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Inorganic and Coordination Chemistry **IC 1**

## Reactions of Cp’$_2$CeH: Breaking C-H and C-O Bonds and Making C-C Bonds

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CA 94720 (USA)

The net reaction of the monomeric lanthanidehydride, bis[1,2,4-$(Me_3C)_3C_5H_2]_2CeH$ abbreviated as Cp’$_2$CeH, and methylhalides is Cp’$_2$CeX and $CH_4$. The mechanism of this metathesis reaction does not proceed through a one-step metathesis transition state; rather, the reaction proceeds buy way of a two-step process in which the first step is an α-CH bond activation generating $H_2$ and the intermediate, Cp’$_2$Ce(η-$CH_2X$), that evolves into the products as $H_2$ traps the methylene fragment. Isolation of the intermediate, when X = OMe in the reaction between $CH_3OMe$ and the hydride, followed by its rearrangement to Cp’$_2$CeOMe and $CH_4$ supports the two-step mechanistic postulate that involves successive CH and CO bond breaking steps. When the ethers contain α- and β-CH bonds, for example in diethylether, the α- and β-CH activation steps are of comparable energy, but only the β-activation intermediate leads to the final product. The net reaction with $CH_3OSiMe_3$ yields Cp’$_2$CeOMe and $HSiMe_3$ is a SiO bond splitting reaction that does proceed by way of a metathesis transition state that involves five-coordinate silicon. In contrast, the net reaction between Cp’$_2$CpH and $CH_3OCMe_3$ yields Cp’$_2$Ce(η-$CH_2OCMe_3$), which rearranges to Cp’$_2$CeOMe, Cp’$_2$CeO$CH_2CMe_3$ (a Wittig rearrangement product), isobutene and isobutane. Evidence for this C-O bond breaking and C-C bond making reaction will be presented. The mechanistic principles developed from these studies are applicable to those metals that cannot underego oxidative addition-reductive elimination steps and therefore of general utility.

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Inorganic and Coordination Chemistry **IC 2**

## Two-photon sensitized lanthanides luminescence: Bio-imaging applications from the green to the infra-red

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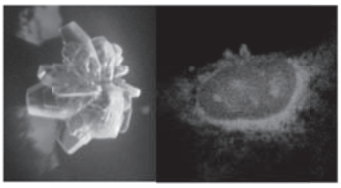
In the last decade lanthanide complexes have been extensively used for their catalytic, magnetic, luminescence properties for applications ranging from material sciences (Laser, color screen, telecommunication devices…) to biological imaging (MRI contrast agent, fluoroimunoassay…). By contrast, the study of the nonlinear optical (NLO) properties of lanthanide remains in its infancy and becomes currently an emerging field of research.



In this context, the sensitisation of lanthanide luminescence in the green (Tb), red, (Eu) even infra-red (Yb) has been achieved by a two-photon antenna effect, a third order NLO phenomenon. Optimisation of the molecular two-photon cross-section involving a new sensitisation process, design of Ln-based nanoparticles as well as applications in bio-imaging using confocal biphotonic microscopy will be presented.

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Inorganic and Coordination Chemistry **IC 3**

## What is alumina ? A molecular point of view

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While alumina is often just considered as a way to support active phases (active sites and nanoparticles), alumina, for instance, readily activates the C-H bond of methane at low temperatures (e.g. 25-100 °C).[1] Moreover, it is often a key component to obtain catalytic activity for heterogeneous catalysts including for the so-called single-site catalysts.[2]

Thus, one might ask what is so special about alumina and more precisely what are the surface sites that allow activation of C-H bond and metal centers.

Here will be described the key structural features of this support, which are essential for generating active sites, by a combined experimental and computational approach. [3]

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Inorganic and Coordination Chemistry **IC 4**

## Rhenium-Catalyzed Trifluoromethylation of Arenes and Heteroarenes by Hypervalent Iodine Reagents

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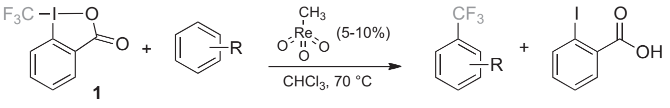
Recently, we reported the trifluoromethylation of N-heteroarenes and activated arenes under mild conditions using electrophilic trifluoromethylating reagents based on hypervalent iodine.[1] These transformation commonly require the use of substoichiometric amounts of tris(trimethylsilyl)silyl chloride or a zinc salt as additives. A novel methodology for the direct trifluoromethylation of both, activated and unactivated arenes and heteroarenes was developed using the easily accessible, shelf-stable trifluoromethylating reagent **1** and methyltrioxorhenium (MTO) as catalyst. Only a small excess of substrate and 5-10% of catalyst are required. To the best of our knowledge, this is the direct aromatic trifloromethylation procedure with the broadest substrate scope so far. NMR, EPR and KIE experiments suggest a radical mechanism triggered by the rhenium-catalyzed oxidation of the aromatic moiety by an activated form of **1**



R = alkyl, aryl, silyl, alkoxy, amino, acyl, halogen, ciano, nitro. Heteroarenes are N-, O- and S- based.

[1] Wiehn, M. S.; Vinogradova, E. V.; Togni, A. *J. Fluorine Chem.* **2010**, *131*, 951.

Inorganic and Coordination Chemistry **IC 5**

## β-Diketiminato Ruthenium(II)-arene Complexes in Homogeneous Lewis-acid Catalysis of the Diels-Alder Reaction

Dominique F. Schreiber and Andrew D. Phillips

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Belfield, Dublin 4, Ireland

There is increasing literature describing the use of β-diketiminate ligands in homogeneous transition-metal catalysis.[1)] The β-diketiminate ligand composed of a chelating diazo scaffold features all the necessary characteristics of a modern, versatile ligand for selective homogeneous catalysis. Most importantly, the presence of the flanking *N*-aryl moieties induces a spatially well-defined substrate pocket that encompasses the metal centre.

The Diels-Alder reaction is a highly atom efficient synthetic method to fuse three unsaturated bonds together to form a six-membered ring. Selectivity and activation of substrates is the central focus of modern homogeneous catalysis. The latter issues are successfully addressed with $\eta^6$-arene ruthenium(II) complexes.[2)] In the present work, the synthesis and characterisation of novel ruthenium(II) complexes featuring strongly electron-withdrawing β-diketiminate ligands is addressed. Furthermore, the application of such complexes towards Lewis acid catalysed cycloadditions between α,β-unsaturated aldehyde and diene substrates is discussed. A detailed examination of the mechanism behind the observed selectivity with NMR and computational models is presented. In particular, the tuning of the Lewis acidic character of the ruthenium centre by alterations of substitution pattern associated with the β-diketiminate ligand is elaborated.

[1] Phillips et al., *Organometallics,* **2007**, *26*, 1120.
[2] Odenkirk et al., *J. Am. Chem. Soc.* **1992**, *114*, 6392. Kündig et al., *Angew. Chem. Int. Ed.* **2001**, *40*(23), 4481. Carmona et al., *Dalton Trans.* **2008**, 3328.

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Inorganic and Coordination Chemistry **IC 7**

## Development of Biopolymeric Drug Carriers for Targeted Delivery of Polyoxometalates

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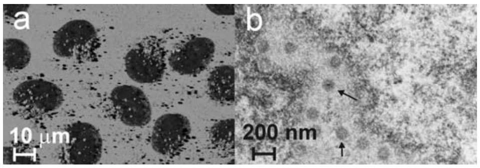
Polyoxometalates (POM) are a class of structurally versatile transition metal oxoclusters with promising antiviral and anticancer properties. However, the adverse effects of these low-cost and easily tunable compounds hinder the exploration of their pharmaceutical potential.[1] We recently showed that the encapsulation of POMs in chitosan derivatives is a suitable approach to significantly reduce these effects.[2] Carboxymethyl chitosan (CMC)/POM composites in a physiological relevant size range (80-150 nm) can be prepared by a facile ionic gelification method. We used several analytical methods, including NMR, FTIR, dynamic light scattering and electron microscopy, to verify the incorporation of intact POMs into the CMC matrix. Furthermore, we could show with confocal laser scanning microscopy and TEM investigations that cells readily take up high amounts of these composites without displaying alterations. All in all, the encapsulation of POMs in a CMC matrix is a promising strategy to design novel POM-based drugs with reduced adverse effects.



POM uptake: (a) Confocal laser scanning microscopy and (b) representative TEM image.

[1] A. Flütsch, T. Schroeder, M. G. Grütter, G. R. Patzke, *Bioorg. Med. Chem. Lett.* **2011**, *21*, 1162.
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Inorganic and Coordination Chemistry **IC 6**

## Homogenous Photocatalytic Hydrogen Evolution from Water under Acidic Conditions

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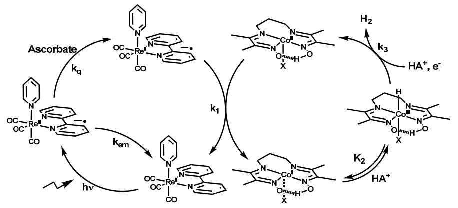
Photocatalytic water splitting is commonly divided into a reductive and a oxidative half reaction, in order to study both processes separately. Therefore sacrificial electron donors and acceptors must be used to mimic the missing counter part of the reaction. For the hydrogen evolving reductive half reaction, tertiary amines are often used for this purpose, limiting the available pH range to basic conditions, which is thermodynamically unfavorable for proton reduction.



Introducing ascorbic acid as sacrificial electron donor expanded the available pH range to acidic conditions and further stabilized the catalytic process. Turnover numbers increased one order of magnitude, indicating a higher stability of the water reduction catalyst under acidic conditions. Furthermore, the photosensitizer was determined to be photo stable under these conditions, probably due to an electron back transfer to the oxidized form of ascorbic acid (dehydroascorbic acid, DHA). This oxidizing agent slowly accumulated during the process. Therefore, DHA was also responsible for shortcutting the electron flow, which eventually terminated catalysis.[1]
Interesting insights to the system and most recent results will be presented.

[1] M. Guttentag, A. Rodenberg, P. Hamm, R. Alberto, submitted

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Inorganic and Coordination Chemistry **IC 8**

## Dative B-N bonds in Supramolecular Chemistry

Erin Sheepwash, Kay Severin

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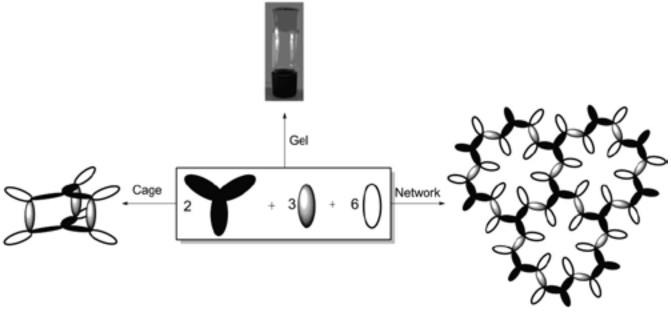
Boronate esters are Lewis acidic compounds, which can form adducts with N-donor ligands. These dative bonds have found applications in the context of materials chemistry and structural supramolecular chemistry.[1] We have employed the B-N dative bond to form crystalline polymers and cages as well as gels.[2,3] The stability of these structures can be tuned by modulating the strength of the B-N dative interaction through the addition of various electron donating and electron withdrawing substituents. Further analysis of B-N dative bond formation through binding studies of simple boronate esters and pyridine derivatives have shown that, depending on the substitution pattern, the $K_a$ value can range from $10^2$ $M^{-1}$ to greater than $10^6$ $M^{-1}$!



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Inorganic and Coordination Chemistry **IC 9**

# NEW FUNCTIONALIZED $\eta^6$ – ARENE RUTHENIUM COMPLEXES FOR BIOLOGICAL APPLICATIONS

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Recently, it was shown that ruthenium possesses several favorable chemical properties, suggesting that it may be a strong candidate to replace platinum and to form a basis for anticancer drug design [1-4]. Besides the rich synthetic chemistry, ruthenium possesses the ability under physiological conditions to adopt a large range of oxidation states ($Ru^{II}$, $Ru^{III}$ and $Ru^{IV}$), an important feature for metal-based anticancer drugs. In addition, ruthenium compounds are generally less toxic than platinum compounds and it is believed that remarkable anticancer activity of ruthenium resides in its ability to mimic iron in binding to several biomolecules, including serum transferrin and albumin.

Like other classes of ruthenium compounds, organometallic ruthenium complexes bearing $\eta^6$-arene ligands have been intensively studied as potential anticancer drugs candidates. In this contribution, we report the synthesis and characterization of new functionalized $\eta^6$-arene ruthenium complexes which were designed in order to improve their cytotoxicity, selectivity against cancer cells, but also to facilitate their uptake by cancer cells.

[1] M. J. Clarke, F. Zhu, D. R. Frasca, *Chem. Rev.* **1999**, *99*, 2511.
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Inorganic and Coordination Chemistry **IC 10**

# Mechanistic Investigations on a Highly Selective Artificial Transfer Hydrogenase for the Reduction of Cyclic Imines

Marc Dürrenberger, Thibaud Rossel, Annette Mutschler, Tillmann Heinisch, Thomas R. Ward*

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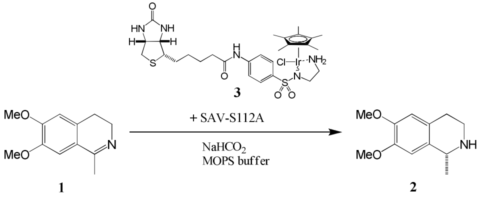
Incorporation of biotinylated piano stool transition metal complexes [ArM(biot-*p*-L)Cl] into streptavidin (SAV) affords artificial metallohydrogenases for the transfer hydrogenation of ketones and cyclic imines. The combination of different biotinylated complexes (M = Ru, Rh, Ir; Ar = benzene, cymene, Cp*) with a library of SAV mutants resulting from saturation mutagenesis at position 112 allowed to optimize the reduction of 6,7-dimethoxy-1-methyl-3,4-dihydroisoquinoline **1** to salsolidine **2** in terms of activity and selectivity. This screening led to the identification of [Cp*Ir(biot-*p*-L)Cl]⊂SAV-S112A **3** as the most active (TON up to 4000) and selective (*ee* up to 96%) hybrid catalyst whose crystal structure was published recently [1]. Based on kinetic and thermodynamic data, a possible enantioselection mechanism will be presented.



up to 96% *ee* (*R*)

[1] M. Dürrenberger, T. Heinisch, Y. M. Wilson, T. Rossel, E. Nogueira, L. Knörr, A. Mutschler, K. Kersten, M. J. Zimbron, J. Pierron, T. Schirmer, T. R. Ward, *Angew. Chem. Int. Ed. Engl.* **2011**, *50*, 3026-3029.

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Inorganic and Coordination Chemistry **IC 11**

# 17 e$^-$ Rhenium CO-Releasing Molecules on a Cobalamin Scaffold

Fabio Zobi, Olivier Blacque, Robert A. Jacobs, Marcus C. Schaub, and Anna Yu. Bogdanova.

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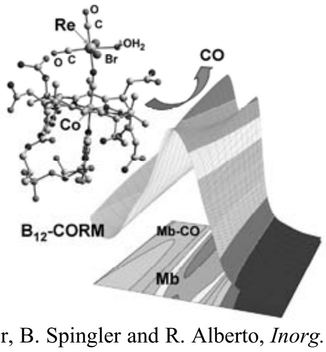
Cyanocobalamin ($B_{12}$) offers a biocompatible scaffold for CO-releasing 17-electrons dicarbonyl complexes based on the *cis-trans*-$[Re^{II}(CO)_2Br_2]^0$ core. A Co-C≡N-Re conjugate is produced in a short time and high yield from the reaction of $[Et_4N]_2[Re^{II}Br_4(CO)_2]$ with $B_{12}$.[1-2] These $B_{12}$-$Re^{II}(CO)_2$ derivatives are characterized by an improved stability in aqueous aerobic media over the metal complex alone, and afford effective therapeutic protection against ischemia-reperfusion injury in cultured cardiomyocytes. The non-toxicity of the resulting metal fragment after CO release, is attributed to the oxidation of the metal and formation in solution of the $ReO_4^-$ anion which is among the least toxic of all of the rare metals inorganic compounds.



[1] F. Zobi, L. Kromer, B. Spingler and R. Alberto, *Inorg. Chem.* **2009**, *48*, 8965.
[2] F. Zobi, A. Degonda, M. C. Schaub and A. Y. Bogdanova, *Inorg. Chem.* **2010**, *49*, 7313.

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Inorganic and Coordination Chemistry **IC 12**

# Coordination chemistry and biological activity of vitamin B12 derivatives with a peptide backbone

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Vitamin $B_{12}$ is essential for humans and plays a key role in cell division. Since fast proliferating cells such as cancer cells are strong consumers of $B_{12}$, catalytically inactive surrogates offer potential medical applications. [1] Most studies with Cbls investigated the coordination chemistry at the β- (“upper”) side of the corrin macrocycle. Rather little is known about the impact of structural changes at the α- (“lower”) side of the molecule. [2]

We are interested in the development of $B_{12}$ derivatives with tuneable coordination and redox properties for physico-chemical studies and biological applications. For this purpose, we modified the f-side chain of $B_{12}$ with different peptide structures. [3] A linear relationship between the “base-on” stability and the reduction potential of cobalt was demonstrated. We also showed that these $B_{12}$ derivatives are useful for the identification of related natural counterparts. [4]

The biological behavior of this class of compounds in enzymatic reactions as well as B12-dependent bacteria growth tests will be discussed.

[1] B. Kräutler, D. Arigoni, B. Golding, *Vitamin $B_{12}$ and $B_{12}$-Proteins*, Wiley-VCH, Weinheim, **1998**.
[2] P. Butler, M. O. Ebert, A. Lyskowski, K. Gruber, C. Kratky, B. Kräutler, *Angew. Chem. Int. Edit.* **2006**, *45*, 989.
[3] K. Zhou, F. Zelder, *Angew. Chem. Int. Ed.* **2010**, *49*, 5178.
[4] K. Zhou, F. Zelder, *Eur. J. Inorg. Chem.* **2011**, 53.

Inorganic and Coordination Chemistry **IC 13**

## A Molecular Pentafoil Knot

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Roy T. McBurney David Schultz.

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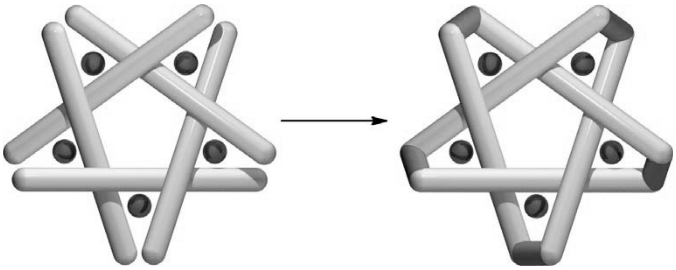

Inspired by the seminal work of Lehn in the development of circular helicates,[1] and the use of dynamic covalent chemistry,[2] the first molecular pentafoil knot has been prepared using metal-directed self-assembly in combination with reversible imine bond formation. The strategy employed is a versatile method for accessing new and molecular topologies in high yields.

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[2] S. J. Rowan, S. J. Cantrill, G. R. L. Cousins, J. K. M. Sanders, J. F. Stoddart, *Angew. Chem. Int. Ed.* **2002**, *41*, 898-952.

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Inorganic and Coordination Chemistry **IC 14**

## Interactions of Ruthenium-based drugs with amino acids, nucleotides, and peptides using NMR Spectroscopy

Federico Giannini[a], Julien Furrer[a],
Bruno Therrien[b],Georg Süss-Fink[b]

a: Departement für Chemie und Biochemie, University of Bern, Freiestrasse 3, CH-3012, Bern, Switzerland
b: Institut de Chimie, University of Neuchatel, rue Emile Argand 11, CH-2009, Neuchâtel, Switzerland

Ruthenium complexes may be strong candidates to replace platinum and to form a basis for rational anti-cancer drug design.[1,2] However, for most of these systems, the mode of action, uptake and biological processes remain poorly understood. In this contribution, we intend to identify their cellular targets and elucidate some of their mechanistic profiles by various NMR techniques.

In this regard, we have synthesized various thiophenolato-bridged dinuclear arene ruthenium complexes of the general formula $[(p\text{-cymene})_2Ru_2(SPh)_3]^+$ with $IC_{50}$ values being in the submicromolar range, and analyzed their interaction with amino acids, nucleotides, glutathione and peptides under physiological conditions.[3,4]

The aim of this initial screening by NMR spectroscopy is to provide the basis for subsequently understanding and characterizing the possible mode of action of these organometallic species with cellular targets in cancer cells and blood plasma at a molecular level. The results presented provide a first insight into their mode of action, and may provide guidance for synthesizing future optimized ruthenium-based drugs.

[1] G. Süss-Fink, *Dalton Trans.* **2010**, *39*, 1673.
[2] G. Gasser, I. Ott, N. Metzler-Nolte, *J. Med. Chem.* **2011**, *54*, 3.
[3] B. Therrien, G. Süss-Fink, P. Govindaswamy, A. Renfrew, P. Dyson, *Angew. Chem. Int. Ed.* **2008**, *47*, 3773.
[4] M. Gras, B. Therrien, G. Süss-Fink, O. Zava and P. Dyson, *Dalton Trans.* **2010**, *39*, 10305.

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Inorganic and Coordination Chemistry **IC 15**

## Metal cluster and functional analysis of plant Metallothioneins

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Metallothioneins (MTs) constitute a large family of ubiquitous, small and cysteine rich proteins. In the case of the plant MTs only little information about their structures and functions is available [1].

Following previous investigations on the MT2 from *Cicer arietinum*, which implicated increased metal ion incorporation into the metal-thiolate cluster in the presence of sulfide ions [2], we analyzed this feature further with different techniques, e.g. UV, CD, MCD, F-AAS, ESI-MS, and colorimetric assays. Owing to their high metal ion binding capacity, a functional role of the plant MTs in metal ion homeostasis and heavy metal detoxification was assumed and yeast complementation assays were performed. The protection system of this model organism against toxic metal ion concentrations was knocked out and replaced by plasmid DNA encoding different plant MTs (Fig.). The ability of the resulting cells to survive high metal ion concentrations was measured via growth curves, and additional tests for the actual intracellular MT and metal ion levels have to be performed.

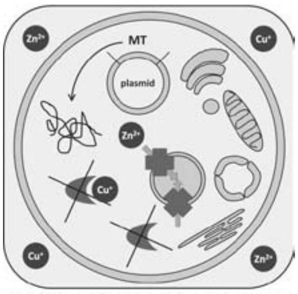

**Fig.** Scheme of yeast complementation assay showing the knock-out of a Cu(I)-specific MT and a Zn(II)-transmembrane transporter.

Financial support from the Swiss National Science Foundation is gratefully acknowledged (SNSF-Professorship PP002-119106/1 to EF).

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[2] X. Wan, *PhD Thesis*, University of Zürich, **2009**.

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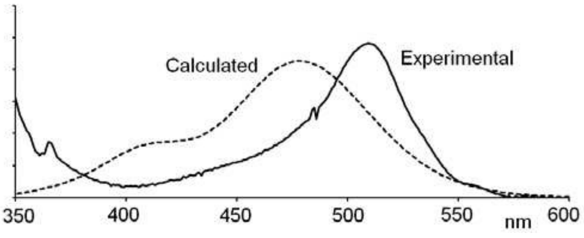
Inorganic and Coordination Chemistry **IC 16**

## Water-soluble alkylated bis{4'-(4-pyridyl)-2,2':6',2''-terpyridine}ruthenium(II) complexes for use as photosensitizers in water oxidation: a complementary experimental and TD-DFT investigation

Edwin C. Constable, Michael Devereux, Emma L. Dunphy, Catherine E. Housecroft,
Jennifer A. Rudd and Jennifer A. Zampese
Department of Chemistry, University of Basel, Spitalstrasse 51, 4056 Basel, Switzerland

We have investigated[1] the effects of attaching different substituents, R, to the pyridyl *N*-position of 4'-pyridyl-2,2':6',2''-terpyridine (L) on the electronic and spectroscopic properties of the $[Ru(LR)_2][PF_6]_4$. Anion exchange was performed on each complex to generate the water soluble $[HSO_4]^-$ complexes. Experimentally, anion exchange has a negligible effect on the electronic and spectroscopic properties and, therefore, TD-DFT calculations were carried out. The calculations showed that the LUMO only extended over the 4'-(4-pyridyl)-2,2':6',2''-terpyridine unit and, therefore, the *N*-substitution has little effect on the electronic and spectroscopic properties of the complexes. The latter are being tested for stability and water-splitting activity.



[1] E. C. Constable, M. Devereux, Emma L. Dunphy, C. E. Housecroft, J.A. Rudd and J. A. Zampese, *Dalton Trans.* **2011,** DOI: 10.1039/C0DT01714K

Inorganic and Coordination Chemistry **IC 17**

## PCsp$^3$P and PCsp$^2$P Palladium (II) Hydride Pincer Complexes: Small Structural Difference – Large Effect on Reactivity

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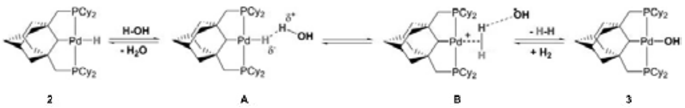
Dihydrogen evolution and formation of a stable palladium(II) hydroxide complex is observed when the aliphatic palladium (II) pincer hydride complex is treated with an excess of water in THF (see below). The reaction is reversible and fast hydrogenolysis is observed [1].



The aromatic analogue shows a strikingly different reactivity [2], which was attributed to the *trans* influence.

[1] R. Gerber, T. Fox, C. M. Frech, *Chem. Eur. J.* **2010**, *16*, 6771-6775.
[2] G.R, Fulmer, R.P. Muller, R.A. Kemp, K. I. Goldberg, *J. Am. Chem. Soc.* . **2009**, *131*, 1346.

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Inorganic and Coordination Chemistry **IC 18**

## Double sensitization of europium III coordinated to dipicolinate derivatives with para-polyoxyethylene-coumarins.

Julien Andres, Anne-Sophie Chauvin

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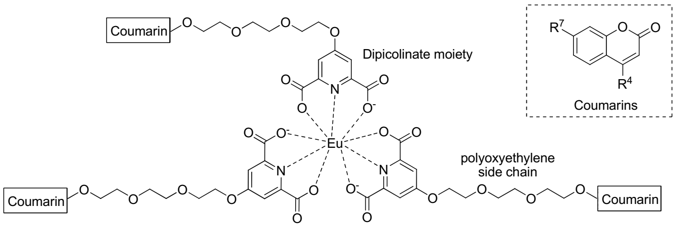
1015 Lausanne, Switzerland

A new class of ligands for luminescent lanthanide ions have been sythesized and investigated.[1] These ligands are made of a polyoxyethylene side chain with a coordinating dipicolinate moiety at one end and a light harvesting coumarin at the other end (see figure) . This framework forms a tris complex with europium III [EuL$_3$]$^{3-}$ and allows a double sensitization of the coordinated lanthanide ion, either by exciting through the coordinated dipicolinate chromophore, or through the distant coumarin fluorophore. The energy flow from absorption to emission has been investigated in details for different coumarin derivatives. The intend is to provide a modulation of the electronically excited levels of the coumarins to further increase the net energy transfer rate to the emissive energy level of europium III.



[1] J. Andres, A.-S. Chauvin, *EJIC.* **2010**, 2700.

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Inorganic and Coordination Chemistry **IC 19**

## New inorganic iridium(III) blue emitters

G. E. Schneider[1], M. Neuburger[1], J. Zampese[1], E. C. Constable[1], C. E. Housecroft[1], R. Costa[2], H. Bolink[2]

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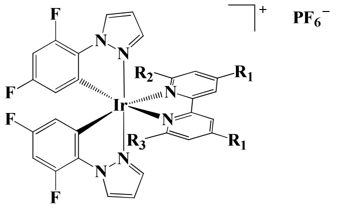
[2]Instituto de Ciencia Molecular, Universidad de Valencia, E-46980 Paterna

Light Emitting Electrochemical Cells (LEEC) are electroluminescent devices with an emissive organic layer, like Organic Light Emitting Diodes (OLED). Up to today, OLEDs are used in a wide range of applications including digital screens and for room lighting.

Compared to an OLED, a LEEC has a significantly simplified architecture. Two electrodes sandwich the emissive layer containing the light emitting molecules. But in LEECs the emitting molecules need to be ionic, unlike in OLEDs. While the OLEDs need a perfect encapsulation to prevent the degradation of the electron-injecting layers, air-stable electrodes like gold or silver can be used with LEECs. Four new iridium(III) complexes have been prepared, which all show a blue emission with quantum yields up to 100%.



**R$_1$: H, $^t$Bu, NMe$_2$**
**R$_2$: H, Ph**
**R$_3$: H, Ph**

[1] H. J. Bolink, E. Coronado, R. D. Costa, E. Ortí, M. Sessolo, S. Graber, K. Doyle, M. Neuburger, C. E. Housecroft, E. C. Constable, *Adv. Mater.*, **2008**, 20, 1 - 4.
[2] S. Graber, K. Doyle, M. Neuburger, C. E. Housecroft, E. C. Constable, R. D. Costa, E. Ortí, D. Repetto, H. J. Bolink, *J. Am. Chem. Soc.,* **2008,** *130*, 14944–14945.

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Inorganic and Coordination Chemistry **IC 20**

## Heteroleptic Copper(I) Complexes for Light-Emitting Electrochemical Cells

J. Schönle[1], S. Graber[1], J. A. Zampese[1], E. C. Constable[1], C. E. Housecroft[1], H. J. Bolink[2], R. D. Costa[2]

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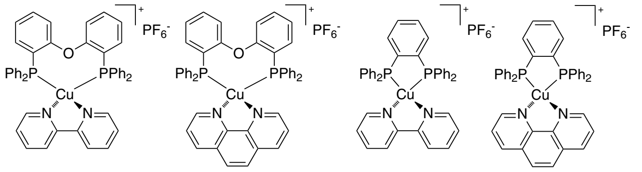
Light-emitting electrochemical cells (LEECs) are single-layer electroluminescent devices consisting of an ionic luminescent material sandwiched between two electrodes. One distinguishes two types of electroluminescent materials: a) conjugated polymers mixed with inorganic salts and b) ionic transition-metal complexes (iTMCs). Up to now, iTMCs based on ruthenium(II) and iridium(III) complexes have been widely investigated with promising results. However, because of the small abundance of these elements in the Earth's crust this metals are very expensive. In contrast, copper is relatively abundant and is also much cheaper. Heteroleptic Cu(I) complexes show promising electroluminescent properties in LEEC configurations.[1]



[1] R. D. Costa, D. Tordera, E. Ortí, H. J. Bolink, J. Schönle, S. Graber, C. E. Housecroft, E. C. Constable and J. A. Zampese, paper to be submitted.

Inorganic and Coordination Chemistry **IC 21**

## [Fe]-Hydrogenase Models Featuring Acylmethylpyridinyl Ligand

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[Fe]-hydrogenase (Hmd) catalyzes the reversible reduction of methenyltetrahydromethanopterin (methenyl-H$_4$MPT$^+$) with $H_2$ to form methylenetetrahydromethanopterin (methylene-H$_4$MPT) and H$^+$.[1,2] Its active site is shown in Figure 1.[1,2]

Herein we present two model complexes which reproduce the main structural features of the active site of [Fe]-hydrogenase.[3,4]

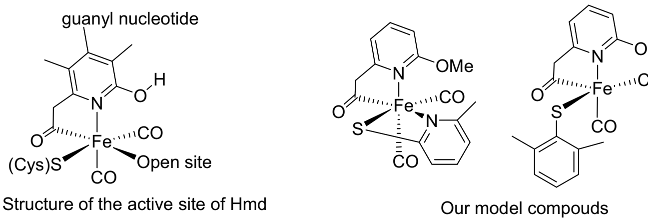

Figure 1. Structures of the active site of Hmd and our model compounds

[1] S. Shima, O. Pilak, S. Vogt, M. Schick, M. S. Stagni, W. Meyer-Klaucke, E. Warkentin, R. K. Thauer, U. Ermler, *Science* **2008**, *321*, 572.

[2] T. Hiromoto, K. Ataka, O. Pilak, S. Vogt, M. S. Stagni, W. Meyer-Klaucke, E. Warkentin, R. K. Thauer, S. Shima, U. Ermler, *FEBS Lett.* **2009**, *583*, 585.

[3] D. Chen, R. Scopelliti, X. Hu, *Angew. Chem. Int. Ed.* **2010**, *49*, 7512.

[4] D. Chen, R. Scopelliti, X. Hu, *Angew. Chem. Int. Ed.* Accepted.

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Inorganic and Coordination Chemistry **IC 22**

## Nano-structured Manganese Based Cathode Material for High Power and Safe Li-ion Batteries

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Recent publications reported that the olivine phase of $LiMnPO_4$ is one of the best alternative cathode materials for Li-Ion Batteries (LIB). The layered rock salt oxides $LiCoO_2$, $LiNiO_2$, and $LiMnO_2$ have been reported that the structure is deformed at overcharging and the transition metal is dissolved into the commercial electrolyte upon cycling[1]. Therefore, it has been researched to replace those layered structures by polyanionic olivine $LiMPO_4$ (M = transition metal) structure due to the excellent cyclability, thermal and chemical stability, low cost and low environmental impact [2].

Despite of its high theoretical capacity (170 mAh/g), high operating voltage (4.1 V vs. Li) and good capacity retention, $LiMnPO_4$ suffers from low intrinsic electronic/ionic conductivity. Particularly, at high current densities the electrochemical performance is poor caused by the slow Li diffusion kinetics within the grains. Reducing the particle size has been found to be one of the effective ways to increase the rate performance because nanoparticles reduce the diffusion path length for $Li^+$ ion and increase the contact area with conductive additives [3].

We synthesized nanoparticles of $LiMnPO_4$ via thermal decomposition method using surfactant. Specific surface area measured by nitrogen adsorption method is 99 $m^2$/g, corresponding to 17 nm of particle size.

We will present the comparative result using two preparative methods and their effects on the size, morphology of the particle and electrochemical performance.

[1] J.R. Dahn and al., Solid State Ionics 69 (1994) 265-270

[2] A. K. Padhi and al., J. Electrochem. Soc., 144 (1997) 1188 - 1194.

[3] Kwon N.H.,and al., Electrochem. Sol. State Lett. 9 (2006) A277-A280.

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Inorganic and Coordination Chemistry **IC 23**

## A Viable Hydrogen-Storage System Based On Selective Formic Acid Decomposition with Heterogeneous Silica-Supported Ruthenium Catalysts in Water

Weijia Gan, Paul J. Dyson, Gábor Laurenczy*

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As an energy carrier, hydrogen holds the potential to provide clean, safe and affordable energy in an easily usable form. Formic acid is an excellent source of hydrogen, having many advantages including weight and safety issues. A viable $H_2$ storage system, based on the selective homogeneous catalytic decomposition of formic acid into $H_2$ and $CO_2$, in a wide pressure range, has been proposed[1,2]. The catalytically active species are formed *in situ* from $RuCl_3$ and TPPTS in aqueous solution[3].

Heterogeneous catalysts could be advantageous for recycling, especially for dilute formic acid solutions, or for small, mobile and portable applications. Several approaches have been used to immobilize/solidify the homogeneous Ru/TPPTS[4]. We will present our recent results concerning the immobilization/solidification of the ruthenium complexes on silica-supports, for hydrogen production from formic acid. These catalysts offer the advantage of high catalytic activity and easy catalyst separation/recycling in dilute HCOOH.

*Acknowledgment:* The Swiss National Science Foundation and EPFL are thanked for financial support.

[1] G. Laurenczy, C. Fellay, P. J. Dyson, PCT Int. Appl. (**2008**), 36pp. CODEN: PIXXD2 WO 2008047312 A1 20080424 AN 2008:502691

[2] C. Fellay, P. J. Dyson, G. Laurenczy, *Angew. Chem. Int. Ed.,* **2008**, *47*, 3966.

[3] C. Fellay, N. Yan, P. J. Dyson, G. Laurenczy, *Chem. Eur. J.*, **2009**, *15,* 3752.

[4] W. Gan, P. J. Dyson, G. Laurenczy, *React. Kinet. Catal. Lett.*, **2009**, *98,* 205.

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Inorganic and Coordination Chemistry **IC 24**

## Beyond Click-Chemistry: Transformation of Azides with Cyclopentadienyl Ruthenium Complexes

Julie Risse, Rosario Scopelliti and Kay Severin

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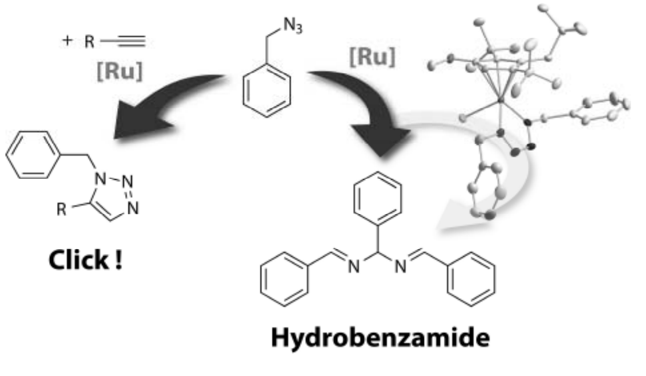
Ruthenium cyclopentadienyl complexes such as Cp*RuCl(cod) and Cp*RuCl(PPh$_3$)$_2$ are active catalysts for the ‘click’ reaction between azides and alkynes. We show that those complexes are also able to catalyze the transformation of benzyl azide into hydrobenzamide. The catalyst precursor [Cp^RuCl$_2$]$_2$ (Cp^ = $\eta^5$-1-methoxy-2,4-di-*tert*-butyl-3-neopentylcyclopentadienyl) was found to be particularly active and selective. The transformation has been extended to other benzylic azides and the mechanism has been studied as well. In the presence of water, benzylic azides are converted to aldehydes.



Inorganic and Coordination Chemistry **IC 25**

### Intercluster Compounds for Nanosized Materials

Fabienne Gschwind, Martin Jansen

Max-Planck-Institute for Solid State Research, Heisenbergstrasse 1, D-70569 Stuttgart, Germany

The term “intercluster compound” refers to assemblies that are constituted of at least two different, large, inorganic building blocks [1, 2]. A few intercluster compounds already exist and it has been possible to determine their crystal structures by single crystal X-ray diffraction.

These results deliver insights into the arrangement of large building units in the solid state material and the underlying intermolecular forces [3, 4].

These first results show that intercluster compounds are very promising for the study of structural and physical properties of nanosized particles.

They also open a wide range for new applications (lithography techniques, electronic or optical devices, study of quantum effects and also of orbital bands). Since only a few compounds have been studied, there is a huge potential for new discovery in this field.

We would like to present new building blocks [5] and their corresponding intercluster compounds.

[1] M. Schulz-Dobrick, M. Jansen, *Eur. J. Inorg. Chem.* **2006**, 4498.
[2] G. Schmid, *Angew. Chem.* **2008**, 120, 3548.
[3] M. Schulz-Dobrick, M. Jansen, Z. Anorg. Allg. Chem. **2007**, 633, 2326.
[4] F. Gruber, M. Jansen, *Angew.Chem. Int. Ed.*, **2010**, 49, 4924.
[5] F. Gschwind, M. Jansen, *Z. Naturforsch.* 2011, *66b,* 1 – 4.

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Inorganic and Coordination Chemistry **IC 26**

### Folding properties of metallothionein $E_c$-1 from wheat (*Triticum aestivum*) investigated by intrinsic tryptophan fluorescence

Barbara Leitenmaier and Eva Freisinger

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Metallothioneins (MTs) are small, cysteine-rich proteins that bind metal ions with high affinity and occur in animals, bacteria, fungi, and plants. The early cysteine-labeled MT $E_c$-1 from wheat (*Triticum aestivum*) was the first MT that has been identified in plants. In this project the folding properties of $E_c$-1 are being investigated via intrinsic tryptophan fluorescence. As $E_c$-1 does not contain tryptophan, three mutants, each one carrying a single tryptophan instead of a valine/glycine respectively, have been generated. With this approach it will be investigated, in which order folding of the two domains of $E_c$-1 takes place under different conditions, e.g. in the presence of various concentrations of cadmium, copper and zinc.

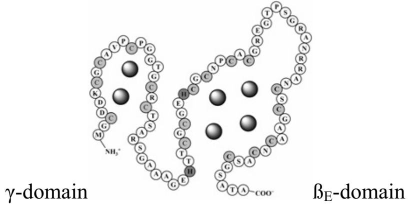

Fig. 1 Amino acid sequence of full-length wheat $E_c$-1. $Zn^{II}$-coordinating Cys and His residues are indicated in grey. The γ-domain on the left and the $ß_E$- domain on the right have been shown to bind 2 and 4 metal ions, respectively [1].

Continuous financial support from the Swiss National Science Foundation (SNSF-Professorship and direct project funding), the Institute of Inorganic Chemistry, and the Faculty of Science of the University of Zürich is gratefully acknowledged.

[1] E. A. Peroza, R. Schmucki, P. Güntert, E. Freisinger and O. Zerbe, *J. Mol. Biol.* **2009**, *387*, 207.

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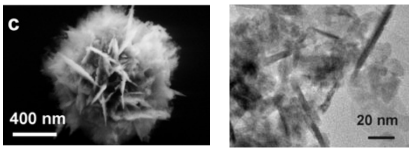
Inorganic and Coordination Chemistry **IC 27**

### Copper-containing Gallium Defect Spinels

Franziska Conrad and Greta R. Patzke*

Institute of Inorganic Chemistry, University of Zurich,
Winterthurerstrasse 190, CH-8057 Zurich, Switzerland

Although impressive progress in oxide nanomaterials synthesis has been reported,[1] many compounds still require the development of individual preparative pathways. This applies for metal-doped defect spinels of the γ-$Ga_2O_3$ type that are far less explored than $CuGa_2O_4$ or $CuGaO_2$.[2, 3] However, by applying state-of-the-art microwave-hydrothermal (MW-HT) techniques, we synthesized hierarchically nanostructured γ-$Ga_2O_3$:$Cu^{2+}$ materials. The implementation of $Cu^{2+}$ ions into nanoscale γ-$Ga_2O_3$ matrices is completed within less than 30 minutes of reaction time, resulting in products with homogeneous distribution of $Cu^{2+}$ and high surface areas. Therefore, the γ-$Ga_2O_3$:$Cu^{2+}$ materials are promising for catalytic processes, such as methanol synthesis, water splitting or the photocatalytic degradation of organic compounds.



Representative SEM and TEM images of MW-HT synthesized γ-$Ga_3O_4$:$Cu^{2+}$.

We thus report on the analytical characterization and catalytic behavior of the obtained γ-$Ga_2O_3$:$Cu^{2+}$ spinels.

[1] G. R. Patzke, Y. Zhou, R. Kontic, F. Conrad, *Angew. Chem. Int. Ed.* **2011**, 50, 826.
[2] T. Moeller, G. L. King, *J. Am. Chem. Soc.* **1953**, *75*, 6060.
[3] K. Faungnawakij, N. Shimoda, T. Fukunaga, R. Kikuchi, K. Eguchi, *Appl. Catal. A* **2008**, *341*, 139.

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Inorganic and Coordination Chemistry **IC 28**

### New protein scaffolds for the design of bio-inspired artificial metalloenzymes

Fabien W. Monnard[1], Elisa S. Nogueira[1], Tillmann Heinisch[1,2], Maurus Schmid[1], Tilman Schirmer[2], Markus Meuwly[1] and Thomas R. Ward[1]

[1]University of Basel, Department of Chemistry, CH-4056 Basel Switzerland
[2]University of Basel, Biozentrum, CH-4056 Basel Switzerland

During the past decade, artificial metalloenzymes based on biotin-avidin technology have been extensively investigated in the Ward group.[1] These artificial metalloenzymes rely on the localization of a catalytically active organometallic moiety within a chiral protein scaffold. In order to develop a new generation of artificial metalloenzyme, we transferred our knowledge of the biotin-streptavidin technology to a sulfonamide-human carbonic anhydrase II system. This protein offers new interesting characteristics including a deeper binding pocket and a monomeric structure allowing a much more straightforward *in silico* modeling of the new artificial metalloenzyme.[2,3]

To ensure localization of the catalytically-active metal complex within carbonic anhydrase, we rely on an arylsulfonamide anchoring strategy and on a chemogenetic protein engineering strategy,[4] i.e. mutagenesis of the protein scaffold to improve binding of the catalytic precursor and influence enantioselectivity.[5]

[1] J. Pierron, C. Malan, M. Creus, J. Gradinaru, I. Hafner, A. Ivanova. A. Sardo, T. R. Ward, *Angew. Chem. Int. Ed.* **2008**, *47*, 701.
[2] F. W. Monnard, T. Heinisch, E. S. Nogueira, T. Schirmer, T. R. Ward, *Submitted.*
[3] M. Schmid, E. S. Nogueira, F. W. Monnard, M. Meuwly , T. R. Ward, *Submitted.*
[4] A. Pordea, T. R. Ward, *Chem. Commun.* **2008**, 4239.
[5] C. Letondor, T. R. Ward, *ChemBioChem* **2006**, *7*, 1745.

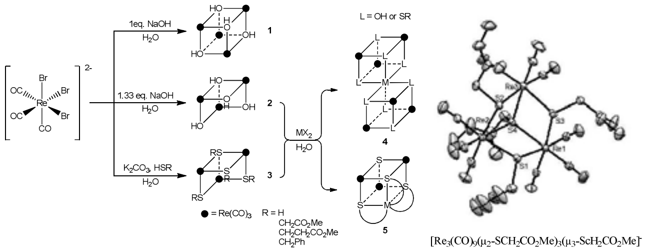
Inorganic and Coordination Chemistry **IC 29**

## Synthesis and Characterization of Re(I) Hydroxy and Mercapto Clusters as Novel Tripodal Ligands with possible Catalytic Activity

A. Degonda, N. von Wolff and R. Alberto

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

Methods for the preparation of cubane-type $[Re_4(CO)_{12}(\mu_3\text{-}OH)_4]$ **1** and incomplete cubane-type $[Re_3(CO)_9(\mu_2\text{-}OH)_3(\mu_2\text{-}OH)]^-$ **2** clusters were described in the early 90's.[1] Especially trinuclear incomplete clusters of type **2** are of high interest due to their rich coordination chemistry. Thus, trinuclear Re(I) cluster **2** acts as a novel tripodal ligand for a wide range of divalent metals ($Cu^{II}$, $Mn^{II}$, $Zn^{II}$, $Co^{II}$) forming the "double-cubane" structure type **4**.[2] By replacing OH with SR these Re(I) clusters are thought to have similar redox-chemical properties as Fe-S-cluster, therefore mercapto analogues like $[Re_3(CO)_9(\mu_2\text{-}SH)_3(\mu_3\text{-}SH)]^-$ **3** are prepared for the Fe-S-cluster mimic. Further, different trinuclear Rhenium mercapto cubane-types $[Re_3(CO)_9(\mu_2\text{-}SR)_3(\mu_3\text{-}SR)]^-$ **3** were prepared in order to extend the coordination number of the tripodal ligand forming the sixfold-coordinated complex **5**. These clusters were synthesized using $[ReBr_3(CO)_3]^{2-}$ as starting material and the condition mentioned in the scheme below. **1** to **5** were structural characterized and electrochemical investigated.



$[Re_3(CO)_9(\mu_2\text{-}SCH_2CO_2Me)_3(\mu_3\text{-}ScH_2CO_2Me]^-$

[1] R. Alberto, A. Egli, U. Abram, K. Hegetschweiler, V. Gramlich and P. A. Schubiger, *J. Chem. Soc. Dalton Trans.* **1994**, *19*, 2815.

[2] W. A. Herrmann, A. Egli, E. Herdtweck, R. Alberto and F. Baumgärtner, *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 432.

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Inorganic and Coordination Chemistry **IC 30**

## Iridium(III) Complexes for Light Emitting Electrochemical Cells

A.Bünzli, E.C. Constable, C.E. Housecroft, M. Neuburger, J. A. Zampese,

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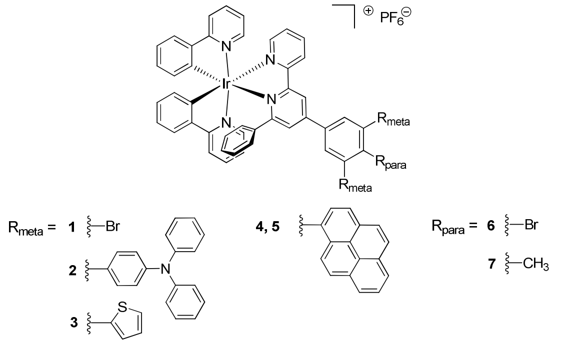
Light Emitting Electrochemical Cells (LEEC) consisting of an iridium based ionic transition metal complex (iTMC), sandwiched between two electrodes show promising properties for highly efficient and low-cost applications in lighting and full-colour displays [1].



The synthesis of some iridium based iTMCs and their photophysical characterization with regard for LEEC applications is presented. Variously substituted 4,6-diphenyl-2,2'-bipyridine ligands were reacted with a chlorido-bridged tetrakis(2-phenylpyridine)iridium dimer to produce orange emitting cyclometallated Ir(III) complexes of the form $[Ir(C^\wedge N)_2(N^\wedge N)][PF_6]$. Their structures and solution properties will be presented.

[1] H.J. Bolink, E. Coronado, R.D. Costa, E. Ortí, M. Sessolo, S. Graber, K. Doyle, M.Neuburger, C.E. Housecroft, E.C. Constable, *Adv. Mater.*, **2008**, *20*, 3910-3913.

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Inorganic and Coordination Chemistry **IC 31**

## Synthesis and Studies of New Iridium Hydride Complexes

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CH-4056 Basel, Switzerland

Cationic iridium complexes incorporating chiral P,N– and heterocyclic carbene–ligands have proven to be highly effective catalysts for the enantioselective hydrogenation of unfunctionalised olefins[1]. For this reason, the chemistry of iridium hydride complexes, which are intermediates in hydrogenation reactions, continues to be of considerable interest[2].

We have synthesized and characterized new iridium hydride complexes via the reaction of iridium COD precursors with molecular hydrogen. The structures of the resulting complexes were established using 2D NMR spectroscopy and X-ray analysis.

[1] a) S. J. Roseblade, A. Pfaltz, *Accounts of Chemical Research* **2007**, *40*, 1402; b) K. Källström, I. Munslow, P. G. Andersson, *Chemistry – A European Journal* **2006**, *12*, 3194; c) X. Cui, K. Burgess, *Chemical Reviews* **2005**, *105*, 3272.

[2] a) R. Crabtree, *Accounts of Chemical Research* **1979**, *12*, 331; b) S. P. Smidt, A. Pfaltz, E. Martínez-Viviente, P. S. Pregosin, A. Albinati, *Organometallics* **2003**, *22*, 1000.

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Inorganic and Coordination Chemistry **IC 32**

## Reaction of $NO^\bullet$ with $O_2$ in Cold Hydrocarbons

Leila Mahmoudi, Reinhard Kissner and Willem H. Koppenol

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We studied the autoxidation of $NO^\bullet$ in 2-methylbutane and in a 8:3 v/v mixture of 2,2-dimethylbutane with *n*-pentane ("rigisolve"). Previous work [1] had led to the discovery of a red intermediate in 2-methylbutane at 110 K, which we characterized further by its infrared spectrum. In "rigisolve" we found a yellow intermediate that precedes the red one at 80-90 K. Upon warming to 110 K it converted to the red intermediate. The yellow material shows UV bands typical for a O=N-O-O function. Warming of the red compound above 110 K results in a colorless solution. Recently, the $NO^\bullet$ autoxidation mechanism was described by a three-step reaction [2]:

$$2NO \rightleftarrows N_2O_2 \qquad N_2O_2 + O_2 \longrightarrow N_2O_2 \cdots O_2 \qquad N_2O_2 \cdots O_2 \longrightarrow N_2O_4$$

This scheme allows only one possible colored intermediate, $N_2O_2 \cdots O_2$. With the EPR results of Ref. [1], we propose a reaction sequence which complies with all observations:

$$\begin{array}{ccc} & NO^\bullet + O_2 \rightleftarrows ONOO^\bullet & \\ & ONOO^\bullet + NO^\bullet \longrightarrow ONOO^\bullet \cdots {}^\bullet NO & \\ & & \textit{yellow} \\ & & \downarrow \\ N_2O_4 & \longleftarrow & ONOONO \\ \textit{colorless} & & \textit{red} \end{array}$$

We conclude that the autoxidation of $NO^\bullet$ proceeds *via* $ONOO^\bullet$, not $N_2O_2$.

[1] B. Galliker, R. Kissner, T. Nauser, W.H. Koppenol, *Chem. Eur. J.* **2009**, *15*, 6161.

[2] H. Beckers, X. Zeng, H. Willner. *Chem. Eur. J.* **2010**, *16*, 1506.

Inorganic and Coordination Chemistry **IC 33**

### Microemulsion approach to antimicrobial nanocontainers

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Within recent years, nanocontainers have attracted increasing interest due to their ability to enclose guest molecules inside their empty core. Because of this potential, hollow nanoparticles may find numerous applications such as drug carriers, reactors, confined reaction vessels, building blocks for photonic crystals or multienzyme biocatalysis.[1]

The microemulsion approach for the production of nanocontainers is a relatively new method enabling dissolution of any substance. Subsequent reaction between reagents on the boundary phase between a micelle and the surrounding phase leads to the formation of a nanocontainer.[2]

The aim of this study is to encapsulate an antimicrobial silver coordination polymer inside inorganic nanocapsules. We have successfully synthesized hollow spheres of a well-defined porous shape with an outer diameter of 41±5 nm and with a wall thickness of 11±2 nm (Fig.1).

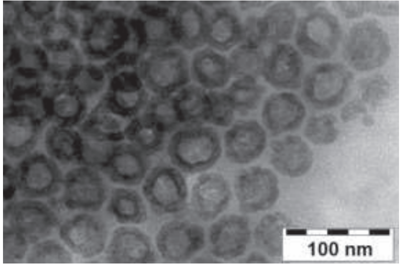

*Figure 1. TEM image of CuS hollow spheres.*

[1] Meier W., *Chemical Society Reviews* **2000**, 29, 295–303.
[2] Feldmann C. et al., *Advanced Materials* **2009**, 21, 1586-1590

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Inorganic and Coordination Chemistry **IC 34**

### New Lanthanoid-Containing Open Wells-Dawson Silicotungstates

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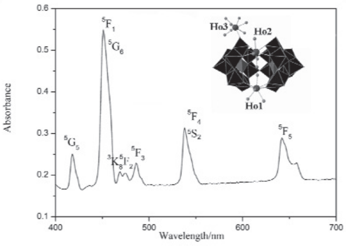
Polyoxometalate (POMs) are early transition metal oxide clusters with manifold application options in catalysis, medicine, electronics, magnetism and optics.[1] A new family of lanthanoid-containing silicotungstates has been constructed from a building block approach based on the open Wells-Dawson anion $[\alpha\text{-}Si_2W_{18}O_{66}]^{16-}$. The $[Ln_2(H_2O)_7Si_2W_{18}O_{66}]_n^{10n-}$ (Ln = $Gd^{III}$, $Tb^{III}$, $Dy^{III}$, $Ho^{III}$) series illustrates the interplay of preparative and crystallographic parameters (radius of the $Ln^{III}$ ion) in the formation of 3D and 2D solid state networks. $Gd^{III}$ gives rise to an interesting polymorphism of POMs with paramagnetic properties, whereas the Ho-compound shows promising photochromic behavior (cf. inset below) and the Tb- and Dy-representatives of the series exhibit photoluminescence.[2]



Solid state UV/vis spectrum and structure (inset) of $[Ho_2(H_2O)_7Si_2W_{18}O_{66}]_n^{10n-}$

[1] (a) *Polyoxometalate Chemistry: From Topology via Self-Assembly to Applications* (Eds.: M. T. Pope, A. Müller), Kluwer, Dordrecht, **2001**. (b) F. Hussain, F. Conrad, G. R. Patzke, *Angew. Chem. Int. Ed.* **2009**, *48*, 9088.
[2] L. Ni, F. Hussain, B. Spingler, S. Weyeneth, G. R. Patzke, *submitted.*

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Inorganic and Coordination Chemistry **IC 35**

### Sodium phosphacyanate as building block for heterocyclic compounds

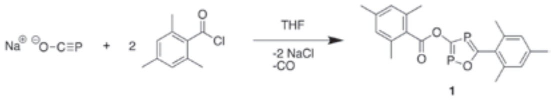
Dominikus Heift and Hansjörg Grützmacher

*Department of Chemistry and Applied Biosciences,*
*ETH Zürich, SWITZERLAND*

The reaction of $NaPH_2$ with carbon monoxide gives the phosphor analogue compound of sodium cyanate, namely Sodium phosphacyanate NaO-C≡P. In a different route carbon monoxide is replaced by ethylene carbonate, which is readily handable.[1]

The phosphacyanate anion is a small molecule, which contains a phosphorus-carbon triple bond and is therefore a very versatile building block in organophosphorus chemistry. Among others NaOCP can act as a nucleophile. Depending on their electronic character, electrophiles attack the phosphacyanate anion either at the phosphorus or the oxygen atom. Furthermore we found that the phosphacyanate anion undergoes cycloadditions.[1] Nevertheless NaOCP has not been widely investigated as a starting material.

Exploring the chemistry of NaOCP we tested its reactivity towards an acid chloride. Surprisingly in the reaction with 2,4,6-trimethylbenzoyl chloride the five-membered heterocyclic compound **1** is formed.



Sodium (I) phosphacyanate reacts in THF with an excess of 2,4,6-trimethylbenzoyl chloride releasing one equivalent of carbon monoxide which was proven by *insitu*-IR spectroscopy.

Literature: [1] Florian Puschmann, Dissertation 19442 ETH Zürich **2011**.

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Inorganic and Coordination Chemistry **IC 36**

### Towards Pd(II/IV) Catalyzed Allylic Trifluoromethylation

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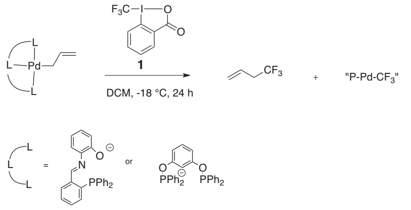
Recently, hypervalent iodine(III) reagents have been used for oxidation of Pd(II)- to Pd(IV)-complexes.[1] In the very same fashion the I-$CF_3$-$\lambda^3$ 1,2-benziodoxole **1** developed in our group[2] has been shown to oxidize Pd(II) bearing ligands of the type N-Aryl yielding a stable Pd(IV)- $CF_3$-complex that upon heating reductively eliminates to give the corresponding trifluoromethylated N-Aryl.[3] Based on this concept we are trying to develop a system for Pd(II)-$\eta^3$-allyl- complexes to trigger allylic trifluoromethylation. However, $\eta^1$-coordinated allyl- Pd(II) complexes bearing tridentate ligands, showed to be more promising as they react with **1** to give 3-(trifluoromethyl)propene. Also, as observed in $^{19}F$ and $^{31}P$ NMR, P-Pd-$CF_3$ species are generated whose structures and roles will be presented and discussed.



[1] Deprez, N.R.; Sanford M.S. *Inorg. Chem.* **2007**, *46*, 1924.
[2] a) Eisenberger, P.; Gischig, S.; Togni, A. *Chem. Eur. J.* **2006**, *12*, 2579.
b) Kieltsch, I.; Eisenberger, P.; Togni, A. *Angew. Chem. Int. Ed.* **2007**, *46*, 754.
[3] Ye, Y.; Ball, N.D.; Kampf, J.W.; Sanford, M. S. *J. Am. Chem. Soc.* **2010**, *132*, 14682.

Inorganic and Coordination Chemistry **IC 37**

## Organic Light Emitting Electrochemical Cells based on new Iridium (III) complexes

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R. Costa[2], H. Bolink[2]

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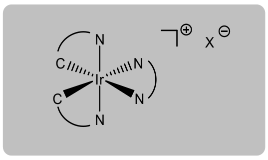
[2]Instituto de Ciencia Molecular, Universidad de Valencia, E-46980 Paterna

Over the past years, Organic Light Emitting Diodes (OLEDs) and Light Emitting Electrochemical Cells (LEEC) have been identified as promising candidates to develop novel and more efficient lighting systems. The LECs are much simpler devices than the OLEDs, requiring no environmental protection. However, both types of device operate at low voltage with no special sensitivity to the thickness of the active layer. Many of the best emitters in both cases are based on iridium complexes.

We have prepared new iridium(III) complexes with an range emission from blue to deep red.



[1] M. A. Baldo et al., *Nature*, **1998**, 395, 151-154.
[2] B. Geffroy, P. le Roy, C. Prat, *Polym. Int.*, **2006**, 55, 572-582.
[3] H. J. Bolink, E. Coronado, R. D. Costa, E. Orti, M. Sessolo, S. Graber, K. Doyle, M. Neuburger, C. E. Housecroft, E.C. Constable, *Adv. Mater.*, **2008**, 20, 3910-3913.

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Inorganic and Coordination Chemistry **IC 38**

## [(Cp-R)M(CO)$_3$] Complexes (M= Re, $^{99m}$Tc) for Potential Application in Tumor Diagnosis and Therapy

S. Sulieman, D. Can, B. Spingler, P. Schmutz and R. Alberto*

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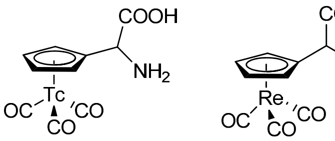
Cyclopentadienyl ($Cp^-$) is a basic ligand in organometallic chemistry. Its properties of low molecular weight, the occupation of three coordination sites in piano stool complexes and its availability for conjugated targeting vectors make it attractive for radiopharmaceutical application. In history several examples showed that cyclopentadienyl i.e. in the form of sandwich complexes like ferrocene are stable and well tolerated in biological media [1]. Even more since we published a fully aqueous synthesis of [(Cp-R)$^{99m}$Tc(CO)$_3$] complexes below 100 °C, a general and easy route for $^{99m}$Tc-labeling of Cp-R was discovered that can be applied for a variety of R-groups [2].



Herein we wish to report about the synthesis and biological evaluation of [(Cp-R)M(CO)$_3$] complexes (M= Re, $^{99m}$Tc), in which R represents an α-amino acid group for LAT1 targeting or a carbonic anhydrase targeting residue. A crystal structure of hCAII, inhibited by the target molecule, bio distribution studies and labelling traces will be presented.

[1] S. Top, A. Vessieres, et. al, *ChemBioChem*, **2004**, 5, 1104.
[2] Y. Liu, B. Spingler, et. al, *J. Am. Chem. Soc.* **2008**, 130, 1554.

* Permanent Address: SYR, AECS, Damascus, P.O.Box: 6091

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Inorganic and Coordination Chemistry **IC 39**

## Synthesis and characterisation of 4,4'-disubstituted-2,2'-bipyridine ruthenium(II) complexes relevant to solar energy conversion.

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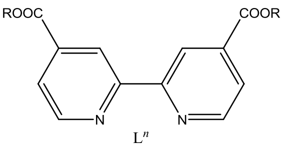
Poly(bipyridine)ruthenium(II) complexes with carboxylate anchoring groups have been extensively studied because of their exceptional photochemical properties: they can be used as tuneable pigments in dye-sensitised solar cells (DSSCs). Complexes with carboxylate anchoring groups bind strongly to the titanium dioxide surface of solar cells. Most complexes have used 4,4'-dicarboxy-2,2'-bipyridine as the anchoring ligand because this ligand facilitates photoinduced electron transfer from the excited ruthenium centre to the surface, which is very important for the efficiency of DSSC.[1]

A series of new ruthenium(II) complexes has been synthesized for their application in photoelectrochemical solar cells using 4,4'-diethylester-2,2'-bipyridine as ligands.[2]



$L^n$

$n = 12$: $R = C_{12}H_{25}$
$n = 16$: $R = C_{16}H_{33}$
$n = 18$: $R = C_{18}H_{37}$

[1] M. Schwalbe, B. Schäfer, H. Görls, S. Rau, S. Tschierlei, M. Schmitt, J. Popp, G. Vaughan, W. Henry, J. G. Vos, *Eur. J. Inorg. Chem.* **2008**, 3310.
[2] A. Bellusci, M. Ghedini, L. Giorgini, F. Gozzo, E. I. Szerb, A. Crispini, D. Pucci, *Dalton Trans.* **2009**, 7381.

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Inorganic and Coordination Chemistry **IC 40**

## Copper(I)-complexes for Dye Sensitized Solar Cells

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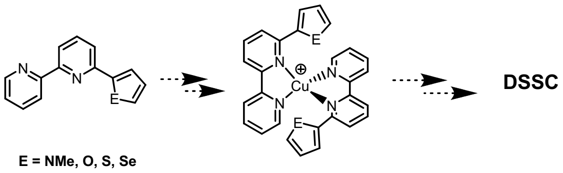
Dye-sensitized solar cells (DSSCs) are possibly cheaper and environmentally more compatible alternatives to silicon-based photovoltaic devices. Typically, DSSCs consist of a semiconductor substrate functionalized with a dye which shifts the absorption of light to the visible region and results in better photon harvesting from the sun. In the commonest type of DSSC (the so-called Graetzel cell), the semiconductor is nanocrystalline, anatase-like $TiO_2$ sensitized with ruthenium(II) oligopyridine complexes.[1] Copper(I) complexes are now under investigation as alternative dyes for DSSCs.[2]



We report here heteroaromatic (HetAr) substituted bpy-ligands (see scheme). Homoleptic [Cu(6-HetAr-bpy)$_2$][PF$_6$] complexes show unusual behaviour in solution and have been studied by NMR spectroscopy. Their incorporation into DSSC devices is also described.

[1] T. Bessho, E. C. Constable, M. Graetzel, A. Hernandez Redondo, C. E. Housecroft, W. Kylberg, Md. K. Nazeeruddin, M. Neuburger, S. Schaffner, *Chem. Commun.*, **2008**, 3717.
[2] D. R. McMillin, M. T. Buckner, B. T. Ahn, *Inorg. Chem.*, **1977**, *16*, 943; N. Armaroli, *Chem. Soc. Rev.*, **2001**, *30*, 113; D. R. McMillin, K. M. McNett, *Chem. Rev.*, **1998**, *98*, 1201.

Inorganic and Coordination Chemistry **IC 41**

## $Mg^{2+}$ binding sites in the κζ region of group II intron Sc.ai5γ

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$Mg^{2+}$ ions are a crucial cofactor of group II intron ribozymes, which need them not only for folding and charge compensation, but also to catalyze self-splicing [1]. The group II intron core structure contains the κζ region of domain 1 (D1κζ), which interacts with the conserved domain 5 (D5) both through a tetraloop receptor (ζ) and a three-way junction (κ). The ζ interaction is known to depend upon di- or multivalent metal ions [2], while there is no information yet on κ.
We are investigating the structure of the isolated D1κζ of *S. cerevisiae* group II intron Sc.ai5γ by NMR spectroscopy. Upon addition of $Mg^{2+}$ we observe large changes in both κ and ζ that allow us to characterize the location and thermodynamics of $Mg^{2+}$ binding.

Financial support by a Marie Curie Intra European Fellowship (RNABIC, 236794 to DD) and in the form of access to the Bio-NMR Research Infrastructure (FP7/2007-2013, grant agreement 261863) within the 7th European Community Framework Programme as well as by the Swiss National Science Foundation (200021-124834 to RKOS) is gratefully acknowledged.

[1] R.K.O. Sigel, *Eur. J. Inorg. Chem.* **2005**, 2281.
[2] J.H. Davis, T.R. Foster, M. Tonelli and S.E. Butcher, *RNA* **2007**, 76.

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Inorganic and Coordination Chemistry **IC 43**

## Molecular computing

Marketa Smidkova[a], Edwin C. Constable[a], Catherine E. Housecroft[a], Alberto Credi[b]

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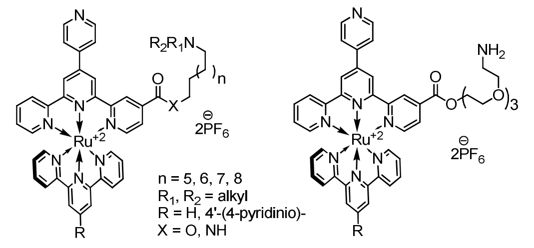
[b]Department of Chemistry, University of Bologna, Via Selmi 2, 40126 Bologna, Italy

Certain compounds can work as so-called molecular switches. Inherent properties of molecules such as conformation, isomerisation, redox properties, pH sensitivity, photoinduced electron transfer and photophysics form the basis of the input and outputs, desirable in a molecular computational device. Our group has reported molecular switching properties of ruthenium(II) terpyridine metal complexes with pendant pyridine units which can exist in different protonation states, each displaying different photophysical characteristics. By observing the change in luminescence is it possible to construct logic gates [1]. The aim of this project is to synthesise heteroleptic ruthenium(II) complexes with a methyl ester substituted pyridyl-terpy ligand. This functionality allows one to further modify the complex with a long side chain containing a secondary or tertiary amine unit which will act as an additional proton acceptor site.



[1] S. Sisvi, E. C. Constable, C. E. Housecroft, J. E. Beves, E. L. Dunphy, M. Tomasulo, F. M. Raymo and A. Credi, *Chem. Eur. J.*, **2009**, *15*, 178.

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Inorganic and Coordination Chemistry **IC 42**

## The influence of divalent metal ions on the folding of large ribozymes characterized by single-molecule FRET

L. Cardo, D. Kowerko, S. L. König, L. Kopp and R. K. O. Sigel.

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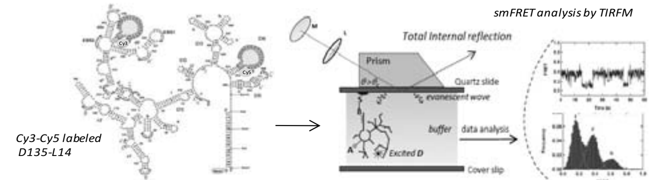
*S. Cerevisiae (Sc.)* ai5γ is a multi-domain RNA (~900 nts) belonging to the class of group II intron ribozymes, whose folding and splicing activities are influenced by metal ions. We designed a derivative of this large ribozyme, named D135-L14, which is labeled with the Cy3-Cy5 fluorophores pair and preserves the dynamics and the catalytic activity of the parent ribozyme [1]. FRET of the labeled RNA has been investigated both in bulk experiments and at the single molecule (sm) level by TIRF microscopy. Particularly, smFRET time trajectories revealed a new paradigm folding for this construct, characterised by three FRET states whose distribution depends on the type and concentration of metal ions in the system [1,2]. In order to assign each FRET state to a specific intermediate in the folding process, different mutated D135-L14 have now been made and analysed by smFRET.



Financial support by the European Research Council (ERC Starting grant to RKOS) and the University of Zurich is gratefully acknowledged.

[1] Steiner M., Karunatilaka K. S., Sigel R. K. O., Rueda D. *Proc Natl Acad Sci USA.* **2008**, *105*, 13853.
[2] Steiner M. Rueda D., Sigel R. K. O. *Angew Chem Int Ed Engl.* **2009**, *48*, 9739.

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Inorganic and Coordination Chemistry **IC 44**

## Luminescent Carbene Platinum(II) Arylacetylide Complexes

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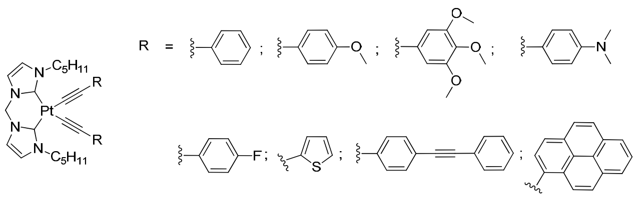
Platinum σ-acetylide complexes bearing phosphine or diimine ancillary ligands which display room temperature phosphorescence have been well investigated for their application in phosphorescence organic light-emitting devices (PhOLED).[1-3] To achieve high efficient blue phosphorescent emitters, *N*-heterocyclic carbene (NHC) was used and a series of *cis* bis-NHC Pt(II) bis-arylacetylide complexes were synthesized.



Structural and photophysical properties were well investigated and few of them indeed display blue phoshphorescence emission. These results open up new avenues in the design and development of triplet blue-emitters, which is being further exlpored in our group.

[1] Hissler, M.; Connick, W. B.; Geiger, D. K.; McGarrah, J. E.; Lipa, D.; Lachicotte, R. J.; Eisenberg, R. *Inorg. Chem.* **2000**, *39*, 447–457.
[2] Chan, C. W.; Cheng, L. K.; Che, C. M. *Coord. Chem. Rev.* **1994**, *132*, 87–97.
[3] Yam, V. W. W.; Lo, K. K. W.; Wong, K. M. C. *J. Organomet. Chem.* **1999**, *578*, 3–30.

Inorganic and Coordination Chemistry **IC 45**

## Copper(I) Complexes for Dye Sensitised Solar Cells and Light Emitting Electrochemical Cells

Alexandra Senger, Edwin C. Constable, Catherine E. Housecroft

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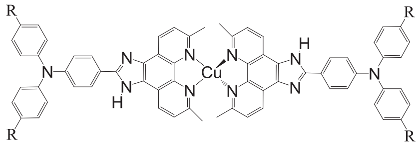
We are developing new types of DSSCs (dye sensitised solar cells) using phenanthroline-based Cu(I) complexes containing electron-withdrawing (EWG) and electron-donating (EDG)-groups as sensitisers:



R = OMe, Br, $NO_2$

In earlier work, Constable *et al* [1] have shown that the structure of the organic ligands in the copper(I) complexes can greatly affect the efficiency of the solar cells. Since the synthesis of phenanthroline ligands proceeds in several reaction steps, and the yields are relatively low, it is of great importance to optimize the syntheses. Furthermore, there is a possible application of our Cu(I) complexes for light emitting electrochemical cells (LEECs) [2], which are currently in competition with OLEDs for optmization of their colour and increased efficiency of the emitted light.

[1] T. Bessho, E. C. Constable, M. Graetzel, A. Hernandez Redondo, C. E. Housecroft, W. Kylberg, Md. K. Nazeeruddin, M. Neuburger and S. Schaffner, *Chem. Commun,* **2008**, 3717.

[2] H. J. Bolink, E. Coronado, R. D. Costa, E. Ortı´, M. Sessolo, S. Gaber, K. Doyle, M. Neuburger, C. E. Housecroft and E. C. Constable, *Adv.Mater.* **2008***, 20,* 3910.

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Inorganic and Coordination Chemistry **IC 46**

## Sawhorse-Type Diruthenium Tetracarbonyl Tweezers

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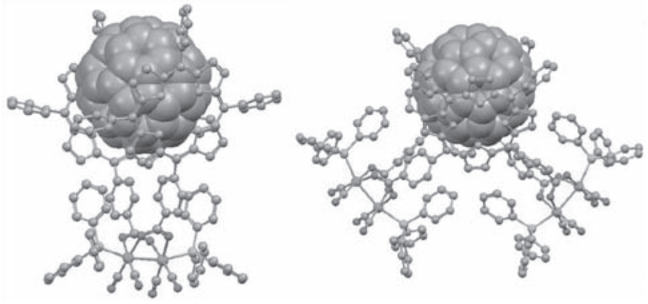
[b] Consiglio Nazionale delle Ricerche, Via Gobetti 101, Bologna, Italia.

Molecular tweezers built from inorganic units and porphyrin derivatives have recently been of central interest.[1] Encapsulation of fullerene in different host molecules has also been investigated by several research groups.[2]



Encapsulation of fullerene molecule in the cavity of sawhorse-type diruthenium complexes built from porphyrin carboxyphenyl panels will be the focus of this poster. In particular, the guest binding properties of these new molecular tweezers using different spectroscopic methods will be discussed.

[1] D. Sun, F. S. Tham, C.A. Reed, L. Chaker, M. Burgess, P. D. W. Boyd, *J. Am. Chem. Soc.* **2000**, *122*, 10704.
[2] K. Tashiro, T. Aida, *Chem. Soc. Rev.* **2007***, 36,* 189.

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Inorganic and Coordination Chemistry **IC 47**

## NMR structural investigation of the κ–ζ region of the group II intron ribozyme *Sc*.ai5γ

Daniela Donghi, Maria Pechlaner, Roland K.O. Sigel

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Group II introns are large self-splicing RNAs that need monovalent and divalent metal ions for folding and activity [1]. They perform the splicing reaction in a way similar to the eukaryotic spliceosome [2].
These ribozymes show a conserved set of six domains, each playing a role in folding and catalysis. The so called κ–ζ region of domain 1 (D1), together with domain 5, represents the minimal required structure for activity. Despite the biological importance of these RNAs, only little structural information on their tertiary architecture is known so far [3].
We are investigating by NMR the 3D structure of the κ–ζ region of D1 of *Sc*.ai5γ group II intron from yeast mitochondria. This RNA contains structural features associated with high mobility. The presence of $Mg^{2+}$ proved to be essential to partially overcome the mobility. NMR experiments run in different experimental conditions and at different magnetic fields allowed the attributions of most of the $^{1}H$, $^{13}C$ and $^{15}N$ NMR resonances. The NMR structure of the κ–ζ region and its $Mg^{2+}$ binding properties will be presented.

Financial support by a Marie Curie Intra European Fellowship (RNABIC, 236794 to DD) and in the form of access to the Bio-NMR Research Infrastructure (FP7/2007-2013, grant agreement 261863) within the 7th European Community Framework Programme as well as by the Swiss National Science Foundation (200021-124834 to RKOS) is gratefully acknowledged.

[1] R.K.O. Sigel, *Eur. J. Inorg. Chem.* **2005**, 2281.
[2] N. Toor, K.S. Keating, A.M. Pyle, *Curr. Opin. Struc. Biol.* **2009**, *19*, 260.
[3] See for example M.C. Erat, O. Zerbe, T. Fox, R.K.O. Sigel, *ChemBio Chem* **2007**, *8*, 306; N. Toor, K.S. Keating, S.D. Taylor, A.M. Pyle, *Science* **2008**, *320*, 77.

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Inorganic and Coordination Chemistry **IC 48**

## Novel synthetic routes toward Bis(acyl)phosphane Oxides (BAPO's)

Hansjörg Grützmacher, Georgina Müller

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

Bis(acyl)phosphane oxides are the most important species in the class of acylphosphane oxide radical-type photo-initiators. BAPO's exhibit good chemical and thermal stability in addition to excellent initiation efficiency and very fast *Norrish type I* photolysis.[1,2]
BAPO's have hitherto been prepared by means of nucleophilic substitution reactions of $NaP(COMes)_2$ (**1**) with alkyl halides. Herein, we present novel synthetic routes toward bis(acyl)phosphane oxides without the need to employ environmentally unfriendly, halogenated starting materials. A synthetic approach has been developed based on a Michael-type addition reaction of $NaP(COMes)_2$ to itaconic anhydride (**Fig. 1**). Furthermore, the addition product of **1** to N,N-dimethylmethyleneimmonium chloride was readily obtained in a Mannich-type reaction. Treatment of the phosphanes under different oxidative conditions, yield the corresponding BAPO's.

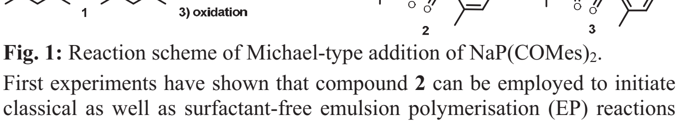

**Fig. 1:** Reaction scheme of Michael-type addition of $NaP(COMes)_2$.

First experiments have shown that compound **2** can be employed to initiate classical as well as surfactant-free emulsion polymerisation (EP) reactions of styrene to yield spherical nanoparticles of about 50 nm in size. Next steps to optimise the reaction conditions for surfactant-free EP and investigations concerning the functionalistion of the anhydride moiety in **3** are in progress.

[1] K. Dietliker, *A Compilation of Photoinitiators Commercially available for UV today*, SITA Technology Limited, Edinburgh, **2002**.
[2] G. Gescheidt et al., *Angew. Chem.* **2009**, *121*, 9523.

Inorganic and Coordination Chemistry **IC 49**

## Dative Boron-Nitrogen Bonds in Structural Supramolecular Chemistry: Multicomponent Assembly of Prismatic Organic Cages

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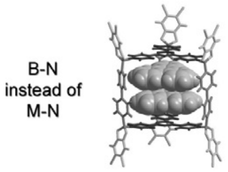

We have recently shown that dative B-N bonds between boronate esters and pyridyl ligands can be used to build macrocycles, rotaxanes, and 1- and 2-dimensional polymers. These results prompted us to explore the possibility to assemble cages via B-N interactions.

The multicomponent reaction of diboronic acids with a catechol and a tripyridyl linker results in the formation trigonal prismatic cages.[1] The cages feature six dative boron-nitrogen bonds as structure-directing elements. The size of the cages can be varied by changing the diboronic acid building block. The cages are able to encapsulate polyaromatic molecules such as triphenylene or coronene. The compounds are close structural analogues of coordination cages described by the group of Fujita.[2]

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Inorganic and Coordination Chemistry **IC 50**

## Dinuclear Arene Ruthenium Complexes Containing Thiolato Bridges

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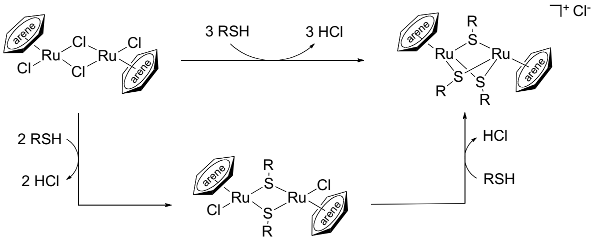
Cationic complexes of the type $[(\text{arene})_2\text{Ru}_2(\text{SR})_3]^+$, easily accessible as the chloride salts, have been found to be highly cytotoxic against human ovarian cancer cells (A2780 and A2780cisR), the $IC_{50}$ values being in the submicromolar range.[1] We now found a new family of thiolato-bridged dinuclear complexes, $(\text{arene})_2\text{Ru}_2(\text{SR})_2\text{Cl}_2$, which are intermediates in the high-yield synthesis of $[(\text{arene})_2\text{Ru}_2(\text{SR})_3]\text{Cl}$.



The isolation and characterization (including structural aspects) of these new complexes $(\text{arene})_2\text{Ru}_2(\text{SR})_2\text{Cl}_2$ and their properties with respect to their $[(\text{arene})_2\text{Ru}_2(\text{SR})_3]\text{Cl}$ counterparts as well as a simple synthetic strategy for the synthesis of mixed complexes of the type $[(\text{arene})_2\text{Ru}_2(\text{SR})_2(\text{SR}')]^+$ will be presented.

[1] M. Gras, B. Therrien, G. Süss-Fink, O. Zava, P. J. Dyson, *Dalton Trans.* **2010**, 10305.

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Inorganic and Coordination Chemistry **IC 51**

## Ferrocenyl-Tethered Ruthenium-Arene Complexes for Asymmetric Catalysis

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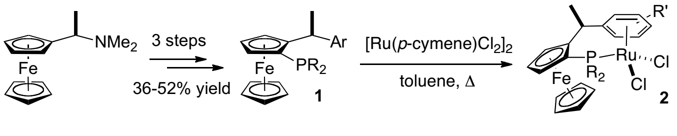
$\eta^6$-Arene ruthenium-based catalysts are widely used in catalytic transformations.[1] 'Piano-stool' complexes with chiral ligands are very well known for their efficiency in asymmetric catalysis.[2] It was shown that tethered systems exhibit improved longevity and higher turnover rates.[3] Aiming for bulky, chiral tethers which do not need additional stereogenic centers, ferrocenylphosphines **1** were synthesized in three steps starting from enantiomerically pure Ugi's amine in good yields. The ligands are highly modular and allow both electronical and sterical fine tuning. Corresponding ruthenium(II)-complexes **2** were obtained quantitatively *via* coordination to $[\text{Ru}(p\text{-cymene})\text{Cl}_2]_2$ and subsequent arene exchange.



Complexes **2** were applied in asymmetric transfer hydrogenation of ketones and Schiff's bases giving moderate to good enantioselectivities.

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Inorganic and Coordination Chemistry **IC 52**

## The Decay of Peroxynitrite:
## Buffer Influence and Kinetics Computation

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Peroxynitrite, $\text{ONOO}^-$ and its conjugated acid ONOOH, are formed in vivo by the diffusion-limited recombination of nitrogen monoxide and superoxide [1]. Because ONOOH is a strong oxidant, peroxynitrite is used in biochemistry to study the oxidation of biomolecules. Various buffers are used to control the pH of the test solutions and are tacitly assumed to be inert. Amine buffers, e.g. HEPES, are reported to influence the product formation during the decomposition of peroxynitrite [2].
We found that, at pH 6.8 and a constant ionic strength of 0.2 M, the decomposition of peroxynitrite is accelerated in Tris buffer and decelerated in phosphate buffer. We found that the simple first-order decomposition, on the basis of the isomerization of ONOOH only (reaction 1), fits the observed decay of $\text{ONOO}^-$ with a systematic error. The decay of peroxynitrite additionally requires inclusion of reactions 2 and 3 [3].

$$\text{ONOOH} \rightarrow \text{HNO}_3 \qquad k_1 = 1.27\ \text{s}^{-1} \tag{1}$$
$$\text{ONOOH} + \text{ONOO}^- \rightarrow \text{HNO}_2 + \text{O}_2\text{NOO}^- \qquad k_2 = 1.93\cdot10^3\ \text{M}^{-1}\text{s}^{-1} \tag{2}$$
$$\text{O}_2\text{NOO}^- \rightarrow \text{NO}_2^- + \text{O}_2 \qquad k_3 = 0.52\ \text{s}^{-1} \tag{3}$$

The values of the rate constants $k_{1-3}$ describe the decay in phosphate buffer.

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[2] M. Kirsch, E. E. Lomonosova, H.-G. Korth, R. Sustmann, H. de Groot, *J. Biol. Chem.* **1998**, *273* (21), 12716
[3] D. Gupta, B. Harish, R. Kissner, W. H. Koppenol, *Dalton Transactions* **2009**, (29), 5730

Inorganic and Coordination Chemistry **IC 53**

## Intermediates in Iridium-Catalysed Imine Hydroogenation

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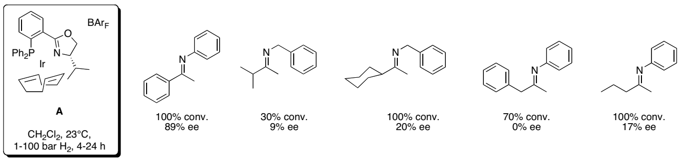
Hydrogenation of acetophenone-, benzophenone or other heteroaromatic-based imines with iridium complexes of bidentate P,N-Ligands like **A** has shown to provide very high enantioselectivities along with full conversion to the corresponding amines. Imines derived from *bis*-alkylketones however still remain challenging substrates with such catalysts as often poor conversion and low enantioselectivites are observed (Picture 1).[1,2,3]



**Picture 1:** asymmetric hydrogenation of aryl/alkylketone-derived imines[1]

In a recent investigation towards a better understanding of the mechanism of imine hydrogenation we identified new structures that were formed under reactions conditions. These new structures bear a cyclometalated imine. The complexes were investigated by *X-Ray* crystallography and *NMR* spectroscopic methods as well as by deuterium labelling, *ESI-MS* and *ReactIR* experiments. They exhibited higher enantioselectivities and reactivities for *bis*-alkyl based imines compared to **A** (Picture 1).

[1] P. Schnider, G. Koch, R. Prétôt, A. Pfaltz, *Chem. Eur. J.* **1997**, *3*, 887
[2] A. Baeza, A. Pfaltz, *Chem. Eur. J.* **2010**, *16*, 4003
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Inorganic and Coordination Chemistry **IC 55**

## Selective Hydrogenation of Furfuryl Alcohol by Hectorite-Supported Ruthenium Nanoparticles

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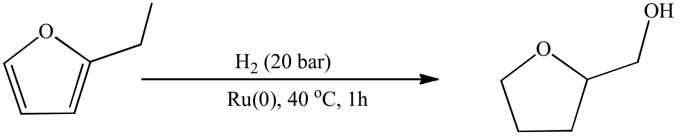
The hydrogenation of furfuryl alcohol (FA) to give tetrahydrofurfuryl alcohol (THFA) is of great importance. This green solvent has an octane number of 83 and it is also being investigated for use as an additive in "clean" fuels, allowing diesel and ethanol to be mixed [1-2]. Furfural, THFA's parent compound, is derived from renewable sources. These favorable properties make THFA a preferred choice for fine chemical synthesis and agricultural, cleaning, coating and pain stripper formulations [3].



We report ruthenium nanoparticles (~4 nm) intercalated in hectorite to be a highly efficient (conversion 100%, turnover frequency 177 h$^{-1}$) and highly selective (selectivity > 99%) reusable catalyst for the hydrogenation of FA to give THFA under mild conditions (methanol solution, 40 °C, 20 bar H$_2$). After a total turnover number of 1423, the hectorite-supported ruthenium nanoparticles are deactivated but can be recycled and regenerated.

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[2] A. Hull, I. Golubkov, *US Pat. 7323020*, **2008**.
[3] UCSAREP review on FA, *USDA National Organic Program*, **2003**.

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Inorganic and Coordination Chemistry **IC 54**

## Neutral Monocyclometalated Au(III) Diaryl Complexes: Syntheses and Photophysics.

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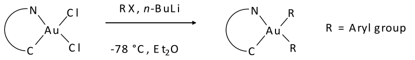
Late transition-metal based phosphorescent OLEDs (PhOLEDs) are much sought owing to the phenomenon of 'triplet-harvesting' which involves effective utilization of both singlet and triplet excitons in a radiative photophysical process [1]. Although, cyclometalated Pt(II) complexes are deeply investigated in this regard, the luminescence properties of isoelectronic Au(III) complexes are less understood and underexplored. In this work, we have shown that, for a class of non-emissive mono-cyclometalated Au(III) dihalides of the type [*cis*-(C^N)AuCl$_2$][C^N = cyclometalating ligand], substitution of the halides with better σ-donating aryl groups leads to stable RT emissive complexes. Further, judicious choice of the cyclometalate and the ancillary ligands leads to emission tunability. Experimental observation and TD-DFT calculations qualitatively suggest the origin of emission to be predominantly of intra-ligand (IL) character with limited participation of the metal [2].



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Inorganic and Coordination Chemistry **IC 56**

## Structural studies on splice site formation during group II intron retrohoming

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Group II introns are large catalytic RNAs that catalyze their own excision from RNA transcripts in the presence of Mg(II). They are also able to reinsert into RNA or DNA [1,2], which is called retrohoming if the recipient molecule is DNA. This enables them to migrate and propagate within the host genome as selfish genetic elements.

Of the six domains of group II introns, domain 1 is the largest and contains the two binding sites, EBS1 and EBS2, for the 5' exon. The correct contact formation between EBS1 and EBS2 with the complementary exonic interaction sequences IBS1 and IBS2 is crucial for initiating the splicing reaction. EBS1 is located in the bulge of a hairpin structure. Its interaction with IBS1 RNA has been well characterized spectroscopically [3,4].

To gain insight into the splice site formation in retrohoming events, we now investigate the structural features of the EBS1-dIBS1 interaction, where dIBS1 is DNA. For this purpose, the solution structure of and metal ion binding to the EBS1-dIBS1 complex is studied by NMR spectroscopy.

*Financial support by the Swiss National Science Foundation and through an ERC Starting Grant 2010 (to R. K. O. Sigel) is gratefully acknowledged.*

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[2] S. Zimmerly, H. Guo, R. Eskes, J. Yang, P. S. Perlman, A. M. Lambowitz, *Cell*, **1995**, *83*, 529-538.
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[4] D. Kruschel, PhD thesis, University of Zurich, **2008**

Inorganic and Coordination Chemistry **IC 57**

### The Effect of the Positively Charged Phosphine Ligands on the Ru Catalysed Hydrogen Production from Formic Acid

Yanouk Cudré, Weijia Gan, Dennis J.M. Snelders, Gábor Laurenczy

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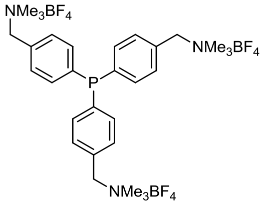
The use of carbon dioxide - formic acid cycle for hydrogen storage and delivery is advantageous for environmental reasons [1]. The formic acid decarboxylation reaction should be selective, to produce only $CO_2$ and $H_2$ (no CO). The hydrogen production should take place under mild conditions, and in aqueous solution; since water obviously preferred to the organic solvents, as reaction medium.
Efficient catalysts have already been developed for this reaction [2], using highly negatively charged hydrophilic sulfonated phosphine ligands with Ru(II).

In this contribution we will present our new results, the application of the tricationic phoshine ligand ([3], see figure), studying the electronic effect of the ligand on the catalytic decarboxylation reaction.



Acknowledgements. Swiss National Science Foundation (FNS) and EPFL are thanked for financial support.

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Inorganic and Coordination Chemistry **IC 58**

### Sustainable Copper Based Materials for OLED Like Devices

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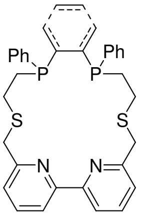
The majority of usable light emitting devices (organic light emitting diodes or light-emitting electrochemical cells) are based upon transition metal or lanthanide emitters or sensitizers [1]. Commonly, second and third row transition metal complexes are used, which have the advantages of efficiency but a disadvantage in terms of cost and abundance of the raw materials.

Recently, *NN-PP* type heteroleptic mononuclear Cu(I) complexes showed promising results as a sustainable alternative to the traditionally adopted compounds of iridium, ruthenium, platinum and rhodium whihc are found in state-of-the-art devices [2]. Our primary objective is to develop the strategies for interconnected *NN-PP* type heteroleptic mononuclear Cu(I) complexes for optimization of light emitting device properties.



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Inorganic and Coordination Chemistry **IC 59**

### Investigations on the Interaction between the *btuB* Riboswitch and Fluorescent $B_{12}$ Derivatives

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Certain natural occurring RNA sequences serve as genetic control elements via specific binding to a variety of metabolites and a subsequent structural change [1]. These so called riboswitches are located in the 5'-untranslated region of bacterial messenger RNAs. The *btuB* riboswitch of *E. coli* binds to coenzyme $B_{12}$ and its derivatives with high selectivity [2, 3]. To investigate the structural changes, we use FRET (Förster Resonance Energy Transfer) by labeling cobalamin and the RNA with one fluorophore each (donor/acceptor). Upon $B_{12}$-*btuB* binding energy transfer between the two fluorophores will occur. We are testing different dye pairs to reach a good quenching efficiency focusing on Cy3 and Cy5 as well as non-fluorescent quenchers BHQ-2 and BHQ-3. By varying the fluorophore position on the RNA, a detailed picture of the folding behavior due to $B_{12}$-binding and on $B_{12}$-binding itself is obtained.

Financial support by the European Research Council (ERC Starting Grant 2010) and the University of Zürich is gratefully acknowledged.

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[3] S. Gallo, M. Oberhuber, R.K.O. Sigel, B. Kräutler, *ChemBioChem* **2008**, *9*, 1408.

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Inorganic and Coordination Chemistry **IC 60**

### Molybdenum and Tungsten Nitrosyl Complexes Bearing Phosphine Ligands and their Catalytic Activity in Homogeneous Hydrogenation of Imines

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Homogeneous hydrogenations of polar C=O and C=N functional groups attract increasing interest in both industry and academia. Most of the transition metal based catalysts enabling reduction of these types of functional groups are based on noble metals like Ru, Rh, Ir.[1] Therefore, in recent years an extensive search for non-precious, low-toxicity metals, such as Mo and W has been initiated. Bullock and co-workers have reported Mo and W complexes that showed catalytic activity in the hydrogenation of ketones,[2] but the TOF values achieved were quite low. Recently our group has developed[3] complexes of the type $Mo(NO)(P^\wedge P)(CO)_2H$ ($P^\wedge P$ = bidentate ligand) which showed hydrogenation activities in the presence of acids towards imines up to TOFs of $121\ h^{-1}$
Our approach to molybdenum and tungsten nitrosyl catalysts has been developed further using tridentate phosphine ligands. The investigations of their hydrogenation catalyses of simple imines, ketones will be reported.

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[2] (a) M. R. Bullock, H. Voges Mark, *J. Am. Chem. Soc.* **2000**, *122*, 12594. (b) F. Wu, V. K. Dioumaev, D. J. Szalda, J. Hanson, R. M. Bullock, *Organometallics* **2007**, *26*, 5079.
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Inorganic and Coordination Chemistry **IC 61**

## $Mg^{2+}$ dependent folding of the *btuB* riboswitch

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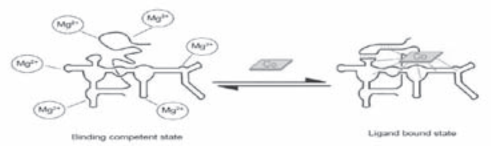
Riboswitches are small conserved sequences in the 5'-untranslated region of bacterial mRNA that follows a structural change upon binding to certain metabolites and thereby altering the gene expression [1]. The 202 nt long *btuB* riboswitch of *E. coli* undergoes a structural rearrangement on interaction with coenzyme $B_{12}$ and some of its derivatives [2]. Although being one of the earliest reported riboswitches, the folding of the *btuB* riboswitch and its interaction with coenzyme $B_{12}$ is not well understood.



The structure of riboswitch's unliganded state is vital to its ability to bind ligand productively. Here, we report the requirement of $Mg^{2+}$ for the formation of a competent unliganded state of the *btuB* riboswitch giving insights into different domains of the riboswitch involved in the structural change. Moreover, the $Mg^{2+}$ binding sites could be mapped on the structure of the *btuB* riboswitch with the help of $Tb^{3+}$.

Financial support by the Swiss National Science Foundation and the European Research council (ERC starting grant) is gratefully acknowledged.

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[2] S. Gallo, M. Oberhuber, R. K. O. Sigel, B. Kräutler, *ChemBioChem.* **2008**, *9*, 1408.

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Inorganic and Coordination Chemistry **IC 62**

## The cyclic analog of the wheat metallothionein γ-$E_c$-1 domain

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The seed-specific metallothionein (MT) $E_c$-1 from common bread wheat is considered to function as a $Zn^{II}$ reservoir for the germination process. It has been shown to contain two metal binding domains, i.e. γ- and $\beta_E$-$E_c$-1, coordinating two and four $Zn^{II}$ ions, respectively. The two metal ions in γ-$E_c$-1 are arranged in a $Zn_2Cys_6$ cluster.

Circular proteins have several advantages compared to their linear analogs, e.g. conformational and entropic stabilization, enhanced resistance to chemical and heat denaturation, and *in vivo* stabilization against proteolytic cleavage (2). Cyclization of MTs is expected to reduce conformational flexibility and might influence the metal binding properties and specificities as well as help to facilitate crystallization. Additionally, γ-$E_c$-1 shows surprising similarities to the cyclotides, the largest group of naturally occurring cyclic peptides, which make comparative studies very interesting. Cyclotides are also rich in Cys residues and contain potential metal-binding sites (3).

The cyclic analog of γ-$E_c$-1 was prepared *in vitro* from a precursor protein obtained with a modified pTWIN2 vector in *E. coli* and identified by mass spectrometry.

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Financial support from the Swiss National Science Foundation is gratefully acknowledged (SNSF-Professorship PP002-119106/1 to EF).

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Inorganic and Coordination Chemistry **IC 63**

## Lead bromide and iodide in ionic liquids

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Lead halides, especially lead bromide and iodide are important materials with interesting optical and electrical properties and they have been frequently used as components in fabrication of acousto-optic and opto-electronic devices, such as light sensitizers for photovoltaic cells.[1] However, due to the low solubility in common solvents and the high melting point of the pure lead halides, incorporation of these metal salts into practical devices are often difficult.

Ionic liquids are very polar with certain anions being highly coordinating and thus can break the coordination network of the lead halides.[2] Being conductive, ionic liquids are also ideal alternative to the pure inorganic salts such as KI, which are often used as component for conducting materials.

We have investigated the interactions of lead bromide and iodide in a series of imidazolium-based ionic liquids. In ionic liquids with bulky anions such as $BF_4$, $BF_6$ and $Tf_2N$, the solubility of lead bromide and iodide are very limited. However, in ionic liquids with bromide and iodide anions, lead bromide and iodide can form stable complexes with melting points significant decreased. Physical properties such as refractive index and conductivity of the obtained lead bromide and lead iodide-ionic liquids composite have been also investigated.

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Inorganic and Coordination Chemistry **IC 64**

## *fac*-$[TcO_3(tacn)]^+$; A Versatile Precursor for the Labeling of Pharmacophores, Amino Acids and Carbohydrates via cycloaddition strategies

Henrik Braband, John F. Valliant and Roger Alberto

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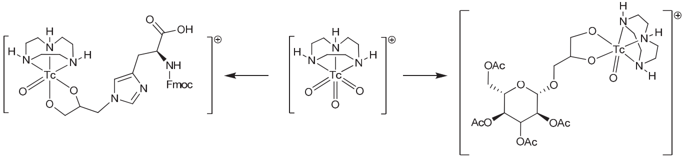
One of the most sensitive methods for non-invasive imaging is the detection of γ-radiation where technetium-99m ($^{99m}Tc$) plays a prominent role. The site specific conjugation of $^{99m}Tc$ to a targeting vector, in a manner in which the product retains the affinity of the parent, is challenging. To address this issue, one can take advantage of the rich coordination chemistry of technetium. In this context complexes containing the $Tc^{VII}$ core, *fac*-$\{TcO_3\}^+$, came into focus of recent research, because they react with alkenes undergonig metal-mediated [3+2] cycloaddition reactions.[1] This reactivity can be used as a creative route to preparing novel molecular imaging probes. We developed a synthesis for the water stable complex $[TcO_3(tacn)]^+$ that is suitable for clinical translation. Furthermore, to explore the potential and general utility of the [3+2] cycloaddition reactions as bioconjugation strategy, three classes of vectors were attached to the core. 4-Nitro-imidazole as a new hypoxia imaging agent, histidine to create a new non-natural amino acid that can be incorporated into peptides and radiolabeled and a simple glucose derivative, because of the interest in preparing $^{99m}Tc$ labelled carbohydrates. In addition to the synthetic work the first biodistribution studies of $[^{99m}TcO_3(tacn)]^+$ and the small [3+2] cycloadduct $[^{99m}TcO(NO_2\text{-}Imi)(tacn)]^+$ were completed, suggesting that theses complexes are stable *in vivo*.



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Inorganic and Coordination Chemistry **IC 65**

## Hydrogenation of carbon dioxide for hydrogen storage

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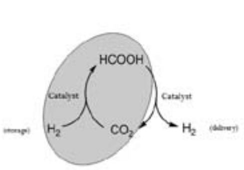
Renewable energy sources are of interest due to the environmental problems resulting from increasing $CO_2$ emission. A new and viable way for hydrogen storage was recently proposed based on the formic acid – carbon dioxide system.

Formic acid can be used as a hydrogen carrier via the selective decomposition of HCOOH into $CO_2$ and $H_2$[1]. To achieve a carbon dioxide neutral system, the $CO_2$ must be recycled via direct hydrogenation. As the delivery of $H_2$ is performed in aqueous - and acidic - solution it is important to find a catalyst for $CO_2$ reduction that is active under the same conditions. At the moment a large number of catalytic systems are known to be active under neutral or basic conditions, which require the presence of a buffer, an amine or a base.



Preliminary studies performed with a water soluble ruthenium complex, $[RuCl_2(PTA)_4]$,[2] have shown certain catalytic activity in the hydrogenation of $CO_2$ in aqueous solution in the absence of amines or other additives. The rate of $CO_2$ hydrogenation was found to be strongly dependent on the pH of the solution.

Acknowledgements: We thank EOS holding and EPFL for financial support.

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Inorganic and Coordination Chemistry **IC 66**

## Investigation into Stable Gold(III) Triplet Phosphors

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Triplet emitters based on late transition metals, especially of the third row, have been well investigated due to their applications in phosphorescent OLEDs (PhOLEDs).[1] In this regard, Pt(II) and Ir(III)-complexes are very well investigated.[2] In contrast, Au(III) complexes have been less explored in this regard mainly because of their instability. Au(III) complexes have in general low-energy d-d ligand field (LF) states, which are responsible for the quenching of the luminescent excited states at r.t. and the high electrophilic character of the Au(III)-center. We have recently reported cyclometalated Au(III) complexes bearing aryl and alkyne as ancillary ligands that are reasonably stable and display room temperature phosphorescence. However, the stability of such complexes is still rather low for applications in OLED devices due to reductive elimination observed in these complexes. In this current work, we have employed different strategies in order to avoid reductive elimination and achieve complexes that are thermally stable. This was accomplished by gaining synthetic access to monocyclometallated Au(III) monoaryl-complexes of the type $\{(N\text{^}C)AuR_1R_2; [N\text{^}C = \text{cyclometallated ligand}]; R_1 = \text{aryl}; R_2 = \text{heteroatom bearing substituents}\}$.

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Inorganic and Coordination Chemistry **IC 67**

## Impact of structural modifications of vitamin $B_{12}$ on its physico-chemical properties and the biological activity.

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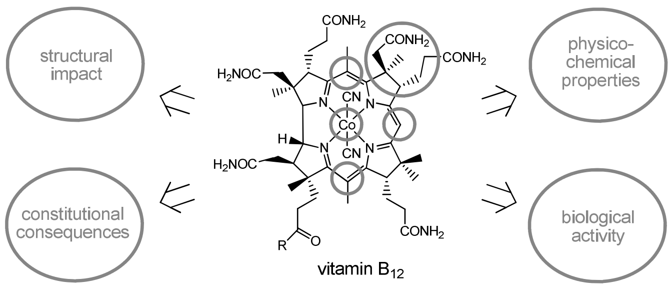
Cobalamins play an essential role in the metabolism of humans. Cellular uptake as well as the reactivity in $B_{12}$-dependent reactions are strongly related to the constitution and the electronic properties of the co-factor.[1] Our group investigates the impact of structural modifications of vitamin $B_{12}$ on its physico-chemical properties and the biological activity.[2,3]

Herein we present such a study with different vitamin $B_{12}$ derivatives having modifications at the π-system as well as the periphery of the corrin mojety.



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Inorganic and Coordination Chemistry **IC 68**

## Orthogonally protected artificial amino acid as a tripodal chelator in solid phases peptide synthesis

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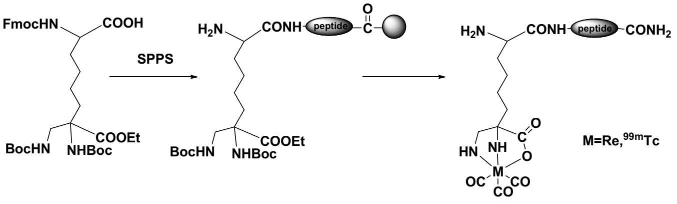
Bombesin (BBN), a 14-amino-acid peptide, shows high affinity for the human gastrin-releasing peptide receptor (GRP-r), which is overexpressed by a variety of tumors. Thus, radiolabeled BBN analogues are potential radioligands for diagnostic and therapeutic use in GRP-R-expressing tumors[1]. The aim of this study was to label analogues of BBN which comprise an artificial amino acid in the sequence with the $[^{99m}Tc(CO)_3]^+$ core. The amino acid is lysine-based and contains a strong and small tripodal chelator. Interference with the receptor binding part is small and high specificity for the GRPr in vivo should be maintained[2]. In this study, the artificial amino acid chelator was attached to the peptide as an additional amino acid using solid peptide phase synthesis (SPPS). Along this strategy, the artificial amino acid can be used for any peptide. The rhenium homologues were prepared by the reaction of $[ReBr_3(CO)_3]^{2-}$ and Lys-$N_2O$-BBN(7-14). Labeling with $^{99m}Tc$ was performed at 90°C for 30 min in PBS buffer. Even at very low peptide concentration, the radiochemical purity was > 95%. It should be emphasized that the $^{99m}Tc$ labelled peptide is hydrophilic which will support rapid excretion from non-targeted sites. Thus, this system represents a universal labelling strategy for biomolecules with a very small, hydrophilic and very potent ligand.



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Inorganic and Coordination Chemistry **IC 69**

## Ditopic ligand, a route to self-assembled cages.

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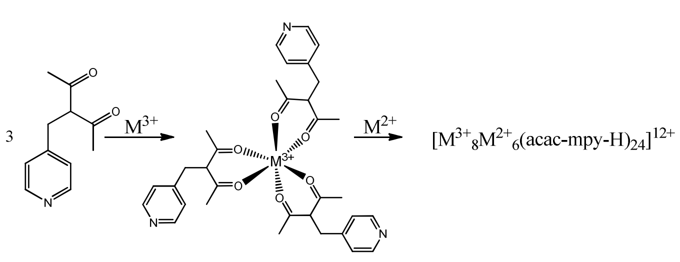
A three-fold and a four-fold axes cannot both lie in the same plane. If the two axes are approximately at 55° to each other, it may lead to a cubic symmetry. A ditopic ligand with two moieties presenting affinities for different metal ions is the way explored to mix three- and four-fold axes. A three-fold node can be obtained by binding three chelate ligands to an octahedral $M^{3+}$ ion. Acetylacetone (acac) is known to have a high affinity for hard metal centers. By attaching a methylpyridine (mpy) group to the acac unit, we obtain a second coordination site. The ligand acac-mpy was synthesized [1] and a first three-fold node [Al(acac-mpy-H)$_3$] (**1**) was obtained. Modelling studies show the pyridyl coordination vector to be oriented at 35° to the three-fold axis as required for a structure of cubic symmetry. The coordination chemistry of this ligand will be presented.



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Inorganic and Coordination Chemistry **IC 70**

## A distinct zinc and cadmium binding site in the mixed $\mathrm{M^{II}_2Cys_6}$ metal cluster of the γ-$\mathrm{E_c}$-1 metallothionein

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The ability of cells to distinguish the essential metal ion $\mathrm{Zn^{II}}$ form toxic $\mathrm{Cd^{II}}$ ions on a molecular level has puzzled researchers from many fields. A class of proteins, believed to be involved in this process, are the metallothioneins (MTs). These small (2-10 kDa), cysteine-rich (up to 33%) metalloproteins are found basically in all phyla of live. They are involved, among others, in the homeostasis of the essential metal ions $\mathrm{Zn^{II}}$ and $\mathrm{Cu^{I}}$ and the detoxification of e.g. $\mathrm{Cd^{II}}$.

The γ-domain of the $\mathrm{E_c}$-1 MT from bread wheat contains a $\mathrm{M^{II}_2Cys_6}$ cluster, and we recently determined the solution structures of the $\mathrm{Zn_2}$- as well as the $\mathrm{Cd_2}$γ-$\mathrm{E_c}$-1 form by NMR spectroscopy [1]. Upon exposure of $\mathrm{Cd^{II}}$ to the fully metallated $\mathrm{Zn_2}$γ-$\mathrm{E_c}$-1 form, we observed formation of a mixed $\mathrm{Zn^{II}/Cd^{II}}$ species, triggering the hypothesis of a certain metal ion specificity of the two metal binding sites. The finding was confirmed by a number of spectroscopic measurements, including UV-vis, CD, MCD as well as multi-nuclear, multi-dimensional NMR, providing information upon the selective character of the metal binding sites. In addition, presence of a ZnCdγ-$\mathrm{E_c}$-1 species was confirmed with ESI-MS.

Financial support from the Swiss National Science Foundation is gratefully acknowledged (SNSF-Professorship PP002-119106/1 to EF).

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Inorganic and Coordination Chemistry **IC 71**

## Template-free co-assembly of Au and $TiO_2$ nanoparticles into a 3D aerogel

Florian J. Heiligtag, Marta D. Rossell, Martin Süess, Markus Niederberger

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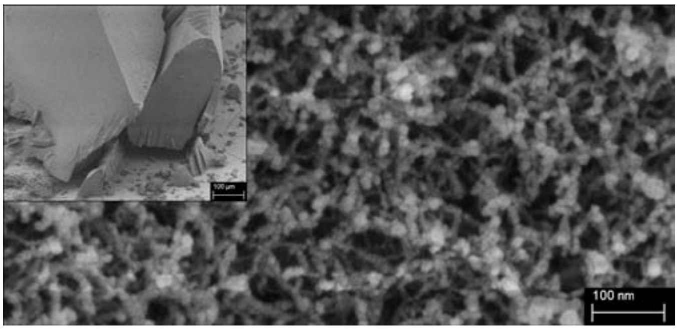
Oriented attachment gives a highly versatile tool for building nanoparticle (NP) superstructures. As presented before, trizma ($(HOCH_2)_3CNH_2$) functionalised anatase NPs assemble into pearl necklace structures after refluxing in aqueous dispersion [1]. In this work, it is shown that increasing the NP concentration leads to the formation of an anatase gel. By supercritical drying, the gel can keep its very fine pore structure and result in an anatase aerogel with a surface area up to 400 $m^2$/g. (figure)



By adding gold NPs to the anatase NP dispersion before the gelation process, the gold particles can be incorporated into the (aero-)gel. This gives new, fascinating possibilities for multicomponent aerogels.

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Inorganic and Coordination Chemistry **IC 72**

## Folding dynamics of the *btuB* riboswitch by fluorescence resonance energy transfer (FRET)

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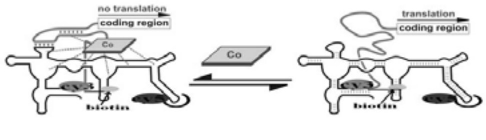
Riboswitches are complex folded RNA domains in the 5'-untranslated region of bacterial mRNA that serve as specific receptors for metabolites [1]. Binding of the metabolite changes the RNA structure and controls thereby gene expression. Conformational changes of the 202nt long *btuB* riboswitch of *E.coli* induced by coenzyme $B_{12}$ (AdoCbl) binding and some of its derivatives lead to an altered gene expression of the downstream *btuB* gene [2]. This interaction of the *btuB* riboswitch with AdoCbl to adopt a folded conformation still remains mostly unclear.

The interaction of the riboswitch with its ligand strongly depends on the initial tertiary structure of the RNA. To monitor the interdomain movements of the RNA, we attached a pair of fluorophores (Cy3 and Cy5) to the *btuB* riboswitch. FRET is then performed to study the folding of the riboswitch upon binding to AdoCbl and derivatives thereof.



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Inorganic and Coordination Chemistry **IC 73**

## Rhenium Based Metal-Ligand Bifunctional Catalysis

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Anorganisch-chemisches Institut, Universität Zürich, Winterthurerstrasse
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There is growing interest in developing new metal ligand bifunctional catalysts for hydrogenations and transfer hydrogenations. The catalytically active species of these catalyses are expected to contain an acidic, as well as a hydridic hydrogen atom, which can be transferred to double bonds of various preferably polar organic substrates. We prepared rhenium complexes isoelectronic to the well-known Shvo ruthenium system $\{[2,3,4,5\text{-}Ph_4(\eta^5\text{-}C_4CO)]_2H\}Ru_2(CO)_4(\mu\text{-}H)$[1] by replacing the RuCO unit with a ReNO fragment. Such complexes of the type $Re(NO)(L)(H)(C_5H_4OH)$ L=P*i*Pr$_3$, PCy$_3$[2] possess reasonable catalytic activity in transfer hydrogenations of aromatic and aliphatic ketones as well as imines applying 2-propanol as a hydrogen donor. For ketones TOF values up to 380 TON/h and for arylimines TOF values up to 60 TON/h were achieved.

Scheme 1. Catalytic cycle of the transfer hydrogenation of acetophenone using rhenium bifunctional complexes.

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Inorganic and Coordination Chemistry **IC 74**

## Synthetic challenges of bis-tridentate ligands incorporating terminal S-Et-S groups to capture Ag$^I$ ions

Nicholas Tart, Emmanuel Terazzi, Daniel Emery, Jiri Mareda, Laure Guénée, Claude Piguet

University of Geneva, Quai E.-Ansermet 30, 1211 Geneva 4, Switzerland

Practical applications of self-assembled lanthanide complexes require the materials to be semi-organised and responsive to external stimuli. This in turn requires well-defined phase boundaries in solution. With this in mind, it has recently been shown that the addition of long thioalkyl chains on the extremities of triple-helicate lanthanide complexes can be achieved.[1] However the thioalkyl chains reduced the solubility of the lanthanide complexes to an unacceptable degree due to the formation of oligo- and polymeric mixtures.

The subsequent addition of Ag$^I$ encouraged the self-organisation of discrete triple-helicates as a result of the soft d$^{10}$ metal interacting with the thiol groups while showing no preference for the tridentate binding site intended for the lanthanide.

Subsequent molecular dynamics studies have shown that the presence of an extra sulphur atom in the alkyl chains may lead to improved interactions between the silver ions and the ligand. With the challenge thus set, thiol-click chemistry has been used to synthesise the modified ligand.

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Inorganic and Coordination Chemistry **IC 75**

## Rhenium Complex Catalyzed Homogeneous Hydrogenations

Balz Dudle, Kunjanpillai Rajesh, Olivier Blacque and H Berke

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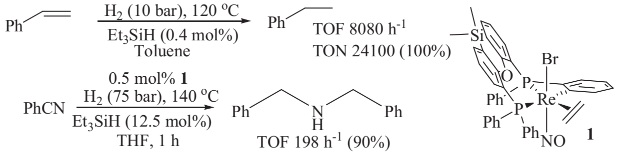
Highly active and selective catalysts are available to hydrogenate various unsaturated substrates and make it a method of choice for environmentally benign and enantioselective reductions.[1] The element rhenium being border to precious metals may have preserved at least some of the precious metal's character, like for instance the preference for interaction with $H_2$ and olefins.[2] These chemical properties made us believe that appropriate rhenium complexes could be also efficient hydrogenation catalysts. We therefore targeted the development of new rhenium nitrosyl complexes on the basis of their isoelectronic relationship to ruthenium carbonyl or phosphine rhodium halide fragments, which comprise essential building blocks of effective hydrogenation catalysts.[3]



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Inorganic and Coordination Chemistry **IC 76**

## Functionalized Triazacyclononane Derivatives as Potential Multimeric Ligands for the *fac*-$\{TcO_3\}^+$ -core

Sebastian Imstepf, Michael Benz, Henrik Braband and Roger Alberto

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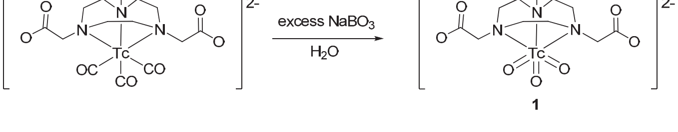
Recently our group has demonstrated the use of 1,4,7-triazacyclononane (tacn) and its derivatives, tacn-R (R= bz, bz-COOH), to stabilize the *fac*-$\{^{99(m)}TcO_3\}^+$-core, even in water [1]. To further extend this array and to develop this chemistry further for radiopharmaceutical applications, derivatives that offer the possibility for conjugation to biomolecules via amide bond formation were scrutinized. Hence, 1,4,7-triazacyclononane-*N,N',N''*-triacetic acid (NOTA) and *N*-benzyl-2-(1,4,7-triazonan-1-yl)acetamide (tacn-BA) were selected as viable candidates for our evaluation. NOTA, with three pendent acid functionalities, is a potential multimeric ligand, which can bind up to three moieties (e.g small peptides) to target a receptor. Thus this ligand could help to develop target specific radiopharmaceuticals with higher receptor binding constants. Tacn-BA on the other hand is a model for a monomeric ligand bearing a biomolecule conjugated via an amide bond.

We report a comparative study of the coordination properties of these two tacn derivatives and their ability to stabilize the *fac*-$\{TcO_3\}^+$-core. Therefore a synthesis for $[^{99}TcO_3(NOTA)]^{2-}$ (**1**), the first negatively charged complex containing the *fac*-$\{^{99}TcO_3\}$ moiety and $[^{99}TcO_3(tacn\text{-}BA)]^+$ (**2**) had to be developed.



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Inorganic and Coordination Chemistry **IC 77**

### Methylated cyanobiphenyls terminated mesogenic complexes: rationalization of interface perturbation in lanthanidomesogens

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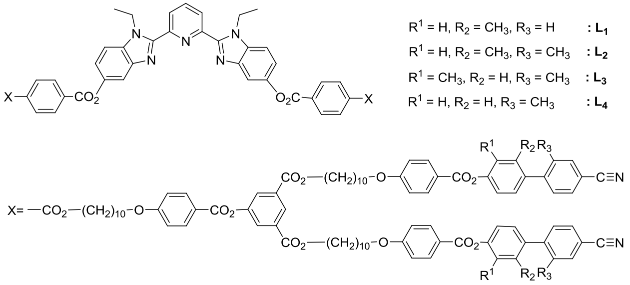
Since lateral intermolecular cohesion is strongly affected by simple methyl substitution in $[Ln(\mathbf{L}_k)(NO_3)_3]$,[1] we developed four different ligands, in which both the location and the number of additional methyl groups were systematically varied. Three lanthanides (La, Eu, Lu) were selected for preparing the associated nitrato complexes $[Ln(\mathbf{L}_k)(NO_3)_3]$. As these complexes undergo dimerization processes in solution, the corresponding thermodynamic parameters will be used for tentatively rationalizing the liquid-crystals properties variations.



The poster will present the synthesis together with the structural, thermodynamic and mesogenic properties of those new ligands and complexes.

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Inorganic and Coordination Chemistry **IC 78**

### Precursors for mixed metal oxides

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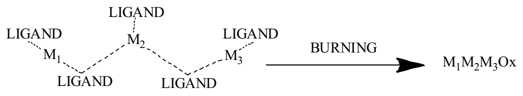
Mixed metal oxides are very important ingredients for material science. In this particular case they are considered for their superconductive properties (for example $YBa_2Cu_3O_7$).

One of the main problems in today's oxide technologies is linked to their formation. Very energetically demanding ways are used [1] and it is difficult to control the ratio of the different metals. Milder ways exist, like chemical vapor deposition techniques, which use single source precursors, but some of them have problems: sensitivity to air, decomposition to undesired side-products and difficulty to scale them up for use in industrial production.

Today a bimetallic oxide is already obtainable with this technique [2].The final idea is to have a trimetallic complex, which will be burned at a lower temperature (no more than 600 °C) and that would give a trimetallic oxide with a well defined ratio. The importance of obtaining a trimetallic oxide will be of interest for superconductors in the first place and for other materials that use mixed metal oxides in the second place.



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Inorganic and Coordination Chemistry **IC 79**

### Preparation of discrete buildings with new bis(bipyridine) ligands

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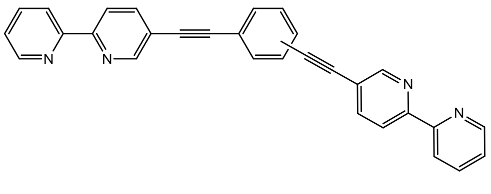
The design of new discrete objects requires the consideration of different elements of symmetry inherent in the clusters considered. For example, the use of bis(bidentate) ligands with an $C_2$ axis, can lead, in the presence of pseudo-octahedral metal centers ($Fe^{2+}$, $Zn^{2+}$...) inducing an $C_3$ axis, to obtain an $M_2L_3$ triple helicate ($D_3$ symmetry) or an $M_4L_6$ tetrahedron ($T$ symmetry). The orientation of these two forms depends mainly on the angle between the $C_2$ and $C_3$ axis (90° and 54.7° respectively for triple helicates and tetrahedron clusters).[1] We are therefore interested in the preparation of new bis(bipyridine) ligands in which the two chelating units are interconnected by a benzene ring. The purpose of this work concerns the effect of the relative position of the aromatic ring in these chelating groups on the geometry of the final cluster.



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Inorganic and Coordination Chemistry **IC 80**

### New ways of $LiCoO_2$ preparation

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Lithium cobalt oxide is currently the most common compound used for lithium ion batteries. Its synthesis requires long and high energy demanding heat treatments.[1]

$$Li_2CO_3 + Co_3O_4 \xrightarrow{600°C,\ O_2\ \text{for 24h}} \text{LT-}LiCoO_2 \xrightarrow{800\text{-}900°C,\ O_2\ \text{for 12h}} \text{HT-}LiCoO_2$$

New ways of preparation of lithium cobalt oxide have been investigated in order to decrease the time and the energy required. These new ways are based on the use of O-donors ligands such as aryloxide and alkoxide for the formation of pre-organized complexes as precursors for high temperature lithium cobaltate.

$$CoCl_2 + \text{Li-Aryloxide or Alkoxide} \xrightarrow[\text{In solution}]{\text{Complexation}} \text{Complex of LiCo} \xrightarrow[\text{In air at 450°C}]{\text{Combustion}} \text{HT-}LiCoO_2$$

Different precursors have been successfully synthesized.[2] The temperature of the heat treatment has been lowered by half, and the time of preparation has been reduced to about half a day. The size of the particles has been tuned to the nanoscopic scale increasing the discharge capacity and the rate capability.[3]

[1] S.-H. Yang, L. Croguennec, C. Delmas, E. C. Nelson and M. A. O'Keefe, *Nat. Mater.* **2003**, *2*, 464-467.
[2] A. Crochet, J.-P. Brog, K. M. Fromm, manuscript in preparation
[3] N.N. Sinha, N. Munichandraiah, *J. Indian. Inst. Sci.,* **2009,** 89, 381-392.

Inorganic and Coordination Chemistry **IC 81**

## Synthesis of New Silver Compounds with Nicotinic acid Derivatives

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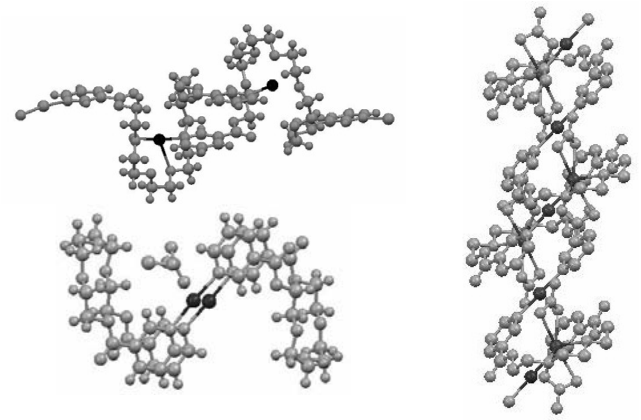
Complexes with silver ions have a great potential for applications in medical uses. Those complexes with ligands derived from nicotinic acid and with polyethylene oxide groups as spacer are synthesized. Upon coordination to silver ions, polymorphism can be observed: symmetric or asymmetric metallacycles, single or double helix and, under special conditions, linear chain structures are obtained.



[1] Adeline Y. Robin, Jorge L. Sagué and Katharina M. Fromm, *CrytEngComm,* **2006**, *8*, 403-416

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Inorganic and Coordination Chemistry **IC 82**

## Fast and High Yelding Post-Synthetic Modification of Metal-Organic Frameworks by Vapor Diffusion

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Metal-organic frameworks (MOFs) have recently emerged as a novel class of crystalline porous polymers with unique properties.[1] MOFs feature high chemical versatility that allows them to undergo post-synthetic modification (PSM) with organic molecules. We present here vapor-phase PSM (VP-PSM) of amino-functionalized MOFs such as IRMOF-3, $NH_2$-MIXMOF-5, and $NH_2$-UiO-66 with anhydrides and aldehydes under static vacuum without solvent to favor the diffusion of the reagents in the vapor phase within the pores. Acetic anhydride smoothly reacted at 100 °C overnight with all $NH_2$-functionalized MOFs to quantitatively give the corresponding amides. Aldehydes reacted with IRMOF-3 and $NH_2$-MIXMOF-5 giving the products with full conversion (**Figure 1**).

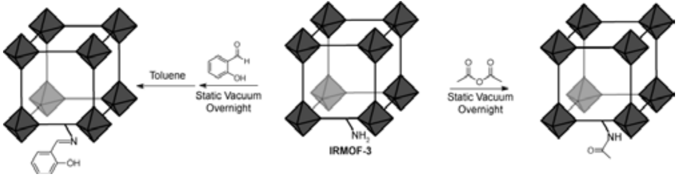

***Figure 1.*** *Vapor-phase PSM of IRMOF-3.*

Generally, PSM is performed in the liquid phase and the relatively slow diffusion of reactants and solvents within the pores requires long reaction times. Our VP-PSM approach provides faster route with high yields.

[1] M. Ranocchiari and J. A. v. Bokhoven *Phys. Chem. Chem. Phys.*, 2011 **13**, 6388-6396 .

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Inorganic and Coordination Chemistry **IC 83**

## Heterophosphorous phenol

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2-Hydroxypyridine has been known for a long time, but it exists as tautomer that is hydrogen will move to the nitrogen to establish its predominant form 2-pyridone. Does the 2-Hydroxyphosphorous exit or perform as the analogue structure of pyridone[1]? To uncover these questions, we prepared the atmospheric stable compound sodium 2-phosphaphenolate through Diels-Alder reactions of α-pyrone and sodium dimethylcarbonate, which further reacted with hydrochloric acid, finally producing a light yellow oil-like product (Fig.1). The DFT calculation at the level of B3LYP/6-311++G(2d,2p) presented that the heterophosphorous phenol structure was more stable than the analogue structure of pyridone by 17.07 kcal $mol^{-1}$. The NMR spectrums of the oil product proved that the proton stayed on the oxygen place.

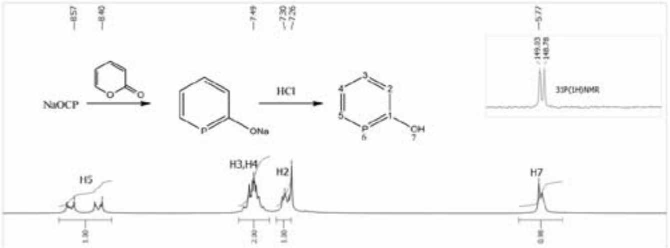

**Fig.1** $^{1}$HNMR and $^{31}P\{^{1}H\}$NMR of 2- Hydroxyphosphorous, the coupling constant between H5 and phosphorous is 42Hz.

[1] Li, W. Q., Tian, W. Q., Feng, J. K., Liu, Z. Z. *Eur. J. Org. Chem.* **2007**, 1669.

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Inorganic and Coordination Chemistry **IC 84**

## Tuning Polynuclear Lanthanide Complexes: Impact of the Ligand Structure on the Self-Assembly

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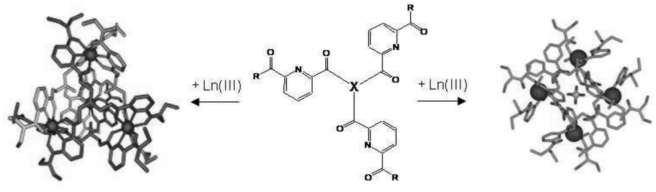
The research of our group is focused on the design and self-assembly processes of new polynuclear complexes, which may find applications in medical imaging, (supra) molecular sensors, and nanomaterials. The lanthanide based systems are of interest due to their similar thermodynamic behavior, but different luminescent and paramagnetic properties.

One of the developed concepts deals with tetranuclear assemblies with three-dimensional arrangements of lanthanide cations. These tetrahedral compounds are formed by the self-assembly of Ln(III) and tripodal ligands bearing three coordinating strands attached to a short spacer.[1] The nanometric complexes within this family may have particular properties depending on subtle structural modifications of the ligand structure. Consequently, we can generate compact tetranuclear complexes or cage-containing assemblies with host-guest interactions. The self-organization and different properties of these unusual complexes will be discussed in this contribution.



[1] a) J. Hamacek, G. Bernardinelli, Y. Filinchuk, *Eur. J. Inorg. Chem.* **2008**, 3419–3422. b) J. Hamacek, C. Besnard, T. Penhouet, P.-Y. Morgantini, *Chem. Eur. J.* **2011**, in press.

Inorganic and Coordination Chemistry **IC 85**

# "Noyori" Asymmetric Transfer Hydrogenation of Imines – a Study of Several Unexpected Influential Parameters

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Asymmetric transfer hydrogenation (ATH) is a reliable way of reducing prochiral ketones and imines to afford optically enriched chiral alcohols and amines.

Noyori-type complexes consisting of a Ru(II) atom, a chiral diamine ligand and a $\eta^6$-arene are able to catalyze the ATH with high enantioselectivities, at promising reaction rates, and under mild conditions.

For this study, a model catalytic complex [RuCl(*S*,*S*-TsDPEN)(*p*-cymene)] was chosen and used to reduce a prochiral imine (1-methyl-3,4-dihydroisoquinoline) to the corresponding amine. An azeotropic mixture of formic acid and triethylamine served as a hydrogen donor for the reduction.

$CO_2$ is formed as a by-product during the reaction and is reportedly [1] able to form a complex with the catalyst. The aim of this study was to evaluate the influence of $CO_2$ on both reaction rate and enantioselectivity of ATH.

It was found that under the conditions favoring the formation of the $CO_2$-catalyst complex, reaction rates notably decreased. Thus, the influence of $CO_2$ as a by-product of the reaction was found to be of major importance and should be taken into consideration.

*This work has been financially supported by the Grant Agency of the Czech Republic (GACR 104 09 1497) and the Ministry of Education (CEZ: MSM 604 613 7301).*

[1] Koike T., Ikariya T., *Adv. Synth. Catal.* **2004**, 346, 37-41.

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Inorganic and Coordination Chemistry **IC 86**

# DFT Calculations in the Asymmetric Transfer Hydrogenation of Imines and Ketones Catalyzed by Noyori Ru(II) Complexes

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Asymmetric transfer hydrogenation (ATH) of imines and ketones using chiral Ru(II)Cl($\eta^6$-*p*-cymene)[*N*-tosyldiphenylethylenediamine] is an excellent and now well-established method for preparing optically pure compounds.

As it has been shown, the reaction mechanism is not a trivial issue. In the case of ketones, the mechanism was described in depth by Noyori e*t al.*, employing extensive density functional theory (DFT) calculations[1]. However, recent experimental evidence suggests that the ATH of imines proceeds via a different, ionic pathway[2].

We set out to investigate both mechanisms computationally using methods which Noyori used in his work[1], although calculating the full molecules instead of simplified structures. The results[3] fully supported the ionic mechanism for imines and the original (Noyori) mechanism for ketones.

Herein, we present the techniques for evaluating transition states and discuss the computational methods exploited.

This work has been financially supported by the Grant Agency of the Czech Republic (GACR 104 09 1497), the Ministry of Education (CEZ: MSM 604 613 7301) and the research intent (AV0Z50200510). Access to the META-Centrum computing facilities (programme LM2010005) is acknowledged.

[1] R. Noyori, M. Yamakawa, S. Hashiguchi, *J.Org. Chem.* **2001**, *66*, 7931.
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Inorganic and Coordination Chemistry **IC 87**

# A quadruple helical cubane-like complex using malic acid bisbenzimidazole derivatives as ligand

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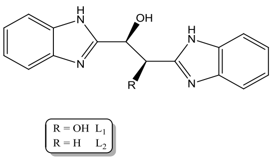
Cubane-like structures are common in transition metal chemistry and one is believed to be present at the active site of the oxygen evolving centre of photosynthesis [1]. Tartaric acid bis-benzimidazole derivatives have been found to generate cubane-like geometry when coordinated to transition metal ions like cobalt(II) and nickel(II) [2]. If the tartaric acid ligand $L_1$ is replaced by the malic acid ligand $L_2$, there are insufficient coordinating groups to satisfy the coordination of the metal ions in an $M_4O_4$ cubane. Diphenylphosphate (DPP) is known [3] to bridge across the face of a cubane, and addition of 2 equivalents of DPP allows the coordination requirements of the metal to be met. The four ligands $L_2$ twist around the cubane core to give a quadruple helical structure.



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[2] K. Isele, F. Gigon, A. F. Williams, G. Bernardinelli, P. Franz and S. Decurtins, *Dalton Trans.*, **2007**, 332-341.
[3] J.-Z. Wu, F. D. Angelis, T. G. Carrell, G. P. A. Yap, J. Sheats, R. Car, and G. C. Dismukes, *Inorg.Chem.,* **2006***, 45,* 189.

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Inorganic and Coordination Chemistry **IC 88**

# Nitrous Oxide Activation by Dinuclear Ru Complexes

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Nitrous oxide's role in ozone depletion and its greenhouse effect has stimulated a lot of interest in activation of this kinetically inert molecule. In addition, $N_2O$ is an appealing oxidant due to its thermodynamic potency and environmentally friendly nature (the only by product in oxygen atom transfer reactions is $N_2$).

Recently, we discovered that dinuclear Ru complexes are able to activate $N_2O$ at room temperature (see picture). NMR spectroscopic and crystallographic analyses show that the Ru complexes mediate a rupture of the N–O bond to give Ru–dinitrogen complexes along with autoxidation products.

Inorganic and Coordination Chemistry **IC 89**

# Chemical Lithiation for New and Better Performing Electrode Materials: A Review

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Transition metal oxides are the state of the art cathodic materials in today's secondary lithium-ion batteries. The high operating voltage and the reversibility of lithium intercalation have encouraged and supported the implementation of these oxides for over 20 years [1]. Coatings, nanoparticles and doping may all contribute to performance improvements, lower costs and greater safety but the complexity of these optimization processes often hinders rational developments [2]. Chemical lithiation addresses precisely this critical issue.

[1] Whittingham S., Chem. Rev., **2004**, *104 (10)*, 4271-4302.
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