Computational Chemistry **105**

Spin-Densities and Magnetic Exchange in Transition Metal Dimers

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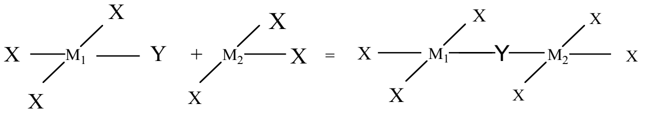
A new conceptual model of calculating magnetic exchange integrals based on spin-densities of the magnetic building blocks of a transition metal dimer complex is presented. It a first step the spin density on the bridging ligand Y resulting from charge transfer and spin polarization due to the open shell M_1 in a M_1X_nY moiety is calculated. In a second step, the coupling of the same ligand Y with a single electron open shell configuration (radical) with the metal on a neighboring M_2X_mY moiety is calculated. Finally, the spin-density from the first step is utilized to properly reduce the exchange integral of the X_mM_2-Y metal-ligand radical coupling bringing it in line with the spin-density distribution in the dimer complex. An application of this recipe to the calculation of the exchange coupling between square planar CuX_4^{2-} entities, sharing a common corner or edge ($Cu_2X_7^{3-}$ or $Cu_2X_6^{2-}$, respectively, X=F$^-$,Cl$^-$) is given. Results are discussed in comparison with the broken symmetry method [1] and a recently proposed DFT-based ligand field computational scheme. [2] The new approach allows to deduce and analyze in a rough but theoretically justified way exchange coupling integrals within a small fraction of computational times compared to usual ab-initio or DFT approaches.



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[2] M.Atanasov, C.A.Daul, *Chem.Phys.Lett*. **2003**, *379*, 209.

Computational Chemistry **106**

The Cycloaddition of Acridizinium cation with Ethylene and Allene: A Theoretical Study

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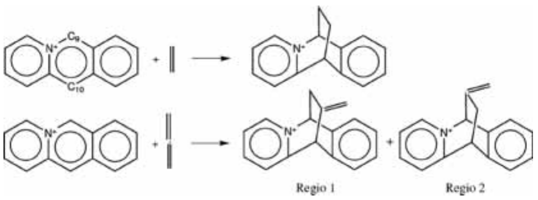
Acridizinium (ACR) cation undergoes cationic Diels-Alder cycloaddition with allene and ethylene. Positive charge on ACR is expected to strongly influence the mechanism of the reaction. Bradsher and coworkers have performed the reaction between ACR and ethylene[1] and proposed concerted mechanism for this reaction because the intermediate carbonium ion could not be detected during the reaction[2].



The cycloaddition of ACR with ethylene and allene have now been modeled at DFT level. Computed Frontier Orbital Energy analysis predict that these reaction are expectedly inverse electron demand type and follows concerted mechanism with extremely asynchronous transition structures. Both frontier orbital control and electrostatic interaction favors high reactivity of C9 over C10 in ACR. The effect of *peri* strain in ethylene reaction and the regio selectivity in allene reaction are examined. Computed bond orders show bond making and breaking in the reaction path in greater detail.

[1] I. J. Westerman, C. K. Bradsher, *J. Org. Chem*, **1978**, *43*, 3002.
[2] C. K. Bradsher, G. L. B. Carlson, N. A. Porter, I. J. Westerman, *J. Org. Chem*, **1978**, *43*, 828.

Inorganic and Coordination Chemistry **107**

The influence of divalent metal ions on the solution structure of a group II intron branch-point domain

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Group II introns are large, highly structured selfsplicing ribozymes found in organellar genes of lower eukaryotes, as well as in bacterial genomes. They all show a common secondary structure consisting of six domains with distinct functionalities. The first step of splicing is initiated by the nucleophilic attack of the 2'-OH of the branch-point, a highly conserved adenosine nucleotide in the intron domain 6 (D6), at the 5'-splice site. Two subsequent transesterification steps eventually lead to the excision of the intron from the pre-mRNA in form of a lariat. Like in most ribozymes, divalent metal ions act as natural cofactors for the splicing reaction. Here we present the NMR solution structure of the branch-region of the yeast mitochondrial intron ai5γ. Our hairpin structure shows a classical A-form helix, interrupted by the branchpoint and closed by a GUAA tetraloop. The branch-point adenosine is sandwiched between two GU wobble pairs. Its 2'-OH group is pointing outwards into the solution, ready to attack as a nucleophile in the first step of splicing. A prominent metal ion binding site has been detected at the branch-point by terbium cleavage [1]. Thus we have also studied the interaction of different divalent metal ions with D6 by NMR. Together with the detailed analysis of our NMR structure, we discuss the effect of divalent metal ions on the conformation of the branchpoint in solution and its implications for branch-point selection and selfsplicing of these intriguing ribozymes.

[1] R. K. O Sigel, A Vaidya, A. M.Pyle, *Nat. Struct. Biol.* **2000,** *7,* 1111-1116.

Financial support by the Swiss National Science Foundation *(SNF-Förderungsprofessur* to R. K. O. S., PP02- 68733/1) is gratefully acknowledged.

Inorganic and Coordination Chemistry **108**

Self-assembled heterotrimetallic d-f-d triple helicates

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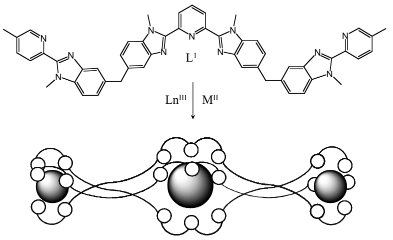
The trisegmental ligand L^1 was used for the self-assembly of heterotrimetallic $[LnM_2(L^1)_3]^{7+}$ helicates (M = Cr^{II}, Zn^{II}), obtained by mixing L^1, M^{II} and Ln^{III} in a 3:2:1 ratio. Following oxidation of $[LnCr_2(L^1)_3]^{7+}$ with air, the inert $[LnCr_2(L^1)_3]^{9+}$ complexes were obtained.



$[LnM_2(L^1)_3]^{7+}$

Structural, thermodynamic and photophysical properties of these $[LnZn_2(L^1)_3]^{7+}$ and $[LnCr_2(L^1)_3]^{9+}$ trimetallic helicates are presented. A particular attention is paid to intermetallic energy transfers occurring between Ln^{III} and Cr^{III}, and comparison with the previously reported bimetallic helicates $[LnCr(L^2)_3]^{6+}$ [1,2] will be discussed.

[1] M. Cantuel, G. Bernardinelli, D. Imbert, J.-C. G. Bünzli, G. Hopfgartner and C. Piguet, *J. Chem. Soc., Dalton Trans.,* **2002**, 1929-1940.
[2] D. Imbert, M. Cantuel, J.-C. G. Bünzli, G. Bernardinelli and C. Piguet, *J. Am. Chem. Soc.,* **2003**, 125, 15698-15699.

Inorganic and Coordination Chemistry **109**

Effective Stereocontrol of Chiral Piano-Stool Metal Complex Geometry by a Coordinating Enantiopure Counterion

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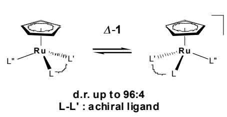
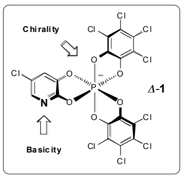
Cationic cyclopentadienyl ruthenium(II) complexes are chiral if four different ligands surround the pseudo-tetrahedral metal atom. These derivatives are configurationally labile and enantiopure bidentate ligands are typically used to control the configuration of the metal center; chiral monodentate or Cp equivalents being usually less efficient for the stereocontrol [1].





We now report the synthesis and resolution of a novel hexacoordinated phosphate anion **1** (*Λ* or *Δ* enantiomer) that exhibits not only counterionic but also *Lewis* basic capacities [2]. This monodentate anion displays unprecedented level of stereocontrol of piano-stool metal complex geometry (d.r. up to 96:4).

[1] H. Brunner *Angew. Chem. Int. Ed. Engl.* **1999**, *38*, 1194; C. Ganter, *Chem. Soc. Rev.* **2003**, *32*, 130.
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Inorganic and Coordination Chemistry **110**

Synthesis of coenzyme B_{12} analogs and investigations on their interactions with the B_{12} responsive riboswitch RNA

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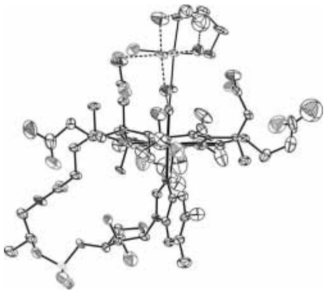
Riboswitches are conserved mRNA sequences, which contribute to gene regulation by direct binding to different metabolites.[1] The *btuB* riboswitch is a 5'-desoxyadenosylcobalamine (AdoCbl) responsive RNA sequence found in the 5'-untranslated region of the *btuB* gene in eubacteria encoding a vitamin B_{12} transport protein. After binding to its substrate, the *btuB* riboswitch RNA is supposed to undergo changes in its tertiary structure leading to premature termination of transcription or inhibition of translation.

AdoCbl is known to be very light sensitive, which makes it difficult to be applied in many biochemical investigations. Thus we are synthesizing light stable AdoCbl analogs, derived from cyano-bridged VitB$_{12}$-*cis*Pt(II),[2] and VitB$_{12}$-enPt(II) (see figure) complexes. Adenine derivates can then be added to the Pt^{II} center.

The investigations on the direct interaction of the different analogs with the 202 nt long *btuB* riboswitch RNA will further be discussed.



Crystal structure of the en-Pt(II)-vitamin B_{12} adduct.

[1] M. Mandal, R. R. Breaker, *Nat. Rev. Mol. Cell Bio.* **2004**, *5*, 451-463.
[2] S. Mundwiler, B. Spingler, P. Kurz, S. Kunze, R. Alberto, *Chem. Eur. J* **2005** *online***.**

Financial support by the Swiss National Science Foundation *(SNF-Förderungsprofessur* to R. K. O. S., PP0268733/1) is gratefully acknowledged.

Inorganic and Coordination Chemistry **111**

Site-Isolated Porphyrin Catalysts in Imprinted Polymers

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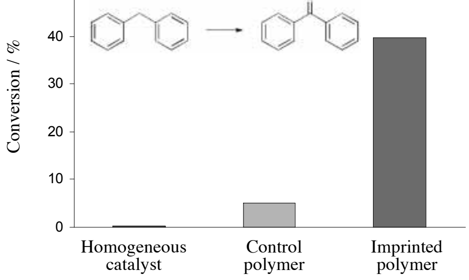
Ruthenium porphyrin catalysts have been widely employed in oxygen transfer reactions with 2,6-dichloropyridine-*N*-oxide as the oxidant.

A molecularly imprinted polymer (MIP), consisting of an immobilized ruthenium porphyrin complex with a substrate pocket next to the active site, was prepared by using a template ("pseudo-substrate") during polymerisation.[1] The resulting heterogeneous catalyst displays enhanced reaction rates for the oxidation of various substrates compared to the control, non-imprinted polymer (NIP) and to the homogeneous catalyst.



Catalyst/substrate ratio : 1/250, 35 °C, values after 6h.

[1] E. Burri, M. Öhm, C. Daguenet, K. Severin, *Chem. Eur. J.* **2005**, in press

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Inorganic and Coordination Chemistry **112**

Thioacetate Functionalised Metal Complexes and Optical Molecular Switches: Precursors for Self Assembled Monolayers (SAMs) on Gold

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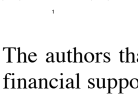
Ruthenium(II)trisbipyridine complexes **1** containing two mercapto-alkyl chains [1] on one of the bipyridyl units have been self assembled on gold and the electrochemical and photophysical properties, thereof, investigated. In the field of sensors, such strong emitting metal complexes can be used for the detection of extremely small quantities of oxygen.

The syntheses and photoisomerisation of a perfluorodithienylcyclopentene [2] based molecular switch **2** has been realized successfully. The immobilisation of this di-thioacetate moiety on gold is underway. Such molecular devices can find application in the fields of data storage and molecular level logic gates.



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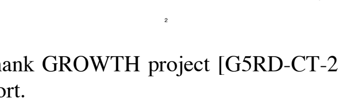

2

The authors thank GROWTH project [G5RD-CT-2002-00776-MWFM] for financial support.

[1] a) J.-C. Chambron, J.-P. Sauvage, *Tetrahedron* **1987**, *43*, 895. b) V. M. Iyer, H. Stoeckli-Evans, A. D'Aleo, L. De Cola, P. Belser, *Acta Cryst. C* **2005**, *C61*, o259.
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Inorganic and Coordination Chemistry **113**

Reactivity of the novel organometallic aqua-ion $[(CO)_2(NO)Re(H_2O)_3]^{2+}$: Kinetics of H_2O substitution and ^{17}O exchange of CO ligands

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The kinetics of water exchange on $[(CO)_2(NO)Re(H_2O)_3]^{2+}$ (**1**) and the ^{17}O exchange between the bulk water and the CO oxygens were investigated by ^{17}O NMR. The water exchange rate constant k_{obs} was analyzed with a two pathways model in which k_{ex} and k_{OH} denote the water exchange rate constants on **1** and on the monohydroxo species $[(CO)_2(NO)Re(H_2O)_2(OH)]^+$ (**2**). $K_{ex}{}^{trans}NO^+$ and $k_{ex}{}^{trans}CO$ were too small to be determined in the presence of the much more reactive species **2**. However, $k_{OH}{}^{trans}NO^+$ and $k_{OH}{}^{trans}CO$ were determined as $(4.2 \pm 2) \times 10^{-3}\ s^{-1}$ and $(0.58 \pm 0.2) \times 10^{-3}\ s^{-1}$, respectively. This is significantly smaller than the value found for $[(CO)_3Re(H_2O)_3]^+$ (**3**) ($k_{OH} = 27 \pm 1\ s^{-1}$) [1]. In addition, we observed a very fast exchange of the CO-oxygens by ^{17}O-H_2O ($\delta(C^{17}O) = 389$ ppm). This was not observed in case of **3** but was reported for $[(CO)_3Ru(H_2O)_3]^{2+}$ (**4**) and $[(CO)_3Mn(H_2O)_3]^+$ (**5**) [2],[3]. Implication on the ligand exchange rates of **1** in aqueous media will be presented.

[1] B. Salignac et al, *Inorg. Chem.* **2003**, *42*, 3516.
[2] U. C. Meier et al, *Inorg. Chem.* **2000**, *39*, 3816.
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Inorganic and Coordination Chemistry **114**

Polynuclear Ln(III) Complexes: Self-Assembled Helix formed by a Chiral Bipyridine-Carboxylate Ligand

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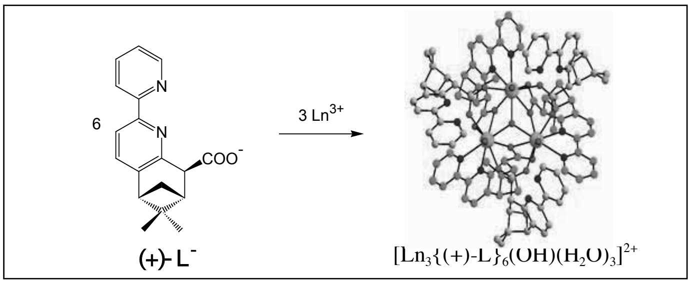
The introduction of a carboxylic moiety onto the pinene bipyridine framework led to a new family of chiral ligands[1] for the diastereoselective synthesis of configurationally stable lanthanide complexes. In particular, the enantiopure, pinene substituted carboxylic derivative L led to the synthesis of oligometallic supramolecular structures through a diastereoselective self-assembly process.[2] The coordination properties and chiral induction ability of this ligand have been tested along the Ln series. The characterization of the new compounds by a variety of physico-chemical methods including chiroptical spectroscopic techniques will be discussed.



[1] M. Lama, O. Mamula, R. Scopelliti, *Synlett,* **2004**, *10*, 1808.
[2] O. Mamula, M. Lama, S. G. Telfer, A. Nakamura, R. Kuroda, H. Stoeckli-Evans, R. Scopelliti, *Angew. Chem. Int. Ed.*, **2005**, 44, 2527.

Inorganic and Coordination Chemistry **115**

Organometallic Receptors for Lithium Ions in Water

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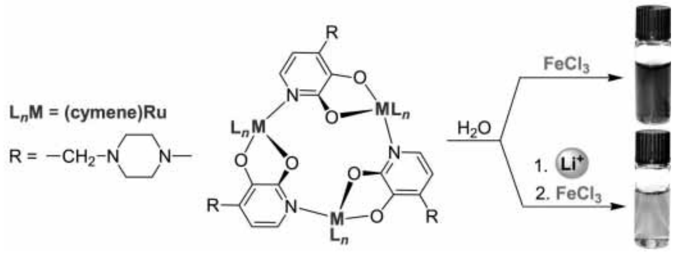
Receptors with high affinity and extraordinary selectivity towards lithium ions in water can be obtained by self-assembly of $[(\pi\text{-ligand})MCl_2]_2$ (M = Ru^{II}, Rh^{III} and Ir^{III}) half-sandwich complexes and functionalized 2,3-dihydroxypyridine ligands.[1,2] The binding affinity depends on the nature of the metal fragment, the ligand and the pH. Associations constants higher than $10^4\ M^{-1}$ are observed for certain complexes. The selectivity of Li^+ over Na^+ is about 10,000:1. The self-assembly process is pH dependent and completely reversible. Upon binding of Li^+ the reversibility of the self-assembly process is inhibited providing the opportunity the sense lithium ions in the mM range by a simple pH measurement. Furthermore, binding of Li^+ results in a change of the oxidation potential offering the possibility to create a "naked-eye" sensor for lithium ions.



[1] K. Severin, *Coord. Chem. Rev.* **2003**, *245*, 3 – 10.
[2] Z. Grote, R. Scopelliti, K. Severin, *J. Am. Chem. Soc.* **2004**, *126*, 16959 – 16972.

Inorganic and Coordination Chemistry **116**

Artificial Metalloenzymes: (Strept)Avidin as Host for Enantioselective Hydrogenation

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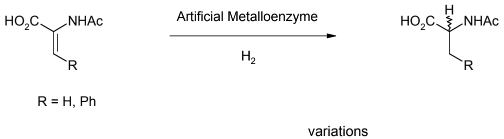
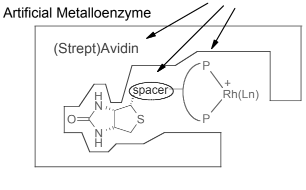
Incorporation of achiral, biotinylated aminodiphosphine–rhodium complexes in (strept)avidin affords catalysts for the enantioselective hydrogenation of enamides[1]. A chemogenetic optimization procedure allows the optimization of the enantioselectivity for the reduction of prochiral enamides in up to 96 % ee. The influence of the nature of the spacer, diarylphosphine residue, guest protein and solvent on activity and selectivity will be presented. Such artificial metalloenzymes based on the biotin–avidin technology display features that are reminiscent of both homogeneous and of enzymatic catalysis.





[1] Skander, M., Humbert, N., Collot, J., Gradinaru, J., Klein, G., Loosli, A., Sauser, J., Zocchi, A., Gilardoni, F., Ward, T. R. *J. Am. Chem. Soc.* **2004**, *126*, 14411

Inorganic and Coordination Chemistry **117**

Microcalorimetry as a Facile Way to Show Properties of Polyamines

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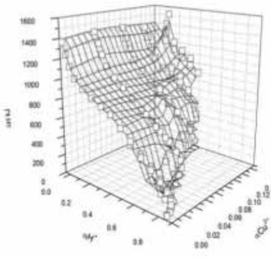
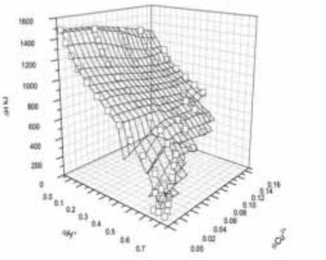
It is well known, that understanding of polyelectrolyte properties in solution is based on the knowledge of the thermodynamic properties. Up to now, there is only a small number of microcalorimetry titrations of polyelectrolyte solutions published. We carried out potentiometric and microcalorimetric titrations of linear and branched polyamines as their hydrochlorides at 25°C and 65°C, to investigate the influence of the structure on the acid-base properties.

In addition we studied the complexation of Cu^{2+} by the polyamines using microcalorimetry and potentiometry. The enthalpy changes measured are presented as function of the degree of protonation and the amount of Cu^{2+}bound.



LPEI -Cu^{2+}



BPEI -Cu^{2+}

The thermodynamic parameters ΔH, ΔG and TΔS were calculated as a function of the degree of protonation and the amount of Cu^{2+} bound at high ionic strength of LPEI, BPEI and PPI. The different behaviour of LPEI, BPEI and PPI is discussed.

Inorganic and Coordination Chemistry **118**

New Dendrimeric Phosphinate Containing Potential MRI Contrast Agent

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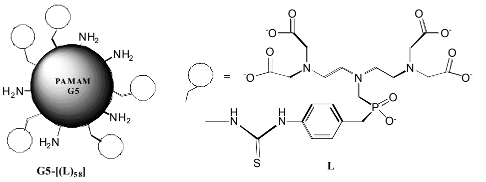
‡Laboratoire de chimie inorganique et bioinorganique, Ecole Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland

The phosphorus analogue of DTPA, promising fast water exchange, was conjugated with PAMAM G5 dendrimer via benzyl-thiourea linkage.



The proton relaxivity of gadolinium(III) complex G5-$[Gd(L)]_{58}$ measured at 37 °C, 20 MHz and pH 6 was 26.8 $mM^{-1}s^{-1}$. The relaxivity decreases with increasing temperature, therefore slow water exchange is not limiting the relaxivity.[1] The phosphinic function allows second sphere water molecules in the system which enhance the overall relaxivity. The ^{17}O and ^{1}H relaxation rates have been analysed using Lipari-Szabo model, modified for the presence of second sphere water molecules. Free NH_2 groups give the possibility to introduce a targeting group into the molecule, which would increase the specificity of this potential MRI contrast agent.

[1] S. Laus, A. Sour, R. Ruloff, É. Tóth, A. E. Merbach, *Chem. Eur. J.* **2005**, *11*, 3064.

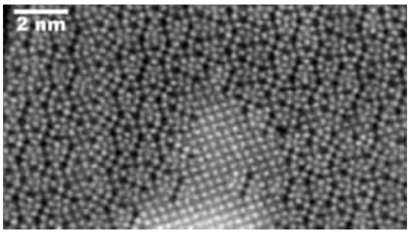
Inorganic and Coordination Chemistry **119**

Oxidation Products of $Nb_4W_{13}O_{47}$

F. Krumeich and R. Nesper

Laboratory of Inorganic Chemistry, ETH Zurich, 8093 Zurich, Switzerland

The members of the solid solution series $Nb_{8-n}W_{9+n}O_{47}$ (0<n<5) crystallize in a threefold superstructure of the tetragonal tungsten bronzes [1]. While an oxidation of these not fully oxidized phases at T_{OX} = 1200 °C leads to a separation into the thermodynamically stable phases, lower oxidation temperatures result in unusual products that contain new structural elements and ordering variants [2,3]. In this contribution, we report on the investigation of the oxidation product of $Nb_4W_{13}O_{47}$ by scanning transmission electron microscopy applying a high-angle annular dark field detector (HAADF-STEM). At the selected imaging conditions (Z contrast), not only the metal positions are revealed by this technique but additional information about the elemental distribution can be obtained as well.



HAADF-STEM image of $Nb_4W_{13}O_{47}$ oxidized at T_{OX} = 1000°C, showing a segregation of WO_3 embedded in the bronze-type matrix.

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[2] F. Krumeich, *J. Solid State Chem.* **119** (1995) 420.
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Inorganic and Coordination Chemistry **120**

Mechanistic Studies of the Reaction of Peroxynitrite with Nitrosyliron(II)myoglobin and Nitrosyliron(II)hemoglobin

Francesca Boccini, Anastasia S. Domazou, and Susanna Herold

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Nitrosyliron(II)hemoglobin ($HbFe^{II}NO$) and nitrosyliron(II)myoglobin ($MbFe^{II}NO$) have been proposed to represent a stabilized form of $NO^{\bullet}$. The dissociation of $NO^{\bullet}$ from these complexes is very slow (10^{-5}–10^{-4} s^{-1}), whereas it occurs at a rate of 1–10 s^{-1} from the oxidized forms, $HbFe^{III}NO$ and $MbFe^{III}NO$. Therefore, it is conceivable that the release of $NO^{\bullet}$ may first require the outer-sphere oxidation of the iron center:

$$(1) \quad HbFe^{II}NO + Oxidant \rightarrow HbFe^{II}NO$$

$$(2) \quad HbFe^{III}NO \rightarrow HbFe^{III} + NO^{\bullet}$$

Among other oxidants, it has been shown that peroxynitrite ($ONOOH/ONOO^{-}$) can oxidize $HbFe^{II}NO$ [1]. Preliminary results show that a similar reaction takes place with $MbFe^{II}NO$, both in the absence and in the presence of carbon dioxide. Peroxynitrite is known to react with carbon dioxide to produce 1-carboxylato-2-nitrosodioxidane ($ONOOCO_2^{-}$). This adduct partly decays to $CO_3^{\bullet-}$ and $NO_2^{\bullet}$. Therefore, to better understand the mechanism of the reactions of peroxynitrite with $HbFe^{II}NO$ and with $MbFe^{II}NO$ in the presence of carbon dioxide, we also carried out a pulse radiolysis study of the reactions of $HbFe^{II}NO$ or $MbFe^{II}NO$ with $CO_3^{\bullet-}$ or with $NO_2^{\bullet}$. Possible mechanistic hypotheses will be discussed.

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Inorganic and Coordination Chemistry **121**

Dithiine-maleimide functionalized ET derivatives. Synthesis and characterization of new building blocks for hydrogen bonded CT compounds, transition metal complexes or TTF-porphyrins or -phthalocyanines

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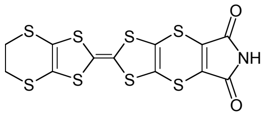
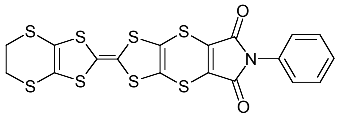
Covalent attachment of metal ion binding groups to bis(ethylenedithio)-tetrathiafulvalene (ET) derivatives and their linkage into supramolecular systems has been chosen as a strategy in the elaboration of functional molecular materials with multiphysical properties.[1-3]
Here, the syntheses and characterization of the two dithiine-maleimide ET derivatives **1** and **2** are reported.



1



2

Compound **1** can be used as precursor for a carboxylate or imide functionalised ET-derivative. It can also be a building block for porphyrins or phthalocyanines with annelated TTF units. Oxidation of **1** could lead to charge-transfer complexes with hydrogen bonding interactions.[4]

[1] F. Iwahori et al., *Inorg. Chem.*, **2001**, *40*, 6541
[2] E. Coronado et al., *Nature*, **2000**, *408*, 447
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[4] Y. Morita et al., *Org. Lett.*, **2002**, *4*, 2185

Inorganic and Coordination Chemistry **122**

High relaxivity confined to a small molecular space: a metallostar-based, potential MRI contrast agent

João Bruno Livramento, Éva Tóth, Angélique Sour, Robert Ruloff, André E. Merbach

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With a crucial role in the development of magnetic resonance imaging (MRI), paramagnetic contrast agents have decisively contributed to the medical diagnosis field.
The purpose of the paramagnetic complex (mainly Gd^{III} complexes) is to enhance the contrast between the healthy and pathological tissues.
Here we present the synthesis and physico-chemical characterization of a bifunctional bipyridine-based poly(amino carboxylate) capable of binding selectively Gd^{III} and Fe^{II} [1]. The ligand self-assembles along with Gd^{III} and Fe^{II} to form a metallostar thus packing into a small space 6 paramagnetic Gd^{III} atoms.This rigid small molecular weight compound displays the highest "relaxivity per molecular mass" ever reported for a Gd^{III} complex as measured by ^1H NMRD profile.

[1] João Bruno Livramento, Éva Tóth, Angélique Sour, Alain Borel, André E. Merbach, Robert Ruloff, *Angew. Chem. Int. Ed.*, **2005**, *44*, 1480.

Inorganic and Coordination Chemistry **123**

Dinuclear Gd^{III} complexes of xylene-based DO3A ligands: aggregation in aqueous solution

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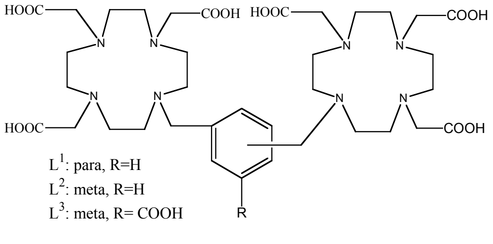
a. Laboratoire de Chimie Inorganique et Bioinorganique, Ecole Polytechnique Fédérale de Lausanne, EPFL-BCH, CH-1015 Lausanne, Switzerland
b. Université de Bretagne Occidentale, UMR-CNRS, 29238-Brest, France

The proton relaxivity, thus the efficacy of Gd-complexes used as MRI contrast agents is influenced by several parameters, such as their hydration number, water exchange rate, or rotation. Due to their increased molecular size and consequent slower rotation, dinuclear complexes are favorable over monomers.

Here we present the results of an ^{17}O NMR and NMRD study on the Gd^{III} complexes of three new, DO3A-derivative dimers (Scheme). In addition, UV-Vis spectrophotometry was used on the Eu^{III} analogues with the objective of assessing the hydration state. Surprisingly, these chelates revealed to be eight-coordinate, with one inner sphere water molecule.

The field dependence of the ^{17}O and ^1H longitudinal relaxation rates evidences strong aggregation in aqueous solution for all three complexes, resulting in remarkably high proton relaxivities. The aggregates can be disrupted by addition of phosphate, which, however, also interferes as a chelating agent by partially replacing the inner sphere water.



Inorganic and Coordination Chemistry **124**

Metal binding of Wheat *E_c-1* Metallothionein

Estevão Peroza, Eva Freisinger

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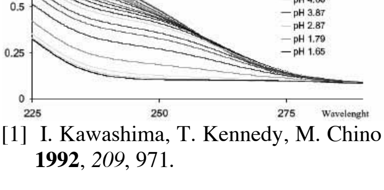
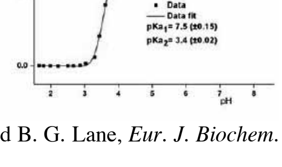
Metallothioneins (MTs) constitute a family of proteins widely present in living organisms (from mammalians to prokaryotes), with the highest known metal content, after ferritins. Involved in the metabolism of metal ions, MTs regulate the levels of essential elements such as Zn^{2+} and Cu^+, and participate in the detoxification of heavy metals like Cd^{2+} or Hg^{2+}. MTs exhibit low molecular weight (~7 kDa) with a high content of cysteine residues, by which they are able to coordinate d^{10} metal ionsWithin the protein molecule, these metals and thiolate ligands are arranged in clusters. For tetrahedral coordination spheres, clusters containing 3 or 4 metals have been reported for MTs so far. Structural information about higher-plant MTs is not available to the same extent as it is for the broadly investigated mammalian isoforms.
Ec-1 from wheat is a 81 amino acids MT[1] and its spectroscopical characterization with respect to metal binding ability as function of pH has been the subject of our late research. pH titration experiments provide information about the protein-metal binding, such as apparent pK_a values, and these and these data will be presented and discussed.





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Inorganic and Coordination Chemistry **125**

Experimental Investigations of Azamacrocomplexes inducing the B- to Z-DNA Transition

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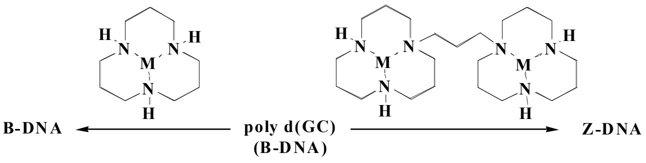
1,3-bis(1,5,9-triazacyclododecyl)propane [1,2,3] has been used as a dinucleating ligand to form the corresponding nickel, zinc and the novel copper and cobalt complexes. A different behaviour was observed when the mono- and dinuclear metal complexes were tested for their ability to induce the B- to Z-DNA transition. Dinuclear Zn, Ni and Cu were able to induce transition; whereas neither the mononuclear complexes nor the dinuclear Co or the ligand alone induced the Z-DNA formation.



M = Cu^{2+}, Ni^{2+} and Zn^{2+}

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Inorganic and Coordination Chemistry **126**

Inter- and Intra-Solid Reactions studied by X-ray Powder Diffraction

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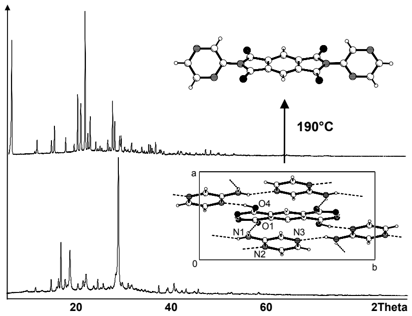
In solid state chemistry when only microcrystalline materials are obtained, X-ray powder diffraction becomes the most important tool for analysing unknown phases. *Ab-initio* structure determinations have been carried out on metal organic compounds obtained in solid state transformation processes [1,2], and on new organic materials. The latter were synthesised by solvent free reactions applying green chemistry principles. The competition of inter- and intramolecular interactions in organic crystals and co-crystals will be discussed.



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Inorganic and Coordination Chemistry **127**

2-D and 3-D Metal-Organic Frameworks: A Crystal Engineering Approach

González Mantero Déborah, Neels Antonia, Fritz Stoeckli
and Helen Stoeckli-Evans

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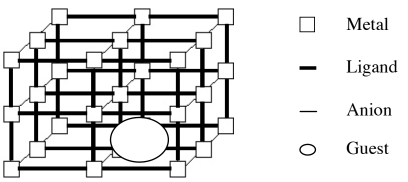
2007 Neuchâtel, Switzerland.

The synthesis of new metal-organic frameworks can be carried out by rational self-assembly using the principles of crystal engineering. Metal ions are usually coordinated to two or more bridging ligands giving a final semi-rigid structure suitable for adsorption, catalysis, etc. Nano-porous materials based on new linear ligands coordinated to metallic centers are presented and have been characterized by physical and chemical methods. These compounds have the general formula $[M(L)A]_n$ where M = Cu^{2+}, Co^{2+}, Ni^{2+}, L = 4,4'-bipyridyl, 4,4′-bipyridyl N,N′-dioxide and A = $S_2O_6^{2-}$, SO_4^{2-} [1].



[1] Neels Antonia, Alfonso Montse, González Mantero Déborah, Stoeckli-Evans Helen, *Chimia* **2003**, *10*, 619.

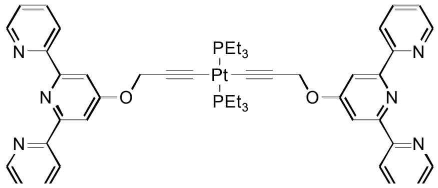
Inorganic and Coordination Chemistry **128**

Formation of heterotetranuclear macrocycles from reactions of platina-homoditopic ligands with M(II) (e.g. M = Fe).

Edwin C. Constable, Catherine E. Housecroft, Markus Neuburger, Sylvia Schaffner and Ellen J. Shardlow

University of Basel, Spitalstrasse 51, CH-4056 Basel, Switzerland.

A series of platinum(II) centred ditopic ligands with 2,2':6',2''-terpyridine binding domains has been prepared. An example is compound **1**.



Compound **1**
1 R = Et

Compound **1** reacts with Fe(II) to give a [2+2] metallomacrocycle [1] in preference to a large macrocycle or polymer. The effects of altering group R in the phosphine and the chain length of the ligand are being investigated and a series of different compounds has been synthesised.
Platinum-alkyne complexes are known for their luminescent properties, and fluorescence studies on these compounds have also been carried out.

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Inorganic and Coordination Chemistry **129**

A Chemosensor Array for the Colorimetric Identification of 20 Natural Amino Acids

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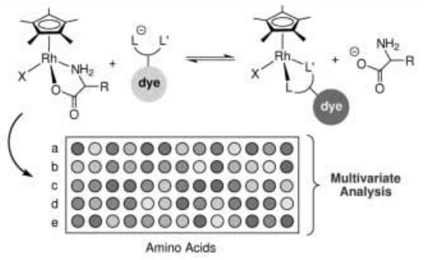
A synthetic receptor, which is bound via non-covalent interactions to an indicator, is able to function as a chemosensor.[1] The combination of several non-specific chemosensors comprises a sensor array.[2] In the following we describe a sensor array, in which the respective sensors are assembled from commercially available building blocks at different pH. This array allows the differentiation of 20 natural amino acids with high fidelity using UV/vis spectroscopy in combination with multivariate analysis.[3]



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Inorganic and Coordination Chemistry **130**

Metal-binding Affinity of Metallothionein 2 from Chickpea (*Cicer arietinum*)

Xiaoqiong Wan, Eva Freisinger

Institute of Inorganic Chemistry, University of Zürich, Winterthurerstrasse 190, 8057 Zürich, Switzerland

Metallothioneins (MTs) are a super-family of small proteins featuring an outstandingly high content of the amino acid cysteine as well as of d^{10} metal ions. MTs are abundant in nearly all kingdoms of life, with the mammalian isoforms being the best studied. Few attempts have been done so far to study metallothioneins in plants [1].
For the present study, the 14 cysteine residues containing metallothionein 2 (MT2) from Chickpea (*Cicer arietinum*) was cloned and over-expressed in *E. coli* and found to bind a number of d^{10} metal ions. The fully loaded Zn- and Cd-forms showed the characteristic absorption spectra for the corresponding metal-thiolate clusters [2]. Metal-to-protein ratios were determined. Apparent binding constants for different metal ions were estimated by following the absorbance change of specific charge-transfer bands in spectrophotometric pH titration experiments. The titration curves reveal two distinct steps of unequal size, suggesting a dissimilarity of metal ion binding sites of some kind.

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Inorganic and Coordination Chemistry **131**

Hyperfine interactions in aqueous solution of Cr^{3+}: an *ab initio* molecular dynamics study.

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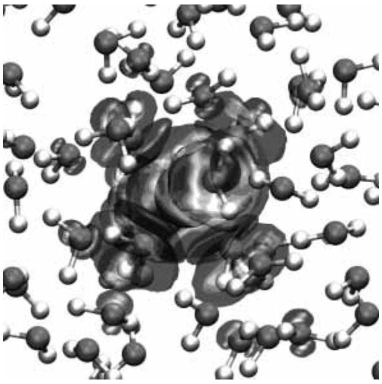
We performed an *ab initio* molecular dynamics simulation of the paramagnetic transition metal ion Cr^{3+} in aqueous solution. Isotropic hyperfine coupling constants between the electron spin of the chromium ion and nuclear spins of all water molecules have been determined for instantaneous snapshots extracted from the trajectory. The coupling constant of first sphere oxygen, $A_{iso}(^{17}O_I) = 1.9$ MHz, is independent on Cr-O_I distance but increases with the tilt angle for the water molecule approaching 180°. First sphere hydrogen spins have $A_{iso}(^{1}H_I) = 2.1$ MHz which decreases with increasing tilt angle and shows a Cr-H_I distance dependence. The hyperfine coupling constants for second sphere ^{17}O is negative and an order of magnitude smaller (-0.20 MHz) compared to first sphere.



Inorganic and Coordination Chemistry **132**

Chiral cyanide-bridged bimetallic networks based on cyclohexane-1,2-diamine

Olha Sereda & Helen Stoeckli-Evans

Institut de Chimie, Université de Neuchâtel, Avenue de Bellevaux 51, CH-2007 Neuchâtel, Switzerland

The hexacyanometallates are interesting synthons for material design as th have the potential to produce fascinating metal-organic frameworks. Chi structures are a new target for the lattice architecture in the field of magne materials. There are a only very few examples where cyclohexane-1,2-diami has been incorporated into cyanide-containing complexes resulting in t formation of ferromagnets [1], [2], [3]. We will present some new chi cyanide-bridged bimetallic networks, $[M(trans\text{-}(1S,2S)\text{-}chxn)_2]_n[Me(CN)$ (where M = Cu, Ni; Me = Ru, Cr, Co; n = 2, 3; m = 1, 2; trans-(1S,2S)-chxn trans-cyclohexane-1,2-diamine), and their structural features and magne properties will be discussed.

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Inorganic and Coordination Chemistry **133**

In situ Monitoring of Transition Metal Catalysts during the Synthesis of Propylene Carbonate in Carbon Dioxide

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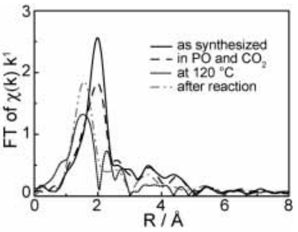
Department of Chemistry and Applied Biosciences, Swiss Federal
Institute of Technology, ETH Hönggerberg, CH-8093 Zürich

The synthesis of propylene carbonate by fixation of carbon dioxide in propylene oxide is an interesting chemical process, because of the direct use of carbon dioxide as reactant and because of the simultaneous use of CO_2 as solvent leading to a “solventless” reaction. Various homogeneous catalysts exist for this reaction, but their activity is still quite low compared to other chemical syntheses. Hence, a better understanding of the reaction mechanism is required. Ni-based catalysts were found catalytically active during the insertion of carbon dioxide in propylene carbonate and XAS measurements were performed to relate their structure to the catalytic activity. Especially, more insight into the reaction has been gained by high pressure *in situ* EXAFS studies with a specially designed batch reactor [1]. An expanded coordination sphere of the transition metal was beneficial for the catalytic activity of the whole complex. Nickel chloride complexes were quite active, in spite of an octahedral coordination. *In situ* EXAFS measurements, which are shown in the figure for methylimidazole nickel chloride, revealed the loss of the chloride during reaction and this resulted in a coordination vacancy. This seems to be beneficial for the performance of the reaction.



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Inorganic and Coordination Chemistry **134**

Ruthenium PNNP Complexes as Catalysts for Asymmetric Nucleophilic Fluorination Reactions

Martin Althaus, Antonio Togni, Antonio Mezzetti*

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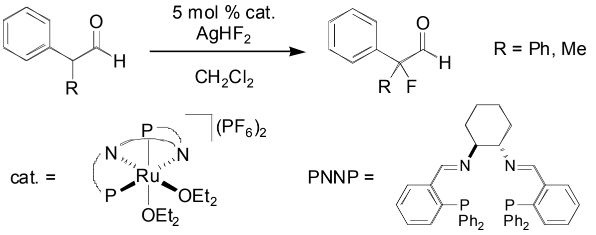
Organic compounds containing a C–F stereocenter are important biomolecules. Highly enantioselective electrophilic fluorinations of 1,3-dicarbonyl compounds using Ti/TADDOLato[1] and Ru/PNNP[2] catalysts have been studied by our group.

Developing catalytic nucleophilic fluorination reactions, we found that Ru/PNNP complexes catalyze the hydrofluorination of *meso*-epoxides. Cyclopentenoxide and cyclohexenoxide give the corresponding 2-fluoroalcohols with $AgHF_2$ as HF source in low yields and with enantioselectivities of 25 and 10 % ee, respectively. In this reaction, phenylacetaldehydes are formed by epoxide rearrangement and subsequently fluorinated at the α-position, as confirmed by the independent reaction of the aldehydes:



We are now investigating the stoichiometry and course of this reaction, for which an “Umpolung” of the aldehyde enol probably occurs.

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Inorganic and Coordination Chemistry **135**

Solvothermal Synthesis and Crystal Chemistry of Fluoromolybdates

Alexej Michailovski and Greta R. Patzke

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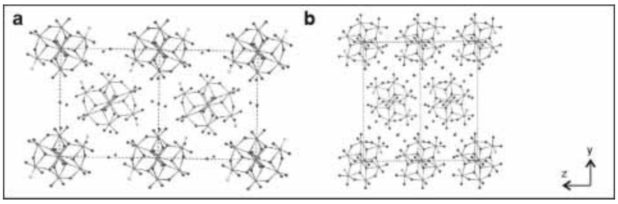
ETH Hönggerberg, 8093 Zürich, Switzerland

Solvothermal methods are a powerful synthetic tool for the preparation of inorganic materials [1], and their full exploration and systematisation would be a major contribution to predictive inorganic synthesis. In the course of our previous studies [2], we have systematically accessed a series of macrocrystalline alkali polymolybdates ($M_xMo_yO_z{\cdot}nH_2O$; y = 2 – 8, 10). This approach has been turned into a targeted search for new structural motifs:

⇒ The combination of specific alkali cations exerts a templating effect upon the Mo-O framework: the packing motif of alkali octafluoromolybdates ($(M, M')_6Mo_8O_{26}F_2{\cdot}nH_2O$; M = K – Rb, M' = Cs), for example, can be controlled by adjusting the cation ratios (cf. Fig.).

⇒ New types of alkali fluoromolybdates, such as $[Mo_6O_{18}F_6]^{6-}$-rings in $(M, M')_6Mo_6O_{18}F_6{\cdot}6H_2O$ compounds ($M = Li – Cs, NH_4^+$), are now available from solvothermal reactions involving fluorine-containing additives.

⇒ The electrostatic interactions between the cations and the polymolybdate surroundings are investigated in terms of MAPLE calculations and electrostatic point potentials.



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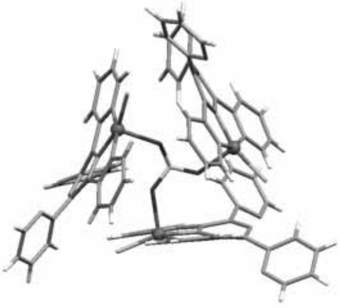
Inorganic and Coordination Chemistry **136**

Triangular copper(II) tetrakis(2-pyridyl)pyrazine supra-molecular species, encapsulating nitrate, sulfite and perchlorate anions.

Gaël Labat, Laurette Schmitt, Gilles Gasser & Helen Stoeckli-Evans

Institut de Chimie, Université de Neuchâtel, Av. de Bellevaux 51,
CH-2007 Neuchâtel, Suisse

Since the publication of the first binuclear copper(II) complex of 2,3,5,6-tetrakis(2-pyridyl)pyrazine (TPPZ) [1] this ligand has been shown to be unusually flexible for the formation of mono- and binuclear compounds, and some polymeric and supra-molecular species. There are more than 60 crystal structures of transition metal complexes involving TPPZ deposited in the Cambridge Crystal Structure Data Base [2]. Recently we have synthesized some unusual triangular copper (II) complexes of TPPZ that encapsulate mono-anions. We shall discuss the formation of these unique triangular supra-molecular species, $\{[Cu(TPPZ)Cl]_3A\}A_2$, where A = NO_3^-, SO_3^-, ClO_4^-, that have been characterized crystallographically, analyzed by cyclic voltammetry and tested for their magnetic properties.



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Inorganic and Coordination Chemistry **137**

Pt-Ba/Alumina NO_x storage-reduction catalysts: influence of Ba loading on NO_x storage behavior

M. Piacentini, M. Maciejewski and A. Baiker

Department of Chemistry and Applied Biosciences,
Swiss Federal Institute of Technology, ETH Hönggerberg, CH-8093 Zurich

A series of $Pt\text{-}Ba/Al_2O_3$ catalysts with Ba loadings in the range 4.5-28 wt. %, used for pollution control of lean engines, has been prepared by wet impregnation of Pt/Al_2O_3 with barium acetate ($Ba(Ac)_2$) as Ba precursor. The build-up, thermal stability and NO_x storage behavior of the deposited Ba-containing species was followed by means of XRD and thermogravimetry (TG) combined with mass spectroscopy (MS). In calcined catalysts three different Ba-containing species could be distinguished based on their crystallinity and thermal stability. The relative concentration of these species varied with the Ba loading [1].

Characterization after NO_x exposure showed that the different Ba-containing phases present in the catalysts possess different reactivity for barium nitrate formation, depending on their interfacial contact [2]. The study revealed that during the NO_x storage process a new thermally instable $BaCO_3$ phase is formed by reaction of evolved CO_2 with active BaO. The fraction of Ba-containing species that are active in NO_x storage depends on the Ba loading, showing a maximum at a Ba loading of about 17 wt. %.

Lower and higher Ba loading resulted in a significant loss of the overall efficiency of the Ba-containing species in the storage process. The loss in efficiency observed at higher loading is attributed to the lower reactivity of the HT-$BaCO_3$ which becomes dominant at higher loading, and the increased mass transfer resistance.

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Inorganic and Coordination Chemistry **139**

A New Family of Nitrosyl Rhenium Complexes with N-Heterocyclic Carbene Ligands

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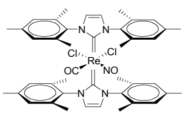
Recently the chemistry of transition metal nitrosyl complexes has attracted growing interest. In our group we have investigated the chemistry of mono and dinitrosyl complexes of rhenium containing various phospohorus donors ligands [1], which were found to be excellent catalysts for hydrogenation and hydrosilylation [2] and show catalysis for some olefin metathesis [3].

Nucleophilic N-heterocyclic carbene ligands are phosphine mimics, which can be used to tune catalytic systems for increased activity and selectivity. Here we report the synthesis of new nitrosyl rhenium complexes, bearing the Imes carbene ligand. The new and well defined complexes **1, 2** and **3** are tested for their catalytic potential.



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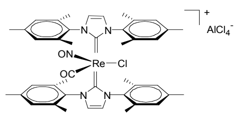

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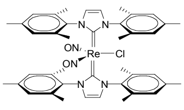

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Inorganic and Coordination Chemistry **138**

Synthesis and Characterization of the New Zintl Phase $Eu_3Mg_2Ge_6$

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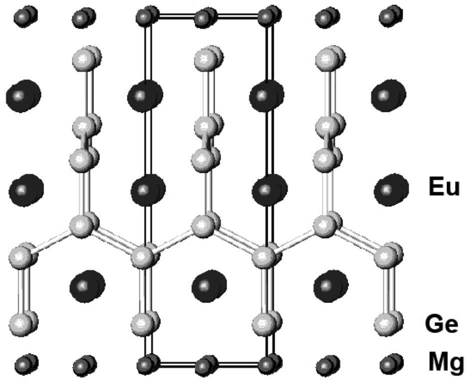
ETH Zürich, Wolfgang Pauli Str. 10, CH-8093 Zürich, Switzerland

The new Zintl phase $Eu_3Mg_2Ge_6$ was prepared and structurally characterized. The compound crystallizes in the tetragonal space group *P*-4*m*2 (No. 115) with a = 4.476(1) Å and c = 12.794(3) Å. The structure contains the novel Zintl anion $^1_4[Ge_6^{10-}]$ with an infinitely branched chain of linked perpendicular zig-zag chains, related to sections of the α-$ThSi_2$ structure type.



The occurrence of diffuse scattering in the [0kl]-layer points to the presence of stacking faults. Different models for stacking faults were developed and discussed, favoring one possibility, which yields a good qualitative explanation of the diffuse scattering intensities [1] and also for the observed residual electron density.

[1] Th. Proffen, R. B. Neder, J. *Appl Cryst.* **1997**, *30,* 171

Inorganic and Coordination Chemistry **140**

Kinetic Studies on Hydride Insertion Reactions of $WH(CO)(NO)(PMe_3)_3$ with Ketones

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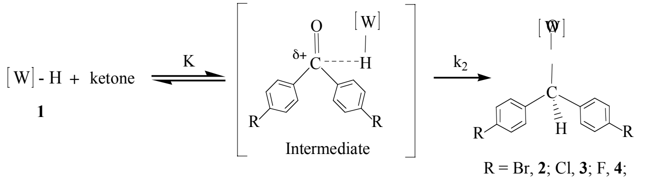
Detailed mechanistic studies showed that transition metal hydride complexes play an essential role in hydrogenation reactions. In the case of the "ionic hydrogenation of ketones", appropriate transition metal hydrides can act as H^- donors while stoichiometric amount of an acidic substrate can act as a H^+ source, together representing an equivalent of H_2 [1], [2].

As a first approach to the understanding of the "ionic hydrogenation", the insertion reaction of complex $WH(NO)(CO)(PMe_3)_3$ (**1**) with 4,4'-dibromo-, -dichloro-, -difluoro-, -dimethoxy-benzophenone and benzophenone was studied to afford the corresponding alkoxide complexes *mer*-$W(CO)(NO)(PMe_3)_3(OCH(C_6H_4)_2R_2)$ (R = Br, **2**; Cl, **3**; F, **4**; OCH_3, **5** and H, **6**). The insertion reactions of **1** with this selection of ketones were pursued at 60°C by ^{31}P NMR spectroscopy under pseudo first-order rate conditions.



R = Br, **2**; Cl, **3**; F, **4**;
OCH_3, **5**; H, **6**

The constants k_1, k_{-1}, K and k_2 were experimentally determined and the constants of the insertion steps ρ were calculated from the Hammet diagrams $\log(k_2/k_2^0)$ vs σ. The rate constants k_2 follow the Hammet constants of substituents and decrease in the ligand order: Br > Cl > F > H > OCH_3. The mechanism of these insertion reactions has furthermore been investigated in the presence of the acidic substrates alcohols that are known to increase dramatically the rate of "ionic hydrogenation" reactions.

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Inorganic and Coordination Chemistry **141**

New Water Soluble Nitrosyl Rhenium Complexes

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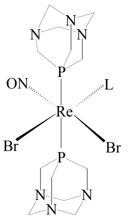
Aqueous homogeneous catalysis is nowadays receiving great attention due to the characteristics of water as inexpensive and nontoxic solvent [1]. Our goal is to prepare new water soluble rhenium hydrides using the neutral water soluble ligand 1,3,5-triaza-7-phosphaadamantane (PTA). At present, just one example of water soluble hydride with this phosphine is known [2],[3],[4]. We report the synthesis and characterization of new water soluble compounds: $[ReBr_2(NO)(PTA)_3]$ and $[ReBr_2(MeCN)(NO)(PTA)_2]$ as potential intermediates for hydride derivatives. Attempts to prepare the corresponding rhenium hydrides as well as investigations on the properties of all these species are presented.



L = MeCN, PTA

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[3] Frost, B.J.; Mebi, C.A. *Organometallics* **2004**, *23*, 5317-5323.
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Inorganic and Coordination Chemistry **143**

Metal halide complexes of thiolate ligands: anion dependence.

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CH-2007 Neuchâtel, Suisse

A series of transition metal thiolate complexes, with the general formula MX_2Y_2, where X = Cl, Br, I and Y = tetramethylthiourea and thiosemicarbazide, have been synthesized and characterized both spectroscopically and crystallographically. It has been found that varying the halide used has a considerable influence of the symmetry of the complex formed.
This aspect of the geometry of the complexes will be discussed and the structures will be compared with those of other transition metal complexes of the same ligands deposited in the Cambridge Crystallographic Data Base [1].

[1] F. H. Allan, Acta Crystallogr., **2002**, *B58, 380.*

Inorganic and Coordination Chemistry **142**

Manganese Alkynyl Complexes – Precursors for Paramagnetic Rigid Rod Materials

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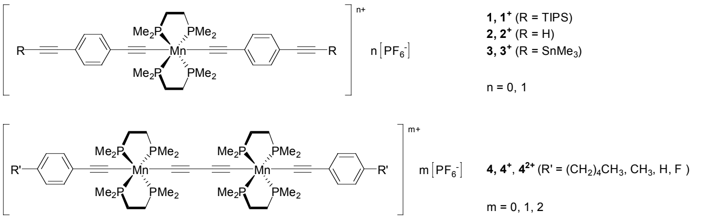
CH-8057 Zürich, Switzerland; e-mail: fritzth@aci.unizh.ch

Complexes in which sp carbon chains span two transition metals $[L_nM\text{-}C_x\text{-}ML_n]$ have attracted great attention, from both the standpoint of fundamental properties and possible applications in molecular devices [1]. Much of this interest has been prompted by their rich redox chemistry, their unique electronic features, and the obvious connection to molecular wires having the ability to shuttle electrons across nanometer distances [2].



We synthesized and studied the properties of paramagnetic mono- and dinuclear manganese-acetylenes acting as potential building blocks for new rigid rod materials [3].

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[2] N. Robertson, C. A. McGowan, *Chem. Soc. Rev.* **2003**, *32(2)*, 96-103
[3] S. Kheradmandan, K. Heinze, H. W. Schmalle, H. Berke, *Angew. Chem.* **1999**, *111(15)*, 2412-2415, *Angew. Chem. Int. Ed. Engl.* **1999**, *38(15)*, 2270-2273

Inorganic and Coordination Chemistry **144**

Novel Coordinating Chiral Hexacoordinated Phosphate Anions for Stereocontrol and Air-Stabilization of Cu(I) Complexes

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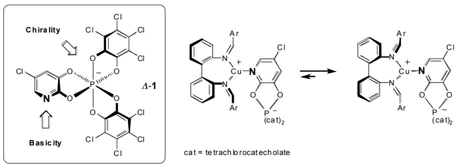
[b] Laboratoire de Cristallographie, Université de Genève, 1211 Genève 4

Configuration of cationic chiral transition metal complexes is generally controlled by non racemic ligands [1]. An interionic strategy, using first or second coordination sphere chiral counterions, can be even so considered [2].



We now report the synthesis and resolution of a novel hexacoordinated phosphate anion **1** (*Λ* or *Δ* enantiomer) that exhibits not only counterionic but also *Lewis* basic capacities. Upon association with chiral *Tropos* Cu(I) complexes, a stereoselective ion pairing occurs. Air-stable zwitterionic derivatives of **1** are readily isolated which can be used in catalytic enantioselective cyclopropanation and aziridination reactions.

[1] A. Von Zelewsky *Stereochemistry of Coordination Compounds*, John Wiley & Sons, Chichester, UK (1996). H. Brunner *Angew. Chem. Int. Ed. Engl.* **1999**, *38*, 1194.
[2] J. Lacour, R. Frantz, *Org. Biomol. Chem.* **2005**, *3*, 15 and references therein.

Inorganic and Coordination Chemistry **145**

Structural studies on the splice site formation of a group II intron ribozyme

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Most functional RNAs are compact, stable and tightly folded into a unique conformation.[1] Numerous of such folded RNA molecules are ribozymes, i. e. "enzymes" that consist completely of RNA. Among these ribozymes, group II introns are of special interest. These autocatalytic introns, which occur in bacterial genomes and in organellar genes of plants, funghi and lower eukaryotes, consist of a conserved set of six domains.[2] Before the RNA can carry out their assigned functions the non-coding introns have to be removed from the coding exons in a process called splicing. This can be performed by self-splicing introns like group II introns.[2] The correct recognition of the 5'-exon through a 10-15 base pairing interaction formed by two regions within the intron (exon binding sites, EBS1 and EBS2) and the last 10-15 nucleotides of the 5'-exon (intron binding sites, IBS1 and IBS2)[2] is decisive for a successful splicing event. Metal ions have not only been shown to be crucial for folding and catalysis,[3] but also to reside at the EBS1-IBS1 complex.[3, 4] We are now investigating the structural and metal ion requirements of this part by various spectroscopic techniques, e.g. NMR. Our data shows that the hairpin including EBS1 consists of a helical region followed by an unstructured single stranded part, which is ready for splice site recognition. The results of the structure analysis will be presented.

Financial support by the Boehringer Ingelheim Fonds (fellowship to D.K.) and the Swiss National Science Foundation (*SNF-Förderungsprofessur* to R.K.O.S.) is gratefully acknowledged.

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[2] K. Lehmann, U. Schmidt, *Crit. Rev. Biochem. Mol. Biol.* **2003**, *38*, 249-303.
[3] R. K. O. Sigel, A. Vaidya, A. M. Pyle, *Nat. Struct. Biol.* **2000**, *7*, 1111-1116.
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Inorganic and Coordination Chemistry **147**

Approaching a New Synthesis of Mononuclear Complexes of Chromium as Precursors to Rigid-Rod Chromium Acetylenes

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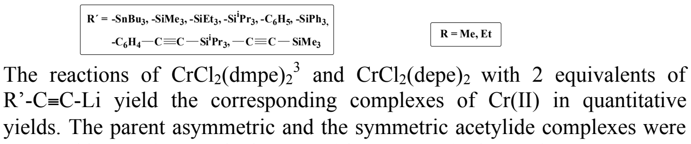
There is growing interest in complexes with two trans σ-alkynyl ligands[1] due to their potential application as building blocks in the synthesis of new dinuclear or oligonuclear rigid-rod complexes. These complexes are expected to display nonlinear optical properties or may have application as electronic materials, such as single electron devices[2]. They are anticipated to possess low energy work functions, which guarantees strong electron delocalization and coupling between the metal centers.



The reactions of $CrCl_2(dmpe)_2$[3] and $CrCl_2(depe)_2$ with 2 equivalents of R'-C≡C-Li yield the corresponding complexes of Cr(II) in quantitative yields. The parent asymmetric and the symmetric acetylide complexes were prepared by treating $CrCl_2(dmpe)_2$ with 1 or 2 equivalents of Na-C≡C-H.

[1] S. Kheradmandan, K. Heinze, H. W. Schmalle, H. Berke, *Angew. Chemi. Int. Ed. Engl.* **1999**, 38, 2270-2273.
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[3] G. S. Girolami, G. Wilkinson, A. M. R. Galas, M. Thorton-Pett and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, **1985**, 1339.

Inorganic and Coordination Chemistry **146**

Monoorganotin(IV) Complexes Containing *cis*-1,2-Bis(diphenylphosphino)ethylene: Solution and Solid State Structural Investigations

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†School of Chemistry, Bharathidasan University, Tiruchirappalli 620 024, India.

Interaction of chelating bisphosphines towards organotin(IV) halides has been the subject of several investigations. Many derivatives containing Sn-O-P fragments formed due to spontaneous aerial oxidation of phosphines are known [1]. On the other hand, the structurally characterized compounds containing direct Sn-P bond are scarce [2]. The comparatively high Lewis acidic monoorganotin(IV) halides, $RSnCl_3$ (R= Me, ^{n}Bu, Ph), are found to react with *cis*-1,2-Bis(diphenylphosphino)ethylene to form stable chelate complexes, in which no ligand oxidation has been observed. The solution and solid state structural studies revealing the molecular structure, the geometry and the *trans* influence of the ligand will be presented.

[1] C. Pettinari, F. Marchetti, A. Cingolani, R. Pettinari, A. Drozdov, S. Troyanov, *Inorg. Chim. Acta,* **2001**, *312*, 125 *and references therein.*
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Inorganic and Coordination Chemistry **148**

Synthesis and structure of new quinoxaline-fused tetrathiafulvalenes

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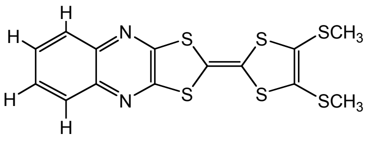
Suitably functionalized tetrathiafulvalenes (TTF) may lead to interesting molecules and materials combining different properties such as conductivity, magnetism and non-linear optics.[1] Fusing a quinoxaline unit to the TTF molecule gives rise to polarized π-extended systems, which might be regarded as A-π-D dyads.[2] There exist only very few quinoxaline-fused TTF's and no structural study was published.[3] We propose an improved synthesis for quinoxaline-fused TTF's and present the structure of quinoxalino-bismethylthio-tetrathiafulvalene (**1**). The crystal packing is determined by π-π stacking interactions and short CH-N contacts.



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[1] J. L. Segura, N. Martin, *Angew. Chem. Int. Ed.*, **2001**, *40*, 1372
[2] Y. Yamashita, M. Tomura, *J. Mater. Chem.*, **1998**, 8(9), 1933.
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Inorganic and Coordination Chemistry **149**

A Novel Photo-Responsive Tetrathiafulvalene Derivative

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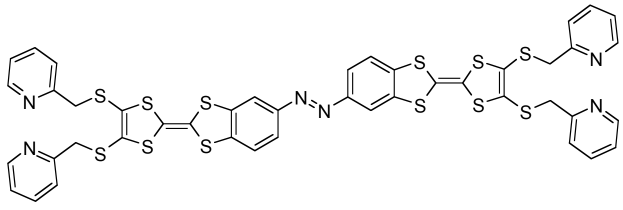
Azobenzene derivatives are known to undergo reversible trans-to-cis photoisomerization and cis-to-trans thermal isomerization [1]. Recently, a multifunctional molecular system, which involves two tetrathiafulvalene(TTF) moieties (π-electron donor) linked to an azobenzene group as a photoantenna unit, was designed and synthesized [2].

In order to search for the novel multifunctional materials, a synthetic route for a TTF derivative with peripheral metal-binding sites has been developed in our group.



Herein, we will describe the synthetic pathway and properties of this compound and exploit its coordination chemistry with a variety of transitions metal ions.

[1] J. Ansai, T. Osa, *Tetrahedron* **1994**, *50*, 4039.
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Inorganic and Coordination Chemistry **150**

Dinuclear Ruthenium Complexes with a Bridging BINAPO-Ligand – Synthesis, Catalysis and Structure

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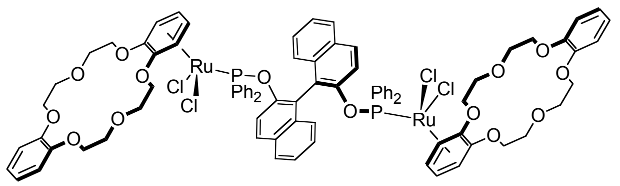
EPF Lausanne, ISIC, BCH 2412, 1015 Lausanne, Switzerland

Relative to the ubiquitious BINAP ligand, only relatively few examples of well-defined metal complexes with BINAPO ligands have been reported to date.[1]

Reaction of $[RuCl_2(\eta^6\text{-arene})]_2$ with BINAPO affords dinuclear complexes in which the two metal centers are bridged by a BINAPO ligand. This is a rare binding mode for dinaphthyl-based phosphine ligands The conformational stability is determined by means of NMR spectroscopy and the catalytic activity of these complexes is evaluated in the enantioselective hydrogenation of β-ketoesters.



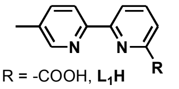
[1] (a) Alerza, V.; Bernardinelli, G.; Corminboeuf, C.; Frey, U.; Kündig, P. E.; Merbach, A. E.; Saudan, C. M.; Viton, F.; Weber, J. *J. Am. Chem. Soc.* **2004**, *126*, 4843-4853. (b) Clyne, D. S.; Mermet-Bouvier, Y. C.; Nomura, N.; RajanBabu, T. V. *J. Org. Chem.* **1999**, *64*, 7601-7611.

Inorganic and Coordination Chemistry **151**

Tridentate Bipyridine-based Ligands bearing Anionic Functions: from Monometallic to Polymetallic Lanthanide Complexes

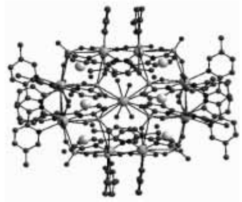
Steve Comby,[†] Daniel Imbert,[†] Anne-Sophie Chauvin,[†] Jean-Claude G. Bünzli,[†] Loïc J. Charbonnière[‡] and Raymond F. Ziessel.[‡]

[†]LCSL, Ecole Polytechnique Fédérale de Lausanne, BCH 1402, CH-1015 Lausanne, Switzerland, [‡]Laboratoire de Chimie Moléculaire,UMR 7008 au CNRS, ECPM, 25 rue Becquerel, 67087 Strasbourg Cedex 02, France



Interaction of trivalent lanthanide ions Ln(III) with tridentate ligands based on 2,2'-bipyridine framework substituted in the 6 position by different anionic functions is reported. Luminescence measurements carried out in solution on 1:3 (Ln:L) complexes at physiological pH point to sizeable quantum yields: 5.1 (L_1) and 7.0 (L_2) %, 34.5 (L_1) and 36.0 (L_2) % for Eu^{III} and Tb^{III}, respectively [1].

On the other hand, L_2 yields astonishing supramolecular assemblies which contain 9 Ln(III) ions and 16 ligands, $Na_6Ln_9L_{16}$; the structure of the monoclinic crystals could be solved for Ln = Eu, Gd, Tb and Er. These species only form under very specific and carefully chosen experimental conditions. Luminescence studies on the $Na_6Eu_9L_{16}$ edifice show that the Eu ions lie in two different environments, characteristics of central and external sites. The photophysical properties of these assemblies are also reported, both for homo- and heterometallic compounds. The magnetic susceptibility of the Gd-containing compound has been studied between 295 and 2K; it substantially decreases in the 7-2 K range, pointing to a weak antiferromagnetic interaction.



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Inorganic and Coordination Chemistry **152**

New tripodal ligands for efficient sensitization of lanthanide NIR luminescence

Steve Comby, Daniel Imbert, Jean-Claude G. Bünzli

Laboratory of Lanthanide Supramolecular Chemistry, Ecole Polytechnique Fédérale de Lausanne, BCH 1405, 1015 Lausanne, Switzerland.

New polydentate ligands have been synthesized to take advantage of the chelating effect of bidentate 8-hydroxyquinolinate subunits connected to a tris(N-amino)ethyl)amine framework. They form stable complexes with Ln(III) ions, the three chromophoric units being coordinated to the metal centre, exploiting the entropic effect generated by the anchor. We describe here their synthesis and their complexation reactions in aqueous media. We focus our work on the thermodynamic properties in water (pK_a's of the ligand, stability constants of the complexes), which have been investigated by the use of UV-vis spectrophotometric and potentiometric methods. Luminescence measurements have been carried out on the ligands and their complexes, revealing good photophysical properties. Moreover, visible excitation of the NIR luminescence, particularly for Nd^{III}, Er^{III} and Yb^{III} lanthanide ions, is also demonstrated.

Inorganic and Coordination Chemistry **153**

From the N_3O_2- Macrocyclic Building Block towards a N_3S_2-TTF Macrocycle

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Supramolecular structures with interesting physical properties can be produced by the combination of inorganic or organic building blocks. In these examples cyanide complexes are used as bridging ligands, whereas the pentadentate N_3O_2- macrocycle provides easily accessible metal coordination sites.

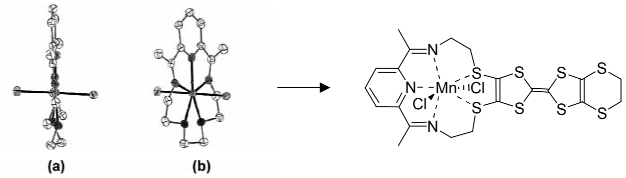

Figure: The pentadentate N_3O_2- macrocycle (a) side view, (b) front view; M(II): center, N: grey, O: black, Cl: light-grey (apical positions)

Metal centers coordinated by labile ligands, will link via μ-cyano bridges to hexa- or octacyano complexes to build up chains, 2-D sheets [1] or 3-D networks [2]. When paramagnetic centers are used, the resulting compounds often show pronounced magnetic interactions as shown in a variety of Prussian Blue analogues [3]. Studies on the new N_3S_2-TTF macrocycle are in progress.

[1] F. Bonadio *et al.*, *Inorg. Chem.*, **2005**, *44*, 969.
[2] P. Franz, *PhD Thesis*, **2003**, 19.
[3] P. Franz *et al.*, *J. Am. Chem. Soc.*, **2004**, *126*, 16472.

Inorganic and Coordination Chemistry **154**

Fluorescent Study on the Effect of M^{n+}-Binding on the Structure of Domain 5 of a Group II Intron Ribozyme

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Group II intron ribozymes are found in organellar genes of lower eucaryotes and plants as well as in bacterial genomes. These large molecular machines are self-splicing introns and they are also capable of acting as mobile genetic elements. Folding of the ribozyme into an active conformation is tightly controlled by the types and concentrations of metal ions present.[1] Monovalent cations like K^+ tend to take part in overcoming the repulsion forces in the negatively charged backbone of the RNA, whereas divalent ions like Mg^{2+} coordinate to specific sites and greatly influence tertiary contact formation and chemical catalysis.

The secondary structure of group II intron ribozymes can be divided into a set of six domains, each one accomplishing specific functions. The domain 5 (D5) of the yeast mitochondrial intron ai5γ forms a stable hairpin of 34 nucleotides, is highly conserved and crucial for catalytic activity. The effect of binding of divalent metal ions to D5 on its structure are presented. The change in structure is followed by fluorescence due to the incorporation of the fluorescent nucleotide base analogue 2-aminopurine (2AP) into the 3-nucleotide bulge in D5. This bulge is known to be flexible and acts as a metal binding platform. The fluorescence intensity change in metal titrations is used to determine apparent dissociation constants for different metal ions (Mg^{2+}, Ca^{2+}, Mn^{2+}, Cd^{2+}).

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

[1] R. K. O. Sigel, *Eur. J. Inorg. Chem* **2005**, online, DOI: 10.1002/ejic.200401007.

Inorganic and Coordination Chemistry **155**

New Rhenium Hydrides with Diazenido Ligands

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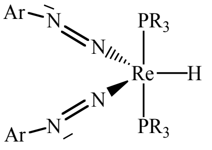
“Ionic hydrogenation” reactions have been known for long in organic chemistry, and recently it was shown [1] that transition metal hydrides can also catalyse these. Earlier homogeneous hydrogenations utilize noble metal catalysts and it would of great advantage if non-noble metal catalysis could be established. “Ionic hydrogenations” would offer the opportunity to develop catalysts based on middle transition metals. Dinitrosyl rhenium hydrides prepared in our group revealed such catalyic activity [2, 3]. Diazenido and nitrosyl ligands are isoelectronic. Therefore rhenium diazenido hydrides were made bearing various phosphine ligands. They have been fully characterized and were studied with respect to their catalytic properties and compared to the related dinitrosyl complexes.



Ar= aryl

R= cyclohexyl, isopropyl, phenyl

Their protonation behaviour was additionally investigated in order to simulate potential intermediates of the “ionic hydrogenation” catalysis.

[1] R. Morris Bullock. *Chem.Eur. J.* **2004**, 10, 2366-2374.
[2] A. Llamazares, H. W. Schmalle, H. Berke, *Organometallics* **2001**, 20(25), 5277-5288
[3] Huang, Wenjing; Berke, Hein.. *Chimia* **2005**, 59(3), 113-115

Inorganic and Coordination Chemistry **156**

Water-soluble arene ruthenium *trans*-1,2-diaminocyclohexane complexes as enantioselective transfer hydrogenation catalysts in aqueous solution

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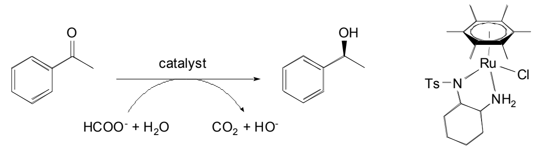
Based on the observation that a mixture of $[(p\text{-MeC}_6\text{H}_4\text{Pr}^i)\text{RuCl}_2]_2$ and *N*-(*p*-toluenesulfonyl)-1,2-diphenyl-ethylenediamine catalyses the transfer hydrogenation of ketones with sodium formate in aqueous solution [1-2], we synthesised two series of water soluble arene ruthenium complexes containing *trans*-1,2-diaminocyclohexane and derivatives thereof as chiral ligand.



The catalytic activity of these isolated and well characterised complexes was studied for the enantioselective transfer hydrogenation of acetophenone to give phenylethanol using HCOONa as hydrogen source in aqueous solution. In the best case, a catalytic turnover of 86 and an enantiomeric excess of 93% are obtained after 2h at 60°C.

[1] X. Wu, X. Li, W. Hems, F. King and J. Xiao, *Org. Biomol. Chem.* **2004**, *2*, 1818.
[2] Y. Ma, H. Liu, L. Chen, X. Cui, J. Zhu and J. Deng, *Organic Lett.* **2003**, *5*, 2103.

Inorganic and Coordination Chemistry **157**

Metal Ions and a Group II Intron - Investigations Into an Exciting Relationship

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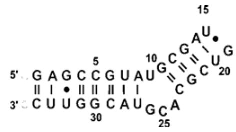
Group II introns are ribozymes - catalytically active RNA molecules - which are able to splice themselves out of pre-mRNA, a process which is essentia for the gene expression in a variety of organisms. In all group II introns the 34 nucleotides long domain 5 (D5) constitutes the central catalytic core.

The presence of divalent metal ions (M^{2+}), particularly Mg^{2+}, is crucial fo the function of the intron [1]. Based on the solution structure of D5 from the yeast mitochondrial intron ai5γ [2] as well as kinetic studies [3], we are now studying metal ion binding to this domain in more detail by NMR. This method allows us, to obtain informations on structural changes within the ribozyme caused by the coordination of metal ions like Cd^{2+} or Mn^{2+}. Moreover we are including sulphur-modified oligonucleotides into our studies; these synthetic derivatives together with Cd^{2+} and various other M^{2+} ions allow chemical and biological studies based on the different affinity of these metal ions towards phosphates and thiophosphates. These so-called thio-rescue experiments are frequently used to study RNA, but presume that the structure of the nucleic acid remains substantially unchanged when Mg^{2+} is replaced by, *e.g.*, Cd^{2+}.



[1] R. K. O. Sigel, *Eur. J. Inorg. Chem.* **2005**, online, DOI 10.1002/ejic.200401007.
[2] R. K. O. Sigel, D. G. Sashital, D. L. Abramovitz, A. G. Palmer, S. E Butcher, A. M. Pyle, *Nature Struct. Mol. Biol.* **2004**, *11*, 187-192.
[3] P. M. Gordon, J. A. Piccirilli, *Nature Struct. Biol.* **2001**, *8*, 893-898.

Financial support by the Swiss National Science Foundation (SNF-Förderungsprofessur to R.K.O.S., PP02-68733/1) is gratefully acknowledged.

Inorganic and Coordination Chemistry **158**

The synthesis and characterization of linked ruthenium-borane compounds using bidentate phosphine ligands and pendant phosphine complexes.

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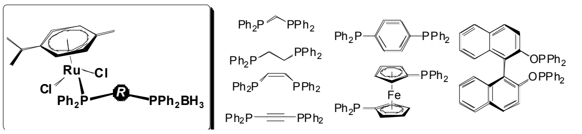
Lausanne, Switzerland

As part of our continuing investigation of ruthenium arene complexes for catalytic hydrogenation reactions we have embarked on developing methodologies for preparing compounds in which the catalytically active ruthenium arene fragment is linked to other metal and non-metal moieties [1]. In this report we describe the synthesis and characterization of several new linked ruthenium-borane systems using a range of different phosphine ligands. The X-ray structures of some of the complexes have been determined.



[1] For recent examples see: T. J. Geldbach, M. R. H. Brown, R. Scopelliti, and P. J. Dyson, *J. Organomet. Chem.*, **2005**, in press; C. Daguenet, and P. J. Dyson, *Organometallics*, **2004**, *23*, 6080; C. Daguenet, R. Scopelliti, and P. J. Dyson, *Organometallics*, **2004**, *23*, 4849; T. J. Geldbach, and P. J. Dyson, *J. Am. Chem. Soc.*, **2004**, *126*, 8114.

Inorganic and Coordination Chemistry **159**

Interaction of Cobalt(III) Complexes with Calf Thymus DNA

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2007 Neuchâtel, Switzerland

During the last decade extensive investigation of the binding of small molecules to DNA has been taken up to develop novel probes of DNA structure [1,2], new therapeutic agents that recognize or cleave DNA, and DNA-mediated electron transfer reactions.

The interaction of metal complexes of polypyridyl ligands with DNA has been extensively studied due to their cationic character and stability in aqueous medium. The characterization of DNA recognition by small transition metal complexes has been substantially aided by the DNA cleavage chemistry that is associated with redox active or photo-activated metal complexes. In addition, some of the transition metal complexes have been used as luminescent markers. The use of octahedral intercalators has permitted the targeting of specific DNA sites by matching the shape, symmetry and functionality of the metal complex to that of the DNA target. This led us to investigate the DNA interactions of the octahedral cobalt(III) bis-complexes of 1,3-bis(2-pyridyliminio)isoindoline [3] and 5,7-bis(2-aminopyridine)-5H-6,7-dihydropyrrolo[3.4-b]pyrazine, and also to study the effect of variation of ligand geometry on the binding mode of the complexes with DNA. The structure of the complexes has been determined and their interaction with DNA studied using various physical methods, such as, UV-Vis, fluorescence and circular dichroism spectroscopy and viscosity measurements.

[1] Holmlin, R. E.; Barton, J. K. *Inorg. Chem.* **1995**, *34*, 7.
[2] Erkkila, K. E.; Odom, D. T.; Barton, J. K. *Chem. Rev.* **1999**, *99*, 2777.
[3] Siegl, W. O. *J. Org. Chem.* **1977**, *42*, 1872.

Inorganic and Coordination Chemistry **160**

Highly *cis*- and Enantioselective Asymmetric Cyclopropanation of 1-Octene with Ruthenium PNNP Catalysts

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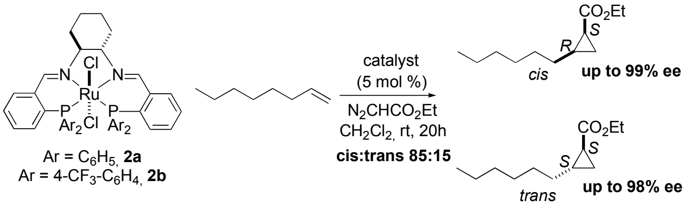
We have previously reported high *cis*-selective $[RuCl(PNNP)]^+$ catalysts for the asymmetric cyclopropanation of styrene [1]. We find now that a modified $[RuCl(PNNP)]^+$ catalyst performs the high *cis*-selective cyclopropanation of 1-octene. To the best of our knowledge, there are no other examples of *cis*-selective asymmetric cyclopropanation of aliphatic 1-alkenes. Silver salts ($AgSbF_6$, $AgBF_4$) abstract one chloride from **2a** and **2b** to give [RuCl(PNNP)]Y (Y=SbF_6, BF_4). The use of the electron-poor ligand **1b**, together with the choice of a low-coordinating counterion (SbF_6^-) resulted in good activity (48 % isolated yield) and excellent selectivities (*cis*:*trans* = 85:15, up to 99 % ee for the *cis* isomer).



The catalyst $[RuCl(\mathbf{1b})]SbF_6$ is superior to its analogue $[RuCl(\mathbf{1a})]SbF_6$ also in the cyclopropanation of styrene and α-methyl styrene. In the case of styrene, 69 % isolated yield, 99:1 *cis:trans* ratio, and 96 % ee for the *cis* isomer were obtained. α-Methyl styrene was cyclopropanated giving 92:8 *cis*:*trans* ratio and 96 % ee for the *cis* isomer.

[1] (a) Bachmann S., Furler M., Mezzetti A. *Organometallics* **2001**, *20*, 2102. (b) Bonaccorsi C., Bachmann S., Mezzetti A. *Tetrahedron: Asymmetry* **2003**, *14*, 845.

Inorganic and Coordination Chemistry **161**

Visualisation of Chirality in Fréchet-type Dendrimers using STM Imaging

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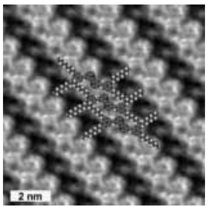
[b]Faculty of Physics/CeNS, LMU Munich, Germany

Nano-assemblies have gained a growing interest recently,[1] due to increased possibilities of probing self-assembled structures using scanning tunnelling microscopy (STM). The recent development of this field has led to potential applications in nanotechnology. There is also considerable potential for the study of structural properties of chemical interest using this new method.

STM images of monolayers of 2,2'-bipyridine ligands, functionalised with Fréchet-type dendrimers, showed the appearance of two different conformers.[2] By introducing chirality into the ligands, the preference for a particular conformer can be altered and the different patterns of the diastereomers can be imaged using STM.



[1] J.-M. Lehn, Supramolecular Chemistry: Concepts and Perspectives, VCH, Weinheim, **1995**.

[2] L. J. Scherer, L. Merz, E. C. Constable, C. E. Housecroft, M. Neuburger and B. A. Hermann, *J. Am. Chem. Soc.*, **2005**, *127*, 4033.

Inorganic and Coordination Chemistry **162**

A novel versatile tetradentate Monophosphorus Triolefin Ligand

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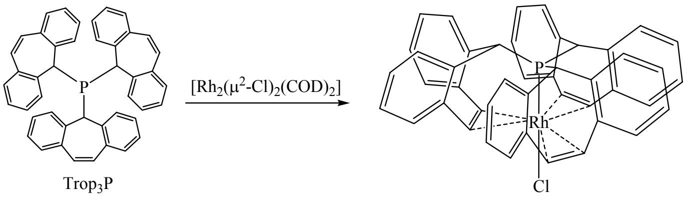
The newly synthesized tertiary phosphine tris(5H-dibenzo[a,d]cyclohepten-5-yl)phosphine (trop$_3$P) shows an interesting coordination chemistry towards various late transition metals (e.g. Pd, Rh, Ir, Pt, Ag, Au). Especially noteworthy is the very rigid structure of this ligand, which makes it perfectly preorganized for a tetradentate coordination (cf. scheme 1). Nevertheless it can also coordinate in a monodentate fashion, making it an extremely bulky triarylphosphine.



Scheme 1

We were able to show that this ligand can serve as a probe for the strength of the metal olefin bonding in the series of the palladium, rhodium and iridium complexes. In these species the anisotropy of the ^{31}P NMR chemical shift directly correlates to the amount of π-backbonding from the metal to the olefins.

Inorganic and Coordination Chemistry **163**

Coordination behaviour of the novel atropisomeric ligand 4,4'-biquinazoline

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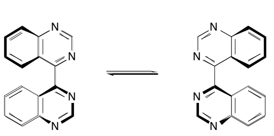
The atropisomeric ligand 4,4'-biquinazoline (**1**) is readily prepared from quinazoline by reaction with KCN followed by oxidation with MnO$_2$. In the solid state, spontaneous resolution occurs to give crystals containing single enantiomers (Space Group C$_2$).



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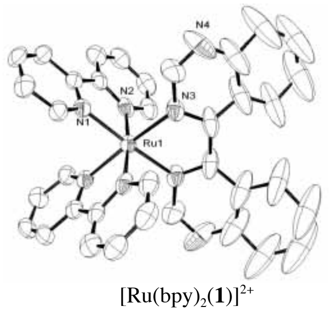

[Ru(bpy)$_2$(**1**)]$^{2+}$

The series of complex ions [Ru(bpy)$_n$(**1**)$_{3-n}$]$^{2+}$ (n = 0-2) have been prepared and the diastereomeric preferences investigated in both the solid state and by solution NMR measurements. In these complexes, the Δ or Λ chirality at the metal centre influences/is influenced by the atropisomerism of the ligands and not all predicted diastereomers are observed.

[1] L. Ademi, E. C. Constable, C. E. Housecroft, M. Neuburger and S. Schaffner, *Dalton Trans.*, 2003, 4565.

Inorganic and Coordination Chemistry **164**

New silver(I) complexes with substituted 3,6-bis(2-pyridyl)-pyridazine

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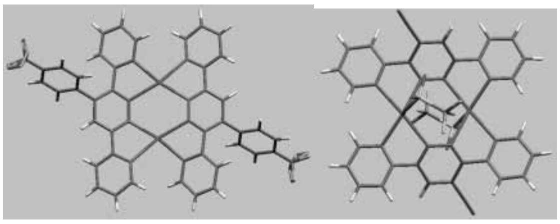
Polytopic ligands incorporating multiple oligo pyridine metal binding domains are important components in the development of metallo supra molecular chemistry$^{(1)}$.

Grid-like structures have particular interest as molecular systems described as binary arrays which may be selectively addressed$^{(2)}$. The majority of grids have been based upon structurally developed analogues of the prototype 3,6-bis(2-pyridyl)-pyridazine ligand introduced by Osborn$^{(3)}$.

The introduction of functional groups allow the incorporation of the ligands and the corresponding metal complexes into larger assemblies and polymers.

We have recently investigated the coordination behavior of functionalized diazines with silver(I).



[1] E.C. Constable, C.E. Housecroft, B.M. Kariuki, N. Kelly, C.B. Smith, *Inorg. Chem. Commun.*, 2002, **5**, 199.

[2] J-P.Sauvage, M.W. Hosseini, (Eds), Pergamon, Oxford, 1996.

[3] M-T. Youniou, N. Rahmouni, J. Fisher, and J.A. Osborn, *Angew. Chem. Int.Ed*, 1992, **6**, 733.

Inorganic and Coordination Chemistry **165**

Ultrafast spectroscopic investigation of a 4,4'-bis(3,5-dimethoxyphenyl)-2,2'-6,6'-dimethylbipyridine copper(I) complex

Amar Boudebous[1], *Edwin C. Constable*[1], *Catherine E. Housecroft*[1]
Hassen Boudebous[2], *Jakob Wirz*[2],

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E-mail:Amar.Boudebous@unibas.ch

The study of luminescence and redox properties of transition metal complexes is of great interest for a variety of fundamental and practical reasons. In the past 20 years most of the attention in this field has been focused on complexes of the 2,2'-bipyridine type family. Such complexes show unique combinations of chemical stability, redox properties, luminescence intensities, and excited states lifetimes. Several hundreds of them have been synthetized and used as photosensitizers in a variety of intermolecular and photochemical processes. Our investigations by steady-state irradiation and laser flash photolysis show that the lifetime of the MLCT state in MeCN is at 725 nm, 30 ps for 4,4'-bis(3,5-dimethoxyphenyl)-2,2'-6,6'-dimethylbipyridine copper(I) complex.

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

Inorganic and Coordination Chemistry **166**

Nanobiotechnology: Discrete, One- and Two Dimensionnal Protein Arrays Triggered By Metal Coordination to Bis-Biotinylated Ligands bound to Streptavidin

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Fax +41 (0)32 718 25 11
E-mail: Thomas.ward@unine.ch

Our group has recently been involved in the use of the biotin-avidin technology to produce efficient artificial metalloenzymes. For this purpose, a ligand is covalently linked to biotin, which when reacted to streptavidin, produces a supramolecular biotin⊂streptavidin complex which displays catalytic properties reminiscent both of enzymes and homogeneous catalysts.

In this study, the linker between the biotin anchor and the ligand is extended to ensure that the metal is located outside of the streptavidin host protein. With this method, and depending on the coordination properties of the transition metal, the {metal-ligand-biotin}⊂streptavidin building blocks can be assembled in various geometries. The resulting discrete, one- and two dimensionnal protein assemblies can be analyzed by atomic force microscopy, revealing well organized protein arrays, reminiscent of molecular tectonics.

[1] Letondor, C., Humbert, N., Ward, T. R., *Proc. Nat. Acad. Sci. USA.* **2005**, *102*, 4683-4687.
[2] Ward, T. R., *Chem. Eur. J.* **2005**, *in press.*

Inorganic and Coordination Chemistry **167**

Line shape of a quadrupolar nucleus coupled to a spin 9/2: application to the determination of the water exchange rate on *fac*-$[(CO)_3Tc(H_2O)_3]^+$ by variable temperature ^{17}O NMR

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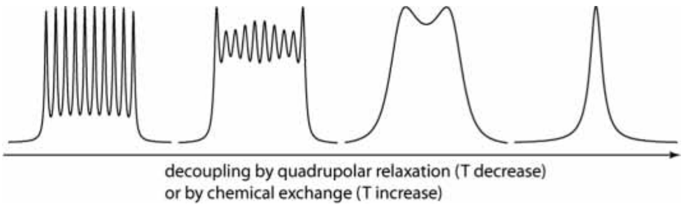
Laboratoire de chimie inorganique et bioinorganique, ISIC,
Ecole polytechnique fédérale de Lausanne, CH-1015 Lausanne

Typically the NMR signal of a nucleus which is spin-spin coupled to another nucleus of a spin I, is expected to have a multiplet structure of equally spaced 2I+1 lines. When the spin I is greater than ½, its electric quadrupole moment will influence the shape of the multiplet due to quadrupolar relaxation. The latter being usually fast, the multiplet is collapsed to a single line. When the quadrupole moment is small or the nucleus with spin I > ½ is in a highly symmetric environment the multiplet can be observed or at least only a partially collapsed one.



From the line shape analysis of variable temperature ^{17}O NMR spectra (272-395 K), taking into account quadrupolar and exchange broadening, the activation parameters for the water exchange on *fac*-$[(CO)_3Tc(H_2O)_3]^+$ were determined. Information about the water exchange on *fac*-$[(CO)_3Tc(H_2O)_3]^+$ are relevant to the investigation of this complex as precursors for radiopharmaceutical agents [1].

[1] Alberto, R. *Eur. J. Nucl. Med. Mol. Imaging* **2003**, *30(9)*, 1299-1302.

Inorganic and Coordination Chemistry **168**

Artificial metalloenzyme for the enantioselective reduction of ketones by transfer hydrogenation

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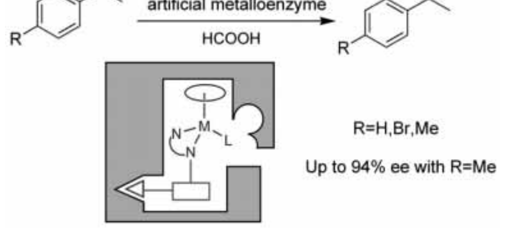
Homogenous- and enzymatic catalysis are in many respects complementary for the synthesis of enantiopure compounds. As the subtle details that govern chiral discrimination are difficult to predict, improving the performance of such catalysts often relies on trial-and-error procedures. Homogenous catalysts are optimized by chemical modification of the first coordination sphere and enzymes can be improved by modification of gene encoding the protein.

The supramolecular anchoring of a biotinylated organometallic catalyst into a host protein ((Strept)avidin) affords versatile artificial metalloenzymes for the reduction of ketones by transfer hydrogenation.[1]



Insertion A combined chemo-genetic procedure to optimize the activity and the selectivity of the metalloenzyme will be presented.

[1] Letondor, C.; Humbert, N.; Ward, T. R. *Proc. Natl. Acad. Sci. USA.* **2005**, *102*, 4683-4687.

Inorganic and Coordination Chemistry **169**

High pressure stopped flow studies of complex formation reactions in ionic liquids

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Ecole Polytechnique Fédérale de Lausanne (EPFL), 1015 Lausanne, Switzerland

Stopped-flow instruments with UV-Vis and fluorescence detectors are very useful to study the kinetics of fast reactions in the liquid phase. High-pressure techniques have been recognized for their utility in the elucidation of reaction mechanisms[1]. These techniques have been combined in a high-pressure stopped-flow instrument designed to measure reaction rates in absorbance and in fluorescence[2].

Ionic liquids are promising alternative solvents offering many new possibilities in organic synthesis, liquid-liquid extraction as well as in electrochemical studies[3]. Their main advantages are their negligible vapour pressure, their tuneability, their large temperature range and their good thermal stability. Furthermore, being ionic, they can influence reaction rates by stabilizing the intermediate state, if it is more polar than the starting material.

Lately, many reactions have been performed and studied in ionic liquids, but the reaction mechanisms have rarely been investigated. We therefore started studying simple complex formation reactions in ionic liquids as test reactions before progressing to reaction mechanisms of catalytic interest. The effect of the presence of water in the ionic liquid has also been investigated.

[1] R. van Eldik and F. G. Klärner, *High Pressure Chemistry*, Wiley/VCH, **2002**..
[2] Bugnon, P.; Laurenczy, G.; Ducommun, Y.; Sauvageat, P.-Y.; Merbach, A. E.; Ith, R.; Tschanz, R.; Doludda, M.; Bergbauer, R.; Grell, E. *Analytical Chemistry* **1996**, *68*, 3045-3049.
[3] (a) Seddon, K. R. *J. Chem. Technol. Biotechnol.* **1997**, *68*, 351 (b) Welton, T. *Chem. Rev*. **1999**, *99*, 2071.

Inorganic and Coordination Chemistry **170**

Routes to new highly electrophilic XCE^+ cations (X = halogen; E = O, S)

Dipl. Chem. Nils Trapp, Prof. Dr. Ingo Krossing

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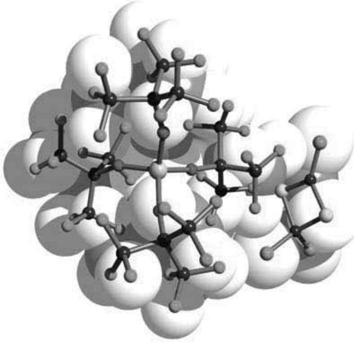
Weakly coordinating anions (WCA) are anions which minimize cation-anion-interactions [1]. WCA are suitable counterions for the stabilization of reactive cations or weakly bound Lewis-acid-base-complexes under mild conditions. In a reaction of the WCA salt $Ag^+[Al(OC(CF_3)_3)_4]^-$ with thiophosgene, a salt of the very reactive $Cl_3C_2S_2^+$ cation (see image) could be synthesized and fully characterized (NMR, IR, XRAY).



This cation is an adduct of $ClCS^+$ and thiophosgene. The Synthesis is a straightforward halogen abstraction by the very polarizing Ag^+:

$Ag^+ + 2\ Cl_2CS \rightarrow Cl_3C_2S_2^+ + AgCl$

It can be deduced from NMR investigations that in solution $ClCS^+$ cations exist in equilibrium with thiophosgene as follows:

$ClCS^+ + Cl_2CS$ # !"! $Cl_3C_2S_2^+$

This equilibrium can be shifted in favor of $ClCS^+$ by utilization of more polar solvents. CH_2Cl_2 Solutions of $Cl_3C_2S_2^+[Al(OR)_4^-]$ ($R=C(CF_3)_3,C(CF_3)_2(C_6F_5)$) are stable at ambient temperature for weeks. Analogous reactions to stabilize other XCE^+ and $X_3C_2S_2^+$ cations (X=Cl-I; E=O,S) have been systematically examined with quantum chemical methods. Results of these calculations as well as further experimental findings will be presented on the poster.

[1] I. Krossing, I. Raabe, *Angew. Chem.* **2004**, *116*, 2116.

Inorganic and Coordination Chemistry **171**

Ruthenium-Catalyzed Allylic Alkylation. Carbonate-Based New Catalysts and Intermediates

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In contrast to Pd(II) catalysed allylic alkylation reactions, which often afford the linear product, the use of ruthenium based catalysts affords primarily branched organic products. To understand the origin of the regioselectivity we prepared the $[RuCp^*Cl(\eta^3\text{-phenylallyl})CH_3CN]PF_6$ complex **2**[1], which was characterized by NMR and X-ray, by stirring $[RuCp^*(CH_3CN)_3]PF_6$ **1** with cinnamyl chloride. DFT calculations and ^{13}C-NMR chemical shifts show that the observed high branched-to-linear regioselectivity for cinnamylchloride using the *tris*-nitrile catalyst **1** has an electronic origin. In an extension of this study we reported[2] that reacting **1** with the branched phenylallyl *t*Bu-carbonate leads to the formation of $[RuCp^*(\eta^3\text{-phenylallyl})(\ OC(O\text{-t-Bu})O)]PF_6$ **3** where the carbonate anion remains in the coordination sphere of the ruthenium. The new Ru(IV) allyl carbonate complex was characterized by NMR and X-ray. We show that the new isolated complex **3** is a relevant intermediate in the catalytic cycle. If used as catalyst **3** is faster than catalyst **1** in the allylic alkylation.

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[2] Hermatschweiler R., Fernández I., Breher F., Pregosin P. S., Veiros L. F., Calhorda M. J., *Angew. Chem. Int. Ed.,* **2005**, accepted.

Inorganic and Coordination Chemistry **172**

Weakly Bound Cationic $Ag(P_4S_3)$ Adducts – Similar Counterions, but Different Structures

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Lewis acid base adducts of small inorganic cluster molecules such as P_4S_3 are of fundamental interest for coordination chemistry, although few examples were known a few years ago, because the P_4S_3 cage often degrades upon the reaction with a transition metal[1,2,3]. But with weakly coordinating fluorinated alkoxy aluminates, it was possible to obtain the first $Ag(P_4S_3)$ adducts[2] which showed new and unprecedented coordination modes. After this initial publication, several reports on such type of coordination appeared[4]. Although the anions $[Al(OC(H)(CF_3)_2)_4]^-$ ($[hf]^-$) and $[Al(OC(CF_3)_3)_4]^-$ ($[pf]^-$) are very similar, the structures of their $Ag(P_4S_3)$ adducts are very different. In order to further investigate the influence of the used counteranion on the structure of the $Ag(P_4S_3)$ complexes, reactions with $Ag[Al(OC(CH_3)(CF_3)_2)_4]$ (Ag[ht]) and $Ag[((CF_3)_3CO)Al\text{-}F\text{-}Al(OC(CF_3)_3)_3]$ (Ag[al-f-al])[5] were performed. While $[P_4S_3Ag[ht]]$ is a molecular species, the adduct $[Ag_2(P_4S_3)_6]^{2+}[al\text{-}f\text{-}al]^-_2$ is a 2:1 salt. The comparison of the structures of all four $Ag(P_4S_3)$ adducts clearly shows the influence of the size and coordination ability of the counterion. With the largest anion, which can almost be called "non-coordinating", isolated cations are formed, whereas with the other aluminates, polymeric cations or even molecular species are obtained.

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[2] A. Adolf, M. Gonsior, I. Krossing, *J. Am. Chem. Soc.* **2002**, *24*, 7111.
[3] One of the rare examples of an P_4S_3 adduct with a transition metal is the apically bound $[(np_3)Ni(P_4S_3)]\cdot 2C_6H_6$: M. di Vaira, M. Peruzzini, P. Stoppioni, *Inorg. Chem.* **1983**, *22*, 2196.
[4] e.g. a) M. Di Vaira, I. de los Rios, F. Mani, M. Peruzzini, P. Stoppioni, *Eur. J. Inorg. Chem.* **2004**, *2*, 293; b) I. de los Rios, F. Mani, M. Peruzzini, P. Stoppioni, *J. Organomet. Chem.* **2004**, *689(1)*, 164.
[5] A. Bihlmeier, M. Gonsior, I. Raabe, N. Trapp, I. Krossing, *Chem. Eur. J.* **2004**, *10*, 5041.

Inorganic and Coordination Chemistry **173**

Electrophilic Trifluoromethylating Reagents based on Hypervalent I(III) Reagents

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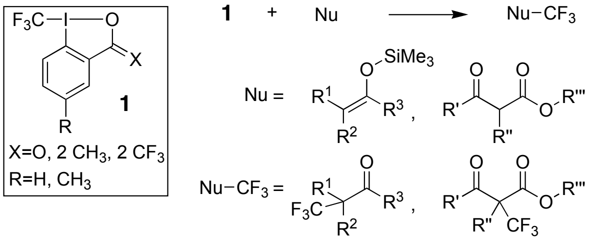
Department of Chemistry and applied Biosciences
ETH Hönggerberg, 8093 Zürich, Switzerland



Fluorinated and perfluorinated compounds have been increasingly targeted in industry during the past decades. The trifluoromethyl unit for instance is often present in synthetic drugs and agrochemicals leading to an altered physical and physiological behavior with respect to uptake, mode of action and metabolism. Therefore the introduction of the trifluoromethyl functionality is a desirable task for synthesis. Direct transfer of a trifluoromethyl moiety in an electrophilic fashion onto nucleophiles still constitutes a major challenge [1]. Recently we prepared new reagents based on the hypervalent iodine scaffold **1** and showed their ability to trifluoromethylate carbon nucleophiles [2]. Here we present the reactivity of these reagents with β-ketoesters and silylenolethers derived from ketons and esters to produce α-trifluoromethylated carbonyl compounds.

[1] T. Umemoto *Chem. Rev.* **1996**, *96*, 1757 – 1777. For asymmetric trifluoromethylations: J. Ma, D. Cahard *Chem. Rev.* **2004**, *104*, 6119 – 6146.
[2] Unpublished results.

Inorganic and Coordination Chemistry[a] **174**

Synthesis and application of Ruthenium(II) complexes containing a helical arrangement built on two ligands with a xylene linker

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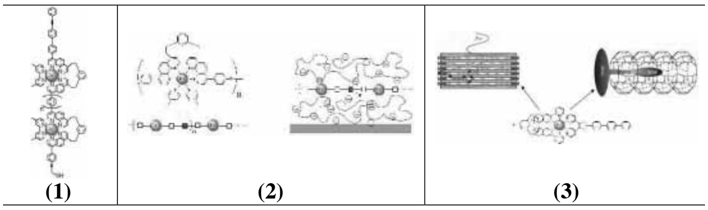
Reactions in restricted geometries have recently been of wide interest. The synthesis of octahedral Ru(II) complexes with well defined shapes[1,2] are the starting point for studying the conductivity of a single molecular wires, the chemical properties of artificial photonic antenna[3] and the chemical properties of polyelectrolytes containing those complexes.[4]

One tool is the calculation of the current intensity and the conductance of photoactive molecular wires based on metal complexes (**1**). An application is to improve conversion and storage of energy by the addition of certain polyelectrolytes to appropriate photochemical systems (**2**) or by incorporating Ru(II) complexes into zeolite crystals (**3**).


(1) **(2)** **(3)**

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Inorganic and Coordination Chemistry **175**

Pulsed-Gradient Spin-Echo Diffusion Measurements on ^{195}Pt, ^{1}H and ^{31}P in Platinum complexes.

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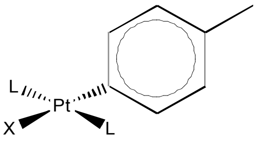
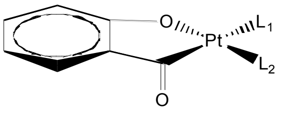
The solvent dependence of the aggregation and/or ion pairing of the hexachloroplatinate dianion in Na_2PtCl_6 and H_2PtCl_6 in methanol is measured using ^{195}Pt PGSE diffusion methods. In water, the ions are well separated. In addition the ^{1}H and ^{31}P diffusion data for *trans*-PtX(Aryl)(L)$_2$ (where L = PEt_3 or PPh_3 and X = Cl or Br) (A) and Pt($C_7H_4O_2$)(L_1)(L_2) (where L_1 and L_2 = different ligand types) (B) show that a substituent on the Aryl ligand of complex (A) does not affect the diffusion constant, whereas a substituent of similar size added to PPh_3 on (B) remarkably changes both D and r_h values.



(A)



(B)

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Inorganic and Coordination Chemistry **176**

Synthesis and characterization of rhodium/phosphoramidites complexes

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Rhodium catalysts containing monodentate P-donor chiral BINOL-based phosphoramidites have recently shown good to excellent activities and selectivities towards catalytic hydrogenation[1] and C-H activation[2]. In order to achieve a better understanding of the chiral induction of the catalysts, rhodium complexes containing one and two ligands have been prepared and characterized, using multinuclear NMR techniques and X-ray diffraction. Reactions of the chiral monodentate *O,O'*-(S)-(1,1'-dinaphthyl-2,2'-diyl)-*N,N'*-di-(S,S)-1-phenylethylphosphoramidite and *O,O'*-(S)-(1,1'-dinaphthyl-2,2'-diyl)-*N,N'*-dimethylphosphoramidite with rhodium salts will be presented.

[1] Jerphagnon, T.; Renaud, J.-L.; Bruneau, C. Tetrahedron: Asymmetry, 2004, 15, 2101.
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Inorganic and Coordination Chemistry **177**

Synthesis, Structure and Bonding of $Ag(\eta^2\text{-}C_2H_2)_n^+[Al(OR)_4]^-$ (n = 1, 2, 4; R = $C(CF_3)_3$, $C(H)(CF_3)_2$, $C(CH_3)(CF_3)_2$)

Reisinger, A.; Krossing, Prof. Dr. I.

Institut de Sciences et Ingénierie Chimiques, École Polytechnique Fédérale de Lausanne; CH-1015 Lausanne;)

Many reactive Cations have already been detected in the gas phase by one of the advanced mass spectrometric experiments. Unfortunately no information about the structure of these species can be given by using this method. One possibility to overcome this problem and to stabilize as well as characterize these cations also in condensed phases consists in using very big and weakly basic anions such as the S_4-symmetric $[Al(OC(CF_3)_3)_4]^-$.[1] Using this anion, we recently synthesized and characterized $Ag(\eta^2\text{-}C_2H_4)_x^+$ (x = 1-3)[2]. Within this poster the synthesis and characterization of Lewis acid base complexes of the Ag^+ cation with ethine will be presented. Inter alia the thermodynamics, details of the bond formation of the $Ag(\eta^2\text{-}C_2H_2)_n^+$ cations as well as some specific features of the single crystal analysis will be discussed.

[1] I. Krossing *Chem. Eur. J.* **2001**, 7, 490; b) I. Krossing, H. Brands, R. Feuerhake, S. Koenig *J. Fluor. Chem.* **2001**, *112*, 83.
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Inorganic and Coordination Chemistry **179**

Nitrogen Monoxide Reacts and the Glutathione Thiyl Radical – A Kinetc Study

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S-nitrosoglutathione (GSNO) is a vasodilator and has numerous other biologial functions [1]. It's biosynthesis is proposed to involve the reaction of nitrogen monoxide ($NO^\bullet$) with the glutathione thiyl radical ($GS^\bullet$). Therefore the reaction $GS^\bullet + NO^\bullet \rightarrow GSNO$ (reaction 1) was studied under various conditions.

The laser flash photolysis at 266 nm of GSNO in $NO^\bullet$-saturated water lead to $GS^\bullet + NO^\bullet$. Their recombination with a rate constant $k1 \leq 6.3 \bullet 10^6\ M^{-1}\ s^{-1}$ was not quantitative. The laser flash photolysis at 266 nm of oxidized glutathione (GSSG) in $NO^\bullet$-saturated water did not show any substantial formation of GSNO at its characteristic absorption at 530 nm. With pulse radiolytic reduction of GSH by $H^\bullet/e^-_{aq}$ in 95% $NO^\bullet$ saturated water a rate constant of $k_1 \approx 2 \bullet 10^7\ M^{-1}\ s^{-1}$ was determined. These results and the low bioavailable concentrations of the participating species indicate that the radical formation pathway is not probable: $[NO^\bullet] \leq 10^{-7}$ M, decay of $GS^\bullet$ by intramolecular $H^\bullet$ transfer is faster than $10^3\ s^{-1}$ [2]. Under such conditions, the yield of $GS^\bullet + NO^\bullet$ is less than 1%.

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[2] L. Grierson, *Int. J. Radiat. Biol.* **1992**, *62*, 265

Inorganic and Coordination Chemistry **178**

Self-Assembly Synthesis of Boronate Macrocycles

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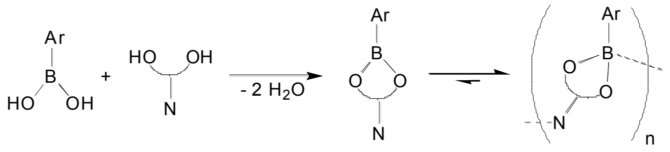
Similar to transition metal complexes, boron compounds can be used as building blocks for the construction of macrocyclic assemblies [1]. In particular, boronic acids are very convenient starting materials, as they easily form cyclic esters with diols. In this context, tridentate N, O, O' chelate ligands are appropriate building blocks to both form boronic esters and promote the self-assembly reaction of macrocycles via formation of a B-N bond [2].



This strategy has been tested with pyridine based ligands of different geometries, allowing for the construction of macrocycles with association number n going from three to five, as evidenced by X-ray crystallographic analyses.

[1] H. Höpfl, *Struct. Bonding* **2002**, *103*, 1.
[2] N. Christinat, R. Scopelliti, K. Severin, *Chem. Commun.* **2004**, 10, 1158.

Inorganic and Coordination Chemistry **180**

$[BX_2]^+$ Cations stabilized by Weakly Coordinated Anions (WCAs)?

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Ecole Polytechnique Fédérale de Lausanne
BCH, ISIC-LCIC
1015, Lausanne

Cations of the type $[BX_2]^+$ (X = F, Cl, Br, and I) isolectronic with CO_2, NO_2^+ and OCX^+ have only been characterized in the gas phase or at very low temperatures by matrix isolation spectroscopy.[1] With Pseudo Gas Phase Conditions[2] stable salts of gas phase cations that where hitherto incompatible with the condensed phase due to anion coordination and/or decomposition could be generated. Here we want to extend this approach to $[BX_2]^+$ salts.

Based on reaction **(i)** where A = the corresponding weakly coordinating anion, the stabilization of di-halogenated boron cations ($[BX_2]^+$) in the condensed phase is investigated.

$$\boxed{BX_3 + Ag[A]^{[3]} \longrightarrow BX_2^+[A]^- + AgX \qquad (i)}$$

Results from recent reactions with BI_3 and BBr_3 will be described.

[1] M.E. Jacox , W.E.Thomson. J. Phys. Chem. **1995**, *102*, 4747.
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[3] a) I. Krossing. *Chem. Eur. J.* **2001**, *7*, 490; b) I. Krossing, H. Brands, R. Feurhake, S. Koenig. *J. Flour. Chem.* **2001**, *112*, 83-90. c) M. Gonsior, I. Krossing. *Z. Anorg. Allg. Chem.* **2002**, *628*, 1821. d) I. Krossing, A. Reisinger. *Eur. J. Inorg. Chem.* **2005**, 1979-1989.

Inorganic and Coordination Chemistry **181**

Synthesis of an Asymmetric Zinc Phthalocyanine with Peripherally Coordinated Ru(II)

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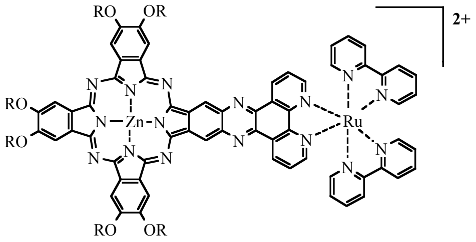
Phthalocyanines display a wide range of interesting physical properties. Most of the applications to-date rely on non-functionalized phthalocyanines. There are only a few examples of phthalocyanines [1,2] or related macrocycles [3] with peripherally coordinated ruthenium(II)-ions or in general with metal ions.

Here we report the synthesis of an asymmetric phenanthroline-appended phthalocyanine of the **AAAB** type, whereby **A** corresponds to phthalocyanine sites with bulky substituents that increase solubility and decrease stacking properties. The phenanthroline unit, which is part of the large π-system of the phthalocyanine moiety, is denoted by **B**. A bis(2,2'-bipyridine)-ruthenium(II) unit has been coordinated to the phenanthroline-appeneded phthalocyanine. The fact that the phenanthroline-ruthenium(II) unit is part of the π-system of the phthalocyanine unit might lead to interesting photophysical properties, which are under investigation.



[1] Kimura M. *et al.*, *Tetrahedron Lett.* **1998**, *39*, 8471.
[2] González-Cabello A. *et al.*, *J. Org. Chem.* **2003**, *68*, 8635.
[3] Montalban A. G. *et al.*, *Inorg. Chim. Acta* **2001**, *317*, 143.

Inorganic and Coordination Chemistry **183**

Metal Binding to a Fruit-specific Metallothionein

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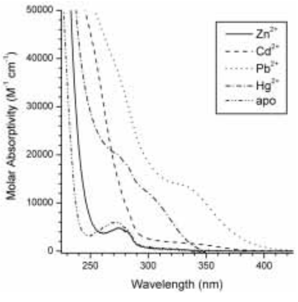
The super-family of metallothioneins (MTs) comprises a wealth of small proteins with an outstanding high cysteine content being able to bind d^{10} metal ions within the cell in form of metal-thiolate clusters. MTs play a role in the homeostasis of essential metal ions, most notably Zn^{2+} and Cu^{+}, and the detoxification of heavy metals, such as Cd^{2+} or Hg^{2+}. Additionally, participation in gene regulation and scavenging of reactive oxygen species (ROS) is discussed. MTs occur in nearly all living organisms, but little is known about the plant isoforms. Their amino acid sequences differ distinctively from MTs of other species, suggesting a significantly different overall three-dimensional structure and metal-thiolate cluster formation. The protein under investigation, *M. acuminata* MT3, belongs to the plant MT fruit-specific p3 subfamily.[1] With a total of 10 cysteine residues, MT3 features a cysteine content and percentage that is more comparable to fungal and prokaryotic MTs than to the well characterized mammalian iso-forms, directly reflected by a lower metal content. The hitherto unknown spectroscopic behavior of MT3 in combination with metal ions will be presented and discussed. - Financial support for this project comes from the Swiss National Foundation (200021-105269/1) and the Research Fund of the University of Zürich (57010101).



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Inorganic and Coordination Chemistry **182**

Pt-Vitamin B_{12} Derivatives

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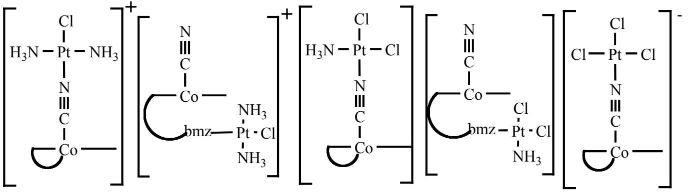
Cisplatin has a dose-limiting toxicity that arises from its interactions with an organism that are remote from the site of cancer [1]. Using vitamin B_{12} as a transporter, the active cytotoxic drug should be released spontaneously inside of cancer cells and no toxicity should be observed in normal cells due to the high consumption of vitamin B_{12} by cancer cells. There are few reactions reported between cisplatin and cobalamins, they showed that the platinum binds to either N^3 of the benzimidazol group in methylcobalamin, to N^7 or N^1 of the adenosyl residue in coenzyme B_{12} [2], or to the cyanide when cyanocobalamin is used [3].

The reactions of vitamin B_{12} with transplatin, $K^+[PtCl_3NH_3]^-$ and K_2PtCl_4 are presented. The reactions in H_2O gave mixtures of complexes with platinum bound to CN or to N^3 in the benzimidazol group. However, in MeOH the main products are the CN-bridged ones. The interaction of these new Pt-B_{12} complexes with 9-methylguanine will be presented.



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Inorganic and Coordination Chemistry **184**

Development of new Weakly Coordinating Anions (WCAs)

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Weakly coordinating anions were continuously developed over the last two decades and are of current interest in basic and applied research.

With WCAs it is possible to stabilize many unusual and very reactive cations in the condensed phase. Applications can be found in homogenous catalysis, polymer chemistry, ionic liquids, electrochemistry or lithium ion batteries.

A relatively new and easily synthesized group of WCAs are fluorinated alkoxy aluminates. By a systematic variation of the fluorinated rest R^F in the WCA $[Al(OR^F)_4]^-$ ($R^F = C(R)(CF_3)_2$; (R = organic rest)) the stability and solubility of the salts is influenced.

A solubility in even non polar solvents like n-hexane could be shown with a new type of alkoxy aluminates: $Li[Al(OC(CF_3)_2(R))_4]$ ($R = CH_2EMe_3$ with E = C, Si). In the synthesized anion $[Al(O(CF_3)_2(R))_4]^-$ with $R = CH_2SiMe_3$ the oxygen atoms are shielded by the sterically demanding $CH_2Si(CH_3)_3$ groups. Because of the non polar $Si(CH_3)_3$ groups the WCA salt $Li[Al(O(CF_3)_2CH_2SiMe_3)_4]$ is soluble in n-hexane and, as a result of no existing ß-H atoms in the CH_2SiMe_3 rest, stable against activation of the C-H bonds.

Lit.: I. Krossing, I. Raabe, *Angew. Chem.* Int. Ed. **2004**, 43, 2066-2090.

Inorganic and Coordination Chemistry **185**

An η^2-Aryl-Metal Interaction Stabilizing a 16-Electron Fragment: Asymmetric Catalytic Cyclopropanation of Olefins

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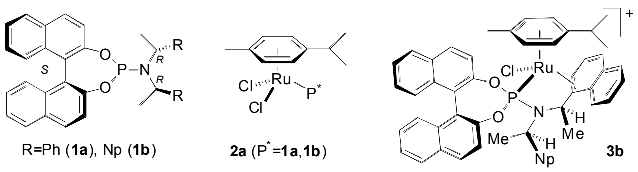
With the intention of developing a new class of *cis*-selective cyclopropanation catalysts, we have prepared half-sandwich ruthenium(II) complexes by reaction of $[RuCl_2(p\text{-cymene})]_2$ with the bulky phosphoramidite ligands P* (P* = **1a** or **1b**) [1] to give the pseudotetrahedral ruthenium complexes $[RuCl_2(p\text{-cymene})(P^*)]$ (**2a** or **2b**):



R=Ph (**1a**), Np (**1b**)

2a (P*=**1a**,**1b**)

3b

Chloride abstraction with Et_3OPF_6 or $TlPF_6$ gives the new species $[RuCl(p\text{-cymene})(P^*\text{-}\kappa P,\eta\text{:}1,2)]PF_6$, which is stabilized by η^2-coordination of a phenyl or 1-naphthyl (**3b**) group of the phenethylamine moiety, as assessed by means of multinuclear NMR spectroscopy techniques. Complex **3b** catalyzes the cyclopropanation of styrene with good enantioselectivity (77 and 68 % ee for the *cis* and *trans* isomer, respectively). High enantioselectivity (86 and 87 % ee, 57:43 *cis*:*trans* ratio) was obtained with α-methylstyrene. Complex **3b** turned out to be a much better catalyst than the initially explored **3a** [2]. Currently, we are investigating further asymmetric catalytic reactions as applications for the ruthenium-phosphoramidite system.

[1] L.A. Arnold, R. Imbos, A. Mandoli, A.H.M. de Vries, R. Naasz, B.L. Feringa, *Tetrahedron* **2000**, *56*, 2865.
[2] D. Huber, A. Mezzetti, *Tetrahedron: Asymmetry* **2004**, *15*, 2193.

Inorganic and Coordination Chemistry **186**

Lanthanide Induced Shift Analysis of Asymmetric Bimetallic Triple Helicates in Solution

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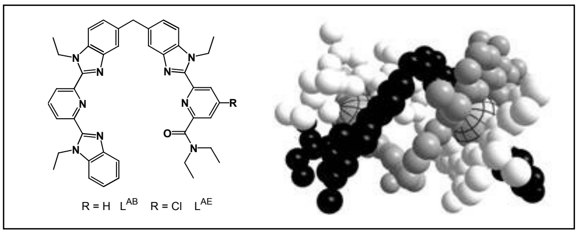
The heterobitopic ligands L^{AB} and L^{AE} self-assemble with lanthanide ions to yield homobimetallic complexes of general formula $[Ln_2L_3]^{6+}$ and with pairs of different lanthanide ions to build heterobimetallic edifices $[LnLn'L_3]^{6+}$. The solid state structure features triple helicate complex ions with the three ligand strands wrapped around the lanthanide ions [1].



R = H L^{AB} R = Cl L^{AE}

^1H NMR measurements of the complexes and analysis of the lanthanide induced shift demonstrate that all complexes are isostructural in solution.

Geometric information obtained from the studies of the solution structure is compared to the structures of the complexes in the solid state. The triple helicate structure found in the solid state is maintained in solution.

It is demonstrated that the individual contributions of two paramagnetic lanthanide ions to the lanthanide induced shifts are additive.

[1] N. André, T. B. Jensen, R. Scopelliti, D. Imbert, M. Elhabiri, G. Hopfgartner, C. Piguet, J.-C. G. Bünzli, *Inorg. Chem.* **2004**, *43*, 515.

Inorganic and Coordination Chemistry **187**

Catalytic Nazarov Cyclization Promoted by Chiral Chlorovanadium(IV) Complexes

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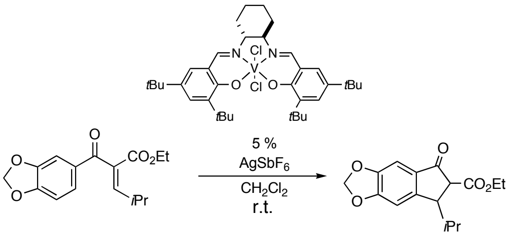
Five-membered carbocycles are widespread in natural products and bioactive molecules. One of the most versatile approaches to their synthesis is the Nazarov reaction [1]. Although a strong Brønsted acid mediated the first Nazarov cyclization, nowadays the substrates are mostly subjected to Lewis acid catalysis [2]. We here report an effective cyclization promoted by a chiral chlorovanadium catalyst, which was prepared by treatment of a known oxovanadium complex [3] with $SOCl_2$ followed by *in situ* activation with $AgSbF_6$.



Cyclized products are isolated in up to 61% yield and high diastereoselectivity.

[1] I. N. Nazarov, I. I. Zaretskaya, *Isv. Akad. Nauk SSSR, Ser. Khim.* **1941**, 211.
[2] W. He, X. Sun, A. J. Frontier, *J. Am. Chem. Soc.* **2003**, *125*, 14278.
[3] Y. N. Belokon *et al.*, *Helv. Chim. Acta* **2002**, *85*, 3301.

Inorganic and Coordination Chemistry **188**

Control over the crystal structure and the shape of CdSe nanocrystals

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The electric and optical properties of semiconductor (SC) nanocrystals (NC) depend sensitively on both their size and shape [1]. Controlling these two parameters has been one of the main goals towards using these materials as building blocks for nanotechnology. SC NCs have been produced at high yield by pyrolysis of precursor complexes in hot surfactant mixtures, achieving a narrow distribution of sizes and shapes (e.g. spheres and rods).

Bulk CdSe exists in two crystalline lattice structures: wurtzite (W, hexagonal) and zinc blende (ZB, cubic). These structures only differ in the stacking sequence of the CdSe hexagonally packed layers, and the energy difference between these two forms is small. Nevertheless most CdSe NCs prepared by this method present a W structure.

The control of the crystal structure is the key to more complex architectures, as it can be used to achieve branching of sections in the anisotropic W on blocks of the more symmetric ZB.

By modifying in various distinct ways the order and the timing of the surfactant addition to the precursors we obtained high quality size-controlled CdSe dots having the less common ZB lattice structure [2], as well as objects based on mixed structures: tetrapods, branched rods, linked dots. Each of these new nanoparticles exhibits specific optical properties.

These results indicate that chemistry among the surfactant molecules plays a more important role in the growth kinetics than usually assumed.

[1] Alivisatos, A. P. *Science* **1996,** *271*, 933.
[2] Mohamed, M.; Tonti, D.; Al Salman, A.; Chemseddine, A.; Chergui, M. *J. Phys. Chem. B* **2005,** *109*, 1533

Inorganic and Coordination Chemistry **189**

Bonding Structures of Planar Branched Chains in Eu_2LiSi_3

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Eu_2LiSi_3, a new phase in Eu/Li/Si ternay system has been successfully synthesized [1]. The structure contains branched infinite silicon chains with 1-, 2- and 3- bonded silicon which are stacked ecliptically along b direction with a distance of 4.597 Å. Interestingly the compound does not crystallize with the same structure as Eu_2LiGe_3 [2]. To predict the electronic properties and to investigate the bonding structures of Eu_2LiSi_3, theoretical calculations in the framework of the Extended Hückel (EHMO) [3] method and the tight-binding Linear Muffin Tin Orbital method in the atomic sphere approximation (TB-LMTO-ASA) [4] were performed. The results indicate that the chains contain double bond contribution, and the π electrons are not distributed uniformly. Because of the ecliptically stacked poly-anions, weak interactions between these π* states along the stacking direction occur, which lead to a band dispersion and crossing of the Fermi level. This also stabilizes the structures, allows for adoptable electron counts and leads to interesting physical properties such as strong anisotropies in the electrical conductivities.

[1] Q. Xie, M. Wörle, R. Nesper, Solid State Chemistry, **2004**, P284, Prague, Czech.
[2] Q.-X. Xie and R. Nesper, *Z. Kristallogr-NCS.* **2004**, 219, 79.
[3] U. Häusserman, S. Wengert, R. Nesper, T. F. Fässler, Program MEHMACC, ETH Zürich, **1997**.
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Inorganic and Coordination Chemistry **191**

Group 11 Metal Complexes of Tris(pyrazolyl)methanide Ligands

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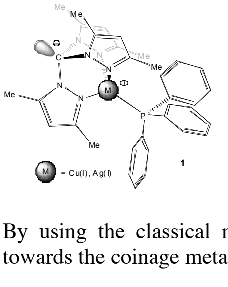
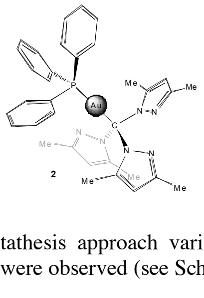
ETH Hönggerberg, Wolfgang-Pauli Strasse, CH-8093 Zürich, Switzerland

Recently, neutral tris(pyrazolyl)methane ligands, that is $HC(R_xpz)_3$, have received renewed interest [1]. However, the isoelectronic tris(pyrazolyl)methan*ides*, which contain an unassociated sp^3-hybridised carbanion in the bridgehead position, are completely underdeveloped in coordination chemistry. A suitable precursor for the synthesis of transition metal complexes is the monomeric, zwitterionic lithium compound $[C(3,5\text{-}Me_2pz)_3Li(thf)]$ [2].



1



2

By using the classical metathesis approach variable coordination modes towards the coinage metals were observed (see Scheme).

[1] H. R. Bigmore, S. C. Lawrence, P. Mountford, C. S. Tredget, *Dalton* **2005**, 635.
[2] F. Breher, J. Grunenberg, S. C. Lawrence, P. Mountford, H. Rüegger, *Angew. Chem. Int. Ed.* **2004**, *43*, 2521.

Inorganic and Coordination Chemistry **190**

Structural Diversity of Polymer Chains in Zintl Phases

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For many decades, the Zintl-Klemm rules [1-3] of formal charge transfer between metals and semimetals have been applied to Zintl phases with great success. According to this, tetrel elements like carbon, silicon, and germanium form structures like sulfur on acquiring of about two charges per atom. Indeed, the infinite polymer chains have been frequently observed in Zintl Phases [4], which are divided in general as branched and unbranched, or planar and unplanar anions. Meanwhile they can also be classified according to the chain conformation. In our work, a systematic investigation was made, and a series of compounds with one-dimensional planar chains which are branched or unbranched have been successfully synthesized. The research in this field is very attractive not only because of the structural similarity of the Zintl anions with the corresponding organic polymers but also their unique properties such as two dimensional conductivity, i.e. along the chain directions and along the stacking vectors of the chains.

[1] E. Zintl, *Angew. Chem.* **1939**, 52, 1.
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[3] R. Nesper, Prog. *Solid St. Chem.* **1990**, 20, 1.
[4] Q. Xie, *Dissertation*, ETH Zürich, No.15626, **2004**.

Inorganic and Coordination Chemistry **192**

Superelectrophilic beryllium cations in solution and in the solid state

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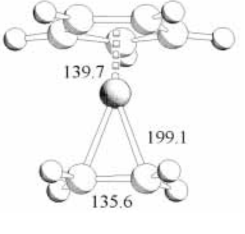
The progress in the development of weakly coordinating anions (WCAs) over the last two decades has opened up new possibilities for chemists to stabilize highly electrophilic cationic species in solution or in the solid state. WCA salts of Ag^+ or carbenium ions should be suitable starting materials to synthesize beryllium cations of the general formula $[XBeL]^+$ (X = halogen, alkoxy, Cp^x; L = weak *Lewis* base, e.g. CO, C_2H_4) *via* halogen or alkyl abstraction:

$$XBeCl + Ag^+[A]^- + L \xrightarrow[{[A]^- = WCA}]{} [XBeL]^+[A]^- + AgCl$$

$$XBeR + R'_3C^+[A]^- + L \xrightarrow[{[A]^- = WCA}]{} [XBeL]^+[A]^- + R'_3C\text{-}R$$

Theoretical calculations, combined with a *Born-Haber* cycle, show that e.g. a $[CpBe(C_2H_4)]^+$ cation should be stable in CH_2Cl_2 solution as well as in the solid state with WCAs (e.g. the $[Al(OC(CF_3)_3)_4]^-$ anion). Recent experiments will be described.



$[CpBe(C_2H_4)]^+$ cation, calculated at MP2 / TZVPP level (distances in pm).

Inorganic and Coordination Chemistry **193**

Enantioselective oxidation with artificial metalloenzymes

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Oxidation reactions are among the most important transformations in synthetic chemistry. In recent years, several discoveries have revealed the potential of manganese catalysts for selective oxidations.

Inspired by the work of the groups of Eric N. Jacobsen and T. Katsuki we have developed biotinylated manganese(salen) complexes for enantioselective oxidation.

Based on the incorporation of achiral biotinylated organometallic complexes within (strept)avidin, artificial metalloenzymes are obtained, with properties reminiscent both of enzymes and of homogeneous catalysts[1]. Having established the proof-of-principle with hydrogenation and transfer hydrogenation reactions, we have recently focused on more challenging oxidation reactions.[1]

The results of aqueous epoxidation of alkenes and aqueous oxidation of sulfides with these artificial metalloenzymes will be presented.

[1] Thomas C.M., Letondor C., Ward T.R., *Journal of Organometallic Chemistry*. **2005**, in press

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Inorganic and Coordination Chemistry **194**

Inorganic and Coordination Chemistry

Design of Rhenium-Based Catalysts for "Ionic Hydrogenation"

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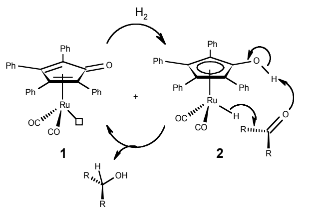
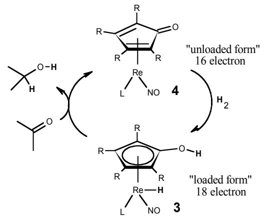
In 1985, Shvo reported that the diruthenium complex (η^4-$Ph_4C_4CO)(CO)_2RuH_2$ was an efficient ketone hydrogenation catalyst [1]. This complex dissociates into the hydroxycyclopentadienyl ruthenium hydride **2** and the coordinatively unsaturated cyclopentadienone **1**. This system is assumed to transfer H_2 in form of an acidic and a hydridic hydrogen to the ketone in a concerted fashion ("Ionic Hydrogenation") as shown below.





We are trying to develop a new "Ionic Hydrogenation" catalyst utilizing polar rhenium hydrides. The catalytic system involves a hydroxyl cyclopentadienyl nitrosyl rhenium complex, isoelectronic to the ruthenium system, bearing an acidic function and a hydride (**3** "loaded form"). After H^- and H^+ transfers a corresponding cyclopentadienone nitrosyl rhenium complex results (**4** "unloaded form"). The loaded form is regenerated by heterolytic H_2 uptake.

Our efforts to be presented are concentrating on the synthesis of "loaded forms" possessing various types of cyclopentadienyl ligands and L = CO.

[1] Y. Blum, D. Czarkle, Y. Rahamim, and Y. Shvo, *Organometal.* **1985**, *4*, 1459.

Inorganic and Coordination Chemistry **195**

Protonated benzimidazoles as synthons for crystal engineering

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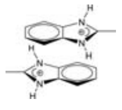
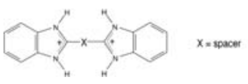
Crystal engineering has been defined [1] as the understanding of intermolecular attractions in the solid state, and seeks the planned synthesis of new solids. Desiraju [2] has introduced the notion of the supramolecular synthon, as a unit that assembles in a crystal in a predictable manner, and which may thus be used to link molecules rationaly in the solid state. We have previously shown [3] that protonated benzimidazoles stack in the solid state as shown below :



We report here a number of crystal structures containing benzimidazole cations of the general type :



We show that they lead to a series of structures in which benzimidazoles stackings and hydrogen bonds networks mainly participate in the crystal cohesion.

[1] G. R. Desiraju in *The Crystal as a Supramolecular Entity*, John Wiley & Sons, **1996**, 41.
[2] G. Desiraju, *Angew. Chem. Int. Ed. Engl.*, **1995**, *34*, 2311.
[3] C. J. Matthews *et al.*, *New J. Chem.*, **2003**, *27*, 354.

Inorganic and Coordination Chemistry **196**

The Pentacyanocyclopentadienyl anion as a bridging ligand

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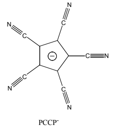
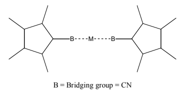
Bridging ligands occupy a central position in modern coordination chemistry : They offer a means of synthesis of extended coordination polymers, or, if some of the coordination sites of the metal are blocked by non-bridging ligands, to oligonuclear species such as boxes and cages. Apart from the structural properties of the bridging ligand, it may also act as electronic link, facilitating electron transfer, energy transfer or magnetic exchange between the metal centers. Our project intends to study the ability of the anionic ligand pentacyanocyclopentadienide, $PCCP^-$ ($C_5(CN)_5^-$) which may be synthesised in three steps from tetracyanoethane [1]. Organocyanide ions such as tricyanomethanide have been used for many years as bridging ligands, but cyanocyclopentadienides have not been studied, with the exception of one paper on complexes of 1,2-bicyanocyclopentadienide [2]. PCCP is particularly interesting as a five-connected node, unknown until now. It is reported to be extremely stable, and its tetraethyl ammonium salt is soluble in water and many organic solvents [1].



$PCCP^-$



B = Bridging group = CN

The simplest method to link the pentagons is to place a metal M between the pentagons as describe above. For the metal, we take an ion which is happy with linear twofold coordination such as silver(I).

[1] O. W. Webster, *J. Am. Chem. Soc.* **1966**, *88*, 4055.
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Inorganic and Coordination Chemistry **197**

Highly cross-linked polymers containing N,N',N''-chelate ligands for the Cu(II) mediated hydrolysis of phosphoesters

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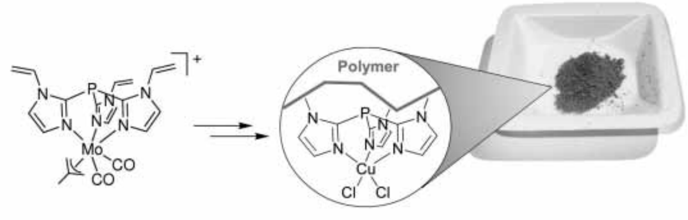
Institut des Sciences et Ingénierie Chimiques, Ecole Polytechnique Fédérale de Lausanne, BCH, 1015 Lausanne, Suisse

Copper(II) complexes of bi- and tridentate N-donor ligands such as bipyridine, terpyridine, and 1,4,7-triazacyclononane and their derivatives have been investigated intensively as artificial phosphoesterases. A general problem of these biomimetic hydrolases was found to be product inhibition and the formation of catalytically inactive hydroxy-bridged dimers. The immobilization of Cu-complexes on solid supports offers a potential alternative to reduce problems of aggregation.



Immobilized Cu(II) complexes were generated by a) homo polymerization of the N,N',N''-chelate ligand tris[2-(1-vinylimidazolyl)]phosphine (**1**) and subsequent metalation with $CuCl_2$; b) by co-polymerization of **1** with EGDMA und metalation with $CuCl_2$ or c) by molecular imprinting with an organometallic Mo-complex of **1** and EGDMA und replacement of Mo(II) by Cu(II). The ability of the polymeric Cu complexes to promote the hydrolysis of phosphoesters was investigated using the model substrates BNPP and NPP. [1]

[1] A. Schiller, R. Scopelliti, K. Severin, *Inorg. Chem.*, submitted.

Inorganic and Coordination Chemistry **198**

Reactions of the $[Re(CO)_2]^+$ core with different ligands

Lukas Kromer, Bernhard Spingler, Roger Alberto

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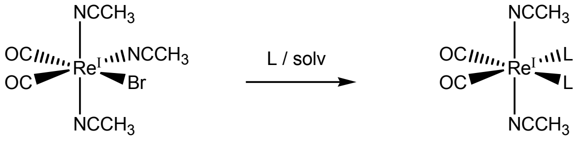
One of the most promising organometallic cores for biomolecule labeling is the *fac*-$[M(CO)_3]^+$ moiety (M = Re, Tc). It has attracted much interest as a precursor for radiopharmaceuticals. It has been speculated that the $[M(CO)_2]^+$ core would allow to label aromatic side chains of peptides. We have synthesized $[Re^{(I)}Br(NCCH_3)_3(CO)_2]$ **1,** a substitution labile but water stable novel precursor, which allows the convenient introduction of different chelators such as bipy, picolinc acid, amino acids and others.



1 **2**

Despite the similarity with the *fac*-$[Re(CO)_3]^+$ containing complexes the reaction products **2** exhibit different chemical and physical properties.

Inorganic and Coordination Chemistry **199**

Halides in ionic liquids: Solvent-solute interactions and consequences on a catalytic hydrogenation reaction

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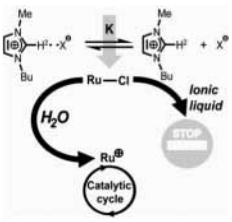
Halides, and especially residual chlorides, are known to poison transition-metal catalysed reactions in ionic liquids (ILs).[1] Compared to water, widely used for biphasic catalysis,[2] ILs afford media in which the solvation of halides is less efficient, providing more nucleophilic species. In an IL, dissolved halides generally interact with the cations of the IL. Therefore, chloride solvation enthalpy, as well as the relative strength of solvation of the halides in a 1-butyl-3-methylimidazolium (bmim)-based IL, were evaluated through the determination of the halide-bmim interaction by variable temperature ^1H NMR spectroscopy.

We found that the solvation of chloride in bmim-based ILs is poor (compared to water). Consequently, a ruthenium-catalysed hydrogenation reaction, which is effective in water, is inhibited in ionic liquids.[3]



[1] Y. Chauvin, L. Mussmann, H. Olivier, *Angew. Chem. Int. Ed.*, **1995**, *34*, 2698.

[2] F. Joó, *Aqueous Organometallic Catalysis, Kluwer, Dordrecht* **2001.**

[3] C. Daguenet, P. J. Dyson, *Organometallics*, **2004**, *23*, 6080.

Inorganic and Coordination Chemistry **200**

Toward a Molecular Switch using the Photophysical Properties of Anthracene

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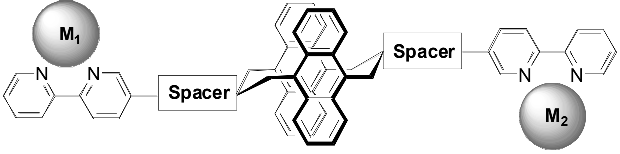
Anthracene and its derivatives show an interesting behaviour if they are irradiated with light of 365nm wavelength; two anthracene units undergo a [2+2]-cycloaddition reaction. This photodimer has different photophysical properties than the anthracene itself. It is well known [1], that the photodimerisation is totally reversible.

These two different states of anthracene can be used in molecular switches. If the anthracene unit is incorporated between two metal centers, it can either be a strong quencher or facilitater of the energy transfer process.

The idea of a new molecular switch is based on the anthracene unit described previously. We want to synthesize a bridging ligand in which an anthracene moiety is incorporated. This bridging ligand should have a linear symmetry and the anthracene units should be fixed in position. The best way to achieve this is to link two anthracenes by a 3-carbonatom bridge and form a 3,3-cyclophane.



By adding functional groups (building blocks and/or ligand molecules) to the anthracene unit, one can further incorporate the new switching molecule between two metal centers.

[1] Bouas-Laurent, Castellan, Desvergne & Lapouyade; *Chem. Soc. Rev.* **2001**, *30*, 248.

Inorganic and Coordination Chemistry **201**

Induction of Z–DNA: When Similar Dinuclear Complexes interact differently with DNA

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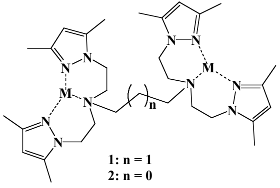
During our studies aimed at better understanding the factors which influence the formation of the left-handed Z-DNA,[1] we speculated that dinuclear metal complexes might induce Z-DNA more efficiently than their mononuclear analogues.[2]

Our aim is to introduce the new family **1** of homodimetallic complexes. They are based on **2** (M = Cu^{2+} and Ni^{2+}) published by Reedijk *et al.*[3, 4] The interaction of **1** and **2** (M = Cu^{2+} and Ni^{2+}) with poly d(GC) has been examined. Furthermore, this allowed to study the influence of the intermetallic distance between the metal centers concerning the transition from B- to Z-DNA. Surprisingly, **1** and **2** (M = Cu^{2+} and Ni^{2+}) showed different interactions as only **1** induced Z-DNA. These unexpected variations in reactivity of structurally very similar complexes with DNA will be discussed.



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Inorganic and Coordination Chemistry **202**

New Phosphorus containing Flame Retardants for Cotton

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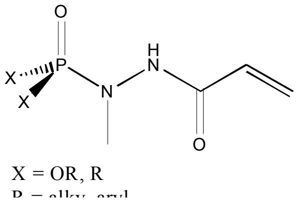
There exist few commercially available flame retardants for cotton. All of these retardants contain phosphaorganic compounds and further additives. Other phosphorus based flame retardants have been synthesized, but are not commercially employed due to toxicological properties or cost.

Here we present a new type of phosphorus containing compounds which we can polymerize onto cotton fabrics to impart flame retardant properties.



The characterization of the treated fabrics was performed by IR-ATR, SEM, TGA, the flame retardant properties were evaluated by limiting oxygen index (LOI) test, and the durability of the surface modification was checked by different washing cycles.

Inorganic and Coordination Chemistry **203**

NMR and X-ray studies on a Ru(IV) allyl complex. An explanation for the observed regioselectivity.

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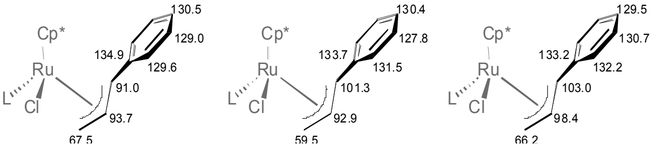
The use of ruthenium based catalysts in allylic alkylation and amination processes, affords primarily branched organic products due the preferred attack at the more substituted carbon.

Here we report NMR and X-ray studies, which together with computational data give an explanation of the observed high branched-to-linear regioselectivity. The oxidative addition of cinnamyl chloride with [Cp*Ru(L)$_3$] (L = CH_3CN) in dichloromethane solution, gives three ruthenium (IV) isomeric complexes. The ^{13}C NMR data for the allylic moieties are shown in the figure.



The NMR data reveal a marked difference between the carbon chemical shifts of the allylic termini in the three complexes. The X-ray structure and computational data show clearly different terminal Ru-C bond distances. These results provide an explanation for the observed control of regioselectivity.

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Inorganic and Coordination Chemistry **204**

Photochromic Dithienylethene-Phenanthroline Hybrid System Containing Ru(II), an Opportunity to Increase Photofatigue Resistance

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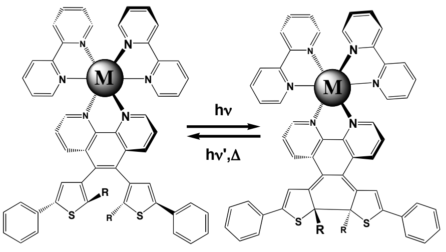
In this work, we have developed a system, in which a photochromic unit (dithienylethene[1]) has been combined with Ru(II) metal complex.[2] By irradiation at 450 nm into the MLCT band of the metal complex, a photosensitized cycloreaction takes place. This low energy light, used to perform the electrocylic reaction, allows an increase of photofatigue resistance.



If light of 254 nm wavelenght is used to close the molecule, after a few cyles, the photochomic properties disappear. On the other hand, irradation at 450 nm, the photochomic properties remain unchanged.

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Inorganic and Coordination Chemistry **205**

Isolation and characterization of the first circular single-stranded polymetallic lanthanide-containing helicate

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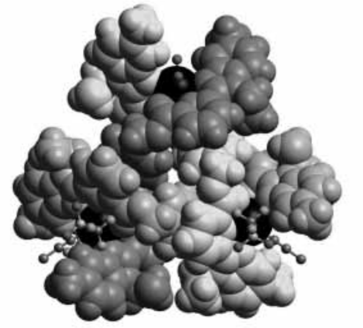
A thorough examination of the disassembly of bimetallic triple-stranded lanthanide helicates $[Ln_2(Li)_3]^{6+}$ in excess of metals shows the competitive formation of standard linear bimetallic complexes $[Ln_2(Li)_2]^{6+}$, and circular trimetallic single-stranded helicates $[Ln_3(Li)_3]^{9+}$.



[1] Jean-Michel Senegas, Sylvain Koeller, Gérald Bernardinelli and Claude Piguet, *Chem. Commun.*, **2005**, 2235-2237.

Inorganic and Coordination Chemistry **206**

Ion Pairing on $[(\eta^6\text{-Arene})Mn(CO)_3]^+,[X]^-$ Complexes

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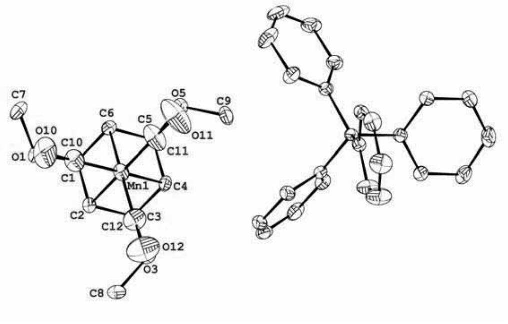
Significant differences in the ion pairing were found in a series of salts $[(\eta^6\text{-Arene})Mn(CO)_3]^+$, $[X]^-$ where the counter ion, X, is either BPh_4 or BArF.



PGSE diffusion measurements in different solvent and NOESY Spectra for those anions confirm these observations, providing unexpectedly strong ion pairing for $[(\eta^6\text{-Arene})Mn(CO)_3]^+$, $[BPh_4]^-$ in CD_2Cl_2.