functionals yield ground-state properties in very close agreement with experiment. The treatment of excited states is not yet as fully developped as is the ground state theory. Although primary difficulties were only formal, the method is now rigorous essentially due to the the work of Gross [1].
In this work, we calculated excited states of some molecules using response theory in time-dependent DFT, as well as ΔSCF method [2] in time-independent DFT, using the ADF program package.
We compared both methods starting from small molecules up to increasingly complex inorganic compounds. We also did investigate the improvement of the results depending upon the basis sets and different functionals, especially the asymptotically correct Van Leeuwen-Baerends potential [3]. We will report results for different types of molecules: e.g. $[Ru(bpy)_3]^{2+}$, $Cr(CO)_6$, CrF_6, Ferrocene, among which we can find different types of transitions, charge transfer, intra-ligand and metal centered.

[1] E.K.U. Gross, J.F. Dobson, and M. Petersilka, in *Density Functional Theory*, edited by R.F. Nalewajski, Springer Series "Topic in Current Chemistry" (Springer, Heidelberg, 1996).
[2] C. Daul, *Int. J. Quantum Chem.* **52**, 867 (1994).
[3] R.van Leeuwen and E.J. Baerends, *Phys. Rev.* **A49**, 2421 (1994).

Computational chemistry **227**

Simulation of the boiling curve of Neon and Argon

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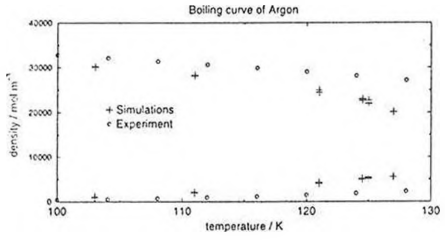
To establish the accuracy of properties calculated by *ab initio* computer simulations, our group has studied several bulk properties of rare gases in the liquid state. The points of interest in this study are: first, how important is the quality of the pair potential; second, how large is the contribution of three body interactions; third, do quantum effects play a significant role.
The boiling curve was simulated using the Gibbs-Ensemble technique, which uses two simulation boxes, that are forced to have the same temperature, pressure and chemical potential.



Although the simulations reproduce the correct trend of the experiment, the accuracy of the boiling curve is poor. This seems to be coupled with the accurate pressure calculation, which is a known problem in simulations. Further more do our results show that it is necessary to use relative large potential cutoff distances to get consistent results.

Computational Chemistry **228**

FRIMOL: Fast calculation of multicenter integrals in a handy package.

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Institut de Chimie Inorganique,
Université de Fribourg, Pérolles, 1700 Fribourg (CH).

The main feature of the new program is that of being a good tool both for standard calculation and for the testing of new computational techniques.
The full use of symmetry in solving Poisson equation has been implemented leading to a considerable computational efficiency.
The computation of important physicochemical properties, such for instance as g-tensor and EFG, is included in the program package as specific modules.
The modular structure of the program will allow the introduction in the main body of the source code of personalised methodologies developed by single users. This feature also simplifies the addition of the computation of new properties.
Although the structure of the program may lead to a loss of efficiency, due to the need of extensive exchange of information between the modules, this drawback can be neglected compared to the whole computational time in the case of complex systems.
The most evident improvement to the current KS-DFT computational techniques, is the introduction of a new way for computing the electrostatic potential. This approach is based on the widely used Becke decomposition of the density space [1-2].
Symmetry is introduced at the level of the grid definition [3] and then improved with the particular expansion of the terms involved in the Poisson equation.

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Physical Chemistry **229**

Similarity Rule and Complementarity Rule

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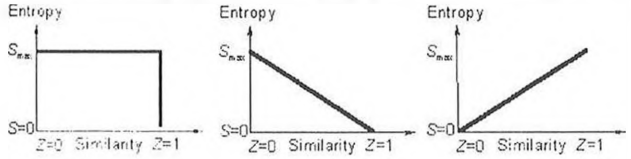
Similarity rule (a component in a molecular recognition process loves others of alike properties) predicts the affinity of individuals of *similar* properties. On the contrary, complementarity rule predicts the affinity of individuals of certain *different* properties. Both types of rule still remain empirical. I am trying to use the concept of entropy as information loss [1] to set up a plausible theoretical foundation for these rules.

Similarity rule can be explained by similarity principle (Fig. c) [1] after rejection of Gibbs' (Fig. a) and revised (Fig. b) relations of entropy-similarity.



Complementarities during all kinds of chemical and physical interaction, such as enzyme and substrate combination, hydrogen baond and electrostatic interation, can be defined and quantitatively calculated as parts of reducible information due to the decrease of the numbers of the information recording individual after any successful tight interaction or combination.

Furthermore, a similarity [1] used to explain similarity rule comforts with symmetry principle [1]. Complementarity rules are related to asymmetry or the concept of asymmetry principle. The Greek word symmetry means the "sameness measure". Symmetry is therefore closely related to distinguishability or similarity.

1 See http://mdpi.org/lin/similarity/similarity.htm and citations.

Chimie Physique **230**

Intramolecular multiple Rehm-Weller plots in photoinduced electron transfer processes: Competition between π- and n-type donor sites in benzylamines

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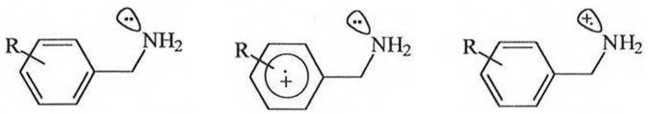
In our earlier work on photoinduced electron transfer processes (PET) we observed that, for a given electron acceptor, distinct π- and n-type electron donors led to distinct Rehm-Weller plots. This was interpreted as due to different Coulomb terms (C-terms) arising between the negative charge in the common acceptor radical anion, and the hole in the π-type (delocalized) or the n-type (localized) hole, respectively, in the donor radical cation after PET.

We discovered now that these two features coexist within a single molecular structure which incorporates both of these types of donor sites in an unconjugated fashion: benzylamines (BA).



The present contribution will discuss the evidence which led us to this conclusion (for detailed information see PCCP, 1999, **1**, 1867).

Hence, the C-term plays indeed a key role in determining PET efficiencies. Alternatively, it provides a further degree of freedom for tuning these efficencies.

Importantly, a PET rate constant is not necessarily related to the easiest oxidizable site in a donor molecule, *i.e.* to its E_{ox}-value as determined by electrochemical techniques.

Physical Chemistry **231**

Intramolecular Vibrational Redistribution in the Chiral Molecule CF_3CHFI: Experiment and *ab initio* Theory

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We have investigated the vibrational spectra and the underlying processes of intramolecular vibrational redistribution (IVR) [1,2] of the chiral molecule tetrafluoroiodoethane (CF_3CHFI) in experiment and ab initio theory. The spectra [3] were measured from the far infrared ($20\,cm^{-1}$) to the visible ($14200\,cm^{-1}$) range by interferometric Fourier transform infrared (FTIR) and photoacoustic techniques at resolutions between 0.004 and $1.0\,cm^{-1}$. The overtone transitions of the C–H chromophore are analyzed by means of an effective Hamiltonian [1 – 4] for the C–H stretch-bend Fermi resonance including the chiral C_S–symmetry breaking coupling constant $k'_{sab} = 30\,cm^{-1}$[3]. We present detailed calculations of the overtone spectra of CF_3CHFI, based on three dimensional ($\nu_{CH} \times \delta_{CH,a} \times \delta_{CH,b}$) and four dimensional ($\nu_{CH} \times \delta_{CH,a} \times \delta_{CH,b} \times \nu_{CF}$) *ab initio* potential energy and dipole moment hypersurfaces (MP2/ C,H,F: 6-311G(d,p); I: LANL2DZ). Explicit incorporation of the CF stretching mode ν_3 turned out to be necessary to describe the experimental spectra properly up to excitation wavenumbers of $12000\,cm^{-1}$. The femtosecond population dynamics of highly excited vibrational states is derived from the effective spectroscopic Hamiltonian in a first step and then compared to the wave packet and population dynamics evolving under the molecular Hamiltonian. In both cases different time scales for IVR processes within the CH modes and between CH modes and the CF frame mode ν_3 are found.

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Physical Chemistry **232**

Very Fast Energy Migration and Trapping by Supramolecular Organisation of Dyes in Zeolite L Nanocrystals

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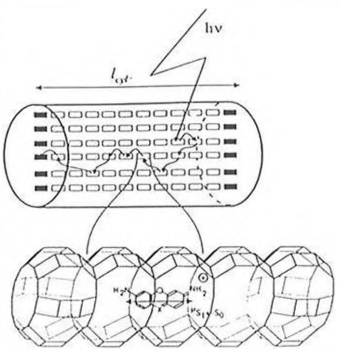
Plants are masters in the direct transformation of sunlight into energy. In the natural antenna system of a leaf, sunlight is transportet by green chlorophyll molecules for the purpose of energy transformation. Our system represents an artificial antenna with a similar light transport, in which the zeolite cylinders adopt the antenna function. As example Zeolite L nanocrystals of about 600 nm length and 800 nm in diameter give rise to more than 100 000 parallel lying channels, each of which bears about 400 sites for the dye molecules. We describe the intercalation of two cationic dyes, in the first step with pyronine (X=C-H) molecules and in the second modified with oxonine (X=N) at both ends of the cylindrical nanocrystals. Light is absorbed by a pyronine molecule located somewhere in one of the channels. The excitation energy migrates preferentially in both directions along the axis of the cylinder and is eventually trapped by an oxonine located at the front or at the back of the nanocrystal. Extremely fast energy migration along the axis of cylindrical crystals has been observed.



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Physical Chemistry **233**

Quantum-Sized Silver Sulfide Clusters in Zeolite A

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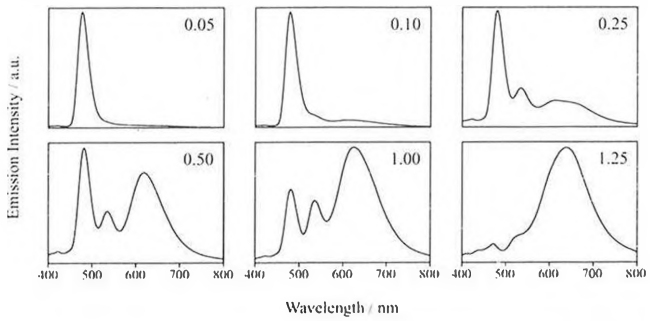
The reaction of H_2S with activated Ag^+-loaded zeolite A leads to silver sulfide zeolite A composites. The optical absorption spectra of samples with different loading densities of silver sulfide suggest the formation of small silver sulfide clusters which are stable under ambient conditions. The composites show a wealth of luminescence behaviors depending on the silver sulfide content. The figure compares the luminescence spectra (measured at 78 K) of six samples with loading densities ranging from 0.05 to 1.25 silver ions per pseudo unit cell of zeolite A.[1] The variety of these spectra offers challenging possibilities to obtain information about the electronic structure of the involved silver sulfide species.



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Physical Chemistry **234**

Efficiency of VUV-induced gas phase oxidation of VOC. Influence of water and reactor geometry

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The use of powerful excimer lamps is of increasing interest for the treatment of waste gas [1-3]. Under these conditions, Volatile Organic Compounds may react with oxygen atoms and hydroxyl radicals which are easily generated if the gas phase containing O_2 and H_2O.

In order to improve the efficiency of the continuous VUV-induced gas phase oxidation, we have investigated the effects of oxygen and water concentrations as well as of the reactor design on the rate of mineralisation. For this propose, tetrahydrofuran or chloro-benzene with initial concentrations of up to 2000 ppm were chosen as model substrates. A coaxial Xe_2-excimer lamp operating at 210 W and a maximum photonic efficiency of approx. 10% at 172 ± 12 nm was used.

The results show that both substrates and their intermediates of oxidative degradation are completely removed from gas stream. The initial oxidation efficiency is slightly smaller in wet mixtures due to the reaction of $O(^3P)$ with water to yield H_2O_2. But humid gas mixtures provide higher rates of mineralisation at equal oxygen concentrations. This indicates that, although, water reduces the initial rate of oxidation, additional paths of chain propagation, similar to those identified in the liquid phase (1), take place.

$$RHOOOOHR + 2\ H_2O \longrightarrow 2\ RO^{\bullet} + H_2O_2 + 2\ H_2O \qquad (1)$$

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Chimie Physique **235**

Barrière à la rotation autour d'une liaison C-P: Variation en fonction de la température du spectre RPE du radical Dibenzobarrellène phosphinyl en phase monocristalline

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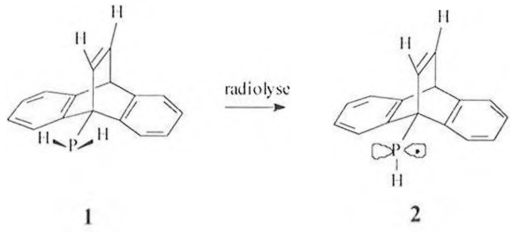
La dibenzobarrellènephosphine **1**, une nouvelle phosphine primaire stable à l'air, a été synthétisée par une addition Diels-Alder suivie d'une cycloreversion thermique et fonctionnalisation de l'intermédiaire lithien. Les tenseurs g et de couplage hyperfin (^{31}P et ^1H) du radical phosphinyl **2** ont été déterminés à 45K et 300K après radiolyse d'un monocristal de **1**. Les orientations des vecteurs propres par rapport aux directions de liaisons sont précisées par référence à la structure cristalline. Les paramètres RPE indiquent qu'entre 50K et 300K, la liaison P-H subit un processus dynamique autour de la liaison P-C. Ce mouvement intramoléculaire est étudié en analysant, pour des orientations connues du champ magnétique, la dépendance en température du spectre RPE. Cette analyse, effectuée à l'aide de la matrice densité, permet de déterminer la barrière à la rotation autour de la liaison C-P. Celle-ci est en accord avec les prédictions de calculs DFT effectués sur ce même radical.



1 **2**

Chimie Physique **236**

Les complexes aqueux de fer(III) en solution diluée : caractérisation et comportement photochimique

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Le comportement thermique d'une solution aqueuse de Fe(III) est régit par les équilibres qui interviennent entre les différents complexes de Fe(III). Dans nos conditions de concentrations et de pH, l'espèce majoritaire initialement présente en solution est le complexe monomère $[Fe(OH)]^{2+}$, complexe qui disparait ensuite avec une vitesse d'autant plus rapide que la température est élevée ou que la solution est diluée. C'est également l'espèce de Fe(III) la plus active photochimiquement, en terme de production de radicaux hydroxyles :

$$Fe(OH)^{2+} \xrightarrow{h\nu} Fe^{2+} + HO^{\bullet}$$

Les radicaux $^{\bullet}OH$ produits peuvent ensuite etre utilisés pour dégrader des polluants organiques. Dans le cas du 4-chlorophénol, nous avons identifié et quantifié les espèces transitoires de la photodégradation et ainsi montré que la somme des rendements quantiques de formation de ces espèces [1] est égale au rendement quantique de formation des radicaux $^{\bullet}OH$ donné dans la littérature [2]. De plus, pour des temps d'irradiation plus longs, la concentration de Fe(II) en solution atteint un plateau qui correspond à une concentration égale à la concentration initiale en complexes monomères. La réaction se poursuit grâce à la réaction de réoxydation du Fe(II) en Fe(III) par les radicaux hydroxyles ($k = 1,4 - 4,3 \times 10^{8}$ L mol^{-1} s^{-1}) [3], ce qui assure par ailleurs la formation de ces radicaux en continu.

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Physikalische Chemie **237**

Modeling of the Photochemically Enhanced Fenton Reaction Using Artificial Neural Networks

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Within the domain of industrial waste water treatment, the photochemically-enhanced Fenton reaction has been found to be one of the most efficient methods for the oxidative degradation of organic pollutants and has been chosen for large-scale development [1]. This process involves a large number of reactions and is therefore difficult to model for the purpose of optimization.
Artificial neural networks are attracting great interest for modeling and predictive purposes [2]. They have the ability to record and learn complex behaviors of an evolutive system from a set of experimental data without a phenomenological model and have proven to be extremely useful for simulating, optimizing and up-scaling complex photochemical processes [3,4].
In this work, 2,4-Xylidine was chosen as a model pollutant. The effects of different parameters (concentrations of pollutant, catalyst and oxidant, as well as reaction temperature) have been investigated in applying the Optimal Experimental Design Methodology, and Artificial Neural Networks have been used to model the process starting with given sets of experimental data. The result provides the possibility to simulate other experiments and to calculate corresponding initial rates of pollutant degradation.

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Ab initio Molecular Dynamics Simulation of Electron Transfer Induced Carbon-Sulfur Bond Cleavage in Rhenium and Technetium Thioether Complexes.

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Abstract

Treatment of hexathioether rhenium and technetium complexes of form $[M(9S3)_2]^{2+}$ (M=Re, Tc and 9S3=1,4,7-trithiacyclononane) with reducing agents such as ascorbic acid, Zn, Cr or $SnCl_2$ results in the immediate carbon-sulfur bond cleavage and release of ethene. This scission takes place under mild conditions, in aqueous solutions and at room temperature. Carbon sulfur bond cleavage processes are of particular interest due to their great technical importance in the hydrodesulfurization of crude oils. The ease with which the bond cleavage can be induced in the hexathioether compounds indicates that these simple homogeneous systems could serve as possible model compounds for the more complex heterogeneous industrial process. Furthermore, hexathioether compounds of Re-188 and Tc-99 are also potential radiopharmaceuticals for targeted radiotherapies and radiodiagnosis. A detailed understanding of their reactivity is thus of great interest.
Therefore we performed ab intio molecular dynamics simulations in order to study the reductive C-S bond cleavage reaction in these hexathioether complexes. From the simulations performed on the rhenium complexes emerges clearly that the oxidized form is stable at room temperature within a run of 4 ps, while the reduced form undergoes the scission of two C-S bonds and splits off the ethylene at only slightly elevated temperatures. Furthermore, we have followed the system along the observed reaction pathway, determining the required activation energies for the cleavage of the C-S bond. At the non local DFT (BLYP) level of theory the obtained values are of 16 and 8 kcal/mol for the oxidized and the reduced form, respectively. Moreover, a detailed analysis of the electronic structure of the rhenium and technetium complexes in the oxidized and in the reduced form confirm the hypothesis [1] of the π back-donation to the C-S σ^* orbital as a possible cause of the C-S bond cleavage. Therefore these results illustrate clearly the pronounced influence of the additional electron and that the C-S bond cleavage is indeed induced via a reductive electron transfer.

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Computational Chemistry **239**

Hybrid Car-Parinnello Simulations as a Tool for the Rational Design of Biomimetics

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Very recently, Wang *et al.* [1] were able to design efficient biomimetic models of the mononuclear copper enzyme galactose oxidase, which reproduce the structural, spectroscopic and functional properties of the native system exceptionally well. In the catalytically inactive (EPR-active) form, the copper ion shows a peculiar non square planar O_2N_2-coordination, which induces a very complex energy level diagram that cannot be related to crystal field models. In order to get more insight into the factors that may augment the efficiency of the synthetic model, we have made a detailed comparison between the synthetic model and the natural system, both in the active and inactive forms. The latter has been described through mixed Car-Parinnello simulations, wheras results for the biomimetic compound are obtained using unrestricted dynamical density functional calculations [2]. The influence of the enzymatic environment and the structural changes upon the electronic structure is discussed.

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Computer Aided Chemistry **240**

Overcoming the time-scale barrier in ab initio molecular dynamics

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The ab initio molecular dynamics method developed by Car and Parrinello[1] combines an electronic structure method based on DFT with a classical dynamics scheme. This provides a powerful, parameter free, tool to study the dynamics of molecular systems in gas or condensed phases. It has become feasable to simulate the finite temperature properties or follow steps in a chemical reaction for systems of a few hundreds of atoms, however, the time-scale covered in a simulation is typically limited to about 10 ps. This limits the type of reactions that can be observed directly by ab initio MD, as only sufficiently fast reactions are likely to be seen.

Due to this limitation, which is apparent in all types of MD simulations, there is considerable interest[2,3] in methods that modify the dynamics of the system to make rare events more likely. Altough the dynamics is modified, these methods still give the thermodynamical properties, including transition state theory rate constants or free energy differences, of the original system. Results obtained with this accelerated dynamics can have exponentially reduced sampling errors. However, depending on the system studied, the way to modify or bias the dynamics is different. We compared different schemes[4] based on bias potentials or forces to find schemes that are well adapted for the particularly steep potential surfaces that are typical for the systems studied with ab initio molecular dynamics.

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Computational Chemistry **241**

Disproving the iceberg effect? The deuterium quadrupole coupling constant of water in DMSO

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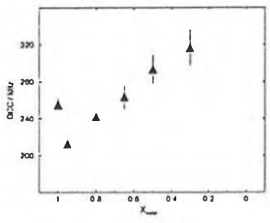

Deuterium quadrupole coupling constant (QCC) of water in the mixture water/DMSO(left $x_{water} = 1$, right $x_{water} = 0$) at 298 K.

The figure depicts the experimental behaviour of the deuterium quadrupole coupling constant (QCC) with changing mole fraction of water. As little DMSO is added, the QCC drops from the pure water value to a value approximately equal to that of solid ice. With increasing concentration of DMSO the quadrupole coupling constant rises to the gaseous water value. The results suggest that an iceberg effect is being observed. Doubts concerning the experiment arose, because the QCC is determined indirectly, i.e. several assumptions are made (amongst them a different correlation time has been taken), and because a similar behaviour is not observed in any other mixture of water and organic solvents. The results of the calculated values differ from the one observed in the experimental study. Evidence for the validity of the simulation is that within statistical error the correct value for pure water is obtained.

Computational Chemistry **242**

Density Matrix Renormalization Group (DMRG) as a tool for Magnetic Properties Calculations.

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The calculation of different spin manifold energies has always been considered as a difficult task both in a post-HF and in a DFT approach due to the intrinsic multi-determinantal nature of the problem. Extensive post-HF treatment is therefore needed in order to obtain reliable (near experimental) values of the exchange coupling constant (related to the different in energy between the different spin states). In this communication we report on the application of Density Matrix Renormalization Group (DMRG) [1] in order to get full-CI energies for different spin states of model and real molecular magnets. DMRG so far applied mainly in solid state physic to describe strongly interacting quantum lattice systems. It is based on an iterative numerical procedure to approximately diagonalize the Hamiltonian of a full CI expansion in a finite basis set. Using Davidsson or Lanczos algorithm in order to reduce the full Hilbert space, we can afford to treat much larger systems that in a standard full-CI procedure (i.e. a larger basis set and therefore a large CI space). Using density matrix projection the less important degree of freedom are integrated out progressively. Therefore we can find the exact solution of the non-empirical molecular Hamiltonian:

$$H = \sum_{i,j,\sigma} h_{ij}^{core} c_{i\sigma}^{\dagger} c_{j\sigma} + \sum_{i,j,k,l,\sigma,\sigma'} \langle ij|kl\rangle c_{i\sigma}^{\dagger} c_{j\sigma} c_{k\sigma'}^{\dagger} c_{l\sigma'}$$

In the current implementation the one (h_{ij}) and two electrons (<*ij*|*kl*>) integrals needed are computed with the Gaussinan98 program in an AO basis set and then transformed in a localised set [2] of orthogonal orbitals.

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Analytische Chemie **243**

Heteronuclear 2D NMR Spectroscopy: The simultaneous Detection of $^{n}J_{CH}$- and $^{1}J_{CH}$-Connectivities

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The correlation of carbon and proton chemical shifts through one-bond ($^{1}J_{CH}$) and long-range ($^{n}J_{CH}$) couplings yields the probably most important information for unravelling molecular structures. Corresponding 2D NMR experiments to detect $^{1}J_{CH}$ - and $^{n}J_{CH}$ -coupling interactions such as HSQC [1] (or HMQC [2]) and HMBC [3] respectively have now progressed to the status of routine procedures and are widely used.
We propose a new 2D pulse sequence based on the gradient enhanced HMBC experiment, which detects simultaneously $^{n}J_{CH}$ - and $^{1}J_{CH}$ connectivities and which allows to edit the corresponding subspectra by simple data processing. Compared to the usual two-step procedure with two 2D experiments (e.g. HMQC and HMBC) applied one after the other to detect these heteronuclear coupling interactions a higher overall sensitivity is achieved with the new pulse sequence which yields the same information in a single step. The experiment sharply discriminates between $^{1}J_{CH}$ and $^{n}J_{CH}$ interactions - most important for „clean" subspectra - for all carbon multiplicities and even for systems containing widely differing coupling constants and/or systems with extensive and strong homonuclear coupling interactions. The suppression of „$^{1}J_{CH}$ - artefacts" in $^{n}J_{CH}$ subspectra obtained with the new method is superior compared to dedicated „state of the art" methods such as the ACCORD-HMBC experiment [4].

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[3] W. Willker, D. Leibfritz, R. Kerssebaum and W. Bermel, *Magn. Reson. Chem.* **1993**, *31*, 287.

[4] R. Wagner and S. Berger, *Magn. Reson. Chem.* **1998**, *36*, 44.

Organische Chemie **244**

Heteronuclear 2D NMR Spectroscopy: The simultaneous Detection of $^{n}J_{CH}$- and $^{1}J_{CH}$-Connectivities

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The correlation of carbon and proton chemical shifts through one-bond ($^{1}J_{CH}$) and long-range ($^{n}J_{CH}$) couplings yields the probably most important information for unravelling molecular structures. Corresponding 2D NMR experiments to detect $^{1}J_{CH}$ - and $^{n}J_{CH}$ -coupling interactions such as HSQC [1] (or HMQC [2]) and HMBC [3] respectively have now progressed to the status of routine procedures and are widely used.
We propose a new 2D pulse sequence based on the gradient enhanced HMBC experiment, which detects simultaneously $^{n}J_{CH}$ - and $^{1}J_{CH}$ connectivities and which allows to edit the corresponding subspectra by simple data processing. Compared to the usual two-step procedure with two 2D experiments (e.g. HMQC and HMBC) applied one after the other to detect these heteronuclear coupling interactions a higher overall sensitivity is achieved with the new pulse sequence which yields the same information in a single step. The experiment sharply discriminates between $^{1}J_{CH}$ and $^{n}J_{CH}$ interactions - most important for „clean" subspectra - for all carbon multiplicities and even for systems containing widely differing coupling constants and/or systems with extensive and strong homonuclear coupling interactions. The suppression of „$^{1}J_{CH}$ - artefacts" in $^{n}J_{CH}$ subspectra obtained with the new method is superior compared to dedicated „state of the art" methods such as the ACCORD-HMBC experiment [4].

[1] A.G. Palmer, J. Cavanagh, P.E. Wright and M. Rance, *J. Magn. Reson.* **1991**, *93*, 151.

[2] R.E. Hurd and B.K. John , *J. Magn. Reson.* **1991**, *91*, 648.

[3] W. Willker, D. Leibfritz, R. Kerssebaum and W. Bermel, *Magn. Reson. Chem.* **1993**, *31*, 287.

[4] R. Wagner and S. Berger, *Magn. Reson. Chem.* **1998**, *36*, 44.

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EUROPEAN COOPERATION
IN THE FIELD OF SCIENTIFIC
AND TECHNICAL RESEARCH

Second Swiss COST Chemistry Symposium

(http://sgich1.unifr.ch/oc/cost/mainpage.html)

Friday, October 15, 1999

ILMAC 99
Convention Center of the Messe Basel
Messeplatz 1
Basel, Switzerland
Room 'Kleiner Festsaal'

Organizer:

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CHIMIA 1999, 53, No. 7/8

WHAT IS COST?

COST (a French acronym for 'Coopération Européenne dans le domaine de la recherche Scientifique et Technique') was set up in 1971 to stimulate and to give a framework for the European cooperation in the field of science and technology. This forum of research brings now together 28 European countries including the fifteen members of the European Union plus Iceland, Norway, Switzerland, the Czech Republic, Slovakia, Hungary, Poland, Turkey, Slovenia, Croatia, Malta, Estonia, and Romania. COST is oriented towards pre-competitive research. COST activities are currently covering the following areas: computer sciences, telecommunications, transports, oceanography, materials, environment, meteorology, agriculture-biotechnology, food technology, social sciences, medical research, urban civil engineering, chemistry, forests-forestry products, physics, and nanosciences.

COST CHEMISTRY

Chemistry is a central science with distinguished history and recent success in Europe (five *Nobel*-prize winners between 1990 and 1998 are European). Chemical Industry is one of Europe's most international, competitive and successful industries and contributes to the prosperity and quality of life of modern European society. In order to maintain and even to improve this position, it was decided to use the COST forum to elaborate a strategic scientific scheme for basic research in chemistry in Europe. In this respect, a Technical Committee (TC) in chemistry was built in 1990. In 1992, through a proposition of the TC, COST decided to launch seven Actions in the field of chemistry. These Actions were followed in 1998 by eight new Actions which will run until 2003. In 1996, the COST CHEMISTRY activities consisted of 117 collaborative projects in which 564 European research groups were involved. The COST system is characterized by the bottom-up approach (the initiative comes from the researcher) and by the fact that the funding of the research is national. In Switzerland, the main sources of funding for COST CHEMISTRY is the Office of Education and Science, and partially the Swiss National Science Foundation.

WHY A SECOND SWISS COST CHEMISTRY SYMPOSIUM?

The goal of this symposium is to present the chemical research which is taking place in Switzerland and in Europe within the COST framework. By inviting ten prominent Swiss and non-Swiss scientists, **we intend to present the different research fields covered by the eight running COST Actions**. A poster session will also give the possibility to the Swiss groups involved in COST programs to present their recent results.

REGISTRATION

Registration is free but necessary in order to get into the ILMAC area. More information will be available at the symposium web site (http://sgich1.unifr.ch/oc/cost/mainpage.html).

CHIMIA 1999, 53, No. 7/8

Scientific Programme

Messeplatz 1, Room 'Kleiner Festsaal'

9h30 Welcome by **Prof. *P. Renaud***
Introduction by **Prof. *A. Merbach***
Chairman of the COST Technical Committee

Morning Session – Chairman: Dr. *H.-P. Schelling*

9h40 **Prof. *Thomas A. Kaden***
Universität Basel, Switzerland
(Action D8: Chemistry of Metals in Medicine)
Labeling Monoclonal Antibodies with Metal Complexes, a Challenge for Coordination Chemists

10h10 **Prof. *Jacques Reisse***
Université Libre de Bruxelles, Belgium
(Action D10: Innovative Methods and Techniques for Chemical Transformations)
Sonochemistry: Scope, Limitations ... and Artefacts

10h40 Coffe break, poster session

11h00 **Prof. *Walter Kohn***
University of California, Santa Barbara, USA
(Action D9: Advanced Computational Chemistry of Increasingly Complex Systems)
Electronic Structure of Matter: Wave Functions and Density Functionals

11h45 **Prof. *Jacques Weber***
Université de Genève, Switzerland
(Action D9: Advanced Computational Chemistry of Increasingly Complex Systems)
Progresses towards the Advanced Computational Chemistry of Increasingly Complex Systems

Poster-Sandwich Session (12h15–13h30)

Action D1–7: Abstracts 1–3

Action D8: Chemistry of Metals in Medicine
Abstracts 4–9

Action D9: Advanced Computational Chemistry of Increasingly Complex Systems
Abstracts 10–17

Action D10: Innovative Methods and Techniques for Chemical Transformations
Abstracts 18, 19

Action D11: Supramolecular Chemistry
Abstracts 20–22

Action D12: Organic Transformations: Selective Processes and Asymmetric Catalysis
Abstracts 23–31

Action D13: New Molecules for Human Health Care
Abstracts 32–40

Miscellaneous: Abstracts 41, 42

Afternoon Session – Chairman: Prof. *M. Grätzel*

13h30 **Prof. *Pier Luigi Luisi***
ETH Zürich, Switzerland
(Action D11: Supramolecular Chemistry)
Membrane-Assisted Polycondensation of Amino Acids and Peptides

14h00 **Prof. *Nigel S. Simpkins***
University of Nottingham, UK
(Action D12: Organic Transformations: Selective Processes and Asymmetric Catalysis)
Enantioselective Proton-Transfer Chemistry

14h30 **Prof. *Alexandre Alexakis***
Université de Genève, Switzerland
(Action D12: Organic Transformations: Selective Processes and Asymmetric Catalysis)
Asymmetric Synthesis Using Organocopper Reagents

15h00 Coffee break, poster session

15h30 **Prof. *Pierre Vogel***
Université de Lausanne, Switzerland
(Action D13: New Molecules for Human Health Care)
Sugar Mimetics: Why and How

16h00 **Prof. *Dieter Seebach***
ETH Zürich, Switzerland
(Action D14: Functional Molecular Materials)
TADDOLs – From Enantioselective Catalysis to Dendritic Cross Linkers to Cholosteric Liquid Crystals

16h30 **Prof. *Roel Prins***
ETH Zürich, Switzerland
(Action D15: Interfacial Chemistry and Catalysis)
The Production and Use of Nanostructured Surfaces as Model Catalysts

17h00 Concluding remarks

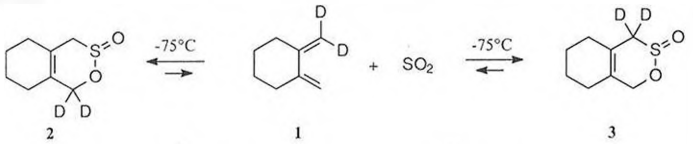
D2/0016/1993 **1**

THE *HETERO* DIELS-ALDER REACTION OF SO_2 TO 1,2-DIMETHYLIDENECYCLOHEXANE IS ASYNCHRONOUS

Frédéric Monnat and Pierre Vogel*

Institute of Organic Chemistry, University of Lausanne, BCH, CH-1015 Lausanne-Dorigny, Switzerland

Most 1,3-dienes add to SO_2 giving the corresponding sultines[1-5] under conditions of kinetic control (low temperature, acidic catalyst). They give the corresponding more stable sulfolenes under condition of thermodynamic control, at higher temperature. With the dideuterated diene **1**, we have been able to show that the *hetero* Diels-Alder reaction is asynchronous, the C-S bond being formed to a larger extend that the C-O bond in the transition state.



$$\frac{k_{obs,2}}{k_{obs,3}} = 1.11 \pm 0.04 \qquad \frac{K_2}{K_3} \rightarrow 1$$

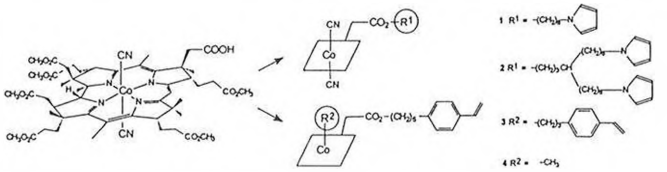
1. Heldeweg, R.F.; Hogeveen, H. *J. Am. Chem. Soc.* **1976**, *98*, 2341.
2. Durst, T.; Tétreault-Ryan, L. *Tetrahedron Lett.* **1978**, 2353.
3. Deguin, B.; Vogel, P. *J. Am. Chem. Soc.* **1992**, *114*, 9210.
4. Fernandez, T; Suarez, D; Sordo, JA; Monnat, F; Roversi, E; de Castro, AE; Schenk, K.; Vogel, P. *J. Org. Chem.* **1998**, *63*, 9490.
5. Fernandez, T; Sordo, JA; Monnat, F; Deguin, B; Vogel, P. *J. Am. Chem. Soc.* **1998**, *120*, 13276.

D5/0010/94 **2**

VITAMIN B_{12} DERIVATIVES WITH POLYMERIZABLE STYRENE AND PYRROL GROUPS

T. Darbre, T. Otten, C. Nachtigal, R. Fraga and R. Keese
Department of Chemistry and Biochemistry, University of Bern, Freiestrasse 3, 3012 Bern, Switzerland

Important features of the coenzyme B_{12} catalyzed reactions have not yet been elucidated. Particularly, the mechanism for the Co-(C5')adenosyl homolysis, considered to be the first step in the catalytic cycle, is still unknown. The chiral recognition, the transfer of chirality in the catalyzed rearrangements as well as the detailed electronic features of these tranformations are other aspects that require further studies. We have prepared polymer-coated electrodes and polymeric materials incorporating derivatives of vitamin B_{12} for this purpose.



Derivatives of vitamin B_{12} with a pyrrole head group attached to the corrin have been prepared (**1**,**2**) and their electropolymerization investigated [1]. In a further developement, two pyrrole groups were grafted to the corrin complex giving **2**, for improved electropolymerization and formation of conducting films on the electrode surface. Polymers of B_{12} derivatives bearing a styryl head group were also prepared. Radical induced polymerization of **3** and **4** led to polymers which are light sensitive and turn red-violet upon exposure to light. Polymers derived from **3** and **4** incorporate a Co-C bond and allow the study of the conditions necessary for the Co-C bond cleavage in the microenvironment of the polymeric support. Low transition temperatures for these polymers have been detected by differential scanning calorimetry.

[1] T. Otten, T. Darbre, S. Cosnier, L. Abrantes, J. Correia, R. Keese, Helv. Chim. Acta **1998**, *81*, 1117.

This work was generously supported by a COST-D5 project, administered by the Swiss National Science Fondation (No. 21228-44'420.95).

D7/0001/1992 **3**

SUPRAMOLECULAR AGGREGATES FROM PHOSPHATIDYLNUCLEOSIDES AND AMINO ACID BASED DOUBLE CHAIN AMPHIPHILES

P. Walde,[1] S. Bonaccio,[1] C. Cescato,[1] P. L. Luisi,[1] D. Capitani,[2] A. Segre[2]
[1] ETH-Zentrum, Institut für Polymere, CH-8092 Zürich, Switzerland
[2] Istituto di Strutturistica Chimica del CNR, I-00016 Roma, Italy

A variety of phosphatdidylnucleosides – phospholipids bearing a nucleosidic head group – and amino acid based double chain amphiphiles have been synthesized and the physico-chemical properties of supramolecular structures formed by these chiral compounds in dilute aqueous solution have been investigated by electron and light microscopy, dynamic light scattering and circular dichroism [1, 2]. Depending on the chemical structure and on the experimental conditions, either rolled, helical, or closed bilayers (vesicles) formed. Vesicles have only been obtained when the amphiphile dispersions were kept below the solid-analogue/liquid-analogue phase transition temperature. Some of the vesicles prepared from phosphatidylnucleosides were characterized by 2D-^{1}H-NMR spectroscopy, and it has been shown that *intra*vesicular interactions between neighbored head groups stabilize the bilayer surface of the vesicles [3].

[1] S. Bonaccio, M. Wessicken, D. Berti, P. Walde, P. L. Luisi (1996) Langmuir 12, 4976.
[2] C. Cescato, P. Walde, P. L. Luisi (1997) Langmuir 13, 4480.
[3] S. Bonaccio, D. Capitani, A. L. Segre, P. Walde, P. L. Luisi (1997) Langmuir 13, 1952.

D8/0001/97 **4**

Eu(II) POLY(AMINO CARBOXYLATES): STABILITY AND RELAXATION PROPERTIES

László Burai, Sabine Seibig, Éva Tóth and André E. Merbach

Institut de Chimie Minérale et Analytique, University of Lausanne BCH-Dorigny, CH-1015, Switzerland

Paramagnetic complexes containing Gd(III) ion have been used in magnetic resonance imaging (MRI) as highly efficient relaxation enhancement reagents. Eu(II) is isoelectronic with Gd(III) which may lead to similar biomedical applications of Eu(II)-complexes. The water exchange rate on $[Eu(H_2O)_8]^{2+}$ has been recently determined and found to be extremely high.[1] These studies have been now extended to complexes of Eu(II) with poly(amino carboxylates) such as DTPA, DOTA and 18-membered macrocyclic derivatives.

The Eu(II) complexes have been synthesised by controlled potential coulometry. Their Eu(III)/Eu(II) redox potential has been measured as a function of the pH. The oxidation of the Eu(II)-complexes was followed by spectrophotometry and potentiometric titration. We concluded that the number of the carboxylic group influences the oxidative stability. The thermodynamic stability and protonation constants of complexes have been determined by pH-potentiometric titration. The equilibrium constants of the Eu(II) complexes are similar to those of the corresponding Sr(II)-chelates. In order to determine the parameters that influence proton relaxivity (rate of water exchange, rotation and electronic relaxation), we have performed ^{17}O NMR, EPR and NMRD measurements at variable field and temperature.

This work was supported by COST D8 program.

[1] P. Caravan and André E. Merbach, *Chem. Commun.*, 1997, 2147.

D8/0001/1997 **5**

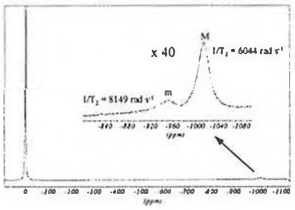
FIRST ^{17}O NMR OBSERVATION OF THE COORDINATED WATER ON A EU(III) COMPLEX: A DIRECT ACCESS TO WATER EXCHANGE

Dunand F. ♣, Barge A. ♦, Helm L. ♣, Botta M. ♦, Aime S ♦, Merbach A.E. ♣.

♣ ICMA, Université de Lausanne, CH-1015 Lausanne, Switzerland.
♦ Dipart. di Chimica I.F.M., Universita di Torino, I-10125 Torino, Italy

It is now well known that DOTA-derivative lanthanides complexes , which are potential MRI contrast agent in the case of Gd(III), exist in two diastereoisomeric forms (M and m).[1] Unlike the case of DOTA where the water exchange rates are too fast to distinguish the contribution of each diastereoisomer to the observed overall exchange rate, the relatively slow water exchange rate of the $[Eu(DOTAM)]^{3+}$ complex allows the observation of both bound water signals and subsequently to quantify each contribution (DOTAM = 1,4,7,10-tetrakis-(carbamoylmethyl)-1,4,7,10-tetraaza-cyclododecane).[2]

The bound water signal was observed for the first time by ^{17}O NMR for this kind of complexes and the temperature dependence of the ^{1}H and ^{17}O NMR bound water signals of both isomers were used to determine the water exchange parameters. Furthermore the pressure dependence measurements for the M-isomer using both ^{1}H and ^{17}O NMR reveal a dissociative interchange mechanism for the water exchange. The M. ·m interconversion rates measured by magnetization transfer are compared to the water exchange and energy profiles for the M/m system are proposed.



^{17}O NMR spectrum of EuDOTAM

We are grateful to the Swiss OFES as part of the European COST D8 action.

[1] S. Aime et al. *Inorg. Chem.* **1997**, *36*, 2059-2068.
[2] S. Aime et al. *Angew. Chem. Int. Ed.* **1998**, *37*, 2673-2675.

D8/0001/97 **6**

PROTEIN-BOUND GD(III) CHELATES : DIRECT ASSESSMENT OF WATER EXCHANGE[1]

Éva Tóth,[1] Kofi Adzamli[2] and André E. Merbach[1]

[1]Institut de Chimie Minérale et Analytique, University of Lausanne BCH-Dorigny, CH-1015, Switzerland
[2]Imaging Division, Mallinckrodt Inc.,675 McDonnell Blvd., P.O.Box 5840, St. Louis, MO 63134 USA.

The Gd(III) complex of 4-pentylbicyclo[2.2.2]octane-1-carboxyl-di-L-aspartyl-lysine derived DTPA, $[GdL(H_2O)]^{2-}$, binds to serum albumin *in vivo* through hydrophobic interaction. The different correlation times that determine proton relaxivity have been obtained for the free GdL, as well as for the protein-bound complex.

A variable temperature ^{17}O NMR has been used to directly evaluate the effect of albumin-binding on water exchange rate. $1/T_1$ NMRD profiles were measured in the magnetic field range 0.24 mT - 14.1 T (0.01 - 600 MHz proton Larmor frequency).

The ^{17}O NMR and NMRD study let us conclude that the non-bound GdL complex is identical to $[Gd(DTPA)(H_2O)]^{2-}$ in respect to water exchange and electronic relaxation. ^{17}O NMR measurements performed in GdL solutions containing BSA indicated that, contrary to the expectations, the water exchange rate on GdL does not decrease considerably when the complex binds to the protein. The lowest limit can be given as $k_{ex,GdL\text{-}BSA} = k_{ex,GdL}/2$. In the knowledge of the water exchange rate for the BSA-bound GdL complex, the analysis of its NMRD profile at 35 °C yielded in a rotational correlation time which is shorter than that of the whole protein, indicating an internal flexibility.

We are grateful to the Swiss OFES as part of the European D8 action.

1. É. Tóth, F. Connac, L. Helm, K. Adzamli and A. E. Merbach, *JBIC*, **1998**,.*3*, 606-613.

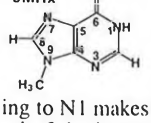
D8/0004/1997 **7**

Acid-Base Properties of the Ternary Complexes Formed with Platinum(II), Diethylenetriamine (Dien) and 9-Methylhypoxanthine (9MHx): Pt(Dien)(9MHx-*N7*)$^{2+}$ and Pt(Dien)(H;9MHx-*N1*)$^{2+}$

Gunnar Kampf,[a,b] Rolf Griesser,[a] Larisa E. Kapinos,[a] Bernhard Lippert,[b] and Helmut Sigel[a]

[a] *Inst. Inorg. Chem., University, Spitalstr. 51, CH-4056 Basel, Switzerland*
[b] *Dept. of Chem., University, Otto-Hahn-Str. 6, D-44227 Dortmund, FRG*

To understand the effect of nucleobase-coordinated metal ions on the acid-base properties of nucleobases [1,2] we studied the title complexes. The acidity constants of $H(9MHx)^+$ were determined by potentiometric pH titrations in aqueous solution (25 °C; I = 0.1 M; $NaNO_3$) [1] and those of the Pt^{2+} complexes were calculated by us from published [3] ^{1}H-NMR shift data. The results in the Table show that $Pt(Dien)^{2+}$ bound to N7 acidifies the (N1)H site, as one would expect (Δ $pK_{a/N1}$ = 1.54), whereas its binding to N1 makes N7 apparently more basic. However, a more careful appraisal of the latter situation shows that the deprotonation of $(N7)H^+$ is considered once with neutral (N1)H, and once with the $(N1)^-$ site. Hence, the valid comparison needs to be made with the zwitterionic $H(9MHx\text{–}H)^{\pm}$ tautomer of the 9MHx ligand. The corresponding micro acidity constant was now estimated: $pk_{ma/N7} = 4.62\pm0.02$ (for the procedure see, e.g., [1]). If this value is used in the comparison, one obtains for the acidification of the $(N7)H^+$ site by N1-coordinated $Pt(Dien)^{2+}$, Δ $pK_{a/N7} = pk_{ma/N7} - pK^{H}_{Pt(Dien)(H;9MHx\text{-}N1)}$ = (4.62±0.02) – (3.02±0.25) = 1.60±0.25; in other words, this acidification on $(N7)H^+$ corresponds to the one observed for (N1)H.



Acid	pK_a of $(N7)H^+$	pK_a of (N1)H	Δ pK_a
$H(9MHx)^+$	1.87 ± 0.01	9.21 ± 0.01	
$Pt(Dien)(9MHx\text{-}N7)^{2+}$		7.67 ± 0.08	1.54 ± 0.08
$Pt(Dien)(H;9MHx\text{-}N1)^{2+}$	3.02 ± 0.25		−1.15 ± 0.25

Supported by the Swiss National Science Foundation, the Swiss Fed. Office for Education & Science (COST D8), the Novartis Foundation (formerly Ciba-Geigy-Jubilee Found.), and the 'Deutsche Forschungsgemeinschaft'.

[1] B. Song, J. Zhao, R. Griesser, C. Meiser, H. Sigel, and B. Lippert, *Chem. Eur. J. 5* (1999) in press.
[2] H. Sigel and B. Lippert, *Pure Appl. Chem. 70* (1998) 845-854.
[3] J. H. J. den Hartog, M. L. Salm, and J. Reedijk, *Inorg. Chem. 23* (1984) 2001-2005.

D8/0004/1997 **8**

Metal Ion Complexes of 4(5)-Aminoimidazole-5(4)-Carboxamide (AImC). Evaluation of Intramolecular Equilibria

Larisa E. Kapinos,[a] Rolf Griesser,[a] Paolo Carloni,[b] Nityananda Saha,[c] Arati Saha,[d] and Helmut Sigel[a]

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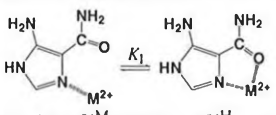
[b] *Internat. School for Advanced Studies SISSA/ISAS, I-34014 Trieste, Italy*
[c] *University of Calcutta, Dept. of Chemistry, Calcutta 700009, India*
[d] *Basanti Devi College, Dept. of Chemistry, Calcutta 700 029, India*

AImC is a precursor in the biosynthesis of purines; since these nucleobases interact with metal ions (M^{2+}), the M^{2+}-binding properties of AImC are also of interest. Chemical reasonings and *ab initio* calculations lead us to conclude that protonation of AImC occurs at the imidazole nitrogen and not at the exocyclic amino group, which has practically no basic properties. This then leads to the interesting question, if not only the imidazole moiety but also the other substituent participates in complex formation giving thus rise to an intramolecular equilibrium between an 'open', $M(AImC)^{2+}_{op}$, and a 'closed' isomer, $M(AImC)^{2+}_{cl}$. The recently established straight-line correlation [1] based on $\log K^{M}_{ML}$ *versus* pK^{H}_{HL} plots of simple imidazole derivatives, like 1-methylimidazole, allows an evaluation of the stability constants available [2] for $M(AImC)^{2+}$ complexes. Application of $pK^{H}_{H(AImC)}$ = 4.02 [2] to the straight-line equations [1] provides the calculated (calcd) stability of the $M(AImC)^{2+}$ species which may be compared with the measured (exptl) values. Any stability enhancement according to $\log \Delta_{M(AImC)} = \log K_{exptl} - \log K_{calcd}$ must be a reflection [3] of the formation degree of the chelated species, $M(AImC)^{2+}_{cl}$. Indeed, the results (Table) show that the formation degree of the chelated isomers involving the carbonyl oxygen is quite significant.



M^{2+}	$\log \Delta_{M(AImC)}$	K_1	% $M(AImC)^{2+}_{cl}$
Ni^{2+}	0.17 ± 0.05	0.48 ± 0.17	32 ± 8
Cu^{2+}	0.59 ± 0.04	2.89 ± 0.38	74 ± 3
Zn^{2+}	0.24 ± 0.14	0.74 ± 0.56	42 ± 18

Supported by the Swiss Fed. Off. for Educ. & Sci. (COST D8); the Swiss Nat. Sci. Found., and the Novartis Found. (formerly Ciba-Geigy-Jubilee Found.).

[1] L. E. Kapinos, B. Song, H. Sigel, *Inorg. Chim. Acta 280* (1998) 50-56.
[2] I. Török, P. Surdy, T. Gajda, et al., *J. Inorg. Biochem. 71* (1998) 7-14.
[3] H. Sigel, S. S. Massoud, N. A. Corfù, *JACS 116* (1994) 2958-2971.

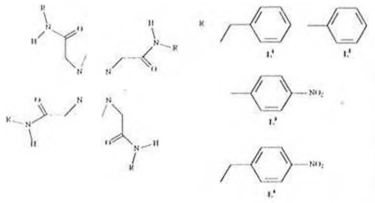
D8/0000/1999 **9**

TUNING THE LUMINESCENCE AND STRUCTURAL PROPERTIES OF LANTHANIDE COMPLEXES WITH CYCLEN DERIVATIVES

Gaël Zucchi, Rosario Scopelliti and Jean-Claude G. Bünzli

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

Until now, the developments in lanthanide coordination chemistry with cyclen derivatives have been essentially focused on the design of powerful contrast agents for magnetic resonance imaging [1]. On the other hand, the peculiar and unique luminescence properties of Ln^{III} ions have been used to develop very sensitive time-resolved fluoroimmunoassays [2]. Our goal is to try to combine the two approaches by using cyclen platforms able to yield both efficient contrast agents and luminescent Eu^{III} and Tb^{III} edifices suitable for biological and medical applications [3].



We investigate here the influence of the pendant arm functionalities on the strucural and photophysical properties of the Eu^{III} and Tb^{III} complexes. In particular, the presence of nitro substituents leads to a good sensitization of the Eu^{III} ion.

[1] R.B. Lauffer, *MRI Clinical Magnetic Resonance Imaging*, eds. R.E. Edelman, M.B. Zlatkin and J.R. Hesselink, W.B. Saunders Co, Philadelphia, **1996**; Vol. 1, Ch. 5.
[2] I. Hemmilä, T. Ståhlberg, P. Mottram, *Bioanalytical Applications of labelling Technologies*, Wallac Oy: Turku, 1995 (2nd ed.) ; G. Mathis in *Rare Earths*, R. Sáez-Puch, P. Caro, eds., Editorial Complutense: Madrid, 1998, pp. 285-297.
[3] G. Zucchi, R. Scopelliti, P.- A. Pittet, J.- C. G. Bünzli, R. D. Rogers, *J. Chem. Soc., Dalton Trans.*, **1999**, 931.

D9/0002/97 **10**

OUTER-SPHERE HYDRATION OF MRI CONTRAST AGENTS: A MOLECULAR DYNAMICS STUDY

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Many factors influence the efficiency of magnetic resonance imaging (MRI) contrast agents but not all of them are directly accessible through experiments. The observed proton relaxation rate enhancement in the presence of a paramagnetic compound is divided into two contributions, namely inner-sphere and outer-sphere relaxivities. The latter is usually described by Freed's force-free model for the solute-solvent interaction[1,2], which could be inadequate depending on the nature of complex solvation. In order to get better understanding of the outer–sphere hydration of MRI contrast agents, we performed molecular dynamics simulations of several Gd^{3+} complexes in water. The structure and dynamics of water around such compounds were studied, as well as the role of chelate structure. We also analysed the impact of our results on outer-sphere relaxivity using numerical calculations.

This work has been supported by the Swiss OFES in the context of the European COST D9 action.

1)Freed, J. H. *J. Chem. Phys.* **1978**, *68*, 4034-4037.
2)Hwang, L.-P.; Freed, J. H. *J. Chem. Phys.* **1975**, *63*, 4017-4025.

D9/0002/97 **11**

The KERUBIN program: An AMBER[1] & GROMOS[2] compatible MD analysis tool

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Kerubin, a molecular trajectories analysis program written in C is a helpful tool in several stages of molecular simulations study, compatible with both AMBER and GROMOS packages. The storage of a sequence of structures or of single structures (PDB files) in a binary file avoids memory overflow for long trajectories and/or big molecular systems.
Besides classical structural analysis (distances, angles, dihedrals,...) the program has some more specific application domains: (i) Hydration and solvation study (rdf, angular distribution, residence time, coordination evolution,...), (ii) EXAFS spectroscopy analysis (double scattering signals simulations).
An atomic filtering method based on dynamic molecular groups can select atoms for which properties are calculated. This procedure refines analysis and reduces drastically the size of the input files.
A simple spreadsheet stores all calculated properties from the active session or previous sessions. Different arithmetical and statistical treatments can be applied before graphic visualization with a GNUPLOT interface and/or saving in ASCII formatted files. XMOL trajectory files or PDB structure files on limited atom groups can be written before visualization with freeware graphic molecular platforms such as MOLEKEL[3].

[1] D. A. Pearlman & *al.* (1995), AMBER 4.1, University of California San Francisco
[2] W. F. van Gunsteren & *al.* (1996), GROMOS96, ETHZ
[3] P. F. Flükiger & S. Portmann (1998), MOLEKEL 3.03, CSCS/SCSC-ETHZ

This work has been supported by the Swiss OFES in the context of the European COST D9 action.

D9/0005/1997 **12**

THE METAL-CARBON MULTIPLE BOND IN IRON(I)- AND IRON(II)-DIBENZOTETRAMETHYLTETRAAZA[14]ANNULENE[1]

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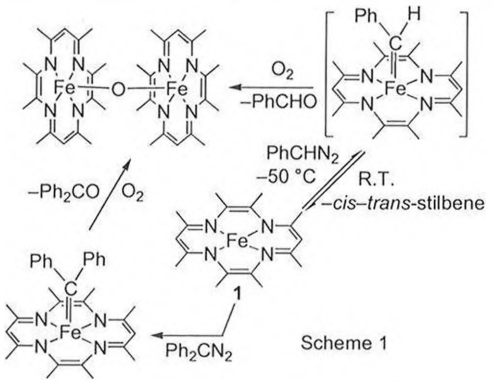
Macrocycles are increasingly considered as ancillary ligands in organometallic chemistry. This trend has been particularly developed in recent years for early transition metals. In the case of middle transition metals, however, the metal-carbon functionalities have been essentially considered for their relationship with biologically occurring systems, namely Vit. B_{12} in the case of cobalt[8] and the cytochrome P450 in the case of iron. The present report deals with the synthesis and the properties of iron(II) and iron(I)-dibenzotetramethyltetraaza[14]annulene [tmtaa] complexes, containing a multiple bond to carbon ligands, namely CO, RNC, carbene, and cyanides (see Scheme 1).



Scheme 1

1. *Organometallics* **1999**, *18*, 360.

We are grateful to Swiss OFES as part of European D9 action.

D9/0005/1997 **13**

MOLECULAR BATTERIES BASED ON METAL-SCHIFF BASE COMPLEXES[1]

Federico Franceschi,[a] Euro Solari,[a] Mario Latronico,[b] Marzio Rosi[c] and Carlo Floriani[a]

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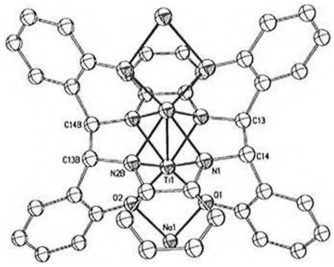
The reduction of metal-salophen [salophen = N,N'-phenylene-bis-(salicylideiminato) dianion] complexes led to the formation of C-C bonded dimers via the coupling of imino groups. These C-C bonds act as a reservoir of $2e^-$ which can be released upon the bond cleavage. Reduction of metal-salophen complexes with one equivalent of sodium metal led to the formation of dimers in which 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. These compounds can reduce a variety of substrates using the electrons stored in C-C bonds, thus restoring the imino functionality.



1. *Chem. Eur. J.* **1999**, *5*, 708.

We are grateful to Swiss OFES as part of European D9 action.

D9/0005/1997 **14**

THE LANTHANIDE ORGANOMETALLIC CHEMISTRY BASED ON THE PORPHYRINOGEN SKELETON: THE TWO-ELECTRON REDUCTION OF DINITROGEN AND ETHYLENE[1]

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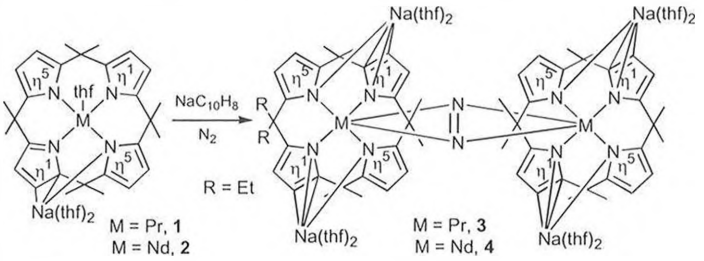
Porphyrinogen tetraanion provides a quite unique binding cavity for electron deficient metals, namely early transition metals. Such metals can exploit the $\eta^5{:}\eta^3{:}\eta^1$ bonding mode of each of the pyrrolyl anions according to the charge and electronic metal requests. In addition, the electron-rich pyrrolyl anions can function as binding countercations in the structure. Although the organometallic chemistry of lanthanides(II) is largely, if not exclusively, limited to samarium(II) and Cp-based ligands, it has been possible, using the *meso*-octaethylporphyrinogen as ancillary ligand, to generate the oxidation state (II) for lanthanides which are usually not available in this oxidation state, and to have them very reactive in the presence of appropriate substrates. The reduction of complexes **1** and **2** with sodium metal in the presence of dinitrogen or ethylene led to their dielectronic reduction, as exemplified in complexes **3**, **4**.



Scheme 1

1. *Chem. Commun.* **1998**,2603.

We are grateful to Swiss OFES as part of European D9 action.

D9/0005/1997 **15**

SYNTHETIC METHODOLOGY DIRECTED TO FUNCTIONALIZABLE ALKYLIDENES[1]

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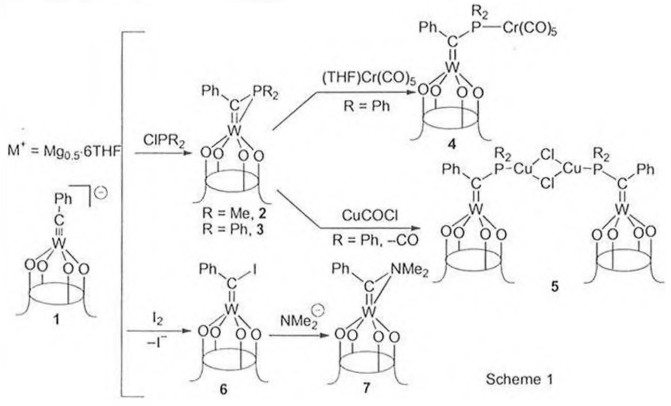
The presence of an heteroatom at the alkylidene carbon moves its properties to the borderline with the Fischer carbene chemistry. The changes in the M=C bond polarization caused by the heteroatom and the introduction of functional groups increases the possible use of the metal-alkylidene synthon both in organic and organometallic synthesis. The anionic tungsten-alkylidene derivatives, exemplified by complex **1** in Scheme 1, are the appropriate starting materials for entering the area of functionalized metal-alkylidenes. Two major complementary synthetic routes have been devised to this purpose (see Scheme 1).



Scheme 1

1. *J. Am. Chem. Soc.* **1999**, *121*, 2797. *Ibid.* **1999**, *121*, 2784. *Angew. Chem. Int. Ed. Engl.* **1999**, *38*, 807.

We are grateful to Swiss OFES as part of European D9 action.

D9/0005/1997 **16**

NOVEL FORMS OF PORPHYRINOGEN PAVING THE WAY TO PORPHYRINS[1]

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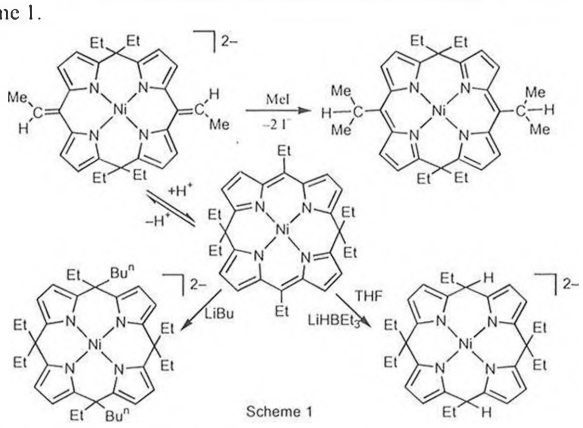
[b] Università della Basilicata, I-85100 Potenza, Italy

The redox and acid-base chemistry of porphyrinogen leads to species which are paving the way of its transformation to porphyrins. The chemistry of porphyrinogen, behind its spontaneous autooxidation to porphyrins, is still quite obscure due to the lack of porphyrinogen forms available for reactivity studies. In order to overcome this major difficulty we used in our approaches *meso*-octaalkylporphyrinogen and porphodimethene metal complexes. The latter compounds are the target of this report, since they allow to enter unusual forms of porphyrinogen through the reactions in Scheme 1.



Scheme 1

1. *J. Am. Chem. Soc.* **1998**, *120*, 12972. *Angew. Chem.*, in press.

We are grateful to Swiss OFES as part of European D9 action.

D9/0005/1997 **17**

THE π-COMPLEXATION OF ALKALI AND ALKALINE EARTH METAL CATIONS INSIDE THE PORPHYRINOGEN CAVITY[1]

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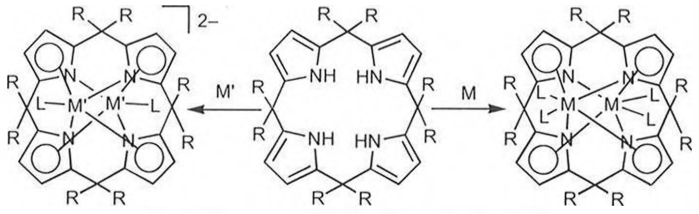
Solvation of alkali and alkaline earth metal cations by a π cavity is a quite remarkable phenomenon in the context of the role played by cation-π interactions in chemistry and biology. Three dimensionally shaped cavities functioning for the π solvation of alkali or alkaline earth metal cations are quite rare. The macrocyclic tetraanion derived from the *meso*-octaalkylporphyrinogen, owing to the presence of *meso* sp^3-hybridized carbon atoms, is particularly suited to arrange the pyrrolyl anions to function as η^3 or η^5 binding sites. We report here how all four pyrrolyl anions function together as π binding sites for alkali or alkali earth metal cations inside the porphyrinogen cavity. This synthetic and structural report (see Scheme 1) emphasizes the role of porphyrinogen as a possible binding cavity for alkali and alkaline earth metal ions. Furthermore, it shows how relevant the solvation of such ions can be using the π-interactions with electron-rich aromatic fragments.



Scheme 1

1. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 2245. *Ibid.* **1999**, *38*, 913.

We are grateful to Swiss OFES as part of European D9 action.

D10/0001/1998 **18**

HOMOGENEOUS CATALYTIC HYDROGENATION OF CARBON DIOXIDE IN AMINE FREE AQUEOUS SOLUTION

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Carbon dioxide reduction into useful starting materials raises several important theoretical and practical questions. Nature has solved this problem very efficiently (photosynthesis) and the inexhaustible/abundant CO_2 reservoirs (air, carbonate rocks, ocean, fuel burning, etc) could serve as raw material for chemical synthesis[1].

Several catalytic systems have been found to be active in the hydrogenation of CO_2 to formic acid (or its derivatives) in homogeneous, supercritical or heterogeneous phases[2-3]. Leitner also studied the reduction of CO_2 in aqueous solutions in the presence of the water soluble amines[4].

In contrast to previous attempts, we have investigated the catalytic reduction of carbon dioxide in amine free aqueous media. The hydrogenation reactions are the fastest at pH above 8 where the bicarbonate concentration shows a maximum. The main role of the amines used in this reaction in aqueous solutions seems to have been misunderstood until now. In aqueous solution, instead of having the role as a thermodynamic sink, they act as bases to increase the $[HCO_3^-]$, the most reactive species in the reduction.

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[2] B. Cornils, W. A. Herrmann, Eds., *Applied Homogeneous Catalysis with Organometallic Compounds*, Vol. 1-2, VCH, Weinheim, **1996**
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[4] W. Leitner, E. Dinjus, F. Gassner, in *Aqueous-Phase Organometallic Catalysis* (B. Cornils, W. A. Herrmann, eds.), Wiley-VCH, Weinheim, **1998**, p. 486

This work was supported by the Office Fédéral de l'Education et de la Science, Suisse (OFES C98.0011). N. L. is grateful for an OFES fellowship. This research is part of the collaboration within the COST D10/0001/1998 Working Group.

D10/0005/1998 **19**

ENZYMIC FORMATION OF SELECTED ALKYL-*O*-GLYCOSIDES UNDER MICROWAVE IRRADIATION

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2-(4-Methoxybenzyl)-1-cyclohexyl-β-D-glucopyranosides and 2-(4-Methoxybenzyl)-1-cyclohexyl-β-D-galactopyranosides, models for glycosidic juvenogens (insect hormonogen substances) were synthesized using either D-glucose or D-galactose [in their natural form or activated form (phenyl-β-D-glucopyranoside and phenyl-β-D-galactopyranoside)], and the respective racemic *cis* or *trans* isomers of 2-(4-methoxybenzyl)-1-cyclohexanol by either enzymic reverse hydrolysis or transglycosylation[1,2] under both, standard heating and microwave irradiation.[3,4] Commercially available β-glucosidase (EC 3.2.1.21) from almond or β-galactosidase (EC 3.2.1.23) from *Escherichia coli* were employed using different acetonitrile / water mixtures [9 / 1 (v / v) for the reverse hydrolysis, and 4 / 1 (v / v) for the transglycosylation]. A positive effect of the microwave irradiation on the chemical yield of the reaction was observed.

Acknowledgment: The COST D10/0005/98 (D10.10) project (MŠMT ČR).

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[2] Vic G., Thomas D.: *Tetrahedron Lett.* **33**, 4567-4570 (1992)
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[4] Jacquault P.: *Eur. Pat.* 549,495 (1992).

D11/0006/1998 **20**

Asymmetric Supramolecular Chemistry of Chiral Anions and Cations

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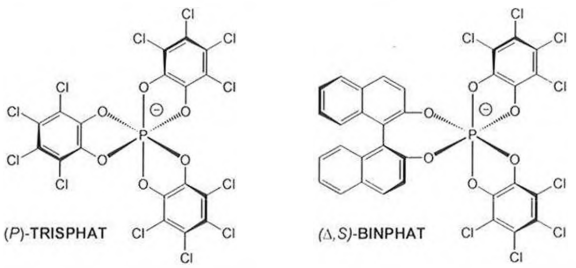
Département de Chimie Organique, Université de Genève, 1211 Genève 4

The induction of optical activity by chiral hosts onto configurationally labile guest molecules is an essential phenomenon (Pfeiffer effect). In this context, our laboratory is engaged in the synthesis of chiral non-nucleophilic anions that can exhibit a high faculty for asymmetric induction onto labile chiral cations. We have shown that D_3-symmetric **TRISPHAT** anion controls efficiently the configuration of a labile $[Fe(diimine)_3]^{2+}$ cationic guest complex (d.c. > 96%).[1] The homochiral or heterochiral nature of the association and its diastereoselectivity strongly depend upon the structure of the diimine ligands. We have also developed the C_2-symmetric **BINPHAT** anion; its use as an anionic auxiliary for asymmetric induction onto $[Cu(diimine)_2]^{2+}$ cations will be presented.



[1] J. Lacour, J. J. Jodry, C. Ginglinger, S. Torche, *Angew. Chem. Int. Ed. Engl.* **1998**, *37*, 2379-2380.

D11/0071/98 **21**

LIPOSOME-ASSISTED SELECTIVE POLYCONDENSATION OF α-AMINO ACIDS AND PEPTIDES

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One of the unsolved problems in the prebiotic chemistry concerns the origin of functional polypeptides. Our work deals with this topic and with the question, whether lipidic bilayers can aid the polycondensation of amino acids and short peptides.

An investigation of the selectivity effects induced by 1-palmitoyl-2-oleoyl sn-glycero-3-phosphocholine liposomes on the polycondensation of hydrophobic α-amino acids and peptides is presented. Two types of reactions are studied: (i) The polymerization of N-carboxy anhydride (NCA) amino acids (i.e., NCA-Trp), and (ii) the polycondensation of dipeptides in the presence of the hydrophobic condensing agent 2-ethoxy-1-ethoxycarbonyl-1,2-dihydroquinoline (EEDQ).

In case (i), the condensation of hydrophobic NCA-amino acids, much longer oligomers (up to 29mer) can be obtained in the presence of liposomes, whereas in the aqueous solution without liposomes the maximal length was around the 7mer. In the case (ii), the membrane-aided polycondensation of dipeptides, such as H-Trp-Trp-OH, led also to higher oligomers (up to H-Trp_8-OH), whereas in the aqueous control experiment only traces of H-Trp_4-OH were found.

If the liposomes were exposed to a small library of four different dipeptides (H-Trp-Trp-OH, H-Trp-Gly-OH, H-Trp-Asp-OH, H-Trp-Glu-OH), only the most hydrophobic H-Trp-Trp-OH was selected by the membrane and underwent oligomerization. Out of the theoretical 16 possible tetrapeptides, H-Trp_4-OH makes about 70% of all the tetrapeptides formed.

Charged membranes can also bind opposite charged amino acids or peptides on the basis of electrostatic interactions. This allows polycondensations on hydrophobic and electrostatic interactions. This can in principle lead to the formation of polypeptide chains consisting of different types of amino acids, which are a prerequisite for obtaining polypeptides with functionality.

D11/submitted **22**

FORMATION AND TRANSFORMATION OF GIANT OLEIC ACID/OLEATE VESICLES

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[2] Max-Planck Institut für Kolloide & Grenzflächen, D-14476 Golm, Germany.
[3] Centre de Recherche Paul Pascale, F-33600 Pessac, France.
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Oleic acid (*cis*-9,10-octadecenoic acid) is a naturally occurring linear, single-chain fatty acid. Upon dispersion of oleic acid in slightly alkaline aqueous solution (e. g. pH 8.5), vesicles form which are composed of several bilayers of oleic acid and oleate molecules. Similarly, addition of a concentrated solution of sodium oleate to an aqueous solution of pH 8.5, the formation of vesicles is observed [1]. Kinetic aspects of this vesicle formation process have been investigated, and it has been shown that the vesicles formed can have diameters of several micrometers (giant vesicles), and therefore a direct visualization by light microscopy is possible. Sub-micrometer-sized oleic acid/oleate vesicles can be transformed into giant vesicles through a dilution process [2]. Mechanistic studies of this vesicle transformation process are in progress.

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D12/0001/98 **23**

Ortho-Halogenoaryl Sulfoxides: A Versatile Chiral Auxiliary for Radical Reactions

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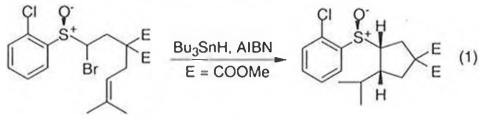
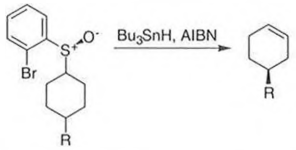
Ortho-halogenoaryl sulfoxides are easily available in enantiomerically pure form via the classical Andersen approach [1]. Theses chiral auxiliaries are excellent for the control of radical cyclization (eq. 1) [2]. Moreover, they eliminate via a radical pathway under very mild conditions (eq. 2), the mechanism of this process is a 1,5-hydrogen atom abstraction followed by a rapid fragmentation of the β-sulfinylated radical.



(1)



(2)

Bringing these two reactions together allows to prepare in a one-pot procedure enantiomerically enriched cycloalkenes.

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D12/0001/98 **24**

Ueno-Stork reaction Controlled by the Acetal Center: A Computational Study

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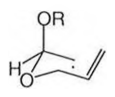
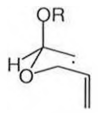
[2]School of Chemistry, The University of Melbourne, Parkville, Victoria, Australia, 3052

We have recently described diastereoselective Ueno-Stork reactions controlled by the acetal center [1]. In continuation of these studies, we report here the combination of ab initio and semi-empirical methodologies for the prediction of selectivity in these reactions with substituted substrates. The importance of anomeric effects will be highlighted.



major TS (→ *cis*)



minor TS (→ *trans*)

[1] Renaud, P.; Villar, F.; *Tetrahedron Lett.*, **1998**, *39*, 8655. Villar, F.; Andrey, O.; Renaud, P. *Tetrahedron Lett.* **1999**, *40*, 3375

D12/0005/98 **25**

Atropconformers for Enantioselective Synthesis

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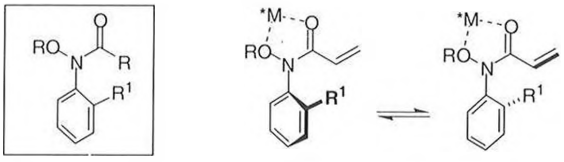
Recently, atropisomers have been used as chiral auxiliary in asymmetric synthesis [1]. We report here a related approach, where enantiomeric atropconformers are differentiated in energy by complexation with a chiral Lewis acid. The chiral axis playing a role of relay between the chiral Lewis acid and the reaction center. This general concept is demonstrated with hydroxamic acid derivatives.



R = H, alkyl M* = chiral Lewis acid

Enantioselective Diels-Alder reactions and radical additions will be described.

[1] J. Clayden, *Angew. Chem. Int. Ed.* **1997**, *36*, 949.

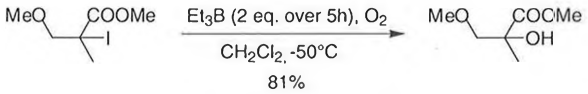
D12/0005/98 **26**

An Efficient Radical Oxygenation of α-Iodocarboxylic Acid Derivatives

Cyril Ollivier, Nobuhiro Kihara and Philippe Renaud

Université de Fribourg, Institut de Chimie Organique, Pérolles
CH-1700 Fribourg, Switzerland

The conversion of iodides into the corresponding alcohols is a useful synthetic procedure wich is usually run under S_N2 conditions. In this account, we report a radical procedure that converts directly α-iodocarboxylic acid derivatives into α-hydroxyacid derivatives. Treatment of the iodide with two equivalents of triethylborane under oxygen atmosphere furnished the α-hydroxycarboxylic acid derivatives in good to excellent yields [1].



Stereochemical control of this reaction with chiral auxiliaries will be discussed.

[1] For the reaction of triethylborane with oxygen, see: K. Nozaki, K. Oshima, K. Utimoto *J. Am. Chem. Soc.* **1987**, *109*, 2547.

D12/0008/98 **27**

A Fluorogenic Oxy-Cope Rearrangement

Nathalie Jourdain and Jean-Louis Reymond*
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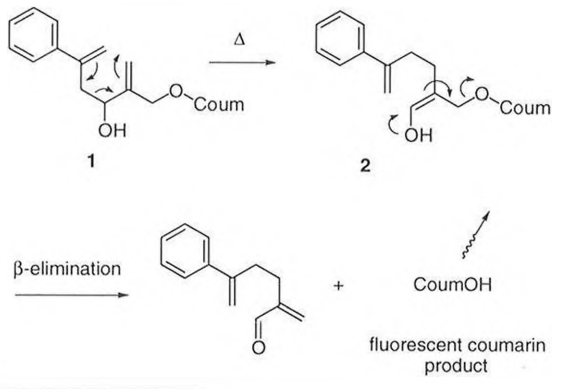
There are only few examples of electrocyclic reactions catalyzed by proteins. These include the chorismate mutase reaction, catalyzed both by enzymes and by catalytic antibodies, and antibody-catalyzed oxy-Cope rearrangement, Diels-Alder Processes, Cope and Selenoxide eliminations.[1] We have recently reported a general principle for fluorogenic reactions based on the secondary β-elimination of 7-hydroxycoumarin.[2] Following that concept, we report here a fluorogenic oxy-Cope rearrangement suited for high-throughput screening of novel oxy-Cope biocatalysts.



[1] J.-L. Reymond, *Top. Curr. Chem.* **1999**, *200*, 59.
[2] a) G. Klein, J.-L. Reymond, *Bioorg. Med. Chem. Lett.* **1998**, *8*, 1113; b) N. Jourdain, R. Pérez Carlón, J.-L. Reymond, *Tetrahedron Lett.* **1998**, *39*, 9415.

D12/0008/98 **28**

Fluorogenic HTS-Assay for Epoxide Opening Reactions

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[b]Dipartimento di Chimica Bioorganica, University of Pisa, I-56126 Pisa

A number of epoxide hydrolase enzymes have been recently described. As a consequence of the reaction mechanism, these enzymes can only produce diols from epoxides.[1] We are interested in developing catalytic antibodies capable of opening epoxides enantioselectively with nucleophiles other than water. We report a novel high throughput screening (HTS) assay for the chemoselective opening of epoxides with nucleophiles. Thus enantiomeric epoxides (*R*)-**1** or (*S*)-**1** react under basic conditions at the terminal carbon with nucleophiles to form the corresponding opening products. In the presence of horse liver alcohol dehydrogenase (HLDH), NAD^+, and BSA,[2] only some of the opening products from enantiomer (*R*)-**1** deliver a fluorescence signal. This chemo- and enantioselective assay is applicable for high throughput screening of catalytic antibody libraries.

(*R*)-**1** (*S*)-**1**

[1] A. Archelas, R. Furstoss, *Top. Curr. Chem.* **1999**, *200*, 159.
[2] a) G. Klein, J.-L. Reymond, *Bioorg. Med. Chem. Lett.* **1998**, *8*, 1113; b) G. Klein, J.-L. Reymond, *Helv. Chim. Acta* **1999**, *82*, 400.

D12/0014/1998 **29**

Asymmetric catalyzed cyclopropanations with sulfonium and iodonium ylides

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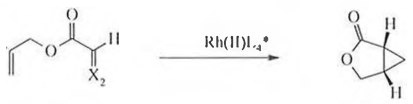
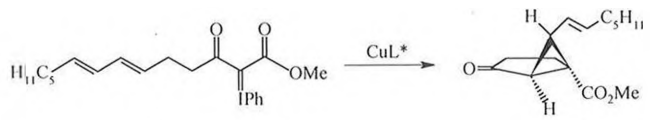
Transition metal-catalyzed decomposition of phenyliodonium and diphenylsulfonium ylides was investigated with regard to applications in asymmetric carbenoïd reactions. With diphenylsulfonium ylide (**1**), the Rh(II)-catalyzed intramolecular cyclopropanation affords (**3**) with 69 % ee.



1 X = SPh_2
2 X = N_2

3

The intramolecular cyclopropanation of iodonium ylide (**4**), in the presence of asymmetric Cu-catalyst, proceeds with 43% e.e., which is unprecedented.



4 5

[1] P.Müller, D. Fernandez, P. Nury and J-C. Rossier, *Helv. Chim. Acta* **1999**, in press.

12/0014/1998 **30**

Asymmetric CC and CO Bond Formation *via* Metal Carbenoids

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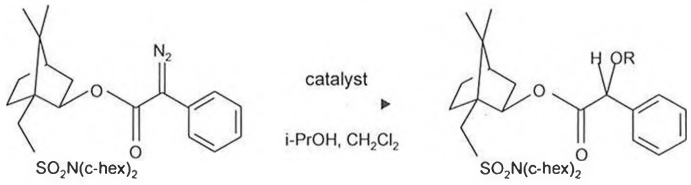
30, Quai Ernest Ansermet, CH-1211-Genève 4

The intermolecular decomposition of diazo carbonyls in the presence of Cu(I) or Rh(II) catalysts may afford products derived from cyclopropanation of double bonds or from insertion into carbon-hydrogen or X-H bonds. We report good enantiocontrol for intermolecular CH insertions which suggests a concerted mechanism analagous with the intramolecular process. The intermolecular transition metal-catalysed insertion of diazo carbonyls into the OH bond of alcohols, however, yields racemic mixtures of products.



1

We report a marked difference in diastereoselectivity as a function of catalyst in the reaction of **1** in the presence of *i*-PrOH suggesting the involvement of the metal at the stage at which the new sp^3 centre is established. Mechanistic implications will be discussed.

D12/0017/1998 **31**

ENANTIOSELECTIVE ALKYLATION OF CYCLANONES *VIA* CHIRAL LITHIOENAMINES

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Inst. of Org. Chemistry & Biochemistry, Flemingovo 2, CZ-16610 Prague 6

A stereoselective alkylation of cyclic ketones at the C(α) and C(α') carbon centers has represented an efficient target of investigation of convenient methods of synthesis of both natural and biologically active compounds. We have applied a modified Michael-type addition reaction to introduce small alkyl groups stereoselectively into the molecules of racemic 2-(4-alkoxybenzyl)-1-cyclanones. Metalloenamines of chiral alkoxy amines have been found to introduce desired chirality into the system which has resulted in an asymmetric alkylation of the ketones at the C(α) or C(α') carbon centers.[1] We have employed (2S)- and (2R)-2-amino-3-phenylpropanoic acids to synthesize (2S)- and (2R)-2-amino-1-methoxy-3-phenylpropanes. Both methoxyamines bear key oxygen-containing functionalities, responsible for a metallo-ligand alignment with a fixed absolute configuration of the molecule. An attack of the electrophile to the C(α) or C(α') carbon centers of the enamine has resulted in producing the alkylated products with controlled absolute configuration.

Acknowledgment: The COST D12/0017/98 (D12.10) project (MŠMT ČR).

Reference:

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D13/0001/1999 **32**

SYNTHESIS OF FLUORINATED C-DISACCHARIDES CONTAINING AN EPOXIDE MOIETY

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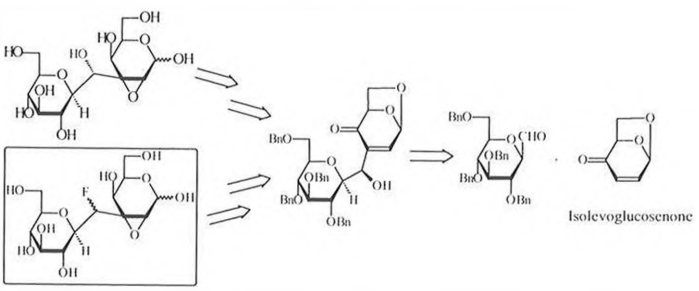
Institute of Organic Chemistry, University of Lausanne, BCH, CH-1015 Lausanne-Dorigny, Switzerland

C-Linked disaccharides are close analogues of saccharides whose interglycosidic oxygen bridge has been replaced by a carbon atom. Such compounds are resistant to hydrolytic enzymes and as such, are potential inhibitors of carbohydrate processing enzymes (glycosidases and glycosyltransferases). Therefore, they could be of great use as pharmacodynamic agents.

Besides, fluorinated compounds are of great interest to organic and medicinal chemist. The strong electronic contribution and negligeable steric demands of fluorine present interesting and unusual properties [1].

Here, we report the synthesis of a new type of C-disaccharides containing an epoxide moiety, one of them bearing a fluorine atom on the carbon bridge of the disaccharide :



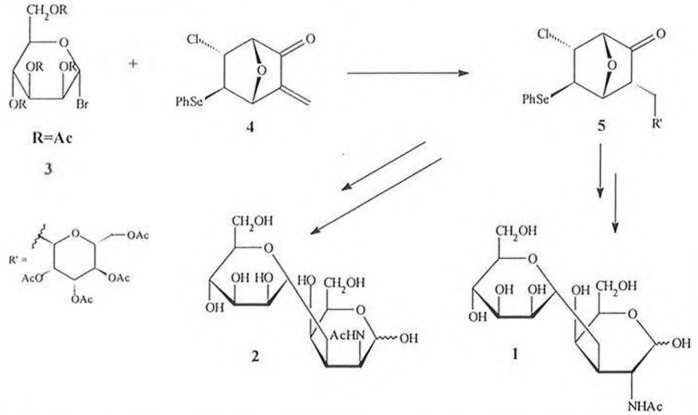
[1] *Organofluorine Compounds in Medicinal Chemistry and Biomedical Applications*, eds. R. Filler, Y. Kobayashi and L. M. Yagupolskii, Elsevier, New York, 1993 ; *Biomedical Aspects of Fluorine Chemistry*, eds. R. Filler and Y. Kobayashi, Elsevier, New York, 1982.

D13/0001/1999 **33**

SYNTHESIS OF NEW INHIBITORS OF GLYCOSIDASES AND GLYCOSYLTRANSFERASES

Carla Pasquarello, Raynald Demange, Sylviane Picasso and Pierre Vogel
Institute of Organic Chemistry of Lausanne, CH-1015 Lausanne, Switzerland

In this work we planned to prepare α-CH_2-(1→3)-mannopyranoside of 2-acetamido-2-deoxygalactose **1** and α-CH_2-(1→3)-mannopyranoside of 2-acetamido-2-deoxytalose **2**. The key step of our approach is the highly stereoselective radical reaction between the acetobromomannose **3** and the enantiomerically pure bicyclic enone **4** following Giese's procedure.[1] The product obtained **5** is the precursor for both acetamido-C-disaccharides **1**[2] and **2**. **1** has been submitted to an inhibition screening and showed inhibiting activities toward glycosidases and glycosyltransferases.



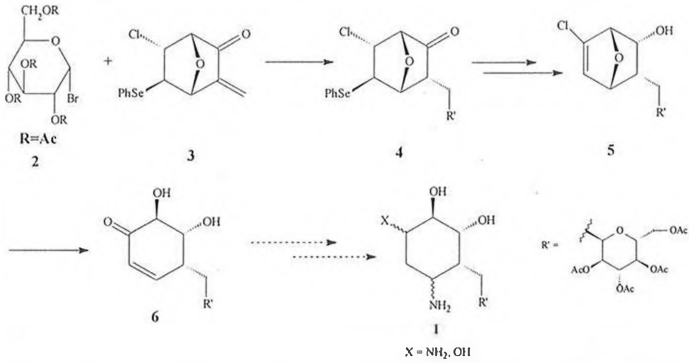
[1] B. Giese, T. Witzel, *Angew. Chem., Int. ed. Engl.* **1986**, *25*, 450.
[2] C. Pasquarello, R. Demange, P. Vogel, *Bioorg. Med. Chem. Lett.* **1999**, *9*, 793-796.

D13/0001/1999 **34**

TOWARDS THE SYNTHESIS OF C-GLUCOSIDES OF AMINOCYCLITOLS

Carla Pasquarello, Carmela De Risi and Pierre Vogel
Institute of Organic Chemistry of Lausanne, CH-1015 Lausanne, Switzerland

Several antibiotics and compound of biological interest incorporate glycosides os cyclohexanepolyols (cyclitols) and amino cyclohexanepolyols (aminocyclitols).[1]
Our synthetic approach to synthesize α-C-glucosides of aminocyclitols **1**, is based on the highly stereoselective radical addition of the acetobromomannose **2** to the enantiomerically pure bicyclic enone **3** following Giese's procedure.[2] Applying known chemisrty[3] compound **4** can be transformed into **5** , the oxa bridge of which is opened to furnish **6**, which is a precursor of the α-C-glucosides of aminocyclitols **1.**



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[2] B. Giese, T. Witzel, *Angew. Chem., Int. ed. Engl.* **1986**, *25*, 450.
[3] R. M. Bimwala, P. Vogel, *J. Org. Chem.* **1992**, *57*, 2076.

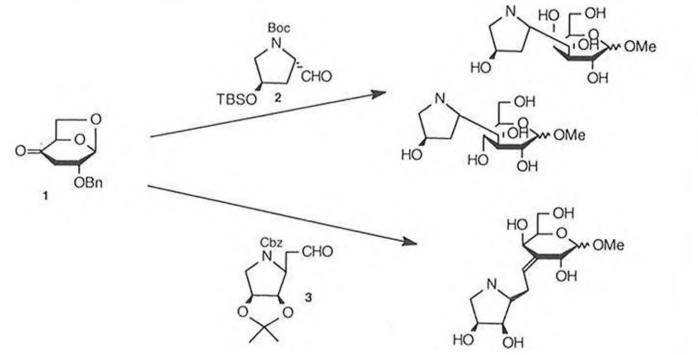
D13/0001/1999 **35**

SHORT SYNTHESES OF IMINO *C*(1→3)-LINKED DISACCHARIDES ANALOGUES

Francesca Cardona, Yao-Hua Zhu, Inmaculada Robina, Pierre Vogel

Section de Chimie de l'Université de Lausanne, BCH, CH-1005-Lausanne-Dorigny, Switzerland
Departamento de Química Orgánica, Universidad de Sevilla, Spain

Imino sugars linked to common sugars by a non-hydrolizable *C*-link (imino-*C*-disaccharides) are valuable synthetic targets as new selective glycosidase inhibitors, and therefore potential antiviral, antibacterial and antitumoral agents.
We report here a short and convergent approach to imino *C*(1→3)-linked disaccharides by joining iminosugar aldehydes **2** and **3** with enolates of the ketone **1**, readily available from D-glucose [1].



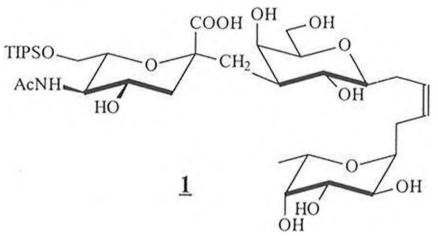
[1] Y.-H. Zhu, P. Vogel, *J. Org. Chem.* **1999**, *64*, 666-669.

D13/0001/1999 **36**

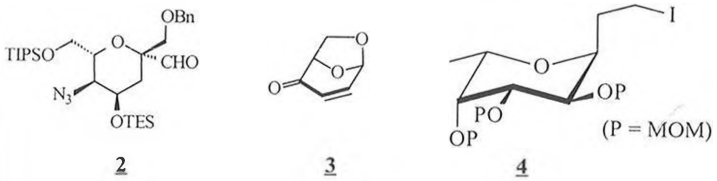
Synthesis of Precursors of Non-hydrolysable Mimetics of Sialyl Lewis X Acid

Frédéric Carrel, Pierre Vogel
Institut de chimie organique, Université de Lausanne
BCH, CH-1015 Lausanne-Dorigny

Our target mimetic is compound **1** and analogues in which all glycosidic bridges are substituted by carbon bridges.



Our approach is based on the cross-aldolisation **2** + **3** followed by a Wittig olefination using **4**.



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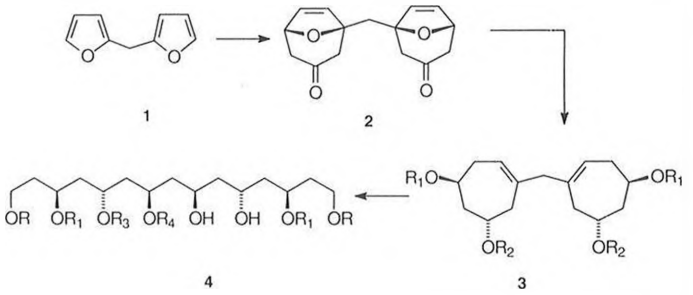
D13/0001/1999 **37**

A new approach toward the synthesis of 1,3-polyol fragments

Marc-Etienne Schwenter, Kai Meilert and Pierre Vogel

Institut de chimie organique, Université de Lausanne, CH-1015 Lausanne

Several novel marine-derived compounds that exhibit extremely potent biological activity are macrolides incorporating 1,3-polyols.[1] We report a new access to this type of fragments by a double opening of the bis-cycloadduct **2** derived from the 1,3-dipolar cycloaddition between bis(α-furyl)methane **1** and two oxyallyl cations.



Desymmetrisation of **3** by Sharpless dihydroxylation and cleavage of the 1,2-diol gives access to a series of 1,3-polyols **4**. The latter can be enlarged to the full family of 64 stereoisomers by selective operations such as steroselective reductions of β-hydroxyketones or/and S_N2 substitutions.

References

[1] (a) Norcoss, R. D. ; Paterson, I. *Chem. Rev.* **1995**, *85*, 2041 ; (b) Rychnovsky, S. D. *Ibid.* **1995**, *95*, 2021.

D13/0001/1999 **38**

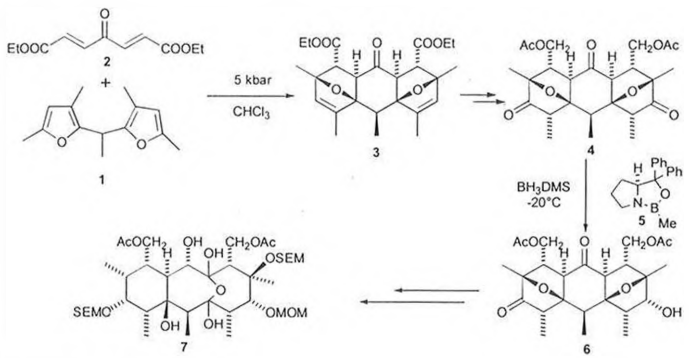
Synthesis of a macrolide precursor. A new convergent and stereoselective approach.

Chiara Marchionni,[a] Kai Meilert,[a] Pierre Vogel[a] and Kurt Schenk[b]

[a]Institut de Chimie Organique, Université de Lausanne, 1015 Lausanne

[b]Institut de Cristallographie, Université de Lausanne, 1015 Lausanne

Long-chain polypropionate fragments occur in a large variety of natural products and antibiotics. We are investigating a new, highly convergent and stereoselective approach to these molecules.[1] A highly diastereoselective tandem Diels-Alder addition between the bisfuran derivative **1** and the bisdienophile **2** gave the cycloadduct **3**. Some further steps led to the triketone **4** which was desymmetrised by catalysed enantioselective reduction. The alcohol **6** was obtained in 90% enantiomeric excess. The macrolide precursor **7** was obtained in an hydrated bridged form after 7 further steps, the latter being an ozonolysis.



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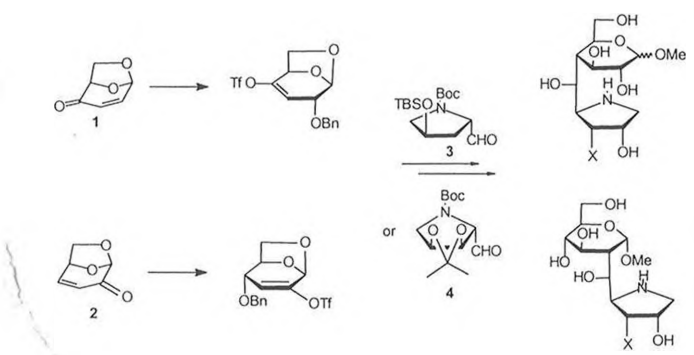
D13/0001/99 **39**

Convergent Syntheses of (1→2) and (1→4)-*C*-linked Imino Disaccharides Appling Nozaki-Kishi Coupling Reaction

Yao-Hua Zhu, Alejandro Dubois Battaner, Isabel Navarro, and Pierre Vogel

Institut de Chimie Organique de l'Université de Lausanne, BCH, CH-1015 Lausanne

Inhibitors of glycosidases and the glycosyltransferases are potential anti-cancer, antiviral, and antidiabetic agents.[1] Disaccharide mimetics such as the C-disaccharides and the dideoxyiminoalditol C-linked to monosaccharides emerge as a new class of specific glycosidase inhibitors and may represent non-hydrolyzable epitopes.[2] We report here that (1→4) and (1→2)-*C*-disaccharides can be prepared by Nozaki-Kishi coupling of iminosugar aldehydes **3** and **4** with isolevoglucosenone (**1**) or levoglucosenone(**2**) derived enol triflate, respectively.



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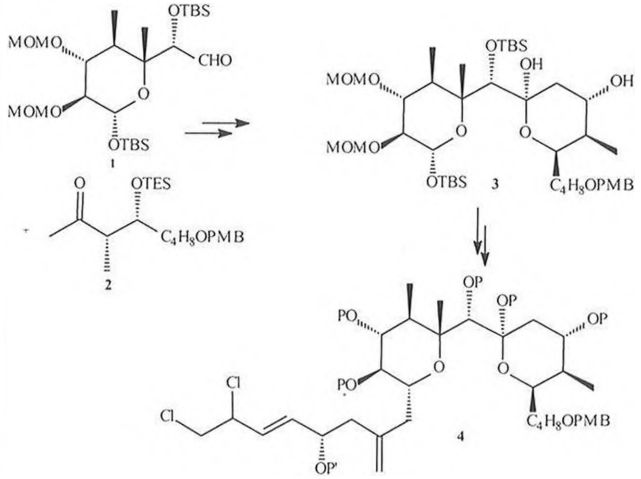
D13 / 0001 / 1999 **40**

CONVERGENT SYNTHESIS OF THE C29-C51 FRAGMENT OF SPONGISTATINS

Sandrine Lemaire-Audoire and Pierre Vogel

Section de Chimie, Université de Lausanne, BCH, 1015 Lausanne-Dorigny, Switzerland

We report our approach to the C_{29}-C_{51} fragment of Spongistatins, marine macrolides which display remarkable inhibitory activity against several chemoresistant cancer cells. The pyranose sub-unit (F-ring) **1** of Spongistatins was elaborated through two sequential stereoselective dihydroxylations A cross-aldol reaction with methylketone **2** afforded the C_{29}-C_{43} skeleton which was cyclized to give the EF fragment **3**. C-glycosidation on C(43) is expected to introduce the trienic side chain and to complete the synthesis of the C_{29}-C_{51} unit of Spongistatins.



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41

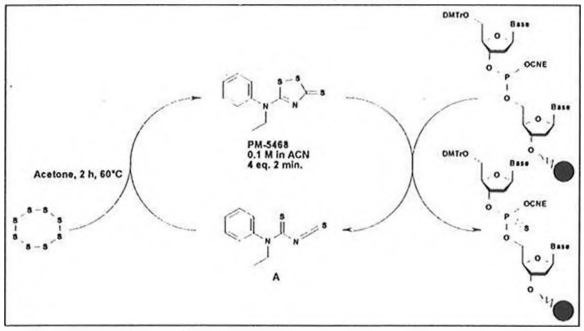
NOVEL SULFUR TRANSFER REAGENT FOR THE SYNTHESIS OF MODIFIED PHOPHOROTHIOATE OLIGONUCLEOTIDES

Pierre Martin, François Natt
Functional Genomics Area, Novartis Pharma Ltd., CH-4002 Basel

Phosphorothioate-containing antisense oligonucleotides (ASO) have proven their value as tools in the inhibition of target gene expression by down-regulation of the corresponding mRNA.

Many reagents (mostly acting by oxidative sulfurization of a phosphite triester linkage) have been intensively investigated. So far, none of them meets all of the requirements for a satisfactory reagent and still contribute for up to 25% of the raw material costs of phosphorothioate-containing ASOs prepared up to kilogram scale for clinical trials.

This poster describes the properties of a novel sulfur transfer reagent for the preparation of ASOs discovered, developed and used at Novartis: the dithiazolthione **PM-5468**. The reagent is very efficient, user-friendly (odourless) and environment-friendly (recycleable).



Use of PM-5468 in oligonucleotide synthesis and recycling thereof

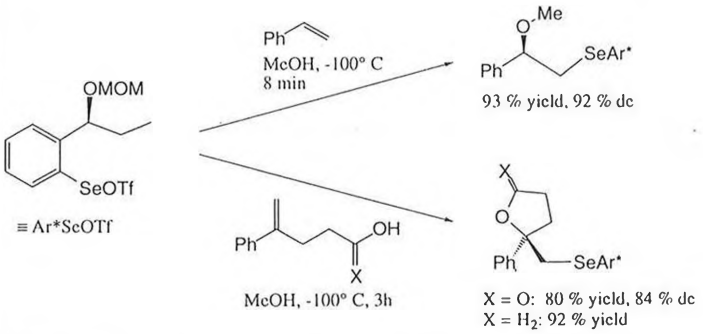
Organic Chemistry **42**

New and Improved Chiral Diselenides for Stereoselective Selenenylation Reactions

Lars Uehlin, Thomas Wirth*

Institut für Organische Chemie der Universität Basel, St. Johanns-Ring 19, CH-4056 Basel, Switzerland

Organoselenium compounds have become standard reagents for synthetic organic chemistry. Although several groups have investigated the use of chiral selenium compounds for stereoselective reactions, the stereoselective functionalization of nonactivated C=C double bonds is still of high interest. We have developed some new, easily accessible, chiral diselenides which can be synthesized in a few steps. These diselenides have been converted *in situ* to the corresponding triflates, which when added to several alkenes, results in the formation of the corresponding seleniraniumions, that were then attacked by nucleophiles. Additionally, intramolecular cyclizations can be carried out with these reagents very efficiently.



Review: T.Wirth, *Tetrahedron* **1999**, *55*, 1

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CONFERENCE REPORT

Chimia 53 (1999) 403–407

ISSN 0009–4293

34th EUCHEM Conference on Stereochemistry, Bürgenstock, April 24–30, 1999

For the last time in this century the Bürgenstock was transformed into the 'Magic Mountain of Chemistry' by the 34th EUCHEM Conference on Stereochemistry. 135 participants with academic as well as industrial backgrounds from 21 countries gathered on Saturday, April 24, to enjoy the different facets of chemistry on the beautiful hillsite high above the Vierwaldstätter See.

When the mystery of the program, which is traditionally kept secret until registration, was unravelled, it became clear that the president, *Javier de Mendoza* (University of Madrid, Spain), along with the organising team (*Hans-Beat Bürgi* (University of Bern), *François Diederich* (ETH Zürich), *Peter Kündig* (University of Geneva), *Klaus Müller* (*Hoffmann-La Roche*, Basel)) had set the stage for a week-long celebration of chemistry. The scientific program, consisting of 14 main lectures, 10 short presentations and 43 posters, covered the wide area from material science and novel structure-elucidation methods, over organic synthesis, to bioorganic chemistry. As a special tribute paid to this year's guest of honor *Jean-Marie Lehn* (University of Strasbourg, France), many lectures were centered around the topic of supramolecular chemistry.

It was a pleasure to have *André Dreiding* (University of Zürich), the founder of the Bürgenstock conference, among the participants as well as many who have had largely formed the Bürgenstock conferences in the past, such as former presidents *Alan Battersby* (Cambridge University, United Kingdom), *Francois Diederich, Jean-Marie Lehn,* and *David N. Reinhoudt* (University of Twente, The Netherlands). Additionally, many young scientists had been given the opportunity to attend thanks to the generous support of the European Science Foundation (ESF) and the Swiss National Science Foundation (SNSF). For most youngsters, the

Fig. 1. *Coffee-break discussion:* J.-M. Lehn *(guest of honor),* J. de Mendoza *(president),* R. MacKinnon (from the left)

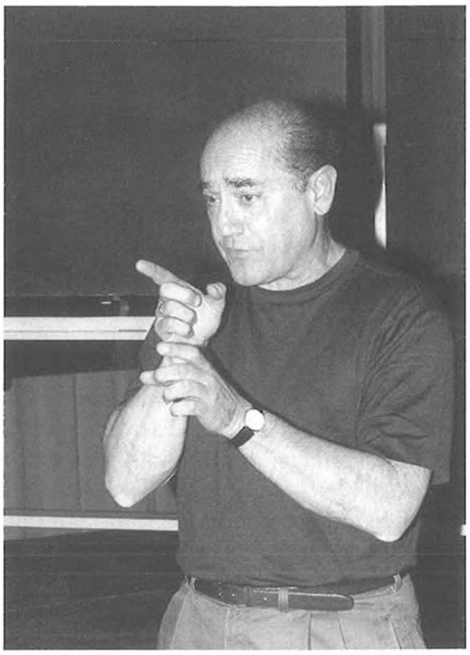

Fig. 2. A. Pines

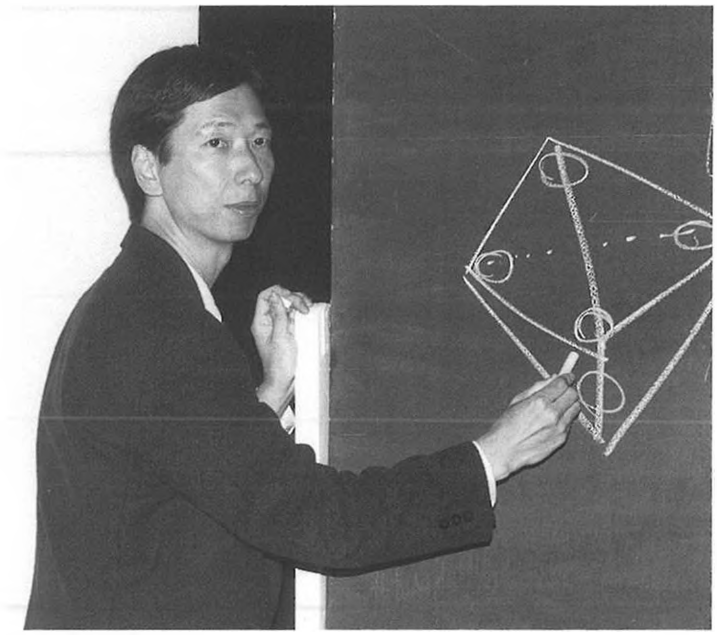

Fig. 3. M. Fujita

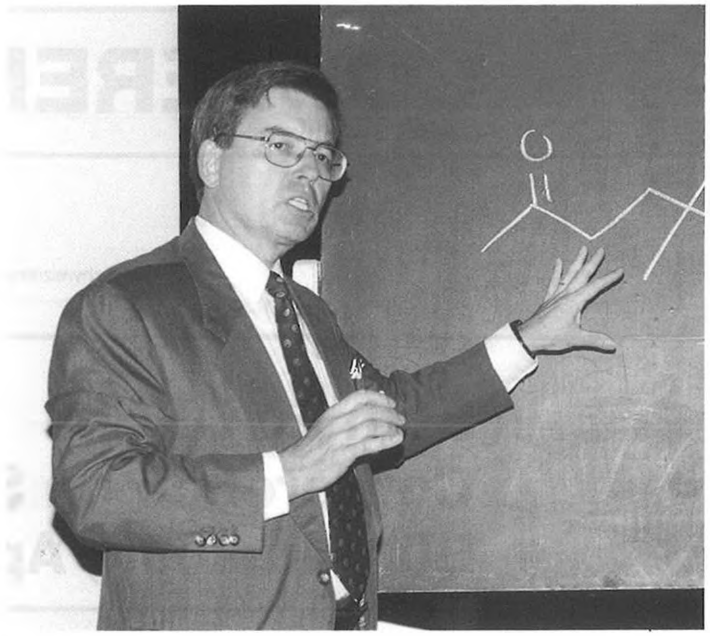

Fig. 4. L.F. Tietze

poster sessions offered an ideal platform for making note of their work. In contrast to many other conferences, the poster sessions, which were preceeded by short 'appetising' oral presentations of a few selected posters, didn't lead a life in the corner but were well attended by all participants.

Structure, Function, and Mechanisms of Biomolecules

In the opening lecture, *Roderick MacKinnon* (Rockefeller University, New York, USA) took us onto the exciting travel of a potassium ion through a transmembrane channel, a process critical for neurotransmission. He elucidated how the channels allow K^+-ions, but not the smaller Na^+-ions, to pass from a highly hydrophilic medium through the hydrophobic membrane into another hydrophilic medium at a speed close to the diffusion limit. Crystal structures as well as sequencing analysis revealed that all potassium channels are tetrameric transmembrane proteins with a highly conserved sequence of five amino acids located on the outer membrane site. These amino acids form a selectivity filter and allow, presumably through steric as well as electrostatic effects, for the discrimination between K^+- and Na^+-ions. The change in the dielectrical environment in- and outside the membrane is kept to a minimum by a widening of the channel inside the membrane. According to crystal structures, the cavity is big enough to accomodate about ten water molecules which can form a sphere around the entering K^+-ions, thereby reducing the energetic cost of passing through the different media.

Fascinated by the specific folding of natural proteins, whose catalytic function is highly dependent on the proper folding pattern, *Samuel H. Gellmann* (University of Wisconsin, USA) showed how the development of unnatural model systems can raise our still very limited understanding of the principles of biological functions. Introducing the term *foldamer* for 'unnatural polymers with well-defined and predictable conformations', he elaborated on the properties of polymeric cyclic β-amino acids. In analogy to natural α-helices, hexamers of cyclic β-amino acids form helices with turn sizes that were predicted by computer modelling and proven by several X-ray crystal structures. The generation of these unnatural helices can be accomplished in organic as well as in aqueous solution. Thus, in the future, it might be possible to modulate foldamers of β-amino acids such that they can perform, *e.g.*, catalytic and other useful functions. Continuing, *Gellmann* elucidated on the importance of cooperative binding for the formation of helices from cyclic β-amino acids as well as for the formation of secondary and tertiary structures of natural proteins.

Picking up the topic of cooperativity, *Dudley H. Williams* (University of Cambridge, United Kingdom) elucidated the interplay of many factors for the antibiotic activity of vancomycin and its analogues. Vancomycin is known to bind to the dipeptide D-Ala-D-Ala, a crucial component for the cell-wall synthesis of bacteria, with high binding affinity and specificity. With a series of elaborate experiments, *Williams* showed that the strong association can only be achieved if the antibiotic is either anchored to the cell membrane or dimerises. Both events allow for a *quasi* 'intramolecular' binding between vancomycin and D-Ala-D-Ala at the surface of the bacteria. That the antibiotic mode of action is probably still more complicated became clear during the lively discussion which was centered around a very recent publication by *Dan Kahne* (Princeton University, USA). *Kahne*'s studies prove

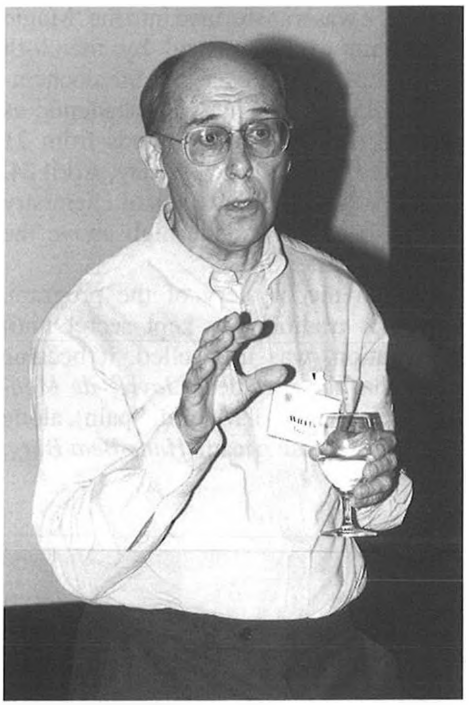

Fig. 5. D.H. Williams

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Fig. 6. S.L. Buchwald

Fig. 7. T. Ebbesen

the saccharide unit of vancomycin, so far believed unimportant for the antibiotic activity, as a crucial component for the antibiotic activity of vancomycin.

Cones, Disks, Dishes, Cages, and Molecular Skyscrapers

David N. Reinhoudt (University of Twente, The Netherlands) opened the reign of self-assembling structures and molecular architecture. His work was a good demonstration how the principles of non-covalent self-assembly can be exploited for the generation of specific receptor molecules that would be difficult to synthesise by conventional means. A steroidal receptor consisting of nine individual subunits was assembled through hydrogen-bond formation around the steroidal guest and then linked covalently *via* a metathesis reaction. Furthermore, he reported on the selective self-assembly of a chiral receptor in the presence of the opposite enantiomer, an example of enantioselective self-resolution in a dynamic hydrogen-bonded assembly.

Continuing on the topic of hydrogen bonds, *José Elguero* (C.S.I.C. Madrid, Spain) presented studies on the hydrogen transfer between tautomers of unsaturated nitrogen heterocycles in their crystal lattices. Based on solid-state NMR-spectroscopic studies he concluded that the hydrogen atoms stay, as one might expect, in defined positions in certain crystals (*e.g.*, triazoles) whereas other crystal lattices show dynamic properties with the hydrogens changing places at a speed of 9000 times/sec – 'a speed that is not even matched by Swiss watches' as *Elguero* pointed out.

Leaving the area of hydrogen-bonded supramolecular structures, *Thomas Ebbesen* (*Pasteur* University, France & NEC Research Institute Princeton, USA) showed how infinite possibilities of new structures can be constructed from simple geometric principles established by *Euler*. He opened our eyes towards the vast amount of naturally occurring geometric objects abiding by the rules of *Euler*'s *Theorem of Geometry* (*e.g.*, viruses, atom-assemblies on surfaces, ancient stone walls, *etc.*). Concentrating on the element carbon, it became clear how carbon atoms can arrange themselves into disks, cones, balls or tubes. Particular emphasis was placed on the properties and widespread application possibilities of carbon nanotubes with a diameter of ~10Å. They can be filled with compounds of low surface tension (*e.g.*, Pb- and Bi-oxides), they can be oxidised at the surface, opening the way for further chemical transformations, and they have even found use in protein crystallisation. At the end of the highly interdisciplinary lecture, one could only agree with *Ebbesen* that the discovery of C_{60} by chemists at the end of this century was somewhat overdue, given its well-defined symmetry, its natural occurrence, and usage in some chinese and indian inks.

'Delicious chemical dishes instead of round the table dishes' were put on stage by *Roeland J.M. Nolte* (University of Nijmegen, The Netherlands). He described the self assembly of flat dish-like porphyrin systems into rods and helices. Electron microscopy and scanning tunnelling microscopy demonstrated that the molecular assemblies are even able to form tertiary structures by twisting around each other. Furthermore, the tertiary fold can be tuned by the addition of metal ions. With the proper choice of functional groups, attached porphyrin molecules of this kind could find applications as molecular wires possessing an isolating mantle.

The excursion into the field of new materials found a splendid finale in *Makoto Fujita*'s (Nagoya University, Japan) lecture. Instead of hydrogen bonds, his molecular assemblies are held together by metal complexation. Exploiting the preferred square-planar coordination of nitrogen ligands around palladium ions, his group has built amazing molecular masterpieces ranging from squares over tubes and 'simple' catenanes to multiply interlocked cages. Moreover, he demonstrated that the generated molecular constructs are not purely beautiful shells but can serve important purposes, *e.g.*, as containers for chemical reactions: Some *Diels-Alder* reactions, redox reactions of ferrocene, as well as a *Wacker* oxidation can only be carried in the inside of a molecular cage.

Structure Elucidation

Monday evening was highlighted by the very vivid and lively lecture of *Alex Pines* (University of California Berkeley, USA). He transformed his audience into spins and the lecture room into a magnetic field to illustrate the basic principles of

solid-state NMR spectroscopy and to allow us at least a grasp at understanding variable-angle correlation spectroscopy (VACSY), dynamic angle spinning (DAS), *etc.* Furthermore, he reported on the most remarkable recent developments in magnetic resonance imaging (MRI) using the noble gas xenon as a probe of the chemical environment. Xenon has found widespread use as a NMR probe due to its chemical inertness, its hydrophobicity, its high polarisability and the long relaxation times of polarised ^{129}Xe nuclei. The enhanced Xe polarisation can be transferred to neighbouring spin systems (*e.g.*, ^{1}H), thereby allowing to gain structural as well as dynamic information on the Xe environment. Using this principle, *Pines* has not only been able to prove the binding of Xe into the hydrophobic core of α-cyclodextrin but has accomplished to look into *in vivo* transport processes even inside the human body. It has been possible to follow the way of Xe from the respiratory system to the blood vessels and the brain. At the end of his lecture, he presented the most stunning intimate picture of his student's bronchial tubes.

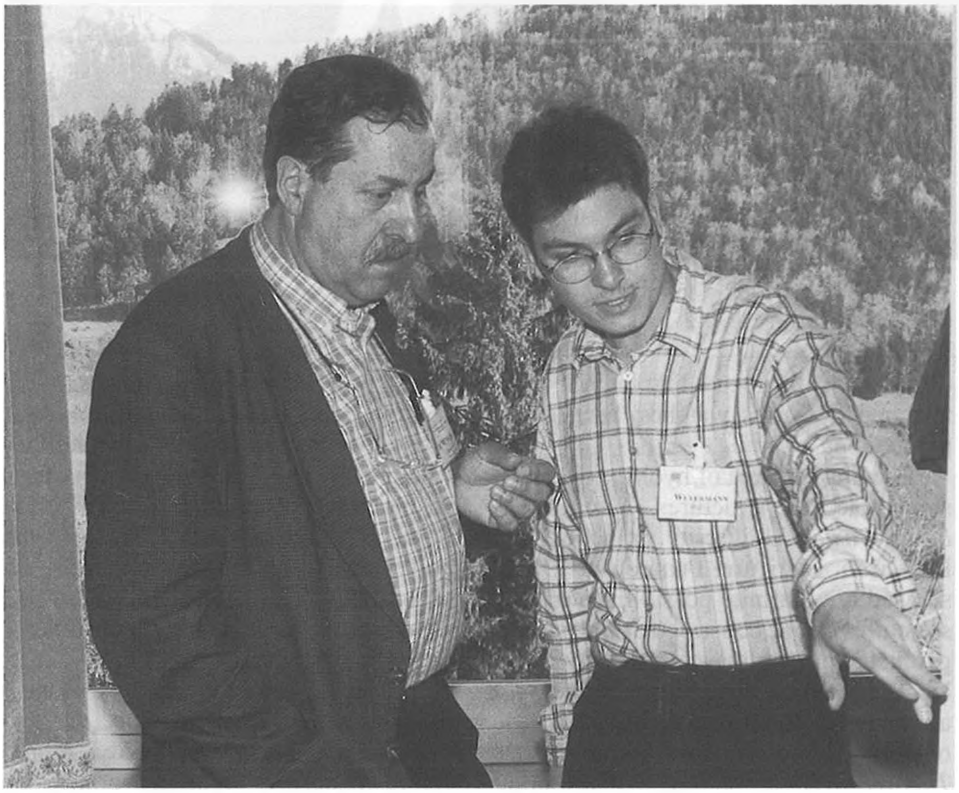

Fig. 8. *Poster session:* J. de Mendoza *(president),* P. Weyermann

Fig. 9. *Chamber music concert:* A. Fiedler, U.S. Schubert, I. Schubert, A. Kreknin, A. Barschewitsch

Synthetic Organic Chemistry

Palladium was the key player for *Steven L. Buchwald*'s (MIT Boston, USA) accomplishments in the development of novel catalytic methodologies for the arylation of amines and phenols. A proper ligand around the palladium, as well as elaborate reaction conditions, allow for the synthesis of polyanilines, indoles, as well as arylated secondary amines with truly catalytic amounts of the Pd-catalysts. Driving the methodology even further, not only aryl bromides but also the less reactive but much more readily available and cheaper aryl chlorides can be employed in the reaction. *Buchwald*'s studies also prove that bulky phosphine ligands with a single coordination site to Pd can be more effective than the generally used phosphine ligands with two coordination sites. The presented synthetic methodologies have already facilitated the synthesis of many important drugs, and it appears certain that we haven't seen the end of the road yet.

Moving from group X to group VI of the periodic table, *José Barluenga* (University of Oviedo, Spain) led us into the rich and versatile world of *Fischer* carbene complexes. The use of chiral *Fischer* carbene complexes allowed for the simultaneous generation of as many as five chiral centres *via* a *Michael*-Aldol reaction cascade. Further examples demonstrated their versatility in cyclopropanations and cycloadditions as well as the use of boron-substituted *Fischer* carbene complexes.

Luis Echegoyen (University of Miami, USA) dedicated his lecture to the electrochemical behaviour and electrochemically induced transformations of fullerenes and their derivatives. Cyclic voltammetry allowed his group the detection of C_{60}-anions up to the hexaanion. Subsequently, he tried to analyse the influence of substituents on C_{60} on the stability of C_{60}-anions. For this purpose, his group, in collaboration with *Françcois Diederich*'s group (ETH Zürich, Switzerland), has synthesized various fullerene derivatives using the *Bingel* reaction. Interestingly, an electrochemically induced retro-*Bingel* reac-

tion was observed during the cyclovoltammetric studies which liberates the fullerene in high yield. Thus, the reaction sequence of *Bingel*/retro-*Bingel* could find useful applications for the generation of enantiomerically pure fullerene cages (*e.g.*, C_{76} and ent-C_{76}) *via* separable diastereomeric intermediates.

Back to 'structures on the molecular level', *Alois Fürstner* (MPI Mülheim, Germany) gave an engaged lecture on the fascinating field of transition-metal catalysed synthesis of carbo- and heterocycles. The synthesis of several natural products (*e.g.*, Roseophilin) with high biological activity has been accomplished using a manifold of Pd-catalysed reactions. Continuing, *Fürstner* concentrated on the metathesis reaction. This reaction has become more and more versatile over recent years but still suffers from a lack of stereocontrol of the newly formed double bond. The synthesis of an alkyne which can be reduced selectively offered an indirect solution. Even more interesting, novel Mo-catalysts were presented that hold a lot of promises for catalysing metathesis reactions with high stereocontrol as judged from initial experiments.

The final act of this years Bürgenstock conference was performed by *Lutz Tietze* (University of Göttingen, Germany). In his interdisciplinary lecture, it became clear how the interplay of organic synthesis and biochemistry opens the way into medicinal chemistry. He showed how the phenotypic as well as genotypic differences of carcinogenic and normal cells can be exploited for the development of anti-cancer drugs. Drugs can be masked such that they are only released in the conditions prevailing in cancer cell. *E.g.*, a drug has been linked to a saccharide *via* an acid-sensitive linker which is stable at the pH of healthy cells but readily cleaved in the slightly more acidic environment of cancer cells. Thus, the drug is selectively released in cancer cells only.

Given the exquisite lectures and poster presentations, it was all but a surprise that lively discussions initiated in the lecture room and continued on strolls around the lake in the lecture-free afternoons or over a glass of beer or wine until late at night. Surely, some students back home will have had to 'suffer' under the explosion of new ideas of their supervisors arising from the exchange of thoughts in the relaxed and interdisciplinary atmosphere on the Bürgenstock. Contributing to the relaxed atmosphere was Tuesday evening, when chemical formulas were replaced by the sounds composed by *De Arriaga* (String Quartet no. 1, d minor) and *Brahms* (Clarinet Quintet op. 115, h mino). The music could not have been chosen more fittingly by our president and was beautifully performed by the *Louis Spohr Quartet* along with *Ulrich S. Schubert* (TU München), a very talented chemist as well as clarinetist.

Fig. 10. J. Barluenga

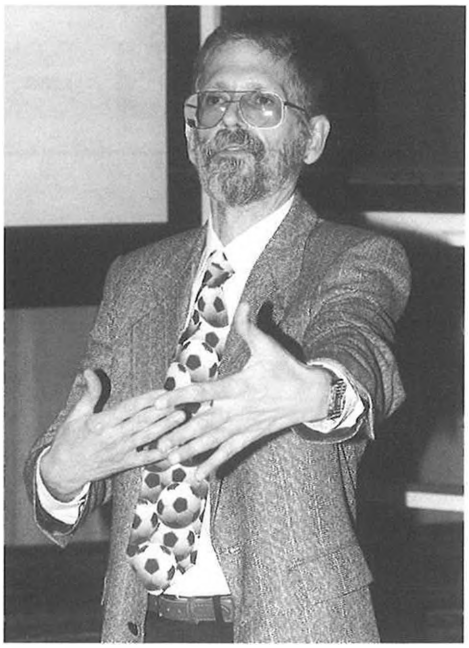

Fig. 11. L. Echegoyen

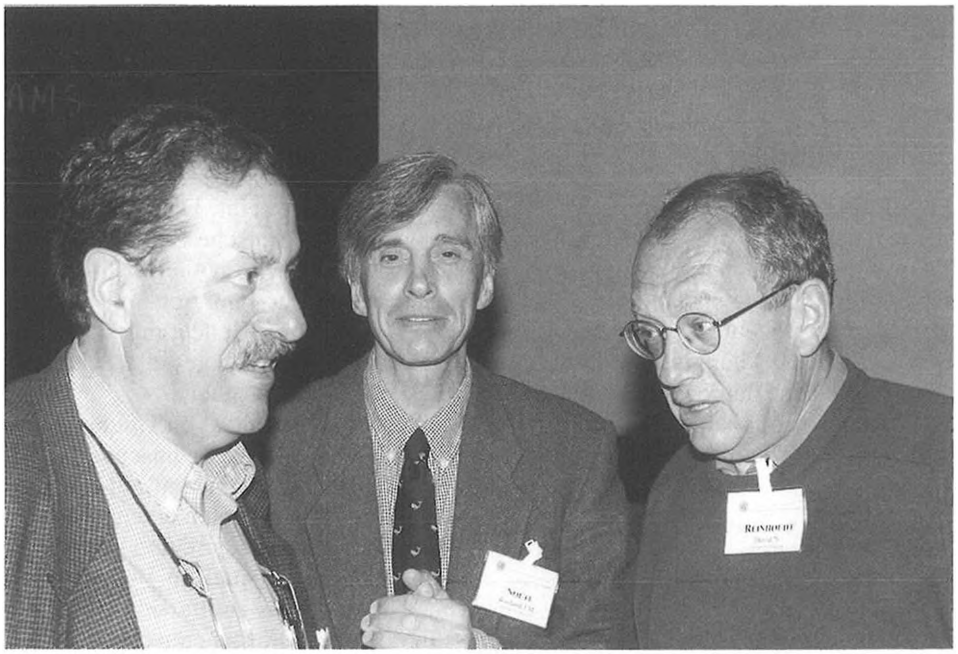

Fig. 12. *After-lecture discussion:* J. de Mendoza *(president),* R.J.M. Nolte, D.N. Reinhoudt (from the left)

Being on the 'Magic Mountain of Chemistry' and having witnessed the intimate picture of human bronchial tubes in *Alex Pines*' lecture, one had to be reminded of the comparatively primitive intimate pictures of a human lung *Thomas Mann* offered to his readers in the novel 'The Magic Mountain' at the beginning of this century. Mankind is left wondering what kind of intimate pictures will be admired at the end of next century. The next series at the Bürgenstock will be played from April 29 to May 5, 2000, with *Jean F. Normant* (University P.&M. Curie, France) as president.

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Die anodische Oxidation von Titan: Eine Semesterarbeit an der HTA Burgdorf

Stefanie May und Ruth Weber*

Anodic Oxidation of Titanium: A Student Project at the HTA Burgdorf

Abstract. The work presented in this article was done by *S. May* in a student project at the HTA Burgdorf. By order of *Aloxyd AG*, Biel, the anodic oxidation of titanium in aqueous electrolyte solution was optimized. Finally, it was possible to produce titanium surfaces with reproducible colors. The worked-out procedure was then used by *Aloxyd AG* to scale up the process for industrial production.

Einleitung

Titan hat dank seiner günstigen Eigenschaften in den letzten Jahren als Werkstoff stark an Bedeutung gewonnen. Eine Besonderheit des Titans besteht darin, dass seine Oberfläche durch elektrochemische Oxidation so behandelt werden kann, dass das Werkstück durch Interferenzphänomene farbig erscheint. Dies macht Titan nicht nur für technische Bauteile interessant, sondern auch für Gegenstände, bei denen neben der Funktionalität ästhetische Aspekte von Bedeutung sind. Beispiele dafür sind Brillengestelle, Schmuckstücke und Velospeichen.

Bei der Herstellung von Titanteilen für den Handel muss die gewünschte Interferenzfarbe reproduzierbar und auf dem ganzen Werkstück homogen erzeugt werden können. Dies war zu Beginn der Semesterarbeit zum Beispiel für Velospeichen nicht gegeben. Es stellte sich daher die Aufgabe, die elektrochemische Reaktion zu optimieren und eine Korrelation zwischen den Prozessparametern und den erzeugten Farben zu finden.

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Interferenzfarben

Dünne Schichten aus lichtdurchlässigen Stoffen erscheinen im reflektierten Licht oft farbig. Die Ursache für diese Farberscheinung ist in *Abb. 1* am Beispiel einer Oxidschicht auf einem Metall dargestellt.

Trifft weisses Licht auf die Oxidschicht, wird ein Teil des Lichts reflektiert. Der

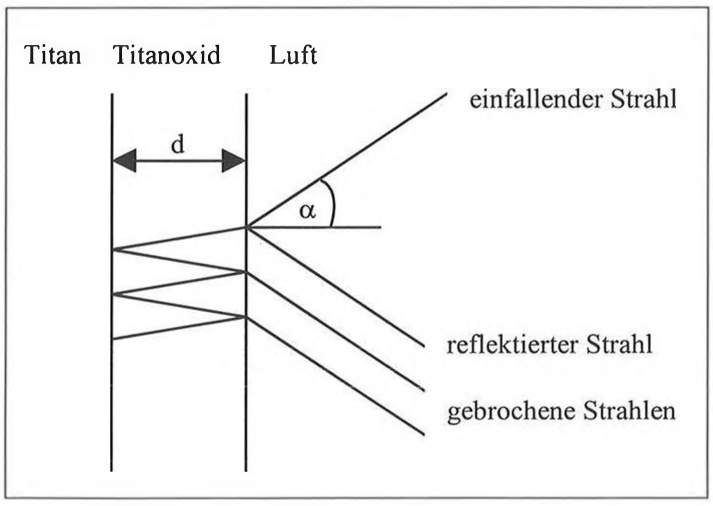

Abb. 1. *Interferenz durch Reflexion*

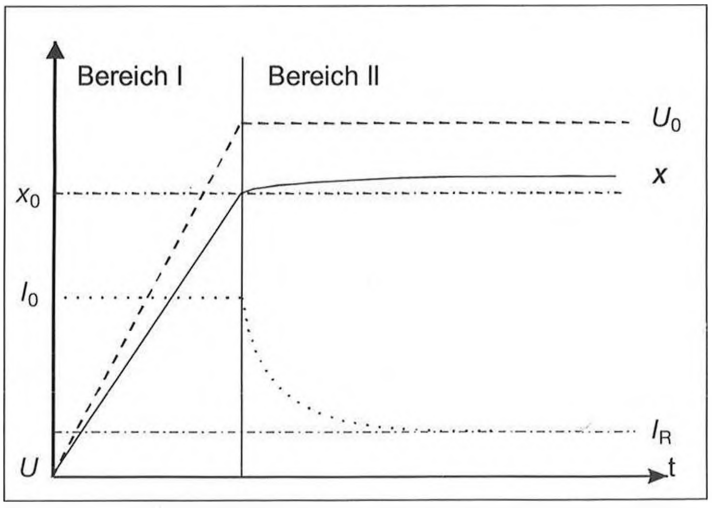

Abb. 2. *Anodische Oxidation: Zeitlicher Verlauf von Spannung, Strom und Schichtdicke*

andere Teil tritt unter Brechung in die Schicht ein und kann dort durch weitere Brechung und Reflexion mehrfach geteilt werden. Die reflektierten und die austretenden Wellen, deren Intensität mit steigender Ordnung abnimmt, sind dank der sehr kleinen Dicke der Oxidschicht kohärent und können interferieren. Dies bedeutet, dass sich die Lichtwellen überlagern und in ihrer Intensität gegenseitig verstärken oder abschwächen. Im Extremfall können sich zwei solcher Wellen nahezu vollständig auslöschen. Diese Wellenlänge fehlt dann im weissen Licht, und der Gegenstand erscheint farbig. Dabei entspricht die wahrgenommene Farbe der zur ausgelöschten Wellenlänge gehörenden Komplementärfarbe.

Damit eine bestimmte Wellenlänge ausgelöscht wird, muss der in *Gl. 1* beschriebene Gangunterschied Δ zwischen reflektierter und austretender Welle die Bedingung $\Delta = \lambda/2, 3\lambda/2, 5\lambda/2$, erfüllen.

$$2d\sqrt{n^2 - \sin^2\alpha} - \frac{\lambda}{2} = \Delta \qquad (1)$$

d = Schichtdicke [nm]
n = Brechungsindex der Oxidschicht
α = Einfallswinkel
λ = Wellenlänge [nm]

Wird die Bedingung $\Delta = \lambda/2, 3\lambda/2, 5\lambda/2, \ldots$ bzw. $\Delta = k\lambda/2$ in *Gl. 1* eingesetzt, dann erhält man für die destruktive Interferenz die *Gl. 2*.

$$d = \frac{k\lambda}{2 * \sqrt{n^2 - \sin^2}} \quad k = 1, 2, 3, \ldots \qquad (2)$$

Gl. 2 besagt, dass es für jede Wellenlänge mehrere definierte Schichtdicken gibt, die zu ihrer Auslöschung und damit zum Erscheinen ihrer Komplementärfarbe führen. Bei kleinen Schichtdicken werden zunächst die kleinen Wellenlängen ausgelöscht. Im sichtbaren Spektrum hat Blau die kleinste Wellenlänge, also ist die erste Interferenzfarbe Gelb. Mit wachsender Schichtdicke durchläuft das reflektierte Licht Gelb, Rot, Blau und Grün. Je dicker die Schicht wird, desto mehr Wellenlängen werden ausgelöscht. Es kommt zu Mischfarben, deren Intensität und Brillianz abnehmen, bis die Farberscheinung verschwindet. Dies bedeutet, dass die Farbe des Gegenstandes durch die Dicke der Oxidschicht gesteuert werden kann.

Anodische Oxidation

Auf Titan ist immer eine natürliche Oxidschicht vorhanden, die jedoch nicht dick genug ist um Licht interferieren zu lassen. Wird das Titanstück aber in einem wässrigen Elektrolyten anodisch geschaltet und mit der entsprechenden Spannung oxidiert, so beginnt die Schicht zu wachsen. *Abb. 2* zeigt qualitativ den zeitlichen Verlauf von Spannung, Strom und Dicke der entstehenden Oxidschicht.

Im Bereich I wird galvanostatisch, das heisst mit konstantem Strom I_0 oxidiert. Dies bedingt eine laufende Erhöhung der angelegten Spannung, da die nichtleitende Oxidschicht in diesem Bereich konstant wächst. Gemäss *Gl. 3* sind die angelegte Spannung U und die Schichtdicke x direkt proportional zueinander.

$$U = k_0 * x \qquad (3)$$

U : Spannung [V]
x : Schichtdicke [nm]
k_0 : Anodisierkonstante [nm/V]

In der Literatur wird die Anodisierkonstante k_0 von Titan mit 3.6–6 nm/V [1] angegeben. Somit kann mit Hilfe von *Gl. 3* die Soll-Formierspannung U_0 für eine geplante Schichtdicke x_0 abgeschätzt werden.

Sobald die Soll-Formierspannung U_0 erreicht ist, geht die Oxidation gemäss *Abb. 2* in den Bereich II über. Die Spannung wird auf dem Niveau von U_0 konstant gehalten, während der Strom mit dem Ausheilen der Schicht exponentiell gegen ein Minimum, den Reststrom I_R, abfällt. Die Grösse des Reststroms ist charakteristisch für den Zustand der Schicht. Allgemein kann gesagt werden, dass Schichten, die bei gleicher Spannung gewachsen sind und den gleichen Reststrom aufweisen, gleich dick sind.

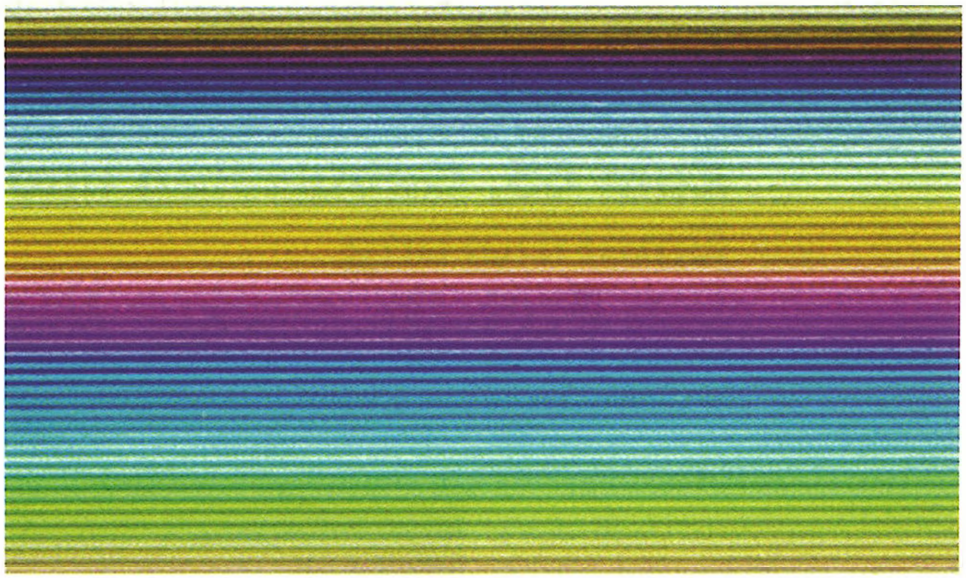

Abb. 3. *Anodisch oxidierte Titanstäbe*

Ergebnisse

Die Optimierung der anodischen Oxidation wurde mit Titanstäben durchgeführt, deren Dicke und Länge jener von Velospeichen entspricht. Die Ergebnisse sind in *Abb. 3* dargestellt.

Wie in *Gl. 2* und *Gl. 3* vorausgesagt, änderten sich die Interferenzfarben mit der Dicke der Oxidschicht und damit mit der gewählten Soll-Formierspannung.

Im Verlauf der Arbeit zeigte es sich, dass die Vorbehandlung der Titanoberfläche und die Kontaktierung der Stäbe entscheidende Parameter für die erfolgreiche Oxidation sind. Untersuchungen zur Vorbehandlung ergaben, dass die Oberflächen für gute Ergebnisse eine gewisse Rauhigkeit aufweisen müssen. Die Kontaktierung der Werkstücke erwies sich für die homogene Farbverteilung über die Länge der Speichen als massgeblich. Die Elektrolytzusammensetzung wurde vorallem im Hinblick auf das Verfahren zur Massenproduktion optimiert. Schliesslich konnten die abgebildeten Farbtöne alle mit einer einzigen Elektrolytzusammensetzung erzeugt werden. Obwohl die Soll-Formierspannug zwischen 7 und 150 V variiert wurde, wurde keine Zersetzung des Elektrolyts beobachtet. Zusammenfassend kann gesagt werden, dass durch die Optimierung der Oberflächenvorbehandlung, der Kontaktierung und der Elektrolytzusammensetzung die gewünschten Farbtöne reproduzierbar über die ganze Länge der Speichen erzeugt werden konnten.

Eingegangen am 30. Juni 1999

[1] M. Metikos-Hukovic, M. Ceraj-Ceric, *Surface Technology* **1985**, *24*, 273–283.

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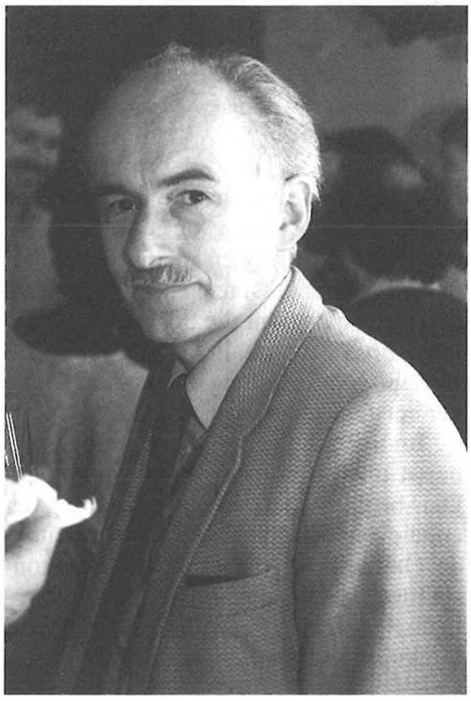
Zum 65. Geburtstag und zur Emeritierung von Prof. Dr. *Markus Neuenschwander*

Lieber *Knüss*

Ich weiss, dass Du Dich grundsätzlich nicht oft öffentlich feiern lässt. Nun ist es aber trotzdem soweit. Die Zeit ist gekommen wo Du Dich einerseits von Deinen 'Jünglingen', andererseits von Deinem 'Privatlabor' offiziell trennen musst. Ich möchte es nicht unterlassen, einen kurzen Rückblick auf Deine Karriere zu machen.

Dem Kanton Bern bist Du bislang immer treu geblieben. So bist Du vor 65 Jahren in Oberdiessbach auf die Welt gekommen. Deine Chemielaufbahn hast Du dann vor mehr als 40 Jahren an der Universität Bern in Angriff genommen, wo Du zwischen 1956 und 1961 Chemie, Mathematik und Physik studiert hast, um Dein Diplom in Chemie zu erlangen. Die Dissertation, mit dem Thema 'Synthese von 6-Vinylfulvenen', hast Du in einer Rekordzeit (so schnell hat es nicht einmal der Author geschafft!) bei Prof. Dr. *H. Schaltegger* im 1963 abgeschlossen. Zwischen 1963 und 1966 warst Du danach als Forschungsassistent tätig und konntest weiter an der Entwicklung neuer Synthesen von Pentafulvenen und 6-Vinylfulvenen sowie an Synthesen von Triazinylcyclopentadienen forschen.

Im Jahre 1966 hast Du es dann aber mutig gewagt, Dich über die Grenzen des Kantons Bern hinaus zu bewegen und ein Post-Doktorat an der TH Darmstadt bei Prof. Dr. *K. Hafner* anzutreten. Dabei hast Du während zwei Jahren auf dem Gebiet der Push-Pull-Acetylene gearbeitet und Dir bei Versuchen zur Herstellung von Push-Pull-Cyclobutadienen die ersten Zähne ausgebissen. Vom Institut für organische Chemie der Universität Bern wurdest Du dann 1968 unter Beförderung zum Oberassistenten wieder zurückgeholt und konntest Deine eigene Forschungsgruppe aufbauen. Von diesem Moment an ging alles sehr schnell: 1970 wurdest Du Privatdozent, 1973 vollamtlicher ausserordentlicher Professor, und seit 1976 bist Du Ordinarius (ordentlicher Professor) in organischer Chemie. Seither hast Du regelmässig Deine Sabbaticals – 1980, 1987 und 1993/94 am IBM Almaden Research Center in San Jose (Kalifornien) – als 'Visiting Professor' dazu benutzt, Deinen Horizont durch Bearbeitung neuer Forschungsgebiete laufend zu erweitern. Du hast bei diesen Gelegenheiten aber auch mittels brillianter Fachvorträge Dein breites Wissen einem gefesselten Publikum weiter vermittelt.



Über alle diese Jahre hast Du vielen Studentengenerationen Unterricht erteilt. Um nur einige Deiner Lieblingsunterrichtsthemen zu nennen: Aromatische Chemie, Anwendung der *Woodward-Hoffmann*-Regeln in der organischen Chemie, Synthesen von Makromolekülen, ^{1}H- und ^{13}C-NMR-Spektroskopie, Strukturaufklärung durch spektroskopische Methoden und viele mehr. Mit Deiner unerreichten Fähigkeit, die trockene Materie dieser Fächer in humorvoller und unterhaltsamer Art an das Publikum zu vermitteln, ist es Dir immer gelungen, die Zuhörerschaft in Deinen Bann zu ziehen.

Auch das Schreiben fällt Dir äusserst leicht. So hast Du bis heute in über 175 Publikationen die Fortschritte Deines Wirkens dem staunenden Publikum mitgeteilt. Lassen wir kurz Deine Forschungsthemen Revue passieren:

Dein Interesse war immer fokussiert auf die Untersuchung von sehr reaktiven Verbindungen mit konjugierten Systemen und überraschenden elektronischen Eigenschaften, die Erarbeitung neuer Synthesewege zu diesen Verbindungen sowie die Untersuchung ihrer Eigenschaften mit spektroskopischen Methoden, vor allem NMR-Spektroskopie. Während über 30 Jahren befasstest Du Dich hauptsächlich mit Fulvenen und Fulvalenen. Dabei handelt es sich um zyklisch konjugierte Verbindungen mit einer exozyklischen Doppelbindung. Das Interesse liegt dabei in der Relation zwischen chemischen Strukturen und elektronischen Eigenschaften wie Delokalisation und Ladungsdichte. Dazu kamen Acetylene mit Elektronendonator- und Elektronenakzeptorgruppen ('Push-Pull'-Acetylene). Neben der Synthese hast Du Dich auch mit Reaktionen dieser Verbindungen befasst, wobei die Säureaddition und das Polymerisationsverhalten im Vordergrund standen.

Die erste Periode Deiner Forschungstätigkeiten zwischen 1968 und 1980 kann folgendermassen beschrieben werden: Ein genereller Syntheseweg für Pentafulvene wurde entwickelt, welcher sich dann später auf Hepta- und Nonafulvene ausweiten liess. Es konnten alsdann zahlreiche der sehr instabilen Heptafulvene, Heptafulvalene und Nonafulvene (da kommt der Autor selbst heute noch ins Schwitzen!) isoliert werden. In Zusammenarbeit mit den Gruppen der Professoren *Heilbronner*, *Philipsborn* und *Bauder* wurden in der Folge die spektroskopischen Eigenschaften dieser nicht-benzoiden aromatischen Systeme untersucht. Dabei wurden grundlegende Er-

kenntnisse über den Übergang von nicht aromatischen zu aromatischen Verbindungen gewonnen.

Die Push-Pull-Cyclobutadien-Arbeiten, die Du ursprünglich bei Deinem 'Freund' *Hafner* begonnen hast, konnten durch eigene Ansätze betr. Synthese, Isolierung und Charakterisierung von Push-Pull-Cyclobutadienen erfolgreich ergänzt und erweitert werden. Zur Hauptaktivität wurden ab 1971 die Reaktionen von Push-Pull-Acetylenen. 1978 konntest Du erfolgreich nachweisen, dass Push-Pull-Acetylene gute und sehr selektive Peptidreagenzien sind. Kinetische Messungen bez. Mechanismen der Addition von Nukleophilen und Elektrophilen an Push-Pull-Acetylene sowie bez. Umlagerungsmechanismen von substituierten Aminoacryl-Derivaten wurden durchgeführt. Auch Bromierungen von Push-Pull-Olefinen sowie der Bildungsmechanismus von Acyloxy-Halo-Methanen wurden untersucht.

Im Zusammenhang mit den Arbeiten an reaktiven organischen Molekülen stieg das Interesse für reaktive Makromoleküle. Basierend auf den Erfahrung mit Fulvenen liessen sich dann erstmals reaktive Polyfulvene durch kationische Polymerisation synthetisieren. Auf einem Nebenschauplatz wurden einige interessante Arbeiten im Bereich der Naturstoffe durchgeführt wie z.B. die Strukturaufklärung von Sesquiterpen-Estern mit Antitumor-Effekt aus der Pestwurz.

In den zwei letzten Jahrzehnten wurden dann die Forschungen auf folgenden Gebieten intensiviert:

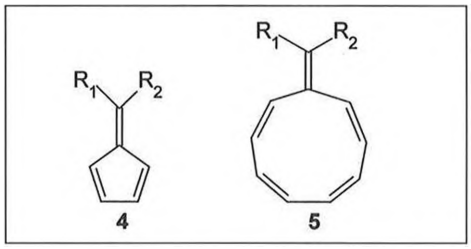
– *Synthetische Betrachtung von gespannten Fulvenen und Fulvalenen*: Ein neuer Syntheseweg zur Herstellung von Triafulven **1** wurde entwickelt (*Schema 1*). Er startet mit einem trifunktionellen Cyclopropan. Dabei konnte **1** als Cycloaddukt von Cyclopentadien nachgewiesen werden.

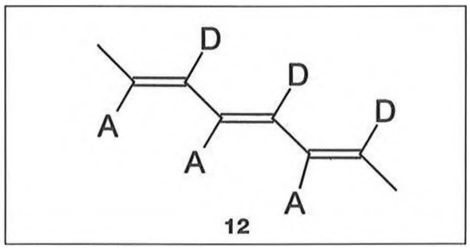
Neue Synthesekonzepte für das bis heute noch unbekannte Calicen **2** und Triafulvalen **3** sind auf gutem Weg. Aus den entsprechenden Vorstufen lassen sich durch eine Retro-*Diels-Alder*-Reaktion die Grundkörper darstellen (*Schema 2*).

– *NMR-Spektroskopische Untersuchungen von Fulvenen und Fulvalenen*: NMR-Untersuchungen von unterschiedlich substituierten Pentafulvenen **4** zeigen, dass Substituenten Änderungen in den Bindungslängen und Ladungsdichten bewirken. Diese Effekte lassen sich durch ^3J-Kopplungskonstanten (Bindungslänge) und ^{13}C-NMR-Signallagen (Ladungsdichte) nachweisen. Es sollte somit möglich sein, den Aromatizitätsgrad von Pentafulvenen **4** und Pentafulvalenen [**4**, $R^1, R^2 = (-CH{=}CH-)_n$] zu eruieren. Somit konnte das erstaunliche NMR-Verhalten von unpolaren und polaren Nonafulvenen **5** erklärt werden.

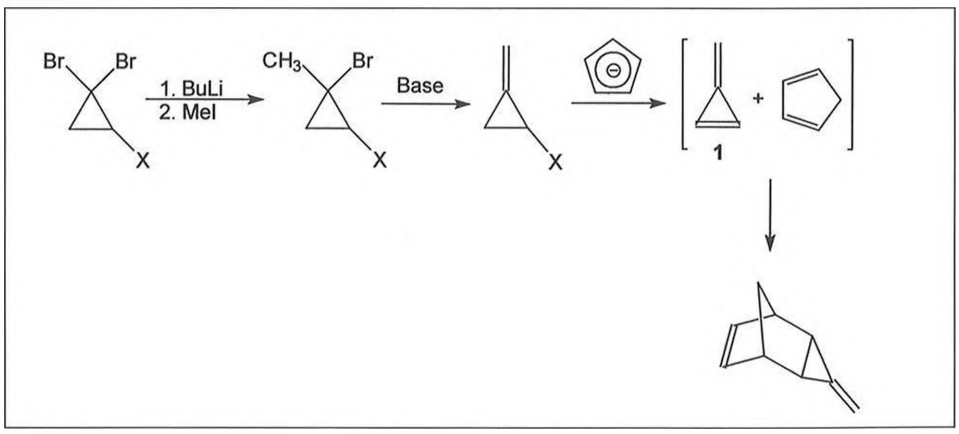
Nach den längeren Arbeiten mit Push-Pull-Acetylenen **6** konnten die ersten Push-Pull-Diacetylene **7** und Push-Pull-Oligoacetylene **8** erfolgreich synthetisiert werden (*Schema 3*). Die Polymerisation von Push-Pull-Diacetylenen in kristalliner Form ergab polymere Polyenine mit interessanten Eigenschaften.

– *Oxidative Kupplungen von* Hückel-*Anionen und Cyclopropyl-Carbenoiden*: Neuliche Versuche haben gezeigt, dass die oxidative Kupplung von *Hückel*-Anionen (wie Cyclopentadienid **9**) oder Cyclononatetraenid in Gegenwart von $AgBF_4$ oder $CuCl_2$ mit hohen Ausbeuten gelingt (*Schema 4*). Sequenzen des Typs **9** →→→ **10** konnten für die Synthesen von Pentafulvalen **10**, sowie Nonapentafulvalen und Nonaful-

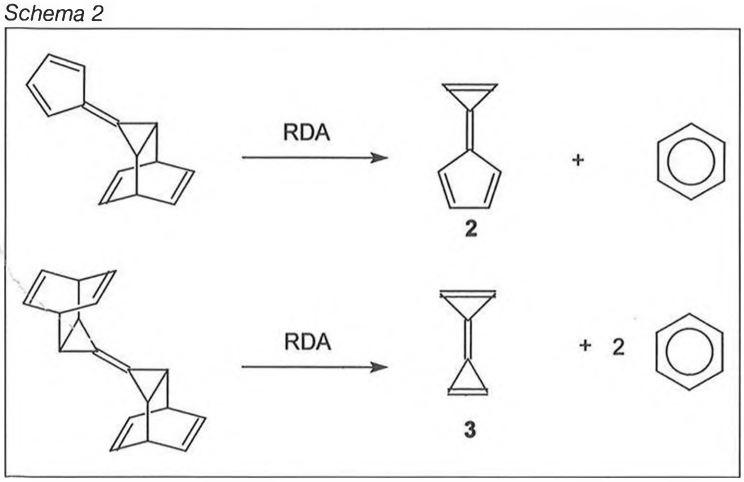




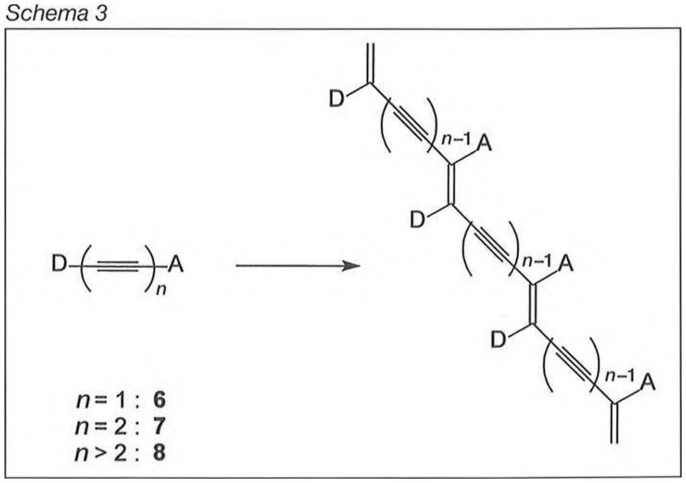
Schema 1

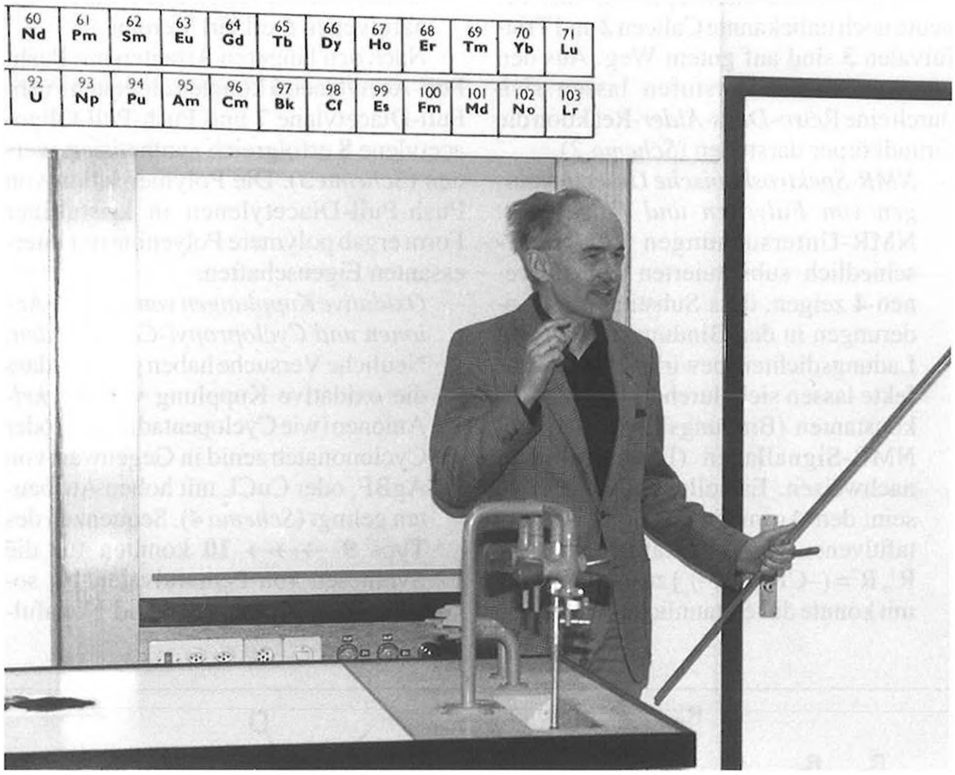


Schema 2

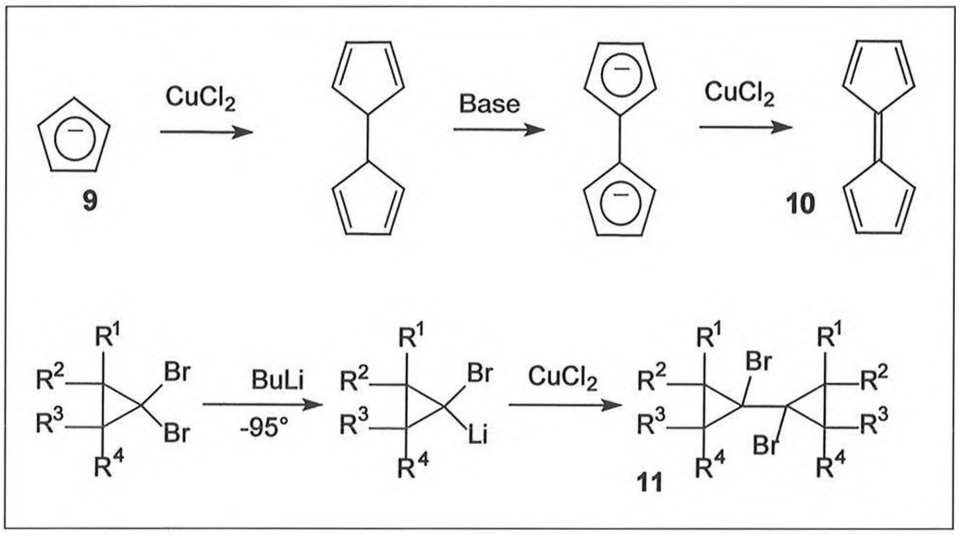


Schema 3

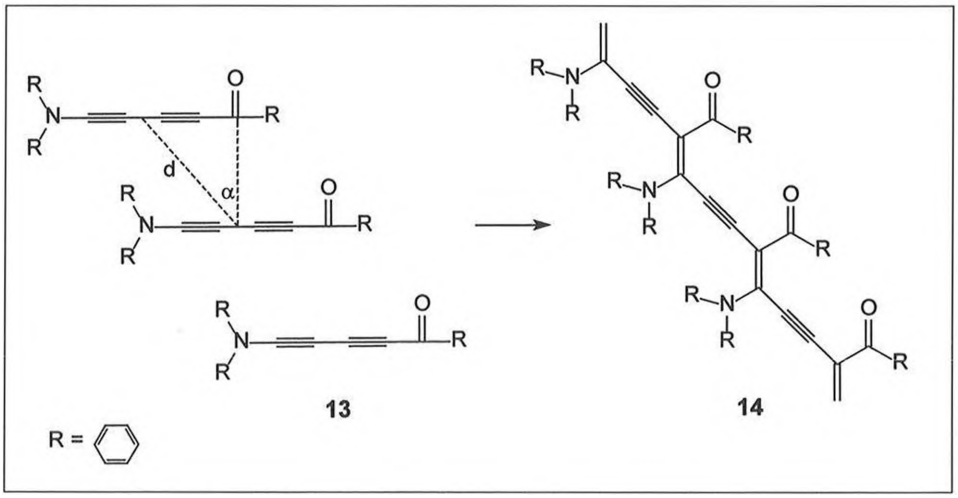




Schema 4



Schema 5



valen angewendet werden. Ähnliche Reaktionen von Cyclopropyl-Carbenoiden ergeben Vorstufen von Triafulvalenen **11**.

– *Polymere Leiter*: Interessante Arbeiten wurden in den letzten Jahren mit potentiell leitfähigen Polymermolekülen des Typs **12** durchgeführt, unter Einbezug verschiedenster Versuche in Richtung Festkörperpolymerisation von 'stacked' Push-Pull-Acetylenen (**13** → **14**) (*Schema 5*).

Lieber *Knüss*, ich habe letzendlich viel zu viel von Deiner Chemie und leider zu wenig über Deine Person selbst geschrieben. In diesen mehr als 30 Jahren Forschung hast Du 50 Doktoranden (davon zu Deinem Leid nur 2 Frauen) ausgebildet und mit zahlreichen Post-DoktorandInnen oder AssistentInnen gearbeitet. Du hast auf uns alle immer als einmaliger, aufgeschlossener und menschlicher Mentor mit grossem Herz (alle diese Attribute zusammen passen sonst nicht immer zu einem Forscher!) gewirkt. So war zum Beispiel die allmorgentliche Kaffepause für Dich ein Heiligtum. Du nahmst Dir immer Zeit, um mit Deinen Leuten über Probleme und Freuden (ob chemische oder private) zu sprechen. Weit über Deine Gruppe hinaus warst Du auch immer bereit, an der Entwicklung des organischen Instituts mitzuarbeiten, das Du zwischen 1983 und 1987 auch geleitet hast. All Deine Studierenden (vom *Greis* über den *Känzer*, den edlen *Tschingg*, den *Bartli*, den *Bonzo*, den *Schädu* oder den *Orso*, um nur einen Bruchteil zu nennen) hast Du mit Deiner Art geprägt. So zitiere ich zusammenfassend aus Deinem Doktorandenbuch den folgenden Spruch von einem Deiner Jünglinge: *'Als ein Original aus dem chemischen Institut, lieber Mensch, als Chemie- und Chompmeister und Geschichtenerzähler werde ich Sie in bester Erinnerung behalten'*.

Dir, lieber *Markus*, wünsche ich von Herzen, dass Dir der Abschied nicht allzu schwer fällt, dass Du bei bester Gesundheit noch die vielen anspruchvollen Jahre geniessen kannst. Jetzt hast Du endlich noch mehr Zeit, Deinen Hobbies nachzugehen und somit Deine Faszination für Kalifornien mit regelmässigen Reisen auszukosten. Vergiss dabei nicht das Sprichwort 'Don't touch your balls, this makes me nervous!'. Und à propos 'balls'... vielleicht reicht es doch noch für einen Chomp-Weltmeistertitel!

Jürg Furrer
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E-mail: juerg.furrer@lonza.ch

CHIMIA 1999, 53, No. 7/8

Wissenschaftliche Auszeichnungen der NEUEN SCHWEIZERISCHEN CHEMISCHEN GESELLSCHAFT

Ausschreibung für die Verleihung 2000

Distinctions scientifiques de la NOUVELLE SOCIÉTÉ SUISSE DE CHIMIE

Mise au concours pour 2000

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 2000 statt. Einreichefrist: 31. Oktober 1999.

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 2000.
Délai de présentation: 31 octobre 1999.

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 2000 statt.
Einreichefrist: 31. Oktober 1999.

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 2000.
Délai de présentation: 31 octobre 1999.

Dr.-*Max-Lüthi*-Preis

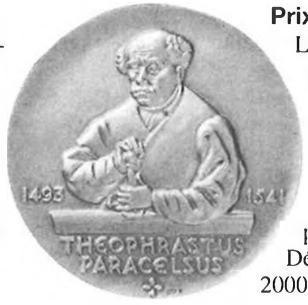
Die Dr.-*Max-Lüthi*-Auszeichnung wird für ausgezeichnete Diplomarbeiten verliehen, die an Chemieabteilungen von höheren technischen Lehranstalten der Schweiz ausgeführt werden. Anträge der Abteilungsvorsteher der Chemieabteilungen müssen bis Ende Dezember 1999 an den Geschäftsführer der NSCG eingereicht werden.
Die Preisverleihung findet im Frühjahr 2000 statt.

Prix Dr.-*Max-Lüthi*

Le prix Dr.-*Max-Lüthi* est attribué à l'auteur d'un travail de diplôme de qualité exceptionnelle 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 1999.
La remise du prix aura lieu au printemps 2000.

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 2001 verliehen.
Einreichefrist: 31. Oktober 2000.



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 2001.
Délai de présentation: 31 octobre 2000.

Vorschläge und Berwerbungen 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.

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CHIMIA 1999, 53, No. 7/8

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NSCG Section of Analytical Chemistry (SACh)

Weiterbildung Analytik im September und Oktober

In den nächsten beiden Monaten führen wir folgende Veranstaltungen durch:

QS-Einführungskurs *4.0.1*
Grundlagen zum Aufbau von Qualitätssicherungssystemen

Ziel:
Sie kennen die Grundlagen und die wichtigsten statistischen Grössen für die Qualitätssicherung. Sie sind dadurch in der Lage, in Ihrem Arbeitsgebiet qualitätssichernde Massnahmen zu treffen.

Inhalt:
- Terminologie in der Qualitätsprüfung
- Grundsätze und Richtlinien in der Qualitätssicherung
- Was muss validiert werden?
- Validierungsumfang und -schwerpunkte
- Durchführung von Validierungen in der Analytik (typisches Validierungsbeispiel)
- SOP's und Dokumentation
- Fehler und Fehlerarten bei der Angabe von Analysenergebnissen
- Messzahlen zur Charakterisierung von Fehlern
- Genauigkeit einer Messung
- Fehlerfortpflanzung

Referenten:
Dr. *R. Looser*, *Novartis Services AG*, Basel
Dr. *P. Radvila*, ehem. EMPA, St. Gallen

Ort/Termin:
Fachhochschule Aargau, Brugg/Windisch
20. September 1999

QS-Einführungskurs *4.0.2*
Statistik in der QS

Ziel:
Sie erarbeiten sich solide Grundlagen in der Statistik und können Ihre Resultate kritisch beurteilen.

Inhalt:
- Begriffe aus der Statistik
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- Tests zur Beurteilung von Messdaten
- Erfassung und Berechnung von Qualitätsmerkmalen für Analyseverfahren (Präzision und Richtigkeit, Linearität, Robustheit, Bestimmungsbereich)
- Korrelation und Regression
- Bestimmung wichtiger Kenngrössen für die Beurteilung von Messgeräten und Messmethoden
- Richtig kalibrieren

Referent:
Dr. *R. Looser*, *Novartis Services AG*, Basel

Ort/Termin:
Fachhochschule Aargau, Brugg/Windisch
21. September 1999

QS-Spezialisierungskurs *4.1.1*
Praxisnahe Qualitätskontrolle

Ziel:
Sie wissen, wie Sie in Ihr Qualitätssicherungskonzept für organische Analytik praktische Aspekte einbauen können, die Ihnen Hinweise über eventuelle Fehlerursachen geben und wie Sie praxisnahe und QC-konforme Methoden entwickeln und validieren.

Inhalt:
- Wie erkennt man Kontaminationen
- Wie werden Nachweisgrenzen definiert
- Wann machen Blindwerte Probleme und wie soll man sich ihnen gegenüber verhalten
- Matrixeffekte und ihre Erkennung
- Das Einsetzen von schlauen Kontrollproben
- Wie wesentlich ist das Erkennen von systematischen Fehlern
- Wann darf quantifiziert werden
- Nichts ist stabil. Vom Aufbewahren von Eichstandards und Referenzproben

Referent:
Prof. Dr. *M. Oehme*, Universität Basel

Ort/Termin:
Fachhochschule Aargau, Brugg/Windisch
25. Oktober 1999

GC-Einführungskurs *1.0.1*
Einführung in die Arbeitstechnik der GC

Ziel:
Sie sind mit den Grundlagen und dem methodischen Vorgehen in der Gaschromatographie vertraut und verstehen, gaschromatographische Trennungen richtig anzugehen und durchzuführen.

Inhalt:
- Überblick über chromatographische Methoden und Techniken
- Grundlagen der Trennungen
- Aufbau von Gaschromatographen

– Einfluss der Betriebsparameter auf das Gaschromatogramm (Trägergas, Temperatur, Säule)
– Wahl der Betriebsparameter
– Phasensysteme, deren Wahl und deren Einsatz in der Praxis
– Analytische und diagnostische Auswertung von Chromatogrammen

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Section de Recherche Chimique SRC
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Assemblée annuelle des membres de la Section Recherche Chimique

Dienstag, 12. Oktober 1999/Mardi 12 octobre 1999: 10.45–10.55
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Messeplatz 21, Kongresszentrum Messe Basel/Centre des Congrès de la foire de Bâle: Auditorium: Montreal

Traktanden/Ordre du jour
1. Protocol of the annual meeting of the Section held on October 15, 1998, in Zürich.
2. Annual report of the chairman
3. Annual report of the treasurer
4. Release of the committee and treasurer
5. Future activities of the section
6. Miscellaneous

PD. Dr. R. Wenger
Chairman of the Section Chemical Research

INFORMATION

News

Materialien für eine bessere Zukunft

Vorschau auf Jugendwettbewerb, Jahrestagung der SATW und Tage der offenen Tür an der ETH Zürich

Am 23.–25. September 1999 findet an der ETH Zürich unter dem Thema 'Werkstoffe der Zukunft' die öffentlich zugängliche Jahrestagung der Schweizerischen Akademie der Technischen Wissenschaften (SATW) statt, gefolgt am 24. und 25. September von Tagen der offenen Tür des Departements Werkstoffe der ETH Zürich zum Thema 'Materialien für eine bessere Zukunft'.

Zahlreiche Forschungsgruppen bieten Demonstrationen und Führungen an. Zu sehen ist ausserdem eine Ausstellung unter Beteiligung von über 25 Firmen aus dem Werkstoffbereich. Alle Veranstaltungen geben wissenschaftlich-technisch wie auch allgemein Interessierten einen vertieften Einblick in neue technische Möglichkeiten dank leistungsfähigeren Materialien. Mit einem vor einiger Zeit gestarteten Jugendwettbewerb soll zudem das Interesse für das zukunftsträchtige Studien- und Forschungsgebiet der Werkstoffwissenschaften geweckt werden.

An der am 23. und 24. September stattfindenden Jahrestagung der Schweizerischen Akademie der Technischen Wissenschaften (SATW) werden einerseits in Vorträgen mit konkreten Beispielen die heutigen Grundlagen und Voraussetzungen der Entwicklung neuer und adaptierter Werkstoffe der Zukunft für technische Innovationen aufgezeigt, und andererseits im Gange befindliche Entwicklungen von Werkstoffen der Zukunft in der Informations-, Kommunikationstechnik sowie Luft- und Raumfahrt und deren Chancen dargestellt. Besonders eingegangen wird an der Tagung auch auf die Tatsache, dass die Natur uns in der Materialentwicklung als Vorbild dienen kann. Die Jahrestagung will zudem auch zeigen, dass sich das Gebiet der Werkstoffentwicklung bzw. der innovativen, neuartigen Werkstoffanwendungen als Basis zur Gründung neuer Firmen durch Ingenieure und Naturwissenschafter sehr gut eignen kann.
Auskunft und Programm:
SATW, Postfach
8023 Zürich
Telefon 01 226 50 11
oder via Internet: www.satw.ch

Die Tage der offenen Tür des Departements Werkstoffe finden am 24. und 25. September 1999 im Hauptgebäude der ETH Zürich und an verschiedenen Forschungsstandorten statt. Forschergruppen geben mit Demonstrationen und Führungen Einblick in den neuesten Stand ihrer Forschung. Dank der Beteiligung von über 25 Industriefirmen aus dem Bereich der Werkstoffe wird zudem in den Hallen des ETH-Hauptgebäudes eine aufschlussreiche Ausstellung zu sehen sein.
Siehe auch Internet:
http://mat.ethz.ch/d-werk/tot/
Programm erhältlich bei
Telefon 01 632 42 44.

Der vom Departement Werkstoffe der ETH-Zürich und Lausanne und der Schweizerischen Akademie der Technischen Wissenschaften gemeinsam ausgeschriebene, gesamtschweizerische Jugendwettbewerb richtet sich an Schülerinnen und Schüler oder Klassen von Mittelschulen und Berufsschulen. Angesprochen sind Jugendliche bis 19 Jahre bzw. Schulklassen. Deren Aufgabe ist es, eine gute Idee auszuarbeiten, die mit dem Einsatz von Werkstoffen zu umweltverträglicheren oder leistungsfähigeren Produkten führen kann. Als Preise winken zwei neueste elektrogetriebene Fahrräder, 'FLYER F6', entwickelt in Zusammenarbeit zwischen der ETHZ und der Firma *BKTech*, sowie CHF 2500.– für die beste Klassenarbeit. Die Unterlagen zum Wettbewerb können auf dem Internet unter http://mat.ethz.ch/d-werk/tot/ eingesehen werden oder können beim Departement Werkstoffe, ETH Zürich, 8092 Zürich bestellt werden.

E-Mail:
heuberger@surface.mat.ethz.ch
Die Preisverleihung findet am Samstag, 25. September, 14.00 Uhr, im ETH-Hauptgebäude statt.

Auskünfte für die Redaktionen:
Tag der offenen Tür und Jugendwettbewerb:
Dr. *Marcus Textor*
ETH Zürich
Oberflächentechnik (Laboratory for Surface Science and Technology)
Wagistrasse 2
CH–8952 Schlieren
Phone +41 1 632 64 51
Mobile +41 79 407 69 17
Fax +41 1 633 10 48
E-Mail
textor@surface.mat.ethz.ch
WWW
http//www.surface.mat.ethz.ch

Auf dem Internet siehe auch:
http://mat.ethz.ch/d-werk/tot/

Jahrestagung SATW:
Dr. *Bertrand Rouvé*
Generalsekretär
Telefon 01 226 50 11
Telefax 01 226 50 20
Internet www.satw.ch

Vorträge

Novartis Chemistry Lectureship 1999/2000

jeweils Mittwoch, 10.30 Uhr
Auditorium Horburg, K-430.3.20
Mühlheimerstrasse, Basel

29. September 1999	Prof. *H. Kunz* University of Mainz, Mainz, Deutschland 'Synthetic Glycoconjugates – Regulatory Tools in Biological Processes and Chemical Conversions'
3. November 1999	Prof. *V. Aggarwal* University of Sheffield, UK 'Catalytic Asymmetric Epoxidation and Related Reactions'
1. Dezember 1999	Prof. *S.L. Buchwald* MIT, Cambridge, USA 'Transition-Metal-Catalyzed Carbon-Carbon and Carbon-Heteroatom Bond Formation: New Catalyst Development and Applications in Organic Synthesis'
12. Januar 2000	Prof. *S. Gibson* King's College London, UK 'Harnessing Organometallic Chemistry: From Amino-Acid Synthesis to Asymmetric Methodology'

2. Februar 2000	Prof. *S. Miller* Boston College, Boston, USA 'Discovery of Minimal Peptides for Asymmetric Catalysis and Synthesis'
6. März 2000	Prof. *W.R. Roush* University of Michigan, Ann Arbor, USA 'Recent Studies in the Synthesis of Stereochemically Complex Natural and Unnatural Products'
5. April 2000	Prof. *U. Kazmaier* University of Heidelberg, Heidelberg, Deutschland 'Chelated Ester Enolates – Efficient Tools for the Synthesis of Unnatural Amino Acids and Peptides'
3. Mai 2000	Prof. *S. Kobayashi* University of Tokyo, Japan 'New Dimension of Catalysis in Synthetic Organic Chemistry'

The Novartis Chemistry Lectureship is set up to recognize the outstanding contributions of academics in natural-product synthesis and the development of synthetic methodology.

Tagungen, Veranstaltungen, Weiterbildung

Fachtagung für angewandte Biotechnologie

8.–10. Mai 2000
Hochschule Wädenswil
CH–8820 Wädenswil
Frau *I. Tinguely*
Fax +41 1 789 99 50

Ehrung

Prof. Dr. *John P. Maier*, Professor für Physikalische Chemie an der Universität Basel, ist zum *Fellow* of the Royal Society, U.K., gewählt worden.

CHIMIA 1999, 53, No. 7/8

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!

Vorhang auf für Labor Veritas!

1889 wurde die 'Schweizerische wissenschaftliche Station für Brauerei in Zürich' gegründet. Die Brauereibranche bezweckte mit dieser Massnahme, die wissenschaftlichen Grundlagen des Brauwesens auszubauen und die angeschlossenen Betriebe bei analytischen, technologischen und technischen Fragen zu unterstützen. Diesem Ziel ist die im Jahr 1900 in 'Versuchsstation Schweizerischer Brauereien (VSB)' umbenannte Genossenschaft bis heute nachgekommen. Der starke Konzentrationsprozess der vergangenen Jahrzehnte in der Brauindustrie führte zwangsläufig dazu, dass die VSB neue analytische Dienstleistungen ins Angebot aufnahm und sich damit auch weitere Kundensegmente erschliessen konnte.

Anfang 1998 erfolgte die Übernahme der auf Wasser-, Abwasser- und Umweltanalytik spezialisierten Labor Roth AG. Am 1. September 1998 ging die Geschäftsleitung von Dr. Heinrich Pfenninger an Dr. René Eisenring über. An der Generalversammlung vom 25. März 1999 haben die Mitglieder nebst der Namensänderung gleichzeitig einer Neufassung der Statuten zugestimmt. Im Zentrum der revidierten Statuten stand die ohne Einschränkung mögliche Öffnung des Mitgliederkreises.

Seit Juli 1999 tritt die VSB neu als Labor Veritas auf und wird damit der bereits heute stark ausgeprägten Diversifizierung gerecht. Die Genossenschaftsform wird beibehalten. Ab sofort kann das neue, umfangreiche Leistungsverzeichnis angefordert werden.

Labor Veritas bedient heute eine äusserst breitgefächerte Kundschaft: Brau- und Getränkeindustrie, Weinkelterer und -abfüllereien, Lebensmittelhersteller, Händler und Lagerhalter von Obst und Gemüse, Halb- und Fertigfabrikatehersteller aus dem pharmazeutischen und chemischen Bereich, Betreiber von Abwasserreinigungsanlagen, Behörden, Ingenieurbüros, Gastronomie- und Verpflegungsbetriebe, Geologen, Grundstoff- und Aromenhersteller, Kunststoffverarbeiter usw. Labor Veritas ist aber nach wie vor eine wichtiger Ansprechpartner für die Brau- und Getränkeindustrie und nimmt im Auftrag des Schweizerischen Bierbrauervereins Branchenvertretungen wahr.

Für die Bearbeitung der Aufträge beziehungsweise als Anlaufstelle für die Erarbeitung von Problemlösungen sind vier Abteilungen mit insgesamt 30 Mitarbeitern nach folgenden Schwerpunkten zuständig:

Mikrobiologie

Getränke- und Lebensmittelmikrobiologie, Hygiene- und Stufenkontrollen vor Ort, Technologie- und Hygieneberatungen vor Ort.

Organische Chemie

Organische Schadstoffe (Pflanzenschutzmittel, Mykotoxine, Nitrosamine usw.), pflanzliche Wirkstoffe, Aromaanalysen, Routineuntersuchungen von Getränken und Lebensmitteln (Überwachung der Verarbeitung, Gesetzes- und Rezepturkonformität).

Wasser- und Umweltanalytik

Untersuchungen aller Arten von Wasser (z.B. Mineral-, Trink-, Oberflächen- und Badewasser), anorganische Rückstandsanalytik (Schwermetalle), Abwasser, Boden, Klärschlamm, Deponiemonitoring.

Beratung

Beratung bei technischen und technologischen Problemstellungen, Qualitäts- und Umweltmanagementsysteme, Arbeitssicherheit, Garantieabnahmen bei Inbetriebnahme von Produktionsanlagen in der Getränkeindustrie.

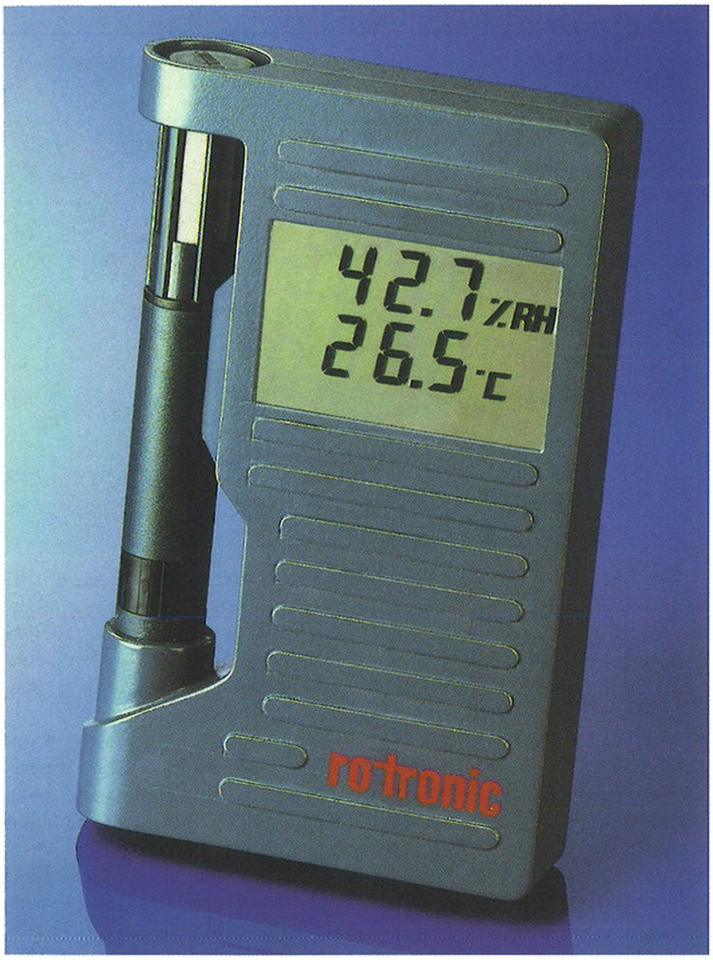
Das Labor Veritas ist dank der Interdisziplinarität eine interessante Adresse für die Bearbeitung von Spezialfällen ausserhalb der Routineanalytik. Es ist nach EN 45001 akkreditiert und verfügt über eine IKS-Bewilligung (Interkantonale Heilmittelkontrolle) zur Durchführung von Arzneimittelprüfungen. Labor Veritas ist ausserdem Koordinationsstelle für Arbeitssicherheit und Gesundheitsschutz der Betriebsgruppenlösung Getränke.

• Labor Veritas
Engimattstrasse 11
CH–8059 Zürich
Telefon 01 283 29 30
Telefax 01 201 42 49
E-Mail admin@laborveritas.ch

Leserdienst Nr. 2

Datenlogger-Hygrolog

Wir bewegen uns mit voller Kraft auf den Jahrtausendwechsel zu. Von den damit verbundenen Computerproblemen wollen wir hier jedoch nicht sprechen. In den folgenden Zeilen beschäftigen wir uns eher mit der Bewältigung von Vergangenheits- und Gegenwartsproblemen. Weltweit bietet unsere Erde ein Kaleidoskop an Kunstschätzen in der Form von historischen Gebäuden, Gemälden oder Skulpturen. Ständig wechselnden Klimasituationen ausgesetzt, ist die Lebensdauer solcher Kulturgüter gefährdet, es sei denn, es werden künstlich verträgliche bzw. optimierte Klimabedingungen geschaffen. Es ist aber dann noch unerlässlich, dass das Einhalten der vorgeschriebenen Bedingungen auch nachgewiesen werden kann. Ähnliche Situationen finden sich beim Transport empfindlicher Güter, handle es sich dabei um sehr teure Musikinstrumente, z.B. einen Flügel, ein Cembalo oder eine Stradivari oder ganz einfach und alltäglich – Kaffee, Gewürze oder Milchpulver. Rotronic bietet hierzu modernste Datenlogger an, z.B. das Modell Hygrolog. Es speichert relative Feuchte und Temperatur als 5000 Wertepaare. Dabei erleichtern drei Betriebsmode (S/S, Loop, Grenzwert-Trigger) und die Alarmwertfunktion die optimale Einrichtung für die Datenspeicherung. Der Logger ist mit dem hochmodernen, 100%-ig austauschbaren Fühlermodul HygroClip ausgestattet und kann ohne Interface direkt über ein Schnittstellenkabel programmiert oder ausgelesen werden. Die Daten können bei



Temperaturen von –10…+50 °C erfasst werden. Die benutzerfreundliche Software erlaubt eine umfassende Datenanalyse über Tabellendarstellung, Kurvengraphik und Zoom-Funktion. Weiterhin können die Kurven mehrerer Geräte in einer Graphik überlagert werden (Multilayer-Funktion), ebenso lassen sich die erfassten Daten problemlos in andere Datenbanken, z.B. EXCEL, exportieren. Eine LCD-Anzeige mit grossen Ziffern ist als Option erhältlich. Als Stromversorgung dienen 3 Standardbatterien AM3, 1,5 V, die vom Anwender sehr einfach ersetzt werden können. Über ein bis zu 5 m langes Verlängerungskabel kann der Fühler im Bereich von –40… +85 °C eingesetzt werden.

- Rotronic AG
  Grindelstrasse 6
  CH–8303 Bassersdorf
  Telefon 01 838 11 11
  Telefax 01 836 44 24
  Internet http://www.Rotronic.ch

Leserdienst Nr. 3

Leica DM IL – Das kleine Inverse mit dem neuen 'Integrated Modulation Contrast' (IMC)

Ergonomie, kompakte Bauweise und Kontrastiermethoden zu einem System vereinigt – die Applikationen in Biologie und Medizin werden somit nahezu grenzenlos.

Das DM IL markiert heute den anspruchsvollen Einstieg in die inverse Mikroskopie. Sein modularer Aufbau und der stets freie Blick auf das Präparat bilden neben den neu entwickelten und optimierten Kontrastierverfahren die von Anwendern gewünschten Praxisvorteile und Gebrauchseigenschaften. Ein neu entwickelter integrierter Modulationskontrast (IMC) bietet jetzt noch hochwertigeren Reliefkontrast und dies alles ohne den Einsatz von zusätzlichen Spezialobjektiven.

Höchste Bildauflösung

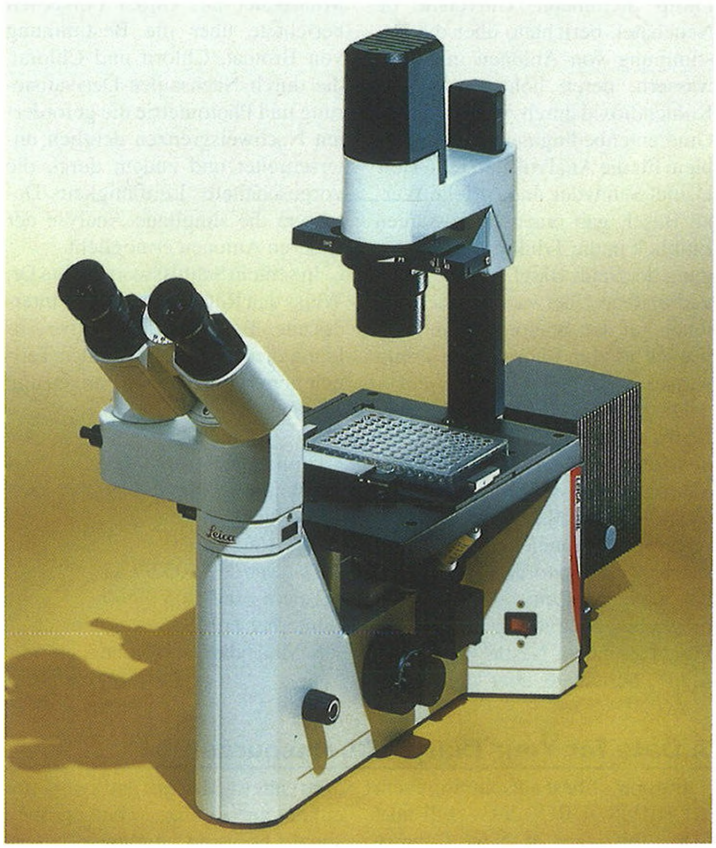
Durch die Adaption des Leica DM IL an die unendlich Optik wird die Integration der Leica HCS (Harmonic Component System) Komponenten erreicht. Somit ergeben sich höchste Bildauflösung, brillante Kontraste und präzise Farbwiedergabe. Die bekannten, eingeführten aufrechten Leica DM Mikroskope der L- und R-Klasse werden damit im inversen Mikroskopiesegment erweitert. Verbessert wurde der Phasenkontrast, der zusammen mit der Auflicht-Fluoreszenz eindeutige Anwendungsvorteile gewährleistet.

Universell für Routine und Labor in Biologie und Medizin

Das DM IL ist das Mikroskop der Wahl für alle Anforderungen im Mikrobiologie- bzw. Zellkulturlabor. Ein universelles inverses Mikroskop für die Routine-Applikation: stabil und platzsparend, flexibel und ausbaufähig mit der Optik der Forschungsstative von Leica Microsystems.

- Leica Microsystems AG
  Kanalstrasse 21
  CH–8152 Glattbrugg
  Telefon +41 1 809 34 34
  Telefax +41 1 809 34 44
  www.leica-microsystems.com

Leserdienst Nr. 4



Tagung Ionenchromatographie

Am 8. Juni 1999 hat die Dionex (Switzerland) AG in Olten eine 'Tagung Ionenchromatographie' durchgeführt. Unter der Leitung von Dr. Joachim Weiss, Technischer Direktor bei Dionex Corp./ International Operations, referierten Gastredner über verschiedenste Anwendungsbereiche der Ionenchromatographie. Mit 60 Teilnehmern übertraf die Resonanz auf die Ankündigung dieser Veranstaltung alle Erwartungen.

In seinem einleitenden Vortrag nahm Dr. Weiss Rückblick auf die Neuerungen, die speziell in den letzten fünf Jahren seit Gründung der Schweizer Dionex-Niederlassung eingeführt wurden, z.B. neue Trennsäulen für Carbonat-Eluenten, hydroxid-selektive Trennsäulen hoher Kapazität oder die elektrochemische Herstellung kontaminationsfreier Eluenten. Passend zum Übergang in das neue Jahrtausend stellte er abschliessend das 'Ion reflux'-Konzept von Hamish Small, dem Begründer der Ionenchromatographie, vor – eine Vision zukünftiger Ionenchromatographie auf der

Basis simultaner elektrochemischer Eluentenherstellung und Suppression.

Dr. Eberhard König, Novartis Services AG/Basel, zeigte die Problemstellungen eines analytischen Auftragslabors auf, das Ionen in unbekannten Proben unterschiedlichster Zusammensetzung unter Berücksichtigung der Qualitätsmanagment-Richtlinien analysiert. Dr. Philip Steinmann, Université de Neuchâtel, berichtete über die Bestimmung von Anionen in Moorwässern, deren hoher Anteil an Kohlendioxid durch Anpassung der Gradientenbedingungen kein Problem für die Analytik darstellt. Herr Daniel Schnyder, Industrielle Werke Basel, gab einen interessanten Einblick in die Trinkwasser-Erzeugung der Stadt Basel und die damit verbundene Überwachung der Anionen auf den Stationen vom Rohwasser bis zum fluoridierten Trinkwasser.

Dr. Fabian Wahl, Fluka AG/Buchs, stellte Resultate der Anionen-Bestimmung in 'Trace Select'-Säuren vor, deren Reinheits-Spezifikationen den Nachweis von Spurenkonzentrationen in einer anionischen Matrix erfordern und damit das unterste Limit der derzeitig möglichen Analytik darstellen. Dr. Pascal Zbinden, Nestlé R&D/Lausanne, berichtete über die Unterscheidung toxischer und nicht-toxischer Arsen-Spezies in Lebensmitteln, die durch die Auftrennung mittels Ionenchromatographie und nachfolgende ICP-Bestimmung ermöglicht wird. Abschliessend stellte Dr. Urs von Gunten, EAWAG/Dübendorf, das in seiner Arbeitsgruppe entwickelte Konzept zur Analytik von Qxyhalogeniden in ozonisiertem Trankwasser vor. Sein Mitarbeiter Dr. Ulrich Pinkernell berichtete über die Bestimmung von Bromat, Chlorit und Chlorat, die durch Nachsäulen-Derivatisierung und Photometrie die geforderten Nachweisgrenzen deutlich unterschreitet und zudem durch die vorgeschaltete Leitfähigkeits-Detektion die simultane Analyse der anderen Anionen ermöglicht.

In seinem Schlusswort dankte Dr. Weiss den Referenten für ihre interessanten Beiträge. Der positive Anklang dieser Tagung bei allen Teilnehmern wird zu einer Fortsetzung führen.

- Dionex (Switzerland) AG
  Solothurnerstrasse 259
  Postfach
  CH–4603 Olten
  Telefon 062 205 99 55
  Telefax 062 205 99 60
  Internet http://www.dionex.ch
  E-Mail dionex@dionex. ch

Leserdienst Nr. 5

A Date for Your Diary – Chemsource 99

Europe's finest outsourcing event – CHEMSOURCE 99 – will take place this year at New Century House, Manchester, England on September 28–29, 1999.

Outsourcing, or contract, custom and toll manufacturing, is the biggest growth area in the fine and specialised chemicals industry.

CHEMSOURCE 99 will provide a forum to meet and build business partnerships regarding both custom manufacture and specialist services with a select group of specialists.

CHEMSOURCE 99 Exhibition is organised by DMG Business Media Ltd, publisher of Speciality Chemicals and Pharmaceutical Manufacturing Review and organiser of the Chemical Specialities Events. The exhibition will be staged on September 29, 1999.

CHEMSOURCE 99 Conference – co-ordinated by The Speciality Chemicals Sector of the Industrial Affairs Division of the Royal Society of Chemistry – is entitled 'Automated Synthetic Methods for Speciality Chemicals' and will run from September 28–29, 1999.

The symposium is directed at R&D chemists working in speciality chemical areas including pharma/agro intermediates, and who are either questioning whether they should be using combinatorial/automated techniques, or who have already begun to use them and are interested in new developments.

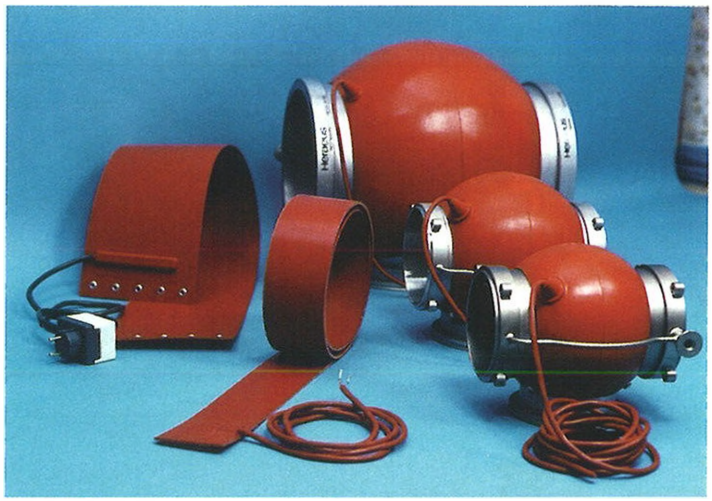
The programme will cover the following aspects: overview, techniques, instrumentation, applications in lead discovery and optimisation, and applications in process development.

For further information please contact:
Dr. W. Hoyle
29 Carrwood Avenue, Bramhall,
Stockport SK7 2PY
Tel./Fax: +44(0)161 439 3547.
Admission to the exhibition is free-of-charge. For free admission tickets contact Jenny Taylor on
Tel.: +44(0)1737 855301.
Fax: +44(0)1737 855474.
Enquiries for exhibition space should be directed to Jaymin Amin on
Tel.: +44(0)1737 855060
Fax: +44(0)1737 855469.

- DMG Business Media Ltd
  Queensway House
  2 Queensway
  Redhill, Surrey RH1 1QS
  England

Lesersdienst Nr. 6

Silikon-Flach-Heizelemente



Wie eine zweite Haut lassen sich flexible Silikon-Flach-Heizelemente, bei einer Dicke von 2–3 mm, auf das zu beheizende Teil, wie z.B. Armaturen, Ventile, Rohre, Trichter, Behälter, Maschinenteile, etc., aufbringen. Die Befestigung erfolgt durch Klebefolie, direktes Aufvulkanisieren oder durch Aufpressen. Dadurch ist ein optimaler, nahezu verlustfreier Wärmeübergang gewährleistet, da zwischen Heizelement und Bauteil keine Luftspalten vorhanden sind.

Die Leistung und die Form des Heizelementes kann an das jeweilige Teil angepasst werden. Je nach Ausführung sind Leistungen bis zu 0.7 W/cm^2 für Temperaturen bis zu 200 °C realisierbar. Dank diesen Flach-Heizelementen kann bei niedriger Temperaturdifferenz eine hohe Energieübertragung erreicht werden. Bezüglich der Leistungsverteilung kann diese den Massenverhältnissen angepasst werden. Punktuelle Überhitzungen oder Kaltstellen sind ausgeschlossen, wodurch eine homogene Wärmeverteilung vorhanden ist.

Wasserdichte Ausführungen der Silikonheizelemente für Anwendungen in Nasszonen sind ohne wesentliche Mehraufwendungen ebenfalls erhältlich.

Geregelt werden die Fachheizer über entsprechend eingebaute Sensoren und externe Regler. Ebenfalls sind auch Wächter oder einfache Bi-Metallschalter in die Heizmatten einbaubar.

- WISAG
  Oerlikonerstrasse 88
  CH–8057 Zürich
  Telefon 01 311 40 40
  Telefax 01 311 56 36
  Internet http://www.wisag.ch

Leserdienst Nr. 7

Leica DSC1 Disc Mikrotom: Innovative Technik in der Mikrotomie

Mit einer völlig neuen Technologie in der Mikrotomie, einem prozessgesteuerten und vollautomatischen Disc Mikrotom, eröffnet Leica Microsystems Nussloch Histopathologen beim Paraffinschneiden die Möglichkeit, jetzt noch wirtschaftlicher, sicherer und effizienter zu arbeiten: Das Leica DSC1 Disc Mikrotom für zeitoptimierte

Probenbearbeitung, die manuelle Tätigkeiten weitgehend vermeidet.

Der Schwerpunkt bei der Entwicklung dieses neuen Gerätes wurde auf die drastische Reduzierung manueller Arbeitsabläufe gelegt. Bei reproduzierbar hoher Schnittqualität lässt sich der Probendurchsatz aufgrund des völlig neuen Konstruktionsprinzips deutlich steigern. Auf einer Kreisbahn wird die Probe dynamisch ausbalanciert zum Messer bewegt – das Ergebnis sind weitgehend stauchungsfreie Schnitte. Jeder Wechsel, ggf. auch die Orientierung der Probe, findet sicher und bequem ausserhalb des Schneidebereichs statt. Der hohe Probendurchsatz ergibt sich durch ein selbstjustierendes Schneidefenster, die hohe Geschwindigkeit der Probe ausserhalb dieses Fensters sowie die vollautomatische Probenannäherung für schnellstes Anschneiden.

Das Gesundheitswesen steht weltweit unter merklichem Kostendruck. Neben der Suche nach Einsparungspotential in allen Bereichen des Gesundheitswesens stehen Investitionen mehr denn je im Zusammenhang mit Produktivitätssteigerungen und anderen Wirtschaftlichkeitsaspekten. Bezogen auf den Geschäftsbereich der Histopathologie führen Bestrebungen zur Produktivitätssteigerung und zur Erhöhung der Wirtschaftlichkeit der Leistungserfüllung zu Privatisierungen der Histopathologie in Europa und zu verstärkter Bildung von gewinnorientierten Gemeinschaftslabors. Mit dem vollautomatischen Disc Mikrotom Leica DSC1 trägt Leica Microsystems bedeutend dazu bei, diesen neuen Marktgegebenheiten gerecht zu werden. Denn im Bereich der histologischen Probenbearbeitung im Routine-Histologielabor führt ein optimierter Personaleinsatz unter weitgehend standardisierten Bedingungen zu einer beträchtlichen Verkürzung der Probendurchlaufzeit.

Das neue Mikrotomkonzept ist für Leica Microsystems die zukunftorientierte Plattformtechnologie für weitere Mikrotomentwicklungen.

- Leica Microsystems AG
  Kanalstrasse 21
  CH–8152 Glattbrugg
  Telefon +41 1 809 34 34
  Telefax +41 1 809 34 44
  www.leica-microsystems.com

Leserdienst Nr. 8

SALVIS LAB Vacucenter mit digitaler Anzeige

Vakuumregelung mit digitaler Anzeige

Seit nun bald 2 Jahren werden die bekannten Salvis Lab Produkte Vacucenter, Thermocenter und Biocenter von der Firma Renggli AG in Rotkreuz produziert. Salvis Lab steht für Qualität und Präzision. Die Geräte dieser Produktelinie finden Sie weltweit in verschiedenen Laborsund gelten seit Jahren als unentbehrliche Arbeitsinstrumente. Auch punkto Innovation setzt die Firma Renggli alles daran, dauernd bedürfnisorientierte Anpassungen und Weiterentwicklungen der Geräte zu verwirklichen. Die digitale Vakuumanzeige für den Vakuumtrockenschrank ist eine davon. Das Vacucenter mit digitaler Anzeige bringt viele Vorteile wie zum Beispiel kontinuierliche Prozesswiederholung oder einfaches, genaues Ablesen von Vakuumwerten, was vor allem beim Arbeiten unter GMP/GLB Grundsätzen verlangt wird.

Auch eine integrierte Vakuumregelung mit digitaler Anzeige ist ab sofort erhältlich. Geräte mit analoger Anzeige können jederzeit nachgerüstet werden.

Wollen Sie noch mehr Genauigkeit beim Vakuumtrocknen? Zögern Sie nicht und kontaktieren Sie:

- E. RENGGLI AG
  Industrie Ost
  CH–6343 Rotkreuz
  Telefon 041 798 14 50
  Telefax 041 798 14 40
  sales@renggli.com
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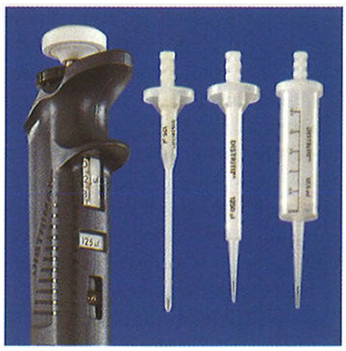
Leserdienst Nr. 9

DISTRIMAN®-Repetierpipette von GILSON



DISTRIMAN® – der neue Standard für repetitives Dosieren.

Der DISTRIMAN® von GILSON ist der erste kontinuierlich einstellbare Dispenser, zum sicheren und präzisen Dosieren von Teilvolumina. Die Handhabung des ergonomisch gestalteten DISTRIMAN® ist so einfach, wie Sie es sich vom bewährten PIPETMAN® gewohnt sind.

Mit nur drei Grössen decken die DistriTips bereits den gesamten Arbeitsbereich der Teilvolumina von 1 µl bis 1.25 ml ab – das spart Platz und Geld. Das eingestellte Teilvolumen ist direkt ablesbar – berechnen des effektiven Volumens mittels Tabellen und Faktoren gehört der Vergangenheit an. Mit jedem DistriTip können bequem über 100 Aliquote abgegeben werden. Microtiterplatten können so in nur einem Arbeitsgang befüllt werden.

Die auf den DistriTips markierten Teilvolumina helfen Ihnen, wertvolle und teure Reagenzien gezielt zu dosieren und damit Ausschuss zu verhindern.

Der auf Direktverdrängung basierende DISTRIMAN® ermöglicht präzises Dosieren wässriger, leichtflüchtiger, viskoser (z.B. Blut, Plasma oder Öle) und schwerer Flüssigkeiten in die unterschiedlichsten Gefässe wie Microtiterplatten, Vi-

als, Röhrchen usw. Cross-Kontaminationen können verhindert werden, weshalb der DISTRIMAN® in anspruchsvollen Gebieten wie z.B. der Molekularbiologie verwendet wird.

Die DistriTips sind autoklavierbar, neu aber auch bereits (-sterilisiert erhältlich. Die aus Polypropylen gefertigten DistriTips sind chemikalienbeständig und von der selben hohen Qualität wie die DIAMOND®-Tips für den PIPETMAN®.

Weitere Informationen finden Sie auf unserer Homepage unter http://www.omnilab.ch.

- OmniLab Biosystems AG
  Untere Bahnhofstrasse 14
  CH–8932 Mettmenstetten
  Telefon 01 768 22 11
  Telefax 01 768 23 21

Leserdienst Nr. 10

Das austauschbare, digitale Feuchte-Sensor-Modul

Feuchtemessung an sich ist eine ungenaue Wissenschaft; der Markt bietet Messgeräte mit höchster Genauigkeit an. Diese kosten jedoch mehrere tausend Franken und sind in der Regel nicht für den täglichen Routineeinsatz geeignet. Geräte im untersten Preisbereich mit den ihnen anhaftenden Messfehlern werden daher oft in weniger kritischen Anwendungen eingesetzt.

Zum ersten Mal bringt nun das neue Feuchte-/Temperaturmessmodul HygroClip von Rotronic höchstmögliche Messgenauigkeit für das untere Preissegment des Marktes – dies dank Verwendung digitaler Datenbearbeitung mit korrigierten Messwerten.

Der HygroClip, ein vollständiges Messmodul, basierend auf modernster ASIC-Technologie, erzielt höchst genaue Messresultate und stellt diese als analoge und digitale Signale zur Verfügung. Sämtliche Kalibrierdaten sind im elektronischen 'Gedächtnis' des HygroClip gespeichert; kommt der Zeitpunkt der Wartung, Kalibrierung oder ist Ersatz angezeigt, kann nun ein neues Modul installiert werden, ohne Genauigkeitseinbusse der Messung.

Ob der HygroClip nun für sich selbst oder in Verbindung mit anderen Peripheriegeräten, z.B. Handgerät oder Datenlogger eingesetzt wird – die Messresultate sind immer höchst genau, die Wartung wird wesentlich vereinfacht. Anwendungen, wo der HygroClip schon erfolgreich eingesetzt wird, umfassen elektronische Gehäuse, Klimasteuerungen, Datenerfassung, Handgeräte und Wetterbeobachtung.

Mit der Genauigkeit von 1.5% rF und Einsatzbereichen von 0–100% rF und –40...+85°C ist der HygroClip bestens geeignet für einen weiten Anwendungsbereich auf nahezu allen Gebieten; Ersatz im Bedarfsfalle ist durch das weltweite Vertriebsnetz innert kürzester Zeit gewährleistet.

- Rotronic AG
  Grindelstrasse 6
  CH–8303 Bassersdorf
  Telefon 01 838 11 11
  Telefax 01 836 44 24
  Internet http://www.Rotronic.ch

Leserdienst Nr. 11

Anaerobier-Werkbank Bug Box

Ab 7 Anaerobentöpfen wird die Bug Box anaerobe Werkbank das wirtschaftlichere Arbeitsinstrument mit vielen zusätzlichen Vorteilen: garantierte anaerobe Bedingungen auch beim Arbeiten, kontrollierte Temperatur und definierte Feuchtigkeit. Das Ein- und Ausbringen Ihrer Proben/Materialien erfolgt über eine Schleuse. Die Bug Box vereinfacht Ihre Arbeiten und garantiert definierte Arbeitsbedingungen. Sie bietet alle Vorteile grösserer Anaerobier-Werkbänke, hat aber einen wesentlich geringeren Platzbedarf bei einer Kapazität von bis zu 180 Petrischalen.

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Leserdienst Nr. 12

PIPETMAN® Service-Center Qualitätssicherung und Werterhaltung

Immer mehr Labors und Betriebe sehen einen enormen Mehraufwand auf sich zukommen, um die GMP/GLP oder ISO-Anforderungen im Bereich Qualitätssicherung zu erfüllen. Alle benötigten Geräte müssen periodisch und nachweisbar gewartet und kalibriert werden.

Um diese Aufgabe zu bewältigen, werden aus Kostengründen oder Personalmangel vermehrt firmenexterne Dienste in Anspruch genommen.

Die offiziellen Vertretungen bieten dabei einige Vorteile: Als vom Werk autorisierte Service-Center stehen sie in direktem Kontakt mit den Herstellern, sind spezifisch geschult, kennen die laufenden Produkteverbesserungen und besitzen die speziellen Werkzeuge und original Ersatzteile zur Reparatur und Kalibration. Der Hersteller stellt die Beachtung der Werksvorschriften sicher, indem das Service-Center regelmässig auditiert wird.

Die ISO 9001 zertifizierte Firma OmniLab Biosystem AG in Mettmenstetten hat als offizielle Gilson-Vertretung schon seit Jahren einen Kalibrations- und Reparaturdienst für Pipetten eingerichtet. Zu ihren Kunden gehören zahlreiche Chemiefirmen, Universitäten und Spitäler in der ganzen Schweiz.

Eine Gilson-Pipette verlässt die Produktion werkskalibriert. Das heisst, die Leistungswerte der Pipette entsprechen den jeweils angegebenen Spezifikationen für Genauigkeit und Präzision. Pipetten sollten, wie andere Geräte auch, in regelmässigen Abständen auf die erforderlichen Spezifikationen überprüft werden.

- Zu prüfende oder defekte Pipetten können einfach per Post dem PIPETMAN® Servicecenter zugeschickt werden.
- Das qualifizierte Serviceteam arbeitet fachgerecht in einem speziell strukturierten und klimatisierten Labor.
- Im Service-Center werden die Pipetten auf Radioaktivität geprüft und chemisch als auch biologisch dekontaminiert.
- Defekte oder Verschleissteile werden gegen original Gilson-Ersatzteile ausgetauscht.
- Mit geeichten Mettler Präzisionswaagen werden die Pipetten auf Herstellerspezifikationen kalibriert.

Ein Prüfzertifikat wird ausgedruckt und dokumentiert die korrekte und GLP-gerechte Funktion der Pipette.

Der 'Lebenslauf' der Pipette wird im eigenen Datenbanksystem lükkenlos aufgezeichnet, ist jederzeit nachvollziehbar und für den Kunden verfügbar.

Nach wenigen Tagen erhält man die Pipetten in neuwertigem Zustand zurück und leistet so einen wesentlichen Beitrag zur Werterhaltung der Laborausrüstung.

Das Pipetten-Service-Center von OmniLab Biosystems AG ist die einzige vom Werk autorisierte Reparatur- und Kalibrationsstelle für Gilson-Pipetten in der Schweiz.

- OmniLab Biosystems AG
  Untere Bahnhofstrasse 14
  CH–8932 Mettmenstetten
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  Telefax 01 768 23 21

Leserdienst Nr. 13

ChemOffice 2000 – Das weltweit führende Chemie-Sofware-Paket ab sofort bei Cherwell Scientific erhältlich!

Cherwell Scientific freut sich, die Auslieferung von ChemOffice 2000, entwickelt von CambridgeSoft Corporation, bekanntgeben zu können. ChemOffice 2000 ist die einzige integrierte Desktop-Chemie-Umgebung für Chemiker mit Applikationen zum Zeichnen von chemischen Strukturen, zur Molekülmodellierung und zum chemischen Informations-Management.

ChemOffice 2000 enthält nun neben ChemDraw Ultra, Chem3D Ultra, ChemFinder Ultra das mathematischem Graphikprogramm, SigmaPlot und weitere Eigenschaften wie Beilsteins Autonom, Connolly Oberflächen und ChemFinder für Excel und erfüllt damit die tagtäglichen Anforderungen eines jeden Chemikers.

Die Neuerscheinung von ChemOffice 2000 stellt eine deutliche Verbesserung gegenüber der vorherigen Version dar; ChemDraw Ultra 5.0 bietet die Möglichkeit, NMR-Linienspektren zu schätzen und Namen zu Strukturen (Name = Struct) umzuwandeln. Mit Chem3D Ultra 5.0 können Sie Reaktionsmechanismen im Publikationsformat zeichnen und Oberflächeneigenschaften von Molekülen visualisieren. Mit ChemFinder Ultra 5.0 erhalten Sie eine voll integrierte MS Excel Schnittstelle und erweiterte Suchfähigkeiten. Mit ChemInfo Pro erhalten Sie Zugang zu unserer

neuesten chemischen Referenzbibliothek, die über 450000 Chemikalien aus 120 Katalogen erhält. Ausserdem können Sie jetzt Ihre Arbeiten durch den Gebrauch des ChemDraw- und Chem3D-Plug-Ins im WWW veröffentlichen.

Cherwell Scientific ist der Distributor von CS ChemOffice, ChemDraw, Chem3D, ChemFinder und ChemInfo, den Warenzeichen von CambridgeSoft Corporation.

Weitere Informationen über Cherwell Scientific und unsere Produkte finden Sie auf unserer Web-Site unter http://www.cherwell.com

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  Telefax 069 970841-41
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Leserdienst Nr. 14

Trends in der Verfahrenstechnik für mehr Wertschöpfung

Trends in der Verfahrenstechnik standen am 'ProTech forum '99' des Technologiekonzerns Bühler im Mittelpunkt. Am 10. und 11. Juni trafen sich am Hauptsitz von Bühler in Uzwil, Schweiz, über 100 Fachleute aus aller Welt zu einem intensiven Erfahrungsaustausch.

Zu Beginn des Forums fesselte der ehemalige Schweizer Botschafter in China und Bühler-Verwaltungsrat, Erwin Schurtenberger, die Teilnehmer mit einem Referat über die Aussichten in den asiatischen Märkten. Nach der Krise sei eine leichte Erholung feststellbar. 'Chancen für ein stärkeres Wirtschaftswachstum in Ostasien bestehen durchaus', sagte er, warnte aber zugleich vor zu grossem Optimismus, weil er nach wie vor auch Risiken sehe.

Aktuelle Entwicklungen aufgezeigt

Die Forums-Teilnehmer hatten danach die Möglichkeit, von verschiedenen Workshops der einzelnen Geschäftsbereiche der Bühler-Division ProTech zu profitieren. Die Division ProTech hat sich auf Prozesstechnologie in der chemischen Verfahrenstechnik spezialisiert. Eigene Referenten und Experten aus den einzelnen Branchen vermittelten ihr Know-how und zeigten aktuelle Entwicklungen auf.

Mit Demonstrationen verdeutlicht

Diskutiert wurden Trends im Bereich der Verfahrenstechnologie für Vermahlungs- und Dispergierverfahren für Druckfarben, für die thermische Kunststoffveredelung, für die Granulation und Extrusion von Zusatzstoffen für die Chemie und weiteren Feinchemikalien, für die mechanische Schüttgutförderung sowie für Nahinfrarotsysteme, die für Analysen in Labor und Betrieb verwendet werden. Im Bühler-Labor wurden zudem Versuche gemacht und Demonstrationen organisiert, welche neue Möglichkeiten aufzeigten und die Entwicklungen verdeutlichten, die für die Zukunft eine höhere Wertschöpfung ermöglichen.

Innovation für den Digitaldruck

Auf Interesse stiess beispielsweise die Technologie von Bühler für Druckfarben, die sich für den Digitaldruck eignen, der in den kommenden Jahren weitere Rationalisierungen ermöglichen wird. Besonderes Augenmerk wurde auf die Prozesse zur Veredelung von PET-Granulat für Getränkeflaschen geworfen: Bühler hat gerade einen Auftrag für die weltweit grösste Anlage dieser Art erhalten und damit neue Massstäbe in diesem Segment geschaffen. Führende Produzenten von Gummi, zum Beispiel aus der Reifenindustrie, und von Russ orientierten über neue Entwicklungen in der Branche. Bühler-Experten gingen zudem auf die pneumatische und mechanische Förderung ein, die in fast allen Industrien eine grosse Herausforderung ist; dabei wurden individuelle Lösungen für die verschiedensten Interessen der breiten Kundschaft beleuchtet. An der Tagung zeigte sich zudem, dass die Nahinfrarottechnologie (NIR) von Bühler in den verschiedensten Bereichen für Analysen eingesetzt werden kann, um die Qualität der Endprodukte sicherzustellen.

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  CH–9240 Uzwil
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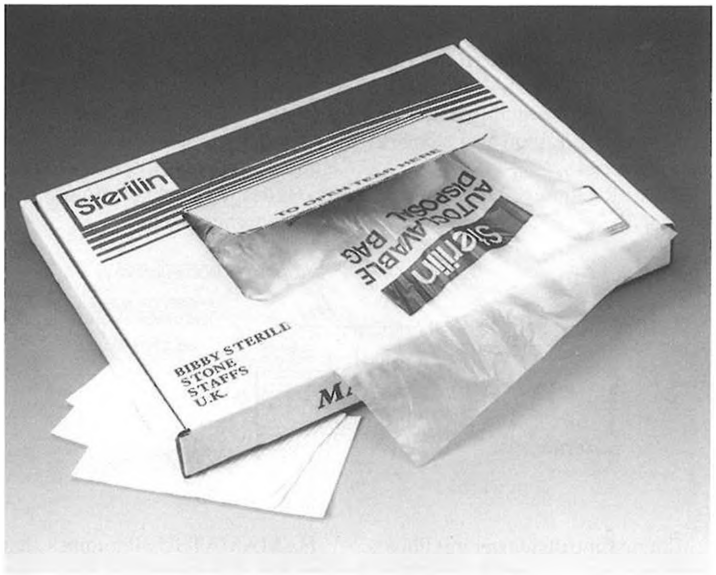
  Telefax +41 (0) 71 955 38 51
  E-Mail
  roman.salzmann@buz.buhler.ch

Leserdienst Nr. 15

Neue benutzerfreundliche Verpackung von Autoklavensäcken



Jetzt herrscht Ordnung auch beim Entsorgen. Vorbei ist das mühsame Suchen des richtigen Autoklavensackes. Jede Grösse kommt jetzt aus dem benutzerfreundlichen Dispenser und dies ohne Mehrpreis. Von Bibby-Sterilin gibt es neu die Autoklavensäcke, wie Sie es von den Taschentüchern her gewohnt sind: einfache Entnahme durch Herauszupfen. Es sind je Entsorgungstemperatur von 131 bzw. 134°C fünf verschiedene Grössen erhältlich.

- IG
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  Räffelstrasse 32
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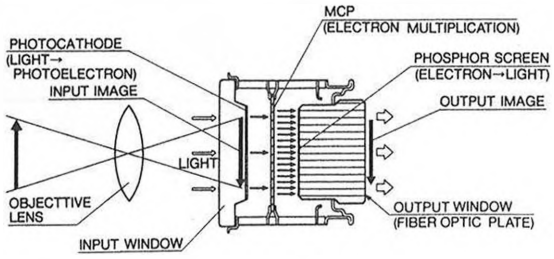
Leserdienst Nr. 16

Elektron-Bombardement CCD (Restlichtverstärker-Kameras)

Schon lange haben CCD-Bildsensoren die guten alten Aufnahmeröhren vom Markt verdrängt und haben sich sogar in Consumer-Anwendungen durchgesetzt. Für einige Anwendungen jedoch genügt die Empfindlichkeit der heutigen CCDs nicht und man ist gezwungen, das zu detektierende Licht, sprich Bild, vor dem CCD zu verstärken. Hierzu verwendet man mehrheitlich sogenannte Bild- oder auch Restlichtverstärker. Die sind uns allen bestens aus dem Golfkrieg bekannt, als CNN uns stundenlang die grünlichen Nachtaufnahmen der Beschiessung Iraks in die guten Stuben zauberte.

Diese Restlichtverstärker bestehen aus:



Einem Eintrittsfenster mit Photocathode, diese wandelt die Photonen in Elektronen, die dann auf einem 'Microchannelplate' fallen und durch diese Mikro-Kanäle Bildpunkt um Bildpunkt verstärkt werden. Die Elektronen-Pakete werden dann auf eine Phosphor-Schicht beschleunigt und in grüne Lichtpunkte umgewandelt. Diese werden dann durch die Fiberoptikplatte transportiert und an der Oberfläche/Grenzfläche sichtbar gemacht. Dort wird das Bild durch eine gewöhnliche CCD-Kamera aufgenommen, gesendet, gespeichert oder auf einem Monitor angezeigt.

Dieser Prozess hat den Nachteil, dass die Mikrokanalplatte aus lauter 'Röhrchen' besteht, und somit ist ein recht grosser Anteil der Fläche des Bildes 'versteckt', bedingt durch die 'Röhrchen-Wände'.

HAMAMATSU Photonics hat nun den Microchannel Plate, die Phosophorschicht und die Fiberoptikplatte durch einen Frametransfer-CCD-Chip ersetzt.

Die Verstärkung wird durch die hohe Beschleunigung der Photoelektronen in den CCD-Chip erreicht. Der CCD sieht somit nicht Licht, sondern das Signal wird durch die ins Silizium eingedrungenen Elektronen entsprechender kinetischer Energie gebildet. (Elektron-Bombardement) Das Bild wird dadurch um einen Faktor 600 verstärkt. Dabei handelt es sich um das volle Bild ohne Verluste, und es steht bereits in der Kamera elektrisch zur Verfügung, um mit einer normalen TV-Ausleserate ausgelesen zu werden.

Mit diesem EB-CCD können darum sehr kompakte Restlichtverstärker-Kameras realisiert werden, die ihren Einsatz in der Biologie, Analytik und Medizin finden.

- HAMAMATSU Photonics
  Richtersmattweg 6a
  CH–3054 Schüpfen
  Telefon 031 879 70 70
  Telefax 031 879 18 74

Leserdienst Nr. 17

Die Vorteile der Quarzglas-Tauchheizer

Maximale Energieausnützung durch Infrarotstrahlung und Wärmeleitung (das Hüllrohr aus Quarzglas ist infrarotdurchlässig und ermöglicht einen besonders guten Wärmeübergang). **Temperaturbeständigkeit** – da Quarzglas praktisch keine Wärmeausdehnung hat, sind derartige Tauchheizer besonders wärmewechselbeständig. **Säurefestigkeit** – Quarzglas-Tauchheizer sind beständig gegen Säuren (ausser Phosphorsäure oberhalb 300 °C und Flusssäure). Sie eignen sich deshalb besonders gut zur direkten Erwärmung von Säuren. **Elektrische Sicherheit** – das Hüllrohr aus Quarzglas ist ein hervorragender elektrischer Isolator – sicherer Berührungsschutz; optimale elektrische Sicherheit durch Erdung des Innenraumes. Die Tauchheizer entsprechen der EG-Richtlinie 89/336/EWG und der EG-Richtlinie 73/23/EWG. Alle Tauchheizer werden mit einer 1,50 m langen Silicon-Anschlussleitung und SEV-Stecker geliefert. Sie sind für 230 V ausgelegt. Sonderanfertigungen bezüglich Formgebung und elektrischer Leistung sind möglich.

- WISAG
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  CH–8057 Zürich
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Leserdienst Nr. 18

Leserdienst 'CHIMIA-REPORT'

CHIMIA-Leserdienst Heft 7·8/99

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