Minisymposium Inorganic and Coordination Chemistry **129**

Coordination Chemistry for the Design of Therapeutic Metal Complexes

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The roles of both the metal ion and its ligands can be crucial in the mechanism of action of therapeutic metal complexes: to achieve targeting to biological sites, and allow specific activation. I will discuss 3 examples from our recent research. Photoactivatable *cis* and *trans* platinum(IV) diazide complexes are relatively non-toxic to cells in the dark, but kill cancer cells by unusual mechanisms when irradiated. For organometallic ruthenium(II) arene anticancer complexes, chemical reactivity, anticancer activity and cellular processing are highly dependent on the nature of the arene and the other ligands, and the contrasting biological behavior of osmium(II) analogues is understandable from studies of their aqueous coordination chemistry under biologically-relevant conditions. Finally binding of antiviral and stem-cell-mobilizing metallomacrocycles to target membrane receptors appears to involve coordination of the metal to specific amino acid side-chains, H-bonding, hydrophobic interactions, and restraint of the configuration of the macrocycle.

Inorganic and Coordination Chemistry **130**

Dynamic combinatorial libraries of dye complexes as flexible sensors for peptides

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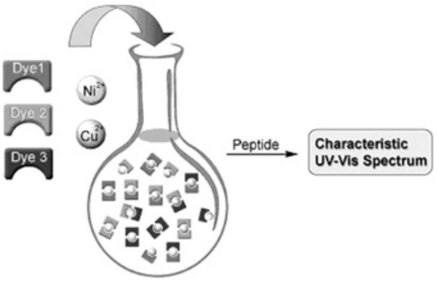
Dynamic combinatorial libraries (DCLs) are adaptive chemical networks formed by combinatorial assembly of molecular building blocks under thermodynamic control. We have constructed a DCL of metal-dye complexes in which the library members have a different color. Any re-equilibration will therefore result in the variation of the UV-Vis spectrum of the mixture. We have shown that such a library can be used to identify dipeptides in aqueous solution with high selectivity.[1] Furthermore we have found that the composition of a library can be optimized in combinatorial fashion for a specific sensing purpose.[2]



[1] A. Buryak, K. Severin, *Angew. Chem. Int. Ed.* **2005**, *44*, 7935-7938.
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Inorganic and Coordination Chemistry **131**

Photochromic Dithienylethene Switches Connected at a Ruthenium(II) Center: Spacer, the Key of Success?

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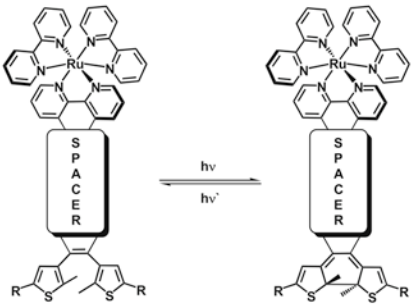
Organic dithienylethene derivatives, commonly called Irie switches, have been extensively studied in recent time [1]. On the other hand, such derivatives involving metal complexes are not often described in literature. By introduction of a metal complex, electronic absorption properties are drastically changed by the appearance of the MLCT transition. It allows the use of visible light to close the switch photochemically by an energy tranfer process from the excited metal centre to the switching unit [2].



We will discuss the crucial influence of the spacer on photochromic properties, thermal stability and fatigue resistance.

[1] M.Irie, *Chem Rev.* **2000**, *100*, 1685.
[2] J. Kühni, V. Adamo, and P. Belser, *Chimia.* **2006**, *60*, 207.

Inorganic and Coordination Chemistry **132**

The cluster structure of a wheat metallothionein

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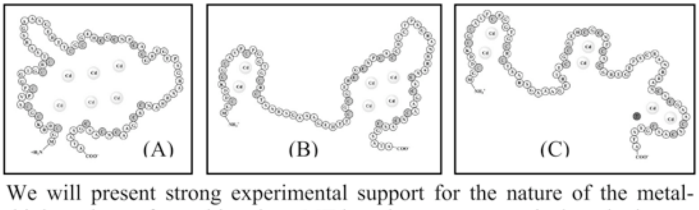
Wheat metallothionein (MT) is a seed specific plant metallothionein. Like the mammalian isoforms, wheat MT is a cysteine-rich protein with low molecular weight and the ability to bind d^{10} metal ions in form of metal-thiolate clusters. Naturally, it is found as a Zn^{II} containing species. As we found the metal-to-protein ratio to be 6 : 1, it is obvious that only sub-stoichiometrically metal-loaded forms have been described in the literature so far. Still unaddressed remains the nature of the metal-thiolate clusters formed. All three arrangements depicted below can be explained purely based on geometrical considerations or even known cluster structures: A “super-cluster” combining all three cysteine-rich regions (A), a two-domain structure consisting of a smaller two- as well as a larger four-metal ion cluster (B), or even a structure consisting of three clusters, each formed by one cysteine-rich segment of the protein (C). An alternative arrangement to (B) featuring two separate clusters of equal size seems less likely solely taking into account geometrical restraints imposed by the peptide chain.



We will present strong experimental support for the nature of the metal-thiolate cluster formed in wheat MT based on spectroscopical methods supplemented by ESI-MS data and results from (bio-) chemical reactions.

Financial support for this project comes from the SNF (200021-105269/1 to EF) and the Research Fund of the University of Zürich (57010101 to EF).

[1] Y. Kojima, P. Binz, J. H. R. Kägi, *Metallothionein IV*, ed. C. Klaassen, **1999**, 3-6.
[2] E. Peroza, E. Freisinger, *submitted*.

Inorganic and Coordination Chemistry **133**

Transition metal anticancer drugs designed to overcome Glutathione-S-Tranferase mediated drug resistance

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Drug resistance represents one of the most serious limitations in chemotherapeutic treatment affecting transition-metal based anticancer drugs such as cisplatin [1]. One important enzyme, known to be responsible for drug resistance in some cancers, is Glutathione-S-Transferase (GST) [2]. Cytosolic GST constitutes the main cellular defense against xenobiotics, catalyzing the conjugation of glutathione with the xenobiotic and leading to its elimination from within the cell [3]. Studies have also found GST enzymes to be over-expressed in several cisplatin-resistant cell lines. With a view to develop anticancer drugs that could also overcome GST-mediated drug resistance, we explored the strategy of conjugating GST inhibitors to transition metal centres to form anticancer drugs with dual modes of activity: *GST-inhibition* and *cytotoxic action*. A series of novel ruthenium and platinum-based compounds were thus developed and *in vitro* studies against established cancer cell lines were carried out [4]. In addition, the binding of the drugs with GST isozymes, namely GSTA1-1 and GSTP1-1, was also examined using mass spectrometry techniques.

[1] Wong, E.; Giandomenico, C. M. *Chem. Rev*. **1999**, *99*, 2451-2466.
[2] Tew, K. D. *Cancer Res.* **1994**, *54*, 4313-4320.
[3] Habig, W. H.; Pabst, M. J.; Jakoby, W. B. *J. Biol. Chem.* **1974**, *249*, 7130-7139.
[4] Ang, W. H.; Khalaila, I.; Allardyce, C. S.; Juillerat-Jeanneret, L.; Dyson, P. J. *J. Am. Chem. Soc.* **2005**, *127*, 1382-1383.

Inorganic and Coordination Chemistry **134**

Palladium-allyl phosphoramidite complexes. Solid-state structures and solution dynamics

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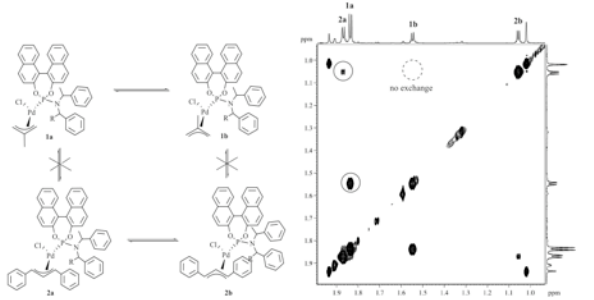
[PdCl(allyl)(phosphoramidite)] complexes have been used in recent years as catalysts in allylic substitution reactions[1]. This class of complexes can be easily synthesized from allylpalladium chloro bridged dimers by addition of P-donor chiral BINOL-based phosphoramidite type ligands. They are present in solution as a mixture of *endo*/*exo* isomers. Exchange NMR spectroscopy studies reveal that the isomers undergo intramolecular dynamics, following selective mechanistic pathways, as well as unexpected intermolecular dynamics in which the dimeric allylpalladium precursors act as reagents, together with the mononuclear complexes.



[1] Boele, M. D. K.; Kamer, P. C. J.; Lutz, M.; Spek, A. L.; de Vries, J. G.; van Leeuwen, P. W. N. M.; van Strijdonck, G. P. F. *Chemistry--A European Journal*, **2004**, 10, (24), 6232

Inorganic and Coordination Chemistry **135**

Mononuclear and Dinuclear Metal Complexes and Their Ability to Induce Z-DNA

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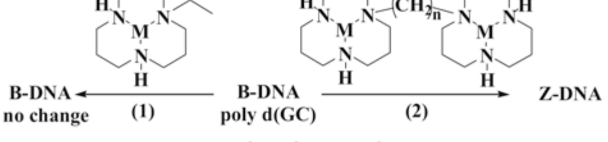
1,2-bis(1,5,9-triazacyclododecyl)ethane, 1,3-bis(1,5,9-triazacyclododecyl)-propane[1] and 1,4-bis(1,5,9-triazacyclododecyl)butane[2] have been used as dinucleating ligands to form the corresponding nickel, zinc and copper complexes. A completely different behaviour was observed when the mono- and dinuclear metal complexes were tested for their ability to induce the B- to Z-DNA transition. Dinuclear Zn, Ni and Cu complexes (**2**) were able to change the DNA helicity from right- to left-handed; whereas neither the mononuclear complexes (**1**), based on the novel 1-ethyl-1,5,9-triazacyclododecane, nor the dinuclear Co(III) complex or the ligands alone induced the Z-DNA formation. The crystal structures of selected metal complexes will also be presented.



M = Cu^{2+}, Ni^{2+} and Zn^{2+}
n = 2 to 4

[1] R. W. Alder, et al., *J. Chem. Soc., Chem. Comm.* **1992**, 507; M. D. Snodin, et al, *J. Chem Soc., Dalton Trans*. **1997**, 3407; K. Junghee and L. Hyujung, *Bull. Korean Chem. Soc*. **1999**, *20*, 491.
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Inorganic and Coordination Chemistry **136**

Synthesis and Characterization of Perovskite-Type Oxides for Geothermal and Solar Thermoelectric Power Generation

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Perovskite-type phases are potential candidates for thermoelectric devices operating at high temperatures due to their chemical and thermal stability in air at T > 400 K. The challenge for materials design is to reduce thermal conductivity, κ, and therefore enhance the figure of merit, $Z = S^2/\rho\kappa$, without affecting the Seebeck coefficient, S, and the electrical resistivity,ρ, using nano-scale materials. To fulfill this task, we are developing new synthesis methods based on the Pechini process which allows us to produce fine perovskites-type phases and to control low level cationic substitution [1-2]. Thus, the thermal conductivity might be reduced by boundary scattering without affecting the electrical transport properties. Moreover, these processes are considered to enhance the ability for particle size control.

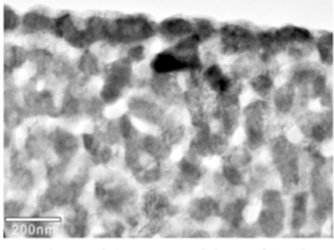

Figure. TEM micrograph picture of powders with composition of $LaCo_{0.85}Ni_{0.15}O_{3-\delta}$ produced at 873 K

[1] Weidenkaff, A. *Adv. Eng. Mater.* **2004**, *6*, 709.
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Inorganic and Coordination Chemistry **137**

Insights into the Relationship Between Cd^{2+} and RNA-Thiophosphate Derivatives

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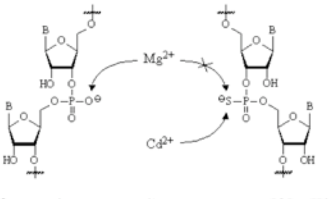
Although Cd^{2+} has no eminent purpose in the human body it is nonetheless of particular interest for biological and medicinal chemists due to its toxicity and carcinogenic potential. Cd^{2+} is also used for a variety of biochemical studies, for instance to restore ('rescue') the activity of sulphur-modified ribozymes. The diminished activity in such RNA derivatives is caused by the deteriorated binding of magnesium ions due to the low affinity of Mg^{2+} towards thiophosphates [1] and can be abrogated by the addition of thiophilic Cd^{2+} ions as shown in the Figure.



We used one- and two-dimensional NMR spectroscopy to investigate the binding of Cd^{2+} and further divalent metal ions to domain 5 (D5) of the mitochondrial group II intron *ai5γ* from the yeast *S. cerevisiae* [2]. This allowed us to gain insight into the chemical background of metal ion-ribozyme interactions. We obtained stability constants for the formation of Cd^{2+}-RNA complexes and compared them with the data available for unmodified D5 [3] and with the results from rescue experiments performed with this domain [4].

Financial support by the Swiss National Science Foundation (SNF-Förderungsprofessur PP002-68733/1 to R. K. O. S.) is gratefully acknowledged.

[1] R. K. O. Sigel, B. Song, H. Sigel, *J. Am. Chem. Soc.* **1997**, 119, 744; C. P. Da Costa, A. Okruszek, H. Sigel, *ChemBioChem* **2003**, 4, 593.
[2] K. Lehmann, U. Schmidt, *Crit. Rev. Biochem. Mol. Biol.* **2003**, 38, 249; R. K. O. Sigel, *Eur. J. Inorg. Chem.* **2005**, 2281.
[3] R. K. O. Sigel, D. G. Sashital, D. L. Abramovitz, A. G. Palmer, S. E. Butcher, A. M. Pyle, *Nat. Struct. Mol. Biol.* **2004**, 11, 187
[4] P. M. Gordon, J. A. Piccirilli, *Nat. Struct. Biol.* **2001**, 8, 893.

Inorganic and Coordination Chemistry **139**

Group 14 Element Cages for Transition Metal Coordination

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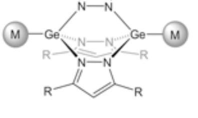
With the aim of determining communication pathways between redox-active transition metal centres, we focussed on group 14 element cages (**I**) as mediating modules featuring Lewis-basic, outward pointing lone-pair electrons suited for metal coordination.[1] Treatment of $[Ge\{N(SiMe_3)_2\}_2]$ with various NH-acidic 3,5-disubstituted pyrazoles H(3,5-R_2pz) leads to free bis(trimethylsilyl)amine and neutral bis(germylenes) consisting of μ^2-bridging and terminal pyrazolyl ligands.[2] By reacting the Ge(II) pyrazolyl compounds with triflic acid (HOTf) one of the pz-ligands can easily be removed. Cationic, triply μ^2-pyrazolyl bridged cages of the general formula $[Ge(\mu^2\text{-pz})_3Ge]^+OTf^-$ are isolated thereby in good yields.[3]

I

II



First investigations revealed that the electron lone-pairs on the germanium atoms are indeed appropriate for metal coordination furnishing linearly bridged binuclear transition metal complexes (**II**).

[1] See for instance: M. Veith et al., *Coord. Chem. Rev.* **1994**, *137*, 297.
[2] For analogous tin(II) compounds see: F. Breher, H. Rüegger, *Angew. Chem. Int. Ed.* **2005**, *44*, 473.
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Inorganic and Coordination Chemistry **138**

Non-classically bound heterocyclic carbene Pd complexes and their catalytic application

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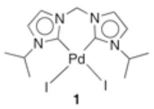
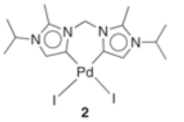
N-heterocyclic carbenes (NHCs), typically derived from imidazolium salts, have provided highly powerful ligands for catalysis [1]. Recently, non-classical C-5 bonding rather than classical C-2 bonding has been discovered as a new carbene bonding mode [2]. We are interested in comparing these two bonding modes, in particular their effect on the catalytic activity of the metal center. Therefore we synthesized two related NHC palladium complexes **1** and **2**, which contain similarly *cis* chelating biscarbenes that bind via C-2 and C-5, respectively [3]. Such chelation increases the stability of the complex and prevents a mutual *trans* rearrangement of the carbenes.



1

classical carbene



2

non-classical carbene

We have compared these complexes by structural and spectroscopic analyses, by theoretical considerations, and by reactivity studies. Our results indicate that non-classical biscarbenes bind stronger to Pd than classical biscarbenes and that they reduce the electron density on the metal center considerably. For example, iodide abstraction from complex **2** gives an unusual dimer which displays short Pd···Pd contacts.
In addition, we will discuss the electronic differences of the metal center in **1** and **2** and the catalytic consequences. Specifically, catalyst performances in Suzuki cross-coupling and aerobic alcohol oxidation will be compared.

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[2] S. Gründemann, A. Kovacevic, M. Albrecht, J.W. Faller, R.H. Crabtree, *J. Am. Chem. Soc.* **2002**, *124*, 2274; A.R. Chianese, A. Kovacevic, B.M. Zeglis, J.W. Faller, R.H. Crabtree, *Organometallics* **2004**, *23*, 2461.
[3] M. Heckenroth, A. Neels, H. Stoeckli-Evans, M. Albrecht, *Inorg. Chim. Acta.* **2006**, *359*, 1929; E. Kluser, M. Heckenroth, A. Neels, M. Albrecht, in preparation.

Inorganic and Coordination Chemistry **140**

Synthesis and Crystallographic Analysis of Coinage Metal Complexes of Mixed Thione and Tricyclohexyl Phosphine Ligands

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Institute de Microtechnique, Université de Neuchâtel, Rue Emile-Argand 11, 2009 Neuchâtel

The use of coinage metal complexes (silver and gold) as antitumor, antibacterial, antifungal and antiarthritic drugs have been well known for centuries.[1-3] Genetic hybridization of microbes is an ever increasing problem due to their resistance to current antimicrobial drugs, such as antibiotics. New compounds are required that will efficiently inhibit the growth of pathogenic micro organisms. Silver(I) compounds commonly prescribed today for their topical antibacterial effects are silver sulfadiazines (silvadene©, Flamzine©) for the treatment of burns, and even dilute solutions of $AgNO_3$ are used prophylactically for infectious bacterial conjunctivitis in infants.[4-5] In the past decades antimicrobial activities of Ag(I) and Au(I) complexes have been actively studied.[6-7]
The main aims of this research are the synthesis of compounds with Ag(I)—N, Ag(I)—S, Ag(I)—O and Ag(I)—P bonds and the establishment of structural relationships of such complexes with antimicrobial activities.

[1] W. Kaim, B. Schwederski, Bioinorganic Chemistry: Inorganic Elements in the Chemis try of Life; John Wiley: New York, **1994**; p373.
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[3] K. Nomiya, S. Takahashi, R.Noguchi, *J. Chem. Soc., Dalton Trans.* **2000**, 2091
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Inorganic and Coordination Chemistry **141**

Asymmetric α-Fluorination of α-Aryl-α-Alkyl Acetaldehydes Catalyzed by Ruthenium PNNP Complexes

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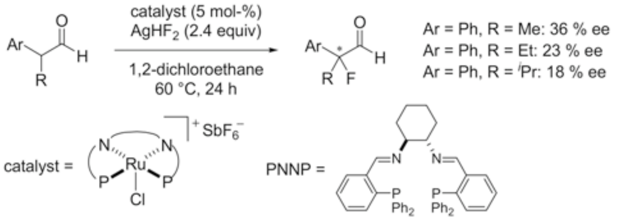
Despite the increasing importance of organic compounds containing a C–F stereocenter, methods for enantioselective C–F bond-forming reactions are still rare. Highly enantioselective electrophilic fluorinations of 1,3-dicarbonyl compounds using Ti/TADDOLato[1] and Ru/PNNP[2] catalysts have been studied in our group. We now find that the five-coordinate complex [RuCl(PNNP)]SbF_6, prepared in situ from [$RuCl_2$(PNNP)] and $AgSbF_6$ (1 equiv), catalyzes the α-fluorination of α-aryl-α-alkyl acetaldehydes with $AgHF_2$ as fluorinating agent, giving enantioselectivities of up to 36 % ee. Primary aldehydes or α,α-dialkyl acetaldehydes do not react under the same conditions.



We are currently investigating the substrate scope by steric and electronic variation of the aryl and alkyl groups to gain insight into the mechanism and course of the reaction, for which an umpolung of the aldehyde enol probably occurs.

[1] Hintermann, L.; Togni, A. *Angew. Chem., Int. Ed.* **2000**, *39*, 4359.
[2] Althaus, M.; Becker, C.; Togni, A.; Mezzetti, A., to be published.

Inorganic and Coordination Chemistry **142**

Metal-templated Macrocyclic (N_3O_2) Coordination Compounds

Christina Ambrus[1], Bo Møller Petersen[2], Jan O. Jeppesen[2], Shi-Xia Liu[1], Silvio Decurtins[1]

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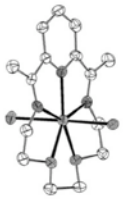
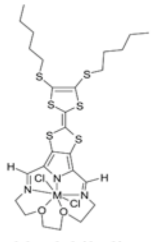
In these examples cyanide complexes are used as bridging ligands, whereas the pentadentate N_3O_2- macrocycle provides easily accessible metal coordination sites.





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_3O_2-TTF macrocycle are in progress.

[1] F. Bonadio, M.-C. Senna, J. Ensling, A. Sieber, A. Neels, H. Stoeckli-Evans, S. Decurtins, *Inorg. Chem.*, **2005**, *44*, 969.
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Inorganic and Coordination Chemistry **143**

Behaviour of Dinuclear Ruthenium and Palladium Complexes When Exposed to DNA

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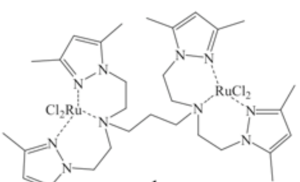
Dinuclear transition metal complexes have proven to be good inducers of Z – DNA. The analogous mononuclear complexes were significantly less efficient in inducing the left – handed Z – DNA[1]. In order to act as useful agents *in vivo*, the system must have additional properties like a tolerance against salts and proteins. In previous studies, dinuclear metal complexes were shown to be highly efficient in model systems such as poly d(GC) at low salt concentrations only.

These present systems, mostly zinc and copper complexes, are neither stable enough nor efficient in high salt concentrations for *in vivo* applications. In order to overcome these problems, more stable dinuclear ruthenium and palladium complexes like **1** with a defined intermetallic distance were synthesised.



1

By varying the intermetallic distance within **1**[2], and examining the kinetics of the induction from B – to Z – DNA, new insights into the formation of the ternary adducts and the mechanism of helical inversion can be made.

[1] B. Spingler, P. M. Antoni, **2006**, submitted.
[2] F. Zobi, P.M. Antoni, A. Medina – Molner, R. Alberto, Chimia, **2005**, *59*, 826.

Inorganic and Coordination Chemistry **144**

Binary CrB-type Silicides of Ca, Sr, Ba and Eu as Hydrogen Storage Materials

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The binary metal silicides of the CrB-type CaSi, SrSi, BaSi and EuSi undergo reversible absorption of hydrogen.[1] Hydrogenations in an autoclave at 432 K and 90 bar of these silicides give rise to significant changes of the crystal structures. Crystal structures of $CaSiH_x$ and $SrSiH_x$ were determined by Rietveld refinement. The lattice parameters change during hydrogenation (table 1). The temperature ranges of hydrogen desorption were determined by a simultaneous thermogravimetric, DTA and mass-spectrometric measurement in a dynamic dry Ar atmosphere. The exact hydrogen content was measured by the inert gas fusion method.

Table 1: *MSi and $MSiH_x$ (M = Ca, Sr, Ba, Eu): Overview.*

	H_2 wt %	Space Group	Lattice Constants Å			Cell Volume Å^3
			a	b	c	
CaSi		*Cmcm*	4.5594(9)	10.731(1)	3.8900(7)	189.67
$CaSiH_x$	1.56	*Pnma*	14.504(8)	3.800(2)	11.169(6)	615.58
SrSi		*Cmcm*	4.8162(4)	11.303(1)	4.0388(4)	219.86
$SrSiH_x$	1.35	*Pnma*	15.1042	3.9539	12.3427	737.11
BaSi		*Cmcm*	5.0430(8)	11.933(2)	4.1395(8)	249.98
$BaSiH_x$	2.08	*Pnma*	15.96	4.1	13.4	876.84
EuSi		*Cmcm*	4.694(5)	11.14(1)	3.981	208.17
$EuSiH_x$	0.99	*Pnma*	15.17	3.95	11.56	692.69

[1] M. Armbruster, M. Wörle, F. Krumeich, R. Nesper, paper in preparation

Inorganic and Coordination Chemistry **145**

Large-Scale Production Of Carbon-Coated Copper Nanoparticles For Sensor Applications

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Copper nanoparticles have attracted considerable interest because of their optical, catalytic, mechanical and electrical properties, resulting in a wide range of applications in the field of metallurgy, catalysis, nano- and opto-electronics.

Here, we use reducing flame spray synthesis for the large-scale production of 1 nm carbon coated metallic copper nanoparticles (10 to 20 nm) [1]. The carbon coating protected the zero-valent copper particles from oxidation in air. Raman Spectroscopy and solid state ^{13}C magic angle spinning revealed that the carbon layers consisted of a sp^2 – hybridized carbon modification in the form of graphene stacks.

Bulk pills of pressed carbon/copper nanoparticles displayed a highly pressure- and temperature dependent electrical resistivity. The negative temperature coefficient (NTC) behavior of the material revealed a similar or greater material constant (beta= 4550 K) than commercial sensing materials. These properties suggest the use of the carbon/copper nanocomposite as novel, low cost temperature sensing material and offer a metal-based alternative to the currently used brittle oxide based spinels and perovskites.

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Inorganic and Coordination Chemistry **146**

Synthesis of New N-Heterocyclic Carbene Complexes of Molybdenum

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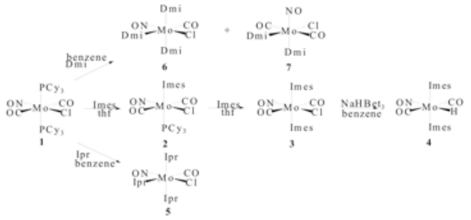
N-Heterocyclic carbenes (NHCs) derived from imidazolium salts act as efficient ancillary ligands in homogeneous catalysis[1,2]. The use of NHCs in the design of homogeneous catalysts is quite recent, but growing rapidly. For many reactions like hydrogenation, hydroformylation, olefin methatesis, Heck-, Suzuki-, and Stille-couplings efficient NHC- based catalysts exist. Here we report the synthesis of NHC based Molybdenumhydrides intended to act as hydrogenation catalysts. Starting from trans, trans-$Mo(Cl)(CO)_2(Pcy_3)(NO)$ (1)[3], three different types of N-heterocyclic carbenes were synthesized, derived from the imidazolium salts: 1,4-dimethylimidazolylidene (Dmi), 1,4- diisopropylimidazolylidene (Ipr) and 1,4- dimesitylimidazolylidene (Imes). Imes reacted to trans, trans-$Mo(Cl)(Pcy_3)(Imes)(CO)_2(NO)$ (2) and trans, trans-$Mo(Cl)(Imes)_2$-$(CO)_2NO$ (3). Treatment of 3 with $NaHBEt_3$ gave the hydride (4). Dmi and Ipr lead to $Mo(Cl)(Dmi, Ipr)_3(CO)(NO)$ (5, 6). In the case of Dmi, also 7 formed.



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Inorganic and Coordination Chemistry **147**

Investigation of metal ion binding to the branch-point of a group II intron ribozyme

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Group II introns are naturally occurring ribozymes in organellar genes of lower eukaryotes, plants and fungi as well as in certain bacterial genomes. They catalyse their own removal from precursor mRNA in a mechanism that is at first sight highly similar to the one performed by the spliceosome *(1)*. A characteristic feature of both systems is the use of an internal adenosine 2'-OH as a nucleophile in the first splicing step, which subsequently leads to the excision of the intron in form of a lariat. In all group II introns, this adenosine resides in domain 6 (D6), consisting of two A-form helical stems interrupted by the single nucleotide bulge of the branch-point adenosine and closed by a (tetra)loop. We have recently solved the solution structure of a shortened domain 6 (D6-27) construct, which contains the main branch-point determinants and has been shown to be active in in vitro trans-branching experiments*(2)*. Metal ion coordination to D6-27 has been studied in detail by mapping the chemical shift changes upon titration with Mg^{2+} and observation of specific linebroadening of resonances at sites that bind to Mg^{2+} or Mn^{2+} *(2)*. We have found high affinity metal ion binding sites close to the 5'-end of the helix, at the tetraloop as well as at the branch-point, mainly involving the two flanking GU-wobble pairs. The latter M^{2+} is potentially crucial for catalysis. To further elucidate the nature of metal coordination at the branch-point, we are incorporating thiophosphates site specifically at the branch region. These derivatives are then titrated with Mg^{2+} or Cd^{2+} and the metal binding characterized by evaluation of the chemical shift change of the ^{31}P resonance around 50 ppm.

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Financial support by the Swiss National Science Foundation (SNF-Förderungsprofessur to R. K. O. S., PP002-68733/1) is gratefully acknowledged.

Inorganic and Coordination Chemistry **148**

Efficient Synthesis of 4-Hydrazone-Functionalised 2,2':6',2''-Terpyridines and Their Iron(II) and Ruthenium(II) Complexes

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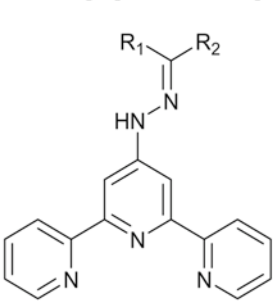
A new family of hydrazone-functionalised terpyridine ligands has been prepared via the reaction of the easily-accessible 4'-hydrazine-2,2':6',2"-terpyridine[1] with various aldehydes and ketones. The reactions occur cleanly and the products are isolated as salts which are stable to both acidic and basic conditions. The natures of these ligands were investigated in solution and in the solid state revealing some interesting protonation behaviour as well as unusual dynamic effects. The iron(II), ruthenium(II) and palladium(II) complexes were also prepared and the properties of these were examined.



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Inorganic and Coordination Chemistry **149**

Straightforward synthesis and characterization of Gd(III) and Eu(III) acetonitrile complexes without counter ion in the first coordination sphere of the metal

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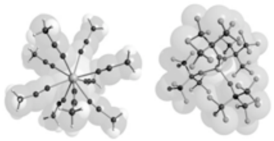
[1] Institut des Sciences et Ingénierie Chimique, Ecole Polytechnique Fédérale de Lausanne, BCH, 1015 Lausanne, Switzerland
[2] Institut für Anorganische und Analytische Chemie, Albert-Ludwigs Universität Freiburg, Albertstr. 21, 79104 Freiburg, Germany

For rare-earth ions high coordination numbers are common. In solution, even equilibrium between differently coordinated species can take place. For understanding the thermodynamic and kinetic properties of metal ion solutions the knowledge of the composition and the structure of the inner-coordination sphere of the metal ion are required. This knowledge is difficult to access in the case of lanthanides, especially in the presence of weakly coordinating ligands like "CH_3CN", since even with the so called "non-coordinating" anions like ClO_4^- or $CF_3SO_3^-$ coordination of the anion in the first coordination sphere of the metal occurs.[1] We report results that support the absence of the counter ion $[Al(OC(CF_3)_3)_4]^-$ [2] in the first coordination sphere of lanthanides, as well as the straightforward synthesis and characterization of the Gd(III) and Eu(III) acetonitrile complexes.



Structure of $[Ln(CH_3CN)_9]^{3+}$ (left side) and $[Al(OC(CF_3)_3)_4]^-$ (right side). Ball-and-stick and space-filling models are superposed.

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Inorganic and Coordination Chemistry **151**

Synthesis of (η^3-allyl)Ru^{IV} Complexes with Bidentate Nitrogen Ligands

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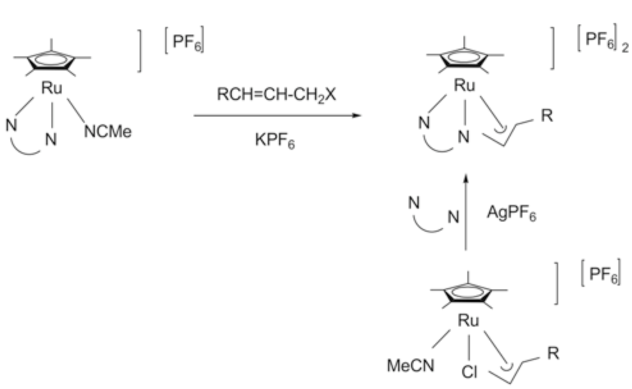
The syntheses of a variety of $[RuCp^*(L_2)(\eta^3\text{-allyl})][PF_6]_2$ complexes are presented, where L_2 is a chelating bipyridine or biquinoline ligand. Two synthetic routes were attempted; oxidative addition of an allylic precursor to $[RuCp^*(L_2)(MeCN)][PF_6]$ and reaction of the L_2 ligand with $[RuCp^*(\eta^3\text{-allyl})(MeCN)Cl][PF_6]$ [1,2,3].



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Inorganic and Coordination Chemistry **150**

Ni-Catalyzed Hydrophosphination of Methacrylonitrile With Halogenated *Pigiphos* Ligands

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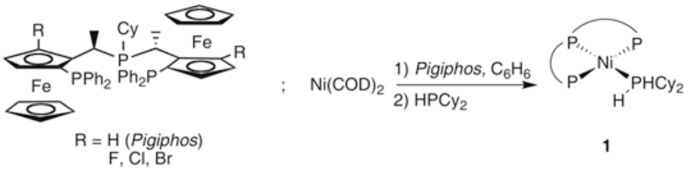
Very few catalytic asymmetric syntheses of chiral phosphines have been described in the literature [1]. Our group recently reported that a dicationic Ni(*Pigiphos*) system catalyzes intermolecular hydrophosphination reactions in good yield and high enantiomeric excess [2]. We now show that the selectivity of the hydrophosphination of methacrylonitrile is influenced by the presence of halogen substituents at position 3 of the ferrocene moiety.



Ni(0)(*Pigiphos*) derivatives containing a secondary phosphine ligand **1** does not undergo P-H activation by oxidative addition and is not a catalyst of the hydrophosphination reaction.

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Inorganic and Coordination Chemistry **152**

Synthesis of Chiral Ferrocenyl-substituted Amidine Ligands

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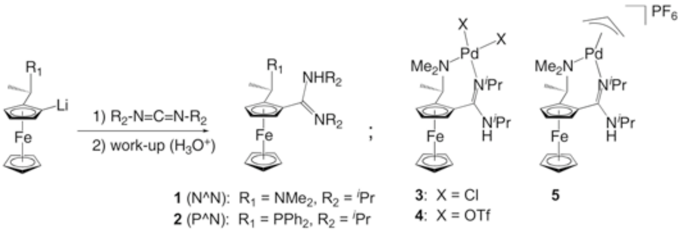
Amidine and amidinato ligands have been widely used in transition metal and in main group chemistry [1]. However their application in homogeneous catalysis remain very rare [2].
Reacting a carbodiimide with a lithiated chiral ferrocene gives rise to planar chiral amidines, where the substituents (R_1, R_2) offers the possibility of a fine tuning of the ligand properties. Using diisopropylcarbodiimide we prepared the new chiral ligands **1** and **2**. The Pd-complexes **3**, **4** and **5** containing ligand **1** were then prepared and characterized by single crystal X-ray diffraction.



Ligands **1** and **2** were tested in asymmetric allylic alkylation using an in situ generated Pd-allyl catalyst with promising 85% ee (**1**) and 71% ee (**2**).

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Inorganic and Coordination Chemistry **153**

Thermal ageing phenomena and strategies towards reactivation of NO_x-storage catalysts

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[1] Institute for Chemical and Bioengineering, Department of Chemistry and Applied Biosciences, ETH Zurich, Hönggerberg, HCI, CH-8093 Zurich
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Lean-burn engines with direct fuel injection, introduced to improve fuel efficiency, require new catalyst concepts for NO_x-reduction. Among them, NO_x-storage/reduction catalysts have received strong attention. They typically consist of precious metals (Pt, Rh), a storage component (e.g. barium containing phases), and carrier oxides with a high surface area (γ-Al_2O_3 or CeO_2). The NO_x conversion observed with such catalysts is high, but deactivation can be caused by different effects, one of them being the formation of mixed oxides from the NO_x -storage material and the support.

In the present study, we therefore focused on the formation of the mixed oxides during thermal ageing and their stability in different atmospheres [1]. In as-prepared state, the Ba-component in $Pt/Ba/CeO_2$ and $Pt/Ba/Al_2O_3$ catalysts was made up of amorphous BaO and crystalline $BaCO_3$. Formation of $BaAl_2O_4$ was observed above 850°C, whereas $BaCeO_3$-formation already started at 800°C and was faster than that of $BaAl_2O_4$. Interestingly, $BaCeO_3$ was transformed to $Ba(NO_3)_2/CeO_2$ in the presence of NO_2/H_2O at 300 – 500°C. $BaAl_2O_4$, in the aged Pt-Ba/Al_2O_3 material could also be decomposed in a H_2O/NO_2 atmosphere but, in contrast to $BaCeO_3$, only below 100°C. Hence, as a potential technical application, the instability of the undesired mixed oxides may be utilized for the reactivation of thermally aged catalysts. Our recent studies confirmed that reactivation of aged catalysts is possible under model gas and engine bench conditions.

[1] M. Casapu, J.-D. Grunwaldt, M. Maciejewski, M. Wittrock, U. Göbel and A. Baiker, *Appl. Catal. B* **2006**, *63,* 232.

Inorganic and Coordination Chemistry **154**

Synthesis of a Molecular Photomagnetic Switch as Information Storage Device

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Av. de Bellevaux 51, CP2, CH-2007, Neuchâtel

The purpose in this research is the development of a molecular photomagnetic switch based on the magnetic properties of four coordinate Nickel (II) complexes[1a]. A Cambridge structural database search of all $NiX_2(PR_3)_2$ complexes reveals that the four coordinate geometry around nickel linearly correlates with the P–Ni–P bite angle. Indeed, large P–Ni–P bite angles favour tetrahedral and thus paramagnetic complexes, while small bite angles yield square planar, diamagnetic ones. Introduction of a photo-isomerizable moiety within a diphosphine backbone may thus allow a reversible photo-induced interconversion between the two nickel spin states. We present the coordination properties of a diphosphine derived from a ferrocene moiety bearing a remote azo functionality [1b]. The photoisomerization of the azo group induces a movement of the scissors blades (diphosphines), which triggers the change in coordination of the nickel (Figure 1).

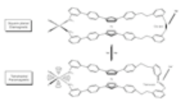

Figure 1. A molecular photomagnetic switch

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Inorganic and Coordination Chemistry **155**

Square-planar dichloro palladium complexes with *trans*-configurated phosphine ligands avoiding *ortho*-metallation: Ligand design, complex synthesis, molecular structure and catalytic potential for Suzuki cross-coupling reactions

Ludovic Chahen, Bruno Therrien, and Georg Süss-Fink*

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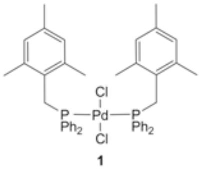
The square-planar palladium complexes *trans*-$[PdCl_2(PPh_2\text{-}CH_2\text{-}2,4,6\text{-}C_6H_2Me_3)_2]$ (**1**) and *trans*-$[PdCl_2(\eta^2\text{-}PPh_2\text{-}CH_2\text{-}2,4,6\text{-}C_6HMe_3\text{-}CH_2\text{-}2,4,6\text{-}C_6HMe_3\text{-}CH_2\text{-}PPh_2)]$ (**2**) have been synthesized from $[PdCl_2(cod)]$ (cod = 1,5-cyclooctadiene) and the corresponding new phosphine or diphosphine ligands [1].



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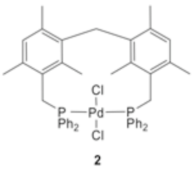
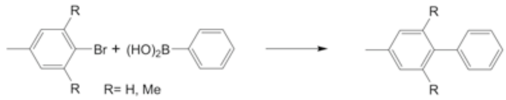


2

Both complexes are found to catalyze Suzuki cross-coupling reactions of deactivated and even bulky arene substrates.



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Inorganic and Coordination Chemistry **156**

The Synthesis And Chelation Kinetics Of Pendant Bis-Phosphine(η^6-*P*-Cymene)Ruthenium(II) Compounds

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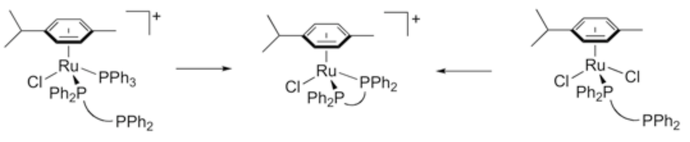
With a view of better understanding the formation of catalytically useful bidenate phosphine ruthenium (II) (η^6-arene) complexes,[1] we have prepared a series of pendant phosphine complexes of the type $[RuCl(PPh_3)(\eta^1\text{-}(P\text{-}P))(\eta^6\text{-}p\text{-cymene})]PF_6$ (P-P = dppm, *cis*-$PPh_2CHCHPPh_2$ (dppv), dppe, dppp, dppf) and studied their chelation kinetics. The chelation kinetics of the related neutral pendant phosphine complexes, $[RuCl_2(\eta^1\text{-}(P\text{-}P))(\eta^6\text{-}p\text{-cymene})]$ (P-P = dppm [2], dppv [3]), have also been determined.



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Inorganic and Coordination Chemistry **157**

Self-Assembly of Boron-Based Dendrimers

Nicolas Christinat, Rosario Scopelliti and Kay Severin*

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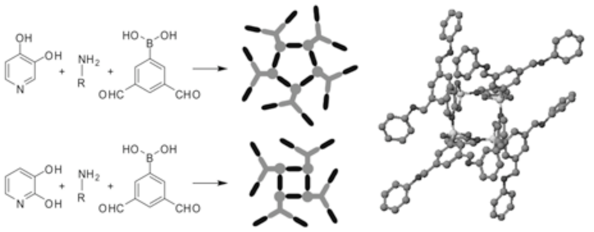
The synthesis of complex supramolecular structures by self-assembly has received considerable attention over the last years. Many of the reported structures have been obtained using transition metal-ligand interactions. An alternative is to use the main group element boron, which is known to reversibly bind oxygen and nitrogen donor ligands. For instance, the condensation of an aryl boronic acid with an N, O, O' chelating ligand produces boronate esters, which then assemble through the formation of a B-N bond to form macrocycles [1].



We now demonstrate that dendrimers can be obtained in a multicomponent reaction of a formyl functionalized boronic acid with a trifunctional ligand and a primary amine. This new methodology allows to access various dendritic structures in a fast and efficient way.

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Inorganic and Coordination Chemistry **158**

Catalysis effect of Lead(II) oxide on Barium Sulphate decomposition studied by DTA.

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Han blue and Han purple, are both man made blue pigments. Their first occurence is dated back until about 600 BC. Earlier investigations in our group showed, that historic artefacts made from chinese purple have a relatively high content in lead compunds. A solid state synthesis [1] of han purple consists of sand (cristobalite) as the silica source, copper minerals and presumably Barite (barium sulfate) as the barium source. Althoug the reactivity of Barite is inferior to Witherite (barium carbonate), Barite was likely to be used as it is much more abundant in China, like in the Hunan and Guangxi Provinces.

Barite is a very stable compound, that melts without decomposition at 1470°C. The synthesis of Han Purple is usually done at about 900°C. At this much lower temperature, Barite is not decomposed yet, and the reaction towards Han Purple is not very effective.

The addition of lead oxide to Barite helps to decompose Barite into Barium oxide. The decomposition of Barite occurs clearly in presence of lead oxide and SiO_2. (these two components are known to form a low melting flux of about 500°C, assuming 24% of PbO vs. SiO_2)

Added to a mixture of Barite, malachite, and sand, the lead oxide, facilitates the formation of Han Purple according to the equations

$BaSO_4 \rightarrow BaO + SO_3$ & $BaO + 2SiO_2 + CuO \rightarrow BaCuSi_2O_6$

We assume a reaction of $BaSO_4 + PbO \rightarrow BaO + PbSO_4$ [2] as a first step. $PbSO_4$ then easily decomposes to PbO and SO_3 at temperatures around 800°C thus forming a catalytic cycle. Decomposition reactions were followed by DTA experiments.

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Inorganic and Coordination Chemistry **159**

Barium Copper Silicates in the Synthesis of Chinese Ceramic Pigments

Tristan Corbière, Ferdinand R. W. P. Wild, Heinz Berke*

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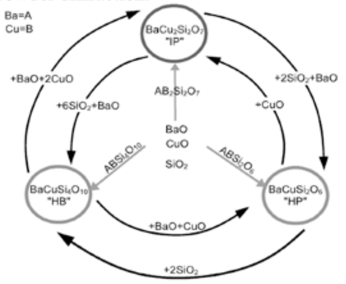
Han Blue (HB) and Han Purple (HP) are two pigments synthesised and used by Chinese craftsmen up to 2600 years ago.[1] Both compounds are barium copper silicate ceramics with different stoichiometry and different crystal structures.[2] Up to now, Han Blue was assumed to be the thermodynamically stable product, whereas the synthesis of Han Purple is kinetically favoured.[3]

We want to report the observation of a third Barium Copper Silicate, $BaCu_2Si_2O_7$, beeing part of the reaction system. and denoted here as "Intermediary Product" (IP).[4] A closer investigation revealed, that all three compounds repeatedly can be transformed into each other by adding the stoichiometrically appropriate mixture of silica gel, barium oxide and copper oxide to them. Pure compounds were obtained separately via sol-gel routes. Thus the quantification of the compounds became possible by means of X-ray powder diffraction.



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Inorganic and Coordination Chemistry **160**

Synthesis, Spectroscopic and Structural Characterization of Dinuclear and Tetranuclear Oxo-Bridged Cobalt(II) Complexes

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The design of polynuclear metal complexes is an active area of research in coordination chemistry and these compounds present interest in various research fields such as magnetochemistry and bioinorganic chemistry. Polynuclear complexes provide an opportunity for the study of magnetic exchange mechanisms involving several metal ions. We have been studying ligands which possess a bridging group (OH) together with two or more terminal ligands. Dinuclear complexes with two metal ions in close proximity show interesting magnetic, catalytic and electron transfer properties. Some reviews are consecrated to the synthesis of ligands likely to generate dinuclear species and to homo- and heterodinuclear complexes of 3d metal ions. Matsumoto & al. have shown that that the formation of dinuclear complexes is favorised with six-membered chelate ring system and that tetranuclear complexes cubane-type structure is often obtained with a five-membered chelate ring system [1]. We have shown that the ring size of the chelate is important to determine the nature of the complex : The replacement of a five-membered chelate ring ((S,S)-1,2-Bis(1-methylbenzimidazol-2-yl)-1,2-ethanediol) by a six-membered chelate ring (1,3-Bis(1-methylbenzimidazol-2-yl)-2-propanol) favours the dinuclear species.

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Inorganic and Coordination Chemistry **161**

The Reactions of the Trioxidocarbonate (•1−) radical, CO$_3^{\bullet-}$, with Cytochrome *c*

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The reactivity of cytochrome *c* towards CO$_3^{\bullet-}$ was determined by pulse radiolysis at pH 8.4 and 10 and room temperature.

The reaction of CO$_3^{\bullet-}$ with Fe(III)cytochrome c takes place only with its amino acids, because no changes in the visible spectrum of cytochrome *c* are observed. The second-order rate constants are $(5.0 \pm 0.2) \times 10^7$ M^{-1} s^{-1} and $(1.0 \pm 0.1) \times 10^8$ M^{-1} s^{-1}, at pH 8.4 and pH 10, respectively. The different rate constant values at pH 8.4 and 10 are attributed to different conformations of the protein and to the pH-dependent reactivity of CO$_3^{\bullet-}$ towards a number of amino acids.

In contrast, CO$_3^{\bullet-}$ oxidizes Fe(II)cytochrome *c* with 100% yield. The second-order rate constants are $(1.07 \pm 0.03) \times 10^9$ M^{-1} s^{-1}and $(7.6 \pm 0.2) \times 10^8$ M^{-1} s^{-1} at pH 8.4 and pH 10 respectively. In the past, this high yield was also observed for negatively charged reductants and is caused by the electric potential field of cytochrome *c* which guides anions to the solvent-accessible haem edge. Different rate constants values at pH 8.4 and 10 may be caused by different charge configurations of the protein.

In conclusion, the present results show that in the intermembrane space of mitochondria cytochrome *c* may effectively scavenge the strongly oxidizing trioxidocarbonate (•1−) radical.

Inorganic and Coordination Chemistry **162**

Construction of 2,2':6',2''-Terpyridine Based Supramolecular Systems via Hydrogen Bonding Aggregation of Amidinium Carboxylates.

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The coordination chemistry of anionic species by hydrogen bond donating receptors is an area of supramolecular chemistry that continues to attract the attention of chemists. The amidinium ion forms salt bridges with carboxylate anions and has been utilised in a variety of supramolecular systems and also as a model to examine the details of proton-coupled electron transfer, by employing both polypyridine and porphyrin based systems [1-3].
A novel terpyridine ligand functionalised with an amidinium group has been synthesised. The association of this ligand, as well as its metal complexes, with various electron acceptor molecules will be presented. Also detailed, are their photophysical and electrochemical properties.

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Inorganic and Coordination Chemistry **163**

A Novel Ru(III) Complex with Sterically Demanding Cyclopentadienyl Ligands - Synthesis and Reactivity

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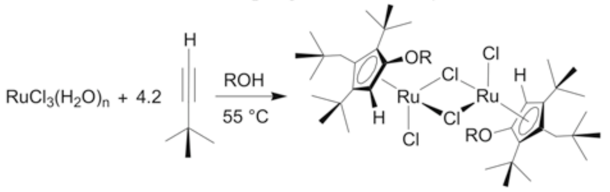
Halfsandwich Ru complexes with Cp and Cp* π-ligands are frequently used as catalysts in organic synthesis. A new Ru (III) complex with a very distinct cyclopentadienyl ligand has been prepared through an unprecedented Ru-mediated coupling reaction of alkynes and an alcohol.



R = Me, Et

The chemical behavior of this Ru-cyclopentadienyl complex with planar chirality is being investigated in order to explore the effect of a different set of substituents on the cyclopentadienyl ligand compared to the more common Cp or Cp* ligands. Reactions of this novel Ru(III) complex with phosphines have resulted in the formation of monomeric complexes which are expected to find high interest in catalytic applications.

Inorganic and Coordination Chemistry **164**

Influence of the Helix Length on Metal Ion Coordination to the Branch-Point in the Group II Intron Ribozyme ai5γ

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Group II introns catalyse their excision from precursor mRNA in a mechanism similar to the spliceosome. Both systems feature an internal adenosine 2'-OH as a nucleophile in the first reaction step. We have solved the solution structure of this so-called *branch-point region D6* of the yeast mitochondrial intron ai5γ by NMR.[1] To improve spectral resolution, the internal loop above the branch-point was removed in our construct D6-27, which splices actively in vitro.[1] Chemical shift mapping and observation of specific line-broadening effects in the NMR have revealed a potentially catalytically important metal ion bound to the GU-wobble pairs that flank branch-A. To further elucidate its effect on the local conformation of the branch-point, we have observed the fluorescence of 2-aminopurine at the branch-A upon addition of Mg^{2+}. Fluorescence quenching indicates increased stacking, as opposed to the effect that Mg^{2+} has on the wild-type D6.[2] We propose that the length of the helix above the branch-A influences the structural effects of a metal ion bound to the branch-site. Thus we solved the solution structure of a D6-construct with the internal loop replaced by a Watson-Crick basepaired region (D6zipGC). Analogous constructs have been shown to be active in branching.[3] To improve the precision of the structure we have implemented residual dipolar couplings (RDCs) obtained from weak aligment of the sample with Pf1-phage. We are currently investigating the metal ion binding sites in this construct by NMR and fluorescence studies.

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Inorganic and Coordination Chemistry **165**

The First Thermotropic Lanthanidomesogens at Room Temperature

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Over the past 20 years, the interest for metallomesogens (i.e., liquid crystals containing metal ions) has considerably increased. In fact, these compounds offer materials with novel magnetic, electrical and optical properties.

The 2,6-bis-[5-(3,4,5-tris-dodecyloxy-benzoyloxy)- 1-[4-(3,4,5-tris-dodecyloxy-benzoyloxy)-benzyl]-1H-benzimidazol-2-yl] pyridine was synthesized and studied for its complexation with $Ln(NO_3)_3$. The tridentate site of the ligand allows the complexation to the lanthanides. This ligand reacts with $Ln(NO_3)_3.xH_2O$ to give neutral 1:1 complexes $[Ln(L)(NO_3)_3]$ (Ln = La to Lu) leading to an inversion of conformation, which does not significantly alter the global anisometry of the molecule.

The gallic ester derivative confers mesogenic properties to the compounds at room temperature, which exhibit columnar mesophases.

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Inorganic and Coordination Chemistry **166**

Functionalization of Ruthenium-complex for Self Assembled Monolayer (SAM) on Gold Surfaces

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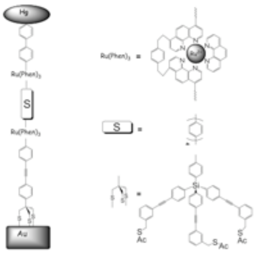
Scanning probe microscopy (SPM) has become a critical tool for atomic-scale imaging. The application of these techniques has impacted chemistry, physics, biology, and materials science. As part of our studies directed toward imaging molecular electronic device architectures, we describe here precisely defined molecular caltrops that may act as SPM probe tips.

The molecular caltrops[1,2] here were prepared by a linear rigid Ru(II) complex and a tetrahedral silicon atom core with three legs bearing thioltipped feet for adhesion to a metallic surface of gold so that their behavior can be studied in the presence of electric fields. The fourth prong is a non-sulfur-bearing arm for projection upward from the surface.



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Inorganic and Coordination Chemistry **167**

High pressure NMR studies on the reaction mechanism of the homogeneous catalytic CO_2 hydrogenation

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The use of carbon dioxide, or limestone and other carbonates, as a chemical feedstock is gaining more and more attention driven by environmental, economical and social factors. In the atmosphere CO_2 is a major cause of the greenhouse effect. Although the use of CO_2 in chemical synthesis can only give a small contribution to the decrease of the CO_2 level in the atmosphere, there are several other factors that render CO_2 an interesting chemical feedstock, such as high abundance, non-toxicity, low cost. A variety of products can be synthesized from CO_2, formic acid and its derivatives have gained particular attention among them.

$$CO_2 /HCO_3^- / CO_3^{2-} + H_2 \rightleftharpoons HCOOH / HCOO^- + H_2O$$

In this contribution we present some results on the reduction of carbon dioxide/carbonate systems using Rh- and Ru-phosphine catalysts. The reactions were followed *in situ* by high pressure NMR spectroscopy under various H_2 and CO_2 pressures.

Acknowledgement: Swiss National Science Foundation is thanked for financial support.

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Inorganic and Coordination Chemistry **168**

One-Step Flame Made Pd/$LaCoO_3$ Catalyst for the Reduction of NO by H_2 Under Lean Conditions

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$LaCoO_3$ and 0,75 wt.% Pd/$LaCoO_3$ were synthesised by the flame spray pyrolysis method [1], using propionic acid as solvent for all the metal precursors, and were characterised by XRD, BET, TEM, MS-TPR-TGA. Their performance for the NO reduction by H_2 in excess O_2 (0.25 vol.% NO/1 vol.% H_2/5 vol.% O_2/He) was monitored between 50 and 450°C [2].

The two materials show high SSA (ca. 100 m^2/g), single perovskite-like structure and consist in aggregate of nano-single crystal spheres of 10 nm average diameter. Based on the instability of Co-perovskites to reducing conditions, their behaviour in H_2/He was studied by TGA-MS and in situ XRD up to 700°C. While the $LaCoO_3$ is reduced in two steps to La_2O_3+Co at 550°C with $La_2Co_2O_5$ as intermediate step at 350°C, the presence of Pd lowers the temperature of the reduction, which occurs via additional formation of a $La_3Co_3O_8$ phase. The reduction is fully reversible, the perovskite structure being restored when the O_2-containing reaction mixture is fed to the catalyst bed. After reduction at 300°C, Pd is likely segregated from the perovskite structure.

The Pd-containing catalyst exhibits full NO conversion at 150°C with 68% selectivity to N_2, whereas $LaCoO_3$ shows no activity at this temperature. Activity drops above ca. 170°C and both materials exhibit oxidation activity to NO_2 for T>350°C likely due to the perovskite.

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Inorganic and Coordination Chemistry **169**

Structural characterization of the catalytic core of a group II intron ribozyme *via* NMR

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Group II introns are one class of naturally occurring catalytic RNAs, i.e. ribozymes, which catalyze a great variety of reactions.[1,2] These large molecular machines are best known for their self-splicing reaction. Among a set of six domains (D) the D1, and D5 as well as the linker regions between the domains are the only regions that are essential for catalysis.[3,4] D5 represents the most critical active-site component with a small hairpin-loop structure.[5,6] It has been shown that metal ions play an essential role for folding and the function of catalytic RNA molecules. We are determining the solution structure of the catalytic D5 of two different classes of bacterial group II introns with distinctly different functionalities. As a next step the coordination of metal ion and their effect on local structure will be investigated in detail by various NMR methods. The structural changes within D5 upon docking to its binding region in D1, being a crucial step in the assembly of the active structure and highly dependent on Mg^{2+},[7] is also part of our work.

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Acknowledgements

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Inorganic and Coordination Chemistry **171**

Acetonitril Promoted Insertion of an Alkylidene into a Nitrosyl Ligand with Fission of the N-O Bond

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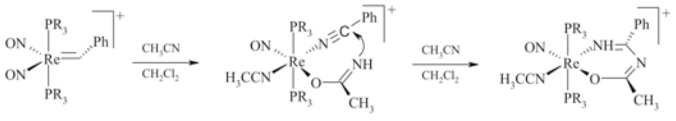
Treatment of the complexes $[Re(NO)_2(PR_3)_2][BAr^F{}_4]$ (R = Cy **1a**; R = ^{i}Pr **1b**) with phenyldiazomethane gave the cationic benzylidene species $[Re\{CH(C_6H_5)\}(NO)_2(PR_3)_2][BAr^F{}_4]$ (**2a** and **2b**) in good yields. When **2a** and **2b** were reacted with acetonitrile the consecutive formation of $[Re(N{\equiv}CCH_3)(N{\equiv}CPh)(NO)(OC(CH_3){=}NH)(PR_3)][BAr^F{}_4]$ (**3a** and **3b**) and $[Re(NCCH_3)(OC\{CH_3\}NH\{C_6H_5\})(NO)(PR_3)_2][BAr^F{}_4]$ (**4a** and **4b**) was observed (see Scheme below)[1].



2a,b **3a,b** **4a,b**

R = Cy **a**
R = ^{i}Pr = **b**

The reaction sequence involves the coupling of coordinated NO, carbene and acetonitrile molecules to yield the (1Z)-*N*-[imino(phenyl)methyl]ethanimidate ligand. Detailed mechanistic studies including labelling experiments and DFT studies were performed.

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Inorganic and Coordination Chemistry **170**

Novel Nitrosyl Tungsten Complexes in Different Oxidation States

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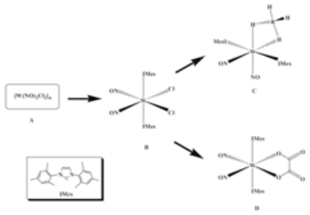
The chemistry of NO is very versatile. With regard to its coordination chemistry it is a well known fact that the NO ligand can contribute to the stabilization of quite different oxidation states of a metal center[1], providing the possibilities of their application as reactive intermediates in organic and organometallic synthesis, as well as in catalytic processes[2].



The reaction of the dichloro complex **B** with $[NEt_4][C_2O_4]$ leads to **D,** an interesting product for photochemical studies. It has been recognized that ultraviolet irradiation of transition-metal oxalate complexes leads to irreversible fragmentation of the oxalate dianion to two molecules of carbon dioxide, with concomitant transfer of two electrons to two metal centers.
The 19-electron organometallic radical **C** could be obtained by reduction of **B** with NBu_4BH_4. Organometallic molecules with more than 18 valence electrons are still rare, and a question of primary importance is to determine "where" the 19th valence electron is located. To complete the characterization, X-ray diffraction studies were carried out on **B**, **C** and **D**.

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Inorganic and Coordination Chemistry **172**

Preparation, separation and chiroptical properties of chiral gold nanoparticles

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We have prepared gold nanoparticles covered with N-isobutyryl-L-cysteine and N-isobutyryl-D-cysteine, respectively. These particles with a mean particle size smaller than 2 nm are highly soluble in water and are amenable to chiroptical techniques like vibrational circular dichroism (VCD) and circular dichroism (CD) spectroscopy. Density functional theory shows that the VCD spectra are sensitive towards the conformation of the adsorbed thiol [1]. Based on the comparison between the experimental VCD spectrum and the calculated VCD spectra for different conformers a preferential conformation of the thiol adsorbed on the gold particles can be proposed. In this conformation the carboxylate group interacts with the gold particle in addition to the sulfur. The particles could furthermore be separated according to their charge and size into well-defined compounds. The optical absorption spectra revealed a well-quantized electronic structure and a systematic redshift of the absorption onset with increasing gold core size, which was manifested in a color change with particle size. Some compounds showed basically identical absorption spectra as analogous gold particles protected with L-glutathione. This shows that these particles have identical core size (10 – 12, 15 and 18 gold atoms, respectively) and indicates that the number and arrangement of the adsorbed thiol is the same, independent of the two thiols, which have largely different size. Some separated compounds show strong optical activity with opposite sign when covered with the D- and L-enantiomer, respectively, of N-isobutyryl-L-cysteine. The observations are consistent with a mechanism based on a chiral footprint on the metal core imparted by the adsorbed thiol.

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Inorganic and Coordination Chemistry **173**

Chiral Arene-Ruthenium(II) Metallo-Prisms Bearing Triazine Derivatives: Synthesis and Structural Characterization

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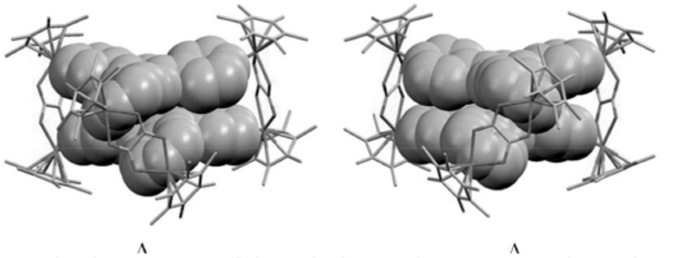
The reaction of dimeric arene-ruthenium chloro complexes $[(\eta^6\text{-arene})RuCl_2]_2$ (**1**) (a: arene = *p*-cymene; b: arene = hexamethlybenzene) with 2,4,6-(n-pyridyl)-1,3,5-triazine (tpt) [n = 3 ($\mathbf{L_1}$), n = 4 ($\mathbf{L_2}$)] gives the corresponding trinuclear complexes $[(\eta^6\text{-arene})RuCl_2]_3(L_1)$ (**2**) and $[(\eta^6\text{-arene})RuCl_2]_3(L_2)$ (**3**), which can be converted into hexanuclear cationic complexes $\{[(\eta^6\text{-arene})RuCl]_6(L_1)_2\}^{6+}$ (**4**) and $\{[(\eta^6\text{-arene})RuCl]_6(L_2)_2\}^{6+}$ (**5**) upon treatment with $AgCF_3SO_3$. The oxalato complexes $[(\eta^6\text{-arene})RuCl]_2(\mu\text{-}O_4C_2)$ (**6**) react with $\mathbf{L_2}$ in the presence of $AgCF_3SO_3$ to afford trigonal-prismatic complexes $[\{(\eta^6\text{-arene})Ru\}_6(O_4C_2)_3(L_2)_2]^{6+}$ (**7**), which present helical chirality.



The molecular structures of the cationic complexes **5a**, **5b** and **7b** show strong π-stacking interactions between the tpt units. Despite the bigger spacing between the two ruthenium atoms in **7b**, the triazine-triazine distance is shorter (3.42 Å) as compared to **5a** and **5b** (3.64 and 3.62 Å respectively), thus giving rise to a helical twist and hence to chirality.

Inorganic and Coordination Chemistry **174**

Efficient charged separated systems for artificial photosynthesis

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An increasing demand for clean and cheap energy has stimulated development of novel chemical systems capable of efficient solar energy conversion into a more useful form, i.e. chemical energy [1]. This goal can be achieved in systems that allow formation of the charge-separated state with a significant lifetime. For this aim, we propose very simple systems based on transition metal complexes containing the original TTF-dppz ligand (Figure 1).

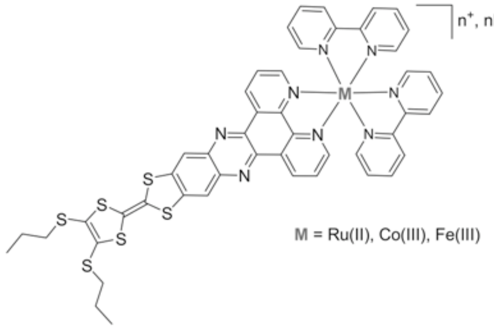

Figure 1

These luminescent complexes exhibit charge separated behaviors with lifetimes which could reach up tol 600 µs.

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Inorganic and Coordination Chemistry **175**

Influence of Gas-Phase Thermodynamics on the Products of Flame Synthesis: From Oxides to Salt I and Metal Nanoparticles

Robert N. Grass and Wendelin J. Stark

Flame synthesis has been applied for several decades for the large-scale manufacturing of metal oxides such as silica and titania. Recent developments including flame spray pyrolysis and reducing flame synthesis further allow the production of biomaterials, carbonates, fluorides and even metal nanoparticles by a cost-efficient gas-phase process. While both the chemical kinetics and mixing properties of highly turbulent flames are poorly understood, gas-phase thermodynamics as well as aggregation and sintering assumptions can be applied for the explanation of shape, size and composition of flame-made nanoparticles.

We show how simple calculations based on solid state chemistry data may be applied together with gas phase thermodynamics to influence the product composition of the flame process. The chemical reaction engineering of flame spray processing is further illustrated by showing possibilities and limitations of a variety of examples starting from cerium oxide[1], calcium-carbonate[2], nano-gypsum, alkali-earth fluorides[3] to metallic bismuth[4], copper[5] and cobalt[6] nanoparticles.

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[6] R. N. Grass, E. K. Athanassiou, W. J. Stark, *EP Patent application 05 019287.1*, **2005**; R. N. Grass, W. J. Stark, *J. Mater. Chem.,* **2006**, *16, 1825.*

Inorganic and Coordination Chemistry **176**

Chemical and Structural Effects on Thermotropic Properties of Lanthanide Complexes

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Driven by the attractive magnetic and optical properties resulting from the introduction of 4f-block metals in mesophases, we focus here on the ternary lanthanide complexes with hexacatenar aromatic tridentate ligands (figure 1). The effect of chemical, structural and electronic organisation on thermotropic properties will be detailed.

Counter-anions in the lanthanide salts affect the affinity of the metal for the additional neutral tridentate ligand, and hence the complexation stability and thermotropic properties [1]. The repartition of the charge density onto the ligand plays an important role in the organisation of the mesogen, and can be related to the intermolecular interactions.

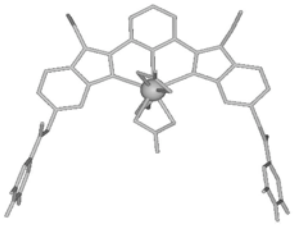

Figure 1. Molecular structure of the rigid core of the complexe $[YbL(NO_3)_3]$.

[1] H. Nozary, S. Torelli, L. Guénée, E. Terazzi, G. Bernardinelli, B. Donnio, D. Guillon and C. Piguet, *Inorg. Chem.* **2006**, *45*, 2989.

Inorganic and Coordination Chemistry **177**

The decomposition of Peroxynitrite at neutral pH revisited

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Peroxynitrite is a potent and versatile oxidant that can attack a wide range of biomolecules. The peroxynitrous acid can react with DNA, proteins, and lipids at physiological conditions, leading to cellular damage and cytotoxity. As the decomposition of peroxynitrite (1 – 10 mM, pH = 7) yields ca. 1 % singlet oxygen ($^1\Delta_gO_2$) [1], we have explored the decomposition of peroxynitrite (1 – 10 mM, pH ca. 7) quenched after 50 – 1000 ms with acids such as $HClO_4$, HNO_3 and H_3PO_4. A few seconds after the addition of acid, all of the ONOOH acid has isomerised to NO_3^- and H^+.

Our studies show the presence of a strongly oxidizing species after quenching, which attacks I^- and Br^- in acetate buffer (pH = 5). The life time of this species is between that of ONOOH and O_2NOOH. It was experimentally verified that HNO_2 and NO_2^- do not cause this oxidation. We, therefore, postulate that the oxidation of I^- and Br^- in acetate buffer (pH = 5) might be due to an adduct of HOONO/$ONOO^-$ or $HOONO_2$ formed from this adduct. These species may also serve as the source for the singlet oxygen. The lifetime of the oxidant was enhanced in phosphate buffer. Additional stopped-flow and quench flow experiments are being carried out to characterize the intermediate(s) formed.

[1] S. Miyamoto, G. R. Martinez, P. Di Mascio, D. Gupta, R. Kissner, W. H. Koppenol, 2006, in preparation.

Inorganic and Coordination Chemistry **179**

Sintering Behaviour of in-Situ Doped Nanoparticles by Flame Spray Pyrolysis for Fuel Cell Applications

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Ceramic oxygen ion conductors play a key role in solid oxide fuel cells (SOFC) with high power output. Ceria-based electrolytes are considered to be very promising due to their high ionic conductivity. Small amounts of transition metal oxides have shown to be very effective sintering aids for Ce0.8Gd0.2O1.9 (CGO20) and Ce0.9Gd0.1O1.95 (CGO10). Adding as few as 1 mol% of cobalt oxide resulted in much lower sintering temperatures, higher shrinkage rates, and grain sizes in the final sintered product in the sub-micron range (~120 nm). Several investigations indicated that the necessary and sufficient dopant concentration lies below the reported 2 mol%. It was argued that improved homogeneity of the dopant phase by using a more suitable doping process would reduce the necessary concentration while maintaining the same sintering effect. In order to test this hypothesis, we used an alternative one-step preparation route to Cobalt oxide doped CGO. Flame spray pyrolysis (FSP) is a continuous high temperature gas process which uses suitable organic derivatives of the desired metals as homogeneous mixtures. The precursors are directly sprayed into a flame where they are rapidly converted into the corresponding mixed oxides. Here, we report on the successful pilot-scale preparation of CGO10 and in-situ cobalt oxide doped CGO10 powders by FSP. We show that cobalt oxide as a dopant is already effective at concentrations as low as 0.1 mol%. At a dopant concentration of 1 mol%, the maximum sintering temperature is lowered by 250°C if compared to undoped CGO10 [1]. The results are further discussed in terms of materials preparation and application.

[1] E. Jud, S.C. Halim, W.J. Stark, L.J. Gauckler, *J. Am. Ceram. Soc.*, accepted, **2006**

Inorganic and Coordination Chemistry **178**

Studies of Phthalocyanine Assemblies by STM

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Over the last few decades, phthalocyanines (Pcs) have been investigated extensively due to their intrinsic properties for many technological applications, such as colorants, dyes, pigments, xerography, sensors, solar cells, catalysts, photodynamic therapy and non-linear optics. Also monolayers of Pcs have been successfully studied by STM methods. Compound **1** [1] and the ZnPc derivative of it have been assembled as monolayers and studied by STM (Fig. 1). Currently, the assembly of more complex phthalocyanine derivatives is in the focus of our investigations.

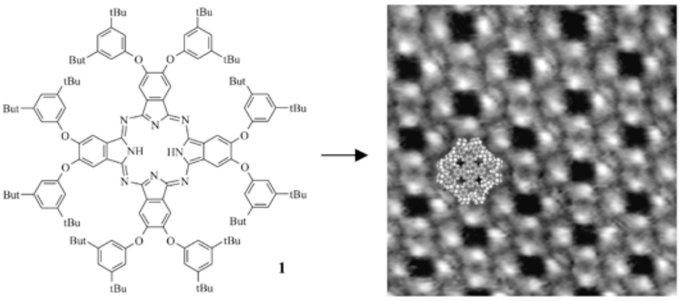

Figure 1. Molecular structure of **1** and STM image (11 x 11 nm) of a monolayer of **1** on Au(111).

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Inorganic and Coordination Chemistry **180**

Ln(III) Tripodal Complexes For Unravelling Preorganisation Effects

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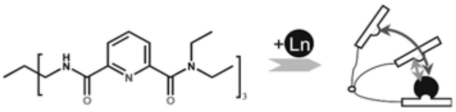
Investigation of the formation kinetics stands for a powerful tool to characterise self-assembly processes, as it has been recently demonstrated for the formation of the Ln(III) bimetallic helicates.[1] The obtained data have been implemented into the thermodynamic models to quantify the key reaction parameters.[2] In this context, a detailed thermodynamic and kinetic study of monometallic Ln(III) complexes with a ligand possessing partially preorganised binding sites appears particularly promising.

In this work, a new tripodal ligand containing three identical strands anchored on the apical carbon has been synthesised. This ligand provides a tight nine-coordinate cavity to bind Ln(III) cations. The resulting C_3-symmetrical complexes have been characterised by NMR, ES-MS and spectrophotometry. The effect of preorganisation on the self-assembly is evaluated using kinetic methods.



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[2] J. Hamacek, M. Borkovec, C. Piguet, *Chem. Eur. J.* **2005**, *11*, 5217.

Inorganic and Coordination Chemistry **181**

Metallopolymer or Metallocycle?

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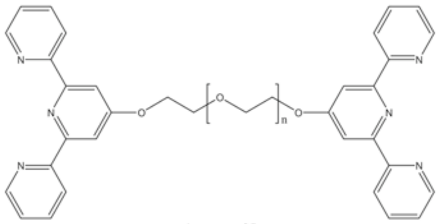
The interactions of ditopic ligands containing two 2,2':6',2''-terpyridine metal-binding domains linked by a variable spacer (see below) with transition metal ions will be presented. The reaction can give metallopolymers (copolymers with alternating metal centres and ligands), discrete molecular macrocycles, or mixtures of the two. The outcome of the coordination depends on the precise reaction conditions and the nature of the metal ion.

Examples will be presented of metallomacrocycles of various sizes and nuclearity together with the dynamic behaviour of some novel chiral species.



$1 \leq n \leq 65$

Inorganic and Coordination Chemistry **182**

Structures of Self Assembled Monolayers of Different Functionalised Dendritic Wedges on Graphite

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[a]University of Basel, Department of Chemistry, 4056 Basel

The study of monolayers on surfaces with scanning tunnelling microscopy (STM) is a very promising field of study with many possible applications such as device fabrication, display manufacture and sensor design[1].

Understanding the self organisation when forming monolayers is a very important part on the road to commercial applications.

The structures of different functionalised second generation dendritic wedges have been investigated by X-ray diffraction structure analysis and by STM on graphite surface.

A remarkable similarity in the structures of three different functionalised dendritic wedges has been found not only in the monolayers that they form on graphite sufaces but also in their crystal structures[2].

Capitalising on the results of dendritic wedges that we have already reported [2], we have now synthesised in high yields amine-functionalised dendritic wedge. This opens the door to new ways of modifying the properties of new compounds.

[1] J.-M. Lehn, *Supramolecular Chemistry: Concepts and Perspectives*; VCH: Weinheim, Germany, 1995
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Inorganic and Coordination Chemistry **183**

Synthesis of New N-Pyridylfulleropyrrolidine-Metal Complexes

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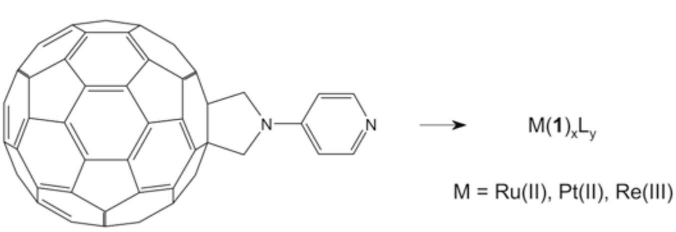
The processes in the photosynthetic reaction centre consist in a variety of short range charge transfer events from a donor to an acceptor molecule. The strong electron accepting properties of C_{60} make it an interesting molecule for studying this kind of light induced electron transfer. N-pyridylfulleropyrrolidine (**1**) is known to have good electronic communication between the fulleropyrrolidine nitrogen and the fullerene core [1], one of the main requirements for an effective charge transfer.



1

Our aim is to synthesize supramolecular systems with long-lived charge separated states by complexation of **1** to different photoactive transition metal ions.

[1] F.T. Tat *et al, J. Org. Chem.* **2004**, 69, 4602.

Inorganic and Coordination Chemistry **184**

Copper(I) complexes as potential photosensitizers in solar cells

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Nowadays, photovoltaic cells are made of nanocrystalline or conducting polymeric materials which contain a semiconductor [1]. Due to the large band gap of these semiconductors, the use of sensitizers is an active field of research.

Up to now, ruthenium has been the most employed metal for spectral sensitization of these films [2] and polypyridine based complexes have been the most studied. Copper(I), however, offers a cheaper alternative to ruthenium, with complexes possessing similar photophysical properties.

A family of novel ligands (eg. 1) with multitopic coordination sites based on nitrogen donors and their copper(I) complexes have been synthesized. Their photophysical properties are under investigation in order to establish their performance in solar cells.

[1] A. Hagfeldt and M. Grätzel, *Acc. Chem. Res.* **2000**, *33*, 269-277.
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Inorganic and Coordination Chemistry **185**

The postulated adduct of peroxynitrite and nitrogen monoxide and its nitrosating properties

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Frein et al [1,2] set up a reaction system which continuously produces superoxide and nitrogen monoxide and has nitrosating properties at moderately acidic pH. They attribute this to addition of a superoxide ion to two nitrogen monoxide molecules. Due to the fast reaction of nitrogen monoxide with the superoxide ion [3] to peroxynitrite, a plausible form is some adduct of this anion or the conjugate acid with nitrogen monoxide.

Stopped-flow studies have shown no observable no reaction of a bulk peroxynitrite / nitrogen monoxide system with various reagents susceptible to nitrosation. Flow reactor EPR measurements did not show any signature that could be assigned to a paramagnetic adduct.

Still, the EPR showed the presence of a paramagnetic species of low concentration, coinciding with nitrogen dioxide. This result allows to determine directly the radical yield of the homolysis reaction of peroxynitrous acid (ONOOH ▯ $NO_2^{\bullet}$ + ${}^{\bullet}OH$) to <1%, considerably lower than a simulation based on previous estimates [4] produces.

[1] Daniel Frein, *Signaling and Redox Regulation by Nitric Oxide, Superoxide and Carbon Monoxide, dissertation in press* **2006.**
[2] Andreas Daiber, Daniel Frein, Dmitry Namgaladze, Volker Ullrich, *Journal of Biological Chemistry* **2002,** *277*, 11882.
[3] R. Kissner, T. Nauser, P. Bugnon, P. G. Lye, W. H. Koppenol, *Chem. Res. Toxicol.* **1997**, *10*, 1285.
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Inorganic and Coordination Chemistry **187**

Preparation of Star-Shaped Pentapyridyl Ligands Towards the Formation of Giant Fullerene-Like Molecule by Coordination Chemistry.

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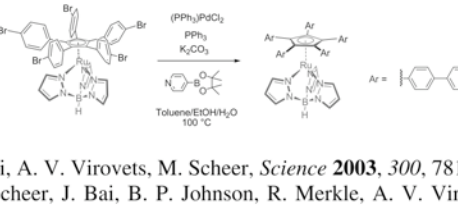
1211 Geneva 4, Switzerland

One of the major goal of supramolecular chemistry is the preparation of complex structures from self assembly of simple building blocks. In this respect, the design of molecular spheroids represents a challenging perspective for chemists.[1-2]
Here, we present the synthesis of star-shaped penta-ligands containing five pyridyls, which could also be considered as starting materials for the preparation of fullerene-like molecules by coordination chemistry. Two synthetic strategies will described, one based on the procedure of M. Nomura *et al.*[3] the preparation of penta-arylcyclopentadiene and one starting from a ruthenium scorpionate.[4]



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Inorganic and Coordination Chemistry **186**

Chiral Phosphoramidites as P,C-Bidentate Ligands in Rhodium(I) and Rhodium(III) Complexes

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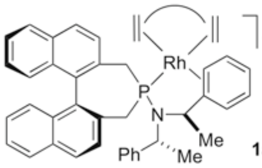
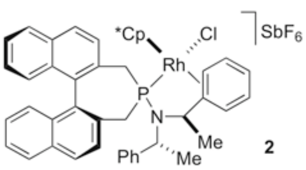
Chiral phosphoramidite ligands have become increasingly important because of their synthetic availability, high resistance to oxidation, and low cost. We have recently reported cyclopropanation catalysts of ruthenium(II) with chiral binaphthol-based phosphoramidites in which one aryl group of the amine moiety coordinates in a η^2-fashion to the metal [1]. We show now that such η^2-interactions are present in Rh(I) and Rh(III) complexes, too.
The reaction of $[Rh(cod)Cl]_2$, $[Rh(nbd)Cl]_2$ or $[Rh(Cp^*)Cl_2]_2$ with (S_a,R_C,R_C)-*O*,*O*'-(1,1'-binaphthyl-2,2'-diyl)-*N*,*N*-bis(1-phenylethyl)phosphoramidite in CH_2Cl_2 solution, followed by addition of $AgSbF_6$, gives the corresponding cationic complexes **1a**,**b** or **2**, in which one pendant phenyl ring coordinates to rhodium in a η^2-fashion.



1a,b



2

These complexes were fully characterized by ^{31}P-, ^{1}H-, ^{13}C-NMR spectroscopy, ^{31}P-^{1}H HMQC, ^{13}C-^{1}H HMQC, ^{13}C-^{1}H HMBC, ^{1}H-^{1}H DQF-COSY and ^{1}H-^{1}H NOESY 2D-NMR measurements, mass-spectrometry, X-ray, and elemental analysis.

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Inorganic and Coordination Chemistry **188**

Dehydrogenation of Amine-Borane Adducts Catalyzed by Rhenium Nitrosyl Complexes

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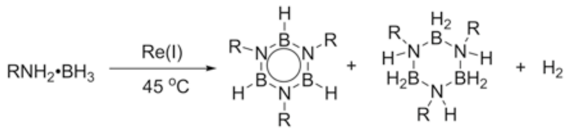
Amine-borane adducts are well-known as potential hydrogen storage systems [1]. Besides thermally controlled H_2 release [2], transition-metal catalyzed H_2 releases from amine-boranes are sought under mild condition. So far, Rh(I) catalyzed dehydrogenation reactions of amine-borane adducts are the only known cases [3].



R = H, Me

Based on a screening of several rhenium nitrosyl diphosphine catalysts, Re(I) species worked best. Our present efforts concentrate on the development of rhenium complexes for reversible amine-borane dehydrogenation/hydrogenation of cases where thermodynamics would allow this.

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[2] Wideman, T.; Sneddon, L. G. *Inorg. Chem.* **1995**, *34*, 1002.
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Inorganic and Coordination Chemistry **189**

Early Stages of the Nitrogen Monoxide – Dioxygen Reaction

Benedikt Galliker and Reinhard Kissner

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Stochiometry and rate law of the title reaction are known for long, with the remarkable decrease of rate with rising temperature, indicating a rapidly settling initial equilibrium which requires an intermediate at steady-state concentration, well concealed in the reaction mixture. N_2O_2 and $ONO_2^\bullet$ are proposed candidates. The former is found in traces only close to 0 K [1] and never at room temperature. Some researchers tried to identify $ONO_2^\bullet$ by infrared spectroscopy but obtained ambiguous results due to the similarity of the other compounds in the gaseous reaction mixture [2].

We used a gas flow reactor in an EPR cavity where we recorded spectra at various $NO^\bullet$ and O_2 flow rates. The compound signal could be numerically decomposed into two strong and one weak regular EPR signals. We also reacted gaseous $NO^\bullet$ with saturated O_2 solution in 2-Methylbutane at 113 K. A novel blood-red and diamagnetic compound was formed around the injection position. On warming to 133 K the red compound disappeared and blue N_2O_3 was formed instead.
Based on our observations we propose the reaction scheme

$$NO^\bullet + O_2 \rightleftharpoons ONOO^\bullet$$
$$ONOO^\bullet + NO^\bullet \longrightarrow ONOONO$$
$$ONOONO \longrightarrow 2\,NO_2^\bullet$$

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Inorganic and Coordination Chemistry **190**

mer-ReBr(NCCH$_3$)$_2$(CO)$_3$: A Precursor for Re(CO)$_2$ Complexes

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The fac-[M(CO)3]+ core (M = Re, Tc) and its many derivatives are promising compounds in various fields of organometallic chemistry. On one hand, it is a precursor for radiopharmaceuticals[1], on the other hand [Re(CO)3(diimine)]+ complexes show activity in the photocatalytic CO2-reduction[2]. Our investigations are now focused in the synthesis of biscarbonyl-complexes [M(CO)2]+. They show different binding, substitution and electrochemical properties that give us the opportunity to extend the field of biomolecule labeling and photocatalysts.

A water-soluble and substitution labile biscarbonyl is the *cis-trans-cis*-(Et_4N)[$ReBr_2(NCCH_3)_2(CO)_2$] **2** which undergoes different substitution reactions with several ligands such as imidazole, bipyridin, 2-picolinic acid etc. Only the two bromide anions were substituted, the acetonitrile ligands were however very strongly bounded. Starting from **2,** we also synthesized *mer*-ReBr($NCCH_3$)$_2$(CO)$_3$ **1,** one of the rare meridional rheniumtricarbonyl compounds.

Substitution reactions with **1** gives again biscarbonyl complexes, but with slightly different composition compared when starting from **2**. Especially the reaction with terpyridine should be mentioned where a two- or threefold coordination could be obtained.

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Inorganic and Coordination Chemistry **191**

Modelling the splice site of a group II intron ribozyme

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Most functional RNAs have to undergo several steps of post-transcriptional modifications before carrying out their assigned function. One of the major modifications is the splicing process, in which the non-coding introns are removed from the coding exons. Group II introns, found in the genes of plants, fungi, lower eukaryotes, and bacteria are ribozymes, i.e. are "enzymes" composed entirely of RNA. These introns splice autocatalytically.[1,2] They consist of a conserved set of six domains (D1-D6) which are defined by characteristic secondary structural elements.[1,2] D1, an independent folding domain and molecular scaffold for docking of the other domains, and D5 are absolutely necessary for catalysis.[3] Splicing can only be successfully carried out if the intron recognizes the two exons at the correct site. 5'-exon recognition occurs through two regions in D1, the exon binding sites 1 and 2 (EBS1 and EBS2) which base pair with two intron binding sites (IBS1 and IBS2) in the 5' exon. It has been shown that metal ions are crucial for folding and catalysis[4] as well as residing at the EBS1-IBS1 complex.[4,5] As the splicing event is dependent on the correct recognition of IBS1 through EBS1, we are focusing on the structural and metal ion requirements of this part by NMR and other spectroscopic techniques. The results of the structure analysis will be discussed.

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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Inorganic and Coordination Chemistry **192**

Polymerisation of Thiophene with {Ru(terpy)$_2$}$^{2+}$ Dyes

William Kylberg, Egbert Figgemeier, Edwin C. Constable and
Catherine E. Housecroft

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In the dye sensitized photovoltaic solar cell a monolayer of metal complexes that absorb light are commonly adsorbed onto a nano-structured TiO_2 film [1]. The cell is completed with a counter electrode and an electrolyte with a redox pair in between. For a variety of reasons it would be advantageous to have a solid-state electrolyte instead of the present liquid one. Polymers that can act as hole conductors are believed to be a possible solid state alternative to liquid electrolytes [2]. One hole-conducting material that has attracted attention is poly-thiophene [3]. In this project attempts were made to modify dye-sensitised TiO_2 films by polymerisation of thiophene monomers directly to thienyl groups of the dye molecule ligands using chemical, electrochemical and photochemical techniques. A new metal complex dye with a 4'-(2,2'-bithienyl)-2,2':6',2"-terpyridine ligand has been synthesized and used to sensitize a TiO_2 film. Photo-electrochemical characterisation has been performed on the modified dye attached to TiO_2 and Sb-doped SnO_2 films. These results have been complemented by solution phase measurements. The growth of poly-thiophene on the surface has been monitored with a scanning electrochemical microscope setup.

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Inorganic and Coordination Chemistry **193**

Substituted Cyclopentadienyl Tricarbonyl Rhenium Complexes

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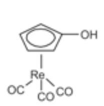
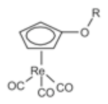
We report here the preparations of various substituted cyclopentadienyl tricarbonyl rhenium complexes. Hydroxycyclopentadienyl tricarbonyl rhenium **1** [1] was synthesised through a new route with bis(trimethylsilyl) peroxide [2]. We were able to obtain different ethers **2a-c** and esters **3a, b** by nucleophilic substitution with acyl chlorides and alkyl bromides [3].

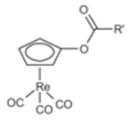


1



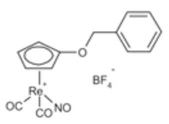
R= Bn a, Et b, iPr c

2



R'= Me a, Ph b

3



4

Nitrosylation of the benzyl ether derivative **2a** led to the corresponding nitrosyl complex **4**. The ether derivatives are ideal precursors for the synthesis of a large range of new interesting complexes such as nitrosyl and phosphine substituted derivatives or hydrides.

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Inorganic and Coordination Chemistry **195**

Synthesis, Characterization and Properties of New Water Soluble Nitrosyl Rhenium Complexes.

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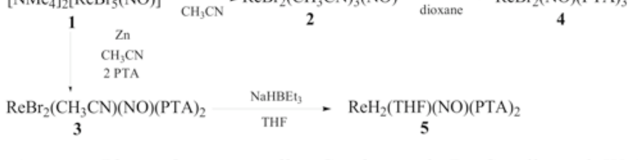
[b] *Department of Chemistry, Wilfried Laurier University, Waterloo, Ontario N2L 3C5, Canada*

Nowadays, there is a growing interest in the field of aqueous homogeneous organometallic catalysis for economical and safety considerations [1]. Our goal is to prepare new water soluble rhenium hydrides using the neutral water soluble phosphine 1,3,5-triaza-7-phosphaadamantane (PTA). Transition metal complexes containing this phosphine were extensively studied and developed mainly by Joó, Darensbourg and coworkers [2], [3]. Starting from the $[NMe_4]_2[ReBr_5(NO)]$ salt (**1**), we report the two steps synthesis of a new water soluble rhenium dihydride $ReH_2(THF)(NO)(PTA)_2$ (**5**). Its characterization, properties and reactivity are also presented.



$$\begin{tikzcd}
\underset{\mathbf{1}}{[NMe_4]_2[ReBr_5(NO)]} \arrow[r, "Zn", "CH_3CN"'] \arrow[d, "\begin{array}{c}Zn\\CH_3CN\\2\ PTA\end{array}"] & \underset{\mathbf{2}}{ReBr_2(CH_3CN)_3(NO)} \arrow[r, "3\ PTA", "dioxane"'] & \underset{\mathbf{4}}{ReBr_2(NO)(PTA)_3} \\
\underset{\mathbf{3}}{ReBr_2(CH_3CN)(NO)(PTA)_2} \arrow[r, "NaHBEt_3", "THF"'] & \underset{\mathbf{5}}{ReH_2(THF)(NO)(PTA)_2} &
\end{tikzcd}$$

[1] *Aqueous Phase Organometallic Catalysis* ed. B. Cornils and W.A. Hermann, Wiley-VCH, Weinheim, Germany, **1998**.
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[3] Darensbourg, D.J.; Decuir, T.J.; Stafford, N.W.; Robertson, J.B.; Draper, J.D.; Reibenspies, J.H.; Kathó, A.; Joó, F. *Inorganic Chemistry* **1997**, *36*, 4218-4226.

Inorganic and Coordination Chemistry **194**

Synthesis and Characterization of Dinuclear Chromium Complexes as Precursors to Rigid-Rod Molecular Wires

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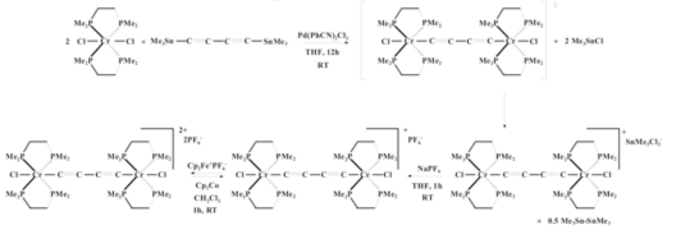
There is growing interest in dinuclear metal complexes $[L_nMC_xML_n]$ bridged by linear unsaturated carbon chains[1] due to their potential application as building blocks for new one-dimensional materials. These complexes are expected to display non-linear optical properties or may have application as electronic materials, such as single electron devices.



The reaction of $Me_3Sn\text{-}C{\equiv}C\text{-}C{\equiv}C\text{-}SnMe_3$ with 2 equivalents of $CrCl_2(dmpe)_2$[2] yields in presence of a palladium catalyst the dinuclear chromium cation in a Cr(II/III) mixed-valent state. By treatment with $[Cp_2Fe][PF_6]$ the Cr(II/III) complex could be oxidized to the corresponding dinuclear Cr(III/III) species. EPR studies and magnetic measurements of the obtained dinuclear complexes indicate a strong antiferromagnetic coupling of the chromium centres through the C_4 bridge. The remaining d-electrons at each Cr centre are not or only very weakly coupled. For the molecular unit this gives rise to class I properties of the Robin-Day classification.

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Inorganic and Coordination Chemistry **196**

Mechanistic Aspects of Enantioselective Hydrogenation by Artificial Metalloenzymes

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Mechanistic investigations on the enantioselective hydrogenation with artificial metalloenzymes based on the biotin-avidin technology reveal that the reaction follows a Michaelis-Menten mechanism ($K_M = 3.18\ mM^{-1}$, $k_{cat} = 0.074\ s^{-1}$). [1,2]

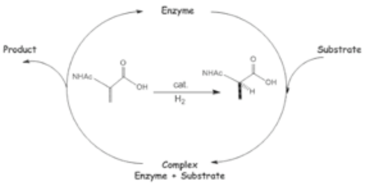

Figure 1. Mechanism of hydrogenation of α-acetamidoacrylic acid

The influence of the spacer, the diarylphosphine residues, the guest protein, and the solvent on the selectivity, the activity and the kinetic parameters will be presented.

[1] Skander, M.; Malan, C.; Ivanova, A.; Ward, T. R. *Chem. Comm.* **2005**, 4815, and references cited therein.
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Inorganic and Coordination Chemistry **197**

Complementary Metal Mediated Self-Assembly

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A common strategy for the construction of supramolecular systems takes advantage of metal ion coordination, whereby metal ions control the self-assembly of ligands to form thermodynamically favoured assemblies.[1] In this poster, we describe the design, modification, and self-assembly of supramolecular structures to create an artificial complementary replicating system based upon metal-ligand interactions.

Resin immobilised (poly)-2,2'-bipyridines have been prepared and used as templates for the copper(II)-mediated assembly of alkene-functionalised 2,2':6',2"-terpyridines which undergo subsequent templated metathesis to form complementary poly-2,2':6',2"-terpyridine strands.[2]

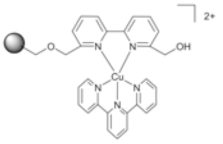

Figure 1 Resin bound self assembled Cu(II) mediated complex. The resin is represented by the shaded sphere.

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Inorganic and Coordination Chemistry **198**

Ruthenium Carbene Complexes for Alkene Metathesis

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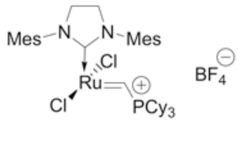
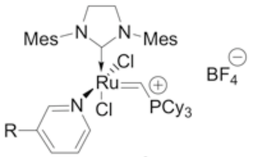
Ruthenium carbene complexes play an essential role in the alkene metathesis reaction [1]. Such species are usually 16-electron complexes, which during initiation step of the metathesis loose one ligand to form an 14-electron intermediate [1]. Recently, an elegant and efficient synthesis of stable "naked" 14-electron carbene complexes **1** was published by Piers *et al.* [2]. These complexes initiate alkene metathesis rapidly, but they suffer from low stability at elevated temperatures [2]. Herein, we report carbene complexes **2** containing weakly coordinated pyridine ligands. According to X-ray analysis, the pyridine ligand is in unusual *cis* position to the heterocyclic carbene ligand. Catalytic activity of complexes **2** in ring-closing metathesis of diallylmalononitrile will also be discussed.



1



R = H, Br

2

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Inorganic and Coordination Chemistry **199**

Evaluation of π Contribution in N-Heterocyclic Carbene Fe(II) Bonds

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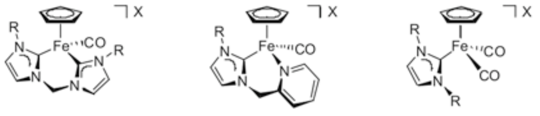
Over the past few years, N-heterocyclic carbenes (NHCs) have emerged as powerful class of ligands in transition metal chemistry [1]. Generally, NHCs have been assumed to be purely σ-donors with negligible π contribution. However, little experimental evidence has been available thus far that supports such a model of π interactions [2].

Our approach for understanding the bonding of NHC is based on a series of Fe(II) complexes (see Figure). In these complexes the carbene ligand can be selectively exchanged by pyridine or CO without significantly modifying the residual moiety. We will present the structural and electronic consequences that arise from such ligand substitution. Most importantly, carbene bonding to Fe(II) is highly similar to pyridine bonding. In line with recent computational analyses [2], these results can be interpreted by substantial metal-to-carbene π backbonding.



R: Me, iPr, Mes
X: I, BF_4

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Inorganic and Coordination Chemistry **200**

Ionic interactions in dicationic Palladium BINAP complexes using diffusion and Overhauser NMR methods.

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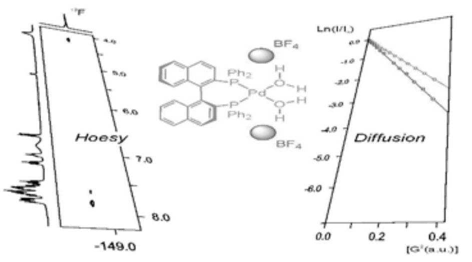
PGSE diffusion, ^{1}H,^{19}F Overhauser and related 2-D NMR studies[1] on salts of the di-cations[2] $[Pd(H_2O)_2(BINAP)]^{2+}$, 1, $[Pd(\mu\text{-}OH)(BINAP)]_2^{\ 2+}$, 2, $[Pd(\mu\text{-}OH)(\mu\text{-}NHR)(BINAP)_2]_2$, 3, (R = *p*-Tol, *p*-$ClC_6H_4$, *p*-$CH_3OC_6H_4$) and $[Pd(\mu\text{-}O_2PF_2)(BINAP)]_2(PF_6)_2$ 4, are reported. These solution NMR results reflect on how the anion interacts with the cation as well as the extent, and the solvent dependence of the ion pairing. The solid-state structure of $[Pd_2(\mu\text{-}OH)(\mu\text{–}p\text{-}TolNH)(BINAP)_2]\,(CF_3SO_3)_2$ has been determined.



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Inorganic and Coordination Chemistry **201**

Synthesis and Structure of A Penta-4-Pyridylferrocene Derivative: A Star-Shaped Building Block for Coordination Chemistry

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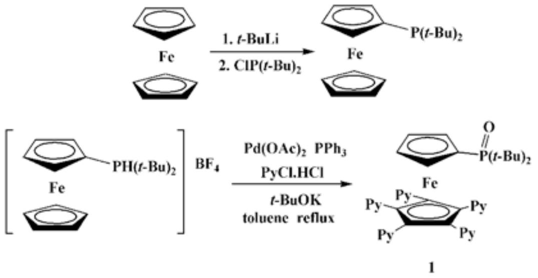
1211 Geneva 4, Switzerland

The design of a molecular spheroid is a very exciting challenge for chemists [1]. Recently, inorganic fullerene-like nanoballs were synthesized from pentaphosphaferrocene and copper derivatives [2]. The structures consist of self assembled cyclo-P_5 rings (pentagonal units) held together by coordination of copper ions.

The new pentapyridyl derivative **1** was obtained in two steps starting from ferrocene. This star-shaped ligand could be used as a building block in order to synthesize fullerene-like molecules. Our present efforts are concentrated on the preparation of complexes with metal salts (Cu^I, Ag^I).



[1] L. R. MacGillivray, J. L. Atwood, *Angew. Chem. Int Ed.* **1999**, *38*, 1018.
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Inorganic and Coordination Chemistry **202**

Energy Consumption During Nanoparticle Production: How Economic is Dry Synthesis?

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The mass production of oxide nanoparticles is increasing rapidly. Newer and faster processes have been developed in the past few years and are already implemented on an industrial level without specifically addressing inherent differences in energy consumption. We have therefore selected a series of wet-chemistry and dry processes and compared them in terms of energy requirements [1].

Clear differences arise for nanoparticle production using electricity-intensive plasma processes, organic- or chloride-derived flame synthesis and liquid based precipitation processes. In spite of short process chains and elegant reactor design, many dry methods inherently require vastly bigger energy consumption than the multi-step wet processes. We have further found that product composition strongly influences the selection of the preferred method of manufacturing in terms of energy requirement: Metal oxide nanoparticles of light elements with high valency, e.g. titania demand high volumes of organic precursors and traditional processes excel in terms of efficiency. Products with heavier elements, more complex composition and preferably lower valency such as doped ceria, zirconia, and most mixed oxide ceramics may be readily manufactured by recently developed dry processes.

[1] N. Osterwalder, C. Capello, K. Hungerbühler, W. J. Stark, *J. Nanoparticle Res.*, **2006**, 8, 1.

Inorganic and Coordination Chemistry **203**

Nanoscale Tungstates: Morphological and Kinetic Studies

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Ragnar Kiebach[2], Wolfgang Bensch[2], Greta R. Patzke[1]

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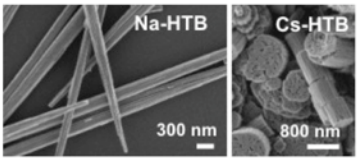
CH-8093 Zürich, Switzerland
[2] Institute of Inorganic Chemistry, University of Kiel, Germany

Tungstates ($M_xWO_{3+x/2}$) are promising materials for electrochromic devices, catalysts and displays. Hydrothermal reactions are a straightforward way of producing nanoscale transition metal oxides in gram quantities through one-step reactions.[1] We have recently investigated the mechanism of hydrothermal MoO_3 rod formation with complementary in situ EDXRD and EXAFS methods.[2] The fibers are formed via a quick dissolution-precipitation mechanism within a few minutes.[2]

This combined technique has now been employed to investigate the hydrothermal formation of nanoscale alkali hexagonal tungsten bronzes (HTBs). The morphology of the HTBs can be tuned by the hydrothermal reaction of ammonium metatungstate with the appropriate alkali chloride, giving rise to highly anisotropic fibers (e.g. Na-HTB) or hierarchical nanorod assemblies (e.g. Cs-HTB). Despite slight differences in the individual kinetics of alkali HTB formation, all reactions proceed on an hour-scale, and they have a nucleation-controlled mechanism in common.



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Inorganic and Coordination Chemistry **204**

Metal Clusters Arrangement in Wheat E_c-1 Metallothionein

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Approximately 50 years ago metallothioneins (MTs) were first isolated from equine kidney as a cadmium-containing protein. Since then, MTs have been found in a wide range of organisms, from plants to fungi. The metal binding ability of MTs, typically via metal-thiolate clusters, is their most distinctive characteristic [1]. MTs have high affinity for d^{10} metals ions, like zinc(II), cadmium(II), copper(I) or mercury(II). Biological functions attributed to MTs are still a subject of discussion. Heavy metal detoxification, zinc and copper metabolism, scavenging of reactive oxygen species, and regulation of metalloenzymes and transcription factors [2] are some of the proposed functions for these unique metalloproteins. So far, only few information is available about plant MTs, which, different from the mammalian MTs, may contain aromatic amino acids and longer linker regions (30~45 amino acids) between the cysteine-reach domains.

E_c-1 (early cysteine labelled protein) from wheat was the first MT identified in higher plants [3]. The metal clusters stoichiometry and organization within the wheat E_c-1 peptide chain, as for other members of the pec subfamily, was so far unknown. Results from our investigations point towards the presence of two separated metal-thiolate clusters in wheat E_c-1[6]. The experimental evidences supporting this conclusion will be presented and discussed.

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[3] B. Lane, *FASEB J.* **1991**, *5*, 2893.
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Financial support from the Swiss National Foundation (200021-105269/1 to E.F.) is gratefully acknowledged.

Inorganic and Coordination Chemistry **205**

Stability and NO_x storage behavior of Ba-containing species in supported Pt-Ba NSR catalysts: Influence of support and Ba-loading

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Department of Chemistry and Applied Biosciences,
ETH Zurich, Hönggerberg, HCI, 8093 Zurich, Switzerland

Recent studies on Al_2O_3 supported Pt-Ba catalysts used for pollution control of lean engines showed that the interaction of Ba-containing species with the support plays a crucial role on their stability and NO_x storage efficiency [1, 2]. To characterize this Ba interaction a series of Pt-Ba catalysts supported on CeO_2, SiO_2 and ZrO_2 has been prepared with Ba-loadings in the range 4.5-28 wt. % and 1 wt. % of Pt. 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 spectrometry (MS). Ba-containing species possessing different thermal stability, resembling those previously identified over Al_2O_3 supported samples, were found on the different supports. The relative concentration of active LT-$BaCO_3$ and non-active HT-$BaCO_3$ phases was dependent on the Ba-loading and kind of the support revealing a direct correlation between the barium carbonates stability and basicity of the support [3, 4]. This finding explains the higher NO_x storage efficiency shown by more basic supports like CeO_2 and ZrO_2 at low Ba-loadings and the poor NO_x storage potential shown by SiO_2 [4]. The Pt-Ba/Al_2O_3 catalyst possesses a higher efficiency at the standard 16.7 wt. % Ba-loading. The results indicate clearly the influence of the support on the NO_x storage process and offer new insight aiding in the development of efficient NSR catalysts.

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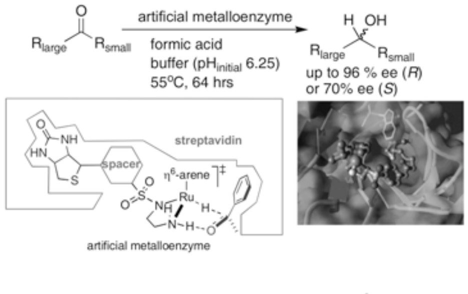
Inorganic and Coordination Chemistry **207**

Artificial Transfer Hydrogenases Based on the Biotin-Avidin Technology

Christophe Letondor [a], Nicolas Humbert [a], Anita Ivanova [a],
Sylwester Mazurek [b], Marjana Novic [b], Thomas R. Ward [a*], Anca Pordea [a]

[a] Institute of Chemistry, University of Neuchâtel, Av. Bellevaux 51, CP 2, CH-2007, Neuchâtel, Switzerland. [b]Laboratory of Chemometrics, National Institute of Chemistry, Hajdrihova 19, SI-1001, Ljubljana, Slovenia



Incorporation of biotinylated racemic three-legged d^6 piano stool complexes in streptavidin yields enantioselective transfer-hydrogenation artificial metalloenzymes for the reduction of ketones. Having indentified the most promising organometallic catalyst precursors in the presence of wild-type streptavidin, fine tuning of the selectivity is achieved by saturation mutagenesis at position S112. This choice for the genetic optimization site is suggested by docking studies which reveal that this position lies closest to the biotinylated metal upon incorporation in streptavidin. For aromatic ketones, the reaction proceeds smoothly to afford the corresponding enantioenriched alcohols in up to 96% ee (*R*) or 70 % (*S*). [1].

[1] Letondor, C; Pordea, A.; Humbert, N.; Ivanova, A.; Mazurek, S.; Novic, M.; Ward, T.R. *J. Am. Chem. Soc., in press.*

Inorganic and Coordination Chemistry **206**

Enantioselective Epoxidation 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 based catalysts for selective oxidations.
Inspired by the work of the groups of Jacobsen and Katsuki, we have developed biotinylated manganese(Schiff-base) 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. Having established the proof-of-principle with hydrogenation and transfer hydrogenation reactions, we have recently focused on more challenging oxidation reactions.
The results of aqueous epoxidation of alkenes with these artificial metalloenzymes will be presented.

[1] Thomas, C.M.; Letondor, C.; Ward, T.R. *J. Organomet. Chem.* **2005,** *690*, 4488**.**

Inorganic and Coordination Chemistry **208**

Photocatalytic Investigation on Novel Rhenium(I)-Tricarbonyl Based Bimetallic Systems

Benjamin Probst, Karlijn van der Schilden, Philipp Kurz,
Christine Männel-Croisé, Roger Alberto

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A systematic investigation of mono- and bimetallic complexes bearing the *fac*-$[MX(CO)_3(diimine)]$ (M=Re,Tc) moiety provided new insights into the mechanism of photocatalytic CO_2 reduction.[1, 2] Sufficient free energy (~2.2 eV for diimine = 2,2'-bipyridine (bipy) or *o*-phenantroline (phen) and X^- = Br^-) is provided to drive a number of reactions including proton reduction. The excited state is reductively quenched by a sacrificial electron donor and the so generated radical species can then be employed as a powerful reducing agent (~ -1.1 V for diimine = bipy or phen and X^- = Br^-).

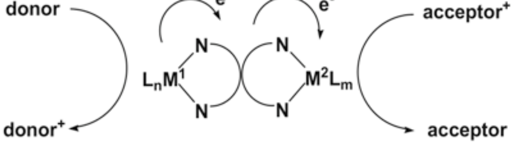

Figure 1 General scheme for photoinduced charge separation in a heterodinuclear complex.

A number of different bridging ligands will be presented and discussed in terms of the excitation processes and involved molecular orbitals. On the other hand different suitable metal fragments for the reduction of the acceptor will be looked at from an electrochemical point of view.

[1] P. Kurz, B. Probst, R. Alberto, *Eur. J. Inorg. Chem.* **2006**, in press.
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Inorganic and Coordination Chemistry **209**

Asymmetric Olefin Aziridination Catalyzed by Ru/PNNP Complexes

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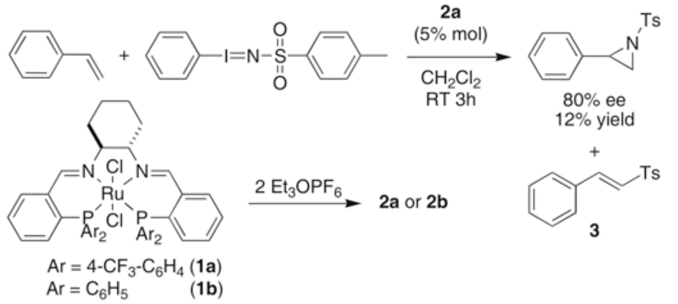
The dichloro complex [$RuCl_2$(PNNP)] (**1a**) catalyzes the fluorination and hydroxylation of dicarbonyl compounds upon activation with Et_3OPF_6 (2 equiv) [1]. We report here that **2a** catalyzes the aziridination of styrene with phenyliodinane to give complete conversion, 12% yield, and up to 80% ee. The low aziridine yield is low because of the formation of **3** as side product.



The activation of **1a** with other chloride scavengers – $TlPF_6$ (1 equiv) and $AgSbF_6$ (1 or 2 equiv) – gives lower conversion and up to 10% ee. The dichloro complex **1b** gives very low conversion and almost racemic products upon activation with any of the chloride scavengers (1 or 2 equiv). No conversion is observed with TsN_3 or chloramine-T as nitrene sources.

[1] Bonaccorsi, C.; Althaus, M.; Becker, C.; Togni, A.; Mezzetti A. *Pure Appl.Chem.* **2006**, *78*, 391.

Inorganic and Coordination Chemistry **210**

Fluorescence Sensors for Lithium Ions

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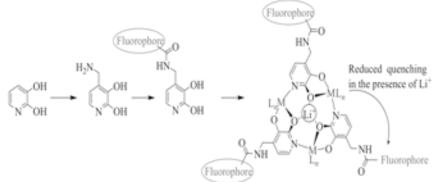
Lithium salts represent a widely used class of drugs for patients suffering from bipolar disorder. The unavailability of Li^+ spectroscopic tool represents severe limitation for investigations in this context.[1] A series of self-assembled macrocyclic receptors displaying an outstanding affinity for Li^+ ions has been described. These receptors can be synthesised and used in water at neutral pH.[2]



Our present efforts are concentered on the attachment of fluorophore to the self-assembled receptors (*cf.* scheme above). The detection of Li^+ ions relies on the fact that the quenching of the fluorescence by the metal centres is reduced in presence of Li^+ ions. Such sensors will certainly find numerous applications in biomedical investigations involving lithium-based drugs.

[1] D. M. de Freitas, M. M. C. A. Castro, C. F. G. C. Geraldes, *Acc. Chem. Rev.* **2006**, *39*, 283-291.
[2] Z. Grote, R. Scopelliti, K. Severin, *J. Am. Chem. Soc.* **2004**, *126*, 16959-16972.

Inorganic and Coordination Chemistry **211**

Syntheses of Fluorescent Vitamin B_{12}-Pt(II) Conjugates and their Pt(II) Release in a Spectroelectrochemical Assay

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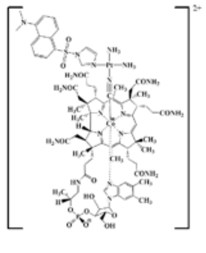
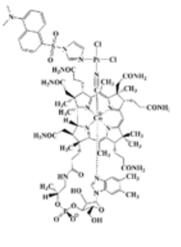
We have synthesized and characterized a series of Pt(II) complexes containing vitamin B_{12} (B_{12}) as a ligand.[1] The precursors $[PtCl_x(NH_3)_{4-x}]^{2-x}$ react with the cyanide of B_{12} to form the {Co-C≡N-Pt} conjugates. Corrinoid adenosylation assays of these adducts with CobA[2] enzyme showed recognition and conversion to AdoCbl and release of Pt(II) species. We plan to use this Pt-conjugation to B_{12} for specific targeting of cancer cells, thereby avoiding the dose-limiting toxicity of cisplatin.[3]

The chloride ligands of these complexes can be exchanged by donors which enabled the introduction of fluorescent markers and allow to isolate and characterize the Pt(II) species released from adenosylation assays and to follow their biological fate.





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[2] Fonseca, M. V.; Escalante-Semerena, J.C.; *J. Biol. Chem.*, **2001**, *276*, 32101.
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Inorganic and Coordination Chemistry **212**

Silver Coordination Compounds with a Family of Ditopic Ligands of Varying Flexibility. About Chains, Rings, Helices and Polycatenanes.

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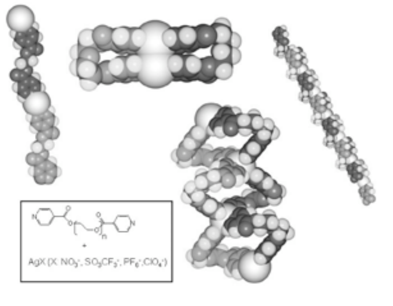
Single crystal structures of coordination polymer networks have helped to understand some concepts of construction in supramolecular chemistry. Nevertheless, the question remains how supramolecular forces subtly direct the final array involving electrostatic interactions, hydrogen bonds, metal-metal, π-π and metal-π-interactions, to name some examples of variables to take into account before a reasonable prediction of the final structure might be achieved. In many cases, the single crystal structures are taken as representative for species present also in solution, although very little is known about what happens when a crystallization starts.



In this study a family of organic ligands derived from the nicotinic/isonicotinic acid ester and polyethylene glycol [1, 2] was used and coordinated to several silver salts. We present here some preliminary results, as well as potential applications for silver coordination polymer networks, as well as an extension of this concept to other metal cations.

Inorganic and Coordination Chemistry **213**

Ruthenium/PNNP Complexes Containing Non-enolized β-Keto Esters in Asymmetric Michael Addition Reactions

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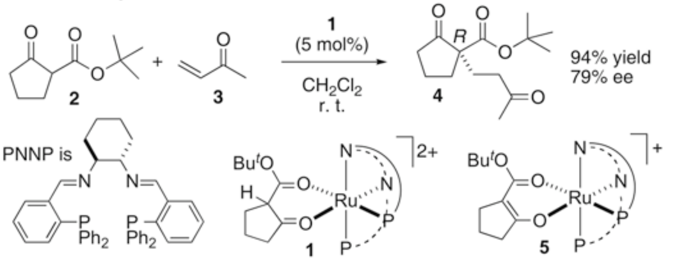
Following our recent report of ruthenium complexes containing non-enolized 1,3-dicarbonyl compounds,[1] we describe here their use in the enantioselective 1,4-conjugate addition of β-keto esters to methyl vinyl ketone. Complex **1**, formed by activation of $[RuCl_2(PNNP)]$ with Et_3OPF_6 (2 equiv), followed by reaction with β-keto ester **2**, reacts with methyl vinyl ketone (**3**, 1.2 equiv) to give the Michael addition product **4** in 93% yield and 90% ee. By using complex **1** as catalyst (5 mol%), the product was obtained in 94% yield and 79% ee:



The activation with Me_3OBF_4 led to an increase of the reaction rate, which hints to a strong anion effect. Interestingly, complex **5**, the enolato analogue of **1**, did not react with methyl vinyl ketone or show any catalytic activity. We also prepared analogues of **1** containing other Michael donors. Their application in catalysis will be reported.

[1] Bonaccorsi, C.; Althaus, M.; Becker, C.; Togni, A.; Mezzetti A. *Pure Appl.Chem.* **2006**, *78*, 391

Inorganic and Coordination Chemistry **214**

Insertion of Heavy Metal Ions Into Metallothionein 1 from *C. arietinum*

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Metallothioneins (MTs) play an important role in the intracellular supply of zinc and copper ions, the protection from oxidative stress, as well as deleterious effects of non-essential transition metal ions such as Cd^{2+} and Hg^{2+} [1]. These small cysteine rich proteins are common to all living organisms and where first reported in 1957.[2] The plant MTs, in comparison to the mammalian isoforms, feature a smaller cysteine content, a different cysteine distribution pattern as well as an additional usually around 30–45 amino acids long cysteine-devoid linker region, which might also include aromatic amino acids. However, not much is known yet about the role, function and structure of plant MTs.

Metallothionein 1 from *C. arietinum*, a member of the MT family 15 subgroup p1, consists of 75 amino acids of which 12 are cysteines. The metal binding capability towards Cd^{2+}, Zn^{2+}, Hg^{2+} and Cu^+ and their cluster formation has been the subject of our late research. UV-visible electronic absorption, CD and MCD spectra of metal ion titrations, starting from the apo- or the Zn^{II}-form, will be presented and discussed.

Financial support from the Swiss National Science Foundation (project funding to E.F., 21-105269/1) is gratefully acknowledged.

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Inorganic and Coordination Chemistry **215**

Photosensitizers Linked to Hydrogenase Acive Sites A Solar to Hydrogen Pathway

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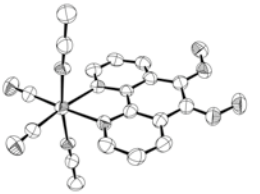
Bernhard Spingler, Roger Alberto

University of Zürich, Winterthurerstrasse 190, 8057 Zürich, Switzerland

Hydrogen is expected to be a major energy carrier in future.[1] Photochemical systems produce hydrogen directly from sunlight and water. We are developing single molecular assemblies for energy conversion based on the cobalt(III) dimethylglyoximato (dmgH) hydrogen producing complex $[Co(dmgH)_2(OH/Cl)L]$ ($L = H_2O$, amine).[2,3] The ligand 1,10-phenantroline-5,6-dioxime (phox) is used to link the cobalt hydrogenase site to rhenium(I) and ruthenium(II) 2,2'-bipyridine photosensitizers.

We have synthesized the biscarbonyl complex *trans-cis*-$[Re(NCCH_3)_2(CO)_2(phox)]Br$ (**1**). Upon reaction with cobalt chloride, the trinuclear complex $[\{Re(NCCH_3)_2(CO)_2(phox)\}_2Co(H_2O)_2]^{3+}$ is formed. The complex is investigated for its production of dihydrogen upon irradiation with visible light. Parallel studies are performed with triscarbonyl rhenium(I) and ruthenium(II) 2,2'-bipyridine derivatives.



1: $[Re(NCCH_3)_2(CO)_2(phox)]^+$

[1] Towards a Hydrogen Economy (special issue). *Science* **2004**, *305*, 901
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Inorganic and Coordination Chemistry **216**

Phase Transformations in Cyanometalate Complexes

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There is growing interest in coordination polymers having high-dimensional structures because of the unique physicochemical properties arising in the bulk. In particular, much effort has been made to the design highly ordered structures with paramagnetic metal centers[1-4]. It is known that hexacyanometalate ions, $[M(CN)_6]^{n-}$, are good building blocks to form bimetallic assemblies, such as Prussian blue, $Fe^{III}_4[Fe^{II}(CN)_6]_3 \cdot n\ H_2O$. We have used $[M'(L)_2]^{2+}$ (L=diamine ligands) complex cations, instead of simple metal ions as in Prussian blue analogues, to prepare bimetallic assemblies. We will present some new cyanide-bridged metal-organic frameworks $[M'(L)_2]_m[M(CN)_n]_2$ (where M'=Cu, M=Ru, Ni), and discuss their structural features and phase transformations, a number of which are reversible.

Powder X-ray diffraction analysis has been used to characterize the new materials obtained after desorption of water by heating. A*b initio*[5] structure solution enabled us to study the structural changes and to explain the desorption processes. Reversibility and selectivity of the solvents has also been proven by adsorption and desorption of solvent followed by X-ray powder diffraction.

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[4] M. Ohba, H. Okawa, T. Ito, A. Ohto, *J. Chem. Soc. Chem. Commun.* **1995**, 1545.
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Inorganic and Coordination Chemistry **217**

Platinum(II) and Gold(I) Centred Bis(2,2':6',2"-terpyridine) Ligands as Metallotectons for the Assembly of Heterometallic Macrocyclic Complexes

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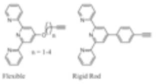
A variety of functionalised 2,2':6',2"-terpyridine (tpy) ligands has been prepared which all contain a terminal alkyne.[1-3] Reaction of these ligands at the alkyne terminus with *trans*-[$PtI_2(PR_3)_2$] or [$(AuCl)_2$dppe] gives either a square planar platinum(II) complex or a linear gold(I) complex with pendant tpy metal-binding domains.

Further reaction of these platinum(II) or gold(I)-containing ditopic ligands with a metal ion (e.g. Fe(II)) results in the formation of a heterometallic metallomacrocycle.[1] We are investigating the way in which varying the flexibility of the bis(tpy) ligand, as well as the phosphine groups, affects the formation of the metallomacrocycle, i.e. macrocycle size and competition with polymer formation.



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Inorganic and Coordination Chemistry **218**

Gold(I)-Catalyzed Ring-Opening of Vinyl Cyclopropane Derivatives (VCP) with Amine

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Recently, gold-catalyzed hydroamination of simple olefins, as a new promising strategy to prepare nitrogen-containing molecules, is attracting much attention [1]. Despite much progress has been achieved in this field, many problems, such as asymmetric transformation and substrate scope, etc., remain great challenges.

As our continuing efforts in hydroamination, herein we reported gold(I)-catalyzed hydroamination of vinyl cyclopropane derivatives (VCP) to afford ring opening addition products, which represents a rare example of ring-opening of vinyl cyclopropane with amine [2]. This discovery not only further extended gold-catalyzed hydroamination, but also enriched VCP's chemistry.

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Inorganic and Coordination Chemistry **219**

Tyrosyl Radical Reduction by Selenocysteine

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ETH Zurich, Wolfgang-Pauli-Strasse 10, CH-8093 Zurich, Switzerland

Current research provides evidence that tyrosyl radicals initiate lipid peroxidation and are precursors of dityrosines which link proteins together [1][2]. In the present study, we explore the reduction of tyrosyl radicals by selenocysteine.

The reaction of tyrosyl radicals by selenocysteine was studied by laser flash photolysis and pulse radiolysis to derive a rate constant. Tyrosine radicals were generated by photolysis or by reaction of N_3• with tyrosine.

The reaction of tyrosyl radicals with selenocysteine has a rate constant of 10^9 M^{-1} s^{-1}, which is 5 - 6 orders of magnitude higher than reduction by cysteine.

Our results support the hypothesis that tyrosyl radical scavenging by selenocysteine may be an important route to trap these radicals and contribute to the preventive effect of selenium against various diseases.

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Inorganic and Coordination Chemistry **220**

$Pt/Ba/Al_2O_3$ NO_x storage-reduction catalysts made by two-nozzle flame synthesis

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[1] Institute for Chemical and Bioengineering, ETH Zurich, Wolfgang-Pauli-Strasse 10, 8093 Zürich, Switzerland
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NO_x storage reduction (NSR) catalysts are applied for the abatement of NO_x from engines operating under lean conditions, where conventional TWC catalysts are inefficient. Here, a novel two-nozzle flame spray pyrolysis (FSP) process was developed for one-step synthesis of $Pt/Ba/Al_2O_3$ NSR catalysts. The use of two nozzles separating the formation of Al and Ba resulted in the formation of individual $BaCO_3$ and Al_2O_3 nanoparticles well-mixed at the nano level exhibiting good NO_x storage capacity [1]. In contrast, amorphous Ba species dispersed over the Al_2O_3 particles were formed by the conventional single nozzle FSP process. In contrast to impregnated $Pt/Ba/Al_2O_3$ at higher Ba loadings, the absence of HT-$BaCO_3$ even increased the relative amount of Ba involved in the NO_x storage process [2]. Pt/Ba supported on ceria/zirconia was prepared by the same flame method [3]. Here, emphasis was placed on the influence of the support composition on the thermal deterioration and the related behavior during NO_x storage and reduction.

[1] R. Strobel, L. Mädler, M. Maciejewski, A. Baiker, S.E. Pratsinis, *Chem. Mater*. **2006**, 18, 2532.

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Inorganic and Coordination Chemistry **221**

The Kinetics of Homolysis of Peroxynitrite Detected by Permanganate

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ETH Zurich, Wolfgang-Pauli-Strasse 10, CH-8093 Zurich, Switzerland

Peroxynitrite is a strong oxidant and nitrating agent. Many decades ago, the reduction of permanganate(VII) to manganate(VI) was used to detemine the concentration of peroxynitrite [1,2]. We investigated the kinetics of this reaction by stopped-flow spectrophotometry.

The rate constant with MnO_4^- in excess over peroxynitrite is $(0.020 \pm 0.002)\ s^{-1}$ at pH 11.7. Similarly, the reaction of permanganate (in excess) with nitrogen monoxide proceeds with a rate constant of $(3.5 \pm 0.7) \times 10^6\ M^{-1}s^{-1}$.

$$ONOO^- \underset{k = 1.6*10^{10}\ M^{-1}s^{-1}\ (3)}{\overset{k = 0.020\ s^{-1}}{\rightleftharpoons}} NO^\cdot + O_2^{\cdot -}$$

The rate of reduction of MnO_4^- by $ONOO^-$ is independent of the MnO_4^- concentration, and we conclude that the reaction $ONOO^- \rightarrow NO^\bullet$ and $O_2^{\bullet -}$ is the rate determining step. Since both $NO^\bullet$ and $O_2^{\bullet -}$ are consumed rapidly by MnO_4^-, we used the rate constant of $0.020\ s^{-1}$ and the backward rate constant of $1.6 \times 10^{10}\ M^{-1}s^{-1}$[3] to calculate a $\Delta_f G^\circ(ONOO^-)$ of 58 kJ mol^{-1}. MnO_4^- can be used conveniently to determine the concentration of H_2O_2-free solutions of $ONOO^-$.

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Inorganic and Coordination Chemistry **222**

Highly Efficient Atom Transfer Radical Addition Reactions with a Ru^{III} Complex as a Catalyst Precursor

Katrin Thommes, Laurent Quebatte and Kay Severin

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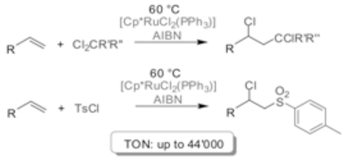
Ruthenium complexes are among the most active catalysts for atom transfer radical addition (ATRA) reactions [1], but they still show a severe disadvantage as they display low catalyst stability. The combination of the air-stable Ru^{III} complex $[Cp^*RuCl_2(PPh_3)]$ with AIBN can be used to catalyze the atom transfer radical addition reactions of polychlorinated compounds and of sulfonyl chlorides to olefins with unprecedented turnover numbers of up to 44'000 [2]. In this new simple but powerful method AIBN is responsible for the in situ generation as well as for the constant regeneration of the active Ru^{II} catalyst.



Given the advantages of low catalyst loadings, high yields and stability as well as easy accessibility of the catalyst, this new procedure or a conceptually related version may find various applications in organic synthesis.

[1] K. Severin, *Curr. Org. Chem*. **2006**, *10*, 217–224.
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Inorganic and Coordination Chemistry **223**

Thiocarbonyl Complexes of Ruthenium (II) and their Reactivity

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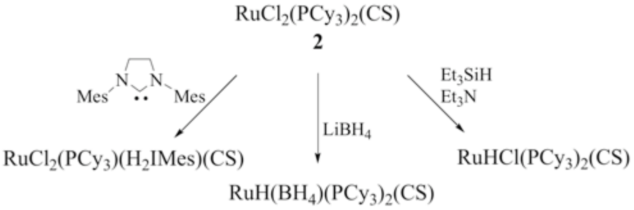
The resemblance in electronic properties of thiocarbonyl (CS) to carbonyl (CO) has stimulated the question about the reactivity of the CS ligand in its metal complexes [1]. As the starting material we used well known thiocarbonyl complex $RuCl_2(H_2O)(PPh_3)_2(CS)$ **1** [2]. Complex **1** reacted with excess of tricyclohexylphosphine to form $RuCl_2(PCy_3)_2(CS)$ **2**. Compound **2** was used in further transformations as shown in the scheme:



All these reactions left the CS moiety intact. Recent literature describes the preparation of carbide species from thiocarbonyl complex [3]. For that reason it is sought to probe the desulfurization of these new thiocarbonyl complexes to the corresponding carbide species.

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Inorganic and Coordination Chemistry **224**

New Applications of Silver Coordination Polymer Networks

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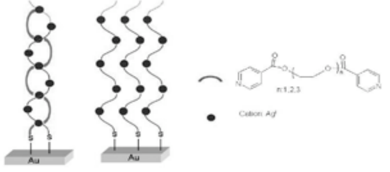
The diversity of silver coordination networks with different bis(isonicotinate) ligands [1,2,3] and the beneficial antibacterial effect of the Ag(I) compounds open new opportunities of their application. The crystalline metal-organic coordination polymers as well as the surface deposited polymer networks provide a starting point for a design of potentially functional materials. Synthesis and characterization of coordination polymers for these new applications will be given. The novel functional materials/surfaces preferably possess different desirable properties such as chirality, hydrophilicity, charges and/or polarity.



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Diverse Cluster Compositions found in Metallothionein 2 from Chickpea (*Cicer arietinum*)

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Metallothionein 2 (MT2) from chickpea (*Cicer arietinum*) belongs to the plant metallothionein superfamily and features the characteristic cysteine distribution pattern typical for the p2 subfamily [1]. The metal-thiolate cluster formation in the presence of Zn^{II} or Cd^{II} ions was studied recently in our lab. In the case of the Cd-thiolate cluster two different cluster compositions were found, one including non-proteinogenic ligands. Metal-to-protein stoichiometries as well as cluster stabilities will be presented. Furthermore, even in the absence of three dimensional data, we were able to assess the number of clusters formed per protein, i.e. to differentiate between a one-domain *versus* a two-domain arrangement. For this, we utilized a plethora of spectroscopic as well as (bio-) chemical methods. The possible biological importance of our findings will be discussed as well.

Financial support for this project comes from the Swiss National Foundation (200021-105269/1 to EF) and the Research Fund of the University of Zürich (57010101 to EF).

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Inorganic and Coordination Chemistry **226**

Cationic and Anionic Substitutions in Functional Perovskite-type Phases

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Perovskite-type phases show a particularly high potential as functional materials for diverse energy conversion processes due to the flexible structure and a variety of properties. Prominent examples are electrode materials in fuel cells and batteries, HTSC based electronics, spintronics, thermoelectric converters, and piezoelectrics. They are also known to be very suitable catalysts for different redox reactions (e.g. as catalysts in fuel cells) resulting from the ability to respond reversibly to oxidising and reducing environment under conservation of their crystallographic structure [1]. By controlled cationic and anionic substitutions the properties can be tuned for the development of novel functional materials.

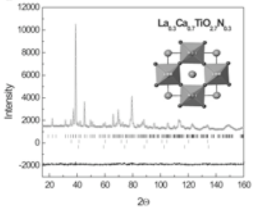

Figure: Rietveld plot of ND/XRD data

The produced oxide and oxynitride materials (e.g. titanates) are characterised with respect to their composition-structure-property-relation with diverse complementary methods, as X-ray and neutron diffraction methods, transmission electron microscopy, Raman- and IR spectroscopy, thermal analysis, and electrical transport measurements.

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Inorganic and Coordination Chemistry **227**

Synthesis and physical chemical properties of $SrMoO_{3-x}N_x$ (x > 1)

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Perovskite type oxynitrides possess unique electronic, optical and magnetic properties differing from those of the corresponding oxides [1]. Thermal ammonolysis is a suitable route to synthesize this type of material from the corresponding oxide precursors. Since ammonia provides both nitriding and reducing atmospheres the phase content and consequently physical properties of the material being obtained are dependant from the starting oxide composition. Among the set of structurally similar oxides of the general formula $AMoO_4$ (A = Ca, Sr, Ba) only the ammonolysis of $SrMoO_4$ is leading to the perovskite type phase formation of the general composition $SrMo^{+5/+6}O_{3-x}N_x$, whereas mixtures CaO-$Mo^{+2/+3}{}_2N$ and $Ba_3Mo^{+6}{}_2O_6N_2$-Mo_2N are formed from $CaMoO_4$ and $BaMoO_4$ correspondingly. The increase of the formal Mo oxidation state with increasing atomic number of the A-site cation can be attributed to an enhanced positive inductive effect when going down the IIA group of the Periodic Table. The synthesized oxynitrides $SrMo^{+5/+6}O_{3-x}N_x$ possess cubic perovskite structure (P m -3 m) and enlarged lattice parameters with increasing nitrogen content. The temperature dependence of the electrical conductivity follows semiconducting behavior. The semiconductor to metal transition can be observed at a temperature around 50 K. Increasing the nitrogen content is leading to the decrease of the conductivity. The Seebeck coefficient of the synthesized oxynitrides is in the range of 20-30 μV/K. The measured properties differ from those of the metal like $SrMo^{+4}O_3$ [2].

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Functionalized tetrathiafulvalene (TTF) derivatives and their coordination chemistry

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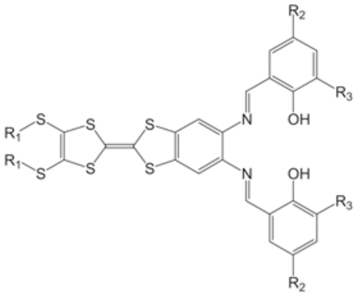
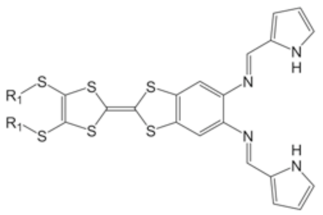
It is a challenge in the field of materials chemistry to design and investigate molecular conductors which are combined with magnetic components and consequently, synthetic efforts are nowadays devoted to the preparation of tetrathiafulvalene (TTF) derivatives with ligating functions for binding metal ions [1]. Accordingly, as a continuation of our previous research work, the following TTF derivatives have been prepared via a well-established Schiff-Base reaction. Herein we report the synthesis and characterization of these promising donors as well as their corresponding transition metal and rare earth metal complexes, aiming to make accessible inorganic/organic hybrid materials with novel and fascinating properties.





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Cp*Rh-Based Indicator-Displacement Assays for the Identification of Amino Sugars and Aminoglycosides

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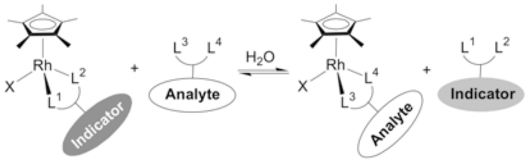
Over the last years, indicator displacement assays (IDAs) have increasingly been employed for analytical purposes. The colorimetric sensing of amino sugars and aminoglycosides with a Cp*Rh-based IDA in buffered aqueous solution is a new approach in this context [1]. The sensing system comprises the organometallic complex $[Cp^*RhCl_2]_2$ and the dye gallocyanine. A 'mini array' of three IDAs at different pH values was sufficient to differentiate three amino sugars and six aminoglycosides with high fidelity. The array was also used to characterize mixtures of aminoglycosides and quantify the respective analytes.



This sensor is especially appealing because of its simplicity. First, the dye and the receptor are both commercially available. Second, the analysis can be realized by mixing the solutions of the Cp*Rh complex, the dye and the analytes and performing UV/Vis measurements. Finally, a mere change of pH is enough to expand the IDA to an array format and thus enhance the analytical power of the sensing ensemble.

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Inorganic and Coordination Chemistry **230**

Structure Determination and Metal Ion Binding Properties of Domain 5 of a Bacterial Group II Intron Ribozyme

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Group II introns, a class of naturally occurring ribozymes, are especially known for their self splicing ability. These introns are found in organellar genes of fungi, plants and lower eucaryotes as well as in certain bacteria like the soil bacterium *Azotobacter vinelandii*, which is very useful as a model organism. To achieve self splicing, it is essential that the RNA is folded in a correct way, which is accomplished by a specific need for metal ions as cofactors (Mg^{2+}, Na^+, K^+). [2]

Structural informations on group II introns are in general very scarce. Here we focus on domain 5 (D5) of an *Azotobacter vinelandii* group II intron, since this domain is known to be the catalytic center of all group II introns. The here investigated D5 distinguishes itself from D5 of other group II introns by specific sequence variation of catalytically crucial nucleotides. It is therefore expected, that also the metal ion binding properties are different.

Our investigation on structural and metal ion binding properties are performed by a multitude of multidimensional NMR experiments. First results indeed show different structure within the so called catalytic triad and the closing loop of D5.

Financial support by the Swiss National Science Foundation (SNF-Förderungsprofessur PP002-68733/1 to R. K. O. S.), the Roche Research Foundation as well as the Novartis Stiftung are gratefully acknowledged

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[2] R. K. O. Sigel, *Eur. J. Inorg. Chem.* **2005**, *12*, 2281.

Inorganic and Coordination Chemistry **231**

Towards a Molecular Switch using the Photophysical Properties of Anthracene

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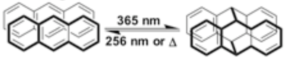
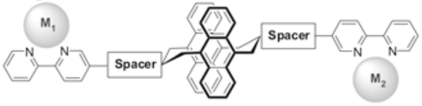
Anthracene and its derivatives show an interesting behaviour; two anthracene units undergo a [2+2]-cycloaddition reaction induced by light. This photodimer has different photophysical properties than the anthracene itself. It is well known [1], that the photodimerisation is totally reversible.



These two conformeres of anthracene can be used in molecular switches as distinguishable situations. If the anthracene unit is incorporated between Ru/Ru or Ru/Os metal centers, it can either be a strong quencher or facilitate an energy transfer process between the metal units.



We are on the way to synthesize a bridging ligand in which an anthracene moiety with a fixed position is incorporated. The two anthracenes are linked by a 3-carbonatom bridge and form a 3,3-cyclophane in position 9 and 10.

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.

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Solid State Chemistry Teaching Projects at ETH Zurich

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The Laboratory of Inorganic Chemistry at ETH Zurich has a long teaching experience with the integrated use of new electronic media [1-2]. "CCI – Experiments on the Web" started 1994, and provides today online more than 200 videos of chemical experiments in different formats, serving the multiple needs of a blended learning environment [3]. Within the project "CCN – The Chemistry Contact Network", the usability of the new technologies for research and education in chemistry where investigated, new research tools where developed [4], and own visual teaching elements where produced [5]. The web-based introduction to electron microscopy started to operate in 2005, and is frequently visited by PhD students world wide [6]. Here we present our new teaching project "SoMaNa: Solid Materials and Nano Science – Basics and Applications", which has the overall goal to cover basic solid state teaching content while reporting on current important research topics as well as on concrete obstacles for applications. Project part 1 started 2005, and focuses on new materials for energy conversion, energy storage, and power transport. Focusing particularly on the present materials and devices problems as well as on possible novel solutions under consideration of nano science, SoMaNa aims at five independent problem based modules to new materials with possible applications (Hydrogen Storage, Photogalvanic Cells, Rechargeable Batteries, Fuel Cells, and Supercapacitors), a crystal structure gallery as well as a teaching resource library for docents.

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[6] http://www.microscopy.ethz.ch.