

Inorganic and Coordination Chemistry, Minisymposium 196

Functional and Supramolecular MetallopolymersIan Manners¹¹School of Chemistry, University of Bristol BS8 1TS England

Polymers containing metal centers are attracting increasing attention as they offer access to new functional macromolecular and supramolecular materials with interesting properties. Our group has developed ring-opening polymerization routes from strained precursors to form metallopolymers such as polymetalloenes with high molecular weights that allows easy processing. Well-defined architectures (e.g. block copolymers) are available through living polymerization processes, including a remarkable recently developed photocontrolled method. This talk will focus on recent efforts to use these metallopolymers to create, for example, photonic crystal devices with applications in displays, and self-assembled supramolecular materials in the form of thin films, which can be used in nanolithographic applications and catalysis.

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2. M. Tanabe, G. W.M. Vandermeulen, W-Y Chan., P.W Cyr, L. Vandermark, D. A. Rider and I. Manners: *Nature Materials* **2006**, 5, 467.
3. Arsenault, A.; Puzzo, D. Manners, I. Ozin, G.A. *Nature Photonics* **2007**, 1, 468.
4. X. Wang, G. Guerin, H. Wang, Y. Wang, I. Manners, M.A. Winnik *Science* **2007**, 317, 644.
5. J. Gilroy, T. Gaedt, Whittell G.R.; L. Chabanne, M. A. Winnik, I. Manners *Nature Chem.* **2010**, in press.

Inorganic and Coordination Chemistry, Minisymposium 198

Coordination Chemistry with Radicals – Where are the Valence Electrons?Karl Wieghardt

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Coordination compounds of transition metal ions containing α -diimine, α -iminoketone, or 1,2-diketone type ligands have been synthesized in the past and their electronic structures have almost invariably been described as species with closed shell, neutral ligands. We show that this is an unduly oversimplification: these ligands are redox-noninnocent and can exist in three oxidation levels, namely neutral ligands (L^{ox}), π radical monoanions ($(L\bullet)^{-1}$) and closed shell dianions ($L^{red}2-$). We will discuss how these forms may be identified by spectroscopy and broken symmetry DFT calculations. Remember, the correct electronic structure matters when you want to understand reactivity – in catalysis and elsewhere.

Inorganic and Coordination Chemistry, Minisymposium 197

Main Group Elements as Transition MetalsPhilip P. Power

University of California, Davis, Department of Chemistry, One Shields Avenue, Davis, California 95616

The main theme of the lecture will concern the reactions of multiple bonded germanium, tin and lead compounds with fundamentally important small molecules such as H_2 , C_2H_4 , NH_3 , O_2 or CO with a view to eventual catalytic applications. The fundamental reasons for the unique behavior of the multiple bonded species in terms of their electronic structures will be discussed in detail.

Inorganic and Coordination Chemistry, Lecture 199

Solar Syngas Production from H_2O and CO_2 via two-Step Thermochemical Cycles based on Zn/ZnO and FeO/Fe_3O_4 Redox Reactions: Kinetic AnalysisA. Stamatou², P. G. Loutzenhiser², A. Steinfeld^{1,2}

¹Solar Technology Laboratory, Paul Scherrer Institute, 5232 Villigen PSI, Switzerland

²Department of Mechanical and Process Engineering, ETH Zurich, 8092 Zurich, Switzerland

Syngas production via a two-step H_2O/CO_2 -splitting thermochemical cycle based on Zn/ZnO and FeO/Fe_3O_4 redox reactions is considered using highly concentrated solar process heat. The closed cycle consists of: 1) the solar-driven endothermic dissociation of ZnO to Zn or Fe_3O_4 to FeO ; 2) the non-solar exothermic simultaneous reduction of CO_2 and H_2O with Zn or FeO to CO and H_2 and the initial metal oxide; the latter is recycled to the first step. The second step was experimentally investigated by thermogravimetry for reactions with Zn in the range 673 – 748 K and CO_2/H_2O concentrations of 2.5–15% in Ar, and for reactions with FeO in the range 973 – 1273 K and CO_2/H_2O concentrations of 15–75% in Ar. The reaction mechanism was characterized by an initial fast interface-controlled regime followed by a slower diffusion-controlled regime. A rate law of Langmuir-Hinshelwood type was formulated to describe the competitiveness of the reactions based on atomic oxygen exchange on active sites, and the corresponding Arrhenius kinetic parameters were determined by applying a shrinking core model.

Hydrogen storage in Formic Acid - Amine Adducts

Albert Boddien^{1,2}, Henrik Junge¹, Gabor Laurency², Matthias Beller¹¹Leibniz Institut für Katalyse e.V (LIKAT), Albert Einstein Str. 29a, 18059 Rostock, Germany²Institute of Chemical Science and Engineering, Laboratory of Organometallic and medicinal Chemistry, École Polytechnique Fédérale de Lausanne (EPFL), Switzerland

The liquid Formic Acid (FA) represents a benign source of hydrogen gas for future energy supply, affluents a high hydrogen content by mass (4.4%) with a good stability, coupled to the usage of carbon dioxide as hydrogen vector (figure 1).[1] There are several reports on the formation of hydrogen via the homogeneous decomposition of HCO₂H with metal catalysts and, recently, the catalytic efficiency has been significantly improved.[2]

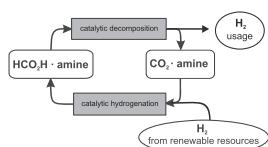


Figure 1. Hydrogen storage in formic acid amine adducts.

We will present here our studies on a highly active catalyst system, for storage and generation of hydrogen using CO₂ as vector. Applying a catalyst system containing [RuCl₂(benzene)]₂ and dppe, a fast hydrogen generation from formic acid amine adducts, as well as a fast hydrogenation of CO₂ was observed.

- [1] C. Fellay, P. J. Dyson, G. Laurency, *Angew. Chem. Int. Ed.* **2008**, *47*, 3966–3968; B. Loges, A. Boddien, H. Junge, M. Beller, *Angew. Chem. Int. Ed.* **2008**, *47*, 3962–3965.
 [2] B. Loges, A. Boddien, F. Gärtner, H. Junge, M. Beller, *Top. Catal.* **2010**, in press.

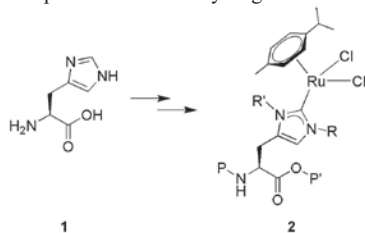
Histidine-based NHC-ruthenium complexes and their catalytic activity

Angèle Monney, Martin Albrecht

School of Chemistry and Chemical Biology, University College Dublin, Belfield, Dublin 4, Ireland

N-Heterocyclic Carbenes (NHCs) have become ligands of great importance in organometallic chemistry. Their good σ -donor properties and their ability to form strong bonds with most metals render them unique spectator ligands in homogeneous catalysis [1].

A few examples of chiral NHC ligands have been reported recently and catalysis with their Pd complexes showed promising ee's for example in α -arylation of amides [2]. We have successfully used histidine (**1**) as starting material for the synthesis of different chiral imidazole-2-ylidene ruthenium complexes (**2**). We will discuss synthetic aspects and the catalytic activity of these bioinspired complexes in transfer hydrogenation.



- [1] Díez-González, S.; Marion, N.; Nolan, S. P. *Chem. Rev.* **2009**, *109*, 3612–3676
 [2] Jia, Y.-X.; Hillgren, J. M.; Watson, E. L.; Marsden, S. P.; Kündig, E. P. *Chem. Commun.* **2008**, 4040–4042; Luan, X.; Mariz, R.; Robert, C.; Gatti, M.; Blumentritt, S.; Linden, A.; Dorta, R. *Org. Lett.* **2008**, *10*, 5569–5572

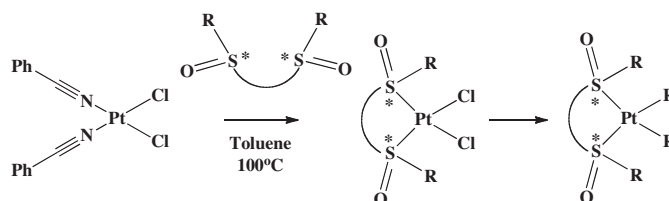
Interactions of chiral bis-sulfoxides with precious metals: synthesis, characterisation and possible catalytic applications

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A family of enantiomerically pure bis-sulfoxide ligands have been prepared in straight forward procedures, as an alternative to phosphine ligands in late transition metal catalysis. The flexibility of the syntheses of these ligands has allowed various steric and electronic variations to be made to these structures.

Previous work from our group has already shown rhodium complexes of these ligands as excellent precatalysts in 1,4-addition reactions^{1,2}. We have now investigated the interactions of these ligands with other late transition metals, particularly palladium and platinum. A range of predominantly S-bound complexes has been synthesised. We will present these structures, and their reactivities in organic reactions.



- [1] Mariz, R.; Luan, X.; Gatti, M.; Linden, A.; Dorta, R. *J. Am. Chem. Soc.* **2008**, *130*, 2172.
 [2] Bürgi, J. J.; Mariz, R.; Gatti, M.; Drinkel, E.; Luan, X.; Blumentritt, S.; Linden, A.; Dorta, R. *Angew. Chem. Int. Ed.* **2009**, *48*, 2768.

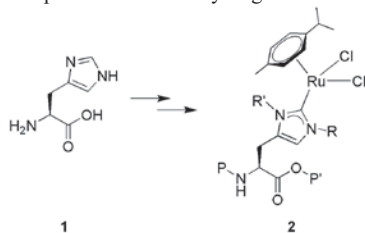
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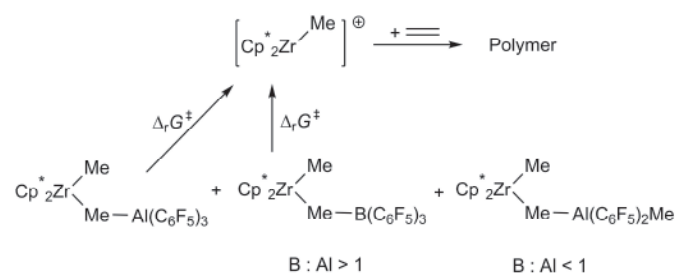
- [1] Díez-González, S.; Marion, N.; Nolan, S. P. *Chem. Rev.* **2009**, *109*, 3612–3676
 [2] Jia, Y.-X.; Hillgren, J. M.; Watson, E. L.; Marsden, S. P.; Kündig, E. P. *Chem. Commun.* **2008**, 4040–4042; Luan, X.; Mariz, R.; Robert, C.; Gatti, M.; Blumentritt, S.; Linden, A.; Dorta, R. *Org. Lett.* **2008**, *10*, 5569–5572

Active Species for Metallocene Olefin Polymerization: $\Delta_r G^\ddagger$ by VT-NMR, DFT Calculations and Activities in Ethylene Polymerization

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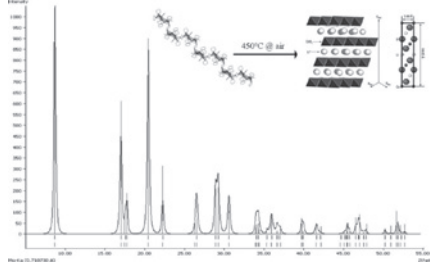
A full picture is presented of the activation mechanism of Cp^{*}₂ZrMe₂ by B(C₆F₅)₃ / [CPh₃][B(C₆F₅)₄] in combination with a trialkylaluminum species, as studied by ¹H and ¹⁹F NMR spectroscopy. Due to rapid transmetalation of the C₆F₅ ligands from boron to aluminum [1], different species are formed depending on the reagent ratio (Scheme 1). Activation barriers $\Delta_r G^\ddagger$ are determined by variable-temperature NMR studies and compared to DFT calculations (M06-L). Furthermore, the different species are tested for their activity in ethylene polymerization.

Scheme 1. The reaction outcome between Cp^{*}₂ZrMe₂, B(C₆F₅)₃ and AlMe₃ depends on the reagent ratio.

- [1] Klosin, J.; Roof, G.R.; Chen, E.Y.-X.; Abboud, K.A. *Organometallics* **2000**, *19*, 4684

Lithium metal aryloxy clusters: starting products for oxide materialsAurélien Crochet¹, Katharina M. Fromm¹¹University of Fribourg, department of chemistry, Chemin du musée, 9; CH-1700 Fribourg, Switzerland

The use of alkali aryloxides^[1] reagents in organo-metallic synthesis often depends on their solubility, a property derived from their structure. The regain of interest of alkali aryloxides also resides in the discovery of high-temperature superconducting compounds which has generated a great interest in the formation of oxide materials and other ceramics. With the broad use of electronic devices, the interest for oxide materials used in batteries increases. For lithium batteries using LiCoO₂, the cathode half reaction is: LiCoO₂ ↔ Li_{1-x}CoO₂ + x Li⁺ + xe⁻. This oxide is synthesized as powder from a stoichiometric mixture of Li₂CO₃ and Co₃O₄ at 600 °C under O₂ for 12 h, followed by two subsequent thermal treatments at 900 °C under O₂ for 24 h and 12 h.^[2] We will present an alternative method to form the lithium cobaltite starting from complex of cobalt(II) aryloxy.^[3]



[1] W. Maudez, M. Meuwly, K. M. Fromm, *Chem. Eur. J.*, **2007**, 13, 29, 8302-8316; W. Maudez, D. Häussinger, K. M. Fromm, *ZAAC*, **2006**, 632, 2295-2298, A. Crochet, K. M. Fromm, *ZAAC*, **2010**, *accepted*

[2] S.-H. Yang, L. Croguennec, C. Delmas, E. C. Nelson and M. A. O'Keefe, *Nat. Mater.*, **2003**, 2, 464-467.

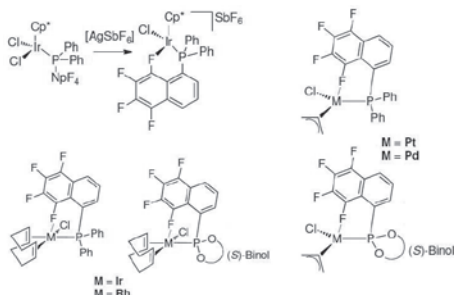
[3] A. Crochet, K. M. Fromm, *in preparation*

Remote CF-metal Interactions in Late-Transition-Metal ComplexesBarbara Czarniecki, Kyrill Stanek, Raphael Aardoom, Heinz Rüegger[†], Antonio Togni[†]

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There are some examples for CF-metal coordination, but the investigation of such remote interactions is focused on group 1 and 2 metal cations¹ and only scattered reports concern late-transition metal complexes.²

We discovered and investigated remote CF-metal interactions in a series of late-transition metal complexes bearing monodentate phosphorus ligands containing the 5,6,7,8-tetrafluoronaphth-1-yl group (NpF₄) using X-ray-crystallography and NMR spectroscopy. In the case of Pt- and Rh-complexes the remote interaction was directly detected in rare 2D NMR heteronuclear correlation experiments.



[1] H. Plenio, *Chem. Rev.* **1997**, 97, 3363.

[2] e.g. (a) S. D. Perera, B. L. Shaw, *Inorg. Chim. Acta* **1995**, 228, 127.

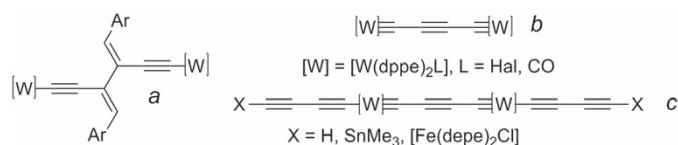
(b) T. Ritter, M. W. Day, R. H. Grubbs, *J. Am. Chem. Soc.* **2006**, 128, 11768. (c) R. J. Kulawiec, E. M. Holt, M. Lavin, R. H. Crabtree, *Inorg. Chem.* **1987**, 26, 2559. (d) I. G. Phillips, R. G. Ball, R. G. Cavell, *Inorg. Chem.* **1987**, 26, 4074.

Electron Transfer in Tungsten Acetylides, Cumulenes and Carbynes

S. N. Semenov, O. Blacque, T. Fox, K. Venkatesan, and H. Berke

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Molecular electronics is an intensively growing field of science. Due to a need for further miniaturization and also for principle reasons to explore for instance quantum effects in electronics, fundamental studies are sought.¹ In our study, we first deeply explored the chemistry of [W(dppe)₂] fragment based on cumulenes and carbynes to get access to the long polynuclear conjugated systems. Complexes of three types were obtained (see scheme).^{2,3} Almost all compounds were characterized by single crystal structural analysis. The electronic communication was investigated by Cyclic voltammetry, EPR, NIR, IR spectroscopy and magnetization measurements.



Those investigations reveal that the system **a** provides only a weak communication. The system **b** provides moderate coupling of metal centers due to the orthogonality of the metal SOMO (d_{xy}) and the bridge orbitals. Study of the system **c** showed that it is an efficient mediator for electron transfer through long distance. In addition the stability of these compounds is impressive compared to C_n polynes.

[1] C. Joachim, J. K. Gimzewski, A. Aviram, *Nature* **2000**, 408, 541-548.

[2] S. N. Semenov, O. Blacque, T. Fox, K. Venkatesan, H. Berke, *Angew. Chem. Int. Ed.* **2009**, 48, 5203-5206.

[3] S. N. Semenov, O. Blacque, T. Fox, K. Venkatesan, H. Berke, *J. Am. Chem. Soc.* **2010**, 132, 3115-3127.

Complexes containing the fac-{^{99m}TcO₃} Core as Multifunctional Platforms for the Development of Dual-Modality Imaging Agents

Sebastian Imstef, Henrik Braband and Roger Alberto

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Molecular imaging has gained enormous importance over the last decade in order to visualize biological events and in terms of non-invasive diagnostics. ^{99m}Tc-compounds are amongst the most favorable radiolabels due to their physical properties and availability. The classical bifunctional chelator (BFC) approach has been proved to be an effective tool in the development of new radiotracers. In addition, the unprecedented [3+2]-cycloaddition reactivity of the fac-{TcO₃}⁺-core has been established to be an effective functionalization tool of novel ^{99m}Tc complexes by us.^[1] Thus the combination of these two tools, the mixed BFC-[3+2]-cycloaddition approach may present an excellent opportunity for novel dual-modality labeling agents.



A variety of technetium(VII) complexes containing functionalized 1,4,7-triazacyclononane (TACN) derivatives have been reported so far.^[1]

We would like to extend this array by reporting the synthesis and characterization of mono- and trisubstituted TACN complexes ([^{99m}TcO₃(TACN-R/R₃)]^p, R = biomolecule, fluorescent marker) that allow further functionalization via the discussed [3+2]-cycloaddition approach. This concept may directly be transposed into [^{99m}TcO₃]-labeling procedures leading to highly versatile, dual-modality radiolabels.

These new results may likely support the ongoing endeavors toward combined optical/SPECT imaging agents.

[1] H. Braband, Y. Tooyama, T. Fox, R. Alberto, *Chem. Eur. J.* **2009**, 15, 633-638.

RNA Forms a Three-way Junction with a Supramolecular Iron(II) Cylinder

J. Schnabl,^a E. Freisinger,^a B. Spingler,^a M.J. Hannon,^b R.K.O. Sigel^a

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^bUniversity of Birmingham, School of Chemistry, Edgbaston, Birmingham B152TT, UK.

Supramolecular dinuclear iron(II) cylinders $[\text{Fe}_2\text{L}_3]^{4+}$ are complexes that have the ability to interact with DNA molecules in various modes. These interactions are enabled through the helical shape, the size and the high positive charge of the cylinder complexes. Treatment of tumor cell lines with the cylinder results in increased cell death by a non-genotoxic activity of the iron(II) supramolecule,^[1] making it a potential anti cancer drug.

Short palindromic DNA strands are forced into a three-way junction with the $[\text{Fe}_2\text{L}_3]^{4+}$ cylinder present.^[2] RNA has the ability to form a huge variety of secondary and tertiary structures. This makes it a perfect target for investigations on cylinder interactions. To study how the characteristics of RNA *in vitro* and eventually *in vivo* would be influenced we conduct a variety of investigations of the supramolecular iron(II) helicates with several RNA molecules. Co-crystallization of the $[\text{Fe}_2\text{L}_3]^{4+}$ cylinder with a palindromic RNA sequence yields single crystals that diffract to a resolution of 1.9 Å. The crystal structure unveils a $[\text{Fe}_2\text{L}_3]^{4+}$ complex amidst three surrounding RNA oligonucleotides, forming a cylinder-stabilized RNA three-way junction. The X-ray structure is presented in full detail.

[1] A. C. Hotze, N. J. Hodges, R. E. Hayden, C. Sanchez-Cano, C. Paines, N. Male, M. K. Tse, C. M. Bunce, J. K. Chipman, M. J. Hannon, *Chem. Biol.* **2008**, *15*, 1258-1267.

[2] A. Oleksi, A. G. Blanco, R. Boer, I. Uson, J. Aymami, A. Rodger, M. J. Hannon, M. Coll, *Angew. Chem., Int. Ed.* **2006**, *45*, 1227-1231.

Financial support by the Swiss National Science Foundation and the State Secretariat for Education and Research (COST D39) is gratefully acknowledged.

Polymer or Macrocyclic? Cobalt Complexes of Ditopic 2,2':6',2''-Terpyridine Ligands with Flexible Spacers

Kate Harris, Edwin C. Constable, Catherine E. Housecroft, Markus Neuburger, Silvia Schaffner and Jennifer A. Zampese

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The reaction of transition metal ions with ditopic ligands containing two 2,2':6',2''-terpyridine units linked by flexible spacers can give metallosupramolecular polymers, discrete metallamacrocycles or mixtures of the two. The outcome of the coordination depends on the precise reaction conditions as well as the nature of the spacer and the transition metal salt.

A detailed ¹H NMR spectroscopic study of the product mixtures obtained from reactions of bis(terpyridyl)oligo(ethylene glycol) ligands with cobalt(II) salts revealed a complex dependence of the speciation on the ligand, anion, solvent, concentration and equilibration time. Using PGSE NMR spectroscopy and X-ray crystallography, the thermodynamic products of the reaction were shown to be metallamacrocyclic complexes, while the kinetic products are significantly larger species.

In addition, the reaction of the ditopic ligands with cobalt(II) acetate tetrahydrate in pure alcohol was found to cause the decomposition of the ligand and the formation of mononuclear bis(4'-alkoxy-2,2':6',2''-terpyridine)cobalt(II) complexes.

Multi-Organometallic-Containing Peptide Nucleic Acids: Preparation and Biological Applications

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Peptide nucleic acids (PNAs) are non-natural nucleic acid analogues.¹ Their neutral pseudopeptide backbone is made of *N*-(2-aminoethyl)glycine units which are ligated via a methylene carbonyl to the four nucleobases (Figure 1).¹ Due to their favourable properties, PNAs have found application in various research areas, e.g. antisense and antigene therapies or biosensing.

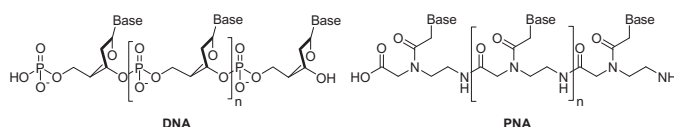


Figure 1. Structure comparison between DNA and PNA.

In order to modify the intrinsic properties of PNAs or in order to add new functionalities and/or spectroscopic properties to PNAs, organometallics have been synthetically attached to these non-natural DNA analogues. We will present our recent advances on the preparation and biological evaluation of multi-organometallic-containing PNA monomers and oligomers.²⁻⁵

[1] P.E. Nielsen, M. Egholm, R.H. Berg, O. Buchardt, *Science* **1991**, *254*, 1497.

[2] G. Gasser, N. Hüskén, S.D. Köster and N. Metzler-Nolte, *Chem. Comm.* **2008**, 3675.

[3] G. Gasser, O. Brosch, A. Ewers, T. Weyhermüller and N. Metzler-Nolte, *Dalton Trans.* **2009**, 4310-4317

[4] N. Hüskén, G. Gasser, S.D. Köster and N. Metzler-Nolte, *Bioconjugate Chem.* **2009**, *20*, 1578.

[5] A. Sosniak, G. Gasser and N. Metzler-Nolte, *Org. Biomol. Chem.* **2009**, *7*, 4992.

SYNTHESIS OF DITOPIC AND TRITOPIC 2,2':6',2''-TERPYRIDINE LIGANDS AND THEIR RUTHENIUM(II) AND EUROPIUM(III) COMPLEXES

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

We report here the synthesis of new ditopic and tritopic tpy ligands with different lengths of oligo(ethylene glycol) chains and the spectroscopic and the electrochemical characterization of complexes of these ligands and ligands itself.

[1] *2,2':6',2''-Terpyridines ... from chemical obscurity to common supramolecular motifs*, Constable, E.C. *Chem. Soc. Rev.* **2007**, *36*, 246-253.

[2] *Metal-directed assembly of a conformationally restricted metallamacrocyclic* Chow, H.S.; Constable, E.C. and Housecroft, C.E. *Dalton Trans.* **2003**, 4568-4569.

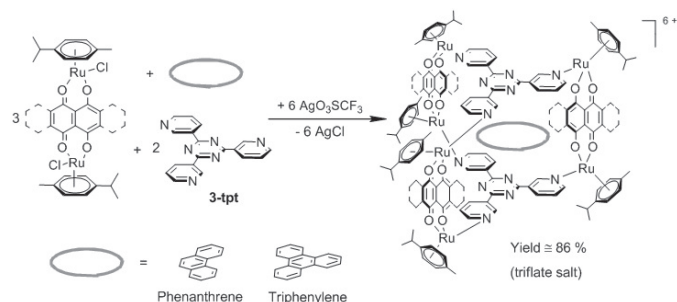
Template-Directed Synthesis of Hexanuclear Arene Ruthenium Prisms

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The synthesis of discrete metalla-assemblies with 2,4,6-tri(pyridin-3-yl)-1,3,5-triazine (3-tpt) ligands is difficult and only a few examples are found in the literature^[1]. Previous work using the isomeric 4-tpt ligand for the synthesis of hexacationic metalla-prisms demonstrated the capacity of these cages to permanently encapsulate or temporarily host aromatic molecules^[2].



We found that cationic trigonal prismatic arene ruthenium complexes containing 3-tpt instead of the isomeric 4-tpt as trigonal panels are obtained only in the presence of an aromatic molecule which acts as a template.

[1] (a) M. Fujita, S.-Y. Yu., T. Kusakawa, H. Funaki, K. Ogura, K. Yamaguchi, *Angew. Chem. Int. Ed.*, **1998**, *37*, 2082-2085. (b) P. Govindaswamy, G. Süss-Fink, B. Therrien, *Organometallics*, **2007**, *26*, 915-924.

[2] J. Freudenreich, N. P. E. Barry, G. Süss-Fink, B. Therrien, *Eur. J. Inorg. Chem.*, **2010**, submitted.

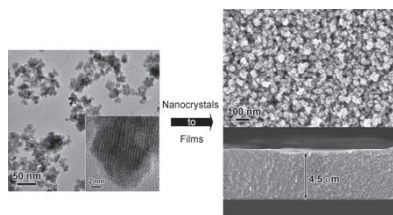
From Al-doped ZnO Nanocrystals to Transparent Conductive Films

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Transparent conductive films (TCF) have great potential in photoelectric applications. Currently, Sn-doped In₂O₃ (ITO) is the material used for most of the TCF applications. But, ITO is rather expensive and lacks thermal stability. As a promising alternative to ITO, Al-doped ZnO (AZO) has moved into the focus due to its lower cost, large band gap, chemical and thermal stability, and abundance in nature [1].

In this work, a microwave-assisted non-aqueous sol-gel process, which has been proved to be a fast synthesis route for metal oxide nanocrystals [2], was used to synthesize AZO nanocrystals. The morphology of the nanocrystals is spherical-like, and the average crystal size is ~9 nm. AZO thin films were either directly deposited on different substrates during the reaction or dip-coated from nanocrystals dispersions. Homogeneous and nanoporous films were formed. The transmittance of the AZO powders is ~90% in the range of visible light, and the electrical resistivity of AZO pellet at room temperature is 72 Ωcm after sintering at 800°C for 10h in air.



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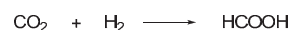
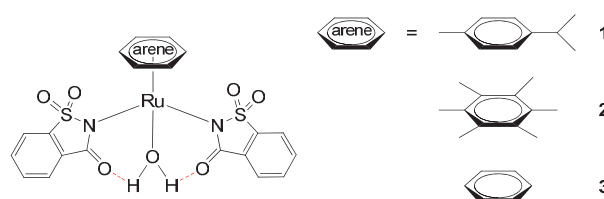
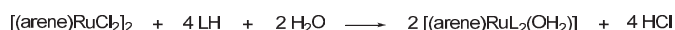
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Arene Ruthenium Bis(saccharinato) Aqua Complexes: Synthesis, Molecular Structure and Catalytic Properties

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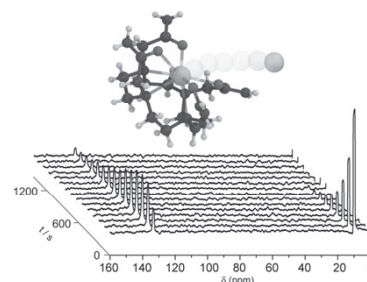
A new family of arene ruthenium bis(saccharinato) aqua complexes of the type [(arene)RuL₂(OH₂)] (arene = MeC₆H₄Prⁱ, C₆Me₆, C₆H₆) was synthesized from [(arene)RuCl₂]₂ and saccharin (LH) or saccharin sodium salt (LNa). The X-ray crystal structure analysis shows these neutral complexes to have a piano-stool geometry with the arene ligand, two saccharinato ligands and the aqua ligand surrounding the ruthenium center in a pseudo-tetrahedral fashion.



The new complexes were found to catalyze the hydrogenation of carbon dioxide to give formic acid in aqueous solution under basic conditions with catalytic turnover number up to 812.

Kinetics of Yttrium-Ligand Complexation Monitored Using Hyperpolarized ⁸⁹Y as a Model for Gadolinium in Contrast AgentsPascal Miéville¹, Sami Jannin¹, Lothar Helm¹, Geoffrey Bodenhausen^{1,2}¹Institut des Sciences et Ingénierie Chimiques, Ecole Polytechnique Fédérale de Lausanne (EPFL), Batochime, 1015 Lausanne, Switzerland²Département de Chimie, associé au CNRS, Ecole Normale Supérieure, 24 Rue Lhomond, 75231 Paris Cedex 05, France

Hyperpolarization by dissolution dynamic nuclear polarization (DNP) enhances ⁸⁹Y spin magnetization by 3 to 4 orders of magnitude and provides a way to monitor yttrium-ligand complexation "on the fly" by means of ⁸⁹Y NMR. In this communication, we show an example of free yttrium Y³⁺ being complexed with DOTAM to form [Y(DOTAM)(H₂O)]³⁺ as a model for gadolinium in contrast agents.



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Gold(I) phosphine derivatives of 4,4'-dialkynyl substituted 2,2'-bipyridine and 4'-ethynyl-2,2':6',2''-terpyridine

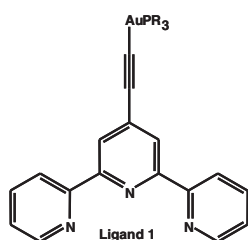
Marzena Kocik, Edwin C. Constable, Catherine E. Housecroft, Jennifer A. Zampese, Markus Neuburger and Silvia Schaffner

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Gold(I) phosphine derivatives have the potential to be luminescent and have interesting optical properties [1].

The family of ligands **1** can be synthesized from 4'-ethynyl-2,2':6',2''-terpyridine and trialkyl- or triarylphosphine gold(I) chlorides. A similar way of synthesis was used to obtain derivatives of 4,4'-dialkynyl substituted 2,2'-bipyridine.

We are presently investigating zinc(II), cadmium(II) and platinum(II) complexes of series of these compounds and studying their absorption and emission properties.



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Turning Apo-Streptavidin into an Osmate-Dependent Dihydroxylase

Tillmann Heinisch^{1,2}, Jincheng Mao², Anca Pordea², Alessia Sardo², Marc Creus², Yvonne Wilson², Valentin Köhler², Tilman Schirmer¹ and Thomas R. Ward²

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Different strategies for the creation of artificial metalloenzymes have been successfully elaborated in recent years; e.g. by building complexes of proteins with either high-affinity or covalently bound metal-cofactors. A more direct approach makes use of the potential of amino acids to ligate metal ions. Herein, we present the conversion of apo-streptavidin into an artificial dihydroxylase based on the dative anchoring of osmate. Various olefin substrates could be converted into the corresponding glycols with stereoselectivities ranging amongst the highest reported in literature. Upon structural characterisation of potential catalytic sites by X-ray crystallography and single-site mutant catalysis stereoselectivity and conversion could be genetically improved for a number of substrates.

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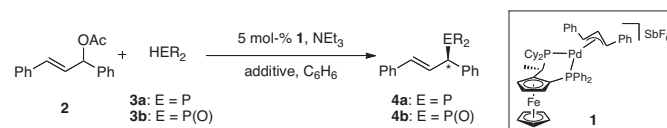
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Enantioselective Allylation of Phosphines and Phosphine Oxides: Synthesis and Application

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Chiral phosphines are among the most important classes of ligands for asymmetric catalysis.¹ Therefore, synthetic procedures which enable enantioselective transformations to chiral phosphines are highly desired. In this field our group has recently reported an asymmetric allylation of secondary phosphines (**3a**) catalysed by a chiral Palladium complex (**1**).² The allylic phosphine (**4a**) generated can be isolated with up to 96% ee in high yield.



We have now found that the reaction also proceeds under the same conditions with secondary phosphine oxides (**3b**) directly furnishing the allylic phosphine oxide (**4b**). Product **4b** precipitates from the reaction solution to yield analytically and enantiomerically pure (>99% ee) material after filtration. In addition, all components are air-stable, thus the reaction can be carried out without the need of a protective atmosphere even in wet solvents without affecting the reaction efficiency.

The allylic phosphination can be used as the key step to introduce stereogenicity in the synthesis of chiral phosphine ligands. Examples of such ligand syntheses will be shown.

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

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In the past years, 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 metalloenzymes we transferred our knowledge of the biotin-streptavidin technology to a sulfonamide-human carbonic anhydrase II system. This protein offers promising characteristics for the creation of artificial metalloenzymes. These include: a deep hydrophobic binding pocket, high affinity for arylsulfonamides and a monomeric structure.

To ensure localization of the catalytically-active metal complex within carbonic anhydrase, we relied upon *in-silico* docking of an arylsulfonamide bearing an organometallic moiety. Site-directed mutagenesis allowed us to tailor the environment to accommodate and influence the catalytic event. This strategy was confirmed by X-ray crystallography.

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Development of Artificial Enzymes: A Computational Study

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By linking a catalytically active metal complex into a protein, it is possible to combine the activity of a metal with a chiral protein environment to generate an enantioselective artificial metalloenzyme [1,2]. A requirement for such an artificial enzyme is a deep binding pocket to allow catalysis, with a stable connection between the two building blocks.

In the past, we have relied on the biotin-avidin technology to anchor the metal moiety within a protein environment. Now we extend the approach to sulfonamide ligands binding to human carbonic anhydrase 2.

To develop the most efficient artificial enzymes, molecular dynamics studies are carried out with different linkers connecting the catalytic metal to the protein or with tailoring the protein moiety by mutation to the needs of the metal. The evaluation of the linkers is done by calculation of the respective binding free energies using MM-GBSA. The force field is validated against experimental results for several small sulfonamide aryl ligands, e.g. ArSO_2NH^- , $\text{NH}_2\text{ArSO}_2\text{NH}^-$, $\text{CH}_3\text{ArSO}_2\text{NH}^-$ or $\text{BipySO}_2\text{NH}^-$. For these ligands, the dissociation constant differs by several magnitudes which makes them convenient for validation. Furthermore the simulation is compared to a QM/MM simulation using the SCCDFTB [3] approach.

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NMR investigation of the catalytic core of a group II intron ribozyme

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Group II intron ribozymes are naturally occurring catalytic RNAs, found mainly in organellar genes of plants, fungi and lower eukaryotes. These special RNAs are best known for their ability to undergo self splicing, in a manner that resembles the eukaryotic spliceosome. [1] Their structure comprises six domains that must adopt a specific 3D arrangement to carry out catalysis. It is known that metal ions are essential in both folding and catalytic activity. [2] Biochemical studies showed that the most crucial atoms for compaction are located within a small section of domain 1 (D1) that includes the κ and ζ elements. This small substructure controls the specific collapse of the molecule and forms the docking site for the catalytic domain 5, so becoming the *catalytic core* of the ribozyme. No structural information on D1 is available so far, and, in general, only little structural information is known on these molecules. [3] We are currently investigating by means of multinuclear and multidimensional NMR techniques the solution structure of the κ - ζ region of D1 of Sc.ai5 γ group IIB intron, from yeast mitochondria. This is a 45 nucleotides long RNA molecule, comprising an unusual three way junction with two flexible tetraloops and one internal loop. The structural modifications as well as the different NMR experiments used to overcome the intrinsic mobility of the object molecule will be presented.

This research is supported by a Marie Curie Intra European Fellowship (RNABIC, n° 236794) within the 7th European Community Framework Programme as well as by the Swiss National Science Foundation.

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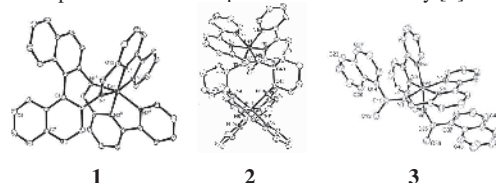
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Controlling the diastereoselectivity of octahedral metal complexes with chiral scaffolds

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The use of chiral ligands to control the configuration of stereogenic metal centres is an important theme in supramolecular chemistry [1].



We have recently developed a suite of chiral Schiff base and reduced Schiff base ligands prepared by the condensation of 2,2'-bipyridine-6-carbaldehyde and chiral diamines or monoamines followed, where appropriate, by borohydride reduction. By reacting these ligands with Fe^{II} , Zn^{II} or Ag^{I} , single-, or double-helicates (e.g. **1** and **2**) and mononuclear complexes (e.g. **3**) have been synthesized. Complete control of diastereoselectivity was observed in the solid state [2-4].

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Solution structure of the catalytic core of a bacterial group II intron

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Group II introns are large self-splicing and retrotransposable ribozymes. Their common ancestry with the eukaryotic spliceosome as well as possible applications in biotechnology and gene therapy have evoked much interest in their structure and mechanism. Their highly conserved secondary structure features six domains that fold into a compact tertiary structure in the presence of Mg^{2+} [1]. Domain 5 (D5), a 34-35 nt hairpin situated in the solvent-inaccessible core of the ribozyme, is the most conserved part of the ribozyme. Both the so-called catalytic triad (usually AGC) close to its stem and its dinucleotide bulge are indispensable for the formation of the catalytic center [2].

Here we present the NMR solution structure of domain 5 of the *Azotobacter vinelandii* group II intron I5 (Av.I5) [3]. A sheered G·A pair makes the catalytic triad region considerably more dynamic compared to the *Saccharomyces cerevisiae* Sc.ai5 γ D5 [4]. Strongest Mg^{2+} binding in Av.I5 D5 is observed in the bulge region, which agrees with the recent crystal structure of a group IIC intron and the proposed two metal ion mechanism of catalysis [5]. In contrast, Mg^{2+} binding affinities in the UAGUU pentaloop are very small.

Financial support by the Swiss National Science Foundation and the University of Zurich is gratefully acknowledged.

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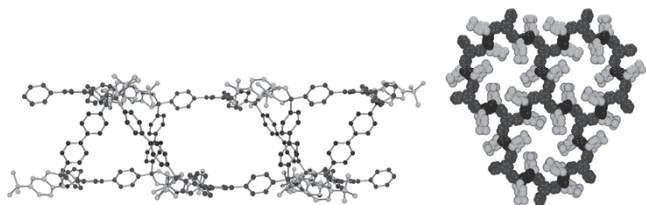
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Boron-Based Crystalline Two-Dimensional Organic Networks

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The development of porous, low density materials are of great interest for their applications in gas storage, catalysis and separations. [1] We have synthesized the first examples of 2D organic polymers for which structural information could be obtained through single crystal X-ray analysis. The networks were synthesized through the use of simple building blocks in a three component reaction utilizing both boronate ester bonds and B-N dative interactions.



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New inorganic iridium(III) complexes for photonic applications

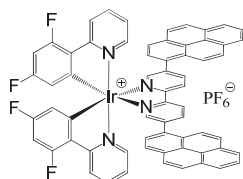
G. Schneider¹, M. Neuburger¹, J. Zampese¹, E. C. Constable¹, C. E. Housecroft¹, R. Costa², H. Bolink²

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

Compared to an OLED, a LEEC has a significantly simplified architecture. Two electrodes sandwich the emissive layer containing the light emitting molecules. In LEECs the emitting molecules need to be ionic, unlike in OLEDs. Compared to an OLED, LEECs are independent of the work function of the electrodes. 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.

The new iridium(III) complex below has been prepared and it shows two emissions yielding a blue-white colour. Its synthesis, structural and physical properties will be described.



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The plant Metallothionein 2 from *Cicer arietinum* increases its metal ion binding capacity by incorporation of sulfide ions

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Metallothioneins (MTs) constitute a large family of ubiquitous, small, and cysteine rich proteins. Previous investigations on the plant MT2 from *Cicer arietinum* (cicMT2) have shown, that the protein has the ability to bind metal ions of groups 11 and 12 forming metal-thiolate clusters, which dictate the tertiary structure of the protein. [1,2] Recent findings also indicate an increased cadmium ion binding ability of the protein with recruitment of sulfide ions as additional ligands generating a form with the stoichiometry Cd₉S₇cicMT2 from the initial Cd₅cicMT2 species. Upon sulfide incorporation, a characteristic shoulder between 260 and 280 nm emerges in the UV-Vis spectra, and the CD spectrum shows intense dichroic bands at positions (+) 248 nm, (-) 262 nm, and (+) 281 nm with the two inflection points located at 256 nm and 269 nm.

Ongoing experiments showed that also higher amounts of other metal ions such as Zn²⁺ can be inserted in presence of additional sulfide ions, although to a smaller extend. In an attempt to investigate the biological relevance of such sulfide containing metal-thiolate clusters we will also present our results to isolate such complexes directly from *E. coli*. In addition, NifS, an enzyme integrating metal-sulfur clusters in proteins, was employed to reconstitute the clusters *in vivo*.

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

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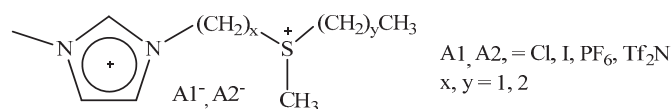
Synthesis and characterization of dicationic imidazolium-sulfonium salts

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Interest in ionic liquids (ILs) has grown rapidly in the last few years.[1] Theoretical studies combined with traditional spectroscopic methods have provided a deeper understanding about the nature of the ILs.[2] However, the studies are almost exclusively based on single-charged ILs systems.

We have prepared a series of thioether-functionalized imidazolium halides. Subsequent reaction of these salts with methyl iodide affords imidazolium-sulfonium salts composed of doubly charged cations and two different anions. Imidazolium-sulfonium salts containing a single anion type are obtained either by a solvent extraction method or by anion exchange.



In the solid state, crystallographic disorder of the dication is observed in nearly all these salts. Despite the heavy disorder and thus the packing inefficiency, all the salts with dications are solid at room temperature.

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New Chiral Rhenium Complexes for Homogeneous Catalysis)

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We have prepared a series of new Re complexes containing chiral ferrocenyl ligands of the Josiphos¹ and Pigiphos² families, starting from commercially available rhenium sources. These materials are air- and moisture-stable in various oxidation states (I, III, V and VII) and with different accompanying ligands such as, halides, hydrides, oxygen and nitrogen. To the best of our knowledge, these complexes are the first examples of chiral rhenium compounds with non-C₂ symmetric ligands.

In particular, a series of Re(V) oxo and nitrido species, showed to be active in the asymmetric transfer hydrogenation of acetophenone using 2-propanol as the hydrogen source. The reaction proceed cleanly with good to excellent yields (50-99%) but still with moderate enantioselectivity (up to 55%). A monohydride mechanism is proposed with the intermediacy of a Re-alkoxyde which was actually isolated. The reduction of these complexes give the corresponding polyhydride derivatives which also showed activity in hydrogenation with molecular hydrogen, hydrosilylation and Michael addition reactions. The scope and limitations of these transformations is currently under study.

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Copper(I) Complexes for Dye Sensitised Solar Cells and LEECs

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We are developing new models of DSSCs (dye sensitised solar cells) using copper(I) 2,2'-bipyridine (bipy) complexes as sensitizers. The structure of the organic part of the complex can consequently affect the efficiency of the solar cells. In previous work by Grätzel, the use of bipy ligands with thiophenes and various conjugated π -systems was found to increase the efficiency of solar cells. Since the synthesis of ligands of this type (**Figure 1**) proceeds in several reaction steps, and the yields are relatively low, it is of great importance to optimize the synthesis method.

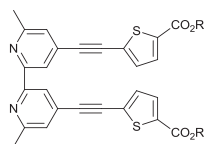


Figure 1

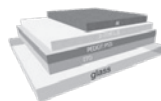


Figure 2

Our Cu(I) complexes may be applied to light emitting electrochemical cells (LEECs) (**Figure 2**), which are currently in competition with OLEDs for optimization of the colour and increased efficiency of the emitted light.

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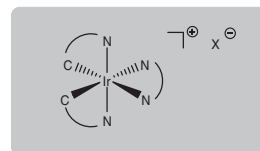
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Organic Light Emitting Electrochemical Cells based on new Iridium (III) complexes

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In recent years, the reduction of energy consumption, by developing novel and more efficient lighting systems, has become an attractive goal. Organic Light Emitting Diodes (OLEDs)¹ and Light Emitting Electrochemical Cells (LEC)² have been identified as promising candidates for such a challenge. The LECs are much simpler devices than the OLEDs, requiring no environmental protection and can be processed from benign solvents³. They operate at low voltage and are not especially sensitive to the thickness of the active layer. Many of the best emitters in both types of device are based on iridium complexes.

We are developing and synthesising new iridium complexes which can increase significantly the lifetime of the devices and shift the emission into the white-blue region.



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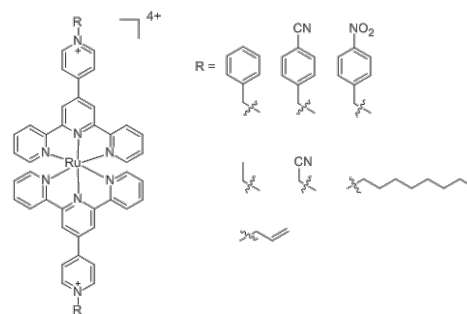
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Photophysical, photochemical and electrochemical investigations of functionalised bis 4'-pyridyl-2,2':6',2''-terpyridine Ru(II) complexes

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Following the discovery of the water-splitting activity of a 4'(4-methylpyridinio)-2,2':6',2''-terpyridine ruthenium(II) complex¹, research is being carried out into the effects of different substituents at the pyridyl *N*-position of the 4'-pyridyl-2,2':6',2''-terpyridine moiety on the electronic and spectroscopic properties of the complex.



R = C₃H₇, C₇H₇, C₈H₆N, C₂H₂N, C₂H₅, C₇H₆NO₂ and C₈H₁₇

After full characterization, anion exchange is performed on each complex to generate the water soluble [HSO₄]⁻ complex which will then be tested for water-splitting activity and stability.

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Carboxymethyl chitosan as a drug carrier for polyoxometalates

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Carboxymethyl chitosan (CMC) is a promising, biocompatible and non-toxic biopolymer that can be used for a wide range of drug delivery and catalytic applications.^[1] We have employed CMC to encapsulate polyoxometalates which are well known for their bio-medicinal potential, e.g. as antiviral and anticancer agents.^[2] For the synthesis of the first model CMC/POM composites, $[\text{Co}_4(\text{H}_2\text{O})(\text{PW}_9\text{O}_{34})_2] \cdot x\text{H}_2\text{O}$ (Co-POM)^[3] was selected and the nanocapsules were prepared by ionic gelification with Ca^{2+} . The CMC/Co-POM composites were analysed by DLS, SEM, IR (Fig. 1a) and solid state NMR (Fig. 1b) and the quantitative encapsulation of the POMs was monitored with UV/Vis-spectroscopy. The nanocapsules are in a physiological relevant size range (100–200 nm) which renders them promising compounds for cellular uptake studies and antiviral assays as well as for catalytic tests.

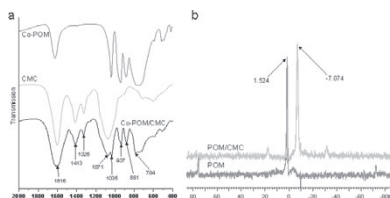


Fig. 1 FT-IR (a) and solid state NMR (b) spectra of Co-POM/CMC composites.

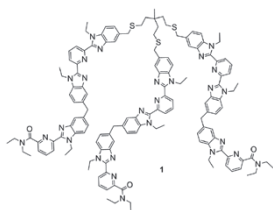
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Thermodynamic investigation of a binuclear podate complexes in solution.

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The formation of polynuclear objects using recognition processes is a great challenge in supramolecular chemistry. Recent research has demonstrated this possibility by creating linear polynuclear helicates. It is even more challenging to be able to establish a good model to understand, control and program the self-assembly process of those polynuclear complexes. The result of more rigorous analysis has shown that those linear helicates present a very weak preorganisation.¹ Is it possible to create polynuclear helicates with enhanced preorganisation? To investigate this question the podate **1**, which incorporated a flexible covalent tripod, has been synthesised. The preliminary results show that it is possible to build a discrete binuclear helicate complex, but what is the effect of the capping unit? Does having a preorganised podate really increase the efficiency to create helicates? This poster presents the results of a thermodynamic study and shows whether preorganised podates are a real improvement compared to the linear ligand strand.



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New Ligands for Photochromic Spin Crossover Complexes

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Our group is active in the synthesis of photochromic ligands.¹ Organic diethylenethene derivatives have been extensively studied because of their potential applications in the field of photochromic and photonic devices.² Various iron(II) tris(diimine), bis(diimine) and bis(terimine) systems on the other hand were reported to undergo a temperature dependent spin crossover process.³ In this context it is highly interesting to use photochromic switches incorporated in diimine or terimine ligands. Assuming that the photoactive opening and closing process of the ligand system changes the ligand field properties sufficiently, we should obtain a system that undergoes a spin crossover upon irradiation with light at room temperature. This concept has already been studied by a few other groups and was called ligand-driven light-induced spin change LD-LISC.^{4,5} The photochromic and magnetic properties of a variety of iron(II) complexes have been studied in solution.

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CO Releasing Properties of *cis-trans*- $[\text{Re}^{\text{II}}(\text{CO})_2\text{Br}_2\text{L}_2]^n$ Complexes: A Feature Modulated by Ligand Variation.Fabio Zobi¹, Alois Degonda¹ and Anna Yu. Bogdanova²

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Carbon monoxide (CO) plays a fundamental role in the circulatory system by improving vasorelaxation and cardiac blood supply. It also suppresses arteriosclerotic lesions associated with chronic graft rejection.^{1,2} An approach to the administration of carbon monoxide is the use of CO-releasing molecules (CO-RMs) based on transition metal carbonyl complexes. To date the *fac*- $[\text{RuCl}(\text{glycinato})(\text{CO})_3]$ complex (CO-RM-3) represents the most promising compound for the CO release *in vivo*.³

In here we show that complexes of the type *cis-trans*- $[\text{Re}^{\text{II}}(\text{CO})_2\text{Br}_2\text{L}_2]^n$ (where L = monodentate ligand)⁴ act as CO-releasing molecules and that under physiologically relevant conditions the rate of CO release is comparable to that of CO-RM-3. No physical stimuli (e.g. UV radiation) are needed in order to elicit dissociation of CO from the metal core. The rate of CO release of *cis-trans*- $[\text{Re}^{\text{II}}(\text{CO})_2\text{Br}_2\text{L}_2]^n$ complexes is pH dependent and can be modulated by ligand variation. The cytoprotective effects of selected molecules against hypoxia-reoxygenation in cardiomyocytes is also described.

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Vitamin B₁₂ Derivatives with Tuneable Properties

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Cobalamines (CbIs) are corrinoids that can adopt different constitutional and electrochemical states.^[1, 2] The accompanying equilibria play important roles for the delivery, the transformation and the reactivity of vitamin B₁₂ (CNCbl) and its organometallic analogues.^[3] We are interested in the design of B₁₂ derivatives with adjustable coordination and redox-properties.

We will present a new class of B₁₂ derivatives with tuneable electrochemical properties, which is designed to disturb the function of the trafficking chaperone *MMACHC* and may alter reactivity in B₁₂ dependant reactions.^[4]

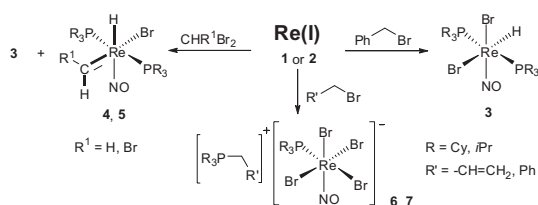
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Facile Synthetic Access to Rhenium(II) Complexes via Activation of Carbon Halogen Bonds

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Rhenium is an extraordinarily redox-active element spanning a wide range of oxidation states from –III to VII.^[1] Among these redox states the 17-electron Re(II) chemistry is particularly interesting due to its potential application in inorganic medicinal chemistry and other material science oriented studies which for instance have demonstrated its potential application in molecular magnetism.^[2] However, Re(II) chemistry is surprisingly scarce with just a few mononuclear Re(II) compounds reported.



In recent years our group focused on the exploration of low valent rhenium hydride chemistry. Lately, it was found that five-coordinate, 16-electron Re(I) hydride complexes [Re(Br)(H)(NO)(PR₃)₂] (R = Cy **1a**, *i*Pr **1b**), derived from easily accessible Re(I) dihydrogen dibromides [Re(Br)₂(NO)(PR₃)₂(η²-H₂)] (R = Cy **2a**, *i*Pr **2b**), exhibited versatile reactivity toward H₂, olefins, *n*BuLi, NHCs carbenes and terminal alkynes. We report here the reactions of **1** and **2** toward alkyl bromides including allyl-, benzylbromide, dibromomethane and bromoform, which are often seen as radical initiators.^[3]

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Spectroscopic and Spectrometric Characterization of the Fungal Metallothionein necluMT1 from *Heliscus lugdunensis*J. Loebus,¹ O. Zerbe,² D. Wesenberg,³ G. J. Krauss,³ E. Freisinger,¹

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Metallothioneins (MTs) are small (2–10 kDa), cysteine-rich (20–35%) proteins, coordinating various essential and toxic metal ions including Zn^{II} and Cd^{II} [1]. The MT necluMT1 from the aquatic fungus *Heliscus lugdunensis* was isolated from a heavy metal polluted mining area (25 μM Cd^{II}, 209 μM Cu^{II}, 40 mM Zn^{II}, 0.04 μM As^{III/V}) [2]. The MT form evidenced *in vivo* by HPLC-MS was shown to coordinate two Cd^{II} ions thereby representing the first native Cd^{II} coordinating protein in fungi [2]. Yet, the strategy, on how the organism and hence the MT differentiates and consequently incorporates the metal ions remains illusive. To elucidate the binding characteristics of necluMT1 for different metal ions flame atomic absorption, UV-vis and CD spectroscopy as well as mass spectrometry (MS) were used. ¹¹³Cd-NMR has provided first evidence of the nature of the Cd^{II} ligands, and titration with Co^{II} allowed the investigation of the metal cluster formation. Moreover the binding stability for Zn^{II} and Cd^{II} ions was evaluated, exhibiting clearly a difference in apparent stability. pH-titration showed that Cd^{II} coordinates significantly stronger to necluMT1 than Zn^{II}. In addition, possible dimerization was investigated via MS and multidimensional NMR spectroscopy in order to understand the putative biological implications of the MT in fungal heavy metal detoxification.

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

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Structure of flame-made vanadia/silica and catalytic behavior in oxidative dehydrogenation of propane

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Catalyst based on supported vanadia showed promising results for the ODH reaction. [1, 2] Here vanadia/silica particles with a specific surface area up to 330 m²g⁻¹ and a V₂O₅ content up to 50 wt.% or V surface density up to 27.6 V nm⁻² were prepared by flame-spray-pyrolysis. Selected samples were tested for the ODH of propane. The as-prepared flame-made catalysts showed dominantly isolated monomeric VO_x surface species for V-loadings exceeding even the typical “monolayer coverage” (2 V nm⁻²) of classic wet-impregnated materials as confirmed by Raman and NMR analysis. The turnoverfrequency of flame-made catalysts decreased with increasing vanadia loading while the presence of small V₂O₅ crystallites seemed to be less critical. The conversion (global activity), however, showed a maximum for the 20 wt.% V₂O₅/SiO₂ (4.6 V nm⁻²) catalyst. Catalysts consisting dominantly of isolated monomeric VO_x-species exhibited higher selectivity to propylene than those where crystalline V₂O₅ prevailed. Nevertheless, the highest propylene yield was measured for catalysts with high V surface density containing both monomeric VO_x and crystalline V₂O₅. Flame-spray-pyrolysis proved to be a very versatile method for synthesis of V₂O₅/SiO₂ catalysts with high dispersion and well defined structure of the active sites.

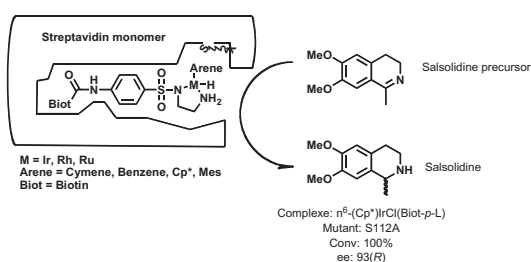
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Artificial Metalloenzymes for Enantioselective Transfer Hydrogenation of Cyclic Imines

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Incorporation of biotinylated racemic three-legged d⁶ piano stool complexes into streptavidin yields artificial metallohydrogenases for transfer hydrogenation reactions of imines. A library of biotinylated complexes was combined with a library of proteins resulting from saturation mutagenesis at position S112. This approach allowed us to optimise the conversion and enantioselectivity for the reduction of the drug-precursor 6,7-dimethoxy-1-methyl-3,4-dihydroisoquinoline. The best variant S112A achieved 100% conversion and an ee up to 96% (*R*) using the S112A mutant. Michaelis-Menten kinetics demonstrate that the metalloenzyme increases the reaction rate 3 fold compared to the free complex (in absence of protein). The X-ray structure of the most active artificial imine reductase will be presented.

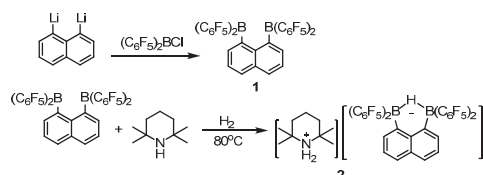


Metal-Free Hydrogen Activation and Hydrogenation of Imines by 1,8-Bis(dipentafluorophenylboryl)naphthalene

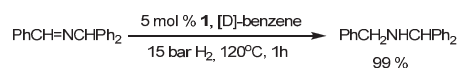
Chunfang Jiang, Olivier Blacque and Heinz Berke*

Anorganisch-chemisches Institut, Universität Zürich, Winterthurerstr.190, 8057 Zürich, Switzerland

The concept of Frustrated Lewis Pairs (FLPs) put forth by D. W. Stephan demonstrated that sterically hindered Lewis donors and acceptors preclude the formation of Lewis acid-base adducts, but as encounter complexes they possess their "unquenched" reactivity enabling activation of small molecules.^[1]



We expected that double Lewis acids (DLAs) would increase the potential activation of FLPs. The DLA, 1,8-bis(dipentafluorophenylboryl)naphthalene **1**, was found to activate H₂ heterolytically under mild condition in the presence of bulky Lewis bases, like 2,2,6,6-tetramethylpiperidine (TMP). Furthermore, compound **1** proved to be a fairly good catalyst for the direct hydrogenation of sterically demanding imines.



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One enzyme two activities: the metal says it all?

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About one third of proteins and perhaps up to half of enzymes are thought to contain a metal crucial for activity. The selectivity of an enzyme for a particular metal and how a metal controls enzymatic activity are two (interrelated) questions of fundamental interest.

Here we propose to investigate an enzyme that has two curiously independent activities *in vivo* according to the nature of catalytic metal bound: a manganese-dependent peptidase activity and a zinc-dependent desuccinylase activity. We are implementing a platform for the directed evolution toward these two separate activities, as a model of how bacteria control intracellular manganese availability and zinc/manganese metallohydrolyase function.

The investigation of the subtle differences in metal coordination leading to different enzymatic activities may be useful for elucidating mechanistic details of interactions between metals and target proteins (e.g. manganese versus zinc uptake of bacteria) as well as how metalloenzymes are controlled by metal-availability. We suggest that these data may also afford insights toward useful de-novo protein design.

Influence of Arene Ligand, Metal Center and the Leaving Group on the *in Vitro* Anticancer Activity of Organometallic Compounds Linked with Carbohydrate Based Ligands

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²Institut des Sciences et Ingénierie Chimiques, Ecole Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland

Metal-arene compounds have demonstrated potential for the development of pharmaceuticals for cancer treatment and different approaches have been explored in recent years. Cancer cells are known to upregulate glycolysis due to increased energy demand, which results in enhanced glucose uptake in cancer cells as compared to healthy cells. Therefore, attaching a carbohydrate functionality to a metal-arene moiety, provides new metal-based compounds that might exploit the biochemical and metabolic functions used for transport and accumulation of sugars in living organisms [1].

The synthesis of a series of anticancer active dihalogenido(η^6 -*p*-cymene)(3,5,6-bicyclophosphite- α -D-glucufuranoside)ruthenium(II) compounds [2] will be presented and the effect of structural variations, such as exchange of the arene, metal center and leaving groups on the anticancer activity will be discussed, especially with regard to interaction with biomolecules such as DNA models and proteins.

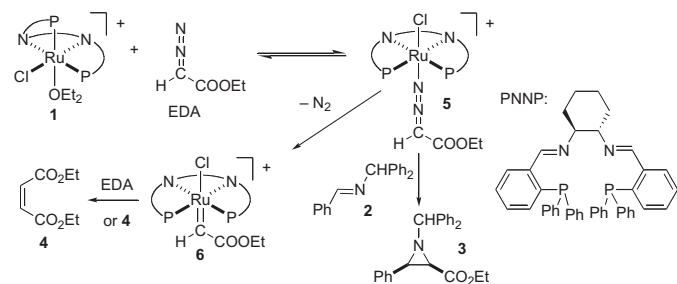
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Ru/PNNP-Catalyzed Asymmetric Imine Aziridination

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Aziridines are important substrates for the synthesis of amino acids as well as building blocks in drugs with antitumor effect^[1]. In this context, enantiomerically pure aziridines are of particular interest. Our group has recently reported the open-cyclic Ru/PNNP catalyst **1** for the aziridination of *N*-benzylidene-1,1-diphenylmethanamine (**2**) with ethyl diazoacetate. Only the *cis*-aziridine **3** is formed with up to 28% yield and 85% ee, along with diethyl maleate (**4**) from the dimerization of EDA^[2].



We have also shown that the formation of aziridine involves the ruthenium EDA complex **5**, which decays to the carbene complex **6** that is an intermediate in maleate formation. Our present goal is to increase the aziridine yield by inhibiting carbene formation and suppressing the formation of diethyl maleate. As this optimization requires additional mechanistic insight, we are performing kinetic studies by NMR spectroscopy and by stopped-flow methods, whose results will be reported.

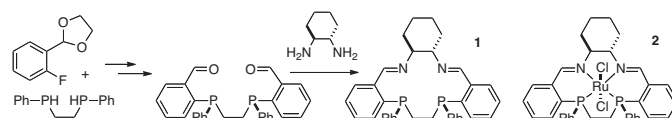
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Chiral macrocyclic PNNP ligands

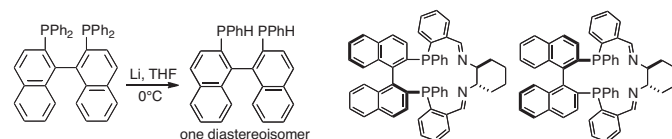
A. Schira, A. Mezzetti*

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Chiral macrocyclic ligands containing P donors are highly interesting for asymmetric catalysis as they are expected to form stable, conformationally rigid complexes. We have recently reported the first chiral macrocyclic PNNP ligand (**1**), which is easily reduced to the diamino analogue, and prepared their ruthenium(II) dichloro complexes:²



The diimino complex **2** catalyzes the transfer hydrogenation of acetophenone to 1-phenylethanol with modest enantioselectivity (30% ee). The low enantioselection is not surprising in view of the pseudo *meso* relationship between the P atoms. Therefore our efforts are now directed toward the synthesis of C₂-symmetric macrocycles with the procedure already used for bis(diphenylphosphino)alkanes. To this goal, we have prepared the secondary analogue of BINAP, which will be used to prepare 16- and 17-membered PNNP macrocycles, whose complexes and catalytic applications will be presented.



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The Nano-Catalyst CuGa₂O₄

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The impact of oxidic nanostructured materials on new technologies has continuously increased over the last years.^[1] Therefore, we develop new and straight forward synthetic methods for functional ternary oxides, such as copper substituted zinc gallium oxides^[2] or CuGa₂O₄. Up to date, even the bulk material has rarely been accessed with conventional methods.^[3,4]

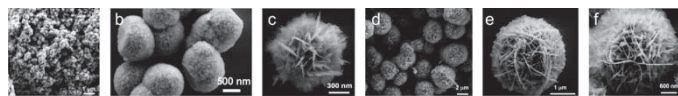


Figure 1. Representative SEM images of microwave-assisted and conventional hydrothermally synthesized CuGa₂O₄ at different pH.

However, we obtained the hitherto rather unexplored inverse spinel CuGa₂O₄ on a minute scale with a microwave-assisted approach. This state-of-the-art technique also offered nanostructured materials as an additional benefit. Within the "inert" gallium sublattice, the Cu²⁺ cations are distributed on tetra- and octahedral sites and they can reductively be transferred into catalytic nanoscale Cu centers that are embedded in the gallium matrix. These copper-containing ternary oxides are under investigation for methanol steam reforming as well as for photocatalytic reactions. In addition to the analytical, magnetic and catalytic characterization of the microwave-synthesized CuGa₂O₄ spinel particles, we also tested their applicability in gas sensors.

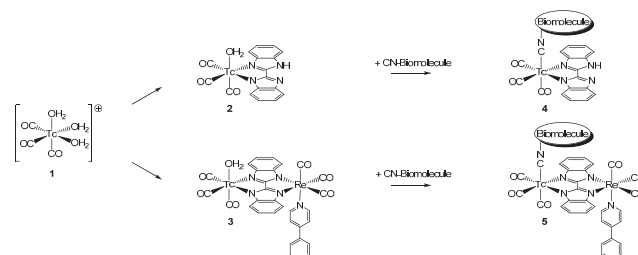
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The Development of Model Systems for Dual Modality Imaging Agents by Applying the [2+1] Approach for the *fac*-[^{99m}Tc(CO)₃]⁺ Core

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The combination of a radionuclide and fluorescent ligands can be used to synthesize new compounds with potential as dual modality imaging agents.¹ On that way it is possible to take advantage of both properties. Aiming at the synthesis of target specific radio-fluorescence labels, the [2+1] approach was applied. In this two-step procedure a fluorescent bidentate ligand is first coordinated to the common precursor **1**.² In a second step a targeting function (peptide) is attached to the metal complex by coordination of an isonitrile group of the biological vector. 2,2'-Bisbenzimidazole (BiBzIm) and [Re(CO)₃(BiBzIm)(4-PhPy)] (4-PhPy = 4-Phenylpyridine) were chosen as fluorescent ligands due to their interesting fluorescence properties. The reaction of BiBzIm and [Re(CO)₃(BiBzIm)(4-PhPy)] yield compound **2** and **3** respectively in very good yield. As a biological vector a heptapeptide and benzyl isonitrile as a model compound were used. The reaction of **2** and **3** with this monodentate ligands gave the fluorescent complexes **4** and **5**. As model complexes **4** and **5** containing benzyl isonitrile have been verified on the macroscopic level by synthesizing the ⁹⁹Tc and Re complexes.

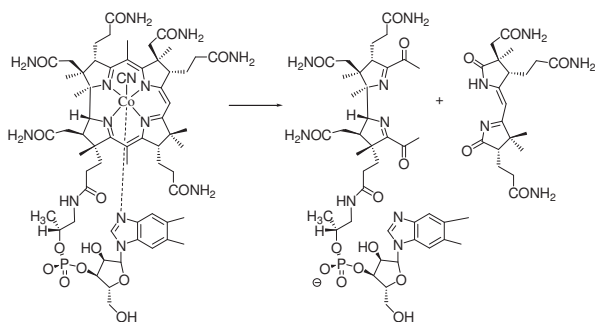


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One-pot synthesis of metal-free AD and BC fragments of vitamin B12René M. Oetterli, Christian Buchwalder, Roger Alberto, Felix H. Zelder¹¹University of Zurich, Winterthurerstr. 190, 8057 Zurich, Switzerland

The synthesis of 'met-balamins' (i.e. B12 derivatives that contain other metals than cobalt) is an unsolved chemical challenge. Based on the work of Kräutler *et al.* [1] we developed a method to cleave B12 photooxidatively into its metal-free AD and BC fragments [2]. These building blocks are structurally related to the "westside" and "eastside" fragments used in the first total synthesis of B12 [3] and can be considered as promising precursors to afford 'met-balamins'.

Synthesis and physico-chemical properties of the fragments, as well as recent progress are presented.



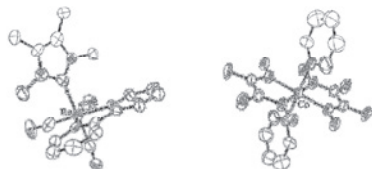
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New Rhenium and Cobalt Complexes for improved photocatalytic H₂ production

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The photocatalytic H₂ generation by the Re/Co based system in DMF as reported by our group^[1] gave high TONs in Re (photosensitizer, PS) and Co (water reducing catalyst, WRC). By modifying the PS, we recently found that the H₂ evolving reaction can be done in pure water. Still, the catalytic system in DMF and in water needs improvements with respect to complex stabilities of the Co WRC and better physico-chemical properties of the PS. The PS should absorb light in the more visible region and the WRC not undergo deterioration during catalysis. To achieve higher TONs, TOFs and long term stability, the Re and the Co complex are to be modified.



We have synthesized novel [ReL(bipy)(CO)₃]⁽⁴⁺⁾ complexes with different monodentate ligands "L" for lifting the HOMO involved in MLCT, to prolong life time of the excited state and PS stability. A complex with L=NHC is shown in the figure. The dmgH ligand of the WRC as used in the original systems was also modified by replacing the two -CH₃ in dmgH with other groups. We will present a series of new Re based PSs, Co based WRCs and discuss the efficiency of the new complexes in photocatalytic H₂ formation.

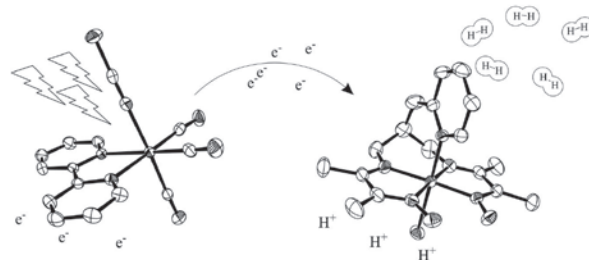
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Mechanistic investigation on cobalt/rhenium based photosystems for catalytic H₂ production

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We reported a mechanistic study for cobalt and rhenium based photocatalytic H₂ production in DMF.^[1] Further mechanistic and synthetic investigation of the catalytic cycle revealed highly significant results for the further development of such systems in aqueous solution, the aim for a final application.



Time resolved FT-IR spectra were recorded for different photosensitizers and different solvents.^[2,3] For the better understanding of the cobalt cycle, in situ UV/VIS spectra and hydrogen evolution measurements were performed. Mechanistic and synthetic insights will be presented.

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New CeO₂-based catalysts for the SCR of NO with NH₃Maria Casapu¹, Oliver Kröcher¹, Martin Elsener¹¹Paul Scherrer Institute, 5232 Villigen, Switzerland

Among the various technologies which have been proposed for the elimination of NO_x emissions, the selective catalytic reduction (SCR) with NH₃ is believed to be the most suitable to fulfill this task. However, the catalytic systems proposed so far as being the most promising still have serious problems. The conventional vanadia-based catalysts have a very low thermal stability due to the volatilization of vanadia species above 650 °C [1]. The limited thermal stability under humid conditions represents also a problem for metal-exchanged zeolite SCR catalysts [2].

The catalyst proposed here, as an alternative to the vanadia-based and metal-exchanged zeolite systems, is composed mainly of niobium oxide and cerium oxide. The NO_x removal performance obtained with this new catalytic system is very similar to that determined with a conventional V₂O₅/WO₃-TiO₂ catalyst. At 250 °C 72% of NO is converted to N₂, whereas almost full conversion is achieved between 300 and 450 °C. Besides, the concentration of the undesired side-product N₂O remained below 15 ppm during the SCR process even at 550 °C. The catalyst possesses also a very good thermal stability and high sulfur poisoning resistance.

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Polymerization of arylmethyl alcohols using tungsten oxide nanoparticles synthesized in a nonaqueous sol-gel process

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Hard and brittle monolithic tungsten oxide-polybenzylene nanohybrids can be obtained in one step by reacting tungsten iso-propoxide with benzyl alcohol. First, crystalline tungsten oxide $W_{18}O_{49}$ nanowires with a diameter of about 1.5 nm form via ether elimination reaction. Subsequently, the large residue of the benzyl alcohol is transformed to dibenzyl ether, which then polymerizes to polybenzylene, incorporating the nanoparticles into the forming polymer. The catalytic effect of the tungsten oxide nanowires on the quantitative formation of polybenzylene is proven by reacting them in different concentrations and at varying temperatures either with benzyl alcohol or with dibenzyl ether. Complete polymerization of benzyl alcohol is achieved within just 30 min by using a particle-to-monomer molar ratio of 1:115 at 160°C. Further studies show that the tungsten oxide nanoparticles are able to completely polymerize various other alcohols with an aryl methanol group.

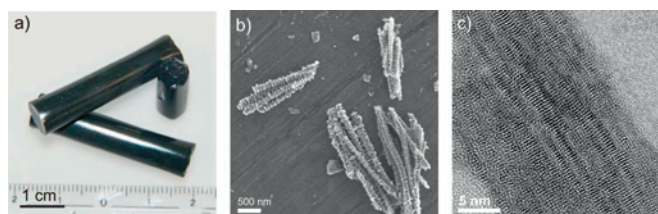


Figure 1: a) Photograph of the as-synthesized hybrid material. b) SEM image of isolated tungsten oxide particles showing rod-like features with rough surfaces. The HRTEM image (c) reveals an internal structure of thin nanowires with diameters of 1.3 to 1.5 nm.

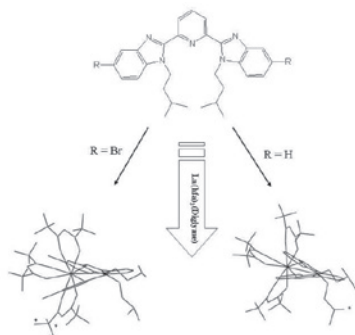
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SYNTHESIS AND CHARACTERIZATION OF NOVEL TRIDENTATE RECEPTORS FOR THE PREPARATION OF LUMINESCENT LANTHANIDE-CONTAINING MATERIALS

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In recent years, considerable effort has been focused on the development of new luminescent materials based on lanthanide metal-ion complexes.¹ A new synthetic strategy has been developed to obtain bent aromatic tridentate 2,6-bis(benzimidazol-2'-yl)pyridine cores functionalized with bromine atoms. A series of new lanthanide complexes has been synthesised by treating the bromo-substituted tridentate receptors with fluorinated lanthanide β -diketonates $[Ln(hfa)_3(diglyme)]$. In order to understand the effect of the bromine substituents on the stability and on the electronic and photophysical properties of these complexes, the analogous unsubstituted complexes have been prepared. The thermodynamic, X-ray crystal diffraction and photophysical data collected for these two families of lanthanide complexes will be presented and interpreted.



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Study of Zinc Oxide Nanoparticle Crystallization in Benzyl Alcohol

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The interest in high quality nanoparticles with well defined sizes and shapes increased rapidly over the last decade due to their fascinating and unique properties. Coming along with this increasing demand chemists all over the world face the challenge of developing rational synthetic strategies to various kinds, sizes and shapes of nanomaterials. Within this task solution-based processes have shown to be particularly versatile with respect to control the particle morphology and composition, and thus to establish general principles for rational synthesis protocols. However, this development of general rules for a well-directed production of nanoparticles demands studies of fundamental principles during particle formation including the underlying reaction and crystallization mechanisms.

The current contribution will show a study on the zinc oxide nanoparticle evolution within the synthesis in benzyl alcohol. Zinc oxide, as a material with great technological relevance, shows a variety of different particle morphologies when synthesized with different solution-based processes. Up to now there are very few studies about the basic mechanistic principles leading to these differences in morphology. Our work will give a deeper insight into the formation of zinc oxide fans obtained in benzyl alcohol and show the whole process being a particle based mechanism.

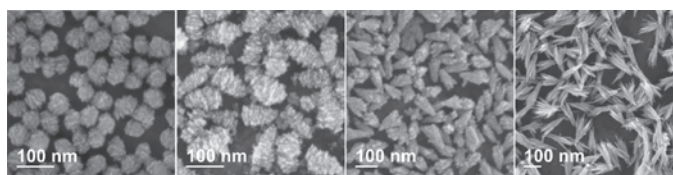


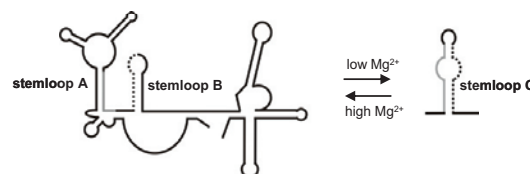
Figure 1: SEM images of ZnO particles after a reaction time of 3, 10, 20 and 120 min.

Structural Investigations on a Mg^{2+} Riboswitch by NMR

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The intracellular Mg^{2+} level in *Salmonella enterica* can be autonomously regulated by a riboswitch sequence in the 5'-UTR of the Mg^{2+} -influx mediator *mgfA*. At high Mg^{2+} concentration the transcription stops within the 5'-UTR before the coding region of the *mgfA* gene is reached. This down regulation of the gene is achieved by a structural change induced by specific Mg^{2+} recognition. By alternative base pairing in distinct parts of the sequence, the 5'-UTR switches between two predicted stemloop structures (Figure).^[1] According to this model, stemloop C stands out as an antiterminator loop that promotes the transcription of the full length gene.



Here we present our NMR studies on the structure and the Mg^{2+} binding properties of a shortened stemloop C construct. To gain insight on the dynamics of the stemloop equilibrium we also examined a construct constituting the shortest necessary sequence to perform the switch between stemloop B and stemloop C. Here we focus on the observation of imino resonances to investigate the base pairing pattern.

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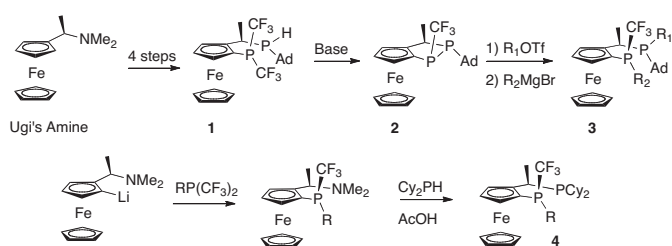
Financial support by the Swiss National Science Foundation and the University of Zürich is gratefully acknowledged.

Bis(trifluoromethyl)phosphines as Precursors for the Synthesis of P-stereogenic Monotrifluoromethylated Phosphine Ligands

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Although Josiphos-type ligands are a well established class of compounds, they do not include examples of trifluoromethyl substituted phosphines. Recently, we discovered that one of the CF₃ groups in **1** undergoes intramolecular nucleophilic substitution by the secondary phosphine giving the cyclic diphosphine **2**.^[1] Alkylation and subsequent nucleophilic ring opening of the cyclic structure **2** yields the twofold P-stereogenic diphosphine **3**. From commercially available Ugi's amine, phosphine **1** can be synthesized in good yield.^[2] Also intermolecular versions of this reaction were investigated. Thus, starting from lithiated Ugi's amine, we were able to synthesize monotrifluoromethylated bidentate ligands **4** in two steps. The bidentate ligands **3** and **4** showed high activities and enantioselectivities in the Rh-catalyzed hydrogenation.



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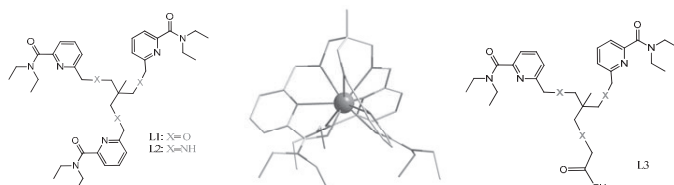
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Complexes of f-elements with short tripodal ligands: Investigation of their potential for sensing applications.

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Recently, we have reported on short tripodal organic receptors providing tetranuclear complexes with lanthanides [1]. However, a small modification of the ligand backbone leads to the formation of monometallic helicates. In this work we present our investigations of these symmetrical and unsymmetrical systems. First, the multistep synthesis of two symmetric tripodal ligands L1 and L2 has been optimized. The lanthanide complexation is achieved by the coordination units of the type 'O-N-O' or 'N-N-O' respectively. Resulting monometallic helicates are characterized by X-ray crystallography. The luminescent and thermodynamic properties will be also discussed.



The second part deals with the study of unsymmetrical tripodal ligands derived from L1. Their lanthanide complexes are investigated in view of their potential applications as relaxation probes or sensors for anions.

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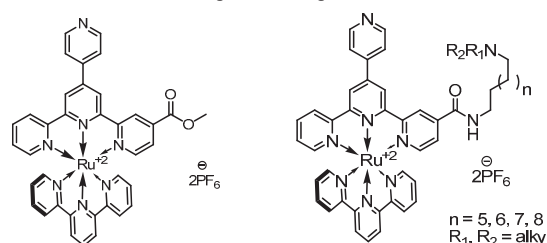
Molecular computing

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There are known compounds which 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 it is 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.



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Synthesis of Aqueous Gold Nanoparticles and their Transfer into Ionic Liquids

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In recent years, ionic liquids (IL) have received increasing attention as reaction media because of their properties which, for number of cases, are more favorable than conventional organic solvents in terms of higher polarity, negligible vapor pressure, greater ionic conductivity and an increased thermal stability.¹ The synthesis of gold nanoparticles, GNPs, in room-temperature ionic liquids is not a straightforward process, as growing evidence demonstrates that these class of nanoparticles are susceptible to rapid aggregation, particularly in the absence of stabilizers² or functionalized task-specific ILs.³ The use of imidazolium based ionic liquid functionalized polymers allows the transfer of nanoparticles, NPs, from aqueous solutions to ionic liquids by anion exchange. Moreover, excellent results were also obtained with palladium- and platinum-based NPs.⁴ Consequently, GNP containing solutions were prepared using new water soluble ionic polymers as stabilizers and further transferred in several ionic liquids: the GNPs were finally characterized by UV-VIS and transmission electron microscopy.

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Evolution of the hierarchical order in nanostructured colloids with the thermal treatmentEugenio Otal^{1,2}, Myriam Aguirre², Anke Weidenkaff²¹ Empa, Swiss Federal Laboratories for Materials Testing and Research, Solid State Chemistry and Catalysis, Ueberlandstr. 129, CH-8600, Dübendorf, Switzerland² CINSO CITEFA CONICET, San Juan Bautista de La Salle 4397 (B1603ALO) Villa Martelli, Buenos Aires - Argentina

The ZnO wurzite nanocrystals show a high dipolar moment [1], this dipolar moment is the reason of different nanostructure formation [2-4].

In this work we study the changes in the morphology and hierarchical structure of spherical colloids obtained by forced hydrolysis methods and thermally treated to different temperatures. The evolution of the hierarchical structure is a convolution of the dipolar moments of the nanocrystals and the welding of the nanocrystals [5]. At low temperature, the dipolar moment of the nanocrystals are strong and the colloids will show a texture due to the orientation of the nanocrystals. Otherwise, at high temperature, the welding of the nanocrystals will tend to form a microcrystal from every spherical colloid.

The evolution of the morphology of the colloids will be followed by scanning electron microscopy and the changes in the nanocrystals average orientation will be followed by diffraction and high resolution electron microscopy.

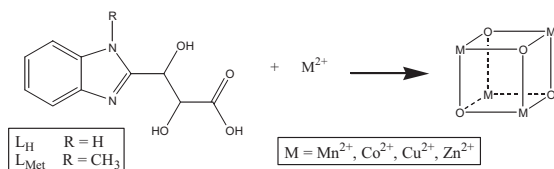
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Tertranuclear complexes of transition metals with ligands containing benzimidazole and carboxylic acid groups

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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 [2] have been reported to generate cubane-like structures with different transition metal ions [3]. One of the two hydroxyl groups could be deprotonated and serves as a bridge between three metal ions in the core of the cubane (see figure). We present here the complexation of the (2*R*,3*S*)-3-(1*H*-benzimidazol-2-yl)-2,3-dihydroxypropanoic acid ligand, where one benzimidazole is replaced by a carboxylate with Mn²⁺, Co²⁺, Cu²⁺ and Zn²⁺ metal ions. The formation of M₃L₄ species is observed by mass spectrometry, using the Pseudoisotopic Molecule Mass Spectrometry method [4]. A solution of two similar ligands, one with R = H and the other one with R = CH₃ is used to complex the metal ions. The M₃L₄ species is believed to adopt a cubane-like structure.



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Optimization of single crystal Ca₃Co₄O₉ flux growth through *in-situ* optical observationMoser, D.^{1,2}, Shkabko, A.¹, Karvonen, L.^{1,3}, Ota, E.¹, Yoon, S.¹, Hulliger, J.², Weidenkaff, A.^{1,2}¹Laboratory for Solid State Chemistry and Catalysis, EMPA, CH-8600 Dübendorf, Switzerland.²Department of Chemistry & Biochemistry, University of Berne, CH-3012 Berne, Switzerland³Laboratory of Inorganic Chemistry, Aalto University School of Science and Technology, FI-00076, Aalto, Finland.

A number of oxides consisting of CoO₂ conducting layers having CdI₂ type of structure and insulating layers of rocksalt structure have gained interest due to their promising thermoelectric properties. Thermoelectric devices based on oxide materials are resistant towards high-temperature oxidizing atmospheres and therefore suitable for the waste heat recovery *e.g.* from car engine exhaust.

[Ca₂CoO_{3-δ}]_{0.62}CoO₂ is a promising *p*-type material forming plate-shape crystallites. Figure of merit (ZT) for single crystalline samples have been reported to reach 0.87 at 973 K. ¹ Since electrical conductivity exhibits pronounced anisotropy parallel and perpendicular to the layered structure, ² parallel alignments of the crystallite platelets is seen as a promising route to improve thermoelectric properties of a polycrystalline leg material.

For aligning the platelets by uniaxial pressing, single crystallites with large dimensions are requested. In our work, an *in-situ* optical observation of the crystal growth from flux is used in order to systematically optimize the temperature program and time required for crystallization. Technique and analytical strategies together with results are highlighted.

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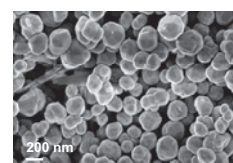
Nanomaterials for Photocatalytic Applications

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The photocatalytic splitting of water into H₂ and O₂ (artificial photosynthesis) is a much sought-after goal of modern inorganic chemistry.[1] The photocatalytic degradation of organic pollutants in water is an efficient option to remove residual organic contaminants in sewage treatment plants. BiVO₄ in its monoclinic modification and SnWO₄ are very promising visible-light-driven photocatalysts for degradation of organic pollutants and for the O₂-production half-reaction of water splitting.[2]

Here, we report on a facile hydrothermal route to monoclinic BiVO₄ nanoparticles with high surface area in the presence of potassium sulfate as an inorganic ionic additive.[3] We discuss the effect on the particle morphology and crystallinity on the catalytic performance for the decomposition of organic compounds and photocatalytic O₂ evolution, respectively. Also we present a low temperature synthesis of tin tungstate nanoparticles and their photocatalytic properties.

**Figure 1:** BiVO₄ nanoparticles

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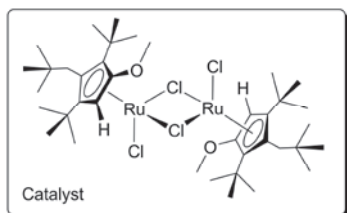
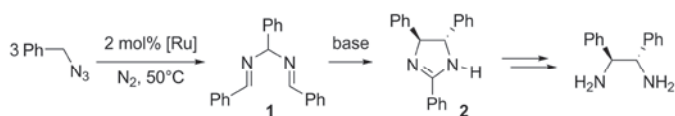
Ruthenium-Catalyzed Synthesis of Triaryl-2,4-diazapenta-1,4-dienes from Benzyl Azides

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Triphenyl-2,4-diazapenta-1,4-dienes, also called "hydrobenzamide" **1**, is a useful organic precursor, which can be converted into "iso-amarine" **2** or "amarine" via reported procedures (see Scheme). Hydrobenzamide is accessible from the reaction of benzaldehyde with liquid ammonia or also by flash vacuum pyrolysis of benzyl azides. However, these procedures suffer from harsh conditions.

Our group has developed a new ruthenium based catalyst, $[\text{RuCp}^*\text{Cl}_2]_2$, an analogue of the well-known complex $[\text{RuCp}^*\text{Cl}_2]_2$. We report a novel catalytic application of $[\text{RuCp}^*\text{Cl}_2]_2$: the formation of triaryl-2,4-diazapenta-1,4-dienes under mild conditions from benzyl azide as starting material (Scheme).



In Situ High Pressure Hydrogen Generation from Formic Acid with Homogeneous and Heterogeneous Ruthenium Catalysts

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As an energy carrier, hydrogen holds the potential to provide clean, safe and affordable energy for a wide range of applications. Formic acid is well known source of hydrogen, having several advantages in terms of weight and safety issues (Table 1).

Table 1. Volumetric hydrogen densities for different storage systems.

Storage	Pressure	Temperature	H "density"
hydrogen gas	350 bar	25 °C	28 g/L
liquid hydrogen	1 bar	-253 °C	70 ^a g/L
formic acid	1 bar	25 °C	53 g/L

^a about 20 % of H₂ is lost to cool down/liquefy

Viable systems, based on the selective homogeneous catalytic decomposition of formic acid into H₂ and CO₂, have been proposed recently.^[1-3] The catalytically active species are formed *in situ* from RuCl₃ and TPPTS in aqueous solution. We present our results on the effect of different water-soluble sulfonated phosphine ligands on this homogeneous catalytic system. For small, mobile and portable applications, immobilized/solidified catalysts for hydrogen production from formic acid have also been investigated.^[4]

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

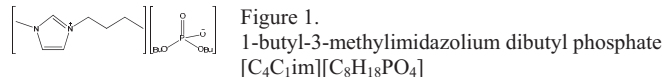
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Formic acid for hydrogen storage: hydrogen production and separation in ionic liquid media

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H₂ has the potential to become an important alternative energy carrier and fuel if the storage and delivery problems associated with its use are solved. Formic acid as a hydrogen storage material has several advantages including a high flash point and high volumetric hydrogen density. H₂ generation from HCOOH has been intensively studied recently.[1] The process could be enhanced by using ionic liquids (ILs), the catalyst can be well immobilized in ILs, and the generated CO₂ and H₂ gas mixture can be separated based on the very different solubilities in ionic liquids.[2] The use of task-specific ionic liquid for HCOOH decomposition has been presented recently.[3] In this work we present our results on the H₂ generation from HCOOH in ILs. Notably, 1-butyl-3-methylimidazolium dibutyl phosphate (Fig. 1) has been shown to be an appropriate reaction media for the H₂ generation.



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

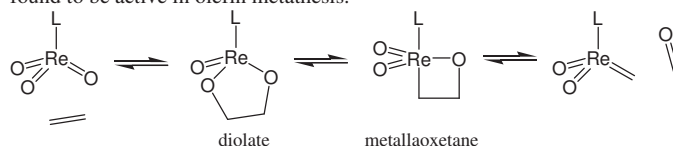
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Self-Activating Rhenium-based metathesis catalysts

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The system Re₂O₇/Al₂O₃ or its related system, MeReO₃/Al₂O₃-SiO₂, is an effective heterogeneous catalyst for carrying out olefin metathesis at ambient temperature. Among plenty of mechanistic investigations reported in the literature, a pseudo-Wittig mechanism is considered the most promising one. Our earlier experimental and computational studies^{1,2,3,4} on high-valent rhenium trioxo complexes in the gas phase also supported the pseudo-Wittig mechanism and furthermore elucidated the structural requirements for a self-activating homogeneous metathesis catalyst. In those works, qualitative molecular orbital arguments, as well as high-level quantum chemical calculations, supported the experimental observation that dissociation of a rhenium diolate complex to an aldehyde and a rhenium carbene (via rearrangement to a metallaoxetane) would be energetically competitive with the expected dissociation to an olefin and a rhenium trioxo complex when (i) the rhenium center is four-coordinate, (ii) the supporting ligand is a σ-donor ligand, and (iii) the σ-donor is electron-deficient. Accordingly, we synthesized and characterized a series of high-valent rhenium trioxo complexes which fulfill the list of structural conditions delineated in the above-mentioned. They were found to be active in olefin metathesis.



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Preferential Pt and Pd deposition on K/Al₂O₃ NO_x storage-reduction catalystsRobert Büchel^{1,2}, Sotiris E. Pratsinis¹, Alfons Baiker²¹ Particle Technology Laboratory, ²Institute for Chemical and Bioengineering, ETH Zurich, CH-8092 Zürich, Switzerland

To decrease automobile emission of lean engines, NO_x storage-reduction (NSR) catalysts have been developed. These catalysts trap NO_x under fuel lean conditions on an alkali or alkaline-earth metal in the form of metal-nitrates, which are subsequently reduced (decomposed) under rich conditions. As noble metal, typically Pt or Pd is used. With a two flame spray pyrolysis (FSP) unit [1], Pt/Pd/K/Al₂O₃-catalysts were prepared with Pd and Pt clusters selectively deposited on the K-storage component or the alumina support and the effect of the noble metal was investigated. Both noble metals were selectively deposited [2] on the K-storage component or the Al-support in various combinations to examine the best location of the noble metal and the most favorable Pt/Pd weight ratio.

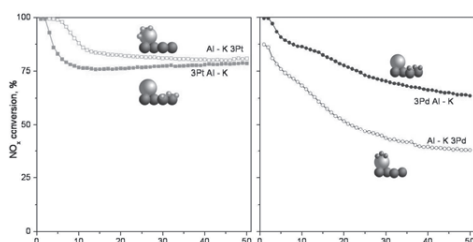
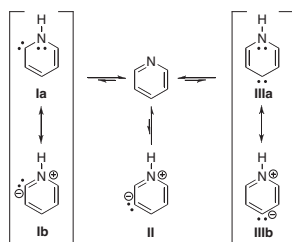


Fig. 1: Pt performed better when supported on the K-component while Pd deposited on Al₂O₃ showed higher NO_x reduction performance.

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Pyridinium-derived carbene ligands:**Normal, abnormal and remote bonding in pyridylidene complexes**Oliver Schuster¹¹University of Fribourg, Ch. du Musée 9, CH-1700 Fribourg, Switzerland

While the term N-heterocyclic carbene (NHC) is widely employed as a synonym for 2-imidazolylidenes and related ligands, there is a growing interest in NHC ligands with reduced heteroatom stabilisation.^[1] We are particularly interested in the complex chemistry of pyridinium-derived carbenes which offer a variety of bonding modes.



Herein we report the first comparative investigation of isomeric normal (I), abnormal (II) and remote (III) pyridylidene complexes. Both experimental and computational studies have been carried out in order to assess the nature of the metal carbon bond.^[2]

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Mixed-Linker MOFs Based on MIL-53(Al)

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The MIXMOF concept is a new strategy to tune the properties of a MOF by incorporation of two different linker molecules into the framework structure. This concept has been applied to the metal-organic framework compound MIL-53(Al). The random incorporation of benzene-1,4-dicarboxylate (BDC) and 2-aminobenzene-1,4-dicarboxylate (ABDC) and its influence on the thermal stability were proven using several complementary techniques.

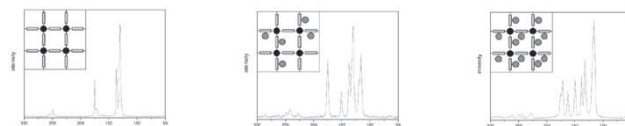


Figure 1: MAS NMR of mixed MIL-53MOF with different degrees of substitution

It could be proven by XRD that the stepwise substitution of BDC by ABDC leads to an isorecticular mixed linker MOF bearing the same framework structure like the pure MIL-53(Al). The incorporation of the functionalized ABDC linker molecule was proven by solid state MAS-NMR (Figure 1) and ATR-IR. TG and DTG measurements showed that the thermal stability of the mixed-linker MOFs is dependent on the composition and that it could be tuned by varying the BDC/ABDC ratio.

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Azulene Based Metal-Organic Frameworks for Strong Binding of H₂Samir Barman¹, Hiroyasu Furukawa², Olivier Blacque¹, Koushik Venkatesan¹, Omar M. Yaghi² and Heinz Berke¹¹Anorganisch-Chemisches Institut, Universität Zurich, Winterthurerstrasse 190, CH-8057, Zurich, Switzerland²Center for Reticular Chemistry, Department of Chemistry and Biochemistry, University of California-Los Angeles, 607 Charles E. Young Drive East, Los Angeles, California 90095

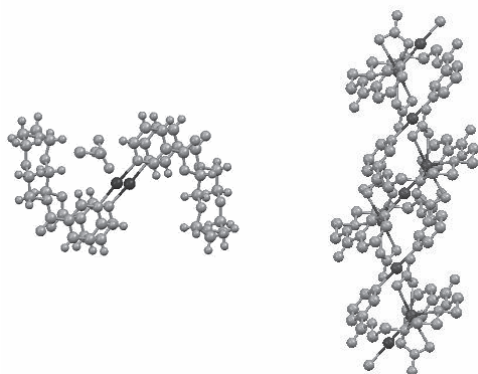
In the last few decades an extensive research focus have been devoted towards finding a suitable Porous Coordination Polymers (PCPs) or Metal-Organic Frameworks (MOFs) as an on-board hydrogen storage system.^[1] Based on theoretical and experimental studies it has become pertinent that the increase in the binding energy of the materials up to 15-20 kJ/mol is the most crucial step towards designing the ambient temperature storage systems.^[2]

Azulenes constitute dipolar aromatic systems and we anticipated that these contained in a MOF could contribute to build up of columbic fields required for the polarization and polarized binding of H₂. Therefore, we strove to prepared MOFs namely MOF-646 [Zn₄O(link)₃] (**icy** net) and MOF-645 [Zn₅(OH)₂(link)₄] (**bcu** net) comprised of polarized angular 1,3-azulenedicarboxylate and Zn²⁺. Indeed, the guest free MOF-646 demonstrates excellent volumetric H₂ uptake of 20.9 g L⁻¹ at 77 K and 1 bar, and more interestingly the isosteric heat of adsorption was as high as 7 kJ mol⁻¹ even at 13.3 mg g⁻¹ of H₂ loading. This reveals the significant impact of internally polarized azulene backbone to stabilize H₂ molecules in the framework.

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Synthesis of New Silver Compounds with Nicotinic acid DerivativesInès Chevrier, Katharina M. Fromm¹University of Fribourg, Chemin du Musée 9, CH-1700 Fribourg,
Switzerland

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: metallacycles and, under special conditions, chain structures are obtained.



Finally we propose the development of complexes with longer spacers to study the possible formation of liquid crystals.

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