doi:10.2533/chimia.2008.595 CHIMIA **2008**, *62*, No. 7/8

Minisymposium Inorganic and Coordination Chemistry **149**

Playing with anions: 1) Fast, environmentally friendly ruthenium-allylation catalysts and 2) Understanding and predicting ion pairing.

Paul S. Pregosin

ETH Zurich, 8093 Zurich, Switzerland

The lecture will consist of two separate but related themes. The opening section will involve a short excursion into how one can synthesize new, and optimize old, ruthenium based homogeneous allylation catalysts such that they are rapid, environmentally friendly and demonstrate exceptional regioselectivity, and then finish with an NMR approach designed to show how to recognize, understand and even predict the extent of ion pairing in a wide variety of inorganic, organic and organometallic salts.

Inorganic and Coordination Chemistry **151**

Multitopic Ligand Approach for the Synthesis of New Mixed Metal Compounds

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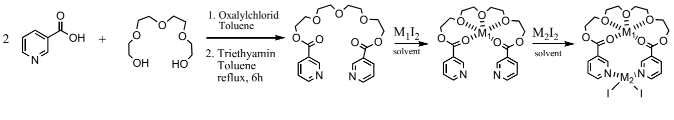
Switzerland

Today, the demand for new materials (superconductors, opto-electronic devices, etc.) is steadily growing. Complexes of alkaline and earth alkaline metal ions may for example provide precursors for the synthesis of high-Tc superconductors [1, 2]. We propose the development of new heterometallic complexes with tailored electronic, optical and/or magnetic properties. Combining different metal ions in molecular devices and analyzing their behavior, is interesting for later applications, and also of fundamental interest [3]. For this purpose we developed a multitopic ligand system based on open polyether molecules, which allows the coordination to different metal ion types by different ligating atoms.



We will show that this concept works by presenting first results. With alkaline earth metal ions such as calcium, the ligand wraps around the metal ion, yielding a complex in which the nitrogen atoms are oriented such as to accommodate another metal ion such as transition metals.

[1] K. M. Fromm, *Dalton Transactions*, **2006**, *43*, 5103-5112.
[2] R. C. Mehrotra, A. Singh, M. Bhagat, *Journal of Sol-Gel Sciences and Technology*, **1998**, *13*, 45-49

Minisymposium Inorganic and Coordination Chemistry **150**

Reticular Chemistry

Omar M. Yaghi

University of California, Los Angeles (UCLA) 607 Charles E. Young Dr.
East Los Angeles, CA 90095-1569 USA

This chemistry is concerned with linking organic and inorganic molecular building units into extended structures using strong bonds. These structures are crystalline and have frameworks in which the inorganic units act as 'joints' and the organic units as 'struts' to produce highly porous and robust metal-organic frameworks (MOFs) and zeolitic imidazolate frameworks (ZIFs). This presentation will outline a simple design strategy and synthesis of these materials including their adsorptive properties and applications to clean energy.

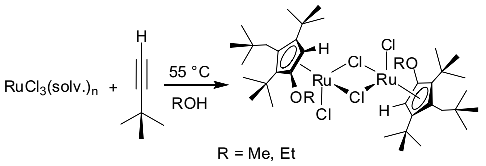
Inorganic and Coordination Chemistry **152**

Sterically Very Demanding Cyclopentadienyl Ligands: Significant Changes in the Behavior of Ru Half-Sandwich Complexes

Barnali Dutta, Kay Severin

Institut des Sciences et Ingénierie Chimiques, Ecole Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland

Ruthenium half-sandwich complexes with new cyclopentadienyl ligands (Cp^) have been prepared through an unprecedented Ru-catalyzed [2+2+1] cyclotrimerization reaction of *tert*-butylacetylene in methanol or ethanol.[1]



- ♦ One pot synthesis
- ♦ Sterically demanding ligands
- ♦ Versatile starting materials

The complexes have shown distinct reactivity in stoichiometric and catalytic transformations arising from the steric demand of the π-ligand. Noteworthy are the interplay between $16e^-$ and $18e^-$ Ru-phosphine complexes.[2] Exceptional reactivity of [Cp^Ru(μ-OMe)]$_2$ includes formation of Cl-bridged Ru^{II} dimers instead of tetramers, unprecedented transformation of cyclooctadiene into ethylbenzene in the coordination sphere of Ru, CO insertion in preference to addition and high catalytic activity for ATRC reactions on a wide range of substrates like *N*–substituted dichloro- and trichloroacetamides, enamides, ethers and esters.[3] [Cp^Ru(PTA)$_2$] possesses increased cytotoxicity on human ovarian cancer cell lines compared to its Cp analogue.[4]

[1] S. Gauthier, E. Solari, B. Dutta, R. Scopelliti, K. Severin *Chem. Commun.* **2007**, 1837
[2] B. Dutta, E. Solari, S. Gauthier, R. Scopelliti, K. Severin *Organometallics* **2007**, *26*, 4791
[3] B. Dutta, R. Scopelliti, K. Severin *Organometallics*, **2008**, *27*, 423.
[4] B. Dutta, C. Scolaro, R. Scopelliti, P. J. Dyson, K. Severin *Organometallics*, **2008**, *27*, 1355.

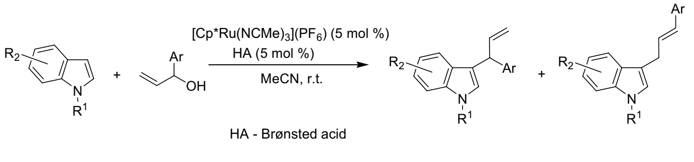
Inorganic and Coordination Chemistry **153**

Efficient allylation of indoles and pyrroles with allyl alcohols catalyzed by complexes derived from [Cp*Ru(NCMe)$_3$](PF$_6$): catalysis, structure and mechanism

Alexey B. Zaitsev, Stefan Gruber, Paul S. Pregosin

ETH Hönggerberg, Wolfgang-Pauli-Str. 10, CH-8093 Zürich, Switzerland

Dicationic ruthenium(IV) allyl complexes are efficient catalysts in the Friedel-Crafts allylation of phenols and indoles.[1,2] We have found that [Cp*Ru(NCMe)$_3$](PF$_6$) together with selected acid co-catalysts in the presence of allyl alcohols allows for *in situ* formation of η^3-allyl Ru(IV) complexes that efficiently catalyze the reaction of indoles and pyrroles with allyl alcohols to form 3-allylindoles and 2(5)-allylpyrroles, respectively, under mild conditions in high yield and regioselectivity.



Aspects of the catalysis, structure and mechanism will be presented.

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[1] I. Fernandez, R. Hermatschweiler, F. Breher, P. S. Pregosin, L. F. Veiros, M. J. Calhorda, *Angew. Chem., Int. Ed.* **2006**, *45*, 6386.

[2] A. B. Zaitsev, S. Gruber, P. S. Pregosin, *Chem. Commun.* **2007**, 4692.

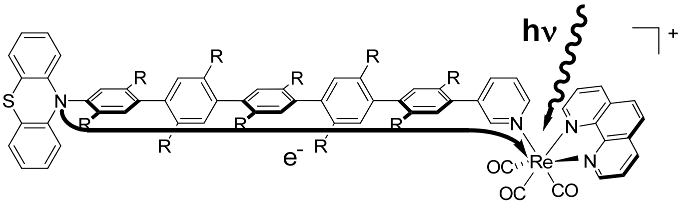
Inorganic and Coordination Chemistry **154**

Electron tunneling through rigid rod-like bridges

David Hanss, Mathieu Walther, Oliver S. Wenger*

Department of Inorganic, Analytical and Applied Chemistry, University of Geneva, 30 Quai Ernest-Ansermet, 1211 Geneva 4, Switzerland

Photoexcitation of a rhenium complex with a covalently attached phenothiazine triggers an intramolecular electron transfer that occurs via a tunneling mechanism. Time-resolved luminescence and transient absorption spectroscopy are used to extract information on both the photoinduced (forward) and thermal (backward) electron tunneling rates.



R = H, CH$_3$, OCH$_3$

Molecules with up to five *p*-xylene spacers have been prepared in good yields.

Of key interest to us is the question how the electronic structure of the covalent bridge between the donor and the acceptor affects the electron tunneling rates.

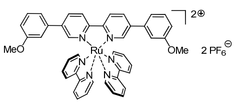
Inorganic and Coordination Chemistry **155**

A Macrocylic Triruthenium(II) Complex

Roesel, P.; Zampese, J.; Schaffner, S.; Neuburger, M.; Housecroft, C. E.; Constable E. C.

Department of Chemistry, University of Basel, Spitalstrasse 51, 4056 Basel, Switzerland.

Ruthenium(II) complexes containing polypyridine ligands continue to attract considerable interest because of their appealing photophysical properties and their incorporation into light-activated devices or photo-activated molecular machines.
Herein we describe the synthesis of a mononuclear ruthenium(II) complex **1**, and its cyclic trinuclear homologue **2**. Both complexes can be synthesized in high yields (90%) starting from the corresponding ligands and [*cis*-Ru(bpy)$_2$Cl$_2$] and are kinetically and thermodynamically stable.



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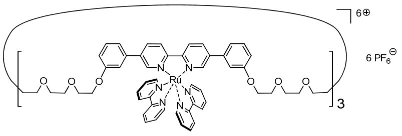


2

Redox and UV-Vis and fluorescence spectroscopic properties of both complexes have been investigated, and the results will be presented.

[1] Balzani, V.; Scandola, F. *Supramolecular Photochemistry*, Horwood, Chichester, **1991**.

[2] Balzani, V.; Campagna, S.; Denti, G.; Juris, A.; Serroni, S.; Venturi, M. *Acc. Chem. Res.* **1998**, *31*, 26.

[3] Badjic, J. D.; Balzani, V.; Credi, A.; Silvi, S.; Stoddart, J. F. *Science* **2004**, *303*, 1845, and refs. therein.

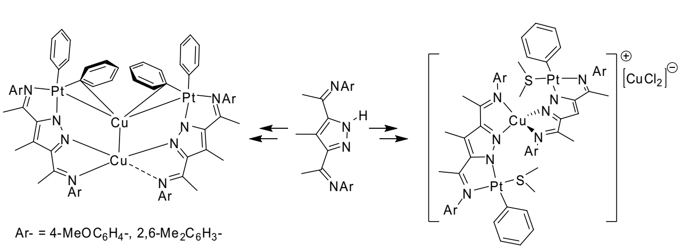
Inorganic and Coordination Chemistry **156**

Mononuclear Organometallic Pt(II) Complexes and Pt(II)-Cu(I) Mixed-Metal Complexes from Pyrazolate Based Compartmental Ligands

Marc-Etienne Moret and Peter Chen

ETHZ, Wolfgang-Pauli-Strasse 10, 8093 Zürich, Switzerland

In an effort towards the use of bimetallic cooperative effects in the field of platinum(II) mediated C-H activation[1], we synthesized mononuclear complexes of 3,5-bis(iminoacetyl)pyrazolate ligands[2] incorporating the [Pt(II)Me(SMe$_2$)], [Pt(II)Ph(SMe$_2$)] and [Pt(II)Ph$_2$] fragments. The coordination of these complexes to Cu(I) was studied, affording heteropolymetallic compounds[3]. These were structurally characterized, and their dynamic properties in solution were studied by variable temperature ^{1}H NMR. Dative Pt(II)-Cu(I) bonds and cuprophilic interactions were observed in the [Pt(II)Ph$_2$] containing structures.



Ar- = 4-MeOC$_6$H$_4$-, 2,6-Me$_2$C$_6$H$_3$-

[1]M. Lersch, M. Tilset, *Chem. Rev.*, **2005,** *105,* 2471.

[2]G. Noël, J. C. Röder, S. Dechert, H. Pritzkow, L. Bolk, S. Mecking, F. Meyer, *Adv. Synth. Catal.*, **2006,** *348,* 887

[3] M.-E. Moret, P. Chen, *Submitted.*

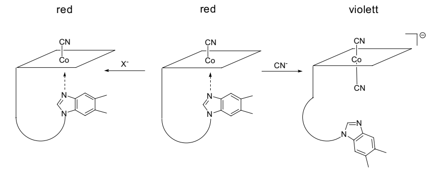
Inorganic and Coordination Chemistry **157**

Colourimetric Sensing of Cyanide with Vitamin B_{12}

Felix Zelder*, Christine Männel-Croisé,

University of Zurich, Winterthurerstr. 190, CH-8057 Zurich, Switzerland

The detection of cyanide in water is of particular importance since this toxic anion is widely used in many industrial applications like mining, electroplating and metallurgy [1]. The toxicity arises from the binding of cyanide to cytochrom a_3 that inactivates the cellular respiration and affects the central nervous systems [2]. Recently, the development of artificial sensors for the so called `*naked eye*` detection of cyanide has attracted much attention [3][4], but most of these methods confront the drawback of poor water solubility as well as interference with many common anions especially certain halides.



X^-: F^-, Cl^-, Br^-, I^-, SCN^-, NO_3^-, ClO_4^-, HCO_3^-, PO_4^{3-}, SO_4^{2-}, AcO^-, $PhCOO^-$

Recently, we demonstrated that commercial vitamin B_{12} is useful for the detection of millimolar cyanide in water [5]. The mode of operation of this sensor is controlled by its natural benzimidazole trigger able to switch between different conformational states. In different competition experiments, it was shown that various other anions as well as a thousand fold excess of Cl^- over CN^- do no interfere with the sensor. In the moment we focus on different approaches to improve the sensitivity of these corrin based sensors.

[1] (a) S. I. Baskin, T. G. Brewer *Medical Aspects of Chemical and Biological Warfare*; Eds.: F. Sidell, E. T. Takafuji, D. R. Franz; TMM Publications: Washington DC, **1997**, 271-286. (b) *Ullman`s Enzyclopedia of Industrial Chemistry*, Wiley-VCH: New York, **1999**.
[2] *Cyanide in biology*; Eds.: B. Vennesland, E. E. Comm, C. J. Knownles, J. Westly, F. Wissing; Academic Press: London, **1981**.
[3] A. Metzger, E. V. Anslyn *Angew. Chem. Int. Ed.* **1998**, *37*, 649-652.
[4] C.-F. Chow, M. H. W. Lam, W.-Y. Wong *Inorg. Chem.* **2004**, *43*, 8387-8393.
[5] F. Zelder, *Inorg. Chem.* **2008**, *47*, 1264-1266.

Inorganic and Coordination Chemistry **159**

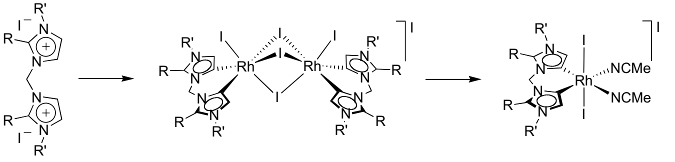
Abnormal NHC Complexes of Rhodium: Synthesis and Catalytic Activity in Transfer Hydrogenation

Anneke Krüger, Liangru Yang, Antonia Neels, Martin Albrecht

Department of Chemistry, University of Fribourg, Ch. du Musée 9,
CH-1700 Fribourg, Switzerland.

Imidazolium-derived carbenes that are bound to the metal centre via C4 (abnormal NHCs) have recently become known to have better electron donor properties than their normal, C2-bound analogues [1][2].

We have now shown that abnormal NHC complexes of Rh, such as **2** and **3**, can be synthesised by direct metallation, using either Rh(I) or Rh(III) precursors [3]. The catalytic activity of the abnormal Rh dicarbene complexes in transfer hydrogenation is far greater than that of their normal analogues. We have demonstrated that transfer hydrogenation catalysed by these Rh complexes proceeds via a monohydride mechanism, thus allowing for regioselective transfer of hydrogen.



1 **2** **3**

[1] A. R. Chianese, A. Kovacevic, B. M. Zeglis, J. W. Faller, R. H. Crabtree, *Organometallics*, **2004**, *23*, 2461.
[2] M. Heckenroth, E. Kluser, A. Neels, M. Albrecht, *Ang. Chem., Int. Ed.*, **2007**, *46*, 6293.
[3] L. Yang, A. Krüger, A. Neels, M. Albrecht, *Organometallics*, **2008**, *27*, in press.

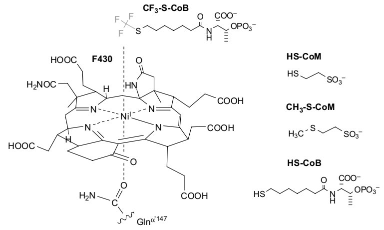
Inorganic and Coordination Chemistry **158**

Dramatic conformational change in the enzyme methyl-coenzyme M reductase (MCR) when the coenzyme B analogue CF_3-S-CoB binds to the active Ni^I state

Sieglinde Ebner, Bernhard Jaun, Meike Goenrich, Rudolf K. Thauer, Dariush Hinderberger, and Jeffrey Harmer

ETH Zürich, Wolfgang-Pauli-Str. 10, 8093 Zürich, Switzerland

Methane formation by methyl-coenzyme M reductase requires binding of the two substrates methyl-coenzyme M (CH_3-S-CoM) and coenzyme B (H-S-CoB). We have synthesized the coenzyme B analogue CF_3-S-CoB and obtained the first structural information on the enzyme in the active Ni^I oxidation state when the substrate CH_3-S-CoM and then H-S-CoB bind to the protein.



This information is obtainable with the substrate analogs H-S-CoM + CF_3-S-CoB and the measurement of the ^{19}F (I = ½) hyperfine interactions to determine the orientation and location of the CF_3 group of CF_3-S-CoB. Using W-band CW-EPR and ENDOR, it was possible to deduce the distance between the nickel center of the hydrocorphin F430 and the fluorine atoms in the CF_3-group. If the geometry within the active site remained as found in the crystal structure of inactive Ni^{II}-forms of the enzyme, this distance should lie in the range of ca. 0.65-0.76 nm for the three F atoms, respectively. In fact, a distance of less than 0.46 nm was found, which brings it within van der Waals contact to the sulfur of coenzyme M.

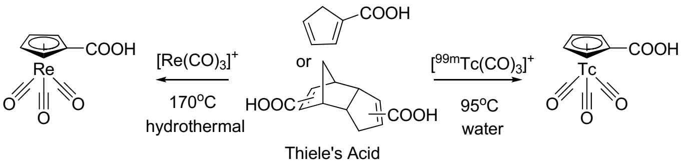
Inorganic and Coordination Chemistry **160**

Labeling Thiele's acid with Re(I)/Tc(I) triscarbonyl through retro-Diels-Alder Reaction in aqueous media

Y. Liu, P. Schmutz, B. Spingler, R. Alberto

Institute of Inorganic Chemistry, University of Zürich, Winterthurerstr. 190,
CH-8057, Zürich, Switzerland

The amino acids coupled with tripodal Dap (Diamino propionic acid) has been introduced in our group to prepare Re(I)/Tc(I) tri-carbonyl complexes, which can be recognized and transported by LAT1 transporter[1]. Based upon this observation, Cp (Cyclopentadiene), with its smaller and more compact size than Dap, should be a good chelator candidate for Re(I)/Tc(I) tri-carbonyl chemistry. Contrary to the conventional view moisture sensitive chemistry of Cp, C_5H_5COOH can react with Re(I)/Tc(I) triscarbonyl to produce $(CO)_3MC_5H_4COOH$ (M=Re(I), ^{99m}Tc(I)) in aqueous media (Scheme). What is more, the Diels-Alder dimer of C_5H_5COOH, Thiele's acid, reacting with Re(I)/Tc(I) triscarbonyl as well in aqueous media, results in the formation of $(CO)_3MC_5H_4COOH$ (Scheme), which gives a first example of retro-Diels-Alder complexation of triscarbonyl compound at low temperature (<100°C) [2].



Scheme

[1] Y. Liu, J. K. Pak, P. Schmutz, M. Bauwens, J. Mertens, H. Knight, R. Alberto, *J. Am. Chem. Soc.*, **2006**, *128*, 15996-15997
[2] Y. Liu, B. Spingler, P. Schmutz, R. Alberto, *J. Am. Chem. Soc.*, **2008**, *130*, 1554-1555

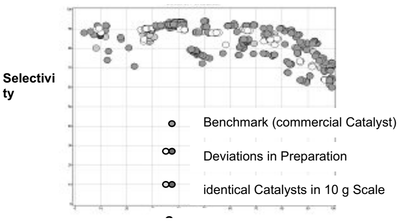
Inorganic and Coordination Chemistry **161**

Development of Heterogeneous Catalysts using Automated High-Throughput Tools

Amira Abou-Hamdan, Ph.D.

Chemspeed Technologies AG, Rheinstrasse 32, CH-4302 Augst (BL), Switzerland

High-throughput tools for the preparation of heterogeneous catalysts are just evolving. However, known techniques such as the impregnation of support wafers with metal salt solutions are often not applicable for industrial purposes, where a subsequent scale-up and commercialization of the developed catalyst is predetermined. The catalysts prepared in the high-throughput scale have to represent the very complex structures and characteristics of commercial heterogeneous catalysts, including for example metal dispersion and distribution, support material, oxidation state of the active compound etc. From the Technical Scale to High-Throughput: Due to the complexity of heterogeneous catalyst preparation, only few variables can already lead to a huge amount of catalyst, requiring high-throughput for both preparation and screening. By using the synthesis robot based on the Chemspeed Accelerator platform, up to 24 heterogeneous catalysts can be prepared in parallel on a 3-15 gram scale, automatically performing tasks such as co-precipitation of mixed metal oxide catalysts as well as impregnation of supports with different metal salts. Downscaling of industrial techniques is easily feasible.



The preparation of heterogeneous catalysts by automated means, allows for the fully automated and unattended screening of a wide range of experiments under highly demanding conditions Furthermore, the obtained results give evidence, that an accelerated, automated development of commercial catalysts is possible and typical development times are significantly reduced by at least 50%.

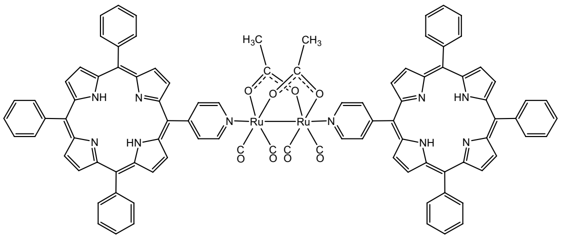
Inorganic and Coordination Chemistry **163**

Sawhorse-Type Diruthenium Complexes Containing Porphyrin-Derived Ligands

Mathieu Auzias,[a] Bruno Therrien,[a] Georg Süss-Fink,[a] L. Juilleret-Jeannerat,[b] F. Schmitt [b]

[a] Institut de Chimie, Université de Neuchâtel, CH-2009 Neuchâtel
[b] University Institute of Pathology, CHUV, CH-1011 Lausanne

Diruthenium tetracarbonyl complexes of the type $Ru_2(CO)_4(O_2CR)_2L_2$ are known to have a stable $Ru_2(CO)_4$ backbone in a sawhorse-type arrangement [1]. To the best of our knowledge, such complexes have never been studied as antitumor drugs. Given the promising results with arene-ruthenium porphyrin derivatives [2], we decided to design diruthenium complexes based on the $Ru_2(CO)_4$ sawhorse unit containing porphyrin-derived ligands for photodynamic cancer therapy.



The synthesis and the photodynamic anticancer activities of these complexes will be discussed.

[1] H. Schumann, J. Opitz, J. Pickardt, *J. Organomet. Chem.* **1977**, *128*, 253-264.
[2] F. Schmitt, P. Govindaswamy, G. Süss-Fink, W. H. Ang, P. J. Dyson, L. Juillerat-Jeanneret, B. Therrien, *J. Med. Chem.* **2008**, *51*, 1811-1816.

Inorganic and Coordination Chemistry **162**

DNA Recognition by Water Soluble Multi – Porphyrin Arrays

Philipp M. Antoni, Bernhard Spingler

University of Zürich, Winterthurerstr. 190, CH – 8057 Zürich, Switzerland

Cationic metal porphyrins can interact with DNA in various ways. Most commonly, these systems intercalate into DNA. The zinc porphyrins $ZnTMPyP^{4+}$ was postulated to coordinate to the N7-guanine of Z form of poly d(GC)[1]. We have shown that Z – DNA can be induced by mononuclear metal complexes having either Ni(II) or Zn(II) centers[2] or by dinuclear metal complexes[3].

Combining those two ways in influencing DNA, we will show a combination of these systems in order to observe a more selective coordination behaviour towards certain DNA conformations. We want to introduce a recognition unit consisting of multiple metal porphyrins linked by metallic linkers. The different coordination spheres of the linking metal centers such as Pt(II), Re(I) will further modulate the coordination behaviour towards different DNA double helices conformations.

[1] M. Balaz, M. De Napoli, A. E. Holmes, A. Mammana, K. Nakanishi, N. Berova, R. Purrello, *Angew. Chem. Int. Ed.* **2005**, *44*, 4006.
[2] B. Spingler, C. Da Pieve, *Dalton Trans.* **2005**, 1637.
[3] B. Spingler, P. M. Antoni, *Chem. Eur. J.* **2007**, *13*, 6617.

Inorganic and Coordination Chemistry **164**

Cu/Zn Superoxide Dismutase- Mimics: Is There a Structure-Activity Relationship for the Metal Binding Region?

Vimalkumar Balasubramanian, Cornelia G. Palivan

Chemistry Department, University of Basel, Klingelbergstrasse 80, CH-4056 Basel, Switzerland

Cu/Zn Superoxide dismutase (SOD), one of the metal proteins which act as an antioxidant enzyme can not be directly administrated, due to its very low bio distribution. One way to solve this problem is to use low-molecular mass copper complexes, which have SOD-like activity (SOD-m). Despite the intensive efforts which have been made to obtain compounds with high SOD-like activity, there are no studies which try to connect the biological activity of all these compounds to their structural properties, in order to model and understand the conformations which promote a better activity.

We constructed a database with the classes of SOD-m previously reported in the literature by taking into account magnetic resonance, spectroscopic characterization, and activity tests. We did a statistical data analysis by taking into account various parameters, such as d-d transitions in electronic spectra, hyperfine coupling constants, distortion factor of the geometry around the metal, and coordination number of copper, in connection with the SOD-like activity. We found out that the most active copper complexes were mononuclear with four-coordination sphere around the metal, and that they belong to a .particular range of structural region which includes d-d transition region (550-680 nm), hyperfine coupling constants (120-160 G), and a distorted geometry which corresponds to a distortion factor of 130-170 cm. We could establish that each structural parameter alone does not have much influence on activity, but when they are interrelated together a structure-activity relationship can be obtained.

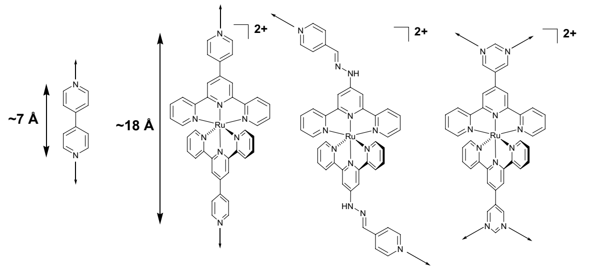
Inorganic and Coordination Chemistry **165**

Crystal Engineering with Extended {M(tpy)$_2$} (tpy = 2,2':6',2"-terpyridine) Units: Coordination Polymers and Networks

Jonathon E. Beves, Edwin C. Constable, Emma L. Dunphy, Catherine, E. Housecroft, Markus Neuburger, Silvia Schaffner, Jennifer Zampese

Department of Chemistry, University of Basel, Spitalstrasse 51, 4056 Basel.

2,2':6',2"-Terpyridine complexes often possess interesting electrochemical or photophysical properties. The inclusion of these groups into extended structures offers the opportunity to build useful functionality into molecular frameworks.



Using self-complementary hydrogen bonding or metal ions, such as Ag(I) or Cu(II), as bridging motifs we are developing [1-3] coordination polymers and networks including {M(tpy)$_2$} groups.

[1] J. E. Beves,. E. C Constable, C. E Housecroft, C. J. Kepert, D. J. Price, *CrystEngComm*, **2007**, *9*, 456.
[2] J. E. Beves, E. C. Constable, C. E. Housecroft, C. J. Kepert, M. Neuburger, D. J. Price, S. Schaffner, *CrystEngComm,* **2007**, *9*, 1073.
[3] J. E. Beves, E. C. Constable, S. Decurtins, E. L. Dunphy, C. E. Housecroft, T. D. Keene, M. Neuburger, S. Schaffner, *CrystEngComm.* **2008**, *in press*.

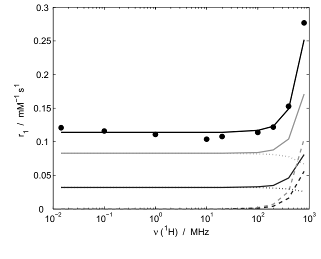
Inorganic and Coordination Chemistry **167**

Acetonitrile exchange kinetics on di- and trivalent lanthanide ions

Gabriella Bodizs, Lothar Helm

Institut des Sciences et Ingénierie Chimique, Ecole Polytechnique Fédérale de Lausanne, BCH, 1015 Lausanne, Switzerland

Our study reports results related to the acetonitrile exchange reaction on some homoleptic lanthanide complexes: $[Ln(CH_3CN)_n][Al(OC(CF_3)_3)_4]_z$ (n = 9, Ln^{z+} = Nd^{3+}, Gd^{3+}, Dy^{3+} and Eu^{2+}; n = 8, Ln^{z+} = Tm^{3+}). During the exchange reaction an acetonitrile molecule from the first coordination sphere of Ln's is replaced by another one from the bulk. The kinetic parameters as well as the electron spin relaxations and the rotational correlation times were obtained by variable temperature ^{14}N NMR, ^{1}H NMRD and EPR techniques. A systematic increase of the acetonitrile exchange rates as the lanthanide ionic radii decrease has been established. This behavior was interpreted by the increase in the steric crowding produced by the coordinated CH_3CN molecules to the metal center.



^{1}H NMRD profile of the of the Dy^{3+} ion in anhydrous acetonitrile at 298 K.

Up to now, the electronic relaxation times for lanthanide ions (other than Gd^{3+}) have been determined only in aqueous solution.[1,2] Since they play a crucial role in the estimation of the solvent exchange rates it seemed to be worth to determine the electronic relaxation times of lanthanide ions in anhydrous acetonitrile. It has been found that the electronic relaxation times of lanthanide ions are independent from the nature of the coordinated solvent molecules.

[1] I. Bertini, F. Capozzi, C. Luchinat, G. Nicastro, Z. Xia, *J. Phys. Chem.* **1993,** *97,* 6351
[2] L. Helm, A. E. Merbach, *Chem. Rev.* **2005,** *105,* 1923

Inorganic and Coordination Chemistry **166**

Microwave-Assisted Non-Aqueous Sol-Sel Routes to Metal Oxide Nanoparticles

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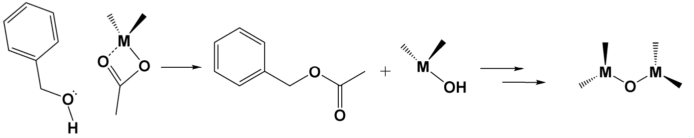
Non-aqueous sol-gel routes offer a simple one-pot approach to a large variety of highly crystalline metal oxide nanoparticles at moderate temperatures [1]. These routes involve the chemical transformation of metal organic precursors in organic solvents making use of simple organic reactions (see Scheme below). Combination with microwave irradiation increases the rate of nanoparticle formation and directly influences the organic reaction pathways. This results on the one hand in an immense acceleration of the process, and on the other hand provides a powerful tool to control the size of the metal oxide nanoparticles by adjusting the experimental conditions such as concentration, time and temperature.



A simple and general approach for the preparation of metal oxide nanoparticles in good yields within minutes or even seconds is presented, offering great opportunities for tailoring the crystal size as well as for the development of predictable size-control strategies [2].

[1] Niederberger M., Nonaqueous sol-gel routes to metal oxide nanoparticles, *Acc. Chem. Res.* **2007**, 9, 793.
[2] Bilecka I., Djerdj I. and Niederberger M., One-minute synthesis of crystalline binary and ternary metal oxide nanoparticles, *Chem. Commun.* **2008**, 886.

Inorganic and Coordination Chemistry **168**

New Efficient Pincer-Type Heck-Catalysts – Mechanistic Investigations

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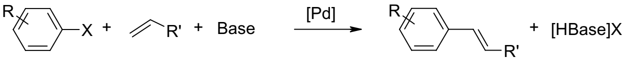
The Heck cross-coupling reaction is one of the most efficient methods for C-C bond formation, which is in our days an indispensable tool in organic synthesis for the catalytic formation of symmetric and non-symmetric olefins.



We would like to introduce new palladium pincer-type complexes as extremely efficient Heck-catalysts which are able to couple aryl bromides and aryl chlorides with various olefins.

The syntheses of these palladium complexes require only cheap starting materials and can be carried out within one day.

Additionally, mechanistic investigations regarding the nature of the active species were performed, because since pincer-type complexes have been successfully introduced as highly efficient catalysts in the Heck reaction, it has been discussed whether a Pd(II)/Pd(IV) mechanism or the formation of palladium nanoparticles leads to their high catalytic activity.

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Gold Nanoparticles Functionalized with Liquid-Crystalline Dendrimer-Thiols

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Thomas Bürgi and Robert Deschenaux

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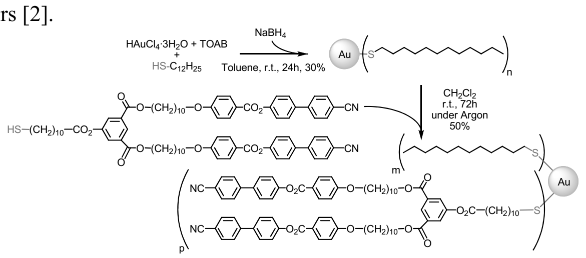
Institutes of Chemistry, Physics and Microtechnology,
Rue Emile-Argand 11, CH-2009 Neuchâtel, Switzerland

Gold nanoparticles have generated a growing interest in the past two decades due to their metallic properties and potential applications [1]. We proposed gold particles stabilized by liquid-crystalline thiolato-dendrimers in order to obtain materials with temperature-dependent optical properties as it was observed with mesomorphic fullerene- and ferrocene-containing dendrimers [2].



These materials were obtained by exchanging stabilizing-alkylthiol ligands for the appropriate liquid-crystalline dendrimer-thiol. As the first attempts for lower generation dendrons did not show a clear mesomorphic behaviour, higher-generation dendrimers of this type will be studied in next experiments and thus thermic behaviour of these new materials will be discussed.

[1] M. C. Daniel, D. Astruc, *Chem. Rev.* **2004**, *104* (1), 293-346
[2] a) Gottis *et al.*, *Helv. Chim. Acta* **2007**, 957; b) Lenoble *et al.*, *J. Am. Chem. Soc.* **2007**, 9941; c) Campidelli *et al.*, *J. Mater. Chem.* **2008**, 1504

Inorganic and Coordination Chemistry **170**

Synthesis of high valent $[^{99m}\text{TcO}_3]^+$ complexes and [2+3] cycloaddition reactions with alkenes in water as a novel direct labeling strategy

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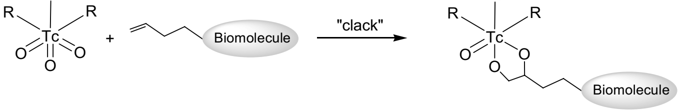
The labeling of small biomolecules with ^{99m}Tc under retention of bioactivity is the major challenge in modern radiopharmacy. For this reason we developed in the past two different synthetic approaches for the synthesis of $\{^{99}\text{TcO}_3\}$ complexes, via an oxidation pathway[1] in water and by the direct activation of $[^{99}\text{TcO}_4]^-$[2] in organic solvents to study stability and properties of this new type of very small complexes. In contrast to the ^{99}Tc chemistry the synthesis of ^{99m}Tc complexes for radiopharmaceutical application has to start form $[^{99m}\text{TcO}_4]^-$ in water, therefore the synthesis of $\{^{99m}\text{TcO}_3\}$ complexes is much more challenging.

Here we report about the first syntheses of complexes $[^{99m}\text{TcO}_3(N^3\text{-R})]^{+/0}$ (N^3-R = triazacyclononane and its derivatives) directly from aqueous solution. These complexes are stable at 37° C in water and in the presence of serum proteins and represent a novel kind of ^{99m}Tc complex for labelling purposes. Furthermore, the $[^{99m}\text{TcO}_3(N^3\text{-R})]^{+/0}$ type complexes react with alkenes in water by a [2+3] cycloaddition, thereby forming the corresponding glycolato complexes at a reasonable rate. We call this "clack chemistry" due to the principal similarity with the well known "click chemistry".[3] "Clack chemistry" represent a novel way of labelling. Substitution does not take place at the metal centre as commonly encountered but on the ligands activated by the metal centre.



[1] H. Braband, U. Abram, *Inorg. Chem.* **2006**, *45*, 6589.
[2] Y. Tooyama, H. Braband, B. Spingler, U. Abram, R. Alberto, *Inorg. Chem.* **2008**, *47*, 257.
[3] H.C. Kolb, M.G. Finn, K.B. Sharpless, *Angew. Chem. Int. Edit.* **2001**, *40*, 2004.

Inorganic and Coordination Chemistry **171**

Antimicrobial Surfaces

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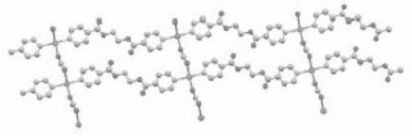
All commonly used implant materials, metals and polymers, seem to present a common problem: bacterial adhesion on their surfaces, mainly S*taphylococci.* The resultant biofilm is resistant to aggressive pharmacological agents as well as host defences [1].

One way to prevent the establishment of infection is to render the implant surface bactericidal, creating a stable environment with a spectrum similar to the soluble antibiotics [2]. The current revival of silver chemistry in this context initiated us to use this metal ion for coating purposes [3].



The combination of molecules derived from antibiotics and silver compounds would provide additive, synergic activity against most microorganisms, and thus the desired protection. Therefore, we propose to avoid or at least strongly reduce bacterial adhesion to implant surfaces using a series of newly developed Ag-antibiotic combinations on implant surfaces.

[1] P.S Stewart, J.W.Costerton, *Lancet*. **2001**, 358, 135.
[2] B. Jose, V. Antoci, A. R. Zeiger, E. Wickstrom, N. J. Hickok C*hemistry & Biology*. **2005**, 12, 1041.
[3] J. L. Clement, P. S. Jarret, *Metal-Based Drugs*. **1994**, 467.

Inorganic and Coordination Chemistry **172**

Palladium-Catalyzed Enantioselective Allylic Phosphination

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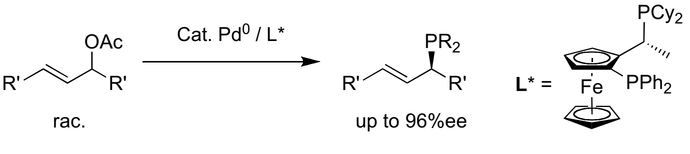
Palladium-catalyzed allylic substitution reactions are known to occur with a variety of carbon, nitrogen and oxygen nucleophiles. However, to the best of our knowledge, the analogous reaction involving a secondary phosphine has never been reported. Recently, our laboratory reported that dicationic Nickel complexes catalyze the intermolecular hydrophosphination of vinyl nitriles with secondary phosphines in good yield and high enantiomeric excess [1]. We now found that the same type of nucleophiles may be used for an unprecedented allylic phosphination. Thus, the model substrate 3-acetoxy-1,3-diphenylprop-1-ene (1) is converted with diphenylphosphine to the corresponding allylic phosphine (2) in the presence of 5 mol-% of a Pd catalyst containing the ferrocenyl ligand Josiphos (3) [2].



Product 2 is isolated in quantitative yield and the enantioselectivity is up to 96 % ee.

This new C-P bond forming reaction can provide a broad set of chiral phosphines with the opportunity of further functionalization of the alkene.

[1] A. D. Sadow, A. Togni, J. Am. Chem. Soc. 2005, 127, 17012.
[2] A. Togni, C.Breutel, A. Schnyder, F. Spindler, H. Landert, A. Tijani, J. Am. Chem. Soc. 1994, 116, 4062.

Inorganic and Coordination Chemistry **173**

Chiral Ferrocenyl Amidines as Modular Ligands for Asymmetric Catalysis

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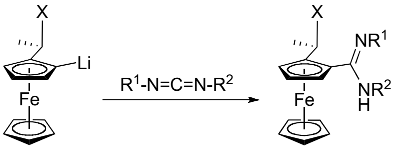
Amidine[1] and especially amidinato[2] ligands have been widely used in transition metal and in main group chemistry. However, their application in homogeneous enantioselective catalysis remains very rare.

We present here the short and highly modular synthesis of new chiral ferrocenyl-substituted amidines combining an amine (**1**,**2**), a pyrazole (**3**,**4**) or a phosphine (**5**,**6**) with an amidine unit as donors.



X	**$R^{1,2}$**
NMe_2	^{i}Pr : (R,S_p)-**1**
NMe_2	Cy : (R,S_p)-**2**
3,5-Me_2-Pz	^{i}Pr : (R,S_p)-**3**
3,5-Me_2-Pz	Cy : (R,S_p)-**4**
PPh_2	^{i}Pr : (R,R_p)-**5**
PPh_2	Cy : (R,R_p)-**6**

Ligands **1**-**6** were tested in the Pd-catalyzed allylic alkylation and amination reaction using the model substrate 3-acetoxy-1,3-diphenylprop-1-ene (**7**) in the presence of 4 mol-% Pd giving in the case of the P^N ligands **5** and **6** full conversion and up to 98% ee showing high catalytic activities.

X-ray and 2D-NMR studies of Pd(π-allyl) complexes containing ligands **1**-**6** will also be presented.

[1] M.P. Coles, *Dalton Trans.* **2006**, 985.
[2] *a)* F.T. Edelmann, *Coord. Chem. Rev.* **1994**, *137*, 403. *b)* J. Barker, M. Kilner, *Coord. Chem. Rev.* **1994**, *133*, 219.

Inorganic and Coordination Chemistry **174**

NOVEL CHIRAL COMPLEXES INCORPORATING ROTATIONALLY RESTRICTED LIGANDS

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CH-4056, Basel, Switzerland.

The $\{M(tpy)_2\}^{n+}$ (tpy = 2,2':6',2"-terpyridine) motif is increasingly used in preference to $\{M(bpy)_3\}^{2+}$ (2,2'-bipyridine) domains in supramolecular chemistry.[1] One major reason is that $\{M(bpy)_3\}^{2+}$ is chiral and the incorporation of multiple centres gives rise to diastereoisomeric structures. This is not to say that $\{M(tpy)_2\}^{n+}$ motifs cannot be chiral; the commonest stereogenic factor is the desymmetrization of the ligand by substitution on one of the two terminal rings. We recently demonstrated that a symmetrical ligands linked through flexible chains can also give rise to chiral structures as a result of the "trapping" of the chain between tpy domains.[2]

We now describe the extension of these observations to new types of bis(2,2':6',2"-terpyridine) ligands and report the spectroscopic characterisation of atropisomeric complexes of these ligands and and the investigation of the dynamic processes interconverting the enantiomers.

[1] *2,2':6',2"-Terpyridines ... from chemical obscurity to common supramolecular motifs*, Constable, E.C. *Chem. Soc. Rev.* **2007**, *36*, 246-253.
[2] *Metal-directed assembly of a conformationally restricted metallomacrocycle* Chow, H.S.; Constable, E.C. and Housecroft, C.E. *Dalton Trans*. **2003**, 4568-4569.

Inorganic and Coordination Chemistry **175**

New Synthetic Strategies towards Oxidic Materials

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Functional oxide-based nanomaterials are essential components of modern materials chemistry. Therefore, we focus on the synthesis and characterisation of ternary oxides, such as $ZnGa_2O_4$. Based on an almost ideal spinel structure, zinc gallate is a transparent and conductive oxide that emits blue light[1] and is well known to be a good low-voltage phosphor material[2]. In order to facilitate the synthesis of nanostructured transition metal oxides[3], we develop microwave-hydrothermal techniques as a highly efficient and time-saving pathway. This technique may replace standard hydrothermal methods due to better crystallisation kinetics. At the moment, we are performing methodological studies on doped zinc gallium spinels that offer important options for the construction of new display types. The morphology and chemical composition of hydrothermal and microwave-assisted synthesized $ZnGa_2O_4$ spinel particles were investigated with respect to the influence of pH, reaction temperature, time and metal ratio of the starting material.

Furthermore, we also apply the above-mentioned methodology on the synthesis of novel (Nb, M)O_x (M = Mo, W) oxides. They combine promising catalytic properties with interesting structural chemistry features, and their nanoscale synthesis still remains a challenging task. Especially the (Nb, Mo)O_x system is currently under investigation with respect to the microwave-assisted synthesis of novel phases.

[1] M. Hirano, M. Imai, M. Inagaki, *J. Am. Ceram. Soc.* **2000**, *84*, 977.
[2] M. Hirano, N. Sakaida, *J. Am. Ceram. Soc.* **2002**, *85*, 1145.
[3] R. Kiebach, N. Pienack, W. Bensch, J.-D. Grunwaldt, A. Michailovski, A. Baiker, T. Fox, Y. Zhou, G. R. Patzke, *Chem. Mater.* **2008**, *20*, 3022.

Inorganic and Coordination Chemistry **176**

Aryloxide clusters of (transition metal ions in analogy to) alkali and alkaline earth metal ions

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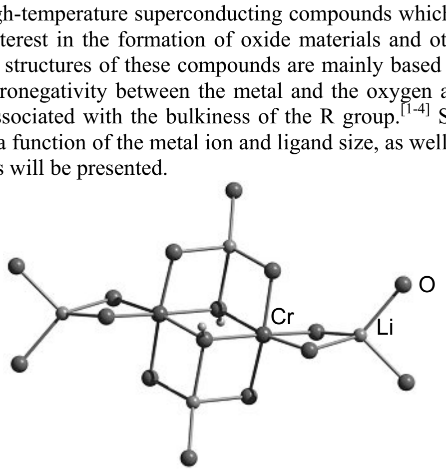
The regain in interest of alkali alkoxides and aryloxides resides in the discovery of high-temperature superconducting compounds which has generated a great interest in the formation of oxide materials and other ceramics. However the structures of these compounds are mainly based on the difference of electronegativity between the metal and the oxygen atom (interaction M-O) associated with the bulkiness of the R group.[1-4] Some relevant examples as a function of the metal ion and ligand size, as well as neutral O-donor ligands will be presented.



[1] W. Maudez, M. Meuwly, K. M. Fromm, *Chem. Eur. J.,* 2007, 13, 29, 8302-8316
[2] K. M. Fromm, E. D. Gueneau, A. Y. Robin, W. Maudez, J. Sague, R. Bergougnant, *Z. Anorg. Allg. Chem.* 2005, *631*, 1725-1740
[3] K. M. Fromm, *Dalton Trans.*, 2006, *43*, 5103-5112
[4] W. Maudez, D. Häussinger, K. M. Fromm, *Z. Anorg. Allg. Chem.*, 2006, *632*, 2295-2298

Inorganic and Coordination Chemistry **177**

Mean Field study of induced magnetic moment in a 2d-multiband Hubbard model. A possible approach to some main group binary compounds.

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CH-8093, Zürich , Schweiz

We set a possible 2-d Hubbard Hamiltonian including an itinerant p-band hybridized with localized orbitals. Inspired in recent studies of magnetism in compounds with no transition metal, we look at the magnetic moment induced by external field. Our model is solved in the Mean field approximation and several thermodynamic quantities are computed. We obtain a variety of behaviors strongly dependent on the fine tuning of the accounted interactions.

[1] S. Wengert, *ETH Diss.* **1997**, *Nr. 12070*, 1.
[2] M. Imada et al, *Rev. Mod. Phys.* **1998**, *70*, 1039.
[3] G. Kotliar et al, *Rev. Mod. Phys.* **2006**, *78*, 865.
[4] G. Y. Gao et al, *J. Phys.* **2007**, *19*, 315222.

Inorganic and Coordination Chemistry **178**

Novel phthalocyanine-based stopcock for zeolite L

Le-Quyenh Dieu[a], André Devaux[b], Ismael López-Duarte[c], M. Victoria Martínez-Díaz[c], Dominik Brühwiler*[a], Gion Calzaferri[b], Tomás Torres[c]

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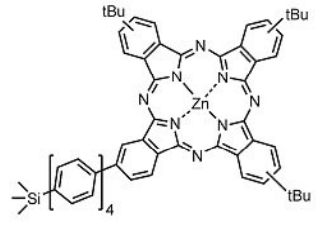
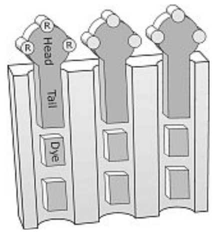
Winterthurerstrasse 190, 8057 Zürich, Switzerland
[b] Department of Chemistry and Biochemistry, University of Bern
Freiestrasse 3, 3012 Bern, Switzerland
[c] Departamento de Química Orgánica, Universidad Autónoma de Madrid
Cantoblanco 28049 Madrid, Spain

The one-dimensional channel system of zeolite L offers possibilities to obtain defined arrangements of monomeric dyes, resulting in efficient energy transfer materials. Communication with external objects is established by functionalization of the channel entrances of the zeolite crystals with fluorescent stopcock molecules. We report the first phthalocyanine-based stopcock for selective adsorption to the channel entrances of zeolite L and the realisation of a new electronic dipole moment coupling situation between dyes in the zeolite channels and stopcock molecules [1]. Photonic antenna systems based on this concept are of particular interest in the design of sensitised organic solar cells [2].





[1] L.-Q. Dieu et al., *Chem. Commun.* **2008**, 1187.
[2] D. Brühwiler et al., *Chimia* **2007**, *61*, 820.

Inorganic and Coordination Chemistry **179**

Insight into fuel cell membrane degradation by pulse radiolysis experiments

S. M. Dockheer, A. Domazou, L. Gubler, G. G. Scherer, W. H. Koppenol, A. Wokaun

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Membrane durability has become a central issue for the progress of polymer electrolyte fuel cells, PEFCs. Accordingly, understanding the mechanism of membrane degradation is crucial to improve suitable membrane materials. Free radical species, such as the $^{\bullet}$OH and $^{\bullet}$OOH, directly produced on the platinum catalyst at the fuel cell electrodes, are assumed to considerably contribute to the ageing process of the polymer. In order to obtain insight into possible polymer-chain-degradation mechanisms relevant for fuel cell applications, this work focuses on the kinetics of the $^{\bullet}$OH towards low-molecular-weight soluble polymers of poly(styrene sulfonic acid) as model systems.

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Repair of Protein Radicals by Ascorbate

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Proteins are significant biological targets for partially reduced oxygen species *in vivo*. The subsequently random formed radicals on the surface of proteins yield often tryptophan and tyrosyl radicals through intramolecular electron transfer. We generated these radicals specifically by azide radicals in insulin, β-lactoglobulin, pepsin, chymotrypsin, and bovine serum albumin. The rate constants measured varied between 10^8 to 10^9 $M^{-1}s^{-1}$, depending on the protein. The formation and disappearance of tyrosyl and tryptophanyl radicals was followed at 405 and 510 nm, respectively. The free tyrosyl and tryptophanyl radical are known to react with monohydroascorbate with rate constants close to 10^8 $M^{-1}s^{-1}$. The rate constants for reactions of protein-bound tryptophanyl radicals with monohydroascorbate in chymotrypsin and pepsin are quite similar, while that of β-lactoglobulin is smaller by a factor of 5. The corresponding rate constant values for protein-bound tyrosyl radicals are ca. 30 – 40 % of that of the free tyrosyl radical, with the exception of that of β-lactoglobulin, which is smaller by a factor of 400. These results are similar to those obtained with lysozyme by others. Previously, we found that glutathione reduces the tryptophanyl radical in lysozyme with a rate constant of 10^5 $M^{-1}s^{-1}$ [1]. Although monohydroascorbate is present in cells in 10-fold smaller concentrations than glutathione, it appears to be more important for the repair of protein radicals. The results suggest that the loss of ascorbate in living organisms subjected to oxidative stress may result from repair of protein radicals.

[1] T. Nauser, W. H. Koppenol, and J. M. Gebicki, *Biochem. J.* **2005**, *392*, 693.

Inorganic and Coordination Chemistry **181**

Rhenium-Catalyzed Ethanolysis of Borane-Amine and Its Use in Transfer-Hydrogenation of Terminal Olefins

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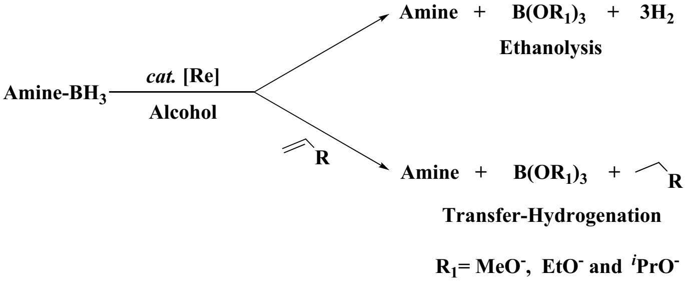
Borane-amine adducts are widely encountered in modern synthetic organic chemistry and industrial processes. Their applications include aqueous reductions of aldehydes and ketones, reductive aminations, olefin hydroborations and amide reductions. Borane-amine adducts are relatively stable, even at 50°C, in ethanol and water maybe due to the high energy barrier of the reactions. It was found that water-soluble complex $[ReBr_2(NO)(CH_3CN)(PTA)_2]$ can activate the ethanolic and hydrolic cleavage of stable borane-amine complexes under mild conditions.



References:
[1] Couturier, M.; Tucker, L. J.; Andresen, M. B.; Dube, P.; Negri, T. J. *Org. Lett.*, **2001**, 3, 465.
[2] Couturier, M.; Tucker, L. J.; Andresen, M. B.; Dube, P.; Brenek, J. S., Negri, T. J. *Tetrahedron Lett.*, **2001**, 42, 2285.

Inorganic and Coordination Chemistry **183**

Photophysical properties of pyridyl fuctionalised 2,2':6'2''-terpyridine ruthenium(II) complexes.

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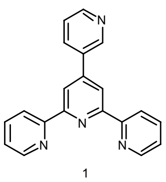
Department of Chemistry, University of Basel, Spitalstrasse 51, 4056 Basel

The optical properties 4-(4'-pyridyl)-2',2':6',2''-terpyridine metal complexes are of interest in supramolecular chemistry due to the change in absorption and emission that occurs with differing protonation states. [1-2]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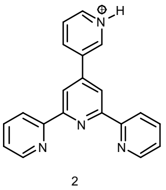

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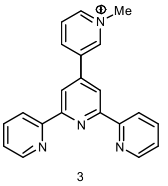

3

Here we describe the photophysical properties of a recently reported [3] series of bis{4'-(*n*-pyridyl)-2',2':6',2''-terpyridine}, (where n = 2, 3, 4), ruthenium(II) complexes and their protonated and methylated analogues exemplified by the ligands 1-3.

[1] E. C. Constable, C. E. Housecroft, A. Cargill Thompson, P. Passaniti, S. Silvi, M. Maestri, and A. Credi, *Inorg. Chim. Acta.,* **2007**, *360*, 1102.
[2] C. Zhang, H. Huang, B. Liu, M. Chen and D. Qian, *J. Lumin.*, **2008**, *128*, 469
[3] J. E. Beves, E. L. Dunphy, E. C. Constable, C. E. Housecroft, C. J. Kepert, M. Neuburger, D. J. Price and S. Schaffner, *Dalton Trans.*, **2008**, *3*, 386

Inorganic and Coordination Chemistry **182**

New insights into the structure and properties of *Musa acuminata* MT3

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Metallothioneins (MTs) constitute a family of proteins present in all animal phyla examined so far as well as in certain fungi, plants and cyanobacteria. MTs are generally small proteins (<10 kDa) featuring a high percentage of cysteine thiolate groups and a large metal ion content [1]. Their function is not finally resolved yet, but has been related to protection against metal ion toxicity, regulation of physiological relevant metal ions (Zn^{II} and Cu^{I}) and protection against oxidative stress.

M. acuminata (banana) MT3 belongs to the plant MT fruit-specific p3 subfamily. It contains a total of 65 amino acids, among them 10 cys and 1 his residues. The ability of MT3 and its H46C-MT3 mutant to bind up to four divalent metal ions has been already described, and apparent pK_a values of the cys residues have been determined [2].

In the present work, we will evaluate the metal ion binding abilities of the apo-proteins with UV and CD spectroscopy. Limited proteolytic digestion experiments give insights into the metal-thiolate cluster organization in the protein, and results are corroborated by measurements performed with dynamic light scattering. Isothermal titration calorimetry studies of both, MT3 and the H46C-MT3 mutant, to access the cluster stability will be presented and discussed as well.

Support from the Swiss National Science Foundation (SNF grant 20-113728/1 and SNF- Förderungsprofessor PP002-119106/1 to E.F.) is gratefully acknowledged.

[1] M. Capdevila, P. González-Duarte, in: J. A. McCleverty, T. J. Meyer (Eds.), *Comprehensive Coordination Chemistry II*, 2004, *8*, 213.
[2] E. Freisinger, *Inorg. Chim. Acta* **2007**, *360*, 369.

Inorganic and Coordination Chemistry **184**

Bimetallic Lanthanide Complexes for Anion Sensing

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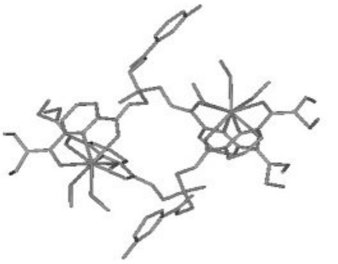
Department of Inorganic, Analytical and Applied Chemistry, University of Geneva, 30 quai E.-Ansermet, CH-1211 Geneva 4



Tripodal[1] ligands are particularly interesting for improving luminescent detection of analytes in Vis and IR. In this context, ligand **L** represents a new asymmetric receptor bearing two tridentate dicarbonylpyridine and one bidentate carbonylpyridine units anchored on the tertiary carbon. This ligand is supposed to provide a cavity for eight-coordinated lanthanide cation. Leaving one free position for interacting with an anionic analyte. However, the X-ray crystal structure of the europium complex ([M]/[**L**] = 1:1) revealed a dimeric form in the solid state. The dimeric structure was confirmed in solution by means of spectrophotometry, ES-MS and luminescence. Introduction of bidentate anions (i.e. acetates) with the complex in acetonitrile solution results in drastic changes of its photo-physical properties.

[1] (a) M. Seitz, M. D. Pluth, and K. N. Raymond, *Inorg. Chem.* **2007**, *46*, 351. (b) J.-M. Senegas, G. Bernardinelli, D. Imbert, J.-C. G. Bünzli, P.-Y. Morgantini, J. Weber, and C. Piguet, *Inorg. Chem.* **2003**, *42*, 4680.

Inorganic and Coordination Chemistry **185**

Charge and energy transfer through salt bridges

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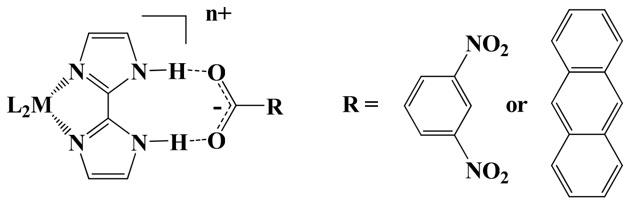
Photoinduced charge and energy transfers play important roles in many bioenergetic conversion mechanisms. In this greater context, we study cationic metal complexes with 2,2'-biimidazole ligands that can form salt-bridges with carboxylates:



M = Ir(III), Ru(II)

L = e. g. 2,2'-bipyridine

Two case studies will be reported: An iridium(III) complex that is useful for proton coupled electron transfer investigations, and a ruthenium(II) complex that transfers energy to an anthracene moiety across the hydrogen bonds.

Inorganic and Coordination Chemistry **186**

Enhanced Spin Crossover through Self-Organization of Iron Complexes

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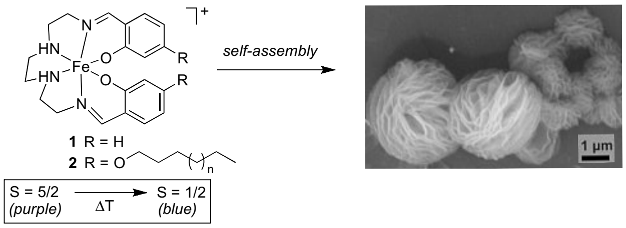
Cooperative spin-crossover systems that show bistability and thermal hysteresis are attractive components for fabricating optical and magnetic memory devices [1]. We aim at self-assembling switchable amphiphilic molecules in order to promote cooperative effects between the metal centers. This approach is expected to eventually amplify the response towards external stimuli.



We have introduced apolar groups in complex **1**, which is known for its thermochromic properties due to a gradual spin transition [2]. The resulting complexes **2** are amphiphilic and therefore self-organize spontaneously at interfaces and in solution. We will present evidence for the formation of self-assembled monolayers and spherical particles. Remarkably, the spin-crossover activity of the metal centers is considerably amplified as a consequence of such spontaneous organization.

[1] O. Kahn, C.J. Martinez, *Science* **1998**, *279*, 44. C. Saioa, M. Gábor, J.A. Real, A. Bousseksou, *Angew. Chem. Int. Ed.* **2006**, *45*, 5786. E. Coronado *et al.*, *Adv. Mater.* **2007**, *19*, 1359.
[2] M.F. Tweedle, L.J. Wilson, *J. Am. Chem. Soc.* **1976**, *98*, 4824.

Inorganic and Coordination Chemistry **187**

ACC-Oxidase model complexes, a possible Cu(I)-OOH intermediate.

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Ethylene is a plant hormone that regulates many stages of a plant life, like germination, fruit ripening and leaf color change. The last step of the biosynthesis of ethylene is catalyzed by ACC-Oxidase, a non-heme iron containing enzyme that utilizes oxygen to oxidize 1-aminocyclopropane carboxylic acid (ACC) into ethylene (Figure 1).

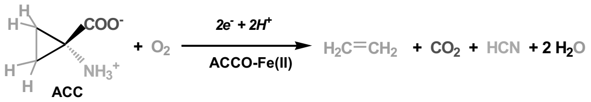

Figure 1: Oxidation of ACC into ethylene by ACC-Oxidase.

Many questions about the enzymatic oxidation mechanism and the role of the metallic ion remain unanswered. Nevertheless, it is accepted that the first step of the reaction is the fixation of ACC and dioxygen on the Fe(II) center. Therefore we were interested in studying the coordination of ACC on metal cations [1].

We succeeded in preparing and characterizing several iron and copper ACC complexes. Reacting these complexes with H_2O_2 generates ethylene [2]. Surprisingly during this oxidation reaction a reduced Cu(I) intermediate was observed and characterized at low temperature [3].

[1] W. Ghattas, C. Gaudin, M. Giorgi, *Chem. Commun.* **2006**, 1027
[2] W. Ghattas, M. Giorgi, C. Gaudin, *BCA*, **2007**, 43424
[3] W. Ghattas, M. Giorgi, Y. Mekmouche, *Inorg. Chem.* **2008**, ASAP.

Inorganic and Coordination Chemistry **188**

Water-soluble arene ruthenium complexes containing pyridinethiolato ligands: Synthesis, molecular structure, redox properties and anticancer activity of the cations $[(\eta^6\text{-arene})Ru(p\text{-}SC_5H_4NH)_3]^{2+}$

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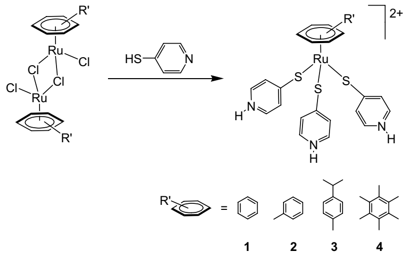
The synthesis of the complexes $[(\eta^6\text{-arene})Ru(SC_5H_4NH)_3]^{2+}$, obtained from the reaction of 4-pyridinethiol with the corresponding precursor $(\eta^6\text{-arene})_2Ru_2Cl_4$, is reported. The reaction involves a transfer of a hydrogen atom from sulfur to nitrogen in the three ligands coordinated to ruthenium.



The molecular structure of these complexes, isolated as the chloride salts, their redox properties and their anticancer activities will be presented.

Inorganic and Coordination Chemistry **189**

Ruthenium(IV)-Catalyzed Allylation of Indoles and Related Ruthenium(IV) Organometallic Complexes

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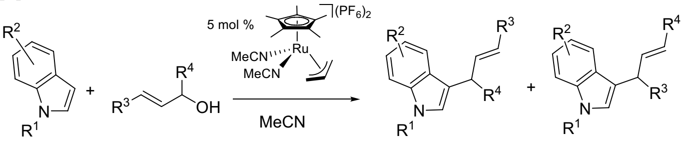
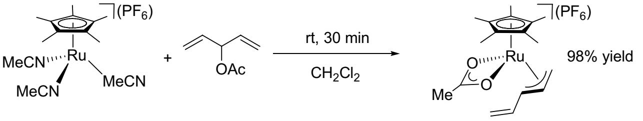
Dicationic ruthenium(IV) allyl complexes are efficient catalysts in the Friedel-Crafts allylation of phenols and related compounds [1]. We have found that related ruthenium(IV) complexes also efficiently catalyze the reaction of indoles with allyl alcohols to form 3-allylindoles under mild conditions in high yield and selectivity [2]. This process offers several advantages over the conventional palladium-catalyzed transformation: a) high regioselectivity with respect to the alcohol, b) very short reaction times at room temperature, and c) there is no need for additives [3].



In order to explain the observed exclusive linear selectivity in the reaction of dienol alcohol with indole, we studied the stoichiometric reactions of dienyl acetate substrates with $[Ru(Cp^*)(CH_3CN)_3](PF_6)$. The structures of the resulting Ru(IV) η^3-vinyl-allyl salts were established using NMR spectroscopy and X-ray analysis.



[1] I. Fernandez, R. Hermatschweiler, F. Breher, P. S. Pregosin, L. F. Veiros, M. J. Calhorda*, Angew. Chem., Int. Ed.*, **2006**, *45*, 6386.
[2] A. B. Zaitsev, S. Gruber, P. S. Pregosin, *Chem. Commun.*, **2007**, 4692.
[3] M. Kimura, M. Futamata, R. Mukai, Y. Tamaru, *J. Am. Chem. Soc.*, **2005**, *127*, 4592.

Inorganic and Coordination Chemistry **190**

Scanning Tunnelling Microscopy examination of monolayers of dendritic complexes of 2-Pyridinecarboxaldehyde-2'-pyridylhydrazone

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Hydrocarbon modified dendritic wedges are able to form stable monolayers on highly ordered pyrrolitic graphite.[1]
The synthesis of these dendritic wedges is a simple and efficient process that can be easily be done on a large scale.
Of special interest to our group is the attachment of metal binding ligands to these wedges. The ligand 2-pyridinecarboxaldehyde-2'-pyridylhydrazone (paphyH) was considered to be a promising candidate. We have coupled first and second generation dendritic wedges with paphyH. We obtained the free ligands of the first and second generations as well as the corresponding iron (II) complexes. The monolayers of these compounds were studied by using scanning tunnelling microscopy (STM).

1 Scherer, L. J.; Merz, L.; Constable, E. C.; Housecroft, C. E.; Neuburger, M.; Hermann, B. A. J. *Am. Chem. Soc.* **2005**, *127*, 4033-4041.

Inorganic and Coordination Chemistry **191**

Toward 3D Helicates: Self-assembly of Tetrahedral Ln(III) Complexes

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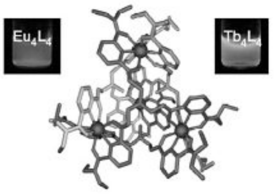
Recently, the thermodynamic modelling has been applied to linear polynuclear helicates with lanthanides in order to extract key energetic parameters for programming the first linear tetrametallic helicate.[1] Here we report on tetrametallic complexes, where 3D arrangement of trivalent lanthanides (Eu-Lu) is controlled through the self-assembly with a new tripodal ligand L. X-ray crystallography shows, that four nine-coordinated cations adopt a regular tetrahedral arrangement, which is maintained in solution, as demonstrated by NMR, ESI-MS and spectrophotometry. These remarkable highly charged structures with four lanthanides in a small volume provide interesting perspectives for exploring intramolecular optical and paramagnetic communication in homo- and heterometallic edifices.



[1] K. Zeckert, J. Hamacek, J.-M. Senegas, N. Dalla-Favera, S. Floquet, G. Bernardinelli, C. Piguet, *Angew. Chem. Int. Ed.* **2005**, *44* 7954. b) N. Dalla-Favera, J. Hamacek, M. Borkovec, D. Jeannerat, G. Ercolani, C. Piguet, *Inorg. Chem*. **2007**, *46*, 9312.

Inorganic and Coordination Chemistry **192**

Cobalt Complexes of Ditopic 2,2':6',2"-Terpyridine Ligands with Flexible Spacers – Polymers or Metallomacrocycles?

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The reaction of transition metal ions with ditopic ligands containing two 2,2':6',2"-terpyridine metal-binding domains linked by variable spacers can give metallopolymers [1] (copolymers with alternating metal centres and ligands), discrete molecular macrocycles [2], or mixtures of the two. The outcome of the coordination depends on the precise reaction conditions as well as the nature of both the spacer and the transition metal ion.

We have used ditopic ligands with two 2,2':6',2"-terpyridine units linked by flexible oligo(ethyleneoxy) spacers to synthesise cobalt(II)-containing metallomacrocycles of various sizes. Their dynamic behaviour in solution has been studied using ^1H NMR. Oxidation of these products to give the cobalt(III) species allowed us to investigate these compounds with diffusion NMR spectroscopy, and thus to determine their relative sizes in solution.

We have isolated neutral mono-2,2':6',2"-terpyridine complexes with labile transition metal ions. The interplay between metallomacrocycles and polymers is also dependent on the counteranion, with the assembly of polymers favoured in the presence of coordinating anions.

[1] H. Hofmeier, S. Schmatloch, D. Wouters and U. S. Schubert, *Macromol. Chem. Phys.*, **2003**, *204*, 2197-2203.
[2] E. C. Constable, C. E. Housecroft, M. Neuburger, S. Schaffner and C.B. Smith, *Dalton Trans.*, **2005**, 2259-2267.

Inorganic and Coordination Chemistry **193**

In Vitro Anticancer Activity and Biologically-Relevant Metabolization of Organometallic Ruthenium Complexes with Carbohydrate-based Ligands

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[b] Institut des Sciences et Ingénierie Chimiques, Ecole Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland
[c] Centro de Química Estrutural, Complexo I, Instituto Superior Técnico, TU Lisbon, Av. Rovisco Pais, 1049-001 Lisbon, Portugal
[d] University Institute of Pathology, Centre Hospitalier Universitaire Vaudois (CHUV), Rue du Bugnon 25, CH-1011 Lausanne, Switzerland

The synthesis and *in vitro* anticancer activity of dihalogenido(μ^6-*p*-cymene)(3,5,6-bicyclophosphite-α-D-glucofuranoside)ruthenium(II) complexes are described. The compounds were characterized by NMR spectroscopy and ESI mass spectrometry, and the molecular structures of the chlorido, bromido and iodide complexes were determined by X-ray diffraction analysis. The complexes were shown to undergo aquation of the first halogenido ligand in aqueous solution, followed by the hydrolysis of a P–O bond of the phosphite ligand and finally formation of dinuclear species. The hydrolysis mechanism was confirmed by DFT calculations. The aquation of the complexes was markedly suppressed in 100 mM NaCl solution, and notably only very slow hydrolysis of the P–O bond was observed. The complexes showed affinity towards albumin and transferrin and monoadduct formation with 9-ethylguanine. *In vitro* studies revealed that the 3,5,6-bicyclophosphite-1,2-*O*-cyclohexylidene-α-D-glucofuranoside complex was the most cytotoxic compound in human endothelial cells and human cancer cell lines .

Inorganic and Coordination Chemistry **195**

Copper(I) bipyridine complexes: the sensitizers of the future for DSSCs

Takeru Bessho,[a] Edwin C. Constable,[b] Michael Graetzel,[b] Ana Hernandez Redondo,[a] Catherine E. Housecroft,[a] William Kylberg,[a] Md. K. Nazeeruddin,[b] Markus Neuburger[a] and Silvia Schaffner[a]

[a]Department of Chemistry, University of Basel, Spitalstrasse 51, CH 4056 Basel, Switzerland; [b] Laboratory of Photonics and Interfaces (LPI), Institute of Chemical Science and Engineering , Faculty of Basic Science , Ecole Polytechnique Federale de Lausanne , CH-1015 Lausanne Switzerland.

Dye sensitized solar cells (DSSC) are nowadays a promising alternative to silicon-based photovoltaic devices and are under active investigation. They are based on a large surface area semiconductor, typically TiO_2, and a dye attached to it having a smaller band gap and acting, therefore, as a sensitizer [1]. These cells are inexpensive and easily prepared.

Up to now, ruthenium(II) polypyridine complexes have been employed as sensitizers. We now show that copper(I) complexes are surprisingly effective for this application. The lower cost and higher abundance of copper versus ruthenium are clearly advantageous.

In our laboratories, we have achieved efficiencies of 2.3 % and we believe that iterative chemical optimization of our copper-based dyes will lead to efficiencies comparable to those where ruthenium complexes are employed as sensitizers [2].

[1] B. O'Regan, M. Grätzel, Nature, **1991**, *353*, 737.
[2] T. Bessho, E. C. Constable, M. Graetzel, A. Hernandez Redondo, C. E. Housecroft, W. Kylberg, Md. K. Nazeeruddin, M. Neuburger and S. Schaffner, 2008, submitted.

Inorganic and Coordination Chemistry **194**

C4-bound *N*-heterocyclic carbenes: exceptionally strong donor ligands for catalytic bond activation

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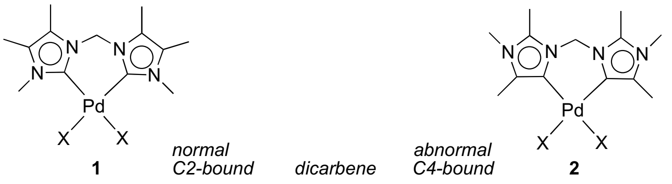
In the last few years, N-heterocyclic carbenes (NHCs) have emerged as versatile ligands in catalysis [1]. Recently, abnormal C4 bonding has been discovered as a new carbene bonding mode [2]. Previous reactivity studies suggested that C4-bound carbenes are stronger donors than normal C2-bound analogs [3]. To probe the influence of electronic factors we prepared two related NHC palladium complexes **1** and **2** with identical steric environment, but containing *cis* chelating dicarbenes bound via C2 and C4 respectively [4].



We will provide evidence that the electron density at the palladium center is markedly higher in C4- than in C2-bound carbene complexes. These electronic properties of the ligand have consequences in catalysis, in particular in oxidative addition and reductive elimination sequences.

[1] W.A. Herrmann, *Angew. Chem. Int. Ed.* **2002**, *41*, 1290.
[2] A.R. Chianese, A. Kovacevic, B.M. Zeglis, J.W. Faller, R.H. Crabtree, *Organometallics* **2004**, *23*, 2461.
[3] M. Heckenroth, E. Kluser, A. Neels, M. Albrecht, *Angew. Chem. Int. Ed.* **2007**, *46*, 6293.
[4] M. Heckenroth, A. Neels, G. Garnier, M. Albrecht, *in preparation*.

Inorganic and Coordination Chemistry **196**

High-driving force dyads for charge transfer in the solid state

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Photoinduced charge separation in molecular systems is commonly observed in fluid solution where solvent reorganization can stabilize the newly formed charge-separated state. When such dyads are taken to the solid state, this is usually not possible any more and as a consequence, electron transfer often shuts down. We aim to overcome this problem with novel donor-bridge-acceptor molecules that provide unusually high driving forces for photoinduced charge separation.

Toward this end, (organic and coordination chemical) synthetic work is complemented by a fair amount of optical spectroscopic and electrochemical studies.

Inorganic and Coordination Chemistry **197**

Irreversibility of Disulfide to Thiyl Photolysis

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Thiyl radicals are a popular target for the research on ageing [1, 2]. Besides generation by pulse radiolysis and steady state γ-radiolyis [3, 4], photolysis of disulfides is often used. Thereby, one assumes, that the photolysis reaction leads to a clean fission of the disulfide bond and provides two thiyl radicals according to

$$RSSR + h\nu \quad 2\,RS^{\bullet} \qquad (1)$$

This reaction is assumed to be fully reversible under clean condition, i.e. if there is no further reaction partner:

$$2\,RS^{\bullet} \quad RSSR \qquad (2)$$

Analysis of this reaction by continuous photolysis, laser flash photolysis, HPLC and NMR techniques show, that there is a considerable formation of side products.

[1] C. Schöneich, *Experimental Gerontology* **1999**, *34*, 19
[2] P. Wardman, C. von Sonntag, *Methods Enzymol.* **1995**, *251*, 31
[3] S. Everett, C. Schöneich, J. H. Stewart, K.-D. Asmus, *J. Phys. Chem.* **1992**, *96*, 306
[4] L. Grierson, K. Hildenbrant, E. Bothe, *Int. J. Radiat. Biol.* **1992**, *62*, 265

Inorganic and Coordination Chemistry **198**

Remarkably high T1 relaxivities of the complex $[Ph_4\{Gd(DTTA)(H_2O)_2\}_3]^{3-}$

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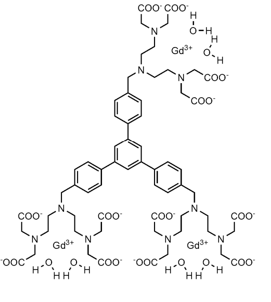
78035 Versailles, France

The compound 1,3,5-tris-(4-DTTA-phenyl)benzene, also called Ph_4DTTA_3, presenting three DTTA chelators linked together by four phenyl cycles, was designed as ligand for a gadolinium based T1 MRI contrast agent. The Gd(III) complex of this compound, $[Ph_4\{Gd(DTTA)(H_2O)_2\}_3]^{3-}$ showed remarkably high relaxivities for such a small molecule. The NMRD profiles present an important relaxation hump at magnetic fields between 0.5 T and 2 T, indicating a long rotational correlation time. Furthermore, the relaxivity, defined as increase of relaxation per mmol of gadolinium, is dependent on the concentration of the complex itself and on the concentration of phosphate buffer.[1] This behaviour suggests the formation of intermolecular structures, probably by □-interactions of the phenyl groups. The objective of this work is to demonstrate the formation of aggregates of $[Ph_4\{Gd(DTTA)(H_2O)_2\}_3]^{3-}$ in water and to characterize the size of these structures and the number of molecules involved.



[1] S. Laus, B. Sitharaman, E. Tóth, R.D. Bolskar, L. Helm, S. Asokan, M.S. Wong, L.J. Wilson, A.E. Merbach, *J. Am. Chem. Soc.* **2005**, *30*, 9368.

Inorganic and Coordination Chemistry **199**

A novel donor-acceptor dyad incorporating TTF and perylene-tetracarboxydiimide units

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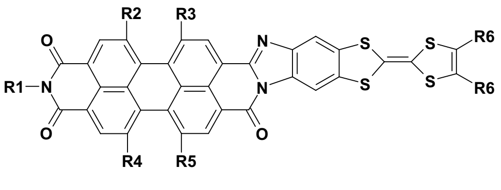
CH-3012 Bern, Switzerland

Perylene-tetracarboxydiimides (PDIs) are most fascinating molecular electron-accepting materials due to their chemical, thermal and photophysical stability, their strong absorption in the visible and their strong inherent luminescence. The idea to fuse PDI as an acceptor with TTF as the donor unit to form donor-acceptor (D-A) ensembles is not from far and several publications on this topic exist. However, so far TTF and PDI units have been combined using linkers and spacers, which is disadvantageous to intramolecular charge-transfer processes [1-3]. In the work at hand, the PDI and TTF moieties will be fused directly, constituting a D-A system expected to show a range of charge-transfer options upon photoexcitation, oxidation and reduction. Chemical and electronic behaviour and material properties of the target structure promise to be tunable (R1 to R6).



[1] X. Guo et Al., *Tetrahedron* **2003**, *59*, 4843.
[2] H. Manikowski, D. Wróbel, K. Lewandowska, A. Graja, *Synth. Met.* **2007**, *157*, 363.
[3] S. Leroy-Lhez et Al., *J. Org. Chem.* **2005**, *70*, 6313.

Inorganic and Coordination Chemistry **200**

Thermotropic Mesophases in Lanthanidomesogens: From Dimeric Cohesion to Rational Organization

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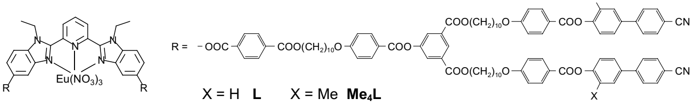
The tridendate dendrimer ligands **L** and **Me$_4$L** form complexes with lanthanides of formula $[Ln(\mathbf{L}/\mathbf{Me_4L})(NO_3)_3]$. The $[Ln(\mathbf{L}/\mathbf{Me_4L})(NO_3)_3] \leftrightarrows [Ln(\mathbf{L}/\mathbf{Me_4L})(NO_3)_3]_2$ dimerization process has been studied in CD_2Cl_2 solution by variable temperature ^1H NMR and thermodynamic parameters have been determined. It is shown that the methyl groups in **Me$_4$L** disfavour the formation of dimeric complexes.



Results obtained from solution studies are used to rationalize measurements (DSC, POM, SAXS) carried out on solid state samples. Complexes with **L** form smectic phases over large temperature ranges with clearing temperatures (SmA→I) around 186 - 200 °C. For the **Me$_4$L** complexes, the clearing temperatures are lower (144 - 159 °C) and nematic phases are observed in a narrow (5 – 14 °C) temperature domain. In line with the thermodynamic results collected in solution, the evolution of layered (SmA) organization toward nematic arrangements reflects the decreasing intermolecular interactions brought by the peripheral methyl groups.

[1] T. B. Jensen, E. Terazzi, B. Donnio, D. Guillon, C. Piguet *Chem. Commun.*, **2008**, 181-183.

Inorganic and Coordination Chemistry **201**

Inorganic anion sensor based on redox-active TTF derivatives

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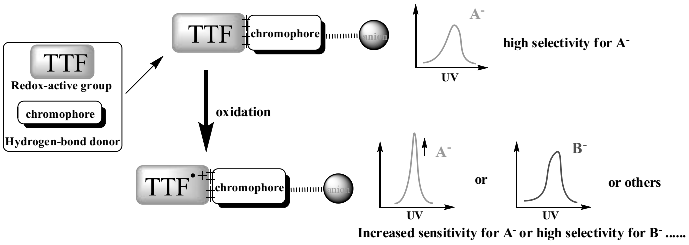
Inorganic anions play an important role in a wide range of industrial, environmental and medicinal processes.[1, 2] Numerous efforts have been devoted to the development of sensors to achieve high selectivity and sensitivity of anions. The common strategy is to introduce the functional groups, such as pyrrole, imidazolium, amide, *etc.*, which can form hydrogen bonds with anions.[2,3] Herein, we describe the synthesis and properties of some electro-optical sensors (Scheme 1), comprising a chromophore and a redox-active TTF (tetrathiafulvalene) unit to generate strong colorimetric and electrochemical signals.

Scheme 1



[1] T. Ghosh, B.G. Maiya, *J. Phys. Chem. A* **2004**, *108*, 11249.
[2] N.J. Singh, E.J. Jun, K. Chellappan, D. Thangadurai, R.P. Chandran, I.-C. Hwang, J. Yoon, K.S. Kim, *Org. Lett.* **2007**, *9*, 485.
[3] P. Anzenbacher, Jr., M.A. Palacios, K. Jursíková, M. Marquez, *Org. Lett.* **2005**, *7*, 5027.

Inorganic and Coordination Chemistry **203**

NMR Investigation of an Oligonucleotide Containing Metal-Mediated Base Pairs

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Metal-modified oligonucleotides are excellent candidates as molecular building blocks in the bottom-up approach for nanodevices according to their self-assembly properties and their repetitive and well-defined structural features. Thus, modified nucleobases are a powerful tool to insert and subsequently array metal ions in a predictable manner into DNA. Such precise control will be necessary for potential applications as nanomagnets, as self-assembling molecular wires or as catalysts in chemical reactions.

Here a 17 nt long oligonucleotide was synthesized containing three imidazole (Im) moieties as nucleobase surrogates. Melting temperature analysis suggests a structure conversion from hairpin to double helix upon addition of Ag(I) ions indicating that Im-Ag^+-Im base pairs were formed.[1] For a detailed understanding of rearrangement of the oligonucleotide in presence of Ag(I) ions and for further characterization of the metal-mediated base pair, several NMR measurements were performed, leading to the three-dimensional structures of the hairpin and the duplex. Determination of the hydrodynamic radii using DLS (Dynamic Light Scattering) and DOSY (NMR) experiments confirm the hairpin structure in absence, and accordingly the duplex formation in presence of Ag(I) ions.

Financial support by the European ERAnet-Chemistry, the Swiss National Science Foundation (20EC21-112708 and *SNF-Förderungsprofessur* PP002-114759 to R.K.O.S.) and the *DFG* (JM1750/2-1 and Emmy Noether programme JM1750/1-3, J.M.) is gratefully acknowledged.

[1] J. Müller D. Böhme, P. Lax, M. Morell Cerdà, M. Roitzsch, *Chem. Eur. J.* **2005**, *11*, 6246-6253.

Inorganic and Coordination Chemistry **202**

Copper-based MOF for the Facile Ring-Opening of Epoxides

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Switzerland

Metal-organic frameworks (MOFs) have generated great interest in the past decade as new promising materials for gas storage, separation, and heterogeneous catalysis. Herein, we developed a simplified and facile route for the synthesis of the flexible Cu-MOF [1] (Figure 1) from $Cu(BF_4)_2$ and 4,4′-bipyridine in aqueous ethanol. The crystalline Cu-MOF is a highly active and selective Lewis acid catalyst in the ring-opening reactions of epoxides with alcohols and aniline under ambient, solvent-free conditions at room temperature (Figure 2) [2]. The catalyst Cu-MOF was found truly heterogeneous and recyclable without any loss of activity.

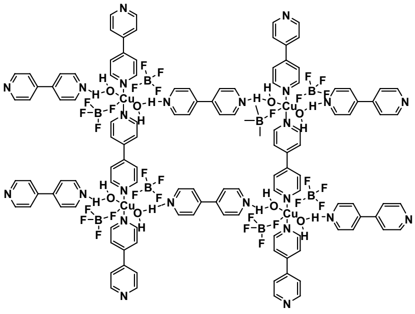

Figure 1.

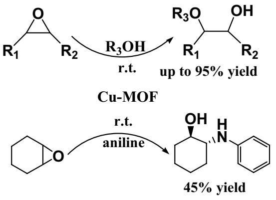

Figure 2.

[1] A.J. Blake, S.J. Hill, P. Hubberstey, W.S. Li, *J. Chem. Soc.-Dalton Trans.* **1997**, 1111.
[2] D.M. Jiang, T. Mallat, F. Krumeich, A. Baiker, *J. Catal.* (submitted)

Inorganic and Coordination Chemistry **204**

Synthesis and characterization of mesoporous oxides

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In the past, heterogeneous catalysts were optimized based on their activity. Modern catalysts have to be both very active and selective to reduce their environmental impact and to design new and better catalysts, the structure-performance relationships have to be known. Because of the heterogeneity of the catalyst structures, however, detailed analysis and understanding are often not possible. In supported metal catalysts in particular the effect of the oxide support remains disputed. Generally, the structure of oxide supports is ill-defined [1]. Goal of this work is therefore to synthesize oxide supports that have very well-defined structures and investigate their role and structure under catalytically relevant conditions. Atomic layer deposition [2] is applied to provide mono- and multi- surface layers of different metal oxides such as alumina, titania and zinc oxide, on a backbone of regular, preformed mesoporous silicas such as SBA-15. Compared to conventionally synthesized supports, these supports exhibit major advantages. Their regular mesoporous structure, which is determined by the silica backbone guarantees optimal diffusion properties. The high surface areas allow the deposition of larger amounts of active metal on a per gram basis. Because of the presence of the metal oxide as a surface layer, only spectroscopic techniques like in situ x-ray absorption spectroscopy can be applied, which only gives limited information about the surface of bulk metal oxides. The mesoporous oxides will be used as support for metal catalysts and their role in chemoselective hydrogenation with selected substrates will be investigated.

[1] M. K. Oudenhuijzen, J. A. van Bokhoven, D. E. Ramaker, D. C. Koningsberger, *J. Phys. Chem. B*, **2004**, *108,* 20247.
[2] M. J. Biercuk, D. J. Monsma, C. M. Marcus, J. S. Becker, R. G. Gordon, *Appl. Phys. Lett.*, **2003**, *83*, 2405.

Inorganic and Coordination Chemistry **205**

Peroxynitrate Formation During Peroxynitrite Decomposition

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Peroxynitrous acid is an unstable peracid which is known to isomerize in a first-order reaction to nitrate with a rate constant of 1.2 s^{-1}. A kinetic anomaly was observed together with dioxygen and nitrite formation at pH= 7-8, just above the pK_a [1]. Since other peracids do undergo bimolecular decomposition regularly [2], we suspected that such a reaction could compete with the unique isomerization. An intermediate was never characterized for the other peracids, it is thought to be too short-lived [3].

We were able to detect the electronic spectrum of peroxynitrate during peroxynitrite decomposition with a quenching method. The peroxynitrate quantities formed were determined by conversion of iodide to iodine after complete elimination of peroxynitrite. The relative yields depend on initial peroxynitrite concentration, as expected for a bimolecular process competing with a monomolecular one. The absolute peroxynitrate yields were more than two times higher than expected from the radical decomposition mechanisms favored by many biochemists [4], providing the second confirmation of a bimolecular interaction. Finally, we could satisfactorily simulate the kinetic anomalies observed earlier.

[1] R. Kissner, T. Nauser, P. Bugnon, P.G. Lye and W.H. Koppenol, *Chem. Res. Toxicol.*, **1997**, *10*, 1285.
[2] J.F. Goodman, P. Robson and E.R. Wilson, *Trans. Faraday Soc.*, **1962**, 1846.
[3] D.F. Evans and M.W. Upton, *J. Chem. Soc. Dalton Trans.*, **1985**, 1151.
[4] G. Merényi and J. Lind, *Chem. Res. Toxicol.*, **1998**, *11*, 243.

Inorganic and Coordination Chemistry **206**

NO autoxidation in aqueous solution studied by electron spin resonance spectroscopy

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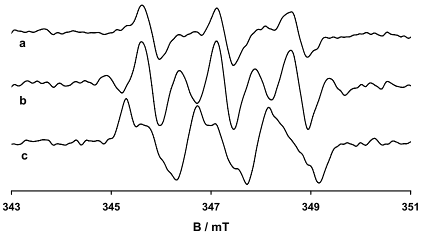
The mechanism of $NO^\bullet$ autoxidation has been proposed via nitric oxide dimer $(NO)_2$ or nitrosyldioxyl radical ($ONOO^\bullet$). We found evidence for $ONOO^\bullet$ being the intermediate in the gas phase by ESR spectroscopy.

Based on the gas phase result, we estimated the steady-state concentration of $ONOO^\bullet$ to be around 10^{-14} M for the autoxidation in aqueous solution, of which the overall rate is also well-known. We show that a spin trap forms different products if treated with a fresh $NO^\bullet$/air mixture compared to the action of the final autoxidation product, $NO_2^\bullet$. The reaction product with $NO_2^\bullet$ in aqueous solution does not correspond to the one obtained in benzene [1]. Further, we present results of the direct EPR detection attempt on $ONOO^\bullet$.



EPR spectra of 20 mM 5,5-Dimethylpyrroline-N-oxide exposed for 1 h to $NO^\bullet$/air (a), air (b) and $NO_2^\bullet$/air (c). 100 mM acetate buffer, pH=5.

[1] P. Astolfi, L. Greci, M. Panagiotaki, *Free Rad. Res.*, **2005**, *39*, 137.

Inorganic and Coordination Chemistry **207**

Modified Metal-Organic Frameworks – Synthesis, Properties and Potential in Catalysis

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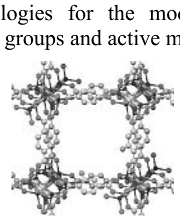
Due to their microporous structure, metal-organic frameworks have become an interesting and promising class of materials for applications in heterogeneous catalysis.[1] Based on MOF-5 and the corresponding IRMOF series[2], we present new methodologies for the modification of metal-organic frameworks with functional groups and active metal centers.



In general, such modification of MOFs with catalytically active groups strongly influences the physical and chemical properties. Therefore special attention is given to the characterization of the resulting catalyst materials under catalytic conditions.

The studies include investigations on the thermal stability of such materials under inert and oxidizing atmosphere as well as the stability in common solvents and supercritical CO_2. Based on these results, we were able to disclose the scope and limitations of our materials for possible catalytic applications. The modified materials could be utilized in gas-phase oxidation reactions as well as in catalytic processes in supercritical CO_2.

[1] U. Mueller, M. Schubert, F. Teich, H. Puetter, K. Schierle-Arndt, *J. Mater. Chem.* **2006**, *16*, 626.
[2] M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O'Keeffe, O.M. Yaghi, *Science* **2002**, *295*, 469.

Inorganic and Coordination Chemistry **208**

Gold(I) phosphine derivatives of 4,4'-dialkynyl substituted 2,2'-bipyridine

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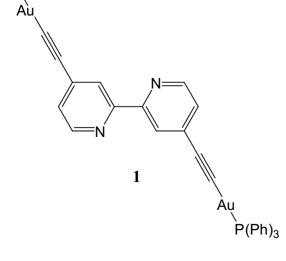
Gold(I) phosphine derivatives have the potential to be luminescent and have interesting optical properties [1]. Ligand **1** can be synthesized from 4,4'-dialkynyl substituted 2,2'-bipyridine and triphenylphosphine gold(I) chloride. This compound had been structurally characterized, and related compounds will also be described and their absorption and emissive properties discussed. We plan to complex this ligand with transition metals like ruthenium(II) and iron(II) in order to investigate the effects of coordination on their electronic spectroscopic properties.



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[1] M.Bardaji, A.Laguna, J.Vicente, P.G.Jones, *Inorg. Chem.*, **2001**, *40*, 2675

Inorganic and Coordination Chemistry **209**

Outersphere Coordination of $[Co(NH_3)_6]^{3+}$ to Domain 6 of a Group II Intron Ribozyme

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Group II intron ribozymes are large RNA molecules that catalyze their own removal from precursor mRNA. For folding into the active three-dimensional structure, as well as for catalysis, the molecular machines require Mg^{2+}.[1] The 2'-OH group of a highly conserved adenosine within domain 6 (D6), i. e. the branch point, acts as the nucleophile in the first step of the self splicing mechanism. The NMR solution structure of a catalytically active 27 nucleotide long D6 construct (D6-27) was recently elucidated[2] and its intrinsic Mg^{2+} binding properties were determined.[3]

Here we investigate possible outersphere coordination of $[Mg(H_2O)_6]^{2+}$ in the branch point region of domain 6. Cobalt(III) hexammine is commonly used as a mimic for the spectroscopically silent $[Mg(H_2O)_6]^{2+}$ and can even show NOE contacts with RNA protons in favorable cases. Chemical shift mapping experiments show binding of $[Co(NH_3)_6]^{3+}$ to the branch-point region. By performing NOESY titration experiments in H_2O and D_2O observing the chemical shift changes at the RNA as well as direct NOE contacts between the ammine protons of $[Co(NH_3)_6]^{3+}$ and RNA protons the exact binding pattern of $[Co(NH_3)_6]^{3+}$ to domain 6 is being elucidated thereby giving information about possible outersphere coordination of $[Mg(H_2O)_6]^{2+}$.

Financial support by the Swiss National Science Foundation (*SNF-Förderungsprofessur* PP002-114759 to R.K.O.S.) is gratefully acknowledged.

[1] R. K. O. Sigel, *Eur. J. Inorg. Chem.*, **2005**, *12*, 2281-2292.
[2] M. C. Erat, O. Zerbe, T. Fox, R. K. O. Sigel, *ChemBioChem*, **2007**, *8*, 306-314.
[3] M. C. Erat, Roland K. O. Sigel, *Inorg. Chem.*, **2007**, *46*, 11224-11234.

Inorganic and Coordination Chemistry **210**

Novel ReO_3-related aluminum tungsten oxides

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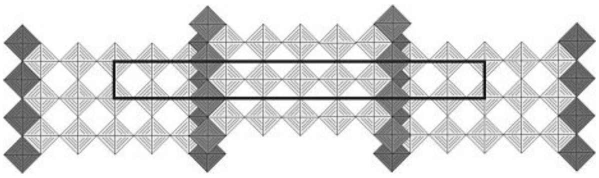
2. Institute of Inorganic Chemistry, University of Zurich, 8057 Zurich

A series of new tetragonal aluminum tungsten oxides with the general formula $Al_4W_{2n}O_{6n+2}$ (n = 4, 5, 6, and 7) was found and structurally characterized by electron diffraction, HRTEM and HAADF-STEM [1]. A structural model for $Al_4W_{10}O_{32}$ (*I*4/*mmm*; $a \approx 0.375$, $c \approx 3.95$ nm) consists of slabs of [5 x ∞ x ∞] corner-sharing WO_6 octahedra that are connected via edge-sharing to AlO_6 octahedra. Simulated HRTEM images agree well with the experimental ones and therefore support the proposed structural model. The connection between adjacent slabs of WO_3 via AlO_6 octahedra can be regarded as a novel variant of crystallographic shear operation for ReO_3-type structures. Frequently, the investigated crystallites show stacking faults and an intergrowth of the different phases.



[1] F. Krumeich, G.R. Patzke, *Microsc. Microanal.* **2007**, *13 Suppl. 3*, 366.

Inorganic and Coordination Chemistry **211**

Electro- and Photoelectro-chemical deposition of Thiophene modified $\{Ru(terpy)_2\}^{2+}$ Complexes

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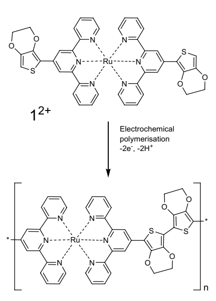
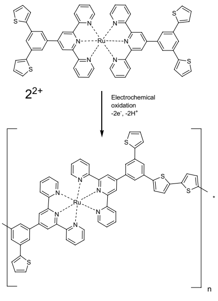
Thienyl substituted 2,2':6',2''-terpyridine metal complexes are known to electrochemically deposit on electrodes and form polymers.[1] Two new bis-terpyridine ruthenium complexes (**1**$^{2+}$ and **2**$^{2+}$) were electrochemically deposited on glassy carbon electrodes and FTO (conducting layer of transparent F-doped SnO_2) glass. The complexes were also photo-electrochemically oxidized by a dye sensitized TiO_2 surface. Scanning electrochemical microscopy (SECM) was used to probe some of the redox chemistry.[2]





[1] J. Hjelm, R. W. Handel, Hagfeldt A., Constable E. C., Housecroft C.E., Forster R. J., *J. Phys. Chem. B*, **2003**, 107, 10431-10439.
[2] D. Mandler, P. R. Unwin, *J. Phys. Chem. B*, **2003**, 107, 407.

Inorganic and Coordination Chemistry **212**

Hydrogen storage – continuous high pressure hydrogen generation

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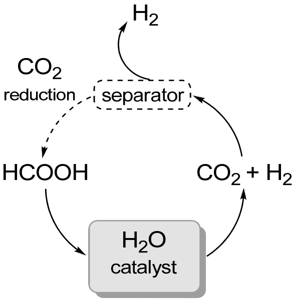
New potential in the use of formic acid as a hydrogen storage material has been demonstrated via the development of a homogeneous catalytic system using ruthenium based water soluble catalysts to selectively decompose HCOOH into H_2 and CO_2. Continuous generation of H_2 of very high purity, over a wide range of pressures and under mild conditions was achieved.

Main advantages

- No need for transport and storage of H_2 gas under pressure (or low temperature liquid hydrogen)
- H_2 generation at any wanted pressure (from 0.5 atm to of 600 atm)
- H_2 production under mild conditions (25-120°C) at very high rate
- The generated hydrogen is free from CO traces (CO < 3 ppm)
- The generated H_2 is easily separated (the carbon dioxide can be captured and recycled)
- The H_2 generator does not require electricity or any particular conditions
- This hydrogen fuel is very economic and ecologic



Swiss National Science Foundation and EPFL are thanked for financial support.

[1] C. Fellay, P. J. Dyson, G. Laurenczy, International patent appl., October **2007**
[2] C. Fellay, P. J. Dyson, G. Laurenczy, *Angew. Chem. Int. Ed.* **2008**, *47,* 3966

Inorganic and Coordination Chemistry **213**

Nonaqueous Sol-Gel Synthesis of Nanocrystalline Zinc Oxide

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Zurich, Switzerland

Coming along with the growing interest in nanomaterials as a result of their unique and fascinating properties, synthetic chemist were faced with the problem of developing new strategies for the synthesis of monodispersed particles with good control over the final size and shape. One solution in the field of metal oxide nanoparticles are nonaqueous sol-gel processes in which a molecular precursor is transformed into a metal oxide in an organic solvent. These synthesis strategies provide several advantages, like robust synthesis parameters and high crystallinity of the product even at low temperature and therefore became a well-known alternative to aqueous routes. Although the reaction system itself is quite simple, it offers a great potential to tailor the final particle characteristics like surface chemistry and morphology [1].

In the current work we will present the results obtained within the syntheses of ZnO nanoparticles, which are of great technological relevance, via nonaqueous sol-gel synthesis by varying the temperature and the solvent.

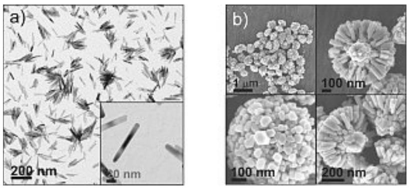

Figure 1: Zinc oxide nanoparticles obtained via nonaqueous sol-gel synthesis in a) benzyl alcohol and b) ^{t}butyl benzyl alcohol

[1] M. Niederberger, G. Garnweitner, J. Buha, J. Polleux, J. Ba, N. Pinna, *J. Sol-Gel Sci. Technol.*, **2006**, *40*, 259.

Inorganic and Coordination Chemistry **214**

Synthesis of New Photochromic Spin Crossover Complexes

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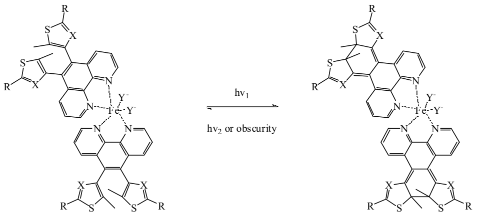
Our group is active in the synthesis of photochromic dithienyl-containing 1,10-phenanthroline ligands. Organic dithienylethene derivatives have been extensively studied because of their potential applications in the field of photochromic and photonic devices. Phenanthroline complexes of Iron(II) on the other hand were reported to undergo a temperature dependent spin crossover process. In this context it is highly interesting to use photoactive 1,10-phenanthroline ligands to build up Iron(II) complexes. Assuming that the photoactive opening and closing process of the ligand system changes the ligand field properties sufficiently, we should obtain a system that undergoes spin crossover upon irradiation with light at room temperature. This concept has already been studied by a few other groups and was called ligand-driven light-induced spin change LD-LISC.



X=C, N,..
R=CH_3, Phenyl, EWG, ERG

[1] Irie, M. *Chem. Rev.*, **2000**, *100,* 1685-1716.
[2] Kuhni, J.; Adamo, V.; Belser, P. *Chimia*, **2006,** *60,* 207-211.
[3] Kolb, J. S.; Thomson, M. D.; Novosel, M.; Senechal-David, K.; Riviere, E.; Boillot, M.-L.; Roskos, H. G. *Comptes Rendus Chimie*, **2007**, *10,* 125-136.

Inorganic and Coordination Chemistry **215**

Encapsulation of Functionalised Aromatic Molecules in Hexanuclear Arene Ruthenium Cages

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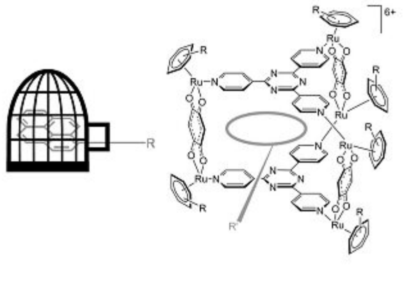
Institut de Chimie, Université de Neuchâtel, Case postale 158, 2009
Neuchâtel, Switzerland

Cationic triangular metallo-prisms, $[Ru_6(arene)_6(tpt)_2(bzq)_3]^{6+}$, incorporating arene ruthenium building blocks, bridged by dihydroxy-1,4-benzoquinonato (bzq) ligands, and connected by two 2,4,6-tris(pyridin-4-yl)-1,3,5-triazine (tpt) subunits allow the permanent inclusion of large aromatic molecules such as pyrene, triphenylene and coronene, or the inclusion of functionalised aromatic molecules in which the aromatic part is encapsulated, while the functional group is hanging out of the cage.[1] These carceplex systems can potentially find applications in molecular recognition, catalysis, or being used as drug delivery containers.



[1] J. Mattsson, P. Govindaswamy, J. Furrer, Y. Sei, K. Yamaguchi, G. Süss-Fink, B. Therrien, submitted.

Inorganic and Coordination Chemistry **216**

Bimetallic Redox Switches Comprising N-Heterocyclic Carbene Spacers

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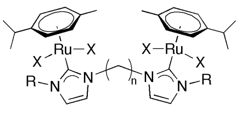
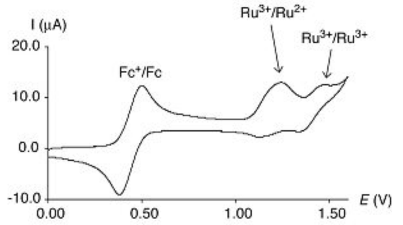
Molecular switches represent an attractive class of functional entities [1]. Multistage switching may be accessible by connecting two transition metal based active sites with a spacer that allows for a certain degree of electronic communication [2].



n = 1-4
R = *n*Bu
X = Cl, Br



We will present our progress in using bifunctional NHC ligands as spacers in binuclear Ru(II) complexes. Specifically, we will focus on the quality of different carbene spacers and spectator ligands in stabilizing mixed-valent species, which has been probed by spectroscopic and electrochemical analyses of the bimetallic systems. Based on the electrochemical measurements, comproportionation constants (K_c) of the mixed-valent species have been determined. These results allow for proposing a mechanism for the electron coupling process.

[1] W. Kaim, G. K. Lahiri, *Angew. Chem. Int. Ed.* **2007**, *46*, 1778.
[2] B. S. Brunschwig, C. Creutz, N. Sutin, *Chem. Soc. Rev.* **2002**, *31*, 168.

Inorganic and Coordination Chemistry **217**

Original Complexation of Silver Ions with Amino Acid

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Amino acids contain many oxygen and nitrogen atoms giving multiple possibilities for a metal ion to be coordinated. We selected silver which has, beside its weak coordination requirements both in term of coordination number and geometry, a biologically interesting activity. Its antibacterial and antifungal properties have been studied, among others, in a histidine complex previously [1]. We show here that silver ions are coordinated in different ways, depending on the reaction conditions. Silver ions may furthermore bind to biomolecules of various size, starting from single amino acids to larger peptides, for which the properties were studied recently [2], or to more complex antibiotics like the vancomycin, where the purpose is to be used as coating on implant materials [3].

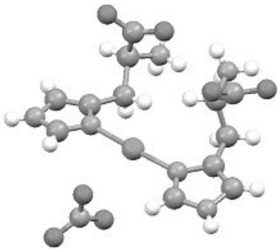

Fig.1: Structure of histidine and silver nitrate

[1] K. Nomiya, S. Takahashi, R. Noguchi, S. Nemoto, T. Takayama & M. Oda, *Inorg. Chem.* **2000**, *39*, 3301-3311.
[2] Kirsten Belser, *Thesis* **2008.**
[3] P. Brunetto & K. M. Fromm, *Chimia* **2008**, 62, 4, 249-252.

Inorganic and Coordination Chemistry **219**

PGSE NMR Diffusion and Overhauser Studies on a Variety of Salts: an Overview of Ion Pairing in Dichloromethane

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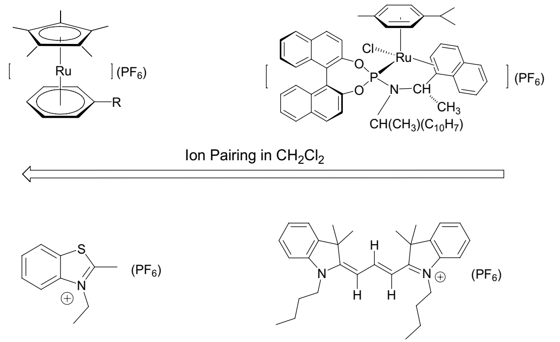
Frequently, the nature of the anion in Transition metal salts is ignored or the anion is considered to be relatively "innocent". However, a number of reports in the recent literature suggest that the choice of the anion can be important, both in terms of structure and reactivity [1].



PGSE diffusion and ^{1}H,^{19}F Overhauser studies on a Variety of Transition Metal, Inorganic and Organic (PF_6^-) Salts are reported. These solution NMR results show that the charge distribution and the ability of the anion to approach the positively charged positions are the determining factors in deciding the amount of Ion Pairing.

[1] Pregosin, P.S; Kumar, P.G.A; Fernandez, I. *Chem. Revs* **2005***, 105*, 2977.

Inorganic and Coordination Chemistry **218**

Coordination Cages of Rhodium and Iridium as Exoreceptors for Alkali Metal Ions

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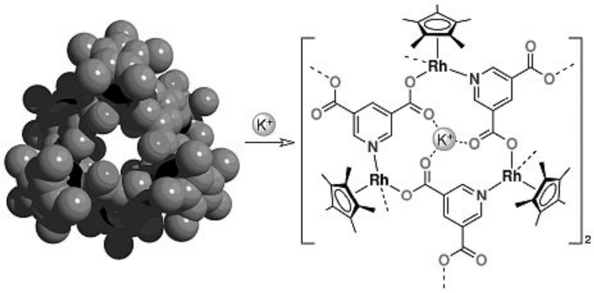
Hexanuclear coordination cages of the formula $[(C_5Me_4R)M(C_7H_3NO_4)]_6$ (M = Rh, Ir; R = Me, H) were obtained by step-wise reaction of $[(C_5Me_4R)MCl_2]_2$ with first AgOAc and then pyridine-3,5-dicarboxylic acid. Crystallographic analyses show that the cages adopt a distorted trigonal anti-prismatic geometry with the pyridine-3,5-dicarboxylates functioning as dianionic, bridging ligands, each of which connects three different $(C_5Me_4R)M$ fragments.



The cages act as exoreceptors for the large alkali metals K$^+$ and Cs$^+$ but show low affinity for Na$^+$. Crystallographic and NMR spectroscopic analyses indicate that two metal ions can be coordinated to the surface of the cages. The respective binding sites are comprised of three carbonyl O-atoms from the bridging pyridine-3,5-dicarboxylate ligand [1].

[1] S. Mirtschin, E. Krasniqi, R. Scopelliti, K. Severin, *Inorg. Chem*. **2008**, in press.

Inorganic and Coordination Chemistry **220**

Lanthanide/ruthenium-based metallostar: characterization, relaxivity and luminescence

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[2] Laboratory of Lanthanide Supramolecular Chemistry, Ecole Polytechnique Fédérale de Lausanne, ISIC, BCH, 1015 Lausanne, Switzerland
[3] Laboratoire de Physico-chimie des Polymères et des Milieux Dispersés, UPMC-ESPCI-CNRS UMR7615, 10 Rue Vauquelin, 75231 Paris Cedex 05, France
[4] Laboratoire de Chimie Organo-Minérale, LC3 du CNRS, Institut de Chimie, Université Louis Pasteur, 4 rue Blaise Pascal, 67070, Strasbourg Cedex, France

The growing interest in magnetic resonance imaging (MRI) requires the development of novel multifunctional contrast agents with high relaxivity (r_1) and possible use in other detection techniques. The first so-called Metallostar, composed of Fe(III) surrounded by three $[(bipyDTTA_2Gd_2)(H_2O)_4]^{2-}$ units has been synthesized and characterized by Livramento et al. in 2005 [1]. Here, we present a ruthenium–based Metallostar, i.e. $\{Ru[Ln_2bpy\text{-}DTTA_2(H_2O)_4]_3\}^{4-}$ with Ln = Y^{3+}, Gd^{3+}, Eu^{3+}, see Chart 1; characterized by different spectroscopic techniques, with application potential as a multi imaging system (MRI + luminescence).

The optical spectroscopic properties of $\{Ru[Eu_2bpy\text{-}DTTA_2(H_2O)_4]_3\}^{4-}$ are studied by means of UV/Vis absorption as well as steady-state and time-resolved luminescence spectroscopy. Aqueous solutions of the complex display sensitized europium luminescence upon visible excitation at 450 nm of the tris(2,2'bipyridyl)ruthenium(II) unit.

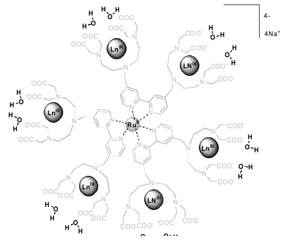

Chart 1

[1] Livramento, J. B.; Toth, E.; Sour, A.; Borel, A.; Merbach, A. E.; Ruloff, R. *Angew.Chem.Int.Ed.*, 2005, **44**, 1480-1484.

Inorganic and Coordination Chemistry **221**

CO_2 capture from atmospheric air via consecutive CaO-carbonation and $CaCO_3$-calcination cycles in a fluidized-bed solar reactor

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A thermochemical cyclic process and associated reactor is proposed for the continuous removal of CO_2 from ambient air via consecutive CaO-carbonation and $CaCO_3$-calcination steps using concentrated solar energy as the source of high-temperature process heat. The thermodynamics of the cycle were examined and the reaction kinetics of both steps were determined by thermogravimetry [1,2]. A fluidized-bed solar reactor is applied to accomplish both steps, with reacting particles directly exposed to high-flux solar irradiation. Five consecutive cycles were performed, yielding complete removal of CO_2 from a continuous air flow containing 500 ppm of CO_2 within a residence time of 1.3 s during each carbonation step, and subsequent complete release of CO_2 and regeneration of the CaO reacting particles during the calcination step.

[1] V. Nikulshina, D. Hirsch, M. Mazzotti, A. Steinfeld. *Energy* **2006,** 31, 1379.
[2] V. Nikulshina, E. Gálvez, A. Steinfeld. *Chem. Eng. J* **2007,** 129, 75.

Inorganic and Coordination Chemistry **223**

Rh and Ir Phosphoramidite Complexes in Cyclopropanation

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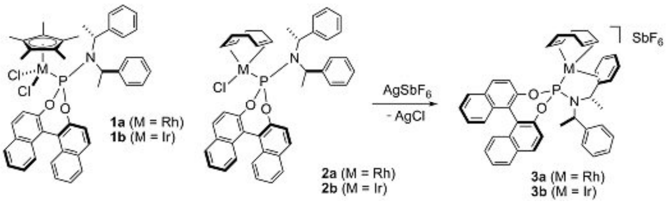
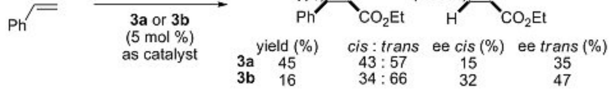
Chiral phosphoramidite (P*) complexes have found increasing application in asymmetric catalysis. Our group has recently reported ruthenium complexes that display an η^2-interaction between the metal and one aryl group of the amine moiety of the binaphthol-based phosphoramidite [1]. These half-sandwich complexes catalyze the cyclopropanation of olefins with moderate efficiency [2]. Therefore, we decided to prepare the Rh(III) (**1a**) and Ir(III) (**1b**) analogues and test them in catalysis. Chloride abstraction with $AgSbF_6$ from **1a** and **1b** gives unstable P,C-chelate complexes.



Upon chloride abstraction, the Rh(I) and Ir(I) analogues [RhCl(COD)(P*)] (**2a**) and [IrCl(COD)(P*)] (**2b**) give the stable P,C-bidentate species **3a** and **3b**, respectively. Preliminary tests in cyclopropanation show modest diastereo- and enantio-selectivity:



	yield (%)	*cis* : *trans*	ee *cis* (%)	ee *trans* (%)
3a	45	43 : 57	15	35
3b	16	34 : 66	32	47

[1] D. Huber, P. S. Pregosin, A. Mezzetti, *Organometallics* **2005**, *24*, 5223.
[2] D. Huber, A. Mezzetti, *Tetrahedron Asymmetry*, **2004**, *15*, 2193.

Inorganic and Coordination Chemistry **222**

Solvent effects and organic reaction pathways in non-aqueous sol-gel processes

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Within non-aqueous sol-gel processes [1] for the syntheses of crystalline metal oxide nanoparticles, the organic component plays an important role. It not only serves as a solvent but also provides the oxygen for the oxide formation. Furthermore the organic solvent respectively the organic reaction products strongly influence the final morphology, size, shape, crystal structure and assembly behavior of the particles [2]. The investigation of organic reaction pathways can establish a better understanding on a molecular level and therefore enables us to intentionally influence and control the particle formation.

In the following work, we will present a short overview of non-aqueous sol-gel processes. In addition the effects of several benzyl alcohol derivatives on the syntheses of transition metal oxide particles and the influence of different precursors will be shown.

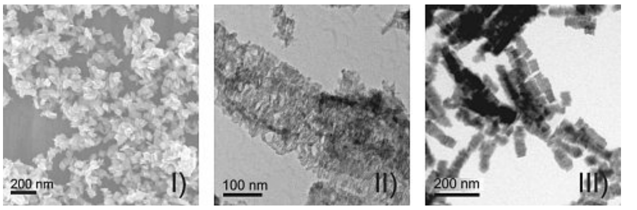

Figure 1: Tungsten oxide particles synthesized in I) benzyl alcohol, II) ^{t}butyl benzyl alcohol and III) fluor benzyl alcohol with tungsten hexachloride as a precursor.

[1] M. Niederberger, G. Garnweitner, *Chem. Eur. J.* **2006**, *12*, 7282.
[2] G. Garnweitner, M. Niederberger, *J .Mater. Chem.* **2008**, *18*, 1171.

Inorganic and Coordination Chemistry **224**

New Nanocomposites with Oxidic Materials

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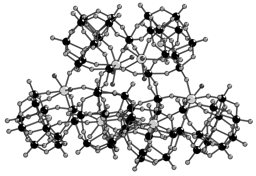
The development of organic-inorganic nanocomposites is a challenging area of synthetic inorganic chemistry to generate compounds with new properties and high application potentials[1]. Thus, we focus on the synthesis and characterization of new organic and inorganic building blocks, such as nanostructured transition metal oxides[2], polyoxometalates (POMs)[3] and polymers. Recently, we have brought forward new types of lanthanide spin cluster polyoxometalates, especially of the $[Ln_6As_6W_{63}O_{226}(H_2O)_{10}]^{38-}$ type (Ln = Eu, Gd and Tb) with interesting magnetic and structural properties:



Furthermore, we have successfully incorporated POMs into polyaniline and the magnetic and optoelectronic properties of the emerging nanocomposites are under investigation. Finally, we cross the border between natural and synthetic products through the combination of highly porous natural chitin skeletons with inorganic nanoparticles.

[1] G. Kickelbick, *Prog. Polym. Sci.* **2003**, *28*, 83.
[2] R. Kiebach, N. Pienack, W. Bensch, J.-D. Grunwaldt, A. Michailovski, A. Baiker, T. Fox, Y. Zhou, G. R. Patzke, *Chem. Mater.* **2008**, *20*, 3022.
[3] A. Michailovski, H. Rüegger, D. Sheptyakov, G. R. Patzke, *Inorg. Chem.* **2006**, *45*, 5641.

Inorganic and Coordination Chemistry **225**

Mercury-Modified Ribonucleic Acids as Potential Molecular Wires

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Metal-modified nucleic acids have become increasingly important as they provide scaffolds, which can potentially be used for molecular wires. A DNA duplex with mismatched T-T pairs can bind Hg^{2+} by forming T-Hg^{2+}-T base pairs, which are as stable as a Watson-Crick base pair.[1] We are interested in the formation of an analogous array of Hg^{2+} by using RNA instead.[2] *In vitro* transcription of the required single-stranded RNA has the potential advantage of providing high yields. We could show that T7 RNA polymerase can incorporate two to twenty consecutive uracil residues into RNA. In the presence of Hg^{2+}, a structural rearrangement from hairpin to regular duplex by forming Hg^{2+}-mediated base pairs takes place for one of the sequences under investigation. This was verified by several techniques, including NMR, DLS, UV and CD spectroscopy.[2] Ongoing investigations now focus on the incorporation of continuous stretches of the chemically more stable thymine into RNA. For this purpose we are using the T7 RNA polymerase mutant Y639F capable of not discriminating between deoxy-ribose and ribose sugars.[3] Indeed we were able to construct RNAs con-taining poly T-sequences, which are now subject to structural studies.

Financial support by the European ERAnet-Chemistry, the Swiss National Science Foundation (20EC21-112708 and *SNF-Förderungsprofessur* PP002-114759 to R.K.O.S.) and the *DFG* (JM1750/2-1 and Emmy Noether programme JM1750/1-3 to J.M.) is gratefully acknowledged.

[1] Y. Tanaka, S. Oda, H. Yamaguchi, Y. Kondo, C. Kojima, A. Ono, *J. Am. Chem. Soc.* **2007**, 129 244-245.
[2] S. Johannsen, S. Paulus, N. Düpre, J. Müller, R.K.O. Sigel, *J. Inorg. Biochem.* **2008**, 102, 1141-51.
[3] R. Sousa, R. Padilla, *EMBO J.* **1995**, 14, 4609-21.

Inorganic and Coordination Chemistry **226**

E_c-1 from wheat: A metallothionein featuring unique metal-binding domains

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Eva Freisinger[a]

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[b]European Mol. Biol. Laboratory, outstation Hamburg at Deutsches Elektronen-Synchrotron, Notkestrasse 85, 22603 Hamburg, Germany

Metallothioneins (MT) are small cysteine-rich proteins with high affinity for metal ions like Zn^{II} and Cu^{I}. *Triticum aestivum* (wheat) **e**arly **c**ysteine labeled protein (E_c-1) was the first MT reported in higher plants.[1] With a total of 81 amino acids, including 17 Cys that are grouped in three regions of the amino acid sequence, E_c-1 has been shown to bind six divalent metal ions (M^{II}) in two separated metal-binding domains.[2] The N-terminal domain, or γ-domain,[3] binds two M^{II} ions presumably via six Cys residues resulting in a metal-thiolate cluster with the stoichiometry $M^{II}_2Cys_6$, which has never been reported before for MTs. The C-terminal part of E_c-1 contains eleven Cys and two His residues and coordinates four M^{II} ions. Recent work from our lab has focused on the study of the separated domains of E_c-1. Results from various spectroscopic investigations substantiate our previous findings and demonstrate the relative independence of the protein domains with respect to each other. In addition, we investigated the lability of the Zn^{II} ions bound to E_c-1 with a mass spectrometry.

[1] Lane, B. G., Kajioka, R. and T. D. Kennedy. *Biochem. Cell Biol.* **1987**, 65, 1001.
[2] Peroza, E. A. and E. Freisinger, *J. Biol. Inorg. Chem.* **2007**, *12*, 377
[3] Peroza, E. A., Al-Kaabi, A., Meyer-Klaucke, W., and E. Freisinger, *to be submitted.*

Support from the Swiss National Science Foundation is gratefully acknowledged: SNF grant 200020-113728/1 and SNF Förderungsprofessur PP002-119106/1 to E.F.

Inorganic and Coordination Chemistry **227**

Synthesis and catalytic properties of palladium complexes containing pyridyl and pyridylidene ligands

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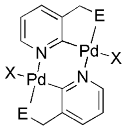
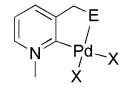
Palladium complexes containing an N-heterocyclic carbene (NHC) ligand are highly active catalysts for cross-coupling reactions.[1] Generally, the NHC ligand of these complexes is derived from imidazolium salts. In the last few years, carbene ligands derived from pyridinium salts (pyridylidenes) have been developed as new types of NHC ligands.[2] Bercaw and coworkers showed that such pyridylidenes are stronger σ-donors and π-acceptors than classical imidazolylidene,[3] which may be useful for improving the catalytic activity of the coordinated metal center.

We synthesized different palladium complexes containing pyridyl (**1**) and pyridylidene (**2**) ligands with a chelating donor group E for supporting the metal-carbon bond and for tuning the properties of the metal center.



(**1**)



(**2**)

E = SMe
SPh
NMe2

We will present structural features of these complexes in the solid state and in solution and will evaluate the influence of the bonding mode (pyridyl vs. pyridylidene) on the catalytic activity of the metal center.

[1] O'Brien C., Kantchev E., Valente C., Hadei N., Chass G., Lough A., Hopkinson A., Organ M. *Chem. Eur. J.* **2006**, *12*, 4743; Navarro O., Marion N., Mei J., Nolan S. *Chem. Eur. J.* **2006**, *12*, 5142.
[2] Raubenheimer H., Cronje S. Dalton Trans. **2008**, 1265; Albrecht M., Stoeckli-Evans H. *Chem. Commun*. **2005**, 4705.
[3] J. Owen, J. Labinger, J. Bercaw, *J. Am. Chem. Soc.*, **2004**, *126*, 8247.

Inorganic and Coordination Chemistry **228**

Metal-Mediated Thiol-Disulfide Interconversion – A New Tool for Metallosupramolecular Chemistry

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Jason R. Price, Silvia Schaffner

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Self-replicating molecular systems represent a challenging target for synthetic chemistry. We have recently become interested in utilising the precepts of metallosupramolecular chemistry[1] for the development of self-replicating systems.[2] Our approach is predicated upon two phenomena: (i) the preference of copper(II) for five-coordinate {Cu(tpy)(bpy)} environments[3] and (ii) the reversible metal-mediated reaction.

$$2RSH \rightarrow RSSR + 2H^+ + 2e^-.$$

Although thiol(thione)-disulfide interconversion has been utilised in the establishment of dynamic combinatorial libraries, disulfides are less commonly encountered in metallosupramolecular chemistry. Establishment of appropriate ligand feeds has lead us to synthesise multiple polypyridyl thiones in order to fulfill redox obligations both potential and electron count.

Presented will be the description of key thione intermediates for the proposed self-replicating systems and describe the metal-mediated oxidation of those compounds to date.

[1] E. C. Constable, *Chem. Ind.*, **1994**, 56.
[2] E. C. Constable, C. E. Housecroft, J. N. Lambert and D. A. Malerek, *Chem. Comm.*, **2005**, 3739.
[3] V. Chaurin, E. C. Constable and C. E. Housecroft, *New J. Chem.*, **2006**, *30*, 1740.

Inorganic and Coordination Chemistry **229**

An efficient homogenous photocatalytic system for the reduction of protons to hydrogen using a Rhenium based photosensitiser

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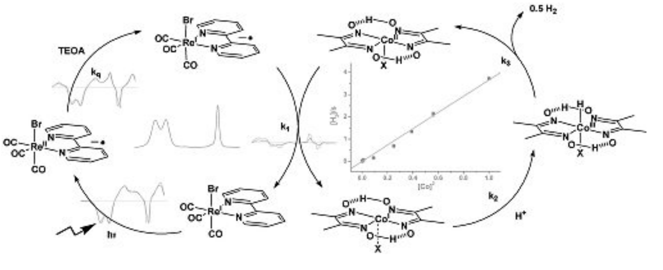

The solar production of hydrogen and oxygen from water remains a major challenge for the coming century.

We wish to report a successful implementation of an homogenous proton reduction cycle as shown above for the production of hydrogen from light and an irreversible electron donor. To our knowledge this is the first artificial mimetic for Photosystem I employing a Rhenium based complex, $[ReBr(CO)_3bipy]$ as chromophore. To overcome the activation barrier for proton reduction a Cobalt based catalyst, $[Co(dmgH)_2]$, is used. Electron transfer between the antenna and the later was observed by time resolved infrared spectroscopy, revealing a forward electron transfer rate of $k_1 = 2.5 \pm 0.1\cdot10^8\ M^{-1}\cdot s^{-1}$. Furthermore we could show that a second order process in cobalt is crucial for the final H_2 generation step, implying a homolytic H_2 formation. Under ambient light conditions the process is controlled by photon flux.[1]

Presently we focus on the linking of our system to an oxidative counterpart.

[1] B. Probst, Ch. Kolano, P. Hamm, R. Alberto, *submitted for publication*.

Inorganic and Coordination Chemistry **230**

Ru/PNNP Complexes with Cyclic PNNP ligands

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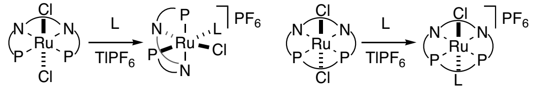
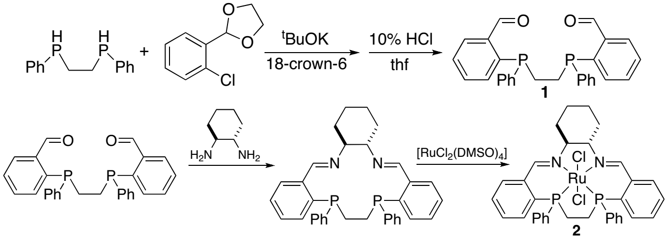
We have used Ru/PNNP complexes as catalysts in the asymmetric cyclopropanation aziridination of olefins.[1] In this reaction, a *trans*-carbene complex must be formed to achieve high enantioselectivity. Therefore, to increase the rigidity of the PNNP ligand and enforce the formation of *trans*-adducts, we prepared the first chiral macrocyclic PNNP ligand (**1**) and the corresponding ruthenium(II) complex $[RuCl_2(PNNP)]$ (**2**), which is expected to form more rigid and stable catalysts upon chloride abstraction.



linear PNNP can give *cis*-β isomers

only *trans*-isomers possible with a cyclic PNNP

The synthesis is performed in four steps starting from 1,2-bis(phenylphosphino)ethane and can be easily scaled up. The most accessible diastereoisomer is obtained from (*R,S*)-2,2'-(ethane-1,2-diylbis (phenylphosphinediyl))dibenzaldehyde (**1**) in 50% overall yield. Applications of **2** in asymmetric catalysis will be reported.



[1] Bonaccorsi, C.; Mezzetti, A. *Organometallics* **2005**, *24*, 4953.

Inorganic and Coordination Chemistry **231**

Ru(II)arene complexes as versatile anticancer agents

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Ruthenium based compounds are an attractive alternative to clinically used platinum drugs due to several features; a wide range of accessible oxidation states, varied synthetic chemistry and low toxicity. One series of Ruthenium(II)-arene-pta (RAPTA; pta = 1,3,5-triaza-7-phophaadamantane) compounds have been found to show particularly high selectivity towards cancer cells in both in vitro and in vivo studies.[1] By varying the ligand sphere, it is possible to control the reactivity and cytotoxicity of the complexes. For example, using a weakly coordinating arene ligand such as $C_6H_5CF_3$ or $FC_6H_4CH_3$ facilitates arene loss allowing increased binding to double stranded DNA Alternatively compounds containing chelate phosphine ligands show reduced hydrolysis rates and much lower reactivity towards DNA though cytotoxicities remain high.

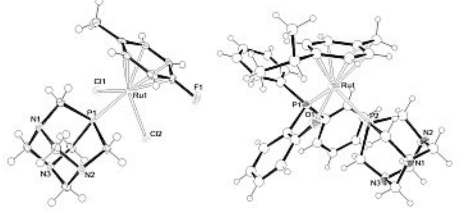

Figure 1: RAPTA-FT and RAPTA-PO

[1] C. Scolaro, A. Bergamo, L. Brescacin, R. Delfino, M. Cocchietto, G. Laurenczy, T. J. Geldbach, G. Sava, P. J. Dyson, *J. Med. Chem.* **2005**, *48*, 4161-4171.

Inorganic and Coordination Chemistry **232**

Postsynthetic Modification of Mesoporous Silica: Methods, Tools, and Perspectives

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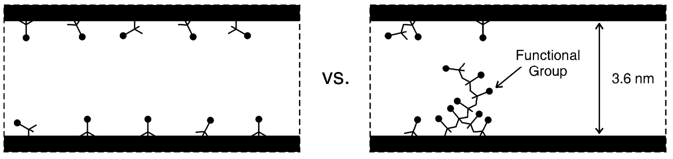
Postsynthetic modification is among the most popular methods for the preparation of functional mesoporous silica [1]. This can be attributed to the fact that the separation of the mesoporous silica synthesis and functionalization steps allows an independent and straightforward control of pore size, periodicity, particle size, and particle morphology. Current problems include the control of the uniformity of surface functionalization, the reliable determination of the functionalization degree, and the analysis of the distribution of the functional groups on the mesoporous silica surface. We are presenting new methods and analytical tools to solve these problems [2,3].



Uniform Distribution of Functional Groups with Site Isolation

Non-Uniform Distribution of Functional Groups with Cluster Formation

[1] F. Hoffmann, M. Cornelius, J. Morell, M. Fröba, *Angew. Chem. Int. Ed.* **2006**, *45*, 3216.
[2] H. Salmio, D. Brühwiler, *J. Phys. Chem. C* **2007**, *111*, 923.
[3] H. Ritter, C. Schütze, D. Brühwiler, *in preparation*.

Inorganic and Coordination Chemistry **233**

Fluorescence Sensors for Lithium Ions

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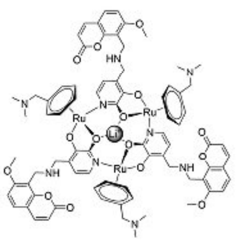
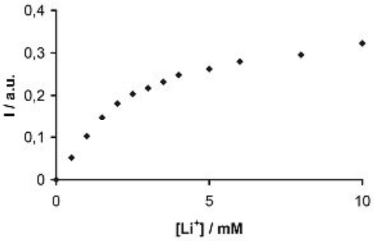
Lithium-based drugs are widely used for patients suffering from bipolar disorders, and applications for the treatment of neurodegenerative disorders have been suggested. However, the unavailability of a sensitive and specific Li^+ tool severely limits investigations in this context.[1]

Macrocyclic receptors, which are known to be water-soluble and selective for lithium ions, have been developed in our laboratory.[2] When a fluorescent dye is attached to them, they can be used to determine the lithium concentration in an aqueous solution by a simple fluorescence measurement.

Sensors of this kind may find applications in biomedical investigations involving lithium-based drugs.





[1] D. M. de Freitas, M. M. C. A. Castro, C. F. G. C. Geraldes, *Acc. Chem. Rev.* **2006**, *39*, 283-291.

[2] Z. Grote, R. Scopelliti, K. Severin, *J. Am. Chem. Soc.* **2004**, *126*, 16959-16972.

Inorganic and Coordination Chemistry **234**

Kinetic Resolution of Chiral Phosphodiesters by Artificial Metalloenzymes Based on Biotin-Streptavidin Technology

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In contrast to organometallic catalysts, enzymes are particularly efficient at hydrolyzing inert phosphodiester and amide linkages. In a biomimetic spirit, incorporation of a biotinylated dinuclear metal complex in streptavidin affords artificial hydrolases for the kinetic resolution of racemic phosphodiesters. A chemogenetic optimization scheme allows to optimize both the activity and the selectivity of the artificial metallonuclease. Combining, kinetic data, mutagenesis and screening of various substrates allows us to present a hypothesis on the key enantiodiscriminating interactions which afford exquise *E* selectivity factors. In addition, our recent efforts on ds-DNA hydrolysis with these artificial nucleases will be presented.

Inorganic and Coordination Chemistry **235**

Syntheses of Vitamin B_{12}-Pt(II) Conjugates and Their Approach as Therapeutic Drug Delivery

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Since fast proliferating cells are high B_{12} consumers, Pt-conjugation to the cyanide of B_{12} can be used for specific targeting of cancer cells and therapeutic drug delivery, thereby avoiding the dose-limiting toxicity of cisplatin.[1] We could show that the Pt(II) complexes released from B_{12} after reduction exerted a cytotoxicity comparable to that of cisplatin itself.[2]
Furthermore, the chloride ligands of Pt(II) in these conjugates could be exchanged by from fluorescence markers, antibiotics or radiopharmaceuticals. The coordination of 2-deoxyguanosine to the released Pt(II) from B_{12} allowed to isolate and characterize the Pt(II) species released from adenosylation assays and to follow its biological fate.
Due to the long half-life of ^{57}Co, ^{57}Co-vitamin B_{12} has a very limited use for humans and imaging of B_{12} metabolism in tumor is almost imposible.[3] We proposed a novel radiolabeled B_{12} without modification of the B_{12} molecule by exchange of Cl^- for ^{131}I in $[\{B_{12}\}\text{-CN-}\{cis\text{-PtCl(NH}_3)_2\}]^+$.[4] Preliminary cancer cell uptake studies will be presented.

[1] Lippert, B. Cisplatin; Wiley-VCH, **1999**.

[2] Ruiz-Sánchez, P; Mundwiler, S.; Spingler, B.; Buan N.R.; Escalante-Semerena, J.C.; Alberto, R. *J. Biol. Inorg. Chem.* **2008**, *13*, 335.

[3] Collins, A.C.; Hogenkamp H.P.C.; Gebhard M.W. *Mayo Clin. Proc.* **1999**, *74*, 687.

[4] Ruiz-Sánchez, P; Mundwiler, S.; Medina-Molner, A.; Spingler, B.; Alberto, R. *J. Organomet. Chem.* **2007**, *692*, 135

Inorganic and Coordination Chemistry **236**

Structural Investigation of an Axial Lanthanide Podates in Solution Using Paramagnetic NMR

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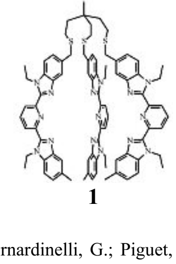
The effective concentration c^{eff} is a measure of the advantages of intra- over intermolecular connection events. In coordination chemistry, it may be used to estimate the extent to which the degree of *preorganization* of a ligand benefits its ability to selectively complex various lanthanide Ln(III) ions. A recent thermodynamic study has investigated the impact of c^{eff} on the stability of a pre-organised nonadentate tripod (**1**) with respect to three separated analogous tridentate binding units. Both systems form triple-helical complexes with Ln(III) ions, but, surprisingly, c^{eff} drastically disfavours the podate, even if both structures are superimposable in the solid-state. Moreover, the size of the lanthanide ion doesn't seem to have a significant influence on c^{eff} in this particular case.[1] To better understand this phenomenon we have studied the solution structure of Ln(III) complexes of the tripodal receptor (**1**) using paramagnetic NMR. In doing this we have been able to ascertain whether or not the apparent unfavourable c^{eff} is due to a major change in structure along the lanthanide series (Ce-Yb). This poster will present and discuss the results obtained from the paramagnetic NMR investigation.



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[1] Canard, C.; Koeller, S.; Bernardinelli, G.; Piguet, C. *J. Am. Chem. Soc.* **2008**, *130*, 1025.

Inorganic and Coordination Chemistry **237**

Ru / PNNP Catalyzed Asymmetric Aziridination of Imines

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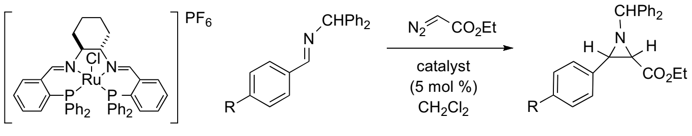
Aziridine-2-carboxylates are valuable precursors for α- and β-amino acids. We report herein the asymmetric synthesis of these versatile organic compounds by catalytic addition of a carbene species to aromatic imines. $[RuCl_2(PNNP)]$ complexes undergo chloride abstraction upon treatment with chloride scavengers to give $[RuCl(PNNP)]^+$ **(1)**. Complex **1** forms the six-coordinate species $[RuCl(L)(PNNP)]^+$ when exposed to oxygen-containing ligands like water and Et_2O (L), and is an efficient enantioselective catalyst for atom-transfer reactions [1][2][3]. We find now that **1** catalyzes the aziridination of N-benzhydryl protected imines **2a-f**, to give **3a-f** in up to 28% yield and with 25% ee with complete *cis*-selectivity.



1 **2a - e** **3a - e**

R = H, NO_2, OMe, F, CF_3

Addition of water or Et_2O to a CH_2Cl_2 solution of **1** increases the enantioselectivity to more than 70% ee. We are studying the details of the mechanism in order to increase the enantioselectivity and suppress the formation of maleate, which limits the yield of **3a - e**.

[1] C. Bonaccorsi, A. Mezzetti, *Organometallics* **2005**, *24*, 4953.
[2] C. Bonaccorsi, M. Althaus, C. Becker, A. Togni, A. Mezzetti, *Pure Appl. Chem.* **2006**, *78*, 391.
[3] M. Althaus, C. Becker, A. Togni, A. Mezzetti, *Organometallics* **2007**, *26*, 5902.

Inorganic and Coordination Chemistry **238**

Highly variable N^1HC^6 ligands: Normal, abnormal and remote bonding in pyridylidene complexes

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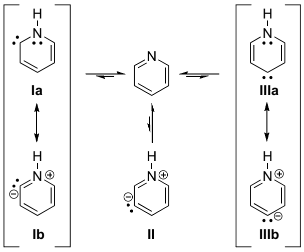
hile the term N-heterocyclic carbene (NHC) is widely employed as a syn- ym for 2-imidazolylidenes and related ligands (*i.e.* five-membered rings ith two N-atoms adjacent to the carbene carbon), there is a growing inter- t in NHC ligands with reduced heteroatom stabilisation *.g.* pyrazolylidenes, 4-imidazolylidenes, pyridylidenes). Our group has en particularly interested in the complex chemistry of pyridinium-derived rbenes which offer a variety of bonding modes (see Figure)[1].



erein we report the first comparative investigation of isomeric rmal (*n*NHC - **I**), abnormal (*a*NHC - **II**) and remote (*r*NHC - **III**) ridylidene complexes. Both experimental and computational studies on mpounds of the general formula $[trans\text{-}(NHC)M(PPh_3)_2Cl]^+$ (M = Pd, Ni) ve been carried out.

] H. G. Raubenheimer, S. Cronje, *Dalton Trans.* **2008**, 1265.

Inorganic and Coordination Chemistry **239**

Synthesis and Structural Determination of Phases in the XSiSn Systems (X=AE, Ln)

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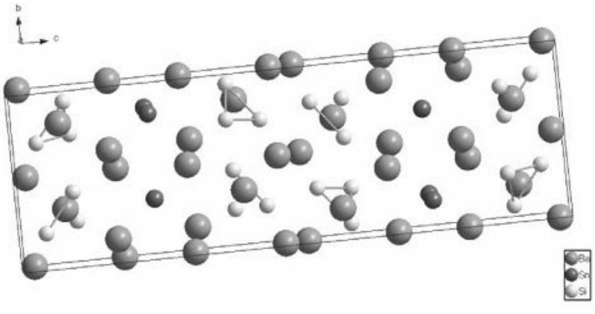
A new Zintl phase Ba_8Si_6Sn was synthesised from the elements. Single-crystal analysis shows that it crystallises in the *Pbcn* space group (orthorhombic, N° 60) with *a*=8.784(5)Å, *b*=8.765(5)=Å and *c*=27.20(2)Å. Interestingly, the structure contains Si_3^{6-} units and Sn^{4-} anions with a counter-intuitive charge distribution. It is related to the previously reported $Ba_8Si_6Br_4$ structure[1]. In the case of Sr and Eu, no analogous structure was found.



From a reaction of Sr, Si and Sn in a ratio of 2:1:1 a crystal was selected and analysed. It crystallises in the *Cmcm* space group (orthorhombic, N° 63) with *a*=4.976(3)Å *b*=11.736(6)Å and *c*=4.306(2)Å. The refinement indicated a mixed occupancy on the Si/Sn site and gives a composition of $SrSi_{0.5}Sn_{0.5}$.

[1] Steffen Wengert, Johannes B. Willems and Reinhard Nesper, *Chem. Eur. J.*, **2001**, *7*, 3209.

Inorganic and Coordination Chemistry **240**

Evaluation of Organometallic Technetium and Rhenium Thymidine Complexes as Substrates for Human Thymidine Kinase Type 1

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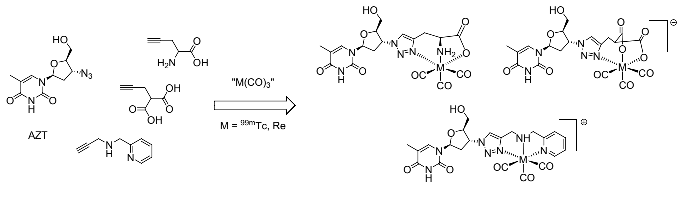
Human cytosolic thymidine kinase (hTK1) shows a higher than normal expression in a wide variety of cancer cells. Technetium labeled thymidine analogues therefore have the potential to act as markers for cancer cell proliferation. Click chemistry can be used to introduce a series of different chelating systems for the $M(CO)_3$ core (M = ^{99m}Tc, Re) into molecules of biological interest.[1] This approach was used to facilitate the synthesis of a series of thymidine derivatives functionalized with a chelating system at the C3' position of thymidine, starting from the commercially available precursor 3'-azido-3'-deoxythymidine (AZT). By varying the chelating system, neutral, cationic and anionic complexes could be readily synthesized. Incubation of the complexes with hTK1 and ATP identified the first organometallic substrates of hTK1 in which thymidine is modified at the C3' position. The synthesis, characterization and relative phosphorylation rates of the novel complexes compared to the natural substrate thymidine will be presented.



[1] H. Struthers, B. Spingler, T. L. Mindt, R. Schibli, *Chem.--Eur. J.* **2008**, in press.

Inorganic and Coordination Chemistry **241**

Homolysis of peroxynitrous acid induced by laser flash photolysis

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We have recently shown that homolysis of $ONOO^-$ at the N–O bond occurs with a rate constant of $0.020 \pm 0.001\ s^{-1}$.[1] From this rate constant and other data, it is possible to calculate a thermodynamically derived rate constant for the homolysis of ONOOH, $0.38 \pm 0.25\ s^{-1}$, for reaction −2. An optional pathway is reaction 3, which would yield products that lie 20 kJ mol^{-1} above the products of reaction 2. To examine this possibility, we used a combined stopped-flow – laser flash photolysis apparatus to determine whether photons cause homolysis of ONOOH via reaction 2 or 3.

$$ONOO^- = NO^\bullet + O_2^{\bullet -} \quad (1)$$
$$ONOOH = NO_2^\bullet + HO^\bullet \quad (2)$$
$$ONOOH = NO^\bullet + HO_2^\bullet \quad (3)$$

We found that absorptions increased in the wavelength range of 235 to 310 nm after excitation at 355 nm, and that these absorptions increase with pH in the range 4–5.5. This suggests strongly that the absorbing species are $HO_2^\bullet$ and $O_2^{\bullet -}$, given the known pK_a of 4.8 of $HO_2^\bullet$ and $O_2^{\bullet -}$, which absorbs more strongly than $HO_2^\bullet$.

In order to clarify whether the O–O or N–O bond breaks, we determined the concentrations of $HO^\bullet$, < 1 µM, and $HO_2^\bullet$, > 20 µM, respectively, which clearly indicates that the induced homolysis takes place at the N–O bond.

Furthermore, we observed a second–order recombination, which ends at the initial absorption level. Hence, we calculated a rate constant of $(2.1 \pm 0.6) \times 10^{10}\ M^{-1}s^{-1}$ for the $NO^\bullet$ and $HO_2^\bullet$ recombination, within the error identical to that of the reaction of $NO^\bullet$ with the $O_2^{\bullet -}$.[2]

[1] Sturzbecher, M., Kissner, R., Nauser T., Koppenol W.H., *Inorg.Chem.* **2007**, *46*, 10655.
[2] Nauser, T., Koppenol, W.H., *J.Phys.Chem.A* **2002**, *106*, 4084.

Inorganic and Coordination Chemistry **242**

Supramolecular Trojan Horse for Cancer Cells

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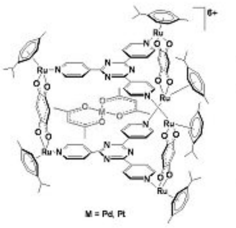
Neuchâtel, Switzerland

Combining the “molecular clip” strategy developed by Stang and the “molecular panelling” strategy developed by Fujita, we recently synthesised the "complex-in-a-complex" cations $[(acac)_2Pd\subset Ru_6(p\text{-}Pr^iC_6H_4Me)_6(tpt)_2(dhbq)_3]^{6+}$ and $[(acac)_2Pt\subset Ru_6(p\text{-}Pr^iC_6H_4Me)_6(tpt)_2(dhbq)_3]^{6+}$, in which the bis(acetylacetonato)Pd or Pt complexes are encapsulated in the hexaruthenium cage $[Ru_6(p\text{-}Pr^iC_6H_4Me)_6(tpt)_2(dhbq)_3]^{6+}$.[1]



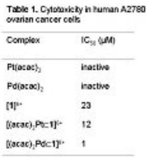


Table 1. Cytotoxicity in human A2780 ovarian cancer cells

Complex	IC_{50} (µM)
$Pt(acac)_2$	inactive
$Pd(acac)_2$	inactive
$[1]^{6+}$	23
$[(acac)_2Pt\subset 1]^{6+}$	12
$[(acac)_2Pd\subset 1]^{6+}$	1

The cytotoxicity of the two host-guest systems, the empty hexaruthenium cage and the free complexes $Pd(acac)_2$ and $Pt(acac)_2$ have been evaluated as anticancer agent against A2780 human ovarian cancer cells. The difference in cytotoxicity of the different systems suggests that like a “Trojan Horse”, once inside a cell, passive leaching of the guest from the cage accelerates and increases the cytotoxic effect.

[1] B. Therrien, G. Süss-Fink, P. Govindaswamy, A. K. Renfrew, P. J. Dyson, *Angew. Chem. Int. Ed.* **2008**, *47*, in press.

Inorganic and Coordination Chemistry **243**

ATRA and ATRC Reactions Catalyzed by a Mixture of $[Cp^*RuCl_2(PPh_3)]$ and Mg

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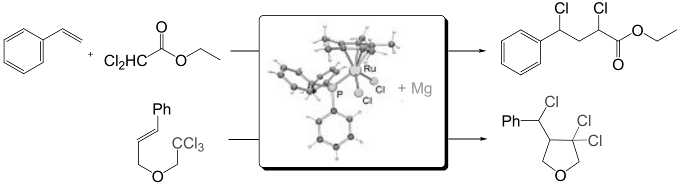
The main disadvantage of active Ru catalysts for atom transfer radical addition (ATRA) and cyclization (ATRC) reactions has been their low stability. The combination of the air-stable Ru^{III} complex $[Cp^*RuCl_2(PPh_3)]$ with Mg allows to perform these reactions under mild conditions with high efficiency [1]. It is suggested that Mg acts as a reducing agent that generates and regenerates the catalytically active Ru^{II} species.



Intramolecular ATRA reactions are especially interesting from a synthetic point of view. With the new system, cyclizations can be performed under mild conditions with low catalyst loadings and good stereoselectivities.

So far, consecutive reactions using ATRA and ATRC products have been rare or mainly limited to cyclization products [2]. In this context, possible following transformations are investigated. They would be of great interest for tandem catalysis reactions, which have attracted a lot of attention in organic synthesis.

[1] K. Thommes, B. Içli, R. Scopelliti, K. Severin, *Chem. Eur. J.,* **2007**, *13,* 6899.
[2] C. D. Edlin, J. Faulkner, P. Quayle, *Tetrahedron Lett.* **2006**, *47*, 1145.

Inorganic and Coordination Chemistry **244**

Molecular Mechanics Modeling of the Trans Influence in Organometallic Complexes Applied to Asymmetric Catalysis

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University of Basel. Klingelbergstrasse 80, 4056 Basel, Switzerland

Efficient calculation of metal-containing complexes relevant to catalysis is of major interest for better characterizing and optimizing the catalysts. Based on an existing force field for organometallic compounds (VALBOND[1]), extensions to include electronic effects such as the trans influence of ligands on the bond lengths and energies are discussed. Parameters and results for model octahedral complexes of Ru, Os, Rh, and Ir are presented, as well as an application to the study of reactive intermediates involved in asymmetric hydrogenation catalyzed by iridium complexes with chiral phosphinooxazolines (PHOX) ligands. The new force field allows for the separation of electronic and steric effects on the stability of different geometric isomers and reproduces DFT results which are consistent with experimental observations

[1] C. R. Landis, T. Cleveland, T. K. Firman. *J. Am. Chem. Soc.* **1998**, *120*, 2641.

Inorganic and Coordination Chemistry **245**

Crystal Structures and Diffuse Scattering of Compounds with Graphite-like (B,C)-Nets

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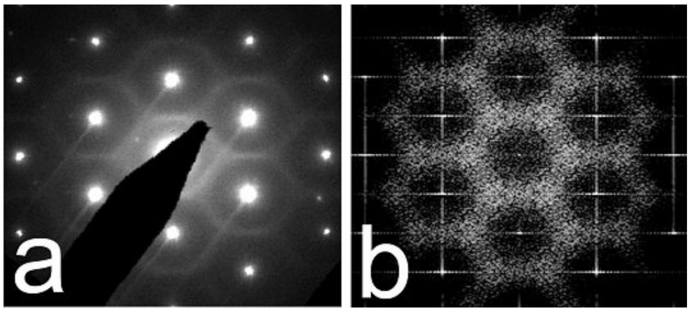
The crystal structures of the new compounds $Ca(B,C)_6$ (hexagonal, a = 4.563 Å, c = 4.396(1) Å) and $Ca(B,C)_8$ (hexagonal, a = 2.588(1) Å, c = 4.434(1) Å) were determined from powder diffraction data. The compounds consist of planar graphite-like (B,C)-nets, intercalated by calcium atoms. In $Ca(B,C)_6$ one third of the hexagonal prismatic voids formed by the (B,C)-layers is occupied by Ca. In $Ca(B,C)_8$ the Ca-atoms are disordered, which gives rise to honeycomb-like diffuse scattering visible in the electron diffraction pattern (Fig.1a). A model for the calcium distribution was developed and the diffuse scattering could be simulated successfully with the program DISCUS [1] (Fig. 1b).



[1] Proffen T., Neder T., *J. Appl.. Cryst.*, **1997**, *30*, 171

Inorganic and Coordination Chemistry **246**

$[^{99}TcO_3]^+$ complexes as model compound for a novel direct labeling strategy for radiopharmaceutical applications

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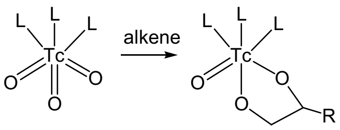
Molecular imaging emerged as a novel and powerful strategy for the visualization of biological events in a molecular level. Due to its availability and physical properties ^{99m}Tc is still the favored radionuclide for radioimaging purposes. In the past decades labeling strategies for Tc were mainly based on the bifunctional chelator concept. Here we report about a completely new strategy for the direct labeling of biomolecules.

$[^{99}TcO_4]^-$ can be activated by strong lewis acids in organic solvents, the highly active intermediate can be substituted by bi- or tridentated ligands and yield the corresponding $\{^{99}TcO_3\}$ complexes.[1] It is known that $\{TcO_3\}$ complexes react with alkenes by a [2+3] reaction[2]. This reaction could offer a new way for labeling of biomolecules containing double (or triple) bounds. We investigated this reaction with a series of $\{^{99}TcO_3\}$ model complexes and biological relevant model alkenes in detail. In all cases a relatively fast biomolecular reaction occurred under quantitative formation of the corresponding $^{99}Tc^V$ complex (e.g. figure 1). The kinetic data we optioned for this reactions support an associatively driven mechanism.



Scheme. The reducing reaction of $[TcO_3]^+$ type complexes by alkenes (L = bi- or tridenate ligands, R = H, Ph, $PhSO_4$ and alkyl group)

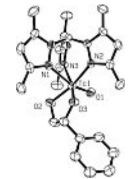


Fig.1 the crystal structure of [(tpzm*)TcO(1-phenyl-1,2-ethanediolate)]

[1] Y. Tooyama, H. Braband, B. Spingler, R. Alberto, et al, *Inorg. Chem.* **2008**, *47*, 257.
[2] M.Ronald and Alan Davison. *Polyhedron* **1988**, *7*, 1981-1989

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Investigation of Lanthanide Complexes with a Family of Tripodal Ligands

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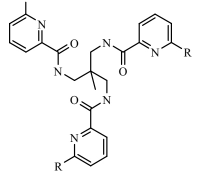
Recently, several tripodal [1] were prepared in order to develop stable binding Ln(III) luminescent and paramagnetic devices. Herein we report on the synthesis of tripodal ligands **L1, L2** and **L3**, which have been designed for Ln (III) coordination by taking advantage of the chelating effect of 2,6-dicarbonylpyridine subunits.



L1: R = –COOMe
L2: R = $–CO-N(CH_2-CH_3)_2$
L3: R = –COOH

The Ln(III) complexes with **L1** and **L2** are characterised in acetonitrile by spectrophotometry, NMR and ES-MS titration. Interestingly, the reaction of **L2** with Ln (=Eu-Lu) provides tetrahedral tetrametallic complexes [2]. In addition, thermodynamic parameters and photophysical properties of Eu(III) complexes with L1-L3 will be discussed.

[1] M. Seitz, M. D. Pluth, and K. N. Raymond, *Inorg. Chem.* **2007**, *46*, 351; J.-M. Senegas, G. Bernardinelli, D. Imbert, J.-C. G. Bünzli, P.-Y. Morgantini, J. Weber, and C. Piguet, *Inorg. Chem.* **2003**, *42*, 4680.
[2] J. Hamacek, G. Bernardinelli, Y. Filinchuk, *Eur. J. Inorg. Chem.* **2008**, Submitte

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Bi_2O_3 Nanowires: Structure Control and Visible-Light-Driven Photocatalytic Activity

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The five polymorphic forms of bismuth trioxide, including α-, β-, γ-, δ- and ω- type, display high dielectric permittivity, high oxygen conductivity as well as remarkable photoconductivity. Therefore, Bi_2O_3 is widely used in gas sensors, optical coatings, photovoltaic cells, photocatalysts, and related applications[1]. The availability of Bi_2O_3 nanowires may bring forward new types of application or enhance the performance of the currently existing devices. Despite its high application potential, up to now, only few researchers have developed synthetic pathways towards one-dimensional (1D) nanostructured Bi_2O_3, and most of them are based on gas phase methods[2, 3]. To the best of our knowledge, a large-scale solution-based synthesis of different modifications of 1D nanostructured Bi_2O_3 has not been achieved until now. Here, we report a simple method for the selective synthesis of different Bi_2O_3 nanowires through hydrothermal treatment of commercial Bi_2O_3 powders in the presence of ionic additives. Furthermore, the relationship between the photocatalytic activities and the morphology of Bi_2O_3 and related ternary compounds, such as bismuth tungstates/vanadates, was investigated through the degradation of organic compounds (methyl orange, methylene blue) under visible-light irradiation.

[1] F. Gao, Q. Lu, S. Komarneni. *Chem. Comm.* **2005**, 531.
[2] Y. Qiu, D. Liu, J. Yang, S. Yang. *Adv. Mater.* **2006**, *18*, 2604.
[3] G. R. Patzke, Y. Zhou. *Mater. Res. Soc. Symp. Proc.* **2008**, *1056*, 1056-HH05-01.

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Inorganic and Coordination Chemistry **249**

Ligand-Mediated Decarbonylation as an Efficient Synthetic Method to Re(I) and Re(II) Dicarbonyl Complexes

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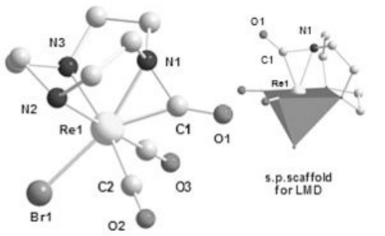
Chemistry of rhenium (II) is the least developed among the eight common oxidations states of this element. This is likely to be true due to a lack of versatile Re(II) precursors as starting material. Compounds of d^5 Re are attractive for medicinal inorganic chemistry and as precursors for single-molecule magnets.[1]-[2] A synthetic approach to Re(II) complexes would therefore be useful for a systematic exploration of the reactivity patterns of these molecules. We present an efficient high yield synthesis of Re(I) and Re(II) dicarbonyl complexes via an unprecedented ligand-mediated decarbonylation (LMD) reaction. We show that the LMD may be considered as generally applicable to *fac*-$[Re(CO)_3]^+$ complexes of tridentate aliphatic amine ligands. Structural authentication of key intermediates is presented.



[1] E. J. Schelter, F. Karadas, C. Avendano, A. V. Prosvirin, W. Wernsdorfer and K. R. Dunbar, *J. Am. Chem. Soc.*, 2007, **129**, 8139-8149.
[2] E. J. Schelter, A. V. Prosvirin, W. M. Reiff and K. R. Dunbar, *Angew. Chem. Int. Ed.*, 2004, **43**, 4912-4915.

Organic Chemistry **250**

Rotaxanes *via* Palladium Active-Metal Template Strategies

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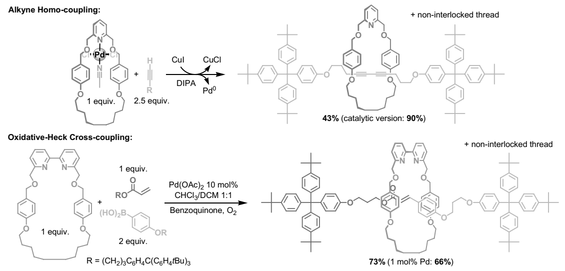
In contrast to the classic 'passive template' approach,[1] an 'active-metal' template strategy[2] involves a metal center which acts as both a template *and* the catalyst for covalent bond formation in the construction of mechanically interlocked architectures.



Palladium-catalyzed reactions are often the method of choice for the formation of C-C bonds in chemical synthesis. The development of both homo[3] and heterocouplings[4] based on Pd active-metal templates opens the possibility to use these methodologies for the assembly of [2]rotaxanes. The reactions are mild, high-yielding, versatile and only a catalytic amount of the template is required.

[1] M. C. Thompson, D. H. Busch, *J. Am. Chem. Soc*. **1964**, *86*, 3651-3656; [2] V. Aucagne, K. D. Hänni, D. A. Leigh, P. J. Lusby, D. B. Walker, *J. Am. Chem. Soc.* **2006**, *128*, 2186-2187; [3] J. Bernà, J. D. Crowley, S. M. Goldup, K. D. Hänni, A.-L. Lee, D. A. Leigh, *Angew. Chem. Int. Ed.* **2007**, *46*, 5709-5713; [4] J. D. Crowley, K. D. Hänni, A.-L. Lee, D. A. Leigh, *J. Am. Chem. Soc.* **2007***, 129*, 12092-12093.

Organic Chemistry **251**

Synthesis, properties and applications of Nickel(II) bisimidazol-2-ylidene complexes

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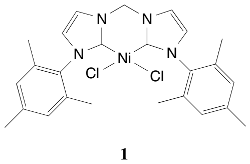
Since their discovery [1], *N*-heterocyclic carbenes (*N*HCs) especially derived from imidazolium salts have been used as ligands in different organometallic catalysis [2], but few have been used for olefin polymerisation. On the other side, the growing importance of nickel complexes as olefin polymerisation catalysts [3], led us to develop a new olefin polymerisation catalyst containing bisimidazolium ligands.



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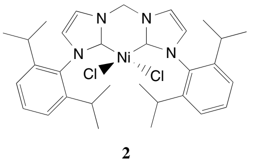

2

In this work, the synthesis of two new nickel(II) bisimidazolium-2-ylidene complexes is described. They are obtained by transmetalation from the corresponding silver carbene complexes. Surprisingly the two complexes differ very much both with respect to structure and catalytic behaviour. Most interestingly the violet pseudotetraedric complex **2** reversibly binds dioxygen, a feature totally absent in the square planar complex **1**.

[1] A. J. Arduengo, R. L. Harlow, M. Kline, *J. Am. Chem. Soc.*, **1991**, *113*, 361-363.
[2] W. A. Herrmann, *Angew. Chem. Int. Ed.*, **2002**, *41*, 1290-1309.
[3] S. Benson, B. Payne, R. M. Waymouth, *J. Polym. Sci., Part A: Polym. Chem.*, **2007**, *45*, 3637-3647.

Organic Chemistry **252**

The Biomimetic Synthesis and Final Structure Determination of (–)-Centrolobine

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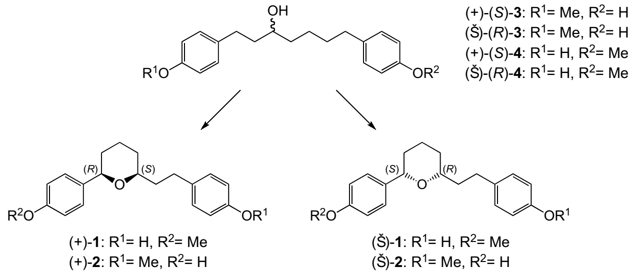
In previous work we have shown that 2,6-disubstituted tetrahydropyrans could be biomimetically synthesized by oxidative cyclization of their corresponding phenolic alcohols [1].



In order to correct structural inconsistencies of (–)-centrolobine ((–)**1**) [2], a physiologically active constituent of *Centrolobium robustum* [3], the congeners **1** and **2** were prepared from their precursors **3** and **4** (*ee* > 99%). The key step is the oxidative cyclization by DDQ, a biomimetic equivalent of phenoloxidase.

[1] P. Rüedi, M. Juch, *Curr. Org. Chem.* **1999**, *3*, 623.
[2] L. V. Alegrio, R. Braz-Filho, O. Gottlieb, *Phytochemistry* **1989**, *28*, 2359; A. F. de C. Alcântara, M. R. Souza, D. Piló-Veloso, *Fitoterapia* **2000**, *71*, 613; V. Böhrsch, S. Blechert, *J. Chem. Soc., Chem. Commun.* **2006**, 1968.
[3] I. L. De Albuquerque, C. Galeffi, C. B. Casinovi, G. B. Marini-Bettòlo, *Gazz. Chim. Ital.* **1964**, *94*, 287.