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Herbstversammlung 1995 / Assemblée d'automne 1995
20. Oktober 1995 / 20 octobre 1995

20. Oktober 1995 / 20 octobre 1995
Chemische Institute, Universität Bern
Instituts de chimie, Université de Berne
Freiestrasse 3, 3012 Bern

09.00 Eröffnung/Cérémonie d'ouverture
Prof. ***A. von Zelewsky***
Hörsaal/Auditoire UG 113

Vorträge der *Werner* Preisträger 1995
Conférences des lauréats du prix *Werner* 1995

Andreas Manz
SmithKline Beecham Chair of Analytical Chemistry
Department of Chemistry, Imperial College of Science, London
What Can Chips Technology Offer for Next Century's Chemistry and Life Sciences?
Abstract W1

Claude Piguet
Département de chimie minérale, analytique et appliquée, Université de Genève
Supramolecular Lanthanide Building Blocks for Organized Luminescent Materials
Abstract W2

Informationen:

Keine Anmeldung erforderlich, der Eintritt ist frei.

Studierende, die Mitglied der NSCG sind, erhalten folgende Reisekosten zurückerstattet: Bahnbillet nach Bern, 2. Kl., ½Tax (Anreise aus dem Ausland: Rückerstattung der Reisekosten ab Schweizer Grenze). Das Bahnbillet ist dem Rückerstattungsantrag beizulegen. Der Rückerstattungsantrag ist unter Angabe der Arbeits- und Privatadresse, des Bank- oder PC-Kontos sowie womöglich Beilage eines Einzahlungsscheines beim Sekretariat für Weiterbildung und Symposien der NSCG, Frau *B. Köchli*, Institut für organische Chemie, Universität Bern, Freiestrasse 3, CH–3012 Bern, einzureichen.

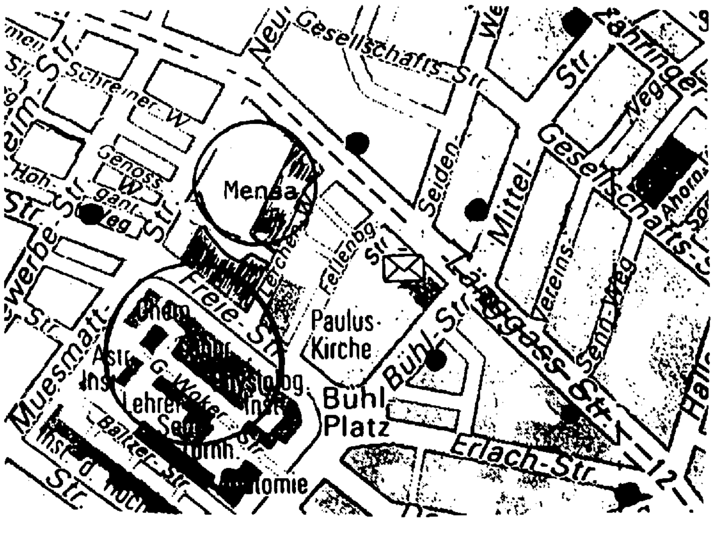
Informations:

Pas d'inscription, l'entrée est gratuite.

Les étudiants qui sont membre de la NSSC peuvent demander un remboursement des frais de voyage. Billet de train Berne et retour, 2e classe, ½prix (pour des membres qui vienent de l'étranger, les frais de voyage à partir de la frontière suisse sont remboursés). Le billet doit être joint à la demande de remboursement. Veuillez indiquer l'adresse du lieu de travail et privée, le compte bancaire ou postal et joindre, si possible, un bulletin de versement. La demande est à adresser au Secrétariat de formation continue et des congrès de la NSSC, Mme *B. Köchli*, Institut de chimie organique, Université de Berne, Freiestrasse 3, CH–3012 Berne.

Lunch:

- Cafeteria Sousol
- Mensa Unitobler (2 Minuten Fussweg, 2 minutes de marche)
- Restaurants



CHIMIA 49 (1995) Nr. 7/8 (Juli/August)

Programm der Herbsttagung
Programme de l'assemblée d'automne

09.00 Eröffnung/Céremonie d'ouverture
Vorträge der *Werner* Preisträger 1995
Conférences des lauréats du prix *Werner* 1995

Analytische Chemie/Chimie analytique
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- **Computerunterstützte Chemie/Chimie informatique**
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- **Anorganische Chemie/Chimie minérale et de coordination**
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Analytische Chemie
Chimie analytique

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Vorträge/Conférences:

10.30–11.30 ***R. Zenobi**, E. Pretsch, R. Schwarzenbach*
Laboratorium für Organische Chemie, ETH-Zürich/EAWAG Dübendorf
Das Kompetenzzentrum für Analytische Chemie an der ETH-Zürich
Abstract 0

11.40–12.00 ***S.R. Müller**, M. Berg, R.P. Schwarzenbach*
EAWAG Dübendorf/Eidg. Technische Hochschule, Dübendorf
Analytik von Atrazin und seinen Metaboliten in Regenwasser, Grundwasser und Oberflächengewässern
Abstract 1

12.00–12.20 ***R. Falter**, H.F. Schöler*
Institut für Umwelt-Geochemie, Universität Heidelberg
Entwicklung einer neuen HPLC-UV-PCO-CVA-AS-Methode zur Quecksilberspeziation in verschiedenen Matrices
Abstract 2

12.20–12.40 ***G. Sabbioni**, O. Sepai*
Institut für Pharmakologie und Toxikologie, Universität Würzburg
Biomonitoring of Workers Exposed to Arylamines and Isocyanates
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Chimie thérapeutique

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10.20–10.40 ***C. Bisang**, C. Weber, J.A. Robinson*
Institut für organische Chemie, Universität Zürich
Stabilization of β-Turn Conformations in the NPNA-Repeat Motif of a Synthetic Malaria Vaccine
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10.40–11.05 ***R. Sedrani**, S. Cottens, T. Fehr, J. Kallen, W. Schuler, M. Walkinshaw,*
Sandoz Pharma AG, Preclinical Research, Basel
Probing the Role of the Triene and Cyclohexyl Moieties in the Immunosuppressive Activity of Rapamycin
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11.05–11.25 *Q. Branca, R. Jakob-Røtne, R. Kettler,* ***S. Röver****, M. Scalone*
F. Hoffmann-La Roche AG, PRPN, Basel
Design and Synthesis of Novel and Potent Monoamine Oxidase Inhibitors
Abstract 30

11.25–12.00 ***J. Zimmermann****, D. Fabbro, H. Mett, M. Müller, U. Regenass, Th. Meyer*
Ciba-Geigy, Oncology-Research, Basel
Phenylamino-Pyrimidines – A New Class of Highly Selective Kinase-Inhibitors
Abstract 31

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14.00–14.20 ***U. Obst****, F. Diederich, L. Weber, D.W. Banner*
Laboratorium für Organische Chemie, ETH-Zürich/F. Hoffmann-La Roche AG, Präklinische Forschung, Basel
De Novo Design of Novel Nonpeptidic Thrombin Inhibitors
Abstract 32

14.20–14:40 ***S. Cottens****, A. Enz, H. Jundt, C. Rufener*
Sandoz Pharma AG, Basel
Synthesis and Anticholinesterase Activity of Some New Fluoroalkylarylketones
Abstract 33

14.40–15.20 ***H. Rüeger****, J. Maibaum, V. Rasetti, N.C. Cohen, R. Göschke, R. Mah, J. Rahuel, M. Grütter, F. Cumin, J. Wood*
Ciba-Geigy AG, Pharmaceutical Division, Basel
Design and Synthesis of Novel Potent, Non-Peptide and Orally Active Renin Inhibitors
Abstract 34

15.20–15.40 ***S. Altmann****, A. Labhardt, M. Billeter, K. Wüthrich, W. Leupin*
F. Hoffmann-La Roche AG, Structural Analysis and Gene Technologies, Basel/Institut für Molekularbiologie und Biophysik ETH-Hönggerberg, Zürich
NMR Studies of DNA Duplexes Stabilized by Different Synthetic Linkers
Abstract 35

15.40–16.00 ***R. Hochstrasser****, C. Strupp, W. Leupin*
Department of Biophysical Chemistry, Biocenter, Basel/Institut für physikalische Chemie, Universität Basel
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Chemische Forschung
Recherche chimique

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10.20–10.40 ***O. Loiseleur****, A. Pfaltz*
Institut für organische Chemie, Universität Basel
Chiral Phosphinodihydrooxazoles in Asymmetric Catalysis: *Heck* Type Reactions
Abstract 40

10.40–11.00 *W. Oppolzer,* ***J. De Brabander****, E. Walther, G. Bernardinelli*
Département de chimie organique, Université de Genève
Asymmetric Synthesis of (–)-Denticulatins A and B *via* Group-Selective Aldolization of a *Meso* Dialdehyde with a Chiral *N*-Propionylsultam
Abstract 41

11.00–11.20 *D. Gala , T.M. Chan,* ***I. Mergelsberg***
Werthenstein Chemie AG, Schachen/Schering Plough Research Institute, Kenilworth
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Abstract 42

11.20–11.40 *M. Juch,* ***P. Rüedi***
Organisch-chemisches Institut, Universität Zürich
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Abstract 43

11.40–12.00 ***G. Thoma****, F. Schwarzenbach, R.O. Duthaler*
Ciba, Central Research Laboratories, Basel
Synthesis of a Sialyl *Lewis* x Mimic with Fixed Carboxylic Acid Group – Chemical Approach towards the Elucidation of the Bioactive Conformation of Sialyl *Lewis* x
Abstract 44

12.00–12.20 *D. Amurrio, G. Anderson,* ***K. Khan****, E.P. Kündig, A. Quattropani*
Département de chimie organique, Université de Genève
New Asymmetric Approaches to Alicyclic Ring Systems from Tricarbonyl Chromium Arene Complexes
Abstract 45

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10.20–10.40 ***H. Zipse****, L.-H. Wang*
Institut für organische Chemie, TU Berlin
Catalysts for Ester Aminolysis in Apolar Solution – Can Catalysts Be Designed from Scratch?
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10.40–11.00 ***L. Weber****, S. Wallbaum, C. Broger, K. Gubernator*
F. Hoffmann-La Roche Ltd., Preclinical Research, Basel
Compound Libraries from Parallel Chemistry
Abstract 47

11.00–11.20 ***P. Waldmeier****, D. Obrecht, A. Trzeciak, K. Müller*
F. Hoffmann-La Roche AG, Pharma Research, Basel
Hochsubstituierte Xanthentemplate zur Synthese zyklischer, β-Turn-stabilisierter Tetrapeptidbibliotheken
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11.20–11.40 ***C.B. Bucher****, H. Heimgartner*
Organisch-chemisches Institut, Universität Zürich
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Abstract 49

11.40–12.00 ***C. Wyss****, B. Giese, M. Neuburger, S. Sauer, M. Zehnder*
Institut für organische Chemie, Universität Basel
Photochemische Synthese von cyclischen Aminosäuren
Abstract 50

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14.10–14.30 ***T. Bourquard****, M. Zahouily, P. Renaud*
Institut de chimie organique, Université de Fribourg
Control of the Diastereoselectivity of the Allylation and Deuteration of 2-Hydroxyalkyl Aryl Sulfoxides
Abstract 51

14.30–14.50 ***G. Jaeschke****, D. Seebach*
Laboratorium für Organische Chemie, ETH-Zürich
Hoch enantioselektive Öffnung cyclischer *meso*-Anhydride zu Halbestern mit Ti-TADDOLaten
Abstract 52

14.50–15.10 ***J. Maynollo****, M. Puchberger, B. Kräutler*
Institut für organische Chemie, Universität Innsbruck
[4+2]-Cycloaddition – Ein Zugang zu hochsymmetrischen Sechsfachadditionsprodukten des Fullerens C_{60}
Abstract 53

15.10–15.30 ***T. Wirth***
Institut für organische Chemie, Universität Basel
Stereoselektive Selenenylierungen aromatischer Alkene
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15.30–15.50 ***V. Helbling****, R. Keese*
Institut für organische Chemie, Universität Bern
Trans-Bicyclo[3.3.0]octane
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14.10–14.30 ***M. Bolli****, C. Leumann*
Institut für organische Chemie, Universität Bern
Bicyclo-DNS: ein Nucleinsäure-Analogon mit aussergewöhnlichen Paarungseigenschaften
Abstract 56

14.30–14.50 ***Th. Koch****, J.-L. Reymond, R.A. Lerner*
Departments of Molecular Biology and Chemistry, The Scripps Research Institute, La Jolla
Katalyse von Aldolreaktionen durch monoclonale Antikörper
Abstract 57

14.50–15.10 *S. Bronco, G. Consiglio,* ***M. Sperrle***
Laboratorium für Technische Chemie, ETH-Zürich
Enantioselective Co-Oligomerisation and Copolymerisation of Propene with Carbon Monoxide
Abstract 58

15.10–15.30 ***U. Diederichsen****, H. Schmitt*
Institut für organische Chemie & Biochemie, TU München
Lineare Paarungskomplexe einer Alanyl- oder Homoalanyl-PNA
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Vorträge/Conférences:

Vormittag/Le matin: Chairman: *S. Leutwyler*

10.20–10.40 ***M. Aeschlimann**, M. Bauer, S. Pawlik*
Laboratorium für Technische Chemie, ETH-Zürich
Femtosekunden-Dynamik von Oberflächenprozessen
Abstract 85

10.40–11.00 ***Y. Georgiadou**, E. Oliveros, A.M. Braun*
Engler-Bunte-Institut, Umweltmesstechnik, Universität Karlsruhe
Steady-state Detection of the Luminescence of Singlet Oxygen ($O_2(^1\Delta_g)$) in the Near-infrared: a New Equipment for Measurements in Aqueous Media
Abstract 86

11.00–11.20 ***M. Eschle**, J. Moser, M. Graetzel*
Institut de Chimie physique, EPFL, Lausanne
Triplet States of 1,4-Diketo-pyrrolo[3,4-*c*]pyrroles (DPP)
Abstract 87

11.30–11.50 ***A. Henseler**, E. Vauthey*
Institut für physikalische Chemie, Universität Freiburg
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11.50–12.10 *G. Calzaferri, R. Imhof, **C. Marcolli***
Institut für anorganische, analytische und physikalische Chemie, Universität Bern
Vibrations of Monosubstituted Octasileasesquioxanes
Abstract 89

12.10–12.30 ***A. Inauen**, S. Leutwyler*
Institut für anorganische, analytische und physikalische Chemie, Universität Bern
Chiral Discrimination in Gas-Phase Pair Complexes
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Postersession/Session des posters: Abstracts 91–104:
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Vorträge/Conférences Abstracts 105–109:
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14.10–15.50 *Hörsaal/Auditoire S 481*

Postersession/Session des posters: Abstracts 110–114:
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Nachmittag/L'après-midi: Chairman: *J. Weber*

14.10–14.30 *V.G. Malkin, O. Malkin, **G. Steinebrunner**, H. Huber*
Institute of Inorganic Chemistry, SAV, Bratislava
Institut für physikalische Chemie, Universität Basel
Solvent Effect on the NMR Chemical Shieldings in Water Calculated by Molecular Dynamics and Density Functional Theory
Abstract 105

14.30–14.50 ***J. Mareda***
Département de chimie organique, Université de Genève
Ab initio Investigation of the $C_7H_{11}^+$ Potential Energy Surface
Abstract 106

14.50–15.10 ***T.A. Wesolowski**, J. Weber*
Département de chimie physique, Université de Genève
Applications of *Kohn-Sham* Equations with Constrained Electron Density
Abstract 107

15.10–15.30 ***A.C. Stückl**, C.A. Daul, H.U. Güdel*
Institut de chimie inorganique et analytique, Université de Fribourg/Institut für anorganische, analytische und physikalische Chemie, Universität Bern
Optical Spectra of Transition Metal Tetraoxo Compounds: A Comparison between Experiment and DFT Results
Abstract 108

15.30–15.50 ***S. Graf**, T. Brgi, S. Leutwyler, W. Klopper*
Institut für anorganische, analytische und physikalische Chemie, Universität Bern/Interdisziplinäres Projektzentrum für Supercomputing, ETH-Zürich
An *ab initio* Derived Torsional Potential Energy Surface $(H_2O)_3$
Abstract 109

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Anorganische Chemie
Chimie minérale et de coordination

Minisymposium: Small Inorganic Molecules in Biological Systems
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Minisymposium: Small Inorganic Molecules in Biological Systems

Chairman: *E. Constable*

10.30–11.10 ***H. Dalton***
Department of Biological Sciences, University of Warwick
Methane Activation by Biological Systems
Abstract 115

11.15–11.55 ***W.H. Koppenol***
Laboratorium für anorganische Chemie, ETH-Zürich
Peroxanitrite, an Inorganic Toxin
Abstract 116

12.00–12.40 ***B. Meunier***
Laboratoire de chimie de coordination du CNRS, Toulouse
Potassium Monopersulfate: a Useful Oxidant in DNA Cleavage
Abstract 117

Abstracts

W1

What can Chips Technology offer for Next Century's Chemistry and Life Sciences?

Andreas Manz,
Imperial College of Science, Technology and Medicine, Department of Chemistry, South Kensington, London SW7 2AY, U.K.

The recent developments in fabrication of microstructures have started to influence chemistry, biochemistry and microbiology in a very broad sense. This technology is based on the photolithography, etching and layer deposition used in microelectronics. Already in the 70s, researchers started to investigate the fabrication and use of microstructured for ink jet nozzles, micro optical benches, micro coolers, pressure and acceleration transducers, micro mirrors, micro mechanical light modulators, electro mechanical switches and gas chromatography. A significant increase in activities focused on chemical and biological applications can be observed in the last 5 years.

The possibility to obtain specifically designed volumes in the range of 1 mL down to 1 fL, including fluid handling and sensing may have a large variety of applications. These microstructures can be obtained as single test structure or as an array of hundreds to millions of identical structures on the same chip. Photolithographically defined areas for synthesis or activity assays, integrated components such as microelectronics, pumps, valves, spectrometers and light sources can be included into the same structure.

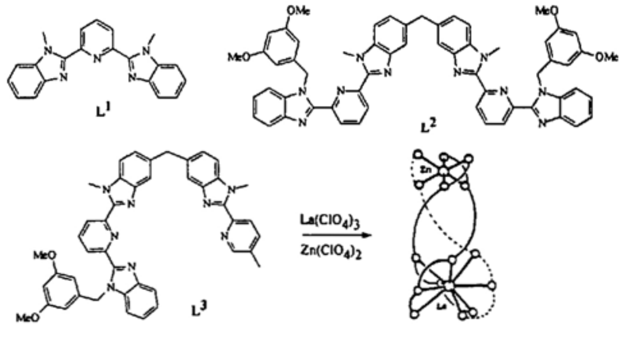
A few examples of results obtained at Ciba-Geigy in analytical chemistry, like electrophoresis and small volume mixers will be shown. They offer good quality separations and chemical reactions in only a few seconds. This is an estimated 50 to 100 times faster than a comparable conventional method, and may play an important role in keeping the analytical expenses of, e.g., pharma research reasonably low.

W2

Supramolecular Lanthanide Building Blocks for Organized Luminescent Materials

Claude Piguet
Département de Chimie Minérale, Analytique et Appliquée, Université de Genève, CH-1211 Genève 4

Ligand **L**^{1} reacts with $Ln(NO_3)_3$ to give strongly luminescent 1:1 complexes $[Ln(L^1)(NO_3)_3(CH_3OH)]$ which act as UV→vis light-converting devices (Ln=Eu, Tb). The use of $Ln(ClO_4)_3$ in acetonitrile leads to the formation of the *pseudo*-cylindrical D_3 cation $[Ln(L^1)_3]^{3+}$ where Ln(III) is coordinated by nine heterocyclic nitrogen donor atoms in a *pseudo*-tricapped trigonal prismatic arrangement. The helical wrapping of the ligands produces interstrand interactions which control the coordination sphere around the metal ion leading to a promizing size discriminating effect for the selective complexation of Ln(III). **L**^{2}, which possesses two tridentate receptors analogous to **L**^{1}, leads to self-assembled dinuclear lanthanide complexes $[Ln_2(L^2)_3]^{6+}$ allowing the detailed investigation of Tb→Eu energy transfers in the heterodinuclear complex $[EuTb(L^2)_3]^{6+}$. The level of molecular programming can be increased by the introduction of different binding units into the segmental ligand. Reaction of **L**^{3} with a mixture of 4f-block (Ln=La to Lu) and 3d-block metal ions (M=Fe, Zn) gives selectively the heterodinuclear d-f complexes $[LnM(L^3)_3]^{5+}$ in acetonitrile. A judicious choice of the pair of metal ions leads to new lanthanide materials with controlled and predetermined structural, magnetic and photophysical properties.



CHIMIA 49 (1995) Nr. 7/8 (Juli/August)

Analytische Chemie **0**

Das Kompetenzzentrum für Analytische Chemie an der ETH Zürich

Renato Zenobi und Ernö Pretsch, Laboratorium für Organische Chemie, ETH Zentrum, CH-8092 Zürich
René Schwarzenbach, EAWAG, 8600 Dübendorf

Am 20. Juni 1995 wurde das neue Kompetenzzentrum für Analytische Chemie ins Leben gerufen, das in diesem Vortrag vorgestellt werden soll. Die Zielsetzungen dieses Zentrums sind eine verbesserte Zusammenarbeit und ein intensiverer Austausch in Forschung und Unterricht unter analytisch-chemisch tätigen Forschern auf dem Platz Zürich (und darüber hinaus !). Beteiligt daran sind zur Zeit Personen von der ETH Zürich, den Forschungsanstalten des ETH-Bereiches (EMPA, EAWAG, PSI, WSL), der chemischen Industie, sowie der Universität Zürich.

Konkrete Schritte, die auch für andere Analytischen Chemiker, oder solche, die analytische Dienstleistungen in Anspruch nehmen, von Interesse sein werden, sind eingeleitet worden. Einige Beispiele seien hier angegeben:

- Organisation eine Kolloquiums Analytische Chemie an der ETHZ
- Organisation von Kursen, Workshops und Tagungen
- Aufbau einer Datenbank über analytisch-chemische know-how, Instrumente, und Dienstleistungen. Diese Datenbank soll unter anderem via elektronische Medien zugänglich gemacht werden.
- Einrichtung eines "Wilhelm Simon Fellowship" für internationalen Austausch

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Analytische Chemie **1**

Analytik von Atrazin und seinen Metaboliten in Regenwasser, Grundwasser und Oberfächengewässern

Stephan R. Müller, Michael Berg, René P. Schwarzenbach

Eidgenössische Anstalt für Wasserversorgung, Abwasserreinigung und Gewässerschutz (EAWAG)
und Eidgenössische Technische Hochschule (ETH), CH-8600 Dübendorf

Atrazin ist in der Schweiz das wichtigste Herbizid im Maisanbau (ca. 60t/Jahr). Daher wird es z.B. im Regen, in Oberflächengewässern und im Grundwasser nachgewiesen. Im Kanton Zürich tritt es z.B. in mehr als 10% der Trinkwasserfassungen mit Konzentrationen von grösser 0.1 µg/L (Toleranzwert) auf.

Es ist aber wenig bekannt über das Verhalten und das Schicksal von Atrazin und seinen Metaboliten in den verschiedenen Umweltkompartimenten. Das Hauptproblem war bisher die gleichzeitige Erfassung von Atrazin und seinen Metaboliten (z.B. Hydroxyatrazin). Uns ist es jetzt gelungen, eine analytische Methode zu entwickeln, welche die simultane Erfassung der Triazine und Ihrer Metaboliten im Spurenbereich erlaubt (Nachweisgrenze 10 ng/L).

Sie basiert auf einer Festphasenextraktion mit Carbopack B und anschliessender Trennung und Erfassung mittels RP-HPLC-DAD (interne Standarts: Propazin und Hydroxypropazin). Die Wiederfindungsraten der verschiedenen Triazine in gepikten natürlichen Wässern sind im Bereich von 82 - 100% (RSD 4%). Diese neue analytische Methode wird mit einer GC/MS Methode verglichen, welche deuteriertes Atrazin als internen Standart verwendt.

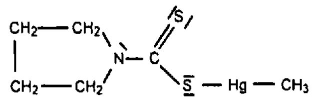
Die gemessenen Konzentrationen werden weiter mittels Modellrechnungen interpretiert und dadurch gezeigt, dass für ein besseres Verständnis der in der Umwelt ablaufenden Prozesse eine präzise Analytik notwendig ist.

Analytische Chemie **2**

Entwicklung einer neuen HPLC-UV-PCO-CVAAS-Methode zur Quecksilberspeziation in verschiedenen Matrices

R. Falter, H.F.Schöler, Insitut für Umwelt-Geochemie
Universität Heidelberg, D-69120 Heidelberg, INF 236.

Es wird eine neue instrumentelle HPLC-Methode zur Bestimmung einfach substituierter quecksilberorganischer Verbindungen vorgestellt. Mit dieser Methode können quecksilberorganische Verbindungen getrennt und verbindungsspezifisch mittels Kalt-Dampf-AAS (CVAAS) detektiert werden. Die Neuentwicklung hat gegenüber den derzeit angewandten HPLC-Methoden den Vorteil, daß eine Oxidation der komplexierten Quecksilberverbindungen mit einer on-line UV-Bestrahlung durchgeführt wird und deshalb auf eine Zuführung von Oxidationsmittel verzichtet werden kann, was ansonsten eine Peakverbreiterung verursacht. Methyl-, Ethyl-, Phenylquecksilber und Hg^{2+} können im Bereich von 4 ppb detektiert werden. Durch die Verwendung von SPDC (Natriumpyrrolidindithiocarbamat) als Komplexierungs-Reagenz ergibt sich ein weiterer Vorteil gegenüber der Verwendung von 2-Mercaptoethanol, dem bisher am häufigsten angewandten Komplexierungsreagenz. $Hg(PDC)_2$ eluiert nach den quecksilberorganischen Verbindungen als letzte Verbindung und kann somit im Gegensatz zu 2-Mercaptoethanol den Methylquecksilberpeak bei der Messung von Realproben nicht überdekken. Die neu entwickelte HPLC-PCO-UV-CVAAS-Methode (**H**igh **P**erformance **L**iquid **C**hromatography - **U**ltra **V**iolet - **P**ost **C**olumn **O**xidation - **C**old **V**apour **A**tomic **A**bsorption **S**pectrometry) zeichnet sich durch ihre einfache Handhabbarkeit und gute Reproduzierbarkeit aus. Es werden Applikationen zur Quecksilberspeziation in Böden, Sedimenten, biologischen Matrices, Erdgaskondensaten und aquatischen Proben gezeigt.



Analytische Chemie **3**

Biomonitoring of Workers Exposed to Arylamines and Isocyanates

G. Sabbioni and O. Sepai

Institut für Pharmakologie und Toxikologie, Universität Würzburg, Versbacher Str. 9, D-97078 Würzburg, Germany.

Arylamines and isocyanates are very important intermediates in the production of plastics and polyurethanes. In order to biomonitor people exposed to these chemicals we developed GC-MS methods to measure blood protein adducts adducts of over 30 arylamines. We have applied these methods to biomonitor workers from 4 factories.

In a group of 75 workers coming from a factory with a high incidence of bladder cancer we found extremely high levels (up to 200 ng/g) of hemoglobin (Hb) - adducts of 2-methylaniline (2MA) and aniline, but normal levels of other arylamines.

Two groups of workers investigated were exposed to 4,4'-methylenedianiline (MDA) and 4,4'-methylenediphenyl diisocyanate (MDI). The air levels of MDA and MDI were below detection limits. Hb-adducts of MDA were found in 94% and *N*-acetyl-MDA (AcMDA) in 61% of the MDA-workers. Hb-adducts of MDA were found in 38% of the MDI-workers. In MDI workers higher levels were found to be bound on serum albumin (SA). Urine of MDA- and MDI-workers was extracted at alkaline pH with and without preceeding acid treatment. MDA and AcMDA were found in the urine of 79% MDA-workers and 67% MDI-workers. In order to release MDA from AcMDA and possible conjugates, urine was treated under strong acidic conditions. Following this procedure MDA was detected in all MDA-workers and in 78% of the MDI-workers.

Another group of workers was exposed to 1,5-naphthalene diisocyanate (NDI). In 65% of the workers 1,5-naphthalenediamine was found in urine and SA treated with acid. No hydrolysable Hb-adducts were found.

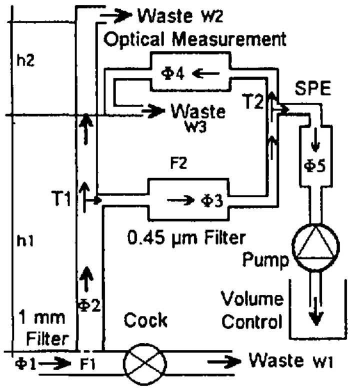
In summary for chronically exposed workers urine metabolites can be used as exposure markers. However, toxicologically more relevant data may be accessible by measurement of SA and Hb adducts.

Analytische Chemie **4**

River Water Online Filtration for Online Monitoring

N. A. Corfù, I. Gallert, M. Zehringer
Gewässerschutzamt Basel-Stadt, Hochbergerstrasse 158, CH-4019 Basel

For automated optical measurements of any kind of water it is of basic importance to have a permanent flow of filtered (0.45 µm) sample water at a certain flowrate. Our filtration system shown in the figure delivers filtered water (0.45µm) at a flowrate of 5-80 mL/min depending on the turbidity of the water and the age of filter capsule F2 [1]. The flowrate Φ1 of the native sample water is large but laminar (ca. 15 L/min). Depending on the height h1+h2 the flowrate Φ2 is regulated with the cock so that Φ2 is laminar and low. Filter F1 (grid of 1 mm) prevents the penetration of large particles into the tube leading upwards. They are transported into waste W1. With the junction T1 and the open outlet W2 the pressure difference over filter F2 [1] is regulated with the height h2. This pressure difference has to be very small and is crucial for the function of the system and the lifetime (2-6 weeks) of F2. With the age of the filter capsule Φ3 is decreasing depending on the amount of sand and suspended matter in the sample water. Therefore the capsule should be cleaned (on working days) by removing sand and by reversed water flux. In our experience no maintenance is necessary for the weekends and - normal conditions assumed - also not for 3-4 days. The system delivers at least Φ4 = 5 mL/min for continuous optical measurements. At junction T2 water for solid phase extraction (SPE) with a cartridge is diverted at Φ5 = 1 L/24 h regulated with the tight damming pump. This litre has to flow continuously and constantly over the cartridge. The system has to be absolutely tight.



[1] GelmanScience Mini Capsule Nr. 12123 (0.8 & 0.45 µm, 500 cm^2)

Analytische Chemie **5**

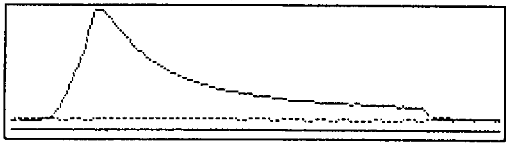
Barium in River Water by Zeeman-Graphite-Furnace-AAS

N. A. Corfù, S. Stadelmann
Gewässerschutzamt Basel-Stadt, Hochbergerstrasse 158, CH-4019 Basel

Barium (Ba) forms carbides and stable oxides. So problems arise measuring Ba in a graphite furnace. The following method works for river water:

Calibration:	Standard addition (each sample), peak height
Addition steps:	3, each 0.25 ng
Wavelength:	553.6 nm (reduced slit)
Background compensation:	Zeeman
Ashing temperature:	500° C, 10 sec
Atomisation temperature:	2800° C, 3 sec
Tube:	pyrolytic coated partition tube
Modifier:	5 µg Si preinject
Sample:	20 µL, 0.06 - 0.5 ng
Accuracy of 20 ppb Standard:	95 - 105 %
Linearity.	0.1 - 1.5 ng
Determination limit:	0.06 ng (= ¼ of 1. addition; in 20 µL: 3 ppb)

The standard addition method is to be preferred as it pays regard to the yield of atomised Ba atoms, the matrix etc. As modifier we tested Al and Si. Al alone shows absorption at 553.6 nm and in the presence of Ba the signal is a double peak. These problems don't arise with Si. To build up a layer between the pyrolytic graphite and the dried sample the modifier is preinjected. The ashing temperature is kept low at 500° C to avoid formation of fritted oxides. The signal shows a pronounced tailing. In the figure the signal corresponds to 0.8 ng Ba giving 0.56 absorption. The blank after several measurements is < 0.01 ng (< 0.01 absorption) so no memory effect is observed. The measured concentrations of several rivers (small and large) are 15-50 ppb.



Analytische Chemie **6**

Hoch-sensitive Detektion von pH-Wertänderungen mit der Methode der Photoakustik als analytisches Werkzeug

B. Schlageter[a], J. Straßburger[b], S. Pörting[b], M. C. Moreno-Bondi[c], S. E. Braslavsky[b], A. M. Braun[a] und E. Oliveros[a]
[a]Lehrstuhl für Umweltmeßtechnik, Engler-Bunte-Institut, Universität Karlsruhe; [b]MPI für Strahlenchemie, Mühlheim a.d.Ruhr;
[c]Compultense University, Madrid

In der Photochemie wird der auf Thyndall und Bell zurückgehende optoakustische Effekt schon seit geraumer Zeit zur Bestimmung von strahlungslosen Relaxationsprozessen herangezogen. In dieser Arbeit soll Laser Induced Photoacoustic Spectroscopy (LIPAS) [1] als analytisches Werkzeug eingesetzt werden, um pH-Änderungen in wässerigen Systemen zu erfassen. Die pH-Wertänderungen werden über eine selbstentwickelte Membran erfaßt, die mit einem pH-sensitiven Farbstoff überzogen und in einer Pufferlösung eingelagert ist [2]. Eine pH-Änderung der Puffer-Lösung bewirkt eine Veränderung des Absorptionsspektrums des immobilisierten Indikatorfarbstoffs und damit eine Veränderung der absorbierten Lichtenergie. Da absorbierte Lichtenergie und photoakustisches Signal proportional sind (1), kann letzteres als Maß für die pH-Änderung benutzt werden.

$$H \sim E_0 * (1-10^{-A}) \qquad (1)$$

Der Einsatz von Photoakustik in einem heterogenen System, bestehend aus pH-sensitiver Membran und Pufferlösung, ermöglicht im Vergleich zur konventionellen Spektroskopie eine enorme Steigerung der Empfindlichkeit von pH-Wertmessungen.

[1] S. E. Braslavsky, G. E. Heibel, Chem. Rev. **1992**, 92, 1381-1410

[2] G. Orellana, M. C. Moreno-Bondi, E. Segovia, M. D. Marazuela, Anal. Chem. **1992**, 64, 2210-2215

Analytische Chemie **7**

Methanol, ein alternativer Aktinometer zur Bestimmung des Photonenflusses in wässrigen Systemen unter Vakuum-Ultraviolett-Bestrahlung ?

Gernot Heit, Pierre-Yves Saugy, André M. Braun
Lehrstuhl für Umweltmeßtechnik, Engler-Bunte-Institut,
Universität Karlsruhe, 76128 Karlsruhe

Durch Vakuum-Ultraviolett (VUV)-Photolyse von wässrigen Systemen, z.B. mit Xe-Excimer-Strahlern, die eine fast monochromatische Strahlung bei 172 nm Wellenlänge emittieren, ist es möglich, darin gelöste organische Verbindungen abzubauen. Diese Abbaureaktionen werden hauptsächlich durch die bei der Wasserphotolyse entstehenden Hydroxylradikale und Wasserstoffatome initiiert.

$$H_2O + h\nu \rightarrow HO^\bullet + H^\bullet$$

Durch die räumliche Trennung von Gasentladungsraum und Elektroden ergeben sich für den Einsatz und das Design dieser Strahler sowie die Reaktorgeometrie vielfältige Alternativen, bei denen allerdings die emittierte Strahlungsleistung desselben Strahlers variieren kann. Da die Strahlungsleistung den für den Betrieb und die Konzeption von Photoreaktoren zentralen Parameter darstellt, ergibt sich die Notwendigkeit einer "in situ"-Aktinometrie.

Im Rahmen dieser Arbeit wurde Methanol als organische Modellsubstanz eingesetzt und die Abhängigkeit der Methanolabbaurate von der Reaktorgeometrie, der Verweilzeit und der Konzentration an gelöstem Sauerstoff untersucht.

$$CH_3OH + HO^\bullet \rightarrow {}^\bullet CH_2OH + H_2O$$

Die über die Methanolabbaurate ermittelten Strahlungsleistungen wurden mit denen auf physikalischem Wege ermittelten Werten verglichen.

Analytical Chemistry

8

Nitrogen determination according to Kjeldahl: A comparison of three different techniques

Cosimo A. De Caro
Mettler-Toledo AG, Analytical, Sonnenbergstr. 74, CH-8603 Schwerzenbach

Classical Kjeldahl Analysis (CKA) is a well established technique for the quantitative determination of organic nitrogen. It is based on three steps:

1) Kjeldahl digestion:
The sample (between 100 mg and 1-3 g) is strongly heated in a Kjeldahl flask with 98% sulfuric acid during 2-3 hours. Nitrogen is released from organic materials and is present in the digested solution as ammonium.

2) Distillation step:
After adding a 30% NaOH solution to the digested sample, ammonia is distilled using water steam and collected in a 2% boric acid solution.

3) Determination of ammonium by titration:
The ammonium content is determined by titration with 0.1M NaOH solution.

The CKA technique is a standard procedure for nitrogen and protein determination in food. The protein amount is determined by multiplying the nitrogen content with a factor f depending on the sample analyzed, for instance f = 6.38 for dairy products (milk, cheese, ..).

The distillation step represents an *additional error source* and an *increase of the analysis time*. This step can be avoided by direct determination of nitrogen by means of 1) an ammonia *gas-sensing electrode* or 2) by reaction of ammonium with *formaldehyde* to urotropine ($(CH_2)_6N_4$, Hexamethylenetetramine). In the first case, ammonia diffuses through the membrane of the gas-sensing electrode and leads to a change of the electrolyte pH-value inside the electrode. On the other side, ammonium reacts with formaldehyde to urotropine according to:

$$2\,(NH_4)_2SO_4 + 6\,HCHO \rightleftharpoons (CH_2)_6N_4 + 2\,H_2SO_4 + 6\,H_2O$$

The ammonium content can be finally determined by titration of sulfuric acid.

In this contribution it will be shown how these methods can be *automated* using modern automatic titrators. In particular, *accuracy*, *reproducibility* and *time-saving* of the techniques will be illustrated and compared with the results obtained with ammonium sulfate solutions as model samples for Kjeldahl digested solutions. Finally, the protein contents in dairy products determined with each technique will be compared and discussed.

9

Analytische Chemie

Isoelectric focusing of Tamm-Horsfall glycoproteins: A simple tool for recognizing recurrent calcium oxalate renal stone formers

P. Schnierle[1], and F. Hering[2]
[1] Institute of Inorganic Chemistry, University of Basel, Spitalstrasse 51, CH-4056 Basel, Switzerland; [2] Kantonsspital Baden, CH-5404 Baden, Switzerland

Tamm-Horsfall glycoprotein (THP) of healthy probands is a powerful crystal aggregation inhibitor of calcium oxalate, the most common component of renal stones, while THP of recurrent calcium oxalate renal stone formers does not show this physiological function (1, 2).

In the present study, isoelectric focusing (IEF) in ultrathin gels was used to further characterize the physicochemical properties of THPs from recurrent calcium oxalate stone formers and healthy probands.

THPs from healthy probands and a majority of recurrent calcium oxalate stone formers reveal different physicochemical properties when analyzed using IEF. The pI-values of THPs from healthy probands are approximately 3.5 while THPs from recurrent stone formers have pI values between 4.5 and 6. The two groups of THPs exhibit completely different protein patterns. This proves that the functionally different THPs are structurally different. The differences in IEF analysis allow to differentiate between THPs from healthy probands and recurrent calcium oxalate stone formers and may be used as a simple diagnostic method in the recognition of recurrent calcium oxalate stone formers.

1. Schnierle, P., Sialm, F., Seiler, H., Hering, F.,and Rutishauser, G. (1992) Urol. Res. 20: 7
2. Hess, B., Zipperle, L., and Jäger, P. (1993) Am. J. Physiol. 265: F784

ANALYTISCHE CHEMIE

10

Determination of Oligosaccharides in Soil by MALDI-TOF-MS

Schuerch Stefan, Howald Markus, Schlunegger Urs P.
Institute of Organic Chemistry, Berne

In the Valle Onsernone, Ticino, six locations were determined, which show identical climatic parameters and pedological factors, whereat the age of the fallow land is the only varying factor.

In soil samples from these locations, oligosaccharides of different size and structure have been detected. They are the product of plant and animal residue degradation.

They have been identified by matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF-MS).

On the one hand, the MALDI-TOF spectra show a sequence of linear oligosaccharides up to a molecular weight of 2000 Dalton - on the other hand, cyclic structures in the mass range up to 4000 Dalton have been detected. The MALDI-TOF spectra exhibit good reproducibility of the peak intensities. The influence of the age of fallow land to the oligosaccharide distribution have been investigated. A direct correlation of the age of fallow land to the oligosaccharide distribution has been found. Therefore, the MALDI-TOF spectra allow to estimate directly the age of fallow land.

Spectra obtained by MALDI-TOF mass spectrometry do not give any hints about the structure of the oligosaccharides. To get more information, the oligosaccharides have been exposed to enzymatic hydrolysis. The high selectivity of the enzymes allows to determine the subunits the oligosaccharides are based on, and the linkage positions and the occurrence of side chains.

Analytical Chemistry

11

Application of Two-Step Laser Mass Spectrometry (L2MS) to Polymer Additives

Qiao Zhan, Patrick R. R. Langridge-Smith, and Renato Zenobi
Professur für Analytische Chemie, Swiss Federal Institute of Technology, CH-8092 Zürich, Switzerland

Two-step laser mass spectrometry (L2MS) is a modern analytical method that features intact vaporization and efficient soft ionization of high-molecular weight compounds. It utilizes a pulsed CO_2 laser for desorption of neutral molecules, a pulsed, tunable UV laser for resonance-enhanced multiphoton postionization, and a reflectron time-of-flight mass spectrometer for mass analysis. L2MS is a highly sensitive and optically selective analysis method. It can serve as a very powerful tool for the direct chemical analysis of selected compounds in complex sample mixtures, such as tissue matrices, polymer materials, environmental samples, and geo/cosmochemical materials.

We applied L2MS to the direct chemical analysis of polymer additives. Polymers are one of the most important materials used in today's world. Most polymers are synthetic chains or cross-linked macromolecules. To improve their properties, additives protecting them against UV radiation, oxidation, weathering etc. are widely used. In this study direct L2MS experiments were carried out on various polymers to study the anti-oxidants and UV stabilizers. Because the desorption spot is very small, the spatial distribution of additives in the polymer can be investigated by L2MS, which is important to verify their effectiveness.

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ANALYTISCHE CHEMIE

An API-Quistor-Quadrupole Mass Spectrometer for Ambient-Air Analysis

Gälli Markus, Schlunegger, Urs P.
Institute of Organic Chemistry, Berne

In the 1980's an environrmental protection law was passed which set, amongst other things, limits for organic and inorganic substances in ambient air and emissions. Due to this extensive measurements were started.

Commercially available instruments have several drawbacks as low time resolution (minutes for NO_2, SO_2, O_3), narrow field of use (one instrument for each of the substances mentioned above), low selectivity (methane / non-methane hydrocarbons) and size of instrument (transportability). Therefore an instrument without these drawbacks was required.

The instrument described shows none of these. It has a wide field of use (simultaneous determination of organic and inorganic substances), a short response time (seconds), high selectivity (differentiation of the relevant substances) and a moderate size.

The instrument consist of three compartments vvhich are differentially pumped: the inlet region, held at about 1 mbar, the ionization and storage region at 10^{-5} mbar, and the quadrupole detector at 10^{-6} mbar. The air is ionized in a penning ion source, stored up to 2 seconds and then detected in the quadrupole mass filter.

13

ANALYTISCHE CHEMIE

New matrices for Matrix-Assisted Laser Desorption Ionization MS (MALDI)

Krause Joem L., Schlunegger Urs P.
Institute of Organic Chemistry, Berne

Besides the instrumental technique, the search for new matrix compounds is one of the most important fields of interest. A large number of very different matrix compounds have been investigated and published so far.

For this work we focussed on the similarities in the chemical structures of some commonly used matrices. These are compounds like 2,5-dihydroxybenzoic acid (DHB), salicylic acid, 2,4, 6-trihydroxyacetophenone, anthranilic acid and others. All of these compounds are containing a hydroxy group or an amino group in the ortho-position to a carbonyl group in a benzene ring.

All of these compounds show the possibility of a hydrogen bond between the phenolic H-atom and the carbonylic O-atom. Related to this H-bond is another interesting property, reported for salicylic acid and some others: A proton transfer under UV irradiation along the described H-bond from the phenolic group to the carbonylic O-atom yielding a dipolar metastable species. If there is a relation between the observed transition and the ability of a substance to work as a matrix, then it should be possible to find new matrix compounds.

New results will be shown with several compounds, tested as matrices for MALDI. All of these are containing the described structure element and are also showing the discussed proton transfer under UV irradiation.

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ANALYTISCHE CHEMIE

A New MALDI Tandem QUISTOR, Time-of-Flight Mass Spectrometer

Stoeckli, Markus; Kofel, Peter; Krause, Joern; Schlunegger, Urs P.
Institute of Organic Chemistry, Bern.

The combination of matrix-assisted laser desorption/ionization (MALDI) with a time-of-flight (TOF) mass spectrometer is a powerful setup to measure large molecules with high sensitivity. In the ionization process the ions are created with wide angular distribution and high initial energy deposition which leads to a relatively low mass resolution.

Ion trapping in a quadrupole ion store (QUISTOR) is an approach to decrease the velocity and spatial distribution of ions before separation in the time-of-flight analyzer. A TOF-MS with the QUISTOR located directly in the flight tube has been constructed. This setup allows experiments on ion trapping in a wide range of interest. In our instrument, the target is placed at the endcap of the QUISTOR, where the sample molecules are ionized by a short laser pulse. With a pulsed gas valve a high storage gas concentration is generated in the QUISTOR for a short time, which is essential for efficient trapping and cooling. The ions are extracted into the flight tube after storing them for 0.1 - 2 seconds.

Details on the instrument and measurement results are presented, including studies of the storage capability with different trapping parameters, extraction modes and kinetic energy of stored ions. Spectra of different substances, including polymers and proteins, are shown.

15

ANALYTISCHE CHEMIE

Analysis of Hydrophobic Peptides and Proteins using ESI- and APCI-MS

Pellascio, Bernhard; Schlunegger, Urs P.;
Institute of Organic Chemistry, Bern;
Schaller, Johann; Kaesermann , Donald;
Institute of Biochemistry, Bern.

Over the past few years electrospray ionization (ESI) and atmospheric pressure chemical ionization (APCI) have revolutionized the mass spectrometry of biomolecules. The combination of mass spectrometry with on-line separation methods is playing an increasing role in the characterization of biomolecules. Currently the combination of HPLC/MS is one of the most popular and successful separation techniques to deal with the analytical challenges of isolating and identifying biologically important compounds. These include peptides, proteins, oligosaccharides, oligonucleotides and many other compounds important in biochemical processes.

Up to the present, analyses have been performed mainly on biopolymers that are soluble in aqueous solutions. Hydrophobic peptides and proteins are in general not soluble in the solutions typically used in mass spectrometry, therefore mass spectrometric analysis of very hydrophobic species, such as membrane proteins, have seldomly been reported in the literature. The main reason for this is the incompatibility of the mass spectrometric methods with the detergents and salts which are used to retain the proteins in solution.

We present data for bacterioopsin, bacteriorhodopsin and their fragments, generated by proteolytic digestion with S. aureus protease V8 and cyanogen bromide as well as of other hydrophobic proteins, applying ESI and APCI in combination with on-line HPLC.

CHIMIA 49 (1995) Nr. 7/8 (Juli/August)

ANALYTICAL CHEMISTRY **16**

SUPERCRITICAL FLUID EXTRACTION [SFE] OF TRIAZINE HERBICIDES FROM ENVIRONMENTAL MATRICES: A POWERFUL SELECTIVE ANALYTICAL METHOD.

S. Papilloud, W.Haerdi,
Department of analytical chemistry, Sciences II, 30 Q. Ansermet
Geneva, Switzerland

Atrazine and three of its metabolites desethyl-atrazine, desethyl-desiosopropyl-2 -hydroxyatrazine and 2-hydroxyatrazine were extracted from different environmental matrices : soils, sediments and plants. Standard extraction conditions were kept similar with all different types of matrices so that comparison could be possible. The recovery of the target analytes varied drastically from one matrix to one another. An extraction performed with modified supercritical CO_2 is compared to a classical solid/liquid extraction [methanol: water (4:1)]. SFE does not require a clean-up of the extract that the classical methods usually do for any of the sample types. SFE extracts can be analysed directly. The method enables analysis of all target analytes. Recoveries are usually good, however, the natural sample have lower recoveries results than the laboratory spiked sample. The classical extraction procedure gave the best recoveries but does not allow quantitation of metabolites. Clean up of the extracts should be done, but means loss of time and recoveries.

SFE is an accurate analytical method that allows quantification of polar pesticides with high reproducibility and specificity, avoiding coextraction of important quantities of sample matrix. Such properties were seldom demonstrated for supercritical fluid extraction of polar pesticides like atrazine and its metabolites.

Analytical Chemistry **17**

Substituted β-Cyclodextrins: Chiral Stationary Phases for HPLC.

Michel Monzione, S.G. Claude, R. Tabacchi

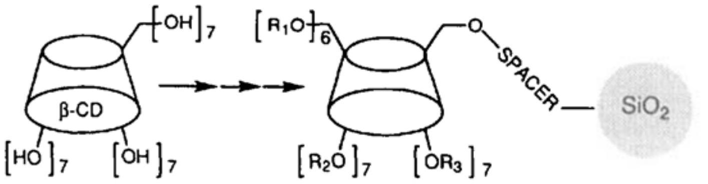
Institut de Chimie de l'Université de Neuchâtel,
Av. de Bellevaux 51, CH-2000 Neuchâtel

The separation of chiral molecules is an area of increasing importance in pharmaceutical and biochemical testing. However, this also represents one of the most difficult challenges in separation science.

The aim of this work is to design new cyclodextrin columns for the separation of enantiomers. Our approach consists in the chemical binding of the substituted β-cyclodextrin via a spacer to a silica support (LiChrospher® Si 100; 5 µm). The coverage density have to be the highest as possible.

Both the linkage and modified β-cyclodextrin must be hydrolytically stable under standard LC conditions.

The reproducibility and the low cost of the synthetic procedure are two important factors to consider to be used in a large scale.



Chimie Analytique **18**

Résolution de mélanges racémiques par GC au moyen de colonnes chirales mixtes

S. Claude, R. Tabacchi
Institut de Chimie de l'Université de Neuchâtel,
Av. de Bellevaux 51, 2000 Neuchâtel
A. Saxer
Institut für Organische Chemie der Universität Bern, Freiestr. 3, 3012 Bern

Des séparations de mélanges racémiques variés ont été réalisées au moyen de colonnes chirales renfermant respectivement du TBDMS-6-, diMe-2,3- [1], et du TBDMS-6, diAc-2,3-β cyclodextrine [2] dilués dans OV 1701.

Ces deux entités possèdent une polarité très différentes, et des énantiosélectivités souvent spécifiques. A l'exemple d'un travail précédent [3], il nous a paru intéressant de concevoir des colonnes à partir de leur mélange en proportions variées.

Les résultats obtenus débouchent sur d'enrichissantes perpectives : gain sur α et maintient des énantiosélectivités respectives, ceci pour les mélanges analysés sur les trois catégories de colonnes.

[1] A. Dietrich, B. Mass, G. Brand, V. Karl, A. Kaunziger, A Mosandl *J. High Resol. Chromatogr.* **1992,** *15*, 769
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Analytical Chemistry **19**

Simultaneous Potentiometric and Optical Investigation of Solvent Polymeric Membranes

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

Poly(vinyl chloride) (PVC) based solvent polymeric membranes are routinely used in ion-selective electrodes (ISEs) and optodes. Recently, a series of questions arose concerning the water uptake of the membrane and the leaching of its components, the deposition of proteins on its surface, and the presence of impurities in membrane components having a considerable influence on the sensor response. New kinds of membrane phases have been developed and are tested on the basis of criteria established from a detailed investigation of the membrane processes.

Here we report on *simultaneous* potentiometric and optical investigations on PVC membranes. Time-dependent concentration profiles are registered after changing the composition of the aqueous sample phase. Diffusion coefficients of different membrane components are evaluated and correlated with long-term potential drifts recorded during the experiment.

The water uptake of PVC membranes depends on the composition of the sample solution. Various new methods have been used to monitor the water diffusion through membranes, large differences being observed between membranes of PVC and of newly synthesized polyurethanes.

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Analytical Chemistry **20**

Automatic Compatibility Check of Structures and Mass Spectra

Bernhard Seebass, David Frank, Tilman Brodmeier, and Ernö Pretsch
Department of Organic Chemistry, ETHZ, CH-8092 Zürich

Computer programs for testing proposed structures against spectra have been developed. Such algorithms are useful both as a tool for automatically validating spectroscopic data and as a filter attached to structure generators for eliminating results incompatible with given spectra.

This contribution focuses on the use of mass spectrometry. Since reliable predictions of mass spectra from chemical structures are not possible as yet [1], the program developed solely examines which signals of the target spectrum *might be* generated on the basis of simple rules [2-3]. These include the simple fragmentation of one or two bonds, H rearrangements, neutral fragment losses, and combinations thereof. The measured mass spectrum is compared with predicted possible fragments and the fraction of the total ion current of unexplained peaks serves as a criterion for rejecting or accepting the constitution proposed.

The fragmentation rules used are to be optimized in order to achieve a high degree of discerning wrong constitutions. Test sets for a variety of compound classes have been prepared by using a mass spectrometric database and generating a series of isomers of the selected entries with the help of a structure generator. Thus, optimization of the comparative process can be done on the basis of training sets containing entries of identical molecular formula.

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Analytische Chemie **21**

Micellar Biooptode Membranes

E. Vaillo, U. E. Spichiger
Centre for Chemical Sensors/Biosensors and bioAnalytical Chemistry,
Department of Pharmacy, ETH Zürich,Technoparkstr. 1, CH-8005 Zürich.

Optical biosensors are mostly two-layers devices: one layer including the immobilized biocatalyst, and the second layer containing the components for chemical and physico-chemical transduction. In such cases, the recognition process of the analyte takes place in a different layer than that hosting the chemical transduction, resulting in a long diffusion pathway and a decrease in sensitivity. A promising new development in the design of biosensors is presented here, using *reverse micelles* to entrap enzymes in bulk optode membranes. The amphiphilic properties of a reverse micellar system allow to combine the specific enzyme for a neutral target analyte with a chemical transduction process in the same polymeric membrane. As a first example, urea-sensitive *reverse micelle based biooptode membranes* were obtained, combining the enzymatic hydrolysis of urea with the components of a NH_4^+-selective optode membrane. The response of the optode is based on an ion-exchange mechanism, as shown in figure 1.

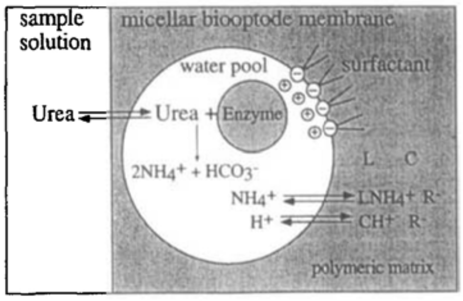


Fig.1: Scheme of the urea-sensitive *reverse micelle based biooptode membrane.*
L: NH_4^+ -selective ionophore
C: H^+ -selective chromoionophore
R^-: lipophilic anions.

Analytische Chemie **22**

Development of New Dyes for Use in Integrated Optical Sensors

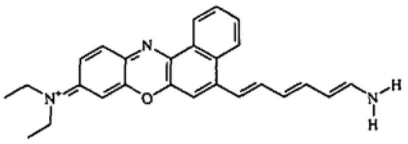
D.Citterio, S.Rásonyi, and U.E.Spichiger.
Centre for Chemical Sensors/Biosensors and bioAnalytical Chemistry,
Department of Pharmacy, ETH-Zürich, Technoparkstr. 1, CH-8005 Zürich.

Several optical sensors, based on plasticized polyvinylchloride membranes have been developed. Contrary to ion-selective electrodes, optodes incorporate pH-sensitive dyes (chromoionophores) to transduce the chemical signal into an optical signal. New measuring techniques e.g. integrated optics allow the miniaturisation of optodes and therefore extend the range of applications of optical sensors.

Using III-V semiconductor based laser diodes, the loss of efficiency is minimal at wavelengths above 800 nm. This is also the spectral region where inexpensive consumer laser diodes have their output maximum. In order to apply the chemically selective membranes in miniaturized and rather cheap sensors, the known system of bulk membrane optodes is adapted to the near-infrared (NIR) range. For this reason, pH-indicators have to be considered, fulfilling the requirements of a chromoionophore for optode membranes (proton selectivity, lipophilicity, membrane solubility, photochemical stability, etc.).

Starting from the nile blue molecule backbone, models for new chromoionophores have been derived. Using the Pariser-Parr-Pople method (PPP) followed by configuration interaction (CI), the wavelength of maximum absorbance was estimated for these dyes. The quality of the estimations was evaluated by comparison with molecules with known absorbance spectra.

In addition, several NIR-dyes (commercially available or synthesized) were tested as chromoionophores. The solubility of charged dye molecules was studied in different membrane compositions.



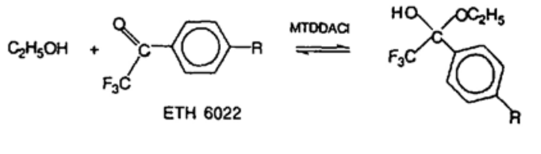
Example of a model compound derived from nile blue
λ_{max} (calculated) = 824 nm

Analytische Chemie **23**

Monitoring of Ethanol in a Bioreactor by a Chemical Sensor.

J. Spichiger, R. Wild, U.E. Spichiger*
Engineering School Wädenswil, CH-8820 Wädenswil,
* Centre for Chemical Sensors/Biosensors and bioAnalytical Chemistry, ETHZ, Technopark, CH-8005 Zürich.

An ethanol-selective chemical sensor, which was developed at the Swiss Federal Institute of Technology in Zürich (ETHZ), and its application to continuous monitoring of ethanol as produced in a bioreactor is shown. The sensing concept is based on a trifluoroacetophenone derivative exhibiting an absorbance at λ=305 nm incorporated in a bulk optode membrane. With increasing concentration of ethanol the equilibrium of the reaction is shifted to the right side and the concentration of the hemiacetale within the membrane increases. The membrane was fixed in a specially designed flow-through cuvette and operated in a commercial photometer. This arrangement was used for continuous monitoring of ethanol production in a bioreactor at the Engineering School Wädenswil (ISW). Each batch of the reactor broth showed an ethanol concentration up to 11% vol/vol after 15-20 hours. Not taking care of any interference by the sample matrix and avoiding any sample pretreatment, the partial pressure of ethanol was monitored in the vapour phase. At constant pressure and temperature, the absorbance decreased linearly with increasing partial pressure of ethanol as compared to the reference procedure.



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Analytische Chemie **24**

Enantioselective Amino Acid Analysis in Fossil Snail Shells for Dating

Monika Jost-Stauffer[1], Hanspeter Kleiber[1], Christian Schlüchter[1], Andreas Saxer[2], Veronika Meyer[2]

[1]Geologisches Institut, Universität Bern, Baltzerstrasse 1, 3012 Bern
[2]Institut für organische Chemie, Universität Bern, Freiestrasse 3, 3012 Bern

After the death of an organism its L amino acids undergo racemization because they are no longer involved in the biological turn-over process. In a calcareous matrix such as the shells of snails or bivalves this racemization runs undisturbed, under constant pH and without amino acid exchange with the environment. The degree of racemization, as found in such types of fossils, represents the geological age although dating is not straightforward due to the strong influence of temperature and biological species. The time range which can be covered by this method is identical to the Quaternary (the last ca. 1.6 million years), a geological time span which suffers from a very limited number of dating possibilities.

Enantioselective analysis of D/L amino acids in trace amounts is possible with gas chromatography on a chiral stationary phase (ChirasilVal). The protocol for shell cleaning, protein hydrolysis, calcium removal, and the necessary derivatization of the amino acids to trifluoroacetyl amides/isopropyl esters is presented. An important question is the problem of which precautions are necessary (and which ones are unnecessary) to prevent the sample contamination with L amino acids from the analyst as well as from reagents and glassware.

First results of dating Quaternary Alpine sediments by amino acid racemization will be presented.

Analytische Chemie **25**

Methode zur quantitativen Bestimmung von Gentamicin und Neomycin in Fleisch, Leber und Niere mit HPLC und Nachsäulenderivatisation

Dominik Guggisberg und Herbert Koch
Bundesamt für Veterinärwesen, Sektion Chemie, Schwarzenburgstrasse 161,
CH-3097 Liebefeld-Bern

Gentamicin und **Neomycin** gehören zur Familie der **Aminoglycosid-Antibiotika** mit breitem Wirkungsspektrum gegen grampositive und gramnegative Bakterien und werden deshalb häufig sowohl prophylaktisch wie therapeutisch in der Tiermast eingesetzt.

Eine HPLC-Methode basierend auf Nachsäulenderivatisation wird zur quantitativen Bestimmung von Gentamicin und Neomycin in Niere und Leber von Schweinen, Rindern und Kälbern beschrieben.

Die Fleischproben (je 5 g) werden homogenisiert, mit wässriger Trichloressigsäurelösung (20 ml) mittels Polytron extrahiert und bei 4'000 U/min (ca. 2900 g) zentrifugiert. Der Ueberstand wird mit 30% NaOH auf pH = 6.2 ± 0.3 justiert und mit Dikaliumhydrogenphosphat/ Natriumphosphat (pH = 6.2) auf 40 ml verdünnt. Die gelbe Lösung wird bei 18'000 U/min (ca. 37000 g) ultrazentrifugiert und anschliessend auf eine konditionierte SCX-SPEC-Disk (schwacher Kationentauscher) appliziert. Gentamicin und Neomycin werden direkt mittels einer Natriumhydroxid-Lösung in ein Autosampler-Vial eluiert und mit Salzsäure auf einen pH < 7 gestellt. Die Analyse geschieht an einer Spezialsäule (Nucleosil AB) mittels Ionenpaar-Reagentien [0.05 M Campher-10-sulfonat/Acetonitril (78/22 v/v)]. Gentamicin und Neomycin werden nach der Analyse mittels o-Phthaldialdehyd derivatisiert und im Fluoreszenzdetektor bei 340 nm, 440 nm nachgewiesen.

Die Wiederfindung für Gentamicin im Bereich 100 - 200 ppb für Leber beträgt 90%. Die Bestimmungsgrenze beträgt 50 ppb.
Die Wiederfindung für Neomycin im Bereich 100 - 200 ppb für Leber beträgt ca 85%. Die Bestimmungsgrenze liegt bei 50 ppb.

Domaine: chimie analytique **26**

Le dosage des hydrocarbures aromatiques polycycliques dans le poisson, les produits carnés et le fromage par chromatographie liquide à haute performance

Oscar Dafflon, Hansjörg Gobet et Herbert Koch
Office vétérinaire fédéral, CH-3097 Liebefeld-Berne

Jacques Olivier Bosset
Station fédérale de recherches laitières, CH-3097 Liebefeld-Berne

Key words: Polycyclic aromatic hydrocarbons, Clean-up, HPLC, Fluorescence detection, Fish, Meat products, Cheese, Smoke

Le présent travail propose un certain nombre d'améliorations et de simplifications au dosage par RP-HPLC des hydrocarbures aromatiques polycycliques de diverses denrées alimentaires, surtout en ce qui concerne la taille et le „clean-up" des échantillons, les volumes de solvants et d'éluants nécessaires ainsi que le choix du diamètre intérieur de la colonne de séparation. La détection est spectrofluorométrique à longueurs d'onde d'excitation et d'émission programmées. Les diverses modifications proposées permettent non seulement des économies de réactifs, mais encore des améliorations des limites de détection et de la résolution chromatographique de ces composés. A 4 exceptions prés, les taux de récupération déterminés par des ajouts connus („spiking" des échantillons) sont supérieurs à 80 %. La répétabilité est voisine de 10 % relatifs. La limite de détection dans les matrices considérées est de l'ordre de 1 µg/kg. L'application en routine de cette méthode, simple et rapide, à un grand nombre de denrées alimentaires provenant du commerce a montré que le fumage est l'une des principales sources de HAP (avant cuisson), l'autre origine étant probablement une contamination par l'environnement. Les HAP mis en évidence dans les produits fumés ne sont pas particulièrement toxiques et leurs teneurs toujours inférieures à 10 µg/kg. Les HAP les plus dangereux pour la santé (cancérogènes) ne se rencontrent que très rarement et généralement en teneurs inférieures à 10 µg/kg. Les HAP présents dans les fromages d'alpages sont dus à la fumée lors du chauffage des laits sur foyers ouverts. Ce sont donc d'excellents marqueurs de telles fabrications puisqu'on ne les trouve en principe pas dans les fromages fabriqués en plaine dans des cuves chauffées à la vapeur (foyers fermés).

Chimie Analytique **27**

Strontium-90 analysis by Ionic Chromatography and On-line Liquid Scintillation Counting.

Philippe G. DESMARTIN[†], Zlatan KOPAJTIC[‡] and Werner HAERDI[†]
[†]Departement of Inorganic, Analytical and Applied Chemistry, Sciences II, University of Geneva, 30, quai Ernest Ansermet, CH-1211 Geneva 4 Switzerland.
[‡]Paul Scherrer Institute, PSI, CH-5303 Würenlingen, Switzerland.

The important role of the beta emiter Strontium-90 in our environnement has been considered since the nuclear age. This long half-life isotope (28.1 years) is produced in a relatively high yield (5.8 % from Uranium-235) during the fission of heavy elements. It has been reported to be the major artificial source of internal irradiation of the human body. Its valence shell electron configuration is the same as Calcium and so this isotope is easily fixed in bones.

The classical analysis of this particular isotope required several weeks since we obtain Yttrium-90 itself also a beta emitor.

We developed a new trace analysis method by coupling High Pressure Ionic Chromotography (HPIC), to separate Strontium-90 from natural or power plant reactor water, and on-line liquid scintillation counting detector, mesuring the beta emission of low concentration Strontium-90 before Yttrium-90 is formed in a significant amount.

We report here some analysis parameters : HPIC setup, scintillation cocktail, window, efficiency of the counting, linearity and detection limits.

We were able to determine very low concentrations of Strontuim-90, dectetion limit : 6.3 10^{-12} mole/L without preconcentration (0.5 ppt from a 200 µL sample). The analysis requires only a few hours.

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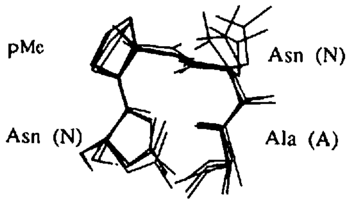
Medizinische Chemie **28**

Stabilization of β-turn Conformations in the NPNA-Repeat Motif of a Synthetic Malaria Vaccine

Christian Bisang, Christoph Weber and John A. Robinson
Institut für Organische Chemie, Universität Zürich, 8057 Zürich

Surface loops on proteins have frequently been identified as important in immune recognition and thus have become the target of peptide based vaccine design. Although anti-peptide antibodies often fail to recognize or only weakly bind the corresponding native protein, this can be explained by poor mimicry of a constrained protein epitope by a small, flexible peptide. Substitution of proline by α-methylproline (P^{Me}) in predicted β-turns has been shown to stabilize turn conformations and improve peptide antigenicity. This approach has been applied to the $(NPNA)_n$-motif of the circumsporozoite surface protein of the malaria parasite *P. falciparum*. The solution structures of $(NP^{Me}NA)_n$ peptides were studied by CD & 2D-NMR spectroscopy. Structure calculations indicate that a type-I β-turn conformation within each $NP^{Me}NA$-unit **1** is significantly stabilized in comparison to the corresponding native peptide [1].



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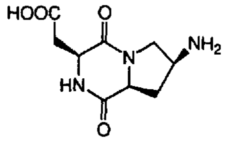

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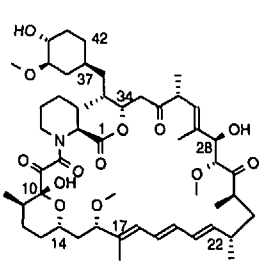
A strong reaction of a rabbit antiserum raised against $(NP^{Me}NA)_3$ to *P. falciparum* sporozoites, as tested by immunofluorescence assay, indicates that we have stabilized a native-like structure.
The NPNA-motif was also used to evaluate the β-sheet/turn inducing propensity of a novel, dipeptidic template **2**. Conformational studies on the template-constrained peptide c(template-ANPNAA) and a related disulphide-bridged octapeptide c(CANPNAAC) are compared with the results obtained for $(NP^{Me}NA)_n$.

[1] Bisang, C. et al., *J. Am. Chem. Soc.* 1995, submitted.

Medicinal Chemistry **29**

Probing the Role of the Triene and Cyclohexyl Moieties in the immunosuppressive Activity of Rapamycin

R. Sedrani, S. Cottens, T. Fehr, J. Kallen, W. Schuler, M. Walkinshaw
Preclinical Research, Sandoz Pharma AG, CH-4002, Basel



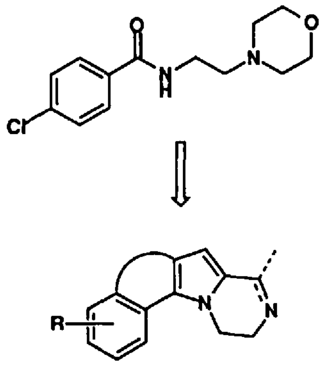
Rapamycin has attracted a lot of interest in recent years because of its potential use in the prevention of allograft rejection or in the treatment of autoimmune diseases. Like the structurally related macrolide FK506, rapamycin binds to a family of intracellular proteins, termed FK506-binding proteins (FKBPs). Despite this similarity, the mechanisms by which these natural products exert their immunosuppressive activity are clearly distinct, indicating that binding to FKBP is not sufficient for immunosuppressive activity. Indeed, whereas the complex FKBP-FK506 binds to and inhibits the serine-threonine phosphatase calcineurin, the complex FKBP-rapamycin binds to another target protein called FRAP.
We have attempted to determine the structural requirements for the immunosuppressive activity of rapamycin. Several modifications of the triene moiety have shown this subunit to be critical: hydrogenation or dihydroxylation of one or more of the double bonds give rise to derivatives which exhibit a significant loss of immunosuppressive activity, although their binding to FKBP is preserved.
Concerning the cyclohexylethyl side chain C35-C42, this moiety is commonly assumed to participate only in binding of rapamycin to FKBP and not to play a major role in the interaction of the FKBP-rapamycin complex with FRAP. We will report structural and conformational variations of this subunit which surprisingly do not affect binding to FKBP, but nevertheless result in reduced immunosuppressive activity.

Medizinische Chemie **30**

Design and synthesis of novel and potent monoamine oxidase inhibitors.

Dr. Q. Branca, Dr. R. Jakob-Røtne, Dr. R. Kettler, Dr. S. Röver, Dr. M. Scalone
F. Hoffmann-La Roche AG, PRPN Bau 15/134, 4002 Basel

RIMA's (Reversible Inhibitors of Monoamine oxidase type A) like moclobemide (AURORIX®, Roche) are potent and safe antidepressants. Based on the structure of moclobemide and some basic assumptions about electronic and steric requirements for reversible inhibitors of monoamine oxidase, new chemical entities were synthetised which potently inhibit the target enzyme. A survey on the design, synthesis and biochemical data of these new chemical entities will be given.



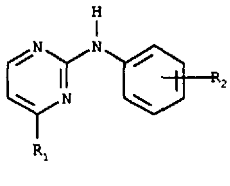
moclobemide, Aurorix®
RO-11-1163

Medizinische Chemie **31**

PHENYLAMINO-PYRIMIDINES - A NEW CLASS OF HIGHLY SELECTIVE KINASE-INHIBITORS

J. Zimmermann, D. Fabbro, H. Mett, M. Müller, U. Regenass and Th. Meyer
CIBA-GEIGY, Oncology-Research, CH-4002 Basel

Protein kinase C, a family of at least 10 distinct subtypes, plays a crucial role in signal transduction as well as in cellular proliferation, differentiation and various regulatory mechanisms. The inhibition of PKC (one subtype?) may therefore provide a new therapy for diseases such as cancer. The functional significance of the existence of multiple closely related enzymes is not yet understood. Different extracellular signals may generate a preferential activation of certain PKC isoenzymes, this information together with the differential tissue distribution and subcellular localization of different isoenzymes suggests that different isoenzymes may perform distinct function. It was now found that some compounds belonging to the class of phenylamino-pyrimidines are selective inhibitors of PKC; some of them even show a significant isoenzyme selectivity. The structure-activity relationship of this compound class for the inhibition of PKC will be discussed, and the surprisingly high selectivity against different protein kinases will be documented. The compounds are antiproliferatively active as demonstrated in the inhibition of the human bladder carcinoma cell line T24. They also show in vivo anti-tumor activity against T24 human bladder carcinoma xenografts in nude mice.



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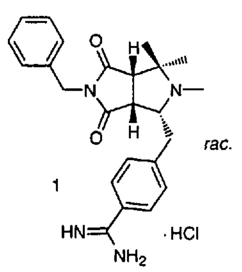
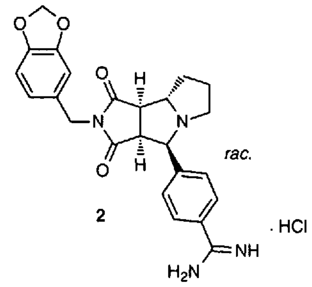
Organische Chemie / Medizinische Chemie **32**

De Novo Design of Novel Nonpeptidic Thrombin Inhibitors

U. Obst,[a)] F. Diederich,[a)]* L. Weber,[b)] D. W. Banner[b)]
[a)] Laboratorium für Organische Chemie, ETH-Zentrum, Universitätstrasse 16, CH-8092 Zürich
[b)] Pharma Division, Präklinische Forschung, F. Hoffmann-La Roche AG, CH-4002 Basel

Thrombin is a serine protease, which plays an important role in the blood coagulation process. A selective inhibition of thrombin has potential therapeutic application against thrombotic diseases. Amidine 1 with a rigid bicyclic core was designed *de novo*, as an inhibitor for this enzyme.





This compound was synthesized and tested for activity as a racemic mixture; it was found to have a K_i of 18 µM. Conformationally more restricted analogs of **1** were even more effective: the most active compound being **2** with a K_i of 90 nM. The binding mode of this compound was elucidated by X-ray crystallography of the thrombin-inhibitor complex. The inhibitor was bound in the active site in the predicted fashion, and only one enantiomer of the racemic mixture was found in the crystal.

[1] U. Obst, V. Gramlich, F. Diederich, L. Weber, D. W. Banner, *Angew. Chem.* **1995**, in press.

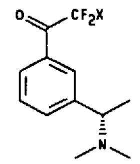
Medicinal Chemistry **33**

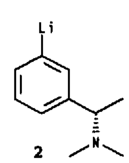
Synthesis and Anticholinesterase Activity of Some New Fluoroalkylarylketones

Sylvain Cottens, Albert Enz, Heinz Jundt and Christian Rufener

Sandoz Pharma LTD, Postfach, CH-4002 Basel

Fluoromethylketones are widely used as inhibitors of serine proteases and esterases due to their ability to form stable reaction intermediates with these enzymes. During our search for new acetylcholinesterase inhibitors as potential drugs to treat Alzheimer's disease we planned the synthesis of the fluoroketones **1a-1c**.


1a X=Cl
1b X=F
1c X=CF3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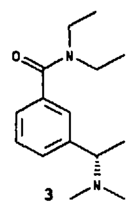
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Attempts to prepare the fluoroketones **1a-c** by reacting the aryllithium intermediate **2** with the corresponding N,N-diethylfluoroacetamides gave only low yields of the desired products. Instead the carboxamide **3** resulting from an haloform reaction was formed as the main or sole product depending on the reaction conditions. The fluoroketones **1a-c** were obtained in good yield by coupling the aryllithium reagent **2** with the ethyl ester of the fluoroacids in place of the N,N-diethylamides.
The *in-vitro* and *in-vivo* anticholinesterase activity of the fluoroketones **1a-c** and of further analogues will be presented and discussed in view of the relative acidity of the corresponding hydrates.

Medicinal Chemistry **34**

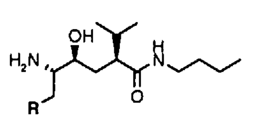
DESIGN AND SYNTHESIS OF NOVEL POTENT, NON-PEPTIDE AND ORALLY ACTIVE RENIN INHIBITORS

H. Rüeger, J. Maibaum, V. Rasetti, N.C. Cohen, R. Göschke, R. Mah, J. Rahuel, M. Grütter, F. Cumin, J. Wood.

CIBA-GEIGY Ltd. Pharmaceuticals Division, Research Department, CH-4002 Basel

The renin-angiotensin system (RAS) plays a central role in the regulation of blood pressure and in the maintenance of electrolyte balance. In an effort to identify potent small molecule renin inhibitors with good oral bioavailability and duration of action we have developed a novel structural concept for the design of such inhibitors as potential antihypertensive agents.

Our approach and the iterative optimization process with the assistance of computer-aided molecular modeling and X-ray crystallographic analyses of r-human renin-inhibitor complexes will be discussed. An intriguing common binding interaction of the new compounds with a hitherto unknown non-substrate binding site of renin has been discovered. Synthesis and SAR data for structurally distinct series of inhibitors of Type I with favourable physico-chemical properties will be presented.


Type I

Potent compounds which induced pronounced and long-lasting blood pressure lowering effects in Na-depleted marmosets will be discussed. These findings may lead to the development of a new generation of renin inhibitors which could be useful for the treatment of hypertension.

Medicinal Chemistry **35**

NMR studies of DNA duplexes stabilized by different synthetic linkers

S. Altmann[1,2], A. Labhardt[1], M. Billeter[2], K. Wüthrich[2] and W. Leupin[1]
[1)] F. Hoffmann-La Roche Ltd, Pharma Research, Structural Analysis and Gene Technologies, CH-4002 Basel, [2)] Institut für Molekularbiologie und Biophysik, ETH Hönggerberg, CH-8093 Zürich

Many physical and biochemical studies involving double-stranded DNA fragments as targets of drugs or other ligands are hampered by the low thermal stability of short (10 to 20 base pairs in length) DNA fragments. In principle, covalent linking of the two single-strands should result in fully double-stranded DNA under the experimental conditions typically employed for biophysical measurements. To further explore this possibility, three singly linked DNA nonamers, d(GTGGAATTC)-L_i-d(GAATTCCAC), were synthesized where the 3'-end of the (+)-strand is covalently connected to the 5'-end of the (-)-strand using three different linkers that have been designed by molecular modelling:

L_1 : -O-$(CH_2)_3$-PO_4-$(CH_2)_3$-O-
L_2 : -O-$(CH_2$-CH_2-$O)_4$-CH_2-CH_2-O-
L_3 : -O-$(CH_2$-CH_2-$O)_5$-CH_2-CH_2-O-

Melting temperatures were measured for the three duplexes and the non-linked nona-deoxynucleotide duplex, and the three linked duplexes were investigated in detail by nuclear magnetic resonance spectroscopy. Sequence-specific resonance assignments of the proton and phosphorous nuclei of the DNA stem were obtained following standard procedures. Distance geometry calculations with NOE-derived distance constraints were performed and the resulting structures were energy-minimized. The analysis of the nuclear magnetic resonance spectra as well as the comparison of the structures revealed that in duplex 1 the nucleotides flanking the propylene-phosphate-propylene-linker are not forming a Watson-Crick base pair, whereas in duplexes 2 and 3 the whole DNA-stem is in a B-type conformation.

Medizinische Chemie **36**

Fluorescently labeled DNA: A new tool for the characterization of DNA and DNA:ligand complexes using time-resolved fluorescence spectroscopy.

Remo Hochstrasser[1], Christian Strupp[1], Werner Leupin[2]

[1]Dept. of Biophys. Chemistry, Biocenter, Klingelbergstrasse 70, 4056 Basel; [2]Institute for Physical Chemistry, Klingelbergstrasse 80, 4056 Basel

The characterization of DNA structures and DNA:ligand complexes is essential for the understanding of many biological processes. It is also the basis for different research efforts for example in drug development. Various methods like absorption spectroscopy, NMR-spectroscopy, X-ray diffraction and electrophoresis techniques are widely used to study DNA and its interaction with ligands like proteins, antisense oligonucleotides, intercalators and minor groove binders. We now have prepared and incorporated into model deoxy-oligonucleotides some new fluorescent DNA base analogs which can replace the natural bases thymine, adenine and cytosine. Also, deoxy-oligonucleotides were labeled with fluorescent dyes at the 5' or 3' end. We will present some applications of these new markers based on fluorescence lifetime and time-resolved fluorescence depolarization experiments. These include determination of the DNA binding constant of peptides and protein domains, the determination of base-pairing in non-trivial DNA structures like hairpins and bulged oligonucleotides and the determination of distances in oligonucleotides using fluorescence resonance energy transfer (FRET).

Medicinal Chemistry **37**

Searching for the Pharmacophore. Correlation of Structure and Antimalarial Activity of Synthetic 1,2,4-Trioxanes

C.W. Jefford[1], J. Weber[2], M. Grigorov[2,3], J.M.J. Tronchet[3], W.K. Milhous[4], B.L. Robinson[5] and W. Peters[5]

[1]Department of Organic Chemistry, University of Geneva, CH-1211 Geneva 4, Switzerland
[2]Department of Physical Chemistry, University of Geneva, CH-1211 Geneva 4, Switzerland
[3]Laboratory of Pharmaceutical Chemistry, University of Geneva, CH-1211 Geneva 4, Switzerland
[4]Department of Experimental Therapeutics, WRAIR, Washington DC 20307, USA
[5]CAB International Institute of Parasitology, St. Albans, Hertfordshire AL4 OXU, UK

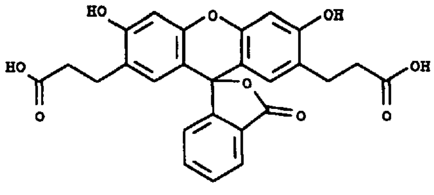
Some synthetic 1,2,4-trioxanes were examined by the *Catalyst* program with the aim of eliciting the factors responsible for antimalarial activity. Among the features offered by the program, hydrophobicity, hydrogen bonding, and polarizability were chosen since they seemed to correspond best to the properties of these neutral heterocycles. Energy-minimized molecular structures were generated for each trioxane. Next, conformational variation was promoted by the "poling" technique in order to obtain uniform coverage of the lower energy portion of conformational space. A hypothetical "pharmacophore" was then created by fitting these features and conformations to the antimalarial activities actually observed. The reliability of the hypothesis was confirmed by its ability to accurately predict the activities of a set of structurally-unrelated trioxanes. As heme is known to be the receptor in the intraerythrocytic parasite, it was also examined by the *Catalyst* program. The surface of heme was scanned for the counterparts of the features present in the active substrates which together would cause tight binding. The results showed that π-π interactions were important for docking.

Chimie thérapeutique **38**

Hydrolysis of nicotinic acid esters catalyzed by human serum albumin : a method to monitor the activation of prodrugs of carboxylic acids.

A. Salvi, J.M. Mayer, P.-A. Carrupt and B. Testa
Institut de chimie thérapeutique, Ecole de pharmacie, Université de Lausanne, CH-1015 Lausanne

A continous spectrofluorimetric assay has been developed to measure initial rate constants of hydrolysis. The method is usable even if the substrate and/or products of the reaction are not fluorescent. This procedure is based on the production of stoichiometric quantities of protons during hydrolysis. The amount of protons produced was coupled to the relative change in fluorescence at two excitation wavelengths of the pH indicator, 2',7'-bis(carboxyethyl)-5(6)-carboxyfluorescein (BCECF), added to the reaction mixture [1].



BCECF

A series of nicotinates were studied at pH 7.4 ± 0.1 and 37°C, the rate constants of chemical and enzymatic hydrolysis being determined.

The degradation of most nicotinates was accelerated by human serum albumin (HSA) by factors up to 300.

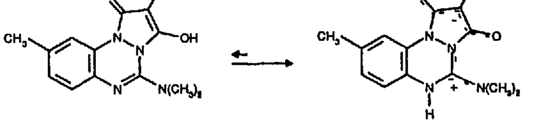
[1] T.R. Sharp and T.L. Rosenberry, *J. Biochem. Biophys. Methods*, 1982, 6, 159.

Medicinal Chemistry **39**

Physicochemical and Structural Properties of the Anti-inflammatory Drug Azapropazone

Caron G., Zhu F., Carrupt P.-A., Tsai R.-S. and Testa B.
Institut de Chimie Thérapeutique, Université de Lausanne, CH-1015 Lausanne

The non-steroidal anti-inflammatory drug (NSAID) azapropazone has been shown to display a pharmacokinetic behaviour very different from that of its structural analog phenylbutazone. This difference could be due to the zwitterionic character of azapropazone, but no evidence has been produced to date to indicate that azapropazone indeed exists as a zwitterion.



In this study we examined the physicochemical and structural properties of azapropazone. Potentiometry in various mixtures of water-methanol and water-dioxane revealed a pK_a of 6.5 for the basic function. The pH-lipophilicity profiles in *n*-octanol/water and *n*-dodecane/water were measured by centrifugal partition chromatography. In both solvent systems, a bell-shaped curve with a large plateau was found. These results suggest that azapropazone is of zwitterionic nature with a weakly basic guanidino group ($pK_a = 6.5$) and a highly acidic dicarbonylmethine group ($pK_a < 1$).

Studies of the acid-base behaviour of azapropazone using ^{13}C-NMR, IR spectroscopy and quantum mechanical calculations (AM1) also confirmed the proposed protonation scheme and demonstrated the zwitterionic nature of azapropazone, a structural feature of high importance for explaining its pharmacokinetic behaviour.

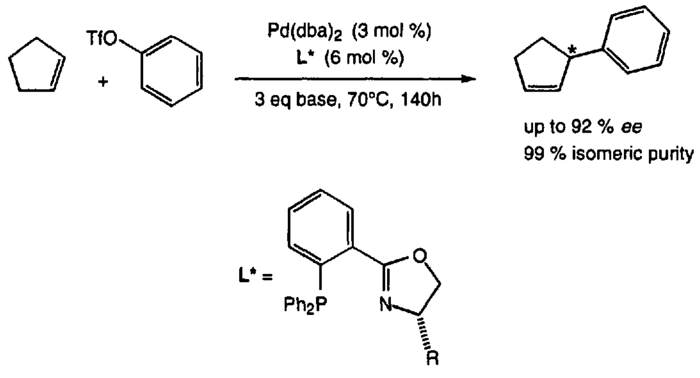
Organic Chemistry **40**

Chiral Phosphinodihydrooxazoles in Asymmetric Catalysis: Heck Type Reactions.

Olivier Loiseleur, Andreas Pfaltz*.

Institut für Organische Chemie, Universität Basel, CH-4056 Basel.

The palladium-catalyzed reaction of an aryl or vinyl triflate with an alkene is an attractive method for C-C bond formation, which has already been used in numerous syntheses of natural products. Recently, enantioselective Heck-type reactions have been developed and excellent enantioselectivities may be achieved in certain cases [1] [2]. Herein, we report on the properties of palladium complexes of chiral phosphino-oxazolines as catalysts for enantioselective arylation and alkenylation of cyclic olefins.



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[1] Reviews: a) A. de Meijere, F. E. Meyer, *Angew. Chem.* **1994**, 106, 2473; b) W. Cabri, I. Candiani, *Acc. Chem. Res.* **1995**, 28, 2.

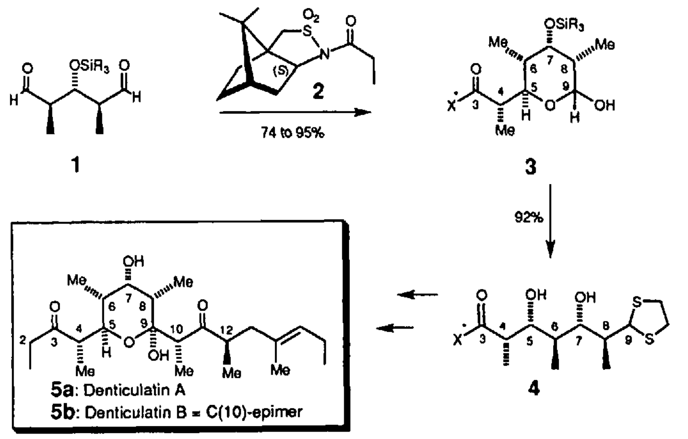
[2] a) F. Ozawa, A. Kubo, Y. Matsumoto, T. Hayashi, *Organometallics*. **1993**, 12, 4188; b) L. E. Overman, *Pure & Appl. Chem.* **1994**, 66, 1423; c) K. Kondo, M. Sodeoka, M. Mori, M. Shibasaki, *Synthesis*. 1993, 920; d) L.F. Tietze, R. Schimpf, *Angew. Chem.* **1994**, 106, 1138; *Angew. Chem. Int. Ed. Engl.* **1994**, 33, 1089.

Organische Chemie **41**

Asymmetric Synthesis of (-)-Denticulatins A and B *via* Group-Selective Aldolization of a *Meso* Dialdehyde with a Chiral *N*-Propionylsultam

W. Oppolzer, Jef De Brabander, Eric Walther and Gérald Bernardinelli
Département de Chimie Organique, Université de Genève, 1211 Genève 4

Aldolization of *meso* dialdehydes **1** with a boryl enolate obtained from chiral *N*-propionylsultam **2**, yields efficiently lactols **3** with simultaneous generation of five stereogenic centers. The enantiotopic group differentiations are <92:8 (R_3= *t*$BuMe_2$) and <95:5 (R_3=*i*Pr_3) in favor of the α,β-syn-β,γ-anti ("anti-Felkin") stereoisomer **3**. Ring opening of lactol **3** (R_3= *t*$BuMe_2$) and chain extension of dithioacetal **4** at C(3) and C(9) leads to the marine polypropionates denticulatin A and B (**5a** and **5b**). [1]



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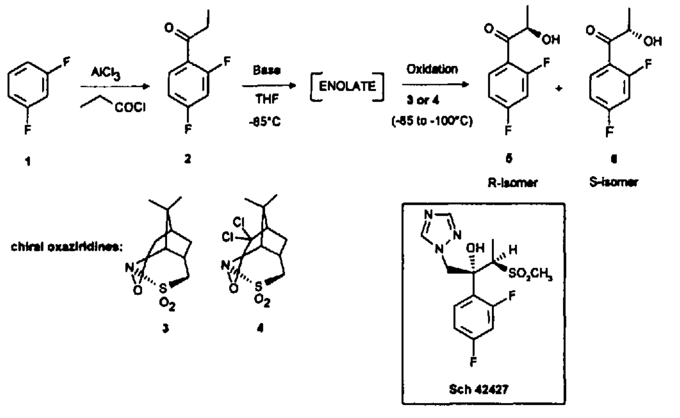
[1] W. Oppolzer, J. De Brabander, E. Walther G. Bernardinelli *Tetrahedron Lett.* **1995**, *36*, in press (issue 25).

Organic Chemistry **42**

Large Scale Chiral α-Hydroxylation of Ketones1) for a Total Chiral Synthesis of Antifungal Sch 42427

D. Gala, T.M. Chan and I. Mergelsberg
Werthenstein Chemie AG, Schachen, Switzerland
Schering Plough Research Institute, Kenilworth, N.J.,USA

The influence of different bases, solvent, temperature and nature of the chiral oxaziridine on the α-hydroxylation of ketone **2** was investigated with regard to enantioselectivity, chemical yield and suitability on pilot plant scale. The synthesis of the chiral oxaziridines **3** and **4** has been improved 2,3) for the preparation on large scale.



1) F.A. Davis and M. Serajul Haque, J. Org. Chem. **1986**, *51*, 4083.

2) I. Mergelsberg, D. Gala, D. Scherer, D.J. DiBenedetto and M. Tanner Tetreahedron Lett. **1992**, *33*, 161.

3) D. Gala, I. Mergelsberg, J. Buckley and D.J. DiBenedetto, Org. Synthesis, in print.

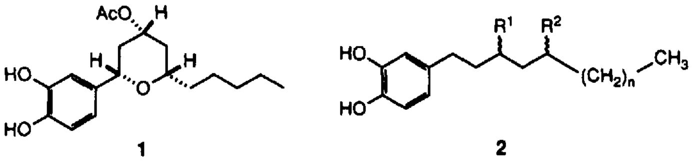
Organische Chemie **43**

Isolierung, Struktur und biologische Aktivität von neuen n-Alkyloxycatecholen aus Labiaten

Mathias Juch und Peter Rüedi

Organisch-chemisches Institut der Universität, 8057 Zürich

Die Suche nach weiteren physiologisch aktiven Inhaltsstoffen aus Labiaten nach dem Leitkriterium der antioxidativen Wirkung [1] ergab aus *Plectranthus sylvestris* eine Reihe neuer Alkylcatechole. Hauptkomponente ist die optisch aktive Verbindung **1**, als Nebenprodukte isolierten wir aus einem komplexen Gemisch die Catechole **2**. Alle Strukturen wurden mit spektroskopischen Methoden und chemischen Transformationen hergeleitet.



R^1 = oder ≠ R^2: =O, OH, H; $\Delta^{3,4}$, $\Delta^{4,5}$, etc.
n = 4,6,8, etc.

Die strukturell mit den [n]-Gingerolen verwandten Verbindungen sind *in vitro* potente Antioxidantien (in der Grössenordnung von BHA und BHT) und Lipoxygenase-Inhibitoren ($IC_{50} \leq \mu M$).

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[1] Ch. Bürgi, P. Rüedi, *Helv. Chim. Acta* **1993**, *76*, 1890.

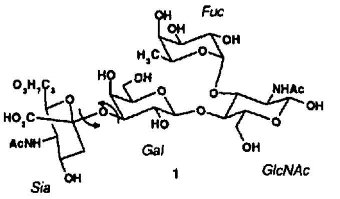
Organische Chemie

44

Synthesis of a Sialyl Lewis x Mimic with Fixed Carboxylic Acid Group -Chemical Approach towards the Elucidation of the Bioactive Conformation of Sialyl Lewis x

Gebhard Thoma, Franz Schwarzenbach and Rudolf O. Duthaler
Central Research Laboratories, CIBA, Postfach,CH-4002 BASEL

The interaction of the endothelium cell surface protein E-selectin with complex carbohydrates on leucocytes is crucially involved in the leucocyte recruitment to sites of inflammation. Control of this process is of high pharmaceutical interest. The sialyl Lewis x tetrasaccharide 1 (s Le^X) appears to be a decisive epitope of the natural E-selectin ligand. In solution the conformation of 1 is fairly rigid with the exception of the two torsion angles of the Sia-Gal linkage[1]. To develop potent inhibitors knowledge of the bioactive conformation of s Le^X is essential. We designed s Le^X analog 2 with fixed carboxylic acid function matching the prevailing solution conformation 1 to probe a potential resemblance of bioactive and preferred solution form.



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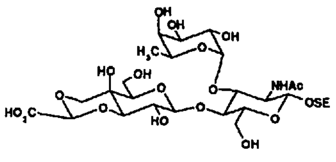

2

Compared to s Le^X 1 an enhancement of the binding of 2 to E-selectin could be expected due to entropy if bioactive and prevailing solution conformation were similar whereas a drop in activity would indicate differences. The synthesis of analog 2 and the biological results will be discussed.

[1] Ichikawa et al; *J. Am. Chem. Soc.* **1992**, *114*, 9283.

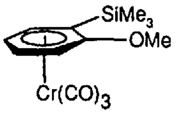
Organic Chemistry

45

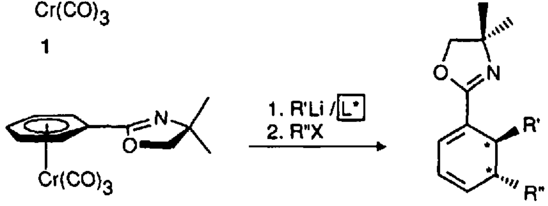
New Asymmetric Approaches to Alicyclic Ring Systems from Tricarbonyl Chromium Arene Complexes

D. Amurrio, G. Anderson, K. Khan, E. P. Kündig, and A. Quattropani
Département de Chimie Organique, Université de Genève, 1211-Genève 4

Temporary complexation of an arene to the electrophilic $Cr(CO)_3$ group opens new synthetic possibilities. Arguably the most striking transformation is the one pot conversion of the metal bound arene into stereoselectively substituted cyclohexadienes.[1] Several asymmetric modifications of this methodology were investigated. Strategies are: i) the use of a chiral auxiliary on the arene ring; ii) the use of a chiral ligand bound to the chromium; iii) the use of planar chiral complexes, and iv) the use of chiral nucleophiles. All four have been realized. In this communication we focus on the application of the nucleophile/electrophile double addition to the planar chiral arene complex 1 and present our preliminary results on reactions of chiral nucleophiles to the prochiral complex 2.



1



2

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

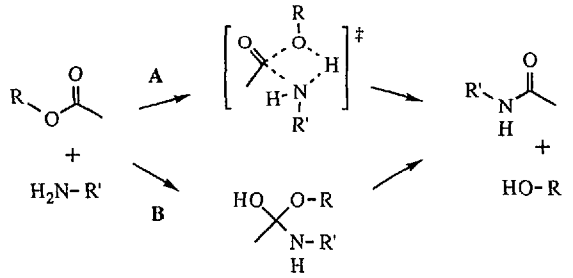
Organische Chemie

46

Catalysts for Ester Aminolysis in Apolar Solution - Can Catalysts be Designed from Scratch ?

H. Zipse* and L.-H. Wang
Inst. Org. Chemistry, TU Berlin, Str. d. 17. Juni 135, D-10623 Berlin

A series of model systems for the reaction of esters with amines has been studied with *ab initio* quantum mechanical methods. In all these model systems, two reaction pathways A and B exist:



On "direct displacement" pathway A the formation of the C-N bond and the cleavage of the C-O bond occur syncronously with proton transfer. On pathway B, addition of the amine to the C-O double bond first leads to the formation of an uncharged tetrahedral intermediate, which then cleaves the C-O bond under concomitant proton transfer in a second step. Catalysis of this reaction is possible by polyethers (electrostatic catalysis), which leaves the original reaction mechanism intact, or by pyridine derivatives (covalent catalysis) through a different reaction pathway. Experimentally determined catalytic efficiencies for various catalysts will be compared to predictions based on either quantum mechanical or force field studies.

Organische Chemie / Medizinische Chemie

47

Compound Libraries from Parallel Chemistry

L. Weber, S. Wallbaum, C. Broger, K. Gubernator
Pharma Division, Preclinical Research, F. Hoffmann-La Roche Ltd.,
4002 Basel

The key task in the initial phase of the discovery of biological effectors is to identify with the least possible synthetic effort a tightly binding ligand for a given biochemical target. Exploiting molecular diversity with combinatorial compound libraries has been proposed to more rapidly arrive at new prototype ligands. We will demonstrate here new approaches to the synthesis of compound libraries by parallel synthesis of single compounds. Dipolar cycloadditions or the Ugi four-component cascade reaction may provide diverse products in high yield in a one-step solution reaction. Thus, parallel solution reactions yield a large number of reaction products in a very short time. Determination of the biological activity of these products in a parallel bioassay provides rapid information about structure/activity relationsships.

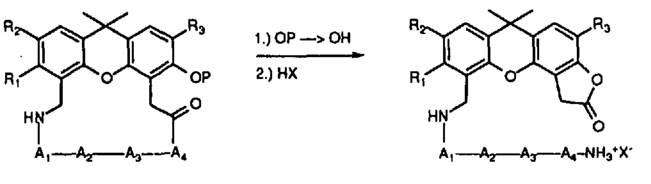
Mathematical optimisation methods like the genetic algorithm were developed to find optimal solutions for complex, multidimensional problems. We demonstrate here the combination of these efficient methods with parallel synthesis using an enzymatic assay as the biological response fitness function, thus constituting an evolutionary feedback loop with high optimising potential for combinatorial compound libraries. A genetic algorithm was applied to optimise the biological activity of compounds from parallel Ugi reactions. The method allowed the fast identification of an inhibitor of the serine protease thrombin with submicromolar binding affinity (Ki= 0.22 µM) out of a library of 160'000 possible reaction products.

Organische Chemie / Medizinische Chemie **48**

Hochsubstituierte Xanthentemplate zur Synthese zyklischer, β-Turn-stabilisierter Tetrapeptidbibliotheken

P. Waldmeier, D. Obrecht, A. Trzeciak, K. Müller
F. Hoffmann-La Roche, Pharma Research, 4002 Basel

Durch eine Folge von regioselektiven Reaktionen wurden hochsubstituierte Xanthentemplate hergestellt, welche lineare Peptide, speziell Tetrapeptide, in β-Turn Konformationen stabilisieren. Durch selektive Spaltung der Schutzgruppe P und nachfolgender säurekatalysierter, durch γ-Lakton Bildung begünstigte, selektive Amidspaltung, wird der N-Terminus des Peptides freigesetzt. Im regioselektiv geöffneten Peptid II ist es möglich, mittels Edman-Abbau die genaue Sequenz der Aminosäuren A_{1-4} zu ermitteln.



I II

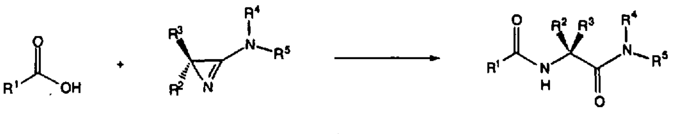
Durch die Einführung einer festphasenkompatiblen Linkergruppe (z.B. $R_{1-3} = CH_2COOH$) sind diese trizyklischen Xanthentemplate ideale Bausteine für die Generierung und biologische Prüfung zyklischer, β-Turn-stabilisierter Peptidbibliotheken an festen Trägern und in Lösung. Die selektive Ringöffnung erlaubt zudem eine eindeutige Bestimmung der Aminosäuresequenz. Diese hochsubstituierten Xanthene können auch als polyfunktionelle Template für kombinatorische Ansätze der Wirkstoffauffindung verwendet werden.

Organische Chemie **49**

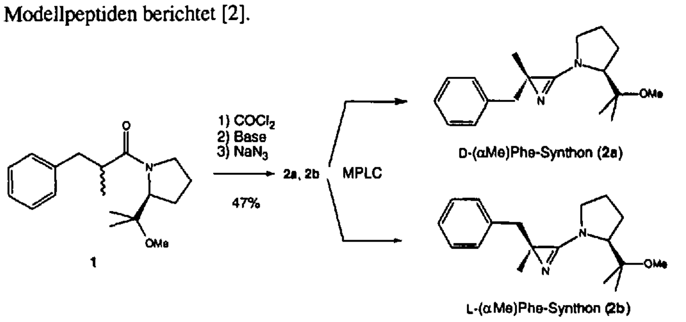
Optisch aktive 3-Amino-2*H*-azirine als Bausteine für α,α-disubstituierte α-Aminosäuren in der Peptidsynthese

Ch. B. Bucher, H. Heimgartner, Org.-chem. Institut der Universität Zürich, Winterthurerstr. 190, 8057 Zürich.

Für die Einführung von α,α-disubstituierten α-Aminosäuren in der Peptidsynthese stellen 3-Amino-2*H*-azirine ideale Bausteine dar [1]. Die Umsetzung von 3-Amino-2*H*-azirinen mit einer Peptidsäure ergibt direkt das um eine Einheit verlängerte Peptid.



Bei verschiedenen Substituenten R^2, R^3 und optisch aktivem R^1 entstehen bei der Umsetzung mit racemischen 3-Amino-2*H*-azirinen Epimerengemische. Es wird nun über die Synthese von optisch aktiven 3-Amino-2*H*-azirinen als Diastereoisomerengemische (chirale R^4R^5N-Gruppe), die Trennung der beiden Bausteine und deren getrennte Anwendung in der Synthese von Modellpeptiden berichtet [2].



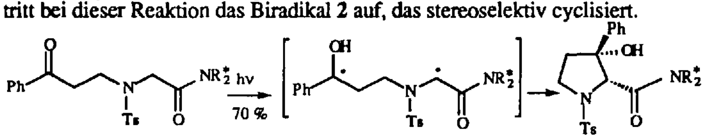
[1] H. Heimgartner, *Angew. Chem.* **1991**, *103*, 271.
[2] Ch. Bucher, A. Linden, H. Heimgartner, *Helv. Chim. Acta*, im Druck.

Organische Chemie / Medizinische Chemie **50**

Photochemische Synthese von cyclischen Aminosäuren

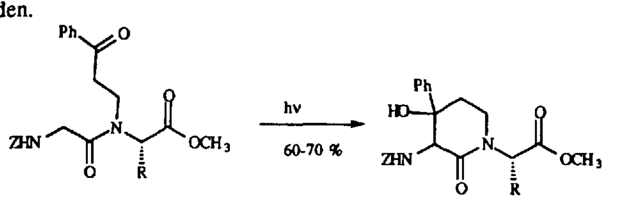
C. Wyss, B. Giese, M. Neuburger, S. Sauer und M. Zehnder
Institut für Organische Chemie, Universität Basel, St.Johanns-Ring 19, CH-4056 Basel

Die photochemische Cyclisierung des mit einem chiralen Auxiliar substituierten Glycinderivates **1** bietet einen neuen Zugang zu Prolinderivaten **3**, welche β-Schleifen in Peptiden hervorrufen können[1].Als Zwischenstufe tritt bei dieser Reaktion das Biradikal **2** auf, das stereoselektiv cyclisiert.



1 **2** **3**

Verwendete man natürliche Aminosäurereste anstelle der Tosylgruppe und des chiralen Auxiliars, konnte die Photocyclisierung direkt im Peptid durchgeführt werden.



4 **5**

So cyclisierte im Dipeptid **4** das Glycinderivat regio- und stereoselektiv in 60-70% Ausbeute zum Sechsring **5**, in dem die OH und NHZ-Substituenten *cis* angeordnet sind (NMR-Spektroskopie).Die absoluteKonfiguration soll durch Kristallstrukturanalyse aufgeklärt werden.

Diese neue Synthesemethode liefert einen Zugang zu modifizierten Oligopeptiden, die als Mimetika für biologisch aktive Peptide Anwendung finden könnten[2].

[1] P.Wessig, P. Wettstein, B. Giese, M.Neuburger, M.Zehnder, *Helv. Chim. Acta* **1994**, *77*, 829.
[2] R.M. Freidinger, D.F. Veber, D. Schwenk Perlow, *Science* **1980**, *210*, 656.

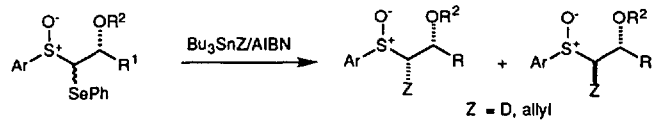
Organic Chemistry **51**

Control of the Diastereoselectivity of the Allylation and Deuteration of 2-Hydroxyalkyl Aryl Sulfoxides

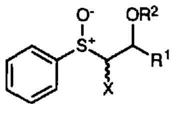
Thierry Bourquard, Mohamed Zahouily and Philippe Renaud

Institut de Chimie Organique, Université de Fribourg, CH-1700 Fribourg.

2-Hydroxyalkyl sulfoxides are easily available in diastereo- and enantiopure form. We have developed a radical procedure for the deuteration and allylation at the C(1) center in order to prepare both diastereosiomeric products.[1-3] We will discuss the influence of the two stereogenic centers on the diastereoselection.



Simple β-hydroxysulfoxides such as **1** as well as glyceraldehyde derivatives such as **2** and **3** were investigated. Moderate to very high selectivities have been obtained. The sense of the diastereoselectivity can be choosen by using appropriate hydroxy protective groups.



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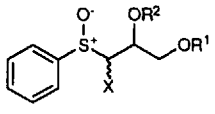

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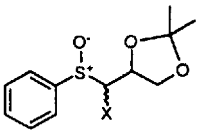


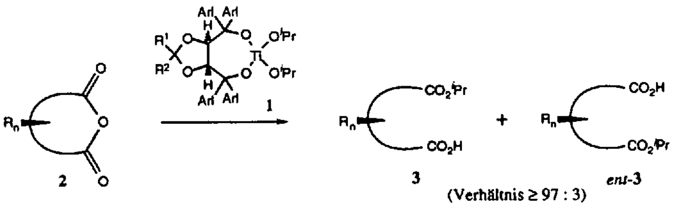
3

(1) Renaud, P.; Carrupt, P.-A.; Gerster, M.; Schenk, K. *Tetrahedron Lett.* **1994**, *35*, 1703-1706.
(2) Renaud, P.; Bourquard, T. *Tetrahedron Lett.* **1994**, *35*, 1707-1710.
(3) Renaud, P.; Bourquard, T.; Gerster, M.; Moufid, N. *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1601-1603.

Organische Chemie **52**

Hoch Enantioselektive Öffnung cyclischer *meso*-Anhydride zu Halbestern mit Ti-TADDOLaten

G. Jaeschke, D. Seebach
Laboratorium für Organische Chemie, Eidgenössische Technische Hochschule, ETH-Zentrum, Universitätstrasse 16, CH-8092 Zürich



Die *Lewis*-Säure-vermittelte Übertragung eines Alkoxid-Liganden aus der chiralen Ligandensphäre des Ti-TADDOLates **1** ermöglicht die hochenantioselektive Öffnung von cyclischen C_S-symmetrischen Anhydriden **2** zu den entsprechenden Halbestern **3** mit Enantiomerenverhältnissen bis 99 : 1. Erste Vorversuche haben gezeigt, daß auch mit $Ti(OiPr)_4$ in Gegenwart einer unterstöchiometrischen Menge an **1** eine enantioselektive Anhydridöffnung möglich ist. Die Fähigkeit zum enantioselektiven Ligandentransfer läßt **1** als eine metallorganische Alternative zu hydrolytischen Enzymen erscheinen, da wie bei diesen allgemein die Differenzierung enantiotoper funktioneller Gruppen in *meso*-Verbindungen und die Racematspaltung chiraler Substrate möglich sein sollte.

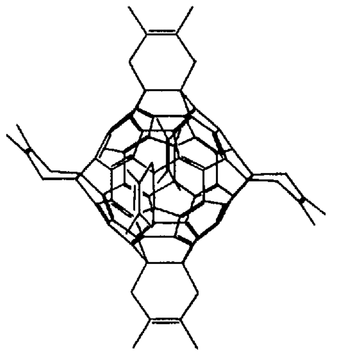
[1] D. Seebach, G. Jaeschke, Y. M. Wang, *Angew. Chem.* **1995**, zur Publikation eingereicht.

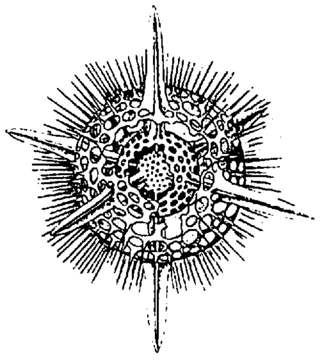
Organische Chemie **53**

[4+2]- Cycloaddition - Ein Zugang zu hochsymmetrischen Sechsfachadditionsprodukten des Fullerens C_{60}

Josef Maynollo, Michael Puchberger, Bernhard Kräutler*
Inst. f. Org. Chemie, Universität Innsbruck, Innrain 52a A-6020 Innsbruck

[4+2]- Cycloadditionen von "gewöhnlichen" Dienen an das Buckminsterfulleren C_{60} führen unter milden Bedingungen und in guten Ausbeuten zu stabilen Monoadditionsprodukten.
Die Cycloaddition von Dienen erweist sich als einfacher Zugang zu hochsymmetrischen Mehrfachaddukten mit ungewöhnlichen Symmetrieeigenschaften. Ein Vorbild für die Gerüststruktur solcher Fulleren-Additionsverbindungen sind die Skelette der Radiolarien.





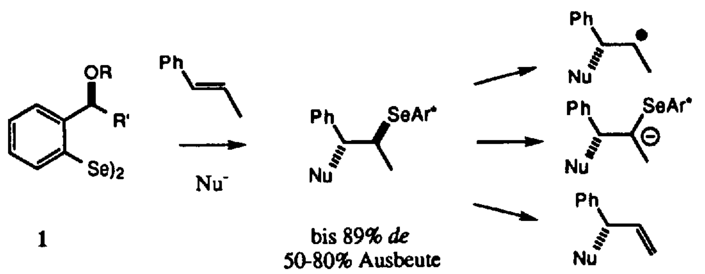
B. Kräutler, M. Puchberger, Helv. Chim. Acta 76, 1626 (1993)
B. Kräutler, J. Maynollo, Angew. Chemie 107, 69 (1995)

Organische Chemie **54**

Stereoselektive Selenenylierungen aromatischer Alkene

Thomas Wirth
Institut für Organische Chemie, Universität Basel, CH-4056 Basel

Die Entwicklung neuer Methoden zur stereoselektiven Funktionalisierung von nicht aktivierten C=C-Doppelbindungen sind herausfordernde Probleme in der organischen Synthesechemie. Chirale Selenverbindungen stellen interessante Reagenzien für solche Umsetzungen dar.
Es werden Diselenide des Typs **1** vorgestellt, die aus einfachen Startmaterialien in wenigen Syntheseschritten leicht zugänglich sind. Diese Selenverbindungen **1** können in guten Ausbeuten an Alkene addiert werden, bei aromatischen Alkenen wurden Diastereoselektivitäten von bis zu 89% *de* gefunden.



Die so erhaltenen Additionsverbindungen stellen attraktive Moleküle für weitere Umsetzungen dar. Durch die Verwendung als Radikalvorläufer steht die ganze Palette radikalischer Reaktionen zur Verfügung. Deprotonierung der Selenide in α-Position zum Selen bietet ebenso wie die oxidative Eliminierung Möglichkeiten zu weiteren Funktionalisierungen.

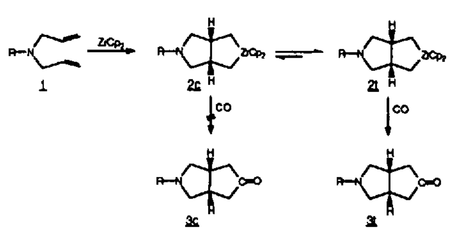
Angew. Chem. **1995**, im Druck

Organische Chemie **55**

Trans-Bicyclo[3.3.0]octane

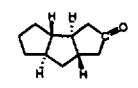
Victor Helbling, Reinhart Keese
Institut für organische. Chemie, Universität Bern, Freiestrasse 3, 3012 Bern

Im Gegensatz zu trans-Hydrindanen und cis-Bicyclo[3.3.0]octanen sind trans-Bicyclo[3.3.0]octane nur nach wenigen Verfahren zugänglich. Typische Methoden bestehen in der Zyklisierung von 1,2-trans-disubstituierten Cyclopentanen oder in der Reaktion auf der endo-Seite der Brückenkopfdoppelbindung von Bicyclo[3.3.0]octenen [1]. Negishi hat vor einiger Zeit ein Verfahren beschrieben, durch das 1,6-Heptadiene mittels Cp_2Zr-induzierter Zyklisierung mit anschliessender Carbonylierung direkt zu trans-Bicyclo[3.3.0]octan-3-on umgesetzt werden können[2].



Unsere Untersuchung dieser bemerkenswerten Stereoselektivität hat ergeben, dass diese Zyklisierung in der raschen Bildung eines cis-3-Zircona-bicyclo[3.3.0]octans 2c besteht, das zu dem thermodynamisch stabileren trans Isomeren 2t reagiert. Durch die Carbonylierung mit CO wird das thermodynamisch weniger stabile trans-Bicyclo[3.3.0]octan-3-on 3t gebildet.

Resultate zur Herstellung trizyklischer Verbindungen vom Typ 4 mit *zwei* trans-Verknüpfungen werden vorgestellt.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[1] D. Bourgin, R. Büchel, P. Gerber, R. Keese, Tetrahedron Lett. **1994**, *35*, 3267.
[2] C. Rousset, D.R. Swanson, F. Lamaty, E. Negishi, Tetrahedron Lett. **1989**, *30*, 5105.

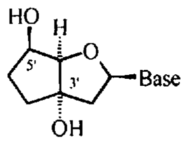
CHIMIA 49 (1995) Nr. 7/8 (Juli/August)

Organische Chemie **56**

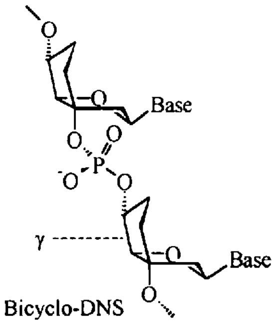
Bicyclo-DNS: ein Nucleinsäure-Analogon mit aussergewöhnlichen Paarungseigenschaften

Martin Bolli und Christian Leumann
Institut für organische Chemie, Universität Bern, CH-3012 Bern

Bicyclo-DNS ist ein konformativ fixiertes Nucleinsäure-Analogon, dessen strukturelle und biophysikalische Eigenschaften im Zusammenhang mit der Antisense und Antigene Therapie von Interesse sind [1,2].



Bicyclonucleoside



Bicyclo-DNS

Untersuchungen zur Basenpaarung dieses DNS-Analogons führten zum Resultat, dass adenin- und thyminhaltige Sequenzen nur dann stabile Duplexe bilden, wenn diese nicht nach dem Watson-Crick sondern nach dem alternativen Hoogsteen Basenpaarungsmuster erfolgen können. In guanin- und cytidinhaltigen Sequenzen ist die Watson-Crick Duplexbildung bei neutralem pH dominant. Bei pH-Werten unter 7 bilden sich äusserst stabile Triplexe.

Die Unterschiede der Basenpaarungspräferenzen vergleichsweise zu natürlicher DNS sind einzig die Folge der Änderung des Torsionswinkels γ in der repetitiven Rückgrateinheit.

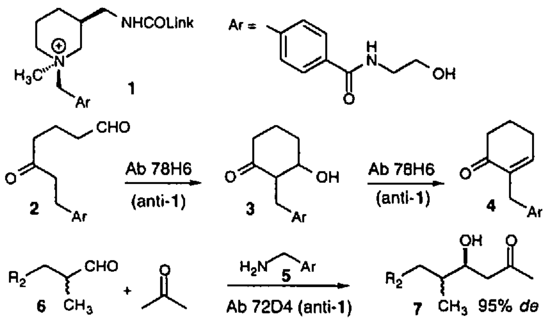
[1] M. Tarköy, M. Bolli, C. Leumann, *Helv. Chim. Acta* **1994**, *77*, 716.
[2] M. Bolli, C. Leumann, *Angew. Chemie* **1995**, *107*, 740.

Organische Chemie **57**

Katalyse von Aldolreaktionen durch monoclonale Antikörper

Thomas Koch, Jean-Louis Reymond* and Richard A. Lerner*
Departments of Molecular Biology and Chemistry, The Scripps Research Institute, 10666 North Torrey Pines Road, La Jolla, CA 92037, USA

Die Technologie der monoclonalen Antikörper ermöglicht einen schnellen und vielfältigen Einsatz von neuen Protein-Katalysatoren. Wir berichten hier von zwei Systemen, mit welchen wir unabhängig voneinander zwei verschiedene Arten von Aldolreaktionen durch den Einsatz von monoclonalen Antikörpern, welche gegen das Hapten **1** gerichtet sind, katalysieren können.



Bei der intramolekularen Aldolreaktion des Keto-Aldehyds **2** erhält man das Aldol-Produkt **3** und nachfolgend Enon **4**. Die Sequenz beinhaltet vier individuelle Reaktionsschritte von denen drei durch allgemeine Basenkatalyse mit dem Antikörper 78H6 beschleunigt werden.

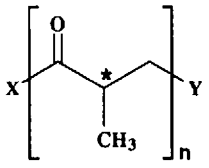
Der Antikörper 72D4 katalysiert bei Zugabe des primären Amins **5** als Cofaktor die Aldoladdition von Aceton an die Aldehyde **6**. Die Produkte **7** werden mit Selektivitäten von bis zu 95% *de* gebildet.

Organic Chemistry **58**

Enantioselective Co-Oligomerisation and Copolymerisation of Propene with Carbon Monoxide

Simona Bronco, Giambattista Consiglio and Martin Sperrle
Laboratorium für Technische Chemie, ETH-Zentrum, CH-8092 Zürich

(L-L)PdX$_2$ complexes (L-L = diphosphine ligand, X = weakly or non-coordinating anion) catalyse the dicarbonylation reaction of propene to low molecular weight diesters or to high molecular weight polyketones depending on the amount of the oxidant *e.g.*, 1,4-benzoquinone.



n = 1, X = CH_3O; Y = $COOCH_3$ 1
n = 1, X = CH_3O; Y = $COCOOCH_3$ 2
n = 1, X = CH_3OCO; Y = $COOCH_3$ 3
n = 2, X = CH_3O; Y = $COOCH_3$ 4
n = large 5

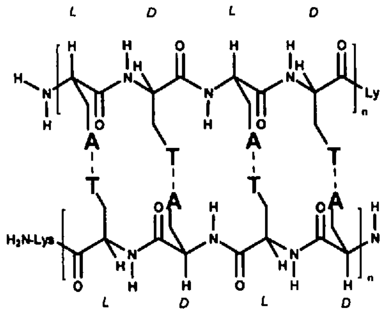
When basic ligands are used (*e.g.*, 1,3-propanediylbis(diethylphosphine)) poly(1-oxo-2-methyltrimethylene) 5 forms, which shows a prevailingly isotactic structure (~80% *l*-diads). The steric control is most probably chain end determined. The use of enantiomerically pure atropisomeric ligands of the type [6,6'-dimethylbiphenyl-2,2'-diyl]- and [6,6'-dimethoxybiphenyl-2,2'-diyl]-bis[dialkylphosphine] allows us to control the stereochemistry of the copolymerisation process. The produced copolymers are regioregular and show different degrees of stereoregularity, namely from almost complete atacticity (~60% *l*-diads) to nearly complete tacticity (>96% *l*-diads). Regioirregular copolymers are formed using aromatic diphosphine ligands. The same catalytic systems can be used to produce, even if with relatively low selectivity, dimethyl 2-methylsuccinate 1. Enantioselectivity is generally low (<30% ee) unless the more basic atropisomeric ligands are used. The enantioselectivity is increased in the formation of the *l*-diastereomer (up to 98% ee) of the dimer 4. The *u*-diastereomer 4 is always formed with lower chemo- and enantioselectivity. A change in the regioselectivity of the insertion process of the olefin affording oxopimelates isomers of 4 always induces a preferential alternation of the enantioface inserted i.e., for these isomers the *u*-diastereomer preferentially forms. Under increased carbon monoxide pressure dimethyl 2-oxo-4-methylglutarate 2 and dimethyl 2-oxo-3-methylglutarate 3 can be obtained with fair enantioselectivity (up to 65% ee).

Organische Chemie **59**

Lineare Paarungskomplexe einer Alanyl- oder Homoalanyl-PNA

Ulf Diederichsen, Harald Schmitt
Org. Chemie & Biochemie TU-München, Lichtenbergstr. 4, 85747 Garching

In der β-Position der Seitenkette mit Nucleinsäurebasen substituierte Alanylpeptide sind nach Modellvorstellungen repetitiv, sobald der Chiralitätssinn der Aminosäureeinheiten alterniert und der Peptidstrang in β-Faltblatt Konformation vorliegt. Es werden lineare Paarungskomplexe erwartet, die auf den klassischen Watson-Crick Basenpaaren A-T und G-C beruhen. Da lineare Stränge keine topologische Einschränkung hinsichtlich Basenpaargröße bedeuten, kann neben Purin-Pyrimidin- auch mit Purin-Purin- sowie Pyrimidin-Pyrimidin-Paarungen gerechnet werden.



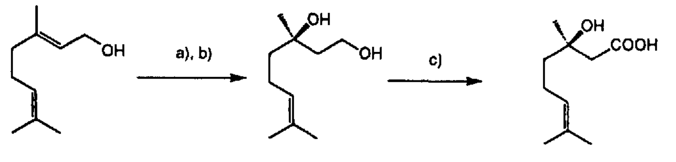
Anhand von Modifikationen des Peptidrückgrats, z.B. Verlängerung der Seitenkette um eine Methylengruppe zu Homoalanyl-Peptiden, lassen sich Rückgrat-Paarungsbeziehungen untersuchen. Selektivität für Watson-Crick- oder Hoogsteen-Paarungen in Abhängigkeit vom Peptidrückgrat wird ebenso diskutiert, wie Strangorientierung, homo-/heterochirale Basenpaaraufhängung und unnatürliche Basenpaarungen.

Organic Chemistry **60**

A Stereoselective Preparation of a new Monoterpene Acid isolated from *CERATOCYSTIS FIMBRIATA PLATANI* and other Derivatives

R. Tabacchi, A. Fkyerat and N. Burki
Institut de Chimie de l'Université de Neuchâtel,
Av. de Bellevaux 51, CH-2000 Neuchâtel

In order to confirm the stereochemistry of the natural monoterpene 1 we prepared with a stereoselective method (R)-3-hydroxy citronellic acid 1 and its isomer on 3 steps starting from geraniol.



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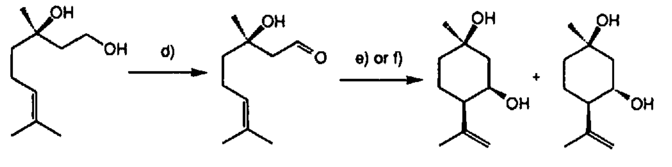
From 3-hydroxy citronellal (intermediate) we prepared as well with high stereoselectivity a new neoisopulegol 2 isopulegol 3 and derivatives which have organoleptic properties. The synthesis of other analogues will be discussed.



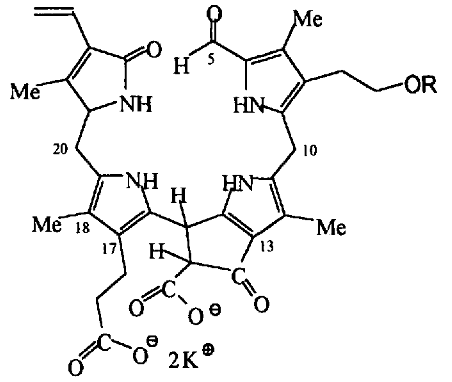
2 3

Organische Chemie **61**

Struktur von nichtfluoreszierenden Chlorophyllkataboliten aus Raps

Walter Mühlecker, Karl-Hans Ongania und Bernhard Kräutler*
Institut f. Organ. Chemie, Universität Innsbruck
Innrain 52a, A-6020 Innsbruck, AUSTRIA

Wir berichten hier über die Konstitutionsaufklärung einer Reihe von farblosen, nichtfluoreszierenden Chlorophyllkataboliten (NCC's), die aus im natürlichen licht-dunkel Rhythmus gealterten Keimblättern von Raps (*Brassica Napus L.*) isoliert werden konnten.
Diese Chlorophyll-Abbauprodukte wurden in der Arbeitsgruppe von Ph. Matile in Zürich entdeckt [1]; die Konstitution eines dieser Kataboliten, Bn-NCC-1, konnte bereits geklärt werden [2].



1 R = $(KOOC)CH_2CO$	K-Salz von Bn-NCC-1
2 R = $C_6H_{11}O_5$	K-Salz von Bn-NCC-2
3 R = H	K-Salz von Bn-NCC-3

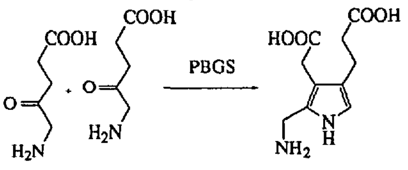
[1] Ginsburg, S., Matile, Ph. *Plant. Physiol.* **1993**, *102*, 521
[2] Mühlecker, W., Kräutler, B., Ginsburg, S., Matile, Ph. *Helv. Chim. Acta* **1993**, *76*, 2976

Organische Chemie **62**

Produktion, Isolation und Versuche zur Aufklärung des Mechanismus der Porphobilinogen Synthase aus *Escherichia Coli*

Matthias Henz[1], Peter Schürmann[2] und Reinhard Neier[1]
1) Institut de Chimie de l'Université de Neuchâtel, CH-2000 Neuchâtel
2) Laboratoire de Biochimie végétale de l'Université de Neuchâtel, CH-2000 Neuchâtel

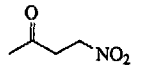
Die Porphobilinogen Synthase (PBGS) ist eines der zentralen Enzyme der Biosynthese der Tetrapyrrole und katalysiert die Kondensation zweier ∂-Aminolävulinsäuren (∂-ALA) zu Porphobilinogen (PBG) [1].



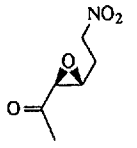
δ-ALA PBG

Von *D. Shemin* und *P. M. Jordan* wurden verschiedene Mechanismen für diesen biosynthetischen Schritt vorgeschlagen [2, 3], die allerdings noch nicht geklärt sind. Es wurden verschiedene Substrat-, Zwischenprodukt - und Produktanaloga synthetisiert, die sich als Inhibitoren erweisen könnten. Nach erfolgter Produktion und Reinigung der PBGS aus *Escherichia Coli* (Strain CR 261) [4] werden zur Aufklärung des Mechanismus Inhibtionsstudien durchgeführt.

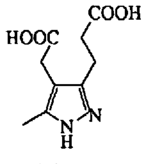
Potentielle Inhibitoren:



Edukt-



Zwischenprodukt-



Produktanaloga

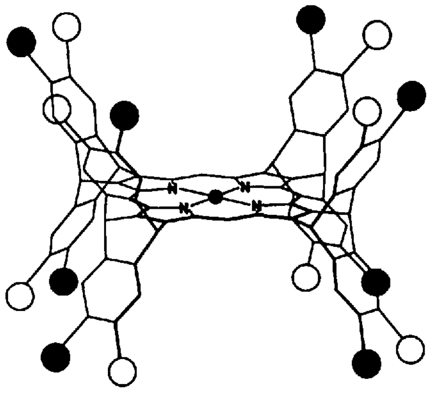
[1] F.J. Leeper, *Natural Product Reports*, **1989**, 171.
[2] D.L. Nandi, D. Shemin, *J. Biol. Chem.*, **1968**, 234 (6), 1236
[3] P.M. Jordan, Biosynthesis of Tetrapyrroles, **1991**, Elsevier, Amsterdam, London, New York, Tokyo
[4] L.W. Mitchell, E.K. Jaffee, *Arch. Biochem. Biophys.*, **1993**, 300, 169

Organic Chemistry **63**

Chiral Biconcave Porphyrins

R.Schwenninger, Y.Ramondenc, B.Kräutler*
Inst. of Organic Chemistry, University of Innsbruck
Innrain 52a, A-6020 Innsbruck, Austria

The synthesis of D_4-symmetric "chiral biconcave porphyrins" is reported, a new class of "sterically protected porphyrins". The chiral biconcave porphyrins are produced from a novel type of a chiral pyrrole, synthesized via a highly diastereoselective Diels-Alder reaction. The porphyrin was calculated to be of an enantiomeric purity of about 10^9:1.
"Chiral biconcave porphyrins" can be used as (diamagnetic or paramagnetic) chiral shift reagents, to discriminate stereoisomeric (enantiomeric) substrates in ^{1}H-NMR-spectra. A series of stereoisomeric substrates (including carboxylic acids, esters, nitriles, alcohols and amines) were analyzed. Sharp and well resolved spectra were obtained, as ligand exchange is fast on the NMR time scale. For all the enantiomerically nonuniform samples analyzed, characteristically separated signals of corresponding protons were observed. Such spectra allow the determination of the enantiomeric purity of the samples with a practical limit of ee's of ca. 99.9%.

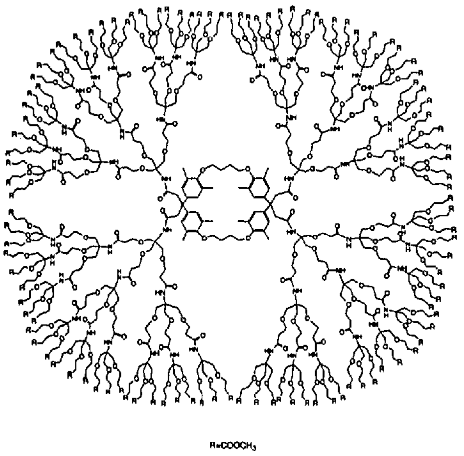


Organische Chemie **64**

Synthese, Charakterisierung und Untersuchung einer neuen Familie von Molekülen: Dendrophane

Sebastiano Mattei, Paul Seiler, François Diederich
Laboratorium für Organische Chemie, ETH-Zentrum, Universitätstrasse 16, CH-8092 Zürich

Eine erste Familie von "Dendrophanen", dendritisch funktionalisierten Cyclophanen, die für die Komplexierung von aromatischen Gästen konzipiert sind, wurde bis zur 3. Generation (Molmasse ca. 19000) synthetisiert und charakterisiert. Erste Ergebnisse der Komplexierung substituierter Naphthaline in Wasser werden vorgestellt.



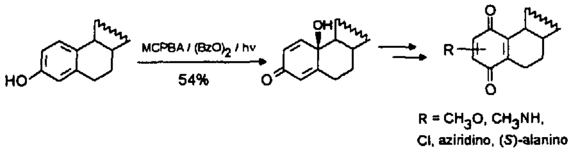
Als Fernziel wird die Synthese von Enzym-Analoga sowie von "Slow drug delivery"-Systemen auf nichtpeptidischer Basis angestrebt.

Organic Chemistry **66**

MCPBA Oxidation of Phenols: An Application to the Synthesis of Steroidal Quinones

B. Šolaja, D. Milić and M. J. Gašić
Faculty of Chemistry, University of Belgrade, P.O. Box 550,
YU-11001 Belgrade

Natural and synthetic products with the quinone moiety in their molecule are of considerable interest because of their pronounced bactericidal and antitumor activities. We focused our research towards the synthesis and biological avaluation of A-ring substituted steroidal quinones, starting from estrone. Our preliminary results on the synthesis, antibacterial and cytotoxicity tests of the A-ring substituted quinones shown in the scheme below will be presented.



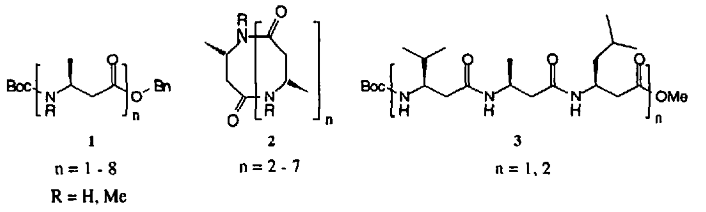
R = CH_3O, CH_3NH, Cl, aziridino, (*S*)-alanino

A new oxidation system for phenol-to-quinol transformation consisting of MCPBA and $(BzO)_2$ in the presence of light was applied to the short synthesis of the desired quinones. The oxidation of other phenols with MCPBA / $(BzO)_2$ / hv system will also be presented. Unexpectedly, only a single regioisomer of the final products, substituted quinones, could be isolated upon addition-oxidation reaction of parent quinone (R = H). The products were found to be C(2) substituted quinones, which were tested against *E. coli* and *S. aureus*, and in preliminary tests, 2,5(10)-estradiene-1,4,17-trione (R = H) exibited the largest antibacterial activity. At the lowest concentration applied (0.001 mg/disk) this compound exibited significant bactericidal activity to both strains. Brine shrimp lethality test was used as indicator of cytotoxicity. In this assay, the most active derivative was 2-methoxy-17β-acetoxy-2,5(10)-estradien-1,4-dione having LC_{50} 0.39 ppm.

Organic Chemistry **65**

The Synthesis of Oligopeptides Consisting of β-Amino Acids

Mark Overhand, Jennifer L. Matthews, Florian M.N. Kühnle and Dieter Seebach
Laboratorium für Organische Chemie, Eidgenössische Technische Hochschule, ETH-Zentrum, Universitätstrasse 16, CH-8092 Zürich



Poly(hydroxyalkanoates) are found in both prokaryotic and eukaryotic organisms [1]. Energy storage is an important function of poly[(*R*)-3-hydroxybutyrate] [P(3-HB)] in bacteria. Chiral building blocks can be obtained by chemical degradation of P(3-HB). Cyclic oligomers have been shown to complex a variety of metal ions, and their ion-transport properties have been studied [1]. Here, we report on the synthesis of linear (**1**) and cyclic (**2**) amide analogs of oligo(3-HB) which will provide a comparison of the structures and properties. The *Arndt-Eistert* reaction can be used to produce a β-amino acid moiety, with concomitant peptide formation [2]. Sequential *Arndt-Eistert* peptide coupling was used in the synthesis of compound **3**. The conformations of oligo-3-aminoacid amides **1**, **2** and **3** have been studied by X-ray diffraction and by CD- and NMR spectroscopy.

[1] Müller, H-M.; Seebach, D. *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 477.
[2] Podlech, J.; Seebach, D. *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 471.

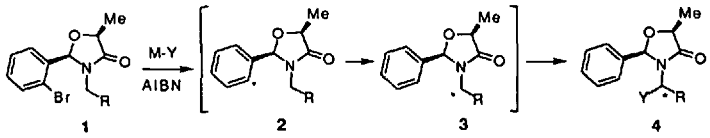
Organic Chemistry **67**

Protecting/Radical Translocating (PRT) Chiral Auxiliaries: A New Concept

Luc Giraud and Philippe Renaud

Institut de Chimie Organique, Université de Fribourg, 1700 Fribourg.

The use of protecting/radical translocating (PRT) groups[1] represents an efficient method for the functionalization at C(1) of alcohols and amines. We present here a further development of this strategy where the PRT group plays also the role of a N-centered chiral auxiliary.[2] Oxazolidinones of type **1** are easily prepared from lactic acid and 2-bromobenzaldehyde. Tin mediated radical chain reactions (M-Y = Bu_3SnD and $Bu_3Sn(allyl)$) gave products of type **4** arising from the expected radical translocation (**2**→**3**). Application of this strategy for the synthesis of enantiopure amines and amino acids is in progress.



(1) D.P. Curran, H. Yu, H. Liu *Tetrahedron* **1994**, *50*, 7343; V. Snieckus, J.C. Cuevas, C.P. Sloan, H. Liu, D.P. Curran, *J. Am. Chem. Soc.* **1990**, *112*, 896. D. Denenmark, P. Hoffmann, T. Winkler, A. Waldner, A. De Mesmaeker *Synlett* **1991**, 621.
(1) For a related N-centered chiral auxiliary, see: W.H. Pearson, A.C. Lindbeck, J.W. Kampf *J. Am. Chem. Soc.* **1993**, *115*, 2622.

Organische Chemie

68

One-step Oxidation of L-Sorbose to 2-Keto-L-gulonic Acid over Supported Pt Catalysts Modified with Tertiary Amines

C. Brönnimann, T. Mallat and A. Baiker*

Department of Chemical Engineering and Industrial Chemistry, Swiss Federal Institute of Technology, ETH Zentrum, CH-8092 Zürich, Switzerland; Fax: + 41 1 6321163

The platinum metal catalyzed oxidation of carbohydrates to the corresponding carboxylic and keto-carboxylic acids is an attractive, environmentally friendly process. High selectivities can be obtained under mild conditions (1 bar, < 60 °C) in neutral or slightly alkaline aqueous medium and with molecular oxygen as oxidant. A great challenge is the application of this method to the direct oxidation of L-sorbose to 2-keto-L-gulonic acid (2-KLG), a substitution for three subsequent steps in the synthesis of vitamine C [1]. Despite the considerable effort which has been made in the past decades, the problems including the rapid deactivation of Pt- and Pd-based mono- and bimetallic catalysts and the low selectivity to the oxidation of the C1 hydroxyl group could not be solved [2].

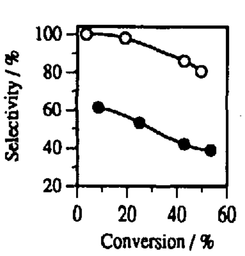


Fig. 1: Selectivity in the oxidation of L-sorbose to 2-KLG over (●) Pt/C and (○) HMTA-modified Pt/C in water (50 °C, pH = 7.3).

We have discovered recently that both the rate and the selectivity of the reaction can be substantially improved by modification of supported Pt with various tertiary amines. Using trialkylamines of high pK value, the average reaction rate could be increased by 150 %. It seems that even in very low molar ratio (amine : $Pt_S = 0.1$) the amines can efficiently catalyze the oxidation of L-sorbose, without promoting the base-catalyzed side reactions in the bulk of the liquid. The promotion of a 5 wt% Pt/C catalyst with hexymethylenetetramine (HMTA) afforded the highest selectivity to 2-KLG, as shown in Fig.1.

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2 C. Brönnimann, Z. Bodnar, P. Hug, T. Mallat, and A. Baiker, J. Catal., 150 (1994), 199.

ORGANISCHE CHEMIE

69

Dendrophanes as Steroid Receptors

Peter Wallimann, François Diederich, Laboratorium für Organische Chemie, Universitätstrasse 16, 8092 Zürich

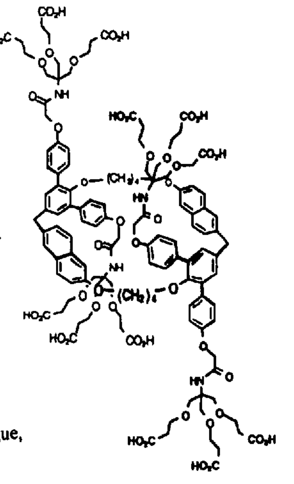
As we have shown lately, cyclophanes are well suited for steroid complexation in aqueous solutions [1]. We now present a novel class of macrocyclic, watersoluble steroid receptors like **1** named *dendrophanes*. They consist of a hydrophobic, rigid cavity buried in a dendritic shell of variable size with peripherial functional groups. The cavity's x-ray structure, synthesis and dendritic functionalization are discussed. Initial complexation studies with steroids were undertaken to investigate potential *slow drug delivery* applications.

First Generation Dendrophane

Formula: $C_{126}H_{148}N_4O_{48}$

Molecular Weight: 2486 g mol^{-1}

1



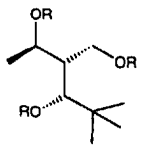
[1] B. R. Peterson, P. Wallimann, D. R. Carcanague, F. Diederich, *Tetrahedron* **1995**, *51*, 401-421.

Organische Chemie

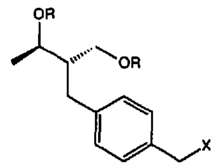
70

Chirale Dendrimere mit zwei- und dreifach verzweigenden chiralen und achiralen Bausteinen

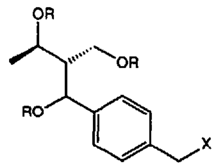
Peter Murer und Dieter Seebach
Laboratorium für Organische Chemie, Eidgenössische Technische Hochschule, ETH-Zentrum, Universitätstrasse 16, CH-8092 Zürich



1



2



3

In unserer Gruppe wurden chirale Dendrimere sowohl mit chiralem Kern und achiralen Ästen [1], als auch mit chiralen Bausteinen im Kern und an den Verzweigungen synthetisiert. Dazu wurde als Kern meistens das Triol **1** (oder verlängerte Derivate desselben) verwendet, und zur Herstellung der chiralen Äste wurden die Diole **2** oder die Triole **3** eingesetzt. Es konnten so chirale Dendrimere erster bis dritter Generation mit bis zu 45 stereogenen Zentren und einem Molekulargewicht von 4900 Da synthetisiert werden. Das grösste "voll chirale" Dendrimer ist eines von 3.52×10^{13} möglichen Stereoisomeren. Es wurden Effekte in CD- und NMR-Spektren sowie ein interessanter Fall von Diastereoselektivität bei der Kupplung von Astbromiden mit einem Kern-triol beobachtet.

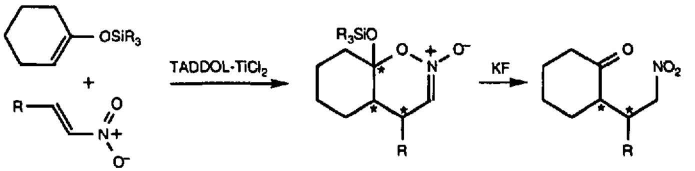
[1] D. Seebach, J.-M. Lapierre, K. Skobridis, G. Greiveldinger, *Angew. Chem.* **1994**, *106*, 457.

Organische Chemie

71

Ti-TADDOLat vermittelte Hetero-*Diels-Alder*-Reaktionen

Robert Dahinden und Dieter Seebach
Laboratorium für Organische Chemie, Eidgenössische Technische Hochschule, ETH-Zentrum, Universitätstrasse 16, CH-8092 Zürich



zwei diastereoisomere Enantiomerenpaare

In unserer Gruppe wurden 1986 cyclische Nitroverbindungen durch Addition von 1-Trimethylsilyloxycyclohexen an Nitrostyrol in Anwesenheit von drei Equivalenten $(i\text{-PrO})_2TiCl_2$ entwickelt [1]. Da die Hetero-*Diels-Alder*-Produkte als Ausgangsmaterialien für interessante Folgereaktionen wie die *Henry*-Reaktion oder 1,3-dipolare Cycloadditionen verwendet werden können, ist eine enantioselektive Synthese mit einem chiralen Ti-TADDOLat ausgearbeitet worden.

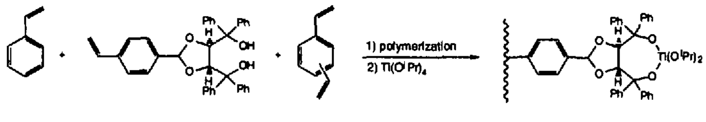
Durch Öffnen der Hetero-*Diels-Alder*-Addukte mit KF gelangt man leicht zu den entsprechenden *Michael*-Addukten. Auf dieser Stufe gelingt die Bestimmung der Stereoselektivität mittels HPLC durch Trennung der zwei diastereoisomeren Enantiomerenpaare auf einer chiralen Phase.

[1] M.A. Brook, D. Seebach, *Can. J. Chem.* **1987**, *65*, 836.

Organische Chemie **72**

Synthese und Anwendung von Polymer-gebundenem TADDOL

R. E. Marti, D. Seebach
Laboratorium für Organische Chemie, Eidgenössische Technische Hochschule, ETH-Zentrum, Universitätstrasse 16, CH-8092 Zürich



1

2
cross-linked polymeric *Lewis* acid

Durch Copolymerisation von **1** mit Styrol und Divinylbenzol erhält man polymer-gebundenes TADDOL, welches sich leicht in das entsprechende Ti-TADDOLat **2** überführen lässt. Dieses Ti-TADDOLat **2** katalysiert die Diethylzink-Addition an Aldehyde mit vergleichbarer Enantioselektivität (er 98 : 2) wie das monomere Ti-TADDOLat [1]. Das Ti-TADDOLat **2** lässt sich vom Reaktionsgemisch einfach abtrennen und kann erneut eingesetzt werden (bis zu vier Durchgänge).

Polymer-gebundene Ti-TADDOLate wurden auch erfolgreich für die enantioselektive Alkyl-Titan-Addition an Aldehyde, für Cycloadditionen und für die Öffnung von cyclischen *meso*-Anhydriden eingesetzt.

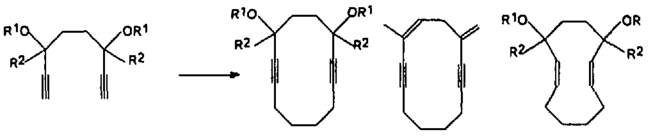
[1] D. Seebach, A. K. Beck, B. Schmidt, Y. M. Wang, *Tetrahedron* **1994**, *50*, 4363-4384.

Organische Chemie **73**

SYNTHESE VON UNGESÄTTTIGTEN CYCLODODECANEN

Christoph Boss und Reinhart Keese, Institut für organische Chemie
Universität Bern, Freiestrasse 3, 3012 Bern

Symmetrisch angeordnete Funktionalitäten in mittleren Ringen spielen für die Ligandeigenschaften und bei transannularen Reaktionen eine ausgeprägte Rolle. Diesbezügliche retrosynthetische Überlegungen haben uns veranlasst, effiziente Verfahren zu entwickeln, mit denen aus $2C_2$- und $2C_4$- Bausteinen in wenigen Schritten funktionalisierte Cyclododecane hergestellt werden können [1]. Als zentrale Reaktion für den Ringschluss war die gleichzeitige Knüpfung von zwei Bindungen vorgesehen, die in den von uns untersuchten Fällen mit erheblich besseren Ausbeuten als bei den bisher bekannten Beispielen gelingt.



1a/b a) R^1 = TBDMS, R^2 = CH_3
b) R^1 = TDS, R^2 = H

2a/b

3

4

So konnte das aus Hexan-2,5-dion zugängliche Dialkin-diol **1** mit 1,4-Dibrombutan zu Cyclododecadiin-diol **2** mit einer Ausbeute von 40% umgesetzt werden; die Diastereomeren werden dabei im Verhältnis von 1:1 gebildet. Bei der Behandlung von **2** mit Ac_2O und $FeCl_3$ entsteht **3**, während bei der Hydrierung mit Lindlar-Katalysator das silylierte Dien-diol **4** erhalten wird. Weitere Cyclisierungen und Umsetzungen der erhaltenen Cyclododecane werden vorgestellt.

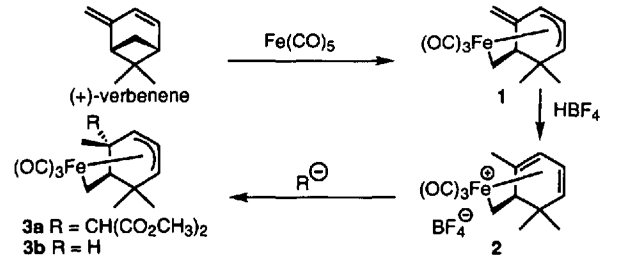
[1] Für ein C_6 + C_6-Beispiel s. B. Bodenmann, R. Keese, Tetrahedron Lett. **1993**, *34*, 1467.

Organic Chemistry **74**

Stereospecific ring opening and functionalisation of verbenene

Titus A. Jenny, Jochen Spuck, David Zeller
Institut de chimie organique, Université de Fribourg, CH-1700 Fribourg

Insertion of iron carbonyl into the four-membered ring of α-pinene leads to a σ–alkyl, π–allyl complex [1]. Other hydrocarbons exhibiting a vinylcyclobutane moiety like *cis*- and *trans*-δ-pinene, apopinene and verbenene react in the same way. Due to its exomethylene group the complex **1** derived from verbenene promises to be a versatile synthon for the construction of higher terpenes.



Protonation of **1** with HBF4 leads to the cationic complex **2**. This compound represents the first example of a pentadienyl-$Fe(CO)_3$-like cation possessing a non contiguous π–ligand. Whereas pentadienyl complexes preferentially add nucleophiles at one of the terminal carbon atoms [2], addition at one of the inner carbon atoms occurs in our case. Complex **3b** was obtained independently from the reaction of *trans*-δ-pinene with $Fe(CO)_5$.

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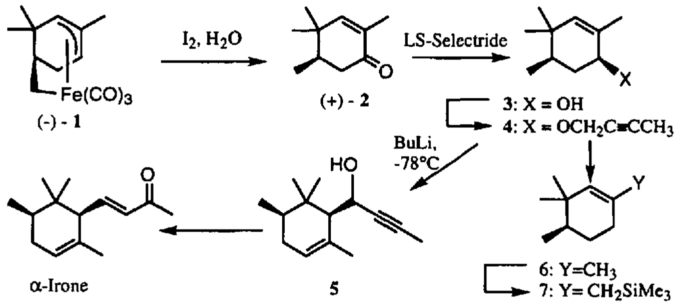
[1] T. A. Jenny, L.Ma, Tetrahedron Letters, **1991**, *32*, 6101.
[2] A. J. Pearson, Iron Compounds in Organic Synthesis, Academic Press London, **1994**.

Organic Chemistry **75**

Short enantioselective synthesis of α- and γ-irone

Stephan Lauper, Thomas Sieber, Liqian Ma, and Titus A. Jenny*
Institut de chimie organique, Université de Fribourg, CH-1700 Fribourg

The iron carbonyl induced ring opening of pinene[1] permits new and short syntheses of optically pure terpenes and terpenoids, because the optical purity of commercial (-)-β-pinene can be easily enhanced to 98% e.e. by crystallization with silver triflat.[2] Using this strategy, a new approach to α- and γ-irone, high priced components of aromas and perfumes, was realized.



Key intermediate (+)-**2** is obtained by oxidation of complex (-)-**1** with iodine and water. LS-Selectride reduction of (+)-**2** leads exclusively to *cis*-**3**. Wittig rearrangement of the butinol ether **4**, obtained by coupling of **3** with 1-bromo-2-butyne,[3] stereospecifically gives alcohol **5**. Different catalysts had to be tested for the isomerization of **5** to *cis*-α-irone, because elimination to the corresponding conjugated dienyne occured in many cases. The synthesis of γ-irone was achieved via deoxygenation of **2** and silylation of the resulting hydrocarbon **6**, followed by a known chain extension procedure.[4]

1. T. A. Jenny, L. Ma, *Tetrahedron Lett.* **1991**, *32*, 6101.
2. S. Lauper, T.A. Jenny, *Helv. Chim. Acta*, to be submitted.
3. K. Mori, M.Amaike, M.Itou, *Tetrahedron* **1993**, *49*, 1871.
4. G. Audran, at alias, *Tetrahedron Lett.* **1993**, *34*, 3417.

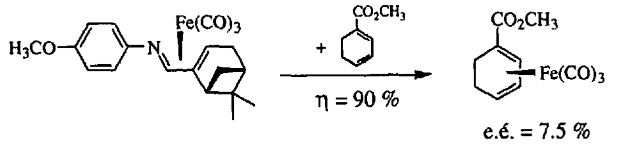
Chimie Organique **76**

Induction de chiralité par échange de ligand des complexes de fer carbonyle des énimines chirales.

T. A. Jenny, P. Aspari
Institut de chimie organique, Université de Fribourg, CH-1700 Fribourg

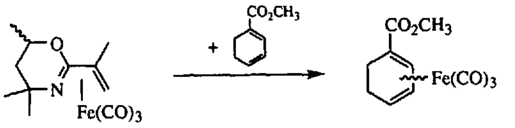
Des échanges de ligands de complexes de fer tricarbonyle entre des énimines achirales vers des ligands diéniques ont été reportés [1]. D'autre part, des études comparables concernant des transferts asymétriques de complexes de fer carbonyle d'énones conjuguées chirales ont montré des résultats prometteurs [2].

Dès lors, différents complexes de fer carbonyle de systèmes d'énimines chirales ont été synthétisés et mis à l'épreuve pour des transferts énantiosélectifs, selon l'exemple suivant:



Les complexes des énimines offrent la qualité appréciable de donner des transferts plus rapides et avec des rendements chimiques bien meilleurs que les complexes des énones précités.

Les recherches ont été ainsi élargies aux complexes de fer carbonyle de différentes oxazolines dont on teste l'aptitude à la réaction d'échange de ligand comme dans le transfert suivant observé:



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[1] H.-J. Knölker, P. Gonser, P. G. Jones, *Synlett*, **1994**, 405-8.
[2] A. J. Birch, W. D. Raverty, G. R. Stephenson, *Organometallics*, **1984**, 3, 1075-79.
T. A. Jenny, V. Schmid, *Chimia*, **1993**, 47, 296.

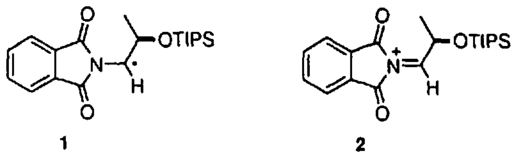
Chimie organique **77**

Stereoselective Reactions Based on Phthalimido Substituted Radicals and Iminium Ions

Aleksandar Stojanovic and Philippe Renaud

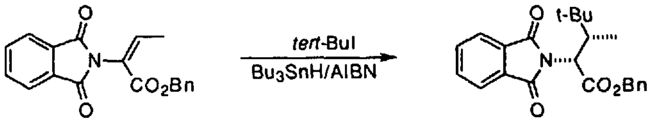
Institut de Chimie Organique, Université de Fribourg, 1700 Fribourg.

Investigation of phthalimido substituted radicalS of type 1[1] and iminium ionS of type 2 is reported. In both cases similar selectivities were observed and explained by a model based on minimization of 1,3-allylic strain ($A^{1,3}$ strain).



1 2

Preparative applications will be presented. For instance, radical addition of tert-butyl iodide to the N-phthaloyl dehydroamino acid 3 gave the protected α-amino acid 4 with a moderate stereoselectivity (70 % ds).



3 4

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(1) For a related work, see: W. Damm, U. Hoffmann, L. Macko, M. Neuburger, M. Zehnder, B. Giese, *Tetrahedron* **1994**, *50*, 7029.

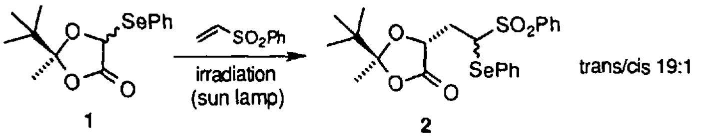
Chimie Organique **78**

Preparation of Enantiopure α-Hydroxy Acids by Phenylseleno Group Transfer Reactions

Sokol Abazi and Philippe Renaud

Université de Fribourg, Institut de Chimie Organique, 1700 Fribourg

Radical additions under non-reductive conditions represent a promising tool for the preparation of highly functionalized compounds. Recently, Byers and others have reported the formation of C-C bonds by transfer of a phenylseleno group.(1) The high versatility of organoselenium compounds renders such reactions particularly attractive. We have already reported that the selenium transfer method allows to perform radical additions with alkoxy-substituted ester radicals despite unfavorable capto-dative stabilization.(2) We report here a general method for the preparation of enantiopure α-hydroxy acids using the 4-phenylseleno-1,3-dioxolan-5-one 1. For example, addition of 1 to vinyl sulfone gave 2 as a trans/cis 19:1 mixture of isomers.



1 2

Both enantiomers of the radical precursor 1 are efficiently prepared from D-mannitol in 5 steps.

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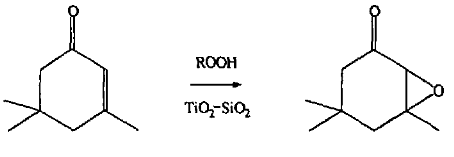
(1) Byers, J. H.; Lane, G. C. *J. Org. Chem.* **1993**, *58*, 3355; Curran, D. P.; Martin-Esker, A. A.; Ko, S. B.; Newcomb, M. *J. Org. Chem.* **1993**, *58*, 4691; Renaud, P.; Vionnet, J. P. *J. Org. Chem.* **1993**, *58*, 5895.
(2) Abazi, S.; Renaud, P. *submitted for publication.*

Organische Chemie **79**

Novel Titania-Silica Aerogels for the Selective Epoxidation of Isophorone with Hydroperoxides

R. Hutter, T. Mallat and A. Baiker
Department of Chemical Engineering and Industrial Chemistry, Swiss Federal Institute of Technology, ETH-Zentrum, CH-8092 Zürich, Switzerland.

The discovery of TiO_2-on-SiO_2 and TS-1 represents two milestones in the history of solid-catalyzed epoxidation of olefins. Presently, the research is aimed at developing new meso- and macroporous materials able to epoxidize bulky olefins under mild conditions. Here we demonstrate that TiO_2-SiO_2 mixed oxides, which are generally considered as catalysts of poor epoxidation activity, can provide excellent reaction rates and selectivities after the proper tuning of the preparation variables. The performance of our sol-gel aerogel catalysts is shown in the epoxidation of a bulky, electron-deficient (unreactive) olefin, isophorone.



The TiO_2-SiO_2 aerogels were synthesized using a sol-gel process followed by supercritical CO_2 extraction [1]. The amorphous aerogels containing 5-20 wt% TiO_2 possess high surface area (460-680 m^2g^{-1}) and mesoporous structure (8-10 nm mean pore diameter). FTIR and UV spectroscopic analysis revealed a high dispersion of Ti in the SiO_2 matrix.

In the epoxidation of isophorone the aerogels provided high selectivity (> 98%) at 333 K, using t-butyl hydroperoxide as oxidant. There is a positive correlation between oxidation rate and Ti-O-Si connectivity, characteristic of Ti-dispersion in the SiO_2 matrix. The suppressed reactivity of isophorone compared to cyclohexene and limonene is attributed to the electron-withdrawing effect of the carbonyl group, whereas steric hindrance by the methyl group is of secondary importance.

Under optimized reaction conditions, the aerogel containing 20 wt% TiO_2 proved to be superior to other well-known TiO_2-SiO_2 catalysts, such as TiO_2-on-SiO_2 (limited number of active sites) and TS-1 (narrow channels).

[1] R. Hutter, D. C. M. Dutoit, T. Mallat, M. Schneider and A. Baiker, J. Chem. Soc., Chem. Comm., 163 (1995).

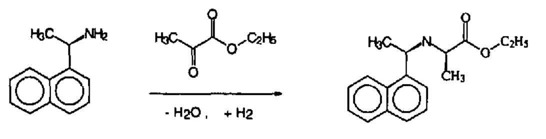
Organische Chemie **80**

Enantioselective hydrogenation of ethyl pyruvate over Pt metals modified by 1-(1-naphthyl)ethylamine and derivatives

B. Minder[1], M. Schürch[1], T. Mallat[1], A. Baiker[1], T. Heinz[2] and A. Pfaltz[2]
[1] Laboratorium für Technische Chemie, ETH-Zentrum, CH-8092 Zürich
[2] Institut für Organische Chemie, Universität Basel, CH-4056 Basel

Recently we have shown that, besides cinchona alkaloids, structurally simple synthetic 1,2-aminoalcohols are efficient modifiers in the enantioselective hydrogenation of ethyl pyruvate (EP) to (*R*)-ethyl lactate. Based on the experience obtained we tested commercially available chiral N-compounds. All these modifiers possess the crucial structural parts, including the flat aromatic moiety promoting the adsorption on Pt, the stereogenic center(s) to induce enantioselectivity and a N-containing group, providing the interaction with EP. One of them, (*R*)-1-(1-naphthyl)ethylamine (NEA) afforded higher enantiomeric excess than cinchonidine under low pressure conditions.

Interestingly, NEA is only a precursor of the actual modifier, which is a secondary amine formed in situ from NEA and EP in a highly diastereoselective (97 %) condensation-reduction reaction, as shown below [1]. The enantioselectivity of EP hydrogenation is determined only by the stereogenic center originally present in NEA. A series of related derivatives has been prepared by reductive alkylation and tested as chiral modifiers. Optimization of reaction parameters provided 82 % ee at full conversion using Pt/Al_2O_3 in AcOH at 8 bar and 282 K.



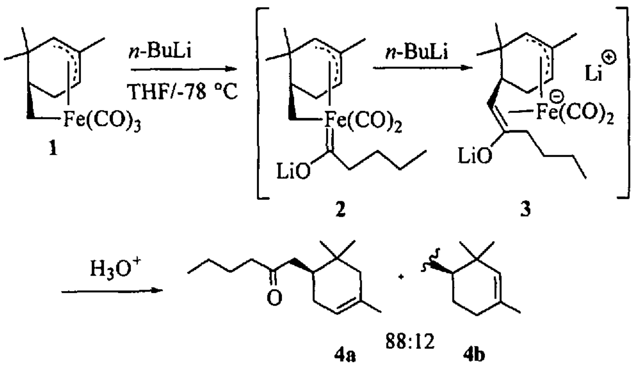
[1] T. Heinz, G. Whang, A. Pfaltz, B. Minder, M. Schürch, T. Mallat and A. Baiker, J. Chem. Soc., Chem. Commun., 1995, in press.

Organic Chemistry **81**

Unexpected Reaction of a Tricarbonyl Iron Complex with *n*-Butyl Lithium

T.A. Jenny, I. Raemy
Institute of Organic Chemistry, University of Fribourg, CH-1700 Fribourg

Treatment of the iron complex **1** (obtained in 60% yield from (-)-α-pinene and $Fe(CO)_5$ [1]) with two equivalents of *n*-butyl lithium quantitatively gives a mixture of the isomeric ketones **4a** and **4b** after work-up and filtration on alox.



The reaction may proceed via deprotonation of the rearrangement product of the primerily formed carben complex **2** to give a lithium enolate iron complex **3**, which is demetallated during the work-up. The position of the double bond in the major isomer **4a** would be in agreement with the iron moiety leaving the complex away from the geminal dimethyl group.

Isolation of the presumed intermediate complex **3**, addition of electrophiles to it, and the influence of other lithium reagents will be further investigated.

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

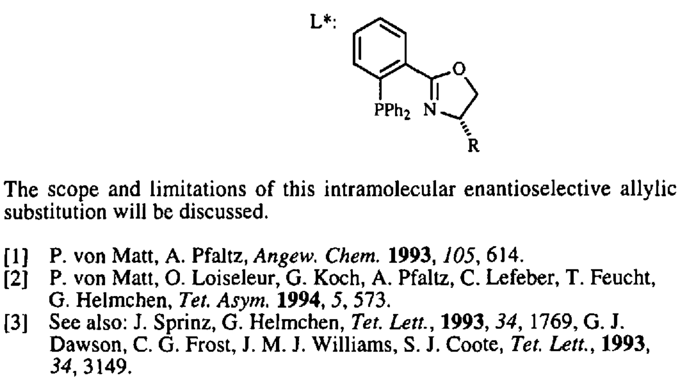
Organische Chemie **82**

Chiral Phosphinoaryl-oxazolines as Ligands in Asymmetric Catalysis: Palladium-Catalyzed Intramolecular Allylic Substitution

Guido Koch, Andreas Pfaltz*.

Institut für Organische Chemie, Universität Basel, St. Johanns-Ring 19, CH-4056 Basel.

Palladium-catalyzed allylic substitution is a versatile, widely used process in organic synthesis and the development of efficient enantioselective catalysts for this reaction is an important goal of current research in this area. We have found that palladium complexes of chiral 2-(2-phosphinoaryl)-oxazolines are effective catalysts for enantioselective intermolecular allylic substitutions [1-3]. In reaction (1), an intramolecular version of the palladium catalyzed allylic alkylation, enantioselectivities up to 87% ee have been obtained.



The scope and limitations of this intramolecular enantioselective allylic substitution will be discussed.

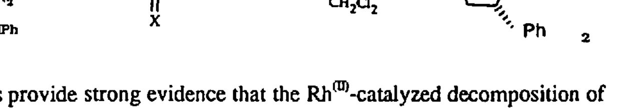
[1] P. von Matt, A. Pfaltz, *Angew. Chem.* **1993**, *105*, 614.
[2] P. von Matt, O. Loiseleur, G. Koch, A. Pfaltz, C. Lefeber, T. Feucht, G. Helmchen, *Tet. Asym.* **1994**, *5*, 573.
[3] See also: J. Sprinz, G. Helmchen, *Tet. Lett.*, **1993**, *34*, 1769, G. J. Dawson, C. G. Frost, J. M. J. Williams, S. J. Coote, *Tet. Lett.*, **1993**, *34*, 3149.

Chimie Organique **83**

Rh$^{(II)}$-Catalyzed Reactions of Iodonium Ylides

Daniel Fernandez and Paul Müller
Département de Chimie Organique, Université de Genève
CH-1211 Genève 4

Phenyliodonium ylides ($R_2C{=}IPh$) are of interest as substitutes for diazocompounds in carbenoid reactions catalysed by Rh$^{(II)}$. In cyclopropanations of substituted styrenes catalyzed with $[Rh_2(OAc)_4]$ the ylides derived from malonic ester ($PhI{=}C(COOMe)_2$) and diazomalonate exhibit the same selectivity. The ρ-value of the corresponding Hammett plot is -0.47 [1]. When appropriately substituted, iodonium ylides, in the presence of $[Rh_2(OAc)_4]$ undergo intramolecular insertions into CH bonds. In intramolecular competition experiments diazo compounds and iodonium ylides exhibit identical product ratios for cyclopropanation and CH-insertion, and identical ee's result upon $[Rh_2(S\text{-ptpa})_4]$-catalyzed CH-insertion [2] of diazocompound **1a** and iodonium ylide **1b** to the ketoester.



The results provide strong evidence that the Rh$^{(II)}$-catalyzed decomposition of diazocompounds and the corresponding iodonium ylides proceeds through the same metallocarbene intermediate.

[1] P. Müller, D. Fernandez, *Helv. Chim. Acta* **1995**,in press.
[2] S. Hashimoto, N. Watanabe, T. Sato, M. Shiro, S. Ikegami, *Tetrahedron Lett.* **1993**, *34*, 5109.

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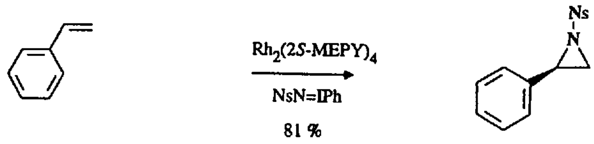
Chimie Organique **84**

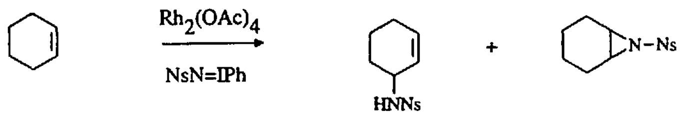
Rh$^{(II)}$-Catalyzed Nitrene Transfer

Corine Baud, Yvan Jacquier, Mary Moran, Yvo Nägeli, Paul Müller
Département de Chimie Organique, Université de Genève
CH-1211 Genève 4

Decomposition of (*N*-(*p*-nitrobenzenesulfonyl)imino) phenyliodinane (PhI=NNs) with [$Rh_2(OAc)_4$] in the presence of olefins affords aziridines in yields of up to 85%. The aziridination is stereospecific with *cis*-hex-2-ene and *cis*-β-methylstyrene, but *cis*-stilbene affords a 3:1 mixture of *cis*- and *trans*-aziridines. In the presence of a chiral catalyst [$Rh_2\{(2S)\text{-mepy}\}_4$] styrene is aziridinated with 80% yield and a modest ee of 21% [1].



The principal competing reaction is insertion into allylic CH-bonds which, with appropriate substrates, may become the predominate pathway. With cyclohexene, the insertion product is formed in 70% yield, while only trace amounts of aziridine form.



Aziridines are also accessible *via* Rh$^{(II)}$-catalyzed carbene addition to imines. However, the yields are low and no asymmetric induction is observed.

[1] P. Müller, C. Baud, Y. Jacquier, *J. Org. Chem.* **1995**, submitted

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Physikalische Chemie **85**

Femtosekunden-Dynamik von Oberflächenprozessen

M. Aeschlimann, M. Bauer, S. Pawlik

Laboratorium für Technische Chemie, ETH Zürich, 8092 Zürich

Photochemische Oberflächenprozesse, durch ultrakurze Laserpulse induziert, haben in der letzten Zeit wachsende Bedeutung für die physikalische Chemie erlangt. Viele Reaktionen zwischen Adsorbaten und Metalloberflächen werden eher durch Austausch von heissen Ladungsträgern als durch thermische Aktivierung induziert. Durch Laserlicht an der Metalloberfläche angeregte Elektronen können in Adsorbatzustände tunneln und dort einen Teil ihrer Energie abgeben, bevor sie wieder in einen unbesetzten Zustand des Substrats streuen. Die von den Adsorbaten gewonnene Energie kann ausreichen, um chemische Bindungen zu brechen oder den Desorptionsvorgang auszulösen. Ein wichtiger Parameter für diese Oberflächenreaktionen ist die Transfer-Rate der *heissen* Elektronen, die stark von den konkurrierenden Mechanismen im Metall abhängt. Dabei handelt es sich zum einen um die Energierelaxation der heissen Elektronen, zum anderen um deren Diffusion von der Oberfläche ins Metallinnere. Beides sind Prozesse, die die Anzahl der für den Ladungstransfer zur Verfügung stehenden angeregten Elektronen reduzieren. Zur Untersuchung dieser Konkurrenzprozesse eignet sich im besonderen Masse die *zeitaufgelöste 2-Photonen-Photoemissions Spektroskopie*, die auf der Pump und Probe Technik basiert. Dabei regt der Pumppuls Elektronen in einen unbesetzten Zustand unterhalb der Vakuumenergie an, aus dem sie innerhalb ihrer Lebensdauer mit Hilfe des zweiten Pulses ins Vakuum emittiert werden können. Unsere Messungen an verschiedenen polykristallinen Metallen zeigen, das der Relaxationsprozess der angeregten Elektronen in Silber sich in Übereinstimmung mit der Fermi-Liquid Theorie verhält, während die Werte für Gold und Kupfer stark abweichen. STM Untersuchungen verdeutlichen, dass diese Abweichung nicht durch Oberflächeneffekte verursacht wird, sondern auf Bulkeffekte zurückzuführen ist. Für Übergangsmetalle ist die Relaxationszeit deutlich kürzer als für Edelmetalle, was darauf hinweist, dass der Zerfall von der Anzahl der unbesetzten d-Orbitale unterhalb des untersuchten Energiezustandes beeinflusst wird. Der Einfluss der Diffusion der angeregten Elektronen ins Metallinnere kann durch die Verwendung von sehr dünnen (200Å) Metallfilmen auf Isolatorträgern vermindert werden.

Physikalische Chemie **86**

Steady-state detection of the luminescence of singlet oxygen (O_2 ($^1\Delta_g$)) in the near-infrared: a new equipment for measurements in aqueous media

Yiola Georgiadou, Esther Oliveros, André M. Braun
Lehrstuhl für Umweltmesstechnik, Engler-Bunte-Institut, Universität Karlsruhe, 76128 Karlsruhe, Germany

We have built a detection system incorporating an InGaAs diode and appropriate pre-amplification based on the phase sensitive detection technique (PSD) for weak signals (<pWatt) in the near-infrared. The high sensitivity achieved even at room-temperature operation is demonstrated by the observation of the NIR-emission (1270 nm) originating from the singlet excited state of molecular oxygen ($^1\Delta_g$) in water (H2O) where the lifetime of this singlet excited state (τ_Δ) is particularly short (about 4µs).This lifetime controls the intensity of the signal as it is directly proportional to the quantum efficiency of emission (Φ_e),

$$\Phi_e = \Phi_\Delta \cdot \tau_\Delta \cdot k_e$$

where Φ_Δ is the quantum yield of singlet oxygen production by the sensitizer, and k_e the rate constant of singlet oxygen emission.

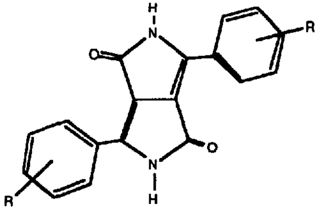
A home-made current amplifier with a high impedance feedback and narrow bandwidth in connection with the PSD technique now enables us to detect signals at low absorbance in water even at small excitation energies.

Chimie Physique: **87**

Triplet States of 1,4-Diketo-pyrrolo[3,4-c]pyrroles (DPP)

Martin Eschle, Jacques Moser, Michael Graetzel
Institut de Chimie Physique, Ecole Polytechnique Fédérale de Lausanne,
CH-1015 Lausanne

Diketopyrrolopyrroles (DPP) have gained interest due to their high light- and weather fastness. Their properties are mainly due to the high crystal stability. Nevertheless emission studies have shown that in pigmented films, monomers are adsorbed on the surface of the particles. These are subject to the photo-induced chemical reactions.



DPP has a particular low triplet energy (30 kcal mol^{-1})^1, allowing sensitization of Δ^1O_2 through the following reaction:

$$^1S^* + {}^3O_2(^3\Sigma g) \longrightarrow {}^3S^* + {}^1O_2(^1\Delta g)$$

The low-lying triplet state is a property of the core structure of the molecule. This can be shown by analysis of the orbitals calculated by the ZINDO method. Comparison of different derivatives allows the conclusion that the energy lowering of the triplet due to the additional term in the exchange integral becomes important for DPP due to the narrow distribution of the HOMO and LUMO.

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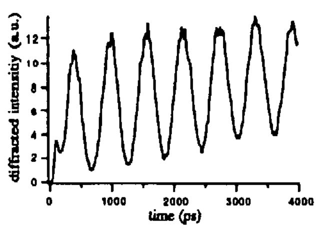
Physikalische Chemie **88**

Transient Phase Grating Study of Photoinduced Electron Transfer Reactions in Solution

Arthur Henseler, Eric Vauthey
Institut für physikalische Chemie, Universität Freiburg, CH - 1700 Freiburg

Transient phase grating spectroscopy is a holographic technique allowing variations of the refractive index, Δn, to be measured. These variations can be induced by density modulations arising from heat releasing reactions produced at the interference maxima of a transient grating[1]. The time dependent intensity of a diffracted probe laser pulse (or cw laser light) provides informations about the kinetic and thermodynamic properties of the observed system.



Diffracted intensity measured upon ET between 0.3 M DABCO and BP in MeCN

We report on the photoinduced electron transfer (ET) reaction between diazabicyclo[2.2.2]octan (DABCO) as the donor and triplet benzophenone (BP) as the acceptor. By using *cw-reading laser* detection in the NIR-region and comparing the intensities associated with the different heat releasing steps, the theoretical value for the enthalpy of free ions, ΔH_{fi}, was confirmed to be around -0.74 ± 0.04 eV[2]. The same technique was used to measure the quantum yield of free ions in the system of dicyanoanthracene with several donors.[3] By using *ps-reading-pulses* the energetics involved in the formation of the geminate ion pair (ip) between BP and DABCO, ΔH_{ip}, was measured, resulting in a value for the Coulomb-term, C, i.e. the term describing the electrostatic interaction between the ions, of about -0.28 ±0.06 eV[4].

The comparison between ΔH_{fi} and ΔH_{ip} opens an alternative way to determine C resulting in a value of -0.18 ± 0.06 eV. The significations of these results will be discussed.

[1] L. Genberg, Q. Bao, S. Gracewski and R. J. D. Miller, *Chem. Phys.* 131 (1989), 81
[2] Eric Vauthey and Arthur Henseler, submitted for publication
[3] Arthur Henseler and Eric Vauthey, J. Photochem. Photobiol. in print
[4] Eric Vauthey and Arthur Henseler, J. Phys. Chem., May 1995

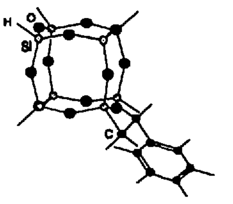
Physical Chemistry **89**

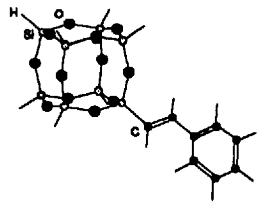
Vibrations of monosubstituted octasilasesquioxanes

Gion Calzaferri, Roman Imhof, Claudia Marcolli

Institute for Inorganic and Physical Chemistry, University of Berne, Freiestrasse 3, CH-3000 Bern 9

Monosubstituted octanuclear silasesquioxanes of the type $RH_7Si_8O_{12}$ have become available in the last years.[1] They can be used to investigate the influence of symmetry reduction on the vibrational behaviour of the $H_8Si_8O_{12}$ cage.





We have recorded the FTIR and FT Raman spectra of $RH_7Si_8O_{12}$ with R = $-CH_2-CH_2-C_6H_5$ and $-CH{=}CH-C_6H_5$. Their vibrational structure was described as a superposition of the spectral features of $H_8Si_8O_{12}$ and of the organic substituents ethylbenzene and styrene. Normal coordinate analyses was applied by combining the force fields of $H_8Si_8O_{12}$ and of the organic substituents. Coordinates and force constants of the vibrations involving the Si-C bond were introduced. Only the new introduced force constants were fitted. All frequencies were assigned and a good agreement between the calculated and the observed frequencies was obtained.

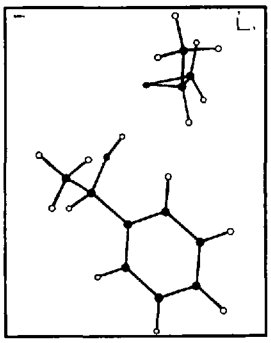
[1] G. Calzaferri, R. Imhof, K.W. Törnroos, J. Chem. Soc., Dalton Trans. 1994, 3123.

Physical Chemistry: **90**

Chiral Discrimination in Gas-Phase Pair Complexes

A. Inauen and S. Leutwyler
Institut für Anorganische, Analytische und Physikalische Chemie,
Freiestr. 3, CH-3012 Bern

The interactions between two chiral molecules M and M' have been studied in supersonic beams by resonant two-photon ionization (R2PI) spectroscopy, combined with time-of-flight (TOF) mass spectroscopy. During the adiabatic jet expansion, cold gas-phase pair complexes of the type M•••M' (besides higher clusters M•••(M')$_n$) are formed. M denotes a hydrogen bond donor, M' the corresponding H-bond acceptor.



MOPAC optimized structure of the R-MBA••R-PO complex

We investigated R(+)-methyl benzyl alcohol (R-MBA) and R(-)-Indanol complexed to either R(+)- or S(-)-propylene oxide. The binary complexes formed are diastereomers, and therefore exhibit different optical spectra. The bare chromophore R-MBA shows a strong electronic origin at 37'623 cm^{-1}, which is almost devoid of low-frequency vibrational structure. The diastereomer complexes show a blue-shift of ≈4 cm^{-1} for R-MBA•••R-PO and a red-shift of ≈36 cm^{-1} for R-MBA•••S-PO. The spectra of both of the complexes differ from that of the bare chromophore R-MBA, and also from each other, which clearly indicates dissimilar structures of the complexes. Also the R-MBA•••S-PO diastereomer is formed much more readily, indicating that the H-bond in the R•S' complex is much stronger.

The spectrum of the R-MBA•••R-PO diastereomer exhibits a low-frequency intermolecular vibrational progression with 12-13 cm^{-1} spacings. This is typical for intermolecular bending and rocking vibrations of hydrogen bonded complexes, and indicates an angular reorientation of the complex upon electronic excitation.

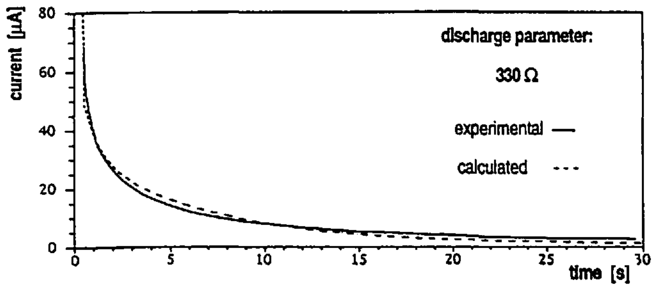
Physical Chemistry **91**

Modelling of a Thin Layer Cell Consisting of Two Polymer Coated Electrodes

A. C. Stückl [a], C. Mehadji [c], C. A. Daul [a], M. Sullivan [b], and E. Deiss [b]
[a] Institut de Chimie Inorganique et Analytique, Université de Fribourg, CH-1700 Fribourg
[b] Paul Scherrer Institut, CH-5232 Villigen
[c] LIMSAG, Université de Bourgogne, F-21004 Dijon Cedex

Redox polymer coated electrodes are an attractive material to construct rechargeable batteries with high charge densities. Because of the different properties of this material in comparison to well studied plane electrodes, a considerable amount of research has been done in modelling the time dependent behaviour of these electrodes in the last years [1], or, very recently [2], to simulate charge and discharge of cells.

A general mathematical formulation is developed in this work that allows the quantitative analysis of a thin layer cell. We present the simulation results of a cell, consisting of two polyvinylferrocene (Cp2Fe) coated electrodes, and show the comparison with the experimentally derived results. The simulation model includes mass transport by diffusion, electron transfer by hopping, and *Donnan* partition kinetics at the interface between polymer and the separator.



[1] E. Deiss, O. Haas, and C. Daul, *J. Electroanal. Chem.*, 337 (1992) 299 - 324
[2] M. Doyle, T. F. Fuller, And J. Newman, *J. Electrochem. Soc.*, 140 (1993) 1526 - 1533

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Physikalische Chemie **92**

Optimization of Pasted Zinc Electrodes for Zinc-Air Batteries

F.Holzer, S.Müller and O.Haas
Paul Scherrer Institute, 5232 Villigen PSI, Switzerland

The demonstration of long cycle life performance for electrically rechargeable zinc-air batteries is an important goal in order to make this system attractive for electric vehicle applications.

Recently we demonstrated very promising cycle-life behaviour of $La_{0.6}Ca_{0.4}CoO_3$-catalyzed bifunctional oxygen elctrodes in an oxygen electrode experiment [1], as well as in a zinc-oxygen cell [2]. From our data we conclude that the stability of the bifunctional catalyst and its support material as well as the change in porosity and pore size distribution at the zinc electrode are the limiting factors of the zinc-oxygen cells. Densification of the pasted zinc electrode seems to be the major reason for the loss of battery capacity at high cycle numbers.

We will discuss the influence of porosity and pore size distribution on the cycle life performance of the zinc-oxygen cell. Therefore, pasted zinc electrodes of various compositions were tested in monopolar cells of 2.5Ah nominal capacity. The pasted zinc electrode contains ZnO, traces of PbO, PTFE and different amounts of cellulose (fig. 1). The porosity and pore size distribution of the pasted zinc electrodes were measured by means of mercury porosimetry.

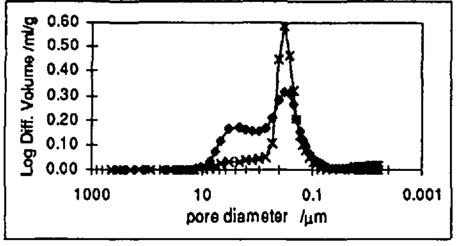


Fig.1 Pore size distribution in pasted zinc electrodes of ~1mm thickness and 2.5Ah capacity.
(X): 1% cellulose
(◆): 20% cellulose

1. S.Müller, K.A.Striebel and O.Haas, *Electrochim. Acta*, **1994**, 39, 1661
2. S.Müller, F.Holzer, O.Haas, Ch.Schlatter, Ch.Comninellis, *Chimia*, 49, **1995**, 27

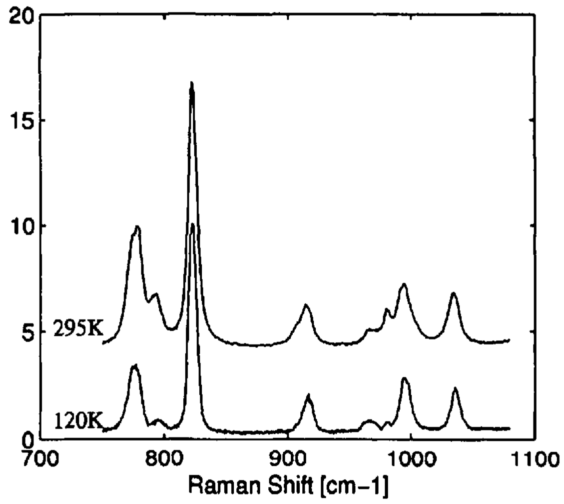
Chimie Physique **93**

Conformational study of 2-butanol using temperature-dependent Raman measurements and MM3 calculations

H. Hagemann, A. Toufiq, J. Mareda and H. Bill

Dépts de Chimie Physique et de Chimie Organique, Université de Genève
30, quai E. Ansermet, 1211 Genève 4, Suisse

Temperature-dependent Raman measurements of 2-butanol at temperatures ranging from 120 K to 360 K have been performed. These data allow to distinguish Raman bands pertaining to different conformers and to evaluate their relative energies. These results are compared with energies calculated by MM3 for a series of conformers and with the computed vibrational spectra.

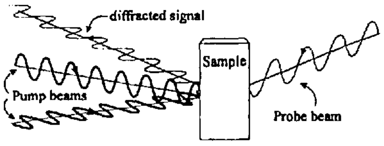


Chimie physique **94**

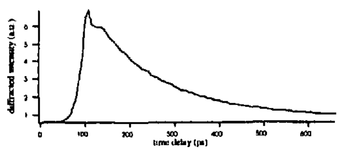
Picosecond polarization grating study of the rotational dynamics of Rhodamin 6 G in different electronic states

J-Claude Gumy, Eric Vauthey
Institut de chimie physique, Université de Fribourg, CH-1700 Fribourg

Picosecond transient grating has already shown to be a very powerful method for ultrafast kinetic studies. For example, decomposition of the signal beam in two perpendicular polarized components permits to determine the variation of the polarization anisotropy and hence, the rotational rate constant.



Scheme of the experimental setup



Decay of polarization grating of R6G in ethanol

In our experiment, we used two orthogonal polarized pump beams to create a polarization grating. The decay of such a grating depends on the lifetime of the excited species and on its rotational time. This allows the variation of anisotropy to be measured directly, without having to handle with some delicate data processing.

This novel method was used to study the rotational dynamic of Rhodamin 6 G (R6G) in protic and non-protic solvents of various viscosity, in the ground and exited states, at two different pump wavelengths.

The use of 355 nm pump beams excites the R6G in the S_2 state that relaxes into S_1 in less than 1 ps, producing a local variation of temperature. On the other hand, pumping at 532 nm does not deliver any excess energy, so that the local temperature can be assumed to be unchanged.

Comparison of the rotational dynamics observed with and without excess energy for both the ground and the excited state will be presented.

Physikalische Chemie **95**

SELECTIVE REDUCTION OF NO_X BY NH_3 OVER COMMERCIAL $DENO_X$ CATALYST:
PARAMETRIC SENSITIVITY AND KINETIC MODELING

R. Willi, B. Roduit, R. Köppel, A. Wokaun and A. Baiker,
Laboratorium für Technische Chemie, ETH-Zentrum, CH-8092 Zürich

Selective catalytic reduction (SCR) by ammonia is the most widely employed technique for the removal of NO_X from stationary combustion sources. Several kinetic and mechanistic studies on the reduction of nitric oxide on vanadia containing catalysts have been reported. Generally, a first order kinetics in nitric oxide and zeroth order in ammonia is assumed. This kinetic behavior can be explained by an Eley-Rideal mechanism involving adsorbed ammonia and nitric oxide from the gas phase.

In this work the kinetics of the selective catalytic reduction of nitric oxide by ammonia have been investigated over a vanadia-based commercial $DeNO_X$-catalyst. For temperatures exceeding 200°C the kinetic data are described well with a model which is based on an Eley-Rideal mechanism. Below 200°C the conversion is higher than predicted. In this temperature range the kinetics could be properly described by accounting for an additional reaction pathway following a Langmuir-type mechanism, which occurs only at low temperatures. Regarding the influence of water and oxygen on SCR, O_2 accelerated and H_2O decreased the reaction rate. The addition of up to 2% H_2O to the dry feed notably reduced the rate of NO_X conversion. The effect levels off for higher H_2O concentrations and between 2.5% and 7.5% H_2O no significant dependence was perceptible. Similarly, the conversion of NO_X is almost independent on O_2 for concentrations between 2% and 10%. Lower oxygen concentrations resulted in a marked decrease of the catalytic activity.

Physikalische Chemie **96**

Untersuchung verschiedener Eisen-Zeolithkatalysatorsysteme auf ihre Einsetzbarkeit zum photochemischen oxidativen Abbau von 4-Chlorphenol

Martina Hill, Esther Oliveros, André M. Braun

Lehrstuhl für Umweltmesstechnik, Engler-Bunte-Institut, Universität Karsruhe, 76128 Karlsruhe

Die photokatalytische Aktivität der Systeme Fe-SM27-Zeolith/H_2O_2 und Fe-Y-Zeolith/H_2O_2 wurde anhand des Abbaus von 4-Chlorphenol untersucht. Die Einbringung der Eisenionen in die Zeolithstruktur wurde durch konventionellen Ionenaustausch oder durch Substitution der Aluminiumionen erreicht. Die Charakterisierung der Zeolithsysteme erfolgte mittels Röntgendiffraktometrie (XRD), Fourietransform-Infrarotspektroskopie (FT-IR) und durch Bestimmung der Adsorptionskapazität (BET). Die photochemischenVersuche wurden in einem Durchflussreaktor durchgeführt. Als Lichtquelle diente eine 150W Quecksilbermitteldrucklampe. Als analytische Untersuchungsmethoden wurden HPLC und DOC benutzt. Überraschend ist die totale Inaktivität der Y-Zeolithe, die wir an Hand von Strukturmodellen zu erklären versuchen

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Physikalische Chemie **97**

Simultaneous photochemical generation of ozone in the gas phase and photolysis of liquid water using one light source

Tarek M. Hashem; André M. Braun
Lehrstuhl für Umweltmesstechnik, Engler-Bunte Institut, Universität Karlsruhe, 76128-Karlsruhe, Germany

The present work describes a new application of a vacuum ultraviolet source based on incoherent xenon excimer radiation originating from a dielectric barrier discharge and providing narrow band radiation at 172 nm. As such a light source is flexible with respect to its geometry and its electrodes configuration a new reactor has been designed making maximum use of the emitted VUV radiation. Hence, with one light source, two simultaneous, separate photochemical reactions have been achieved: (1) photochemical generation of ozone by irradiating oxygen in the gas phase, (2) photolysis of water in the liquid phase.

$$3O_2 \xrightarrow{h\upsilon} 2O_3 \qquad (1)$$

$$H_2O \xrightarrow{h\upsilon} OH^{\cdot} + H^{\cdot} \qquad (2)$$

Analytical experiments were conducted to quantify the photochemically generated ozone in the gas phase and its residual concentration in water after the ozone was introduced into the liquid reaction system and irradiated by the same light source. This work presents the degradation kinetics of chlorinated hydrocarbons in differentiating the effects of VUV photolysis and oxidation by ozone, by applying each of the oxidants separately as well as a combination of both.

Physical Chemistry **98**

Laser-induced thermal desorption of aniline from silica surfaces

Stefan Nettesheim, Pierre Voumard and Renato Zenobi
LOC - Lehrstuhl für Analytische Chemie, ETH-Zentrum
CH-8092 Zürich, Switzerland

Submonolayer coverages of aniline desorb intact from silica surfaces both for classical temperature programmed desorption (TPD) experiments as well as during pulsed laser-induced thermal desorption where heating rates of 10^{10} K/s are reached [1].

We are currently exploring methods to measure these fast surface temperature transients by time-resolved detection of the blackbody-emission in the 3-7 µm range and monitoring the depletion of the aniline layer by time-resolved ellipsometry. This is important to verify whether the kinetic parameters governing the quasi-equilibrium desorption characteristics for TPD sweeps can be applied to the regime of high laser heating rates.

Partitioning of the thermal energy supplied by the laser pulse into kinetic and internal (rovibronic) energy of the desorbing aniline is probed by time of flight measurements combined with resonant multiphoton ionization spectroscopy (REMPI-TOF).

While the surface of the silica sample reaches about 600-700 K at the time of desorption, the kinetic temperature of laser-desorbed aniline was found to be $T_{kin}=420\pm60$ K, $T_{vib}=360\pm60$ K, and $T_{rot}=350\pm100$ K. These results are discussed using different models for laser-induced thermal desorption from surfaces.

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Physikalische Chemie **99**

Thin metal films on mica: a comparative study with XRD, AFM and XPS

J.-D. Grunwaldt, F. Atamny, U. Göbel, A. Baiker
Laboratorium für Technische Chemie, ETH-Zentrum, CH-8092 Zürich

Flat and highly orientated thin films are of great interest in surface science. Among other applications thin metal films with such well-defined structural properties are suitable model systems for studying the relation between the structural and catalytic properties of metals. The crystallographical and morphological properties of thin metal films prepared by physical vapour deposition strongly depend on the deposition parameters.

In this study thin gold films on muscovite mica at different substrate temperatures (410-680 K) and thin silver films of different thicknesses (50-300 nm) using different substrate temperatures (480 K-680 K) were prepared. The residual oxygen partial pressure in the preparation chamber amounted to ca. $2 \cdot 10^{-7}$ mbar. XRD indicated that the gold films were exclusively [111]-orientated, whereas the silver films also showed some [100]-orientation. The amount of silver islands with [100]-orientation was found to be strongly dependent on the deposition parameters: At a substrate temperature of 530 K and low film thicknesses the [111]-orientation was most pronounced (> 99.9 %). Below or above this temperature as well as in thicker films the amount of the [100]-orientated islands increased. AFM-studies revealed that mainly two shapes of crystals - flat islands with hexagonal-like symmetry and higher oval-shaped islands - exist which can be related to the XRD studies.

The size of the islands in the gold and silver films is significantly larger than 500 nm (measured by STM and AFM) and varies significantly with the substrate temperature and film thickness.

XPS-analysis of gold and silver films indicated the presence of a substantial amount of oxygen and carbon on the surface. Most of the contaminants could be removed by sputtering. Interestingly, the differently prepared silver films show a similar carbon content but a different oxygen content on the surface before and after sputtering. Higher oxygen contents were found for silver samples with significant contributions of (100) planes.

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Physikalische Chemie **100**

Comparative Study of Formation of Harmful By-products in Selective Catalytic Reduction of NO_x over Cu/ZSM-5 and Alumina

F. Radtke, R. Köppel and A. Baiker

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

The reduction of nitrogen oxides (NO_x) emissions, both from stationary and mobil sources, is a major task to be solved for environmental protection. Recently, increased attention has been given to the removal of NO_x from lean-burn engines operating under net oxidizing conditions, utilizing hydrocarbons as reducing agent. Although nitrogen has been found as the major nitrogen containing product, other species such as HCN, NH_3, N_2O and HNCO have been observed in the course of the reaction [1,2].

Here we report the formation of by-products in the selective catalytic reduction of NO_x by either ethene or propene in the presence of excess oxygen over γ-alumina and Cu/ZSM-5. The apparatus used for the catalytic studies consisted essentially of a dosing system for the reactant gases, a tubular fixed-bed micro reactor and a FT-IR spectrometer, equipped with a heatable gas cell and a MCT-detector, for gas analysis.

The catalytic performance as well as the formation of undesired by-products are strongly governed by the catalyst, the hydrocarbon used as a reductant, the nitrogen oxide (NO or NO_2) and the presence of water. Substantial quantities of undesirable by-products such as CO, HCN, HNCO, NH_3, N_2O and CH_2O are formed under certain experimental conditions. With alumina, NO_2 is reduced more efficiently than NO with both reductants but with ethene showing a lower tendency to form undesired by-products. Water addition strongly suppresses catalytic activity and formation of by-products. This contrasts the findings with Cu/ZSM-5, where HCN formation is not altered by the presence of water and where ammonia appears in place of HNCO upon adding water.

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Physikalische Chemie **102**

Nickel Thin Films Prepared by MOCVD: Morphological and Electrical Properties

F. Atamny[1] ,M. Becht[2], K.-H. Dahmen[2] and A. Baiker[1]

[1]Laboratorium für Technische Chemie, ETH-Zentrum, CH-8092 Zürich, Fax: +41 1 632 1163
[2]Laboratorium für Anorganische Chemie, ETH-Zentrum, CH-8092 Zürich

In the semiconductor industry, chemical vapor deposition (CVD) is routinely used to deposit a wide variety of thin films. Many different types of reactors, new CVD processes as well as alternative precursors have been developed for this purpose.

Although Ni and Ni alloys have interesting properties for various applications (like microelectronics and catalysis) only a few reports exist about the properties of these films prepared by CVD. In this study, we present thin nickel films prepared by metal organic chemical vapor deposition (MOCVD) using bis(dimethylglyoximato)Ni(II) as precursors. The aim was (i) to investigate alternatives to the very toxic $Ni(CO)_4$ precursor, (ii) to optimize the conditions for Ni film growth, and (iii) to characterize the film morphology and growth mechanism.

The deposition of the films was carried out in a horizontal quartz reactor at reduced pressure in a hydrogen/helium atmosphere. The films were analysed by X-ray diffraction and AFM. Information about the electrical behaviour of the deposited materials was gained from resistivity measurements. Film thicknesses were determined using a profilometer. The combined AFM (morphology and surface roughness) and electrical resistance studies provided interesting information on the growth mechanism of the films which will be discussed.

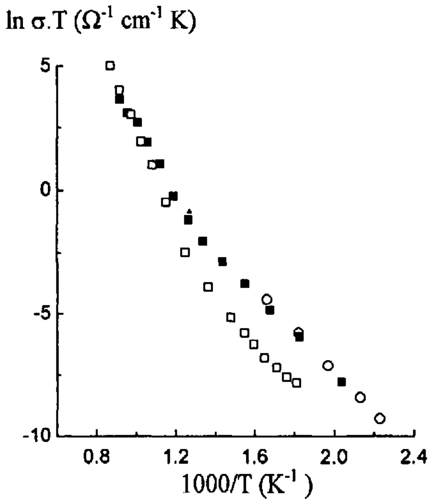
Chimie Physique **101**

Ionic conductivity and superionic behaviour of Na_2S single crystals: an experimental study.

B. Bertheville, D. Lovy, D. Frauchiger and H. Bill

Dépt. de Chimie Physique, Université de Genève, Sciences II, 30 quai E. Ansermet, 1211 Genève 4, Suisse.

Alkali sulfide single crystals are grown in our laboratory. We present results of ionic conductivity measurements performed as a function of temperature (300K-1200K) and frequency (10H-10^{5}Hz) on the Na_2S moiety. The results show at lower temperatures the extrinsic behaviour due to impurities and the intrinsic conductivity at elevated temperatures. Raman experiments have further been performed on this sytem.



Physikalische Chemie **103**

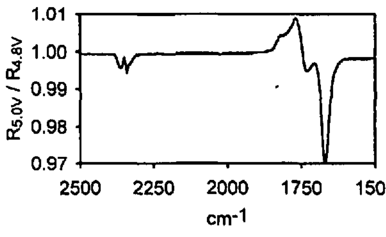
Untersuchungen an organischen Elektrolyten mittels SNIFTIRS (Subtractively Normalized Interfacial FTIR Spectroscopy)

Felix Joho[a,b], Petr Novák[a], Otto Haas[a] und Reinhard Nesper[b]

[a] Paul Scherrer Institut, Sektion Elektrochemie, CH-5232 Villigen PSI
[b] Laboratorium für Anorganische Chemie, ETH-Zentrum, CH-8092 Zürich

Für wiederaufladbare Lithium- oder Ionentransferbatterien sind wässrige Elektrolyte nicht mehr geeignet, weil sie Zellspannungen über 2V kaum ermöglichen. Deshalb müssen organische Elektrolyte verwendet werden, die bei wesentlich grösseren Spannungen noch stabil sind. Im Idealfall bilden diese Schutzfilme aus Zersetzungsprodukten, die zwar für die Lithiumionen immer noch durchlässig sind, aber den flüssigen Elektrolyten wirksam vor weiterer Zersetzung schützen. Die richtige Wahl des Elektrolyten zu den Elektroden verlängert die Lebensdauer einer Batterie erheblich.

Um einen Einblick in die Vorgänge an der Elektrodenoberfläche zu erhalten, haben wir eine spezielle Messzelle entwickelt, womit die Phasengrenze Elektrolyt/ Elektrode in situ mit SNIFTIRS beobachtet werden kann. Zum Beispiel von 1M $LiClO_4$ in Propylencarbonat: Auf dem Bild ist die normalisierte Differenz zweier FTIR-Spektren zu sehen, bei der eine Spannung von 5.0V resp. 4.8V zwischen einer Lithiumgegen- und einer Nickelarbeitselektrode angelegt wurde. Zwischen diesen beiden Potentialwerten beginnt eine intensive Zersetzung des Elektrolyten an der Arbeitselektrode. Die scharfe Bande bei 2342 cm^{-1} ist auf die Entwicklung von CO_2 zurückzuführen. Die Verschiebung der Carbonylschwingungen zu kleineren Wellenzahlen deutet auf eine Ringöffnung des Propylencarbonats hin. Es werden Resultate von verschiedenen Elektrolytsystemen vorgestellt.



Wir danken dem Bundesamt für Energiewirtschaft für die finanzielle Unterstützung.

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Physikalische Chemie **104**

Reibungsmessungen mit dem Rasterkraftmikroskop

A. Schumacher, N. Kruse, R. Prins, Lab. für Techn. Chemie, ETH Zürich
E. Meyer, H.-J. Güntherodt, Institut für Physik, Universität Basel

Das Rasterkraftmikroskop (AFM) ist zu einem wichtigen Instrument zur Untersuchung von Oberflächen im Bereich von einigen Å bis mehreren µm geworden. Neben dem ursprünglichen, nur Topographie abbildenden AFM sind in den letzten Jahren zahlreiche Erweiterungen entwickelt worden, mit denen physikalische und chemische Eigenschaften von festen Stoffen untersucht werden können.

Wir haben das Reibungsverhalten auf MoS_2, Glimmer und Korund mit Hilfe eines Rasterkraftmikroskops eingehend untersucht. Dazu wurde MoS_2 in Form von 1,2 nm flachen Partikeln mit einem Durchmesser von einigen 100 nm, sogenannten "single-layern", auf Glimmer bzw. Korund-Einkristallen aufgetragen. Auf diese Weise war es möglich, die Reibung von zwei verschiedenen Materialien in einer Aufnahme zu messen und zu vergleichen. Das Reibungsverhalten wurde insbesondere bei verschiedenen Feuchtigkeiten untersucht. In trockener Umgebung hat Glimmer einen kleineren Reibungskoeffizienten als MoS_2. Im Bereich zwischen 40 und 60% Feuchtigkeit kehrt sich das Reibungsverhältnis jedoch um. Dies ist auf die Adsorption von Wasser auf der Glimmeroberfläche zurückzuführen. Glimmer ist stark hydrophil. In feuchter Umgebung bildet sich ein Wasserfilm auf der Oberfläche aus, der die Kapillarkräfte zwischen der Spitze des Kraftmikroskops und der Probe erhöht. Das hat zur Folge, dass die lateralen bzw. Reibungskräfte, die während des Abrasterns auf die Spitze wirken, erhöht werden.

Die Adsorption von Wasser auf MoS_2 und Korund ist gering. Entsprechend ändern sich die Reibungskoeffizienten von MoS_2 und Korund mit dem Feuchtigkeitsgehalt der Umgebung nur wenig. Die Reibung auf Korund ist stets kleiner als auf MoS_2.

Computational Chemistry **105**

Solvent effect on the NMR chemical shieldings in water calculated by molecular dynamics and density functional theory.

Vladimir G. Malkin and Olga Malkin, Institute of Inorganic Chemistry, SAV, Dubravska cesta 9, SK-84236 Bratislava, Slovakia

Gerold Steinebrunner and Hanspeter Huber, Institut für Physikalische Chemie der Universität Basel, Klingelbergstr. 80, 4056 Basel

The solvent effect on the NMR chemical shielding in liquid water is calculated from a combination of molecular dynamics simulations and quantum chemical calculations for protons and ^{17}O. The simulations are performed with three different potentials, ab initio as well as empirical ones, to study the influence of the force field. From liquid configurations obtained in these simulations, molecules are randomly chosen together with neighbour molecules to get clusters of water typical for the liquid at the selected temperature and pressure. Different cluster sizes are studied. The clusters are treated as supermolecules in quantum chemical calculations of chemical shifts by sum-over-states density functional perturbation theory with individual gauge for localized orbitals. An average over clusters yields the chemical shielding in the liquid at the selected temperature and density. The best values obtained for the gas-liquid shift, -3.2 ppm (exp. -4.26 ppm) for the proton and -37.6 ppm (exp. 36.1 ppm) for ^{17}O, show fair agreement with experiment, but the results depend strongly on the chosen interatomic potential.

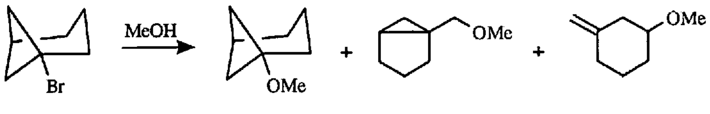
Computational Chemistry **106**

Ab Initio Investigation of the $C_7H_{11}^+$ Potential Energy Surface

J. Mareda
Department of Organic Chemistry, University of Geneva
CH-1211 Geneva 4

Bridgehead halides have a markedly reduced reactivity which was rationalized recently in terms of structure-reactivity relationships [1]. A notable exception to these relationships is provided by the bicyclo[n.1.1]halides, which indeed solvolyse more rapidly than expected on the grounds of the strain energies accumulated in the corresponding cations.

1-bromobicyclo[3.1.1]heptane in particular shows extraordinary reactivity even under mild solvolytic conditions, leading to a mixture of both rearranged and unrearranged products [2]. This halide is at least 8 times more reactive than *tert*-butyl bromide, despite the fact that it has been believed to react *via* the intermediacy of strained bicyclo[3.1.1]heptyl cation [2].



In the present work the $C_7H_{11}^+$ potential energy surface has been investigated with *ab initio* methods in order to provide computational evidence for the enhanced reactivity for the bicyclo[3.1.1]heptyl halides. These results will be discussed and in addition, will be compared with those obtained for other bridgehead carbocations [3]. The computed data will also be correlated with experimental results.

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Computational Chemistry **107**

Applications of Kohn-Sham Equations with Constrained Electron Density

Tomasz Adam Wesolowski and Jacques Weber
Department of Physical Chemistry, University of Geneva
30, quai Ernest-Ansermet, 1211 Geneva 4, Switzerland

Most current applications of Density Functional Theory for studies of molecular properties are based on the Kohn-Sham (KS) approach [1], where the electron density minimizing the total energy functional is derived from molecular orbitals. We proposed recently an alternative approach for searching for the electron density minimizing the total energy[2,3]. In this approach, the total electron density is represented as a sum of two components (ρ_1 and ρ_2). Only ρ_1 is allowed to vary and it is obtained from Kohn-Sham equations with constrained electron density (KSCED). The KSCED equations contain terms representing the coupling between ρ_1 and ρ_2. These terms involve also a new functional, namely the non-additive kinetic energy functional [2] that is not present in the original KS method. The following applications of the KSCED approach will be presented:

a) the ground state properties of interacting H_2 and NCH molecules,
b) the energy gap between states with different symmetry (^2E and $^4A_2$) of $(CrCl_6)^{3-}$ complex,
c) the polarization of water molecules surrounding a lanthanide ion (Gd^{3+}) and the structure of the complex.

In the all cases, the KSCED approach has been shown to lead to accurate results as compared with supermolecule calculations, while requiring a substantially smaller computational effort.

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Computational Chemistry **108**

Optical Spectra of Transition Metal Tetraoxo Compounds: A Comparison between Experiment and DFT Results

A. C. Stückl a), C. A. Daul a), and H. U. Güdel b)
a) Institut de Chimie Inorganique et Analytique, Université de Fribourg, CH-1700 Fribourg
b) Institut für Anorganische und Physikalische Chemie, Universität Bern, CH-3000 Bern

Density Functional Theory is used to predict excited state properties of several transition metal compounds from first principles.
Combining the Transition Operator approach [1] with the Equiensemble DF Formalism in its generalized form [2], a selfconsistent set of symmetry adapted state functions is constructed to calculate transition energies, excited state multiplet splittings [3] and vibrational frequencies from total energies. Results are compared with data obtained from a ΔSCF procedure.

A comparison between experimentally derived and calculated data shows, that the trends in the chemical series are well reproduced for d^0 transition metal oxides (VO_4^{3-}, CrO_4^{2-}, MnO_4^-; MoO_4^{2-}, TcO_4^-, RuO_4;). With the inclusion of relativistic corrections, the results for WO_4^{2-}, ReO_4^-, and OsO_4 are in good agreement with the experimental absorption spectra.
We discuss whether the presented calculation approach is also useful to obtain d-d- and CT-transitions in d^n (n = 1,2) compounds. Examples of the MnO_4^{n-} series are shown.

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Computational Chemistry **109**

An *ab initio* derived torsional potential energy surface for $(H_2O)_3$

Stephan Graf, Thomas Bürgi, and Samuel Leutwyler
Institut für anorganische , analytische und physikalische Chemie,
Freiestr.3, CH-3000 Bern 9

Wim Klopper
Interdisziplinäres Projektzentrum für Supercomputing, Eidgenössische Technische Hochschule, CH-8092 Zürich

An intermolecular potential energy surface was derived for the hydrogen-bonded water trimer as a function of four intermolecular coordinates, the three torsional angles ω_1, ω_2, ω_3 and the symmetric stretch coordinate (equal O•••O distances). The intramolecular geometry of the H_2O molecules is held fixed. This surface is based on MP2-R12 *ab initio* calculations [1], which involve very large basis sets and the most extensive treatment of correlation energy for calculations of $(H_2O)_3$ so far. The *ab initio* interaction energies, multiplied by six due to the S_6 symmetry of the surface, were fitted using a modified EPEN potential function. This potential provides a rapidly computable analytical expression for use in calculations of intermolecular vibrational eigenfunctions and -values and other properties of this cluster. Torsional eigenfunctions have been calculated in one-, two- and three-dimensional model calculations. The low-lying torsional wavefunctions are easily classifiable according to nodal properties.

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Computational Chemistry **110**

Molecular modelling study of hydrophobic interactions between HEL(52-61) and related peptides by I-A^k class II MHC molecule.

Peter Weber1, Pierre-Alain Carrupt1, Joelle Paris2, Denis Gerlier3, Chantal Rabourdin-Combe4, Laurent Ettouati2 and Bernard Testa1.

1 Institut de Chimie Thérapeutique, Université de Lausanne, BEP, CH-1015 Lausanne.
2 Laboratoire de Chimie Thérapeutique, Faculté de Pharmacie, Université Lyon I, 8 avenue Rockefeller, F-69373 Lyon Cedex 08.
3 Immunité et infections virales, IVMC, UMR30, CNRS-UCBL, F-69373 Lyon Cedex 08.
4 Immunologie Moléculaire, UMR 49, CNRS-ENS Lyon, F-69364 Lyon Cedex 07.

The I-A^k class II major histocompatibility complex (MHC) is a protein of the mouse immune system. It is a cell surface macromolecule located on antigen-presenting cells (APC). After endosomal degradation of a foreign protein, I-A^k binds peptidic fragments and brings them to the cell surface to present them to the T cells. This interaction will stimulate the proliferation of the T cells and thus activate the immune response.

This study uses biological *in vitro* data on T-cell activation and competing peptide concentration of 35 peptides derived from the hen egg lysosyme (HEL) fragment 52-61 [1]. A SAR analysis was performed using the molecular lipophilicity potential (MLP) [2] to see if the three-dimensional lipophilicity of the peptides can explain their binding affinity.

The molecular modelling of the I-A^k is based on a crystallographic structure of the human HLA-DR1 molecule complexed with an influenza virus peptide (306-318) [3]. The coordinates were kindly provided by J.H.Brown. The sequence homology is 60%, so the I-A^k molecule was build by "mutating" the non-homologous amino-acids. The MLP applied to the binding groove of the I-A^k in addition to molecular dynamics served as a guide to postulate the conformation of the bound peptide

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Computerunterstützte Chemie **111**

A Computer Program for the Calculation of the Kinetic Parameters of Solid-state Reactions

B. Roduit, M. Maciejewski and A. Baiker,

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

A computer program for the calculation of the kinetic parameters of solid state reactions has been developed in order to simulate the course of processes during isothermal or non-isothermal heating. For the description of the course of the reaction three parameters have to be determined: the preexponential factor *A*, the activation energy *E* (constants of Arrhenius equation) and the function of the progress of the reaction α, which are dependent on the mechanism of the reaction. As a first step the program selects the most suitable model among the 21 models applied in the literature for the description of solid-state kinetics on the basis of the data taken from at least 2 thermogravimetric curves obtained with different heating rates. For each experimental point the program calculates the squared difference between the α value computed for that point and the corresponding experimental value. In the second step the optimisation of the kinetic data is performed by minimising the total residual sum of squares $\Sigma(\alpha(exp)-\alpha(cal))^2$. The applied numerical integration procedure adjusts *A*, *E* and the reaction order *n* in previously chosen $f(\alpha)$ function. After determination of the kinetic parameters the simulation of the course of the reaction under different heating rates (non-isothermal mode) or at different temperatures (isothermal mode) is possible. Input of data can be achieved manually or by using ASCII files. The program runs using Excel 4.0 or 5.0 and has been elaborated for MS-DOS with Windows or Macintosh computers. The application of the program is illustrated by calculating the kinetic parameters of the reduction of NiO by H_2.

Computational chemistry

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Calculation of photophysical properties of $[Cr(NH_3)_6]^{3+}$

Karel Doclo, Claude Daul
Institut de chimie inorganique et analytique
Université de Fribourg, Pérolles
CH-1700 Fribourg
Switzerland

Although the ligand-field spectra, photophysics and photochemistry of chromium (III) amine complexes are very well investigated by many experimentalists, there exist almost no *ab initio* studies about this subject.
In this work, we searched the ground state geometry of $[Cr(NH_3)_6]^{3+}$ using Density Functional Theory (DFT) within the local and non-local approximation. Furthermore, we calculated the multiplet energies within two different approaches : expressing the energies of multiplets in function of the energies of single determinants [1] or in function of electrostatic two-electron integrals [2]. Special attention is given to the $^4T_{2g}$ excited state, which undergoes both large totally symmetric and Jahn-Teller distortions.

[1] C. Daul, Density functional theory applied to the excited states of coordination compounds, *Int. J. Quantum Chem. 1994*, **52**, 867
[2] J. S. Griffith, The theory of transition metal ions, Cambridge University Press, Cambridge, 1961

Computational chemistry

113

Geometry of Coordinatively Unsaturated Two-legged Piano Stool Complexes: A Theoretical Study.

Olivier Schafer and Claude Daul[a], Thomas R. Ward[b], Peter Hofmann[c]
[a]Institut de Chimie Inorganique et Analytique, Université de Fribourg, 1700 Fribourg Suisse
[b]Institut für Anorganische Chemie der Universität Bern, Freierstrasse 3, 3012 Bern Switzerland
[c]Institut der TechnischenUniversität München, 8046 Garching, Germany

The structure of coordinatively unsaturated two-legged piano stool complexes is analyzed with extended Hückel methodology as well as with Density Functional Theory (DFT). Pyramidal, and thus potentially chiral at the metal, geometries are predicted to be preferred for systems containing low lying π-acceptor orbitals, as well as electropositive σ–donors, i.e. silanes. DFT calculations were carried out for the model compounds [CpFeH2]$^-$, [CpFe(CO)2]$^+$ and [CpFe(HCO)H]$^-$.
In all cases, the computed inversion barriers are too low (<45 kJ/mol) to account for retention of configuration at the metal upon dissociative ligand substitution. An η^2-coordination in [CpFe(acyl)NO] is predicted by the extended Hückel calculations which may account for the stereospecific ligand substitution in acyl containing systems. At the DFT level, an η^2-coordination was found for [CpFe(HCO)H]$^-$ but no η^1 minimum was found.

Computational chemistry

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Electron Localization Function (ELF): Application to transition metal complexes

Olivier Schafer and Claude Daul

Institut de Chimie Inorganique et Analytique
Université de Fribourg,
1700 Fribourg
Suisse

The notion of 'electron pair' and 'chemical bond' can be nicely illustrated by a function developped by Becke and Edgecombe [1]. They investigated a way of defining such regions of electron localization. Nice examples of this electron localization function (ELF) from Hartree-Fock calculation are given by Savin et al.[2] and Silvi and Savin[3].
We present a new computer program that derives ELF from Density Functional Theory calculations. Examples for $CoAl_2Cl_8$, $Pd_2Cl_4\mu(CO)_2$, $Cr(NH_3)_6$, $[CpFeH_2]^-$, [CpFe(acyl)H]$^-$ as well as other chosen transition metal complexes will be presented.

[1] A. D. Becke and K. E Edgecombe, *J. Chem Phys.* **92**(1990), 5397
[2] A. Savin, A.D. Becke, J. Flad, R. Nesper, H. Preuss and H. G. von Schnering, *Angew. Chem. Int. Ed. Engl.* **30** (1991), 409
[3] B. Silvi and A. Silvi, *Nature* **371** (1994), 683

Anorganische Chemie
Minisymposium: Small Inorganic Molecules in Biological Systems

115

Methane Activiation by Biological Systems

Howard Dalton
Department of Biological Sciences, University of Warwick, Coventry

Despite the fact that over 150 different bacterial strains have been isolated from Nature capable of growing on methane the enzyme responsible for the initial oxidation of methane to methanol has been thoroughly characterized from only two of these strains. The enzyme responsible for this O_2-dependent oxidation of methane is called methane monooxygenase (MMO) and comprises three proteins, the reductase, a regulatory protein and the hydroxylase. The reductase interacts with reduced pyridine nucleotides to pass electrons to the hydroxylase, the site of methane activation and dioxygen reduction. The hydroxylase is able to effect methane oxidation by activation dioxygen through a μ oxo-bridged diiron centre to produce a ferryl species that is electophilic enough to abstract hydrogen from methane to form a methyl radical. The radical then collapses with captive hydroxyl species to form methanol.

In many respects the mechanism of action closely resembles that of cytochrome P450 wich, although responsible for a wide variety of hydrocarbon oxidations is not able to oxidize methane. Indeed an equally large number of metal-based organic complexes have been synthesized in an attempt to mimic the active site of the enzyme to effect room temperature, ambient pressure oxidation of methane. All but one of these have failed to show methane activation so an obvious question to be asked is 'what is so special about the enzyme that allows methane to be entrapped and activated?' The X-ray crystal structure of hydroxylase has given us some insight into this and recent modelling studies have shown that these are two specific binding sites for various MMO substrates that are located close to the diiron centre. In addition to these modelling studies kinetic and spectroskopic data have given us a reasonable picture of how the enzyme works and is regulated. This presentation will attempt to distill this information into a coherent picture of enzymic methane activation and indicate where future studies might lead.

Anorganische Chemie
Minisymposium: Small Inorganic Molecules in Biological Systems

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Peroxynitrite, an Inorganic Toxin

W.H. Koppenol
Laboratorium für Anorganische Chemie, ETHZ, 8092 Zürich

Nitrogen monoxide has been identified as a biologically important molecule involved in a number of physiological processes including relaxation of vascular smooth muscle, neurotransmission, platelet inhibition and immune regulation Among the important reactions of nitrogen monoxide is that with superoxide to form the toxic compound peroxynitrite [oxoperoxonitrate(1-), $O=NOO^-$] The rate constant for this reaction is diffusion-controlled, which makes this reaction kinetically feasible near activated macrophages and neutrophils.

Oxoperoxonitrate(1-) is a relatively stable species, but its protonated form, O=NOOH, isomerizes readily to NO_3^- and H^+ at a rate of 1.3 s^{-1} at 25°C. Both hydrogen oxoperoxonitrate and its anion are powerful oxidants that damage biological compounds. The reaction of oxoperoxonitrate(1-) with aromatic compounds produces both nitrated and hydroxylated products the ratio of which is pH-dependent. These reactions proceed as fast as the isomerization to nitrate and do not depend on the concentration of the aromatic compound. The nitration reaction is enhanced by metal complexes and Cu/Zn superoxide dismutase. In the case of reactions that are first-order overall, it has been suggested that peroxynitrous acid undergoes homolysis to form hydroxyl and nitrogen dioxide radicals. We have argued that homolysis is unlikely on the basis of thermodynamic and kinetic considerations. Instead, O=NOOH itself is is a strongly oxidizing agent that oxidizes in an activated state. The oxidizing species is believed to be an intermediate closely related to the transition state for the isomerization of hydrogen oxoperoxonitrate to nitrate. In contrast, oxoperoxonitrate(1-) oxidizes methionine, sulfhydryls, tryptophan and ascorbate in second-order reactions. The reaction of hydrogen oxoperoxonitrate with hypochlorite is also bimolecular and results in the formation of nitrosyl chloride, a nitosylating species.

It is clear that hydrogen oxoperoxonitrate uses many different pathways to damage biomolecules. The mechanisms of these reactions are the goal of our research.

Anorganische Chemie

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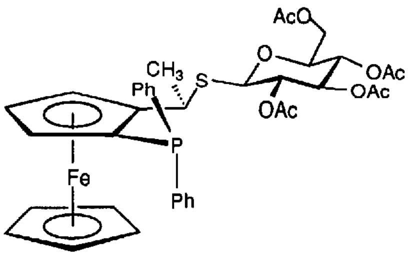
New Metal Complexes Based on a Novel Chiral Ligand
Sugar-Phosphine Chemistry

P.S. Pregosin, K. Wick
Laboratorium für anorganische Chemie, ETH Zürich, CH-8092 Zürich

The preparation and characterisation of a series of transition metal complexes and the new chiral P,S-ligand, 1, will be presented.



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The application of 1 as chiral auxiliary in the Pd(II) catalysed enantioselective allylic alkylation will be shown. There will be a brief discussion on how this and other chiral auxiliaries function in this reaction.

Anorganische Chemie
Minisymposium: Small Inorganic Molecules in Biological Systems

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Potassium Monopersulfate: a Useful Oxidant in DNA Cleavage

B. Meunier
Laboratoire de Chimie de Coordination du CNRS, 205 route de Narbonne, F-31077 Toulouse, cedex

Oxidative DNA cleavage is easily perfomed *in vitro* by using cationic manganese porphyrin complexes activated by potassium monopersulfate, an efficient water-soluble oxygen atom donor [1]. The presentation will be focused on the molecular aspects of DNA cleavage mechanism by these metal-oxo porphyrin species. We recently demonstrated that oxidation at carbon 1' of DNA deoxyriboses by the Mn-TMPyP/$KHSO_5$ system resulted from a cytochrome P-450-type hydroxylation reaction [2].

[1] a) J. Bernadou, G. Pratviel, F. Bennis, M. Girardet, B. Meunier, *Biochemistry* **1989**, *28*, 7268.
b) M. Pitié, G. Pratviel, J. Bernadou, B. Meunier, *Proc. Natl. Acad. Sci. USA* **1992**, *89*, 3967.
c) G. Pratviel, V. Duarte, J. Bernadou, B. Meunier, *J. Am. Chem. Soc.* **1993**, *115*, 7939.
d) G. Pratviel, J. Bernadou, B. Meunier, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 746.
[2] M. Pitié, J. Bernadou, B. Meunier, *J. Am. Chem. Soc.* **1995**, *117*, 2935.

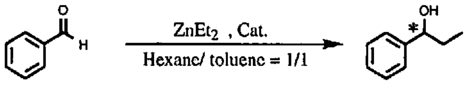
Chimie minérale et de coordination

119

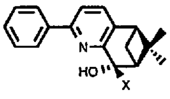
Use of rigid pyridyl-alcohols in asymmetric catalysis

P. Belser, Ph. Collomb and A. von Zelewsky
Institut de Chimie Inorganique et Analytique, Université de Fribourg, CH-1700 Fribourg

Optically active β-aminoalcohols are known to be efficient catalysts for various asymmetric reactions, including the enantioselective addition of diethylzinc to benzaldehyde, giving 1-phenyl-1-propanol[1].



The optically active precursor for the synthesis of the catalysts is the inexpensive (-)-α-pinene. The rigidity of the pinene moiety fixes the conformation of the ligand, where the hydroxy group is out of the plane of the pyridine ring.



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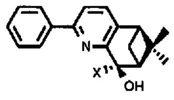

2

1 and 2 are diastereoisomers having very different catalytic efficiencies.

By using 5 % of 1 (X= H), (S)-1-Phenyl-1-propanol was obtained in 87 % yield with an enantiomeric excess of 26 %.
By using 5 % of 2 (X= H), (R)-1-Phenyl-1-propanol was obtained in 98 % yield with an enantiomeric excess of 91 %.

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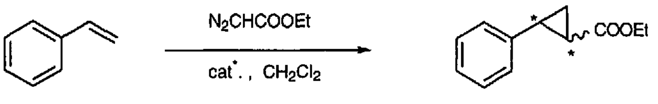
[1] K. Soai, S. Niwa, *Chem. Rev.* **1992**, *92*, 833;
C. Bolm, G. Schlingloff, K. Harms, *Chem. Ber.* **1992**, *125*, 1191;
A. Iuliano, D. Pini, P. Salvadori, *Tetrahedron: Asymmetry* **1995**, *6*, 739

Inorganic and Coordination Chemistry **120**

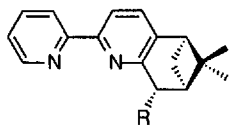
Novel Optically Active Bipyridines as Chiral Ligands in Copper-Catalyzed Asymmetric Cyclopropanations

Stefan Rupprecht and Alex von Zelewsky
Institute of Inorganic and Analytic Chemistry, University of Fribourg, Pérolles, CH - 1700 Fribourg

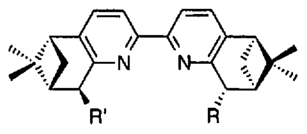
The reaction of carbenes with olefins represents a superb opportunity for the preparation of small ring molecules. Recently, several groups have been working on asymmetric variations of this reaction [1].



The copper-based chiral catalysts presented here show good to moderate chiral inductions for the reaction of diazoacetate with styrene. The different catalytic properties between ligand **I** and **II** in respect to their substituents **R** and **R'** (**R** = H, Me, Et, ^{i}Pr, SiMe3) will be discussed.



I



II

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[1] K. Ito, S. Tabuchi, T. Katzuki *Synlett* **1992**, 575; D. A. Evans, K. A. Woerpel, M. M. Hinman, M. M. Faul *J. Am. Chem. Soc.* **1991**, *113*, 726;H. Fritschi, U. Leuternegger, A. Pfaltz *Helv. Chim. Acta* **1988**, *71*, 1553.

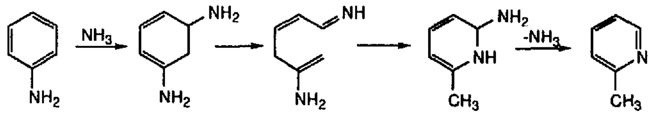
Anorganische/Koordinations Chemie **121**

The Zeolite-catalysed Isomerisation of Anilines to Methyl-substituted Pyridines

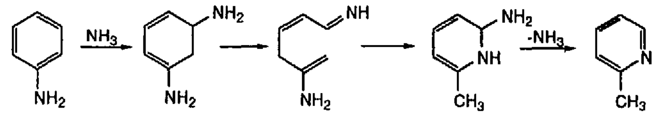
A. Tschumper, T. Stamm and R. Prins

Laboratory for Technical Chemistry, Federal Institute of Technology (ETH), CH 8092 Zürich, Switzerland

Some years ago it was discovered (European Patent no. 0082613 (1982), German Patent no. 3332687 (1983)) that aniline could be isomerised to 2-methylpyridine and m-diaminobenzene to 2-methyl-6-amino-pyridine and 2-methyl-4-amino-pyridine when these reactants were heated under high ammonia pressure in the presence of acid catalysts. We have studied the scope and mechanism of these intriguing reactions, which could be of interest for the synthesis of pharmaceutical and agrochemical intermediates.



Rather severe conditions are required for the isomerisation of aniline, with optimum results around 300°C and 100 atm NH_3. A high NH_3 pressure was absolutely required, pyridine formation took only place in the presence of NH_3. Although many acid materials (zeolites, Al_2O_3, $FeCl_3$, NH_4Cl) catalysed the reactions, zeolites and especially H-ZSM-5 performed best, because of less (fast) deactivation.
All arylamines studied (aniline, toluidines, naphthylamines and anthracylamines) showed the conversion into a methyl substituted aza-aromatic system. For instance, methyl-isoquinolines were produced from naphthylamines. In all cases, the methyl group in the product was positioned ortho to the nitrogen atom in the aromatic ring.
A mechanism which explains the results goes via addition of NH_3 to the aromatic ring, ring opening, reorientation, ring closure and ammonia elimination.



Anorganische/Koordinations Chemie **122**

Katalytische Synthese von Methylaminen aus CO_2, H_2 und NH_3

S.V. Gredig, R. Köppel und A. Baiker
Laboratorium für Technische Chemie, ETH-Zentrum, 8092 Zürich

Die Herstellung von Methanol ausgehend von CO_2 und H_2 sowie die Synthese von Aminen aus CO/H_2-Synthesegas und Ammoniak sind bereits bekannt. Kürzlich wurde gezeigt, dass Methylamine direkt aus CO_2, H_2 und NH_3 hergestellt werden können [1].

Die Reaktion wurde in einem Festbettreaktor unter einem Druck von 6 bar in einem Temperaturbereich von 200-340°C durchgeführt. Das Eduktgas bestand aus 20% CO_2, 60% H_2, 0-20% NH_3 und N_2 als Inertgas. Für alle Experimente wurden 3g Kupfer/Aluminiumoxid-Katalysator mit 33.9 resp. 58.5 Gew.-% Kupferbeladung eingesetzt.

Die einzigen nachgewiesenen kohlenstoffhaltigen Produkte waren Mono-, Di- und Trimethylamin (MMA, DMA und TMA), Methanol und Kohlenmonoxid. Beide Kupfer/Aluminiumoxid Katalysatoren zeigten ein identisches Verhalten, was bedeutet, dass der Kupfergehalt im untersuchten Bereich keinen signifikanten Einfluss hat. Durch die Varrierung der Raumgeschwindigkeit in Bereich von 1500 bis 3000 h^{-1} konnte ebenfalls keine wesentliche Beeinflussung des katalytischen Verhaltens festgestellt werden. Hingegen zeigten der Ammoniakumsatz und die Produkteverteilung deutliche Abhängigkeiten von der Temperatur und vom Ammoniakgehalt des Eduktgases. MMA stellt über den gesamten Temperaturbereich das Hauptprodukt dar, dessen Anteil bei höheren Temperaturen zunimmt, während der TMA-Anteil deutlich zurückgeht. Bei tiefen Ammoniakkonzentrationen stellte TMA das Hauptprodukt dar, während mit steigender NH_3-Konzentration (> 2.5 mol%) bevorzugt MMA gebildet wurde. Die Bildung von Methanol wurde durch die Zugabe von Ammoniak zum Eduktgas vollständig unterdrückt. Dies deutet darauf hin, dass Methanol nicht als Zwischenprodukt dieser Aminierungsreaktion auftritt.

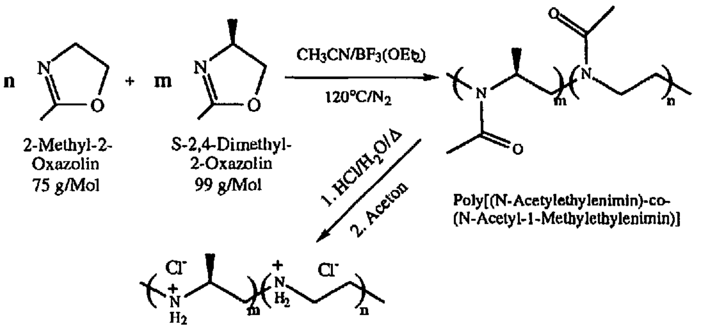
[1] S.V. Gredig, R.A. Köppel und A. Baiker, J. Chem. Soc., Chem. Commun.,1 (1995) 73.

Anorganische Chemie **123**

Komplexe mit optisch aktiven Polyiminen

C.W.Schläpfer, M.Kurt
Institut für analytische und anorganische Chemie, Fribourg

Polymere mit verschiedenen Verhältnissen an 2-Methyl-2-oxazolin und dem optisch aktiven S-2,4-Dimethyl-2-oxazolin wurden synthetisiert.



Poly[(Ethylenimin)-co-(1-Methylenimin)]

Die jeweiligen Molekulargewichte der Polymere wurden mit Dampfdruckosmometrie ermittelt. Das Verhältnis der beiden Monomere im Polymer wurde mit der Elementaranalyse, der NMR-Spektroskopie und der Polarographie bestimmt.
Durch Metalltitration mit Nickel wurde versucht festzustellen, ob sich das Metallion statistisch über das ganze Polymer verteilt anlagert. Bei pH= 7,7 bildet sich ein NiN_6-Komplex, bei pH= 4,5 ein $NiN_4(H_2O)_2$-Komplex. Deshalb wurden die verschiedenen Polymere bei konstantem pH-Wert titriert. Die Titrationen wurden mittels UV/VIS- und CD-Spektroskopie verfolgt. Es wurde beobachtet, dass bei kleinem Anteil an S-2,4-Dimethyl-2-oxazolin im Polymer die Intensitäten im CD-Spektrum langsamer ansteigen als erwartet. D.h., bei geringem Anteil von S-2,4-Dimethyl-2-oxazolin bildet sich am Anfang bevorzugt Komplexe mit optisch inaktiven Abschnitten des Polymers. Die sterisch anspruchsvollere Umgebung der chiralen Zentren wird erst bei höheren Konzentrationen besetzt.

CHIMIA 49 (1995) Nr. 7/8 (Juli/August)

Anorganische Chemie/Koordinations Chemie **124**

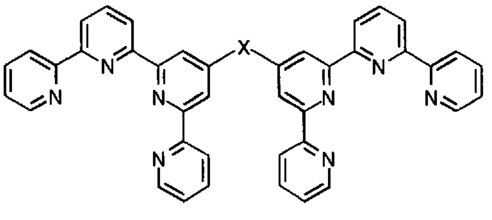
Oligopyridine metal-binding domains for helicates and cyclometallates

E.C. Constable, S. Dunne, F. Heirtzler, D. Rees, D. Smith and L. Whall

Institut für Anorganische Chemie, Universität Basel, CH-4056 Basel

The higher oligopyridines and related oligoheteroaryls have proved to be versatile ligands for the assembly of helicates. Recent results on new ligands in which the oligopyridine metal-binding domains are separated in a variety of ways (*e.g.* **1**) will be presented.

Related studies on a series of ligands in which some of the nitrogen donor heterocycles in the oligopyridine have been replaced by sulfur donor thiophenes or cyclometallating phenyl or phenylene groups will also be reported.



1

New multinuclear complexes in which several helical motifs are covalently linked will be described, as will some novel self-assembly processes.

E.C. Constable, *Prog. Inorg. Chem.*, 1994, 42, 67-138

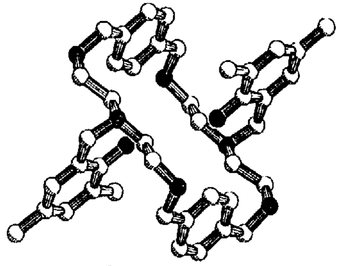
Anorganische Chemie **125**

MODELLING OF THE TYROSINASE AND PHOSPHATASE ACTIVE SITES BY N_6O_2-MACROCYCLIC COMPLEXES

Peter Comba[a], *Dave T.Richens*[b], *Andreas Kühner*[a]

[a]Anorganisch-Chemisches Institut der Universität Heidelberg, 503
D-69120 Heidelberg, Germany
[b]Dept. of Inorganic Chemistry, University St.Andrews Scottl., UK

Our ligand system should be capable of imitating the active sites of tyrosinase (copper enzyme) and PAP (iron enzyme). We have already shown, that the N_3O-Fe^{3+}-complexes are appropriate spectroscopic models. A four step synthesis via amine protection and Mannich reaction leads to the



N_6O_2-pendant arm macrocycle.

The metal-metal distances can be varied by using terephtalaldehyde, isophtal-aldehyde and different alkyl chains as spacers. Our first aim is to model the typical absorption band of purple acid phosphatase (catalytic inactive Fe^{3+}-Fe^{2+}-form λ_{max}= 550 nm, active Fe^{3+}-Fe^{2+}-form at λ_{max}= 505 nm)[1]. Secondly, we intend to determine the solution structures of the Cu^{2+}-systems using the MM-EPR-approach and to carry out some activity studies.[2]

1. K.Doi, P.Aisen, *Struct. Bonding* (Berlin), **1**, 170, (1988)
2. P.V.Bernhardt, P.Comba, T.W.Hambley, S.S.Massoud, S. Stebler, *Inorg. Chem.*, 31, 2644 (1992)

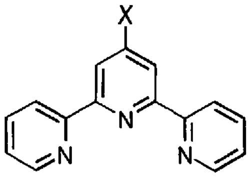
Anorganische Chemie/Koordinations Chemie **126**

Functionalised 2,2':6',2"-Terpyridines as building blocks in metallosupramolecular chemistry

D. Armspach, E.C. Constable, R.-A. Fallahpour, P. Harveson, C.E. Housecroft, T. Kulke, D. Morris, M. Oberholzer, A. Schneider and D. Smith

Institut für Anorganische Chemie, Universität Basel, CH-4056 Basel

Substituted 2,2':6',2"-terpyridines have proved to be ideal building blocks for the assembly of metallosupramolecular systems based. The {M(tpy)2} motif allows the assembly of a variety of functionalised oligomeric, polymeric and dendritic systems.



1

A variety of functionalised ligands will be presented which. *inter alia*, incorporate clusters, hydrogen-bond donors and acceptors, molecular recognition sites, chiral functionality, additional metal-binding domains and solubilising groups. The use of such ligands and of metal-directed reactionsin the assembly of dendrimers will be illustrated.

E.C. Constable, in *Transition Metals in Supramolecular Chemistry*, Eds. L. Fabbrizzi and A. Poggi, Kluwer, Dordrecht, 1994, 81 -100

Anorganische/Koordinations Chemie **127**

MCM-41, a mesoporous material

S. Hitz and R.Prins

Laboratorium für Technische Chemie
Eidgenössische Technische Hochschule, 8092 Zürich

Recently Mobil Oil Company described a new family of mesoporous molecular sieves. One of the materials, MCM-41, exhibits a hexagonal arrangement of uniform pores. As an organic template for the synthesis of the aluminosilicate serves a liquid crystal structure of the surfactant Cetyltrimethylammonium chloride /hydroxide. The material is a breakthrough in Zeolite chemistry as it expands the range of pore size to 25 Å (or even higher).

MCM-41 can be synthesized similar to zeolites. A gel of the composition: SiO_2 : 0.013 Al_2O_3 : 0.016 Na_2O : 0.083 $(CTMA)_2O$: 0.14 $(TMA)_2O$: 19 H_2O was placed in a teflon bottle at 70°C for 14 days without agitation. Afterwards the material it was calcined at 540°C for 6 hours in a flow of air to remove the organic template.

X-ray diffraction patterns show clearly the typical peaks of an MCM-41 material. The four peaks can easily be indexed to a hexagonal cell. For the as synthesised material the strongest peak is at a distance d_0 of ≈43 Å.

Surface area was determined by nitrogen adsorption. The BET surface area of the material is 1020 m^2/g. The sharp step of the isotherm and the narrow pore size distribution show clearly the uniformity of the pores.

Magic angle spinning NMR of ^{27}Al nuclei were recorded. The spectrum showed a single peak at a shift of 51 ppm. This indicates that all of the detectable aluminium is in a tetrahedral coordination.

As a test reaction for the catalytic activity of H-MCM-41 the Friedel-Crafts acylation of 2-methoxy-naphtalene with acetic anhydride was investigated. Reactions were run in batch reactors at a temperature of 100°C in Sulfolane as the solvent. Conversion to 1-acyl-2-methoxynaphtalene was 38 % after four hours reaction time. The selectivity towards 1-acetyl-2-methoxynaphtalene was 95%.

The catalyst performance can be compared to zeolite Beta. This encourages further application of MCM-41 as a mild acidic catalyst for organic reactions.

Anorganische/Koordinations Chemie **128**

The Effect of Phosphorus on the Hydrodenitrogenation of Quinoline over NiMoP/Al_2O_3 Catalysts

M. Jian and R. Prins
Laboratory for Technical Chemistry, Swiss Federal Institute of Technology, 8092 Zürich

Hydrodenitrogenation (HDN) is one of the most important industrial processes in petroleum refinery. It removes nitrogen from oil distillates which pollutes our air when the oil is burned (as NO_x) and which poisons the subsequent refining processes when the oil is further processed. Because of the increasing demand of clear fuel and refining of heavy crudes in recent years, the importance of hydrodenitrogenation has been greatly enhanced since the last decade. The development new HDN catalysts which makes the HDN process more efficient is therefore under pressure.

In the present study, the function of phosphorus in the HDN reaction of quinoline has been studied over NiMoP/Al_2O_3 catalysts. It is found that HDN of quinoline takes place mainly through two reaction paths over the catalysts: C-N bond breaking of the saturated intermediate DHQ→HC and C-N bond breaking of aromatic intermedites THQ-1→OPA→HC (Fig. 1). The relative contributions of these two reaction mechanisms depend on the reaction conditions and the catalyst employed. Presence of phosphorus in the catalyst favours the reaction through OPA, while the presence of H_2S in the reaction stream favours the reaction path through DHQ. In the former reaction path phosphorus exhibits a promotional effect while in the later reaction path phosphorus exhibits an inhibiting effect on the HDN conversion.

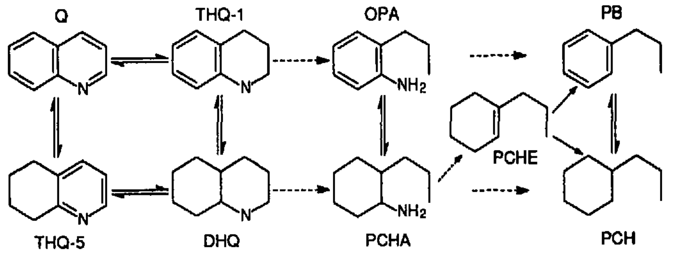


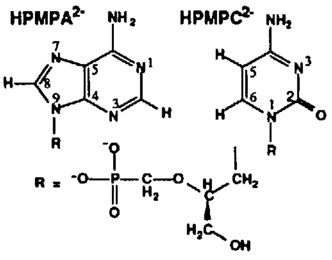
Fig. 1 HDN reaction network of quinoline

Anorganische/Koordinations Chemie **129**

Metal Ion-Coordinating Properties of Antiviral Adenine (HPMPA) and Cytosine (HPMPC) Phosphonate-Derivatives

Claudia A. Blindauer,[a] *Bin Song,*[a] *Matthias Bastian,*[a] *Antonín Holý,*[b] *and Helmut Sigel*[a]
[a] Institute of Inorganic Chemistry, University of Basel, Spitalstrasse 51, CH-4056 Basel, Switzerland; [b] Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Rep., 6610 Prague, Czech Republic

The nucleotide analogues (*S*)-9-[3-hydroxy-2-(phosphonomethoxy)propyl]-adenine and -cytosine are effective against DNA viruses, thus their metal ion-binding properties deserve attention [1]. Our preliminary stability constants determined via potentiometric pH titrations in aqueous solution (25°C; $I = 0.1$ M, $NaNO_3$) for some of their complexes, M(P), are given in the Table. Based on previous $\log K^{M}_{M(R\text{-}PO_3)}$ *vs* $pK^{H}_{H(R\text{-}PO_3)}$ correlations (R = non-coordinating residue) [1] and $pK^{H}_{H(HPMPA)} = 6.84 \pm 0.01$[2] or $pK^{H}_{H(HPMPC)} = 6.86 \pm 0.01$ the stability constant, $\log K^{M}_{M(P)_{op}}$, of the 'open' M(P) complex with only a $\text{-}PO_3^{2-}/M^{2+}$ interaction, can be calculated. Any formation of (a) chelate(s) must be reflected in an increased complex stability, i.e. $\log \Delta_{M(P)} = \log K^{M}_{M(P)} - \log K^{M}_{M(P)_{op}}$ must be positive. These values and results for M(PME) complexes ($PME^{2-} = CH_3CH_2\text{-}O\text{-}CH_2\text{-}PO_3^{2-}$) [1] (columns 4-6) prove that five-membered chelates involving the ether oxygen form and that in Cu(HPMPA) also a metal ion-adenine interaction must occur.



M^{2+}	$\log K^{M}_{M(HPMPA)}$	$\log K^{M}_{M(HPMPC)}$	$\log \Delta_{M(HPMPA)}$	$\log \Delta_{M(HPMPC)}$	$\log \Delta_{M(PME)}$
Mg^{2+}	1.81±0.03	1.83±0.04	0.12±0.04	0.13±0.05	0.22±0.03
Co^{2+}	2.35±0.03	2.29±0.07	0.27±0.07	0.21±0.09	0.29±0.06
Cu^{2+}	4.04±0.03	3.69±0.05	0.87±0.07	0.52±0.08	0.48±0.07
Zn^{2+}	2.73±0.10	2.60±0.06	0.39±0.12	0.25±0.08	0.34±0.06
Cd^{2+}	3.01±0.03	2.92±0.06	0.36±0.06	0.26±0.08	0.30±0.05

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

[1] H. Sigel, A. Holý, et al., *Helv. Chim. Acta 75*, 2634-2656 (1992).
[2] B. Song, A. Holý & H. Sigel, *Gazz. Chim. Ital. 124*, 387-392 (1994).

Chimie minérale et de coordination **130**

Etude du cycle thermodynamique des complexes de chlorure de cobalt(II) avec la 4-picoline

Laurent Audergon, Franzpeter Emmenegger
Institut de chimie inorganique, Université de Fribourg, CH-1700 Fribourg

De récentes analyses ont montré que $CoCl_2$ est parfaitement volatil dans la pyridine gazeuse. L'étude de la formation de complexes dans un tel système permet d'éviter les effets de la solvatation rencontrés en phase condensée et d'estimer ainsi les énergies des interactions métal-ligand. Dans le cadre de ce travail, nous avons étudié la formation de complexes de $CoCl_2$ avec pic (4-picoline), une base plus forte que la pyridine conduisant donc à des complexes sensiblement plus stables. En combinant les résultats des mesures de spectroscopie VIS en phase gazeuse avec les valeurs de la littérature et les données issues des mesures thermogravimétriques de pression de vapeur, nous avons pu déterminer le cycle thermodynamique complet pour l'équilibre solide-liquide-gaz dans le système $CoCl_2$-pic (valeurs en $KJ \cdot mol^{-1}$):

$$\begin{tikzcd}
CoCl_2pic_2(s) \arrow[r, "1", "+88.4"'] \arrow[d, "3"', "+23.4"] & CoCl_2pic(s) + pic(g) \arrow[r, "2", "+115"'] \arrow[d, "4"', "(+34.1)"] & CoCl_2(s) + 2\,pic(g) \arrow[dd, "11"', "(+234)"] \\
CoCl_2pic_2(l) \arrow[r, "7", "(+99.1)"'] \arrow[d, "8"', "+94.3"] & CoCl_2pic(l) + pic(g) \arrow[d, "5"', "+82"] \arrow[dl, "6"', "(-4.8)"] & \\
CoCl_2pic_2(g) \arrow[r, "9", "(+86.8)"'] & CoCl_2pic(g) + pic(g) \arrow[r, "10", "(+232.9)"'] & CoCl_2(g) + 2\,pic(g)
\end{tikzcd}$$

La mesure par spectroscopie VIS des constantes de formation de $CoCl_2(pic)$ et $CoCl_2(pic)_2$ en solution nous a en outre permis de comparer la stabilité des complexes en phase gazeuse et en solution.

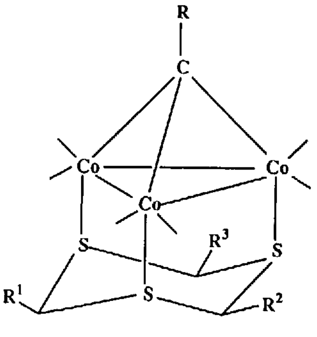
Chimie minérale et de coordination **131**

Coordination of Tridentate Crown Thioethers to Trinuclear Cobalt Clusters : Synthesis and Structure of Complexes of the Type $Co_3(CO)_6(\mu_3\text{-}CR)[\mu_3\text{-}\eta^3\text{-}(SCHR^1SCHR^2SCHR^3)]$

C. Renouard, G. Rheinwald, H. Stoeckli-Evans and G. Süss-Fink*
Institut de chimie, Université de Neuchâtel,
Avenue de bellevaux 51, CH-2000 Neuchâtel

The coordination of different six-membered crown thioethers to the cobalt skeleton of various Co_3C clusters always occur in the axial sites of the three cobalt atoms with preservation of the chair geometrie of the non coordinated ligands.

$$Co_3(CO)_9(\mu_3\text{-}CR) + SCHR^1SCHR^2SCHR^3 \xrightarrow{70°C} Co_3(CO)_6(\mu_3\text{-}CR)[\mu_3\text{-}\eta^3\text{-}(SCHR^1SCHR^2SCHR^3)] + 3\ CO$$



It is known that crown thioethers coordinate more strongly to metals than simple thioethers and the new clusters synthesised appear to be unusually stable.

Anorganische Chemie/Koordinationschemie **132**

Highly Dispersed and Mesoporous Vanadia–Silica Mixed Oxides

D.Dutoit, M.Schneider, P.Fabrizioli and A.Baiker
Laboratorium für Technische Chemie, ETH Zentrum, CH-8092 Zürich

The excellent activities in the epoxidation of bulky olefins by the use of titania–silica low-temperature aerogels prompted us to extend our studies to other silica-based mixed oxides. Silica-supported vanadia, vanadia–silica xerogels, and vanadium-containing silicalites (VS-1, VS-2) have been shown to possess interesting catalytic properties. However, xerogels and V-silicalites suffer from the small pores restricting the access of large organic reactants to the internal surface and thus impeding the use for fine chemical synthesis.

The vanadia–silica mixed oxides were prepared via the sol–gel method involving acid-catalysis together with prehydrolysis in order to achieve matching of the reactivities of vanadium(V) oxide triisopropoxide and tetraethoxysilicon(IV) precursor. Gelation was forced by the addition of basic solution. The as-received gels were either supercritically dried by semicontinuous extraction with supercritical CO_2 at 313 K (low-temperature aerogels) or direct removal of the ethanolic solvent at 533 K, i.e., above its critical point, (high-temperature aerogels) or evaporatively dried at ambient temperature (xerogels). The effects of composition, aging, drying procedure, and calcination temperature on the chemical, structural, and textural properties of the solids were investigated. The oxides were characterized by N_2-physisorption, XRD, vibrational spectroscopy, thermal analysis, UV-Vis, ^{51}V-NMR, and XPS.

The low-temperature vanadia–silica aerogels were mesoporous and highly disperse. The increasing V-content from 5 to 20 wt% nominal V_2O_5 caused a gradual decline in V-dispersion. For 30 wt% "V_2O_5" the continuous formation of V–O–V connectivity resulted in crystallisation of V_2O_5. The effect of aging in basic medium confined to the textural properties, significantly increasing BET surface area and especially pore volume. The high-temperature aerogel with 10 wt% "V_2O_5" was meso- to macroporous and X-ray amorphous but contained significant V–O–V connectivity, indicative of the high drying temperature used. Calcination at ≥ 673 K led to crystalline V_2O_5. The related xerogel possessed similar V-dispersion as the corresponding low-temperature aerogel but was microporous. In general, aero- and xerogels revealed a marked lack of stability against both apolar solvents in the presence of peroxides and polar solvents. In the case of low-temperature aerogels, however, the marked thermal stability in air at ≤ 873 K, combined with mesoporosity and high V-dispersion, rendered these solids most advantageous for fine chemical syntheses in gas phase.

Anorganische Chemie **133**

Formation and Reactivity of Pd-C Solid Solution in the Reaction of CO_2 with H_2 over Supported Palladium Catalysts

P.Dimmer, M.Maciejewski, R.Köppel and A.Baiker

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

Recently we have shown that upon exposure of supported palladium catalysts to pure carbon monoxide at 180°C disproportionation of CO (Boudouard reaction) occurs with subsequent incorporation of carbon into the palladium lattice [1,2]. In the present work we focus on the formation and reactivity of interstitial carbon and the role of the Pd-C phase during carbon dioxide hydrogenation to methane over Pd supported on Al_2O_3, ZrO_2, TiO_2 and SiO_2.

The experimental studies show that methane formation strongly depends on the kind of support material. The temperature of the beginning of CH_4 production changes from 260°C for the most active Pd/ZrO_2 to 400°C for the least active Pd/SiO_2. The activities of supported Pd catalysts for methane formation, characterised as the temperature onset of its formation, are comparable to the sequence of temperatures of carbon incorporation into Pd during CO disproportionation, which increases in the order $ZrO_2<TiO_2<Al_2O_3<SiO_2$.

The carbon incorporated into the Pd lattice was found to be very active. Reaction of Pd-C with hydrogen to form CH_4 starts already at ca. 170°C and reaches its maximum rate at ca. 260°C, independently of the support material. Graphitic carbon deposited on the surface of the catalysts reacts with hydrogen at markedly higher temperatures in the range 600-700°C.

The findings indicate that low temperature methane formation during CO_2 hydrogenation occurs via formation and subsequent reaction of interstitial carbon with hydrogen. The reaction is strongly influenced by the ability of the supported palladium to incorporate carbon.

[1]. M.Maciejewski and A.Baiker, J.Phys.Chem., 98 (1994) 285.
[2]. M.Maciejewski and A.Baiker, Pure & Appl.Chem., (1995), in press.

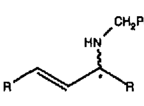
Anorganische und Koordinationschemie **134**

Palladium-katalysierte asymmetrische allylische Aminierung mit neuen Pyrazolyl-haltigen Ferrocenylliganden

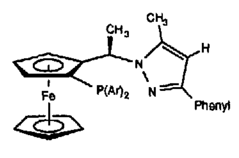
Urs Burckhardt und Antonio Togni

Laboratorium für anorganische Chemie, ETHZ, 8092 Zürich

Wir berichten hier über die Anwendung neuer pyrazolhaltiger Ferrocenylphosphine in der Palladium-katalysierten allylischen Aminierung. Produkte des Typs 1 werden mit hoher Enantioselektivität erhalten (bis 96% *ee*). Die Ligandsynthese erlaubt die einfache Einführung verschiedener Substituenten sowohl am Pyrazolring als auch am Phosphin. Dadurch kann der Ligand in elektronischer und in sterischer Hinsicht massgeschneidert werden [1].

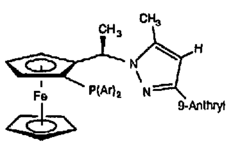


1



2

96% *ee* (***R***)



3

50% *ee* (***S***)

Aus elektronischen Gründen erfolgt der nucleophile Angriff am koordinierten Allylsystem *trans* zum Phosphor. Für einen hohen Enantiomerenüberschuss im gebildeten Produkt ist entscheidend, dass die Konfiguration der Allyleinheit möglichst starr fixiert bleibt. Dies wird durch die Substituenten R^3 und R^5 am Pyrazolring erreicht. Deren Form bestimmt, welche Konfiguration das Allylsystem bevorzugt einnimmt und in welche Richtung somit die Enantioselektivität verläuft. Die Liganden 2 und 3 illustrieren diesen Sachverhalt eindrücklich.

[1] A. Schnyder, L. Hintermann, A. Togni, *Angew. Chem.* **1995**, *107*, 996, und dort zitierte Literatur.

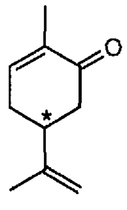
Anorganische Chemie **135**

Mehrdimensionale NMR-Studien an Palladium-Carvon-Komplexen

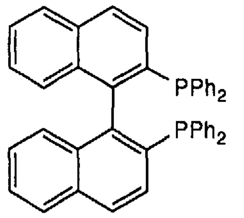
- Neue Allylchemie -

P.S. Pregosin, G. Trabesinger
Laboratorium für anorganische Chemie, ETH Zürich, CH-8092 Zürich

Mit dem Di-Terpen Carvon 1 und den chiralen Phosphin-Liganden BINAP 2 und Chiraphos 3 wurden neuartige Palladium-π-Allyl-Komplexe des Typs 4 synthetisiert und charakterisiert. Mit dem Carvon-π-Allyl-System lassen sich über Studien mit multinuklearer NMR-Spektroskopie Aussagen über die Natur der chiralen Umgebung des Phosphins, Struktur und Dynamik des Komplexes machen.



1



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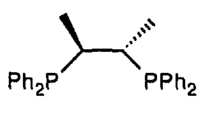

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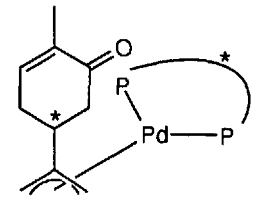


4

Anorganische Chemie **136**

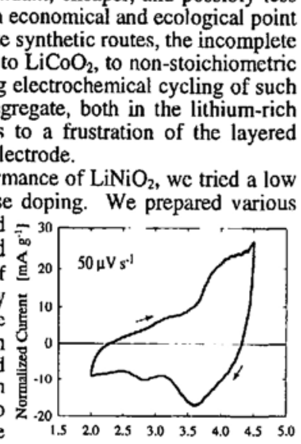
Investigations of the Li-Ni-Mn-O-System using Low Temperature Synthetic Routes towards Novel Lithium Insertion Electrode Materials

Michael E. Spahr [a,b], Petr Novák [a], Otto Haas [a], and Reinhard Nesper [b]

[a] Paul Scherrer Institut, Sektion Elektrochemie, CH-5232 Villigen PSI
[b] Laboratorium für Anorganische Chemie, ETH-Zentrum, CH-8092 Zürich

Recently, metal doped and undoped $LiNiO_2$ have been discussed as a substitute for $LiCoO_2$ as the cathode material in secondary ion-transfer battery systems. Since nickel is more abundant, cheaper, and possibly less toxic than cobalt, it has advantages from an economical and ecological point of view. However, using classical solid state synthetic routes, the incomplete oxidation of Ni^{2+} to Ni^{3+} leads, in contrast to $LiCoO_2$, to non-stoichiometric $Li_{1-x}Ni_{1+x}O_2$ compounds ($0<x<0.4$). During electrochemical cycling of such electrode materials, the Ni^{2+} impurities segregate, both in the lithium-rich and nickel-rich layers. This process leads to a frustration of the layered structure and a capacity drop of the oxide electrode.

In order to improve the electrode performance of $LiNiO_2$, we tried a low temperature synthetic route and manganese doping. We prepared various $LiNi_{1-y}Mn_yO_{2+z}$ samples ($0<y<1$) and tested them electrochemically. Coprecipitated Ni^{+III} and Mn^{+IV} oxide-hydroxides of different compositions were prepared by adding a solution of the appropriate divalent metal nitrates in water to an aqueous Br_2/KOH solution. The filtered and washed precipitates were mixed with lithium hydroxide and heated at 450 °C to get a poorly crystalline material. The obtained $LiNi_{1-y}Mn_yO_{2+z}$ samples allow reversible deinsertion/insertion of lithium ions in electrochemical cells with organic, ethylene carbonate based electrolytes. Specific charges of up to 170 Ah kg^{-1} (referred to the active oxide) could be demonstrated using the potential range between 4.3 V to 2.0 V *vs.* Li/Li^+ and 1.5 M $LiPF_6$ in ethylene carbonate/dimethyl carbonate (1:2 by weight) as an electrolyte (see the inserted figure). A specific charge of 150 Ah kg^{-1} could be stabilized for ten charge/discharge cycles.



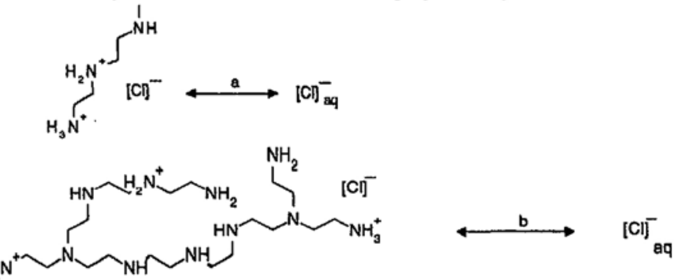
We would like to thank the BEW for financial support.

Inorganic chemistry **137**

Counterion condensation of chloride ions in Polyethyleneimine solutions. Studied by ^{37}Cl- and ^{35}Cl-NMR

C.W. Schläpfer, U. Meier
Institut für Anorganische und Analytische Chemie, Universität Freiburg,
CH-1700 Freiburg

Poly(ethyleneimine) is a typical polymeric amine which exists in a linear (LPEI) , a branched (BPEI) structure. In acid solution the polymer is partially protonated forming a polyelectrolyte. The charge density is controled by the degree of protonation. NMR of quadrupolar ions is a useful method to study the counterion distribution in polyelectrolyte solution.



a) Relaxation of ^{37}Cl and ^{35}Cl in LPEI solutions: The relaxation rates increases with increasing degree of protonation (α). The ratio of the transverse relaxation rates of the two chloride isotopes shows, that dynamic processes contribute to the observed changes in the the relaxation rates. The comparision of the calculated correlation time (τ_c) and the viscosity of the solution indicates that the molecular reorientation of the polyelectrolyte is reponsible for the observed changes of the relaxation rates.

b) Relaxation of ^{35}Cl in BPEI solutions: The relaxation rates increase with increasing α. Mesurements of R_1 and R_2 show that the relaxation is dominated by quadrupolar relaxation.

Anorganische/Koordinations Chemie **138**

Catalytic Dehydrogenation of Iminodibenzyl to Iminostilbene over Potassium-promoted Iron Oxides

A.Knell[a], M.Maciejewski[a], D.Monti[b] and A.Baiker[a]

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

[b] Ciba, Pharmazeutische Abteilung, CH-4002 Basel

The dehydrogenation of iminodibenzyl to iminostilbene has been investigated over potassium-promoted iron oxide catalysts in the presence of steam. The reaction was performed at 550-600°C and steam/iminodibenzyl ratios of 50-300 mol/mol. Under the conditions used, selectivities to iminostilbene up to 80% at nearly 100% iminodibenzyl conversion were achieved. Beside iminostilbene, 9-methylacridine and acridine were detected as major side products.

The reaction behaviour was strongly influenced by the steam/iminodibenzyl ratio in the feed. Both selectivity to iminostilbene and the conversion of iminodibenzyl was increased with higher steam/iminodibenzyl ratios. The addition of steam shifts the equilibrium towards the product side and suppresses non catalytic, unselective reactions resulting in an increase of the iminostilbene selectivity. The activity of the catalyst was found to be strongly influenced by the oxidation state of iron and the amount of carbon deposits on the catalyst surface. Dilution of the iminodibenzyl feed by steam prevents reduction of the active iron oxide phase and reduces drastically the deposition of carbon.

Promotion of iron oxides with 0.5 wt% potassium increases the activity of the catalysts. Potassium improves the reducibility of iron oxides and results in an apparent increase of the number of active sites for the dehydrogenation of iminodibenzyl.

Potassium carbonate and magnetite represent the main phases under reaction conditions in the presence of steam and are proposed as the active phases in the dehydrogenation. Gasification of carbonaceous deposits by steam leads to the formation of carbon dioxide and potassium carbonate under normal reaction conditions.

Anorganische/Koordinations Chemie **139**

Thermogravimetric/Mass-Spectrometric Studies and Reactivity of Heteropoly Acid

M. Baumgartner, B. Krebs and F. Wettstein
Institute of Inorganic Chemistry, University of Zürich, CH-8057 Zürich

Among various Heteropoly Acids (HPAs) the Keggin-anion $[Mo_{12}O_{36}(PO_4^{3-})]^{n-}$ is known since 1826 (*Berzelius*) and used as the "heteropoly blue" in colorimetric determination of PO_4^{3-}. We are investigating the structurally related enlarged Keggin-type anion $[V_{18}O_{42}(x)]^{n-}$ ($X=SO_4^{2-}$, PO_4^{3-}, VO_4^{3-}, a.o.) as selective gas adsorbent and catalytically active compounds. The structural aspects, the electronic and magnetic properties of these mixed valence V^{IV}/V^{V} clusters are reported elsewhere [1, 2].

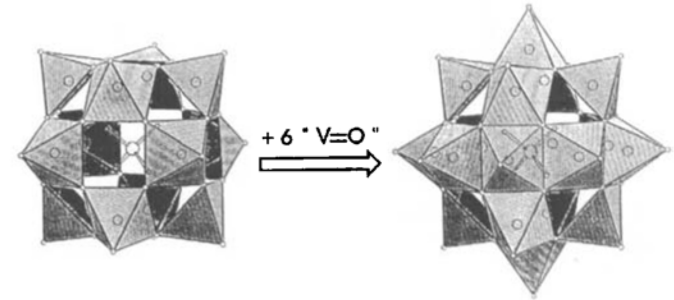


Fig. 1: Structural relationship between the hypothetical $[V_{12}O_{36}(X)]^{m-}$ Keggin-type anion and the $[V_{18}O_{42}(X)]^{n-}$ cluster-type; each V exhibits a square-pyramidal coordination polyhedron.

The thermal stability of these compounds is caused by the central building unit X. The dehydration of these water rich compounds (Weight loss between 15 up to 20%) proceeds slowly over a wide temperature range. In air, an increase of weight was observed above 500°C, which is probably the effect of an oxidation of the V^{IV}; under an inert atmosphere, no such behaviour was observed.

[1] A. Müller, J. Döring, *Z. anorg. allg. Chem.*, 595 (1991), 251-274
[2] J.R. Galan, C. Gimenez-Saiz, C.J. Gomez-Garcia, E. Coronado, Proceedings NATO-ASI 1995 "Localized and Itinerant Molecular Magnetism"

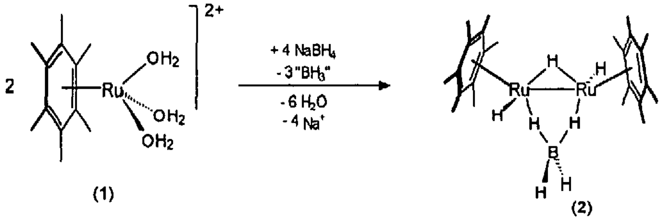
CHIMIA 49 (1995) Nr. 7/8 (Juli/August)

Anorganische und Koordinationschemie **140**

$[(\eta^6\text{-}C_6Me_6)RuH]_2(\mu_2\text{-}H)(\mu_2\text{-}\eta^2\text{-}BH_4)$ - Ein Komplex mit ungewöhnlicher η^2-verbrückender Koordinationsweise des Boranatoliganden.

M. Jahncke, G. Meister, G. Rheinwald, H. Stoeckli-Evans, G. Süss-Fink*
Institut de Chimie, Université de Neuchâtel, CH-2000 Neuchâtel

Die Umsetzung einer wäßrigen Lösung von $[(\eta^6\text{-}C_6Me_6)Ru(H_2O)_3][SO_4]$ (1) mit einem Überschuß an festem $NaBH_4$ liefert $[(\eta^6\text{-}C_6Me_6)RuH]_2(\mu_2\text{-}H)(\mu_2\text{-}\eta^2\text{-}BH_4)$ (2). Dieser ist der zweite bekannte Komplex mit der ungewöhnlichen η^2-verbrückenden Koordinationsweise des Boranatoliganden.



Die Umsetzung von 1 mit 1.5 Äquivalenten einer wäßrigen Lösung von $NaBH_4$ liefert dagegen den kationischen Komplex $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu\text{-}H)_3]^+$, der als Hexafluorophosphat (3) ausgefällt werden kann. Umsetzung von 3 mit einem Äquivalent $NaBH_4$ in THF ergibt ebenfalls den Boranatokomplex 2.

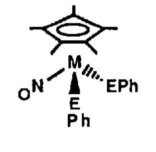
Verbindung 2 wurde vollständig charakterisiert. Die Struktur des Komplexes wurde durch eine Einkristallstrukturanalyse aufgeklärt. Die temperaturabhängigen ^1H-NMR-Spektren zeigen, daß die drei Hydridoliganden einerseits und die Wasserstoffatome der BH_4-Gruppe andererseits einem intramolekularen Austausch unterliegen.

Anorganische / Koordinations Chemie **142**

Heterodimetallic Complexes Derived from $Cp^*M(NO)(EPh)_2$ (M = Ru, Os ; E = S, Se, Te)

A. Béguin, G.–X. Jin, W. Milius and M. Herberhold
Laboratorium für Anorganische Chemie der Universität Bayreuth,
Postfach 101251, D–95444 Bayreuth, Germany

The new halfsandwich ruthenium and osmium dichalcogenolato complexes $Cp^*M(NO)(EPh)_2$ ($Cp^* = \eta^5\text{–}C_5Me_5$; M = Ru, Os ; E = S, Se, Te) have been synthesized from the reaction of $Cp^*M(NO)X_2$ (M = Ru: X = Cl, M = Os: X = Br) with the chalcogenides PhELi.



		E		
		S	Se	Te
M	Ru	Ia	Ib	Ic
	Os	IIa	IIb	IIc

These new dichalcogenolato complexes can act as bidentate chelating ligands towards low-valent transition metals, yielding heterodi- or trimetallic complexes with μ–chalcogenolato bridges. Some reactions have been investigated:

Treating the halfsandwich starting compounds with $(nor\text{–}C_7H_8)M'(CO)_4$ (M' = Cr, Mo) afforded dinuclear complexes of the type $Cp^*M(NO)\text{–}(\mu\text{–}EPh)_2M'(CO)_4$ (M = Ru, Os ; E = S, Se, Te ; M' = Cr, Mo), which surprisingly further reacted to give trinuclear complexes of the type MM'M.

The reactions of Ia–c or IIa–c with $[(nor\text{–}C_7H_8)M'Cl]_2$ (M' = Rh, Ir) led to the neutral, heterodinuclear complexes $Cp^*M'(NO)(\mu\text{–}EPh)_2M'(Cl)\text{–}(nor\text{–}C_7H_8)$, which could be further dehalogenated in the presence of $AgBF_4$ to give the stable salts $[Cp^*M(NO)(\mu\text{–}EPh)_2M'(nor\text{–}C_7H_8)]^+ BF_4^-$.

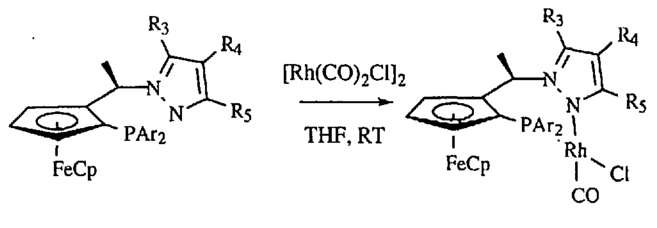
All new complexes were isolated as crystalline solids and were characterized by their infrared, mass and NMR spectra. Some crystal structure determinations have also been carried out.

Anorganische und Koordinationschemie **141**

Elektronische Effekte in der asymmetrischen Katalyse und ihre Einflüsse auf die Rhodium-Carbonyl-Bindung

A. Schnyder, U. Wiesli und A. Togni
Laboratorium für anorganische Chemie, ETH-Z, Zürich

In der asymmetrischen Hydroborierung von Styrol mit pyrazolylhaltigen Ferrocenylliganden konnten starke elektronische Effekte beobachtet werden [1]. Diese Einflüsse untersuchte man nun anhand von Rhodium-Carbonyl-Komplexen. Anhand der CO-Streckschwingung in solchen Komplexen können Aussagen darüber gemacht werden, wie stark der Stickstoffdonor an das Rhodium bindet und welchen Einfluss er auf den *trans*-ständigen Liganden ausübt [2].



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[1] A. Schnyder, L. Hintermann, A. Togni, *Angew. Chem.*, **1995**, *107*, 996
[2] siehe: C. A. Tolman, *Chem. Rev.*, **1977**, *77*, 313

Anorganische/Koordinations Chemie **143**

Effect of metal oxide additives on the CO hydrogenation over Rh/SiO_2 and Pd/SiO_2

A. Gotti and R. Prins
Laboratory for Technical Chemistry,
Eidgenössische Technische Hochschule, 8092 Zürich, Switzerland

The interest in the CO hydrogenation is not only due to its hugh potential industrial applications, but also to the amazing academic challenges. Methane, higher hydrocarbons, methanol, ethanol and other oxo compounds belong to the wide product distribution, which is affected by the choice of the active metal, catalyst support, promoters, cataylst pretreatment and reaction conditions.

The elementary steps in the catalysed conversion of synthesis gas still need more explanations. Whereas the model in which, after dissociative adsorption of H_2 and CO, the formed surface CH_x fragments build hydrocarbons, as well as higher oxygenated compounds through CO insertion, is well accepted, the mechanism of the methanol formation and the nature of the catalytic sites are still debated.

Catalysts were prepared from ultra pure SiO_2, Rh and Pd nitrates and chlorides, and by doping with alkali, alkaline earth and trivalent metal oxides. The activities and selectivities of the Pd and Rh catalysts were investigated in the CO hydrogenation at 553 K, H_2/CO = 2 or 3, and 2.5 or 4 MPa, respectively.

Among the tested systems, the alkali oxides promoted catalysts showed an important decrease of the total activity, probably due to the suppression of the CO dissociation. Those doped with basic oxides, as Ca, promoted the CO hydrogenation to methanol; this effect was attributed to the capacity of such catalysts to form formates and subsequently hydrogenate them to methoxy groups. The catalysts doped with acidic oxides, as Al, denoted a lower oxygenates product activity and an increase in the formation of higher hydrocarbons, as probable consequence of the acid catalysed hydrogenolysis of the oxygen containing compounds.

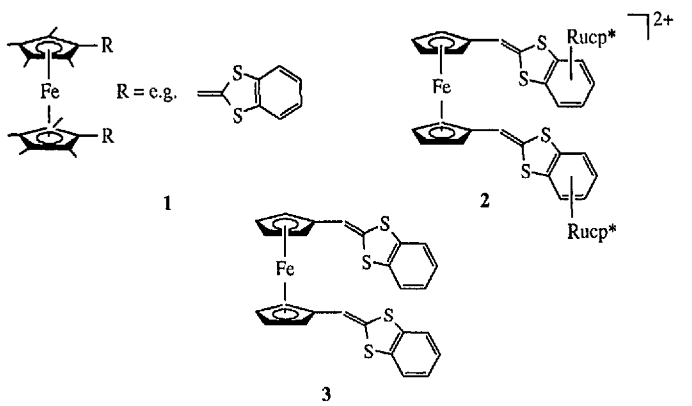
Because of the great interest and the controversous debate about the mechanism and the catalysis of the methanol formation, we focused our investigation on the effect of Ca doped Rh and Pd catalysts. By testing systems with different additive/noble-metal ratios, we found a clear correlation between Ca amount and methanol selectivity, whereas the total activity showed a more complicate dependence, which is the result of superposition of the exponential decrease of the hydrocarbons activity and the volcano-shaped increase of the methanol activity.

Anorganische Chemie/Koordinationschemie **144**

Substituted Ferrocenes and Ruthenocenes as Donors for Charge-Transfer Complexes: Synthesis and Redox Properties.

Oliver Ruppert, Markus Hobi, Antonio Togni
Laboratory of Inorganic Chemistry, Swiss Federal Institute of Technology, ETH-Zentrum, CH-8092 Zürich, Switzerland

The ferrocene derivatives **1** and **2** and their synthesis will be reported.



1 2 3

The properties of compounds **1** and **2**, as compared to **3** [1] and their ability to form CT complexes with suitable electron-acceptors will be described.

[1] A. Togni, M. Hobi, G. Rihs, G. Rist, A. Albinati, P. Zanello, D. Zech, H. Keller, Organometallics, 1994, 13, 1224.

145

Inorganic and Coordination Chemistry

Stereoselective Synthesis of Bridged Binuclear Ruthenium(II) Bipyridyl Complexes

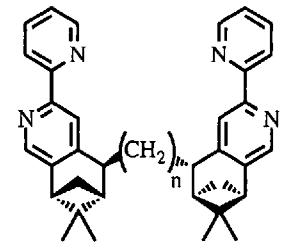
N.C.Fletcher,[a] F.R.Keene,[b] P.Belser,[a] A.von Zelewsky,[a] H.Stoekli-Evans.[c]

a: Institute of Inorganic and Analytic Chemistry, University of Fribourg.
b: Department of Molecular Sciences, James Cook University of North Queensland, Townsville, Queensland 4811, Australia.
c: Insitute of Chemistry, Neuchâtel, Avenue de Bellevaux 51, Neuchâtel.

Previously, the chiral bridging "chiragen" series of ligands have been reported(where n = 5, 6 and 7).[1] Here, we illustrate the synthesis and characterisation of two analogous "chiragen" ligands, with smaller spacer groups (n = 0 and 3), including an X-ray structure determination.

The "Chiragen" ligand

n = 0 and 3



Using the previously described chiral building blocks; $[\Delta\text{-Ru(bpy)}_2\text{(py)}_2]^{2+}$ and $[\Lambda\text{-Ru(bpy)}_2\text{(py)}_2]^{2+}$,[2] the optically pure ΔΔ and ΛΛ diasteriomers of the di-ruthenium centred complexes of both these ligands have been prepared, and their physical properties investigated.

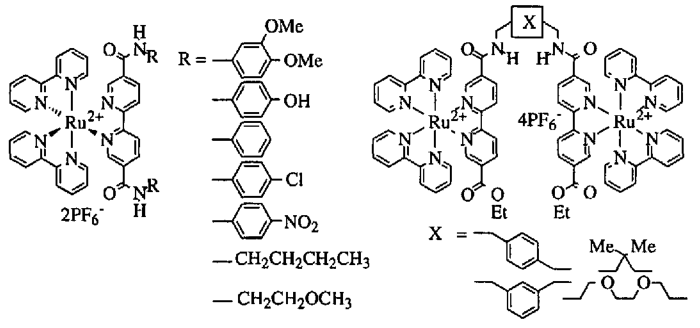
1) P.Hayoz, A.von Zelewsky and H.Stoekli-Evans, *J. Am. Chem. Soc.* 1993, **115**, 5111.
2) X.Hua, A.von Zelewsky, *Inorg. Chem.* 1991, **30**, 3798.

Inorganic and Coordination Chemistry **146**

Acyclic Anion Receptors Containing Ruthenium (II) Bipyridyl Complexes

Nicholas.C.Fletcher,[a] Paul.D.Beer,[b] Trevor.J.Wear.[c]
a: Institute of Inorganic and Analytic Chemistry, University of Fribourg.
b: Inorganic Chemistry Laboratory, University of Oxford, South Parks Road Oxford, UK OX1 3QR.
c: Kodak Ltd. Headstone Drive, Harrow, Middlesex, UK HA1 4TY.

In recent reports we have described the importance of hydrogen bonding of an amide (CON-H) proton in anion recognition in a series of redox active complexes.[1] To extend these ideas further, a series of acyclic mono- and multi-centred ruthenium bipyridyl complexes were prepared containing secondary amide functions. Ruthenium (II) bipyridyl groups have well characterised redox and photo-chemical behaviour, which could provide a suitable method for the detection of bound species.



We illustrate the synthesis and characterisation of these complexes. Further we demonstrate their ability to coordinate anions by a variety of techniques, including ^1H NMR spectroscopy, cyclic voltammetry, and by photo-emission and absorption spectroscopy.

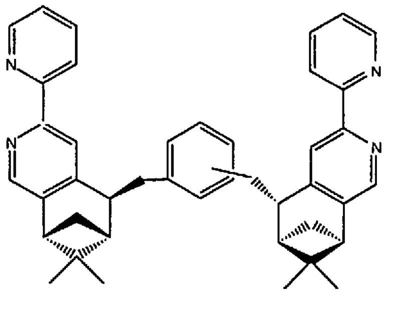
1a) P.D.Beer, C.A.P.Dickson, N.C.Fletcher, A.J.Goulden, A.Grieve, J.Hodacova, T.Wear. *J. Chem. Soc. Chem. Commun.* 1993,828. b) P.D.Beer, M.G.B.Drew, A.R.Graydon, D.K.Smith, S.E.Stokes. *J. Chem. Soc. Dalton Trans.* 1995, 403.

Anorganische Chemie / Koordinationschemie **147**

High yield synthesis of enantiomerically pure Ru(L^L⌒L^L)Cl_2 building blocks

Peter Belser, Hansruedi Mürner and Alex von Zelewsky
Institute of Inorganic and Analytic Chemistry, University of Fribourg

Defined and controlled stereochemistry at the metal centre(s) is a necessity for many areas of research in coordination chemistry. One possibility to predetermine the helicity at OC-6 centres are stereoselectively linked 4,5-pinenebipyridines[1]. With the tetradentate ligands of this family, only Λ- or Δ-Ru(L^L⌒L^L)Cl_2 complexes (depending on the starting pinene-enantiomer) are formed. The two remaining chlorine atoms are easily replaced with a large variety of other ligands.



Bridge : para-, meta-, ortho-Xylene

We report on the high yield synthesis and total characterization of Δ-Ru-(xylenebridged 4,5-pinenebipyridine)Cl_2. Under high dilution in saturated LiCl solutions of MeOH, these chiral building blocks form in 70-90% yield. The dichloro complexes are stable at r.t. under dry conditions. The synthetic value of these building blocks is demonstrated by the preparation of several mononuclear $\Delta\text{-[Ru(L\^{}L}\frown\text{L\^{}L)(L\^{}L)]}^{2+}$ complexes (L^L: bipyridine-derivates).

[1] Hayoz, P.; von Zelewsky, A.; Stoeckli-Evans, H.; J. Am. Chem. Soc. **1993**, *115*, 5111 - 5114.

Inorganic and Coordination Chemistry **148**

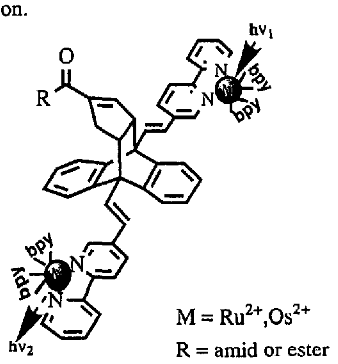
Supramolecular Ru and/or Os-complexes of bisbipyridine ligands connected to a substituted anthracene unit

P. Belser and A. Beyeler

Institute of Inorganic and Analytic Chemistry, University of Fribourg, CH-1700 Fribourg

Supramolecular systems in which photoinduced energy or electron transfer can take place are the basis of new photochemical systems [1]. These could be capable of performing well-defined light-induced functions, for example, switching in electronic devices.
To achieve this, there must be a functional part of the bridge able to undergo a reversible change, so that in one case energy or electron transfer is possible whilst not in the other case [2].

In this context we synthesized the system shown below, consisting of two bipyridines coordinated to separated metal centres, bridged by a 9,10-substituted anthracene moiety. The advantage of the system being the possibility to introduce synthetically, for example, a redox active group prior to complexation.



M = Ru^{2+},Os^{2+}

R = amid or ester

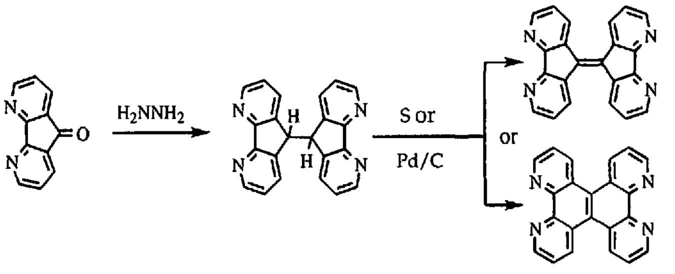
[1] H. Kurreck, M. Huber, *Angew. Chem.*, **1995**, *107*, 929-947.
[2] V. Balzani, F. Scandola, *Supramolecular Photochemistry*, Horwood, Chichester, **1991**.

Inorganic and Coordination Chemistry **149**

Preparation of a symmetrical bridging ligand for the synthesis of polynuclear Ruthenium complexes

M.Riklin, P. Belser, A. von Zelewsky
Institute of Inorganic and Analytic Chemistry, University of Fribourg

Previously we have synthesized stereochemically well-defined chiral tetranuclear Ruthenium complexes: $[Ru(\Lambda\text{-}Ru(bpym)(bpy)_2)_3](PF_6)_8$ and $[Os(\Lambda\text{-}Ru(bpym)(bpy)_2)_3](PF_6)_8$ from the $[Ru(bpym)_3]Cl_2$ (bpym: 2,2'-bipyrimidine) and the chiral building block $[Ru(bpy)_2(py)_2]$[(-)-dibenzoyl-L-tartrate] [1]. However in view of the disappointing yields, we have concluded that the 2,2'-bipyrimidine is a poor bridging ligand, the complexation of one side strongly reducing the coordination ability of the other [2].
Consequently we developed a symmetrical bridging ligand, the bis-(4,5-diazafluorenylidene) prepared by dehydrogenation of the 9,9'-bis-(4,5-diazafluorene) [3] with sulphur or Pd/C. This compound presents a larger distance between the two sites of complexation. Previously Newkome [4] has reported a preparation of this ligand, however our analyses disagree with those published. Consequently we will demonstrate whether the product has rearranged to the isomer tetrapyridonaphtalene.



We have synthesized several Ruthenium complexes from these ligand.

[1] X. Hua, thesis Nr. 1047, University of Fribourg.
[2] M.Riklin, P. Belser, A. von Zelewsky, Assemblée d'automne 1994 de la Nouvelle Société Suisse de Chimie, Poster 43.
[3] K. Kloc, J. Mlochowsky, Z. Szulc, Heterocycles Vol. 9, No. 7, 1978.
[4] G. R. Newkome, J.M. Roper:, J. Org. Chem., Vol. 44, No. 4, 1979.

Anorganische/Koordinations Chemie **150**

Acidification of the H(N-1) Site in 9-Ethylguanine (9-EtG) upon N-7 Coordination of Platinum(II)

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

The interplay between nucleotides and metal ions in biology [1] and the fact that the anticancer drug Cisplatin, i.e. *cis*-$[(NH_3)_2PtCl_2]$, exerts its action mainly via N-7 coordination to guanines of DNA [2], prompted us to use 9-EtG as a model ligand to evaluate the effect of N-7 coordination on the H(N-1) site, which is involved in hydrogen bonding in double stranded DNA. Our preliminary results determined by potentiometric pH titrations in aqueous solution are given in the Table. Deprotonation of the two H(N-1) sites in *cis*-$[(NH_3)_2Pt(9\text{-}EtG)_2]^{2+}$ occurs with $pK_{a/1}$ = 8.02 and $pK_{a/2}$ = 8.67; the difference of 0.65 is close to 0.6 expected statistically, indicating that the mutual influence of the two sites is small; in the *trans* compound this is different (see Table). The micro acidity constants for the two H(N-1) sites must be the average of the two macroconstants, i.e., $pk^{H}_{H(N-1)}$ = (8.02+8.67)/2 = 8.35 using the *cis* complex as example. This value serves to calculate the acidification, i.e. Δ pK_a, as defined by Eq (1) (Table). The results show that N-7 coordination transfers H(N-1) into a better H donor site.

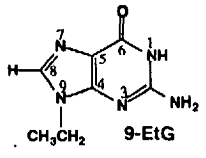


Table. Acidity Constants for H(N-1) Sites (25°C; *I* = 0.1 M, $NaNO_3$)
(MeC = 1-methylcytosine) $\Delta pK_a = pK^{H}_{H(N-1)/9\text{-}EtG} - pK^{H}_{H(N-1)/complex}$ (1)

9-EtG or Complex	$pK^{H}_{H(N-1)}$	Δ pK_a
9-EtG	9.57±0.04	
cis-$[(NH_3)_2Pt(9\text{-}EtG)_2]^{2+}$	8.02±0.01/8.67±0.01	1.22±0.04
trans-$[(CH_3NH_2)_2Pt(9\text{-}EtG)_2]^{2+}$	8.01±0.01/8.81±0.01	1.16±0.04
trans-$[(CH_3NH_2)_2Pt(MeC)(9\text{-}EtG)]^{2+}$	8.12±0.01	1.45±0.04
$Ni(9\text{-}EtG)^{2+}$	7.8 ±0.3	1.8 ±0.3

Supported by the Swiss Nat. Sci. Foundation (H.S.), the 'Deutsche Forschungsgemein.' (B.L.), and the HCM programme (Brussels/Berne).

[1] H. Sigel, *Chem. Soc. Reviews* 22, 255-267 (1993).
[2] B. Lippert, *Biometals 5*, 195-208 (1992).

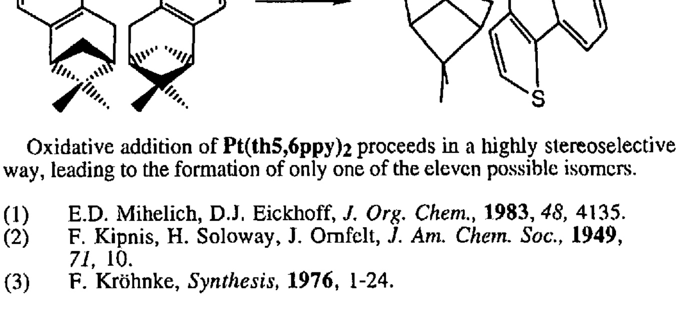
Inorganic and Coordination Chemistry **151**

Synthesis and Study of the Δ-cis-bis-[2-(2-thienyl)5,6-pinene-pyridine]platinum(II) Complex, $Pt(th5,6ppy)_2$, and some of its Addition Compounds.

Peter Belser, Michel Gianini, Helen Stoeckli-Evans‡, Alex von Zelewsky.
Institut de Chimie inorganique et analytique, Université de Fribourg, CH.
‡ Institut de Chimie, Université de Neuchâtel, CH.

A new ligand, 2-(2-thienyl)5,6-pinenepyridine, has been prepared in good yield from (-)-α-pinene following methods published by E.D. Mihelich (1) F. Kipnis (2) and F. Kröhnke (3).

Complexation of this ligand to platinum gives a sterically hindered bis-homoleptic platinum complex, **$Pt(th5,6ppy)_2$**, which shows an important distorsion from the square planar geometry. A consequence of this deformation is that a Δ chirality is induced at the metal center. A complete characterization of **$Pt(th5,6ppy)_2$** has been made, including an X-ray structure analysis.



Oxidative addition of **$Pt(th5,6ppy)_2$** proceeds in a highly stereoselective way, leading to the formation of only one of the eleven possible isomers.

(1) E.D. Mihelich, D.J. Eickhoff, *J. Org. Chem.*, **1983**, *48*, 4135.
(2) F. Kipnis, H. Soloway, J. Ornfelt, *J. Am. Chem. Soc.*, **1949**, *71*, 10.
(3) F. Kröhnke, *Synthesis*, **1976**, 1-24.

Anorganische Chemie **152**

Structure and Magnetic Properties of Novel Ternary Compounds in the Barium-Europium-Silicon System

Michael E. Spahr [a,b], Christina Häussermann [b], and Reinhard Nesper [b]

[a] Paul Scherrer Institut, Sektion Elektrochemie, CH-5232 Villigen PSI
[b] Laboratorium für Anorganische Chemie, ETH-Zentrum, CH-8092 Zürich

Ternary alkali rare-earth silicides are magnetically diluted systems, in which not only novel silicon clusters can be found but also interesting distance dependant magnetical interactions. The distances of the magnetic centers can be tuned varying their dilution degree by the alkali/rare earth ratio. Similar ion radii of Ba^{2+} and Eu^{2+} and the relatively high magnetic moment of free Eu^{2+} in its $^8S_{7/2}$ ground state makes the Ba-Eu-Si system suitable to study in this respect.

Both, the binary BaSi and EuSi crystallize in the CrB-type structure in the space group Cmcm (No. 63), in which the silicon atoms form planar one-dimensional zigzag chains $^1_\infty[Si^{2-}]_n$. In these binary compounds, the cations can successively be replaced forming solid solutions of the ternary compound $Ba_{1-x}Eu_xSi$ with 0<x<1 and a statistical distribution of barium and europium atoms on the metal positions. Vegard's rule is not obeyed for the volumes which may point out a slight clustering of the europium atoms or at least a preferred stability of the ternary phases. Isotropic magnetic measurements of $Ba_{1-x}Eu_xSi$ samples in a SQUID magnetometer show increasing ferromagnetic interactions of the magnetic centers with increasing europium content. For x>0.5, an additional decrease of the magnetic moment with decreasing temperature can be observed in the lower temperature region indicating an antiferromagnetic coupling with a T_N smaller than 30 K. However, this effect disappears in the case of the binary EuSi. Magnetization measurements give a magnetic saturation moment of about 7 μ_B related to 1 Eu atom evidencing that the oxidation state of the europium atoms is +2 in all these compounds.

$BaEu_2Si_4$ and $Ba_2Eu_3Si_7$ form new single phases in the ternary Ba-Eu-Si-system. $BaEu_2Si_4$ crystallizes in the Ba_3Si_4-structure type in the space group $P4_2/mnm$ (No. 136) containing a Si_4^{6-} butterfly anion that can be regarded as a reduced form of tetrahedrane according to the Zintl-Klemm-concept. The crystal structure of $Ba_2Eu_3Si_7$ in the space group $P\bar{6}2m$-D^3_{3h} (No. 189) represents a new structure type with a novel Zintl anion [1]. The silicon atoms form a one-dimensional infinite strand $^1_\infty[Si(Si_3)Si_3^{10-}]$ with di- and trivalent silicon atoms. The latter are coordinated in a trigonal planar way and represent the backbone of the anion, the divalent silicon atoms are located at terminal positions. The Eu atoms form trigonal prisms around the trivalent Si atoms, while Ba coordinates the terminal Si atoms of the strand.

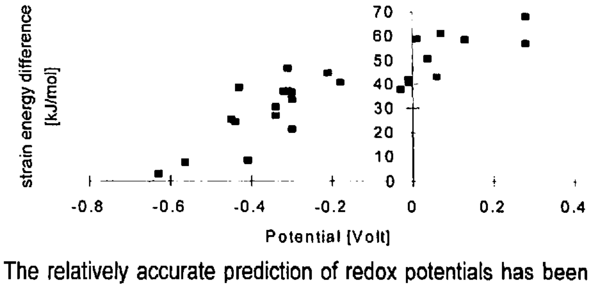
Anorganische Chemie **153**

The dependence of electron transfer properties of transition metal compounds from structural parameters

Peter Comba and Achim Sickmüller

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

Both the thermodynamics and kinetics of electron transfer reactions (redox potentials and electron transfer rates) have steric contributions, and molecular mechanics calculations have been used to identify them. A large amount of experimental data for Co^{2+}/Co^{3+} couples have been reported, and we have used molecular mechanics calculations to interpret them and to design new compounds with specific redox potentials and/or electron transfer rates. The linear dependence of the redox potentials to strain energy differences between the optimised cobalt(III) and Cobalt(II) complexes with a slope of 64 kJ/molV indicates that the variation of the redox potentials is due to a large extent to strain relaxation.



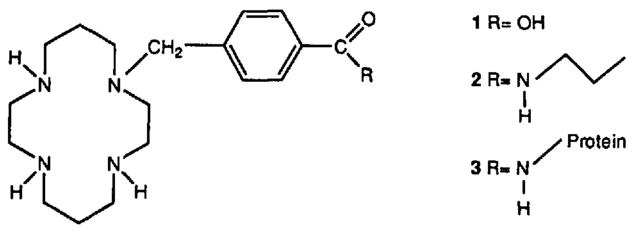
The relatively accurate prediction of redox potentials has been used to determine the structure of a new Cobalt (III) cage compound with a redox potential of +0.8 V (A.M.Sargeson, submitted). These results have been supported by the good agreement between experimentally determined and calculated (MM-AOM) UV-Vis spectra.

Koordinationschemie **154**

Kinetics of the Cu^{2+} Incorporation into Macrocycles Covalently Attached to Proteins - Models for Monoclonal Antibody Labelling.

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

We have previously shown, that the macrocycle 1 can covalently be attached to monoclonal antibodies and that it can be labelled with $^{67}Cu^{2+}$ [1]. We have now studied the kinetics of Cu^{2+} incorporation into the macrocyclic moiety, once it is bound to a protein.



Macrocycle 1 has been activated through formation of the N-hydroxysuccinimide ester and coupled with proteins, such as bovine serum albumin or ribonuclease A. After purification over a *Sephadex G-25* column the number of macrocycles attached to the protein was determined by atomic absorption spectroscopy of its Cu^{2+} complex. Depending on the reaction procedure the modified proteins contain 1-4 macrocycles.

The kinetics of complexation of the two model compounds 1 and 2 as well of the modified proteins 3 have been measured by stopped-flow technique and indicate that the reactivity of the macrocycle is not drastically changed by attaching it to a protein.

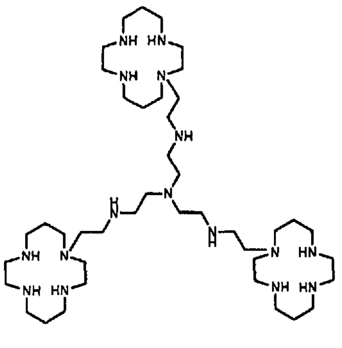
[1] M. Studer, Th.A. Kaden, H. Mäcke, *Helv. Chim. Acta* **1990**, *73*, 149; P.M. Smith-Jones, R. Fridrich, Th.A. Kaden, I. Novak-Hofer, H. Mäcke, P. A. Schubiger, *Bioconjugate Chem.* **1991**, *2*, 415

Koordinationschemie **155**

Trinuclear Metal Complexes of a Tris-Macrocycle

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

In continuation of our studies on metal-metal interactions we have now synthesized the tris-macrocycle 1, by coupling the N-hydroxysuccinimide ester of 1,4,8-tritosyl-1,4,8,11-tetraazacyclotetradecane-11-acetic acid to tris(2-aminoethyl)amine (*Tren*), followed by amide reduction with $BH_3.SMe_2$ and detosylation with CF_3SO_3H.



The new ligand is able to bind 3 Cu^{2+} through the three N_4-macrocycles. The trinuclear complex shows a pH-dependent colour change around pH 4.5, the absorption maximum shifting from 515 nm at low pH to 575 nm at high pH. The colour change is due to the axial coordination of the side-chain amino groups, which become potential ligands at higher pH.

The EPR-spectra are also drastically affected by the coordination geometry change.

Reference
[1] R. Schneider, A. Riesen, M. Zehnder, Th.A. Kaden, *Helv. Chim. Acta* **1986**, *69*, 53 ; L. Fabbrizzi, L. Montagna, A. Poggi, Th.A. Kaden, L. Siegfried, *J. Chem. Soc., Dalton Trans.* 1987, 2631; A. Urfer, Th.A. Kaden, *Helv. Chim. Acta* **1994**, *77*, 23

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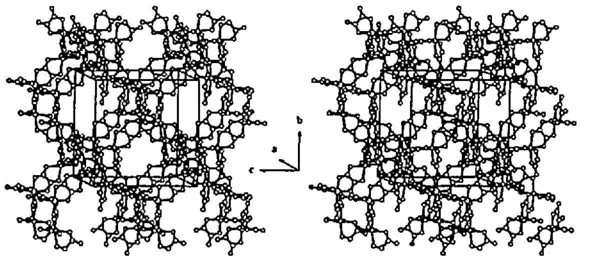
Anorganische Chemie / Koordinationschemie **156**

Magnetic Structure of the Chiral Three-Dimensional Network $[Mn_2(C_2O_4)_3]_n^{2n-}$

R. Pellaux*, P. Fischer**, H.W. Schmalle*, S. Decurtins*, F. Palacio***, G.P. Antorrena***

* Anorganisch-Chemisches Institut der Universität Zürich, CH-8057 Zürich
** Paul Scherrer Institut, Laboratorium für Neutronenstreuung ETH / PSI, CH-5232 Villigen PSI
*** Facultad de Ciencias, ICMA-Universidad de Zaragoza, E-50009 Zaragoza

Tris chelated cations $[M^{II}(bipy)_3]^{2+}$ favour the crystallization of three-dimensional coordination polymers of oxalato-bridged metal complexes $[M^IM^{III}(C_2O_4)_3]_n^{2n-}$ and $[M^{II}_2(C_2O_4)_3]_n^{2n-}$. These anionic networks build up chiral 3-connected 10-gon nets as shown in a stereoplot below:



The homometallic networks $[M^{II}_2(C_2O_4)_3]_n^{2n-}$ are valuable candidates for studies in the field of molecular based magnets because they fulfill the requirements of three-dimesional connectivity of spin carriers, as well as accessibility to a detailed structural characterization.

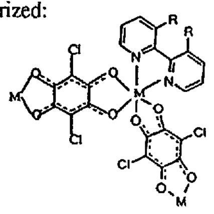
The compound $[Fe^{II}(bipy)_3]^{2+}_n$ $[Mn^{II}_2(C_2O_4)_3]_n^{2n-}$ was synthesized and structurally characterized. DC- and AC-susceptibility and heat capacity experiments indicate a transition to an antiferromagnetic phase at $T_N \approx 12$ K. In order to understand the magnetic structure and it's relationship to the chiral network structure, neutron powder diffraction experiments on a deuterated sample were performed.

Anorganische Chemie / Koordinationschemie **158**

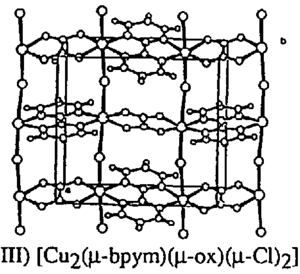
Structural and Magnetic Properties of $[Cu(DCMB)(\mu\text{-}CA)]_n$, $[Mn(bipy)(\mu\text{-}CA)]_n$ and $[Cu_2(\mu\text{-}bpym)(\mu\text{-}ox)(\mu\text{-}Cl)_2]_n$

L.-M. Zheng[a], H.W. Schmalle[a], P. Schneuwly[a], S. Decurtins[a], J. Ensling[b]
[a]Institut für Anorganische Chemie, Universität Zürich, CH-8057 Zürich
[b]Institut für Anorganische Chemie und Analytische Chemie, Johannes Gutenberg-Universität Mainz, D-55099 Mainz

Aiming to design and synthesize novel transition metal compounds with increasing dimensionality, many recent reports have focused on the synthesis and structural characterization of polymeric compounds using oxalate or 2,2'-bipyrimidine as bridging ligands. The dianion of 2,5-dihydroxy-1,4-benzoquinone and its derivatives (chloranilate anion, for example), as potential bis-bidentate bridging ligands, are considered as prominent candidates of building up new polymers of magnetic interest. The following three complexes have been synthesized and structurally characterized:



(I) M=Cu(II), R=CH_3OCO
(II) M=Mn(II), R=H



(III) $[Cu_2(\mu\text{-}bpym)(\mu\text{-}ox)(\mu\text{-}Cl)_2]_n$

Both (I) and (II) show 1D zigzag conformations with a chloranilate bridging ligand and an additional chelating bipyridine ligand. In (III), three different ligands, namely μ-bipyrimidine, μ-oxalato and μ-chloro ligands, conjointly coordinate to copper(II), thus forming a neutral 2D polymeric network. The variable-temperature magnetic susceptibility measurements revealed a weak antiferromagnetic interaction which is transmitted in (I) and (II) through their comparatively large distances between neighboring metal centers [Cu...Cu 7.980(3)Å, Mn...Mn 8.142(1)Å]. While in (III), a strong antiferromagnetic σ-in-plane exchange interaction between the magnetic centers is mediated along the alternating μ-bipyrimidine and μ-oxalato linkages.

Anorganische Chemie/Koordinationschemie **157**

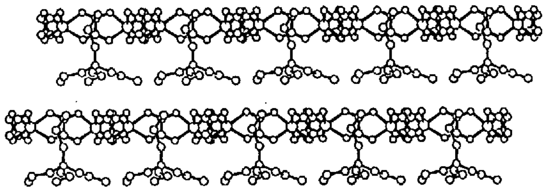
Structural and Magnetic Properties of Two-Dimensional Bimetallic Oxalate-Bridged Networks

R. Huber*, H. W. Schmalle*, S. Decurtins*, F. Palacio** and G. P. Antorrena**

* Anorganisch-Chemisches Institut der Universität Zürich, CH-8057 Zürich
** Facultad de Ciencias, ICMA-Universidad de Zaragoza, E-50009 Zaragoza

One of the strategies for the synthesis of molecular-based magnetic materials is to assemble paramagnetic metal ions as spin carriers by a bridging ligand system thus forming two- or three-dimensional polymeric compounds. The availability of a detailed structural analysis of such networks will be a prerequisite for an understanding of relevant physical properties.

Up to now there are only two publications of two-dimensional bimetallic oxalate-bridged networks based on X-ray studies of single crystals [1,2]. So far, most of the optical and magnetic studies had to be performed with microcrystalline materials. However, the determination of physical properties, e.g. of the magnetic anisotropy, requires single crystals of suitable size.



The structures of $\{[N(Pr)_4][MnCr(ox)_3]\}_n$ and $\{[N(Bu)_4][MnFe(ox)_3]\}_n$ were determined. Magnetic and heat capacity measurements were performed. The former compound orders ferromagnetically at 6 K and exhibits a strong anisotropy in magnetisation, the latter compound is an antiferromagnet ($T_N \approx 40$ K).

[1] L. O. Atovmyan, G. V. Shilov, R. N. Lyubovskaya, E. I. Zhilyaeva, N. S. Ovanesyan, S. I. Pirumova, G. Gusakovskaya, *JETP Lett.* **1993**, *58*, 766.
[2] S. Decurtins, H. W. Schmalle, H. R. Oswald, A. Linden, J. E. Ensling, P. Gütlich, A. Hauser, *Inorg. Chim. Acta* **1994**, *216*, 65.

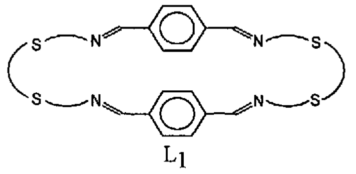
Anorganische Chemie **159**

Double Helical Dinuclear Copper (I) Complexes of Macrocyclic bis-dithiadiimine Ligands.

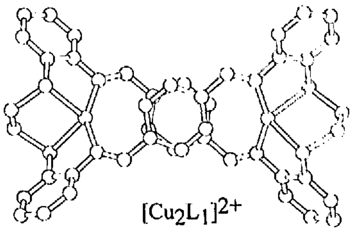
Peter Comba, Andreas Fath and Annette Vielfort

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

Large ring macrocyclic ligands with $(N_2S_2)_2$ donor sets (L_1) were prepared by a 2+2 Schiff base condensation reactions. Upon coordination to copper (I) dinuclear double helical complexes are formed ($Cu_2L_1^{2+}$). The driving force for the novel figure-of-eight motif and the stability of the helices in solution is discussed on the basis of structural, spectroscopic and modeling studies of a variety of free ligands of the type of L_1 and their dimetal complexes.



L_1



$[Cu_2L_1]^{2+}$

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Anorganische Chemie **160**

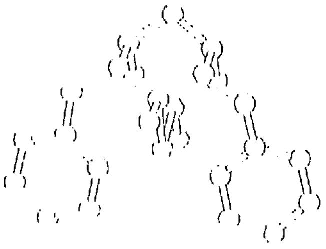
Enforced tetrahedral coordination geometry

Peter Comba, Achim Lienke, Norbert Okon and Anne Ramlow

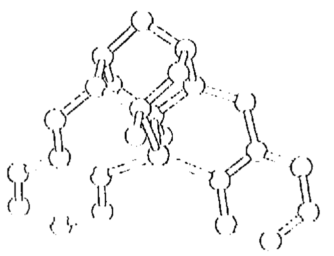
Anorganisch-Chemisches Institut der Universität Heidelberg
69120 Heidelberg, Germany

Ligands enforcing tetrahedral geometry show a wide variety of applications including selective extraction in the recovery of metals. However, only few such ligands are available, and it is difficult to design structures that allow a straight forward synthesis.

Ligands based on the bispidine backbone with pendant arms in cis or trans position (see calculated structures I and II) may enforce a tetrahedral environment around the metal centre. Molecular mechanics calculations are used to predict coordination geometries arising from the compromise between the metal desire and ligand preference. Ligand of type I have been prepared, and the experimental coordination chemistry is compared with predictions based on molecular modelling.



I



II

Anorganische Chemie/Koordinationschemie **161**

Zirconia Aerogels and Xerogels: Influence of Solvent and Acid on Structural Properties

C. Stöcker, M. Schneider, A. Baiker
Laboratorium für Technische Chemie, ETH-Zentrum, CH-8092 Zürich

High-surface-area zirconia aerogels with meso- to macroporosity have been prepared by an acid-catalyzed alkoxide–sol–gel route with tetrabutoxyzirconium(IV) and subsequent high-temperature supercritical drying at 578 K. The effect of solvent (ethanol, propanol, butanol, t-amylalcohol), amount of nitric acid, calcination temperature, and drying method was studied by nitrogen physisorption, X-ray diffraction, Fourier transform Raman and diffuse reflectance infrared Fourier transform spectrosopy, scanning electron microscopy, thermal analysis, and temperature-programmed desorption of NH_3.

After calcination in air at 573 or 773 K, the aerogels possessed specific surface areas of up to 270 or 180 $m^2 \cdot g^{-1}$, respectively. The use of ethanol as solvent resulted in the highest specific surface areas and pore volumes (up to 1.5 $cm^3 \cdot g^{-1}$) among all samples studied, whereas bulky t-amylalcohol caused a shift of the maxima of the broad pore size distributions from 30 to 70 nm. With the corresponding xerogels, prepared via the same wet-chemical procedure but evaporatively dried at ambient temperature, butanol resulted in a maximum at 3 nm and t-amylalcohol in a bimodal pore size distribution with maxima at 3 and 15 nm. The variation of the acid-to-alkoxide ratio in the range 0.08–0.12 at a hydrolysis level of 4 did not significantly influence the structural properties of aerogels and related xerogels. In contrast to the aerogels, the xerogels had significantly lower specific surface areas and prominent microporosity. All uncalcined aerogels contained crystalline ZrO_2, whereas the corresponding uncalcined xerogels were X-ray amorphous and crystallized only during calcination at 573 K. Both aerogels and xerogels possessed Brønsted-type and Lewis-type acid sites. With the xerogels, the density of acid sites on the surface was significantly lower. This behaviour is attributed to the higher amounts of organic residues which persisted in and on the xerogels up to 773 K and thus blocked the acid sites partially.

Anorganische Chemie **162**

Die Aktivierung von Zintl-Phasen

Christian Kronseder und Thomas Fässler
Laboratorium für Anorganische Chemie, ETH-Zentrum, CH-8092 Zürich

Die in Zintl-Phasen präformierten Cluster Anionen sind geeignete Quellen für Cluster vieler Hauptgruppenelemente. Gelingt es die Cluster aus dem Festkörperverband herauszulösen, so steht ihrer Verwendung in der Synthesechemie nichts mehr im Wege. Als Lösungsmittel werden bisher fast ausschliesslich en[1] und $NH_{3,liq}$ eingesetzt. Gibt man zu diesen Lösungen cryptofix222[2] können radikalische Zintl-Anionen in kristalliner Form erhalten werden.

Anstelle dieser „klassischen" Lösungsmittel werden binäre Phasen von K/Sn und K/Ge auch in geschmolzenem Kronenether 18C6[3] rückstandsfrei aufgelöst. Die so erhaltenen Produkte werden auf ihre magnetischen Eigenschaften in Abhängigkeit der eingesetzten Stöchiometrien von Komplexierungsreagenz 18C6 und Phase durch NMR- und ESR-Spektroskopie untersucht.

Die Umsetzung der gelösten, „aktivierten" Phase der Zusammensetzung K_4Sn_9 mit Trialkylzinnhalogeniden R_3SnHal (z.B. R=n-Butyl; 2,6-Diethylbenzol) werden beschrieben.

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[1] cn = Ethylendiamin

[2] cryptofix222 = 4,7,13,16,21,24-Hexaoxa-1,10-diazatricylco[8.8.8]hexacosane

[3] 18C6 = 1,4,7,10,13,16-Hexaoxacyclooctadecan

Chimie minérale et de coordination **163**

A High-Pressure Stopped-Flow Fluorometer for a Study of the Kinetics of Fast Reactions.

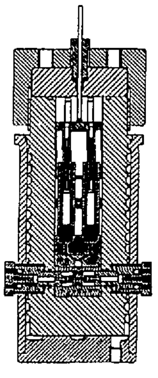
P. Bugnon[a], M. Doludda[b], R. Bergbauer[b], E. Grell[b], A. E. Merbach[a]

[a] Institut de Chimie Minérale et Analytique, BCH, CH-1015 Lausanne, Switzerland

[b] Max-Planck-Institut für Biophysik, Kennedyallee 70, D-60596 Frankfurt a.M., Germany

High-pressure kinetic techniques have been recognised to be very important for the elucidation of chemical reaction mechanisms[1]. Relaxation techniques such as T-Jump, P-Jump or NMR, and flow techniques such as stopped-flow have been used with success at high-pressures[2]. The usual high-pressure stopped-flow apparatus were usually restricted to an absorbance detection. However, recent advances, especially in the domain of biochemistry[3], necessitated the conception and construction of a high-pressure stopped-flow fluorometer.

We present a description of a new generation of our high-pressure stopped-flow capable of measuring rates of reactions simultaneously in absorbance and/or in fluorescence. Using this apparatus, the activation volumes for the reaction of Magnesium(II) 8-hydroxyquinolin complex formation were successfully determined at 278 K.



High-pressure stopped-flow: section trough pressure vessel

1 R.G. Wilkins, Kinetics and Mechanisms of Reactions of Transition Metal Complexes, VCH, Weinheim, 2nd edn., 1991.
2 R. van Eldik (Ed.), Inorganic High Pressure Chemistry, Elsevier, Amsterdam, 1986.
3 M. Doludda, E. Lewitzki, H. Ruf, E. Grell, The Sodium Pump, E. Bamberg and W. Schoner eds, Steinkopff, Darmstadt, 1994, 629-632.

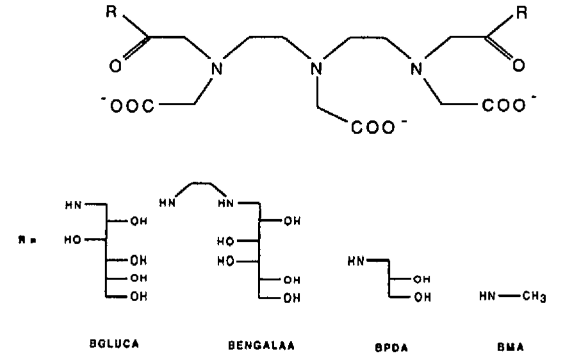
Chimie Minérale et de Coordination **164**

Water Exchange on three Amino Sugar Based [Gd(DTPA-BMA)(H_2O)] Derivatives of Relevance to MRI

Dirk Pubanz[a], Eva Tóth[a], Hendrik Lammers[b], Joop Peters[b], André E. Merbach[a]

Université de Lausanne, Delft University of Technology

A variable temperature and pressure ^{17}O NMR study at 9.4 T on the Gd^{3+} complexes of the amino sugar based DTPA-BMA^{3-} derivatives DTPA-$BGLUCA^{3-}$ (bisglucamide), DTPA-$BENGALAA^{3-}$ (bisethylenegalactamineamide), and DTPA-$BPDA^{3-}$ (bispropanediolamide) yielded the kinetic parameters of the water exchange reaction: the exchange rates k_{ex} are (3.9±0.2), (2.1±0.1), and (3.6±0.3) $\times 10^5$ s^{-1} and the activation volumes (±0.2 cm^3mol^{-1}) are +6.4, +5.2, and +6.5 cm^3mol^{-1}, respectively, indicating that the reaction is dissociatively activated. A comparison is made with the parent compound [Gd(DTPA-BMA)(H_2O)], and the conclusion is drawn that structural changes outside the first coordination sphere do not influence the activation parameters for water exchange on this type of complexes.

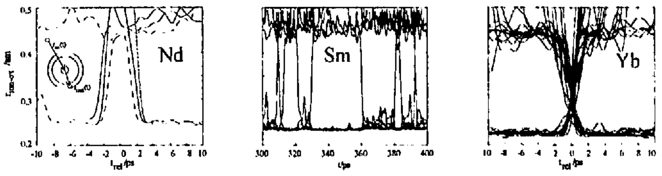


Chimie minérale et de coordination **165**

Mechanisms of Water Exchange between Lanthanide(III) Aqua Ions $[Ln(H_2O)_n]^{3+}$ and Bulk Water: A Molecular Dynamics Simulation Study

Th.Kowall, F.Foglia, L.Helm, A.E.Merbach
Institut de chimie minérale et analytique, Université de Lausanne, Bâtiment de Chimie (BCH), CH-1015 Lausanne

We have analyzed MD-simulations for lanthanide ions Ln(III) in aqueous solution in order to get insight into the water exchange kinetics and the water exchange mechanisms on these ions. The applied potential function took into account the polarization of water in the first hydration shell [1].



For $[Yb(H_2O)_8]^{3+}$ the water exchange follows an interchange-type scheme I with associative character. First a 9-coordinated transition state of tricapped trigonal prismatic geometry is formed that then initiates the leaving of a water molecule from the first shell.

For Sm^{3+} a ninth water molecule is frequently exchanging between the first hydration shell and the bulk and maintains the coordination equilibrium between a $[Sm(H_2O)_8]^{3+}$ and a $[Sm(H_2O)_9]^{3+}$ aqua ion. The resulting trajectory pattern of incoming and leaving water molecules is an alternation of elimination and addition reactions and cannot be classified into the scheme of D, I or A processes for substitution processes.

For $[Nd(H_2O)_9]^{3+}$ the exchange mechanism is clearly dissociative involving an eight-fold coordinated intermediate of square antiprismatic geometry and an activation volume close to the value for a limiting dissociative mechanism. Because the lifetime of the intermediate that is shorter than the reorientational correlation time of the complex and because a preferential relative arrangement between the entering and the leaving water molecule is preserved, a dissociative interchange I_d mechanism with strong dissociative character has been assigned.

[1] Th.Kowall, F.Foglia, L.Helm and A.E.Merbach
J.Am.Chem.Soc. **1995**, *117*, 3790-3799.

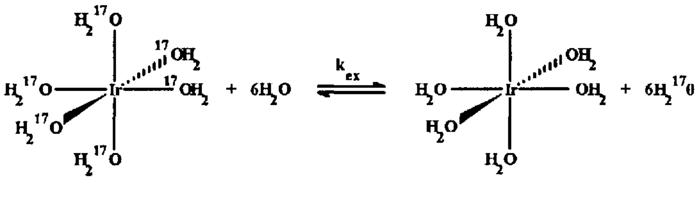
Chimie Minérale et de Coordination **166**

Variable-Temperature and Variable-Pressure Oxygen-17 NMR Study of Water Exchange on Hexaaquairidium(III)

A. Cusanelli,[a] D. T. Richens,[b] and A. E. Merbach[a]

[a] Institut de Chimie Minérale et Analytique, Université de Lausanne, Bâtiment de Chimie (BCH), CH-1015 Lausanne, Switzerland
[b] Department of Chemistry, University of St. Andrews, The Purdie Building, Scotland, KY16 9ST

Since the pioneering work of Hunt and Taube,[1] it has been known that the hexaaquachromium(III) ion is slow to exchange its bound water with solvent. Subsequently, the hexaaqua ion of iridium was shown to be one of the, if not the most, inert monomeric 3+ ion in aqueous acidic media[2] and as a result, little is currently known about the exchange mechanism for this ion. We now report the first definitive quantitative evidence for water exchange on iridium(III). The water exchange rate constants and activation parameters for $[Ir(H_2{}^{17}O)_6][CF_3SO_3]_3$ have been determined by ^{17}O NMR spectroscopy as a function of temperature and pressure. The value for k_{ex}^{298} was calculated to be 1.4 x 10^{-10} s^{-1} (half-life $\tau_{1/2}$: ~ 150 years), corresponding to the *slowest* documented water exchange at a mononuclear metal center.



(1) Hunt, J. P.; Taube, H. *J. Chem. Phys.* **1951**, *19*, 602.
(2) Castillo-Blum, S. E.; Sykes, A. G.; Gamsjäger, H. *Polyhedron* **1987**, *6*, 101.

Anorganische Chemie **167**

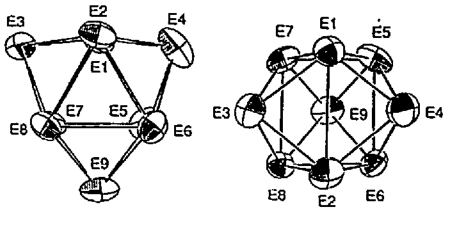
Magnetische- und ESR-Messungen der Verbindungen $[K(crypt)^+]_3E_9$ und $[K(crypt)^+]_6E_9E_9$ (E = Ge, Sn, Pb)

Thomas Fässler und Markus Hunziker
Laboratorium für Anorganische Chemie, ETH Zürich, 8092 Zürich

Die Umsetzungen der in Ethylendiamin gelösten Phasen der nominalen Zusammensetzung $KE_{2,25}$ (E = Ge, Sn, Pb) mit Kryptofix222 ergeben Verbindungen des Typs $[K(crypt)^+]_3E_9$ (1) bzw. $[K(crypt)^+]_6E_9E_9$ (2). In dieser Serie konnten nun alle Verbindungen mit den drei Elementen Ge, Sn und Pb synthetisiert werden. Bei den Clusteranionen handelt es sich bei den Verbindungen des Typs 1 um radikalische Anionen $E_9{}^{3-}$. Im Falle des Verbindungstyps 2 liegen zwei unterschiedliche Clusterisomere pro Elementarzelle vor. Hierbei werden radikalische Einheiten $E_9{}^{3-}$ und gemischt valente Spezies $E_9{}^{2-}$ und $E_9{}^{4-}$ (diamagnetisch) diskutiert.

Hier werden die strukturellen Eigenschaften und Beziehungen der beiden Verbindungstypen verglichen und diskutiert. Des weiteren werden magnetische Messungen und ESR Untersuchungen mit den entsprechenden Strukturen korreliert.

Kryptofix222 = 4,7,13,16,21,24-Hexaoxa-1,10-diazabicyclo[8.8.8]hexacosan



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Name Number of Abstract