

Computational Chemistry

113

Progress on Computation of Molecular Parity Violation Using the Coupled-Cluster Linear Response ApproachLuboš Horný, Martin Quack and Martin Willeke

Physical Chemistry, ETH Hönggerberg, CH-8093 Zürich, Switzerland

Progress has been made in the theoretical description of molecular-parity violation over the last decade¹⁻⁴, and its possible implications for the origin of molecular chirality and biomolecular homochirality, as well as possible experiments on molecular parity violation are of fundamental interest⁵⁻⁸. Following our previous work^{1,2}, we report new developments to computation of molecular parity-violation potential E_{pv} . Particularly, we seek for an effective and controllable way to examine the importance of electron correlation for the parity-violating potential. Since, the coupled cluster method⁹ has proved to be a most rigorous approach to account for the electron correlation in molecules, we show how the linear response function¹⁰ of the coupled cluster wavefunction provides the contributions to E_{pv} . We discuss the algorithms and computational steps, which are being developed, to achieve the effective coding of this property. The results will be important for future accurate analyses of experimental results⁷.

- [1] A. Bakasov, T. K. Ha and M. Quack, *J. Chem. Phys.*, **1998**, 109, 7263.
 [2] R. Berger and M. Quack, *J. Chem. Phys.*, **2000**, 112, 3148.
 [3] R. Berger, In *Relativistic Electronic Structure Theory, Vol. 2*, **2005**, 188.
 [4] M. Quack and J. Stohner, *Chimia*, **2005**, 59, 530.
 [5] M. Quack, *Angew. Chem. Intl. Ed. (Engl.)* **1989**, 28, 571.
 [6] M. Quack, *Angew. Chem. Intl. Ed. (Engl.)*, **2002**, 41, 4618.
 [7] M. Quack, In *Modelling Molecular Structure and Reactivity in Biological Systems, Proc. 7th WATOC Congress, Cape Town January 2005*, **2006**, 3 (Royal Society of Chemistry, Cambridge).
 [8] M. Quack, *Chem. Phys. Lett.*, **1986**, 132, 147.
 [9] J. Paldus, In *Methods in Computational Physics*, **1992**, 99.
 [10] O. Christiansen, P. Jørgensen, and C. Hättig, *Int. J. Quant. Chem.* **1998**, 68, 1.

Inorganic and Coordination Chemistry

115

Small Molecule Activation and Generation by Early Transition Metal ComplexesChristopher C. Cummins

Chemistry Department, Massachusetts Institute of Technology, Cambridge, MA 02139-4307 (USA)

Computational Chemistry

114

Ab Initio Study of Some Persistent Nitroxide RadicalsLuboš Horný, Fabio Mariotti and Martin Quack

Physical Chemistry, ETH Hönggerberg, CH-8093 Zürich, Switzerland

Stable free radicals have a variety of applications. Particularly, the aminoxyl group is frequently used in spin-labeling experiments. Nitroxides may also exhibit intriguing chiral and magnetic properties and must be of interest for studies of molecular parity violation^{1,2}. Three different groups of persistent NO-radicals :i) acyclic³⁻⁵ :dimethylaminoxyl (Me_2NO), bis(trifluoromethyl) aminoxyl (CF_3)₂NO, and [(CMe₃)₂NO]; ii) cyclic⁶⁻⁸ : aziridine-N-oxyl, azetidine-N-oxyl, pyrrolidine-N-oxyl and piperidine-N-oxyl; and iii) nitronyl nitroxides⁹. We used density functional and *ab initio* (MP2, coupled cluster) methods. The molecular structures, harmonic vibrational frequencies, and inversion barriers are reported and compared with experiment when available. The cyclic species exhibit considerable inversion barriers of \sim hc 3500 cm⁻¹ compared to only \sim hc 500 cm⁻¹ for the acyclic ones. Nitronyl nitroxides are theoretically characterized for the first time in our work. We discuss the possibilities that some of the chiral derivatives may be dominated by molecular parity violation in their dynamics.

- [1] M. Quack, *Angew. Chem. Intl. Ed. (Engl.)* **1989**, 28, 571.
 [2] M. Quack, *Angew. Chem. Intl. Ed. (Engl.)*, **2002**, 41, 4618.
 [3] P. W. Harland, *Int. J. Mass Spect. & Ion Physics* **1977**, 25, 61.
 [4] C. Chatgillaloglu et al., *J. Phys. Chem.* **1980**, 84, 3597.
 [5] D. A. C. Compton, C. Chatgillaloglu, H. H. Mantsch, K. U. Ingold, *J. Phys. Chem.* **1981**, 85, 3093.
 [6] I. Komaromi, J. M. J. Tronchet, *J. Phys. Chem.* **1995**, 99, 10213.
 [7] A. Ebrahimi et al., *J. Mol. Struct. (THEOCHEM)* **2001**, 535, 247.
 [8] I. Novak et al., *J. Org. Chem.*, **2004**, 69, 7628.
 [9] C. Hirel, J. Pecaut, S. Choua, Ph. Turek, D. B. Amabilino, J. Veciana, P. Rey, *Eur. J. Org. Chem.* **2005**, 348.

Inorganic and Coordination Chemistry

116

Chemistry with Aminyl Radical Complexes and Related Compounds: New Perspectives for CatalysisHansjörg Grützmacher

Laboratorium für Anorganische Chemie, ETH Hönggerberg, HCI CH-8093 Zürich, Switzerland

Computational Chemistry

113

Progress on Computation of Molecular Parity Violation Using the Coupled-Cluster Linear Response ApproachLuboš Horný, Martin Quack and Martin Willeke

Physical Chemistry, ETH Hönggerberg, CH-8093 Zürich, Switzerland

Progress has been made in the theoretical description of molecular-parity violation over the last decade¹⁻⁴, and its possible implications for the origin of molecular chirality and biomolecular homochirality, as well as possible experiments on molecular parity violation are of fundamental interest⁵⁻⁸. Following our previous work^{1,2}, we report new developments to computation of molecular parity-violation potential E_{pv} . Particularly, we seek for an effective and controllable way to examine the importance of electron correlation for the parity-violating potential. Since, the coupled cluster method⁹ has proved to be a most rigorous approach to account for the electron correlation in molecules, we show how the linear response function¹⁰ of the coupled cluster wavefunction provides the contributions to E_{pv} . We discuss the algorithms and computational steps, which are being developed, to achieve the effective coding of this property. The results will be important for future accurate analyses of experimental results⁷.

- [1] A. Bakasov, T. K. Ha and M. Quack, *J. Chem. Phys.*, **1998**, 109, 7263.
 [2] R. Berger and M. Quack, *J. Chem. Phys.*, **2000**, 112, 3148.
 [3] R. Berger, In *Relativistic Electronic Structure Theory, Vol. 2*, **2005**, 188.
 [4] M. Quack and J. Stohner, *Chimia*, **2005**, 59, 530.
 [5] M. Quack, *Angew. Chem. Intl. Ed. (Engl.)* **1989**, 28, 571.
 [6] M. Quack, *Angew. Chem. Intl. Ed. (Engl.)*, **2002**, 41, 4618.
 [7] M. Quack, In *Modelling Molecular Structure and Reactivity in Biological Systems, Proc. 7th WATOC Congress, Cape Town January 2005*, **2006**, 3 (Royal Society of Chemistry, Cambridge).
 [8] M. Quack, *Chem. Phys. Lett.*, **1986**, 132, 147.
 [9] J. Paldus, In *Methods in Computational Physics*, **1992**, 99.
 [10] O. Christiansen, P. Jørgensen, and C. Hättig, *Int. J. Quant. Chem.* **1998**, 68, 1.

Inorganic and Coordination Chemistry

115

Small Molecule Activation and Generation by Early Transition Metal ComplexesChristopher C. Cummins

Chemistry Department, Massachusetts Institute of Technology, Cambridge, MA 02139-4307 (USA)

Computational Chemistry

114

Ab Initio Study of Some Persistent Nitroxide RadicalsLuboš Horný, Fabio Mariotti and Martin Quack

Physical Chemistry, ETH Hönggerberg, CH-8093 Zürich, Switzerland

Stable free radicals have a variety of applications. Particularly, the aminoxyl group is frequently used in spin-labeling experiments. Nitroxides may also exhibit intriguing chiral and magnetic properties and must be of interest for studies of molecular parity violation^{1,2}. Three different groups of persistent NO-radicals :i) acyclic³⁻⁵ :dimethylaminoxyl (Me_2NO), bis(trifluoromethyl) aminoxyl (CF_3)₂NO, and [(CMe₃)₂NO]; ii) cyclic⁶⁻⁸ : aziridine-N-oxyl, azetidine-N-oxyl, pyrrolidine-N-oxyl and piperidine-N-oxyl; and iii) nitronyl nitroxides⁹. We used density functional and *ab initio* (MP2, coupled cluster) methods. The molecular structures, harmonic vibrational frequencies, and inversion barriers are reported and compared with experiment when available. The cyclic species exhibit considerable inversion barriers of \sim hc 3500 cm⁻¹ compared to only \sim hc 500 cm⁻¹ for the acyclic ones. Nitronyl nitroxides are theoretically characterized for the first time in our work. We discuss the possibilities that some of the chiral derivatives may be dominated by molecular parity violation in their dynamics.

- [1] M. Quack, *Angew. Chem. Intl. Ed. (Engl.)* **1989**, 28, 571.
 [2] M. Quack, *Angew. Chem. Intl. Ed. (Engl.)*, **2002**, 41, 4618.
 [3] P. W. Harland, *Int. J. Mass Spect. & Ion Physics* **1977**, 25, 61.
 [4] C. Chatgillaloglu et al., *J. Phys. Chem.* **1980**, 84, 3597.
 [5] D. A. C. Compton, C. Chatgillaloglu, H. H. Mantsch, K. U. Ingold, *J. Phys. Chem.* **1981**, 85, 3093.
 [6] I. Komaromi, J. M. J. Tronchet, *J. Phys. Chem.* **1995**, 99, 10213.
 [7] A. Ebrahimi et al., *J. Mol. Struct. (THEOCHEM)* **2001**, 535, 247.
 [8] I. Novak et al., *J. Org. Chem.*, **2004**, 69, 7628.
 [9] C. Hirel, J. Pecaut, S. Choua, Ph. Turek, D. B. Amabilino, J. Veciana, P. Rey, *Eur. J. Org. Chem.* **2005**, 348.

Inorganic and Coordination Chemistry

116

Chemistry with Aminyl Radical Complexes and Related Compounds: New Perspectives for CatalysisHansjörg Grützmacher

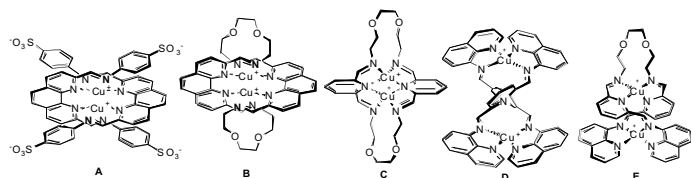
Laboratorium für Anorganische Chemie, ETH Hönggerberg, HCI CH-8093 Zürich, Switzerland

Copper(I) Complexes with Reversibly-Formed Imine Bonds : Synthetic Control via Self-AssemblyMarie Hutin^a, Gérald Bernardinelli^b, Jonathan R. Nitschke^{*a}^aSciences II, University of Geneva, 30 quai Ernest Ansermet, 1211 Geneva 4, Switzerland.^bLaboratory of X-Ray crystallography, University of Geneva, 24 quai Ernest Ansermet, 1211 Geneva 4, Switzerland.

Our group has developed a self-assembly methodology that allows unusual structures to be created in excellent yield. Amine and aldehyde subcomponents are held together by reversibly-formed imine (C=N) bonds that self-assemble around copper(I) templates.

The dynamic behaviour of these complexes allowed novel reactivity: by changing the pH, it was possible to switch between the open topology of helicate **A** and the closed topology of macrocycle **B** [1].

The reaction of "undersaturated" macrocycle **C** (only three nitrogen donors per copper) with "oversaturated" helicate **D** (five such donors) led to the formation of heterocomplex **E**, in which both copper(I) ions and ligands are valence-satisfied [2].

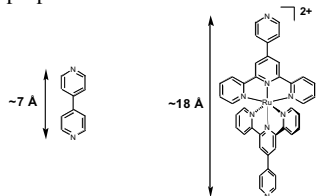


[1] M. Hutin, C.A. Schalley, G. Bernardinelli, J.R. Nitschke, *Chem. Eur. J.*, **2006**, *12*, 4069-4076.

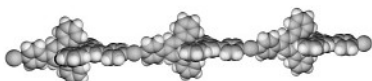
[2] M. Hutin, G. Bernardinelli, J.R. Nitschke, *Proc. Natl. Acad. Sci. USA*, **2006**, *103*, 17655-17660.

The Construction of Coordination Networks Incorporating $\{M(\text{tpy})_2\}_n^{2+}$ (tpy = 2,2':6',2''-terpyridine) GroupsJonathon E. Beves,^a Edwin C. Constable,^a Catherine E. Housecroft,^a Cameron J. Kepert,^b Markus Neuburger,^a David J. Price^b and Silvia Schaffner^a^a University of Basel, Spitalstrasse 51, 4056 Basel, Switzerland^b University of Sydney, 2006 Sydney, Australia

Iron(II) and ruthenium(II) complexes of 2,2':6',2''-terpyridine are the focus of extensive interest in supramolecular chemistry [1]. The inclusion of these groups into extended structures offers the opportunity to build electrochemical or photophysical properties into addressable molecular frameworks.



We are developing [2] coordination polymers containing $\{M(\text{tpy})_2\}$ units. A key building block is the ligand 4'-(4-pyridyl)-2,2':6',2''-terpyridine, which acts as a terdentate ligand with a pendant 4-pyridyl ring. In these structures the $\{M(\text{tpy})_2\}$ moieties act as 'expanded 4,4'-bipyridines' in which the two 4-pyridyl metal-binding domains are separated by metal-containing $\{M(\text{tpy})_2\}$ scaffolds.

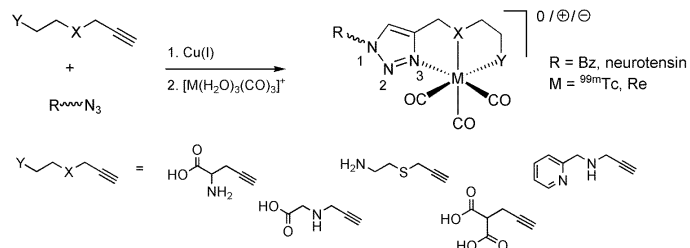


[1] E. C. Constable, *Chem. Soc. Rev.*, **2007**, *36*, 246.

[2] J. E. Beves, E. C. Constable, C. E. Housecroft, C. J. Kepert, D. J. Price, *CrystEngComm*, **2007**, in press.

Design and synthesis of triazole containing metal chelating systems suitable for the $M(\text{CO})_3$ -core ($M = {}^{99m}\text{Tc}$, Re), and their incorporation into tumor targeting peptidesHarriet Struthers¹, Bernhard Spingler², Thomas Mindt¹, Roger Schibli¹¹Department of Chemistry and Applied Biosciences, ETHZ, 8093 Zurich, Switzerland. ²Institute of Inorganic Chemistry, University of Zurich, 8057 Zurich, Switzerland

We have used click chemistry to develop a simple method to introduce a series of different chelating systems for the $M(\text{CO})_3$ -core ($M = {}^{99m}\text{Tc}$, Re) into azide containing molecules of biological interest. The present strategy employs the triazole not only as a stable coupling group between the chelating system and biomolecule, but also as an integral part of the chelator. Suitable alkynes with a variety of functionalities were synthesized and reacted with benzyl azide to form a series of model ligands. Analysis of the organometallic rhenium complexes (NMR, X-ray) proved selective coordination of the triazole via N3. The corresponding alkynes of the most efficient systems were incorporated into an azido derivative of the tumor targeting peptide neurotensin. The synthesis and characterization of the novel compounds will be discussed, as well as in vitro and in vivo data for the ${}^{99m}\text{Tc}$ labeled neurotensin analogues and their potential for use in diagnostic radiopharmacy.

**A closer view at the wheat metallothionein E_c-1 and an evaluation and comparison of its redox properties**

E. A. Peroza, E. Freisinger

Institute of Inorganic Chemistry, University of Zürich, Winterthurerstrasse 190, 8057 Zürich, Switzerland (peroz@aci.uzh.ch)

Metallothioneins (MTs) are small proteins widely present in living organisms. The high cysteine content and affinity for d^{10} metals ions are their most remarkable characteristics. Investigations over the past 50 years have accumulated evidences supporting their involvement in the homeostasis of essential metal ions (like Zn^{II} and Cu^{I}) and in the protection against toxic elements (Cd^{II} or Hg^{II}) and oxygen reactive species (ROS). A biochemical mechanism of action of the MTs, linking the cellular redox state to the pull of available zinc, has been proposed [1].

"Early cysteine-labelled" protein, or E_c-1, from wheat is a member of the pec sub-family of plant MTs and was the first MT recognized in higher plants [2]. In our past investigations we have showed that wheat E_c-1 can bind up to 6 Zn^{2+} or Cd^{2+} and gathered clear evidences supporting that these metal ions are structured in 2 separated metal clusters: one binding 4 metal ions ($\alpha\text{-E}_c\text{-1}$) and another binding 2 ($\gamma\text{-E}_c\text{-1}$) [3].

Details about the metal cluster characteristics will be presented and discussed. Furthermore we will bring data from our studies of the wheat E_c-1 zinc release properties under varying redox environments and comparison to plant MTs from other types.

[1] W. Maret, *J. Nutr.* **2000**, *130*, 1455.

[2] Lane, R. Kajioka, T. Kennedy, *Biochem. Cell. Biol.* **1992**, *65*, 1001

[3] E. A. Peroza, E. Freisinger, *J. Biol. Inorg. Chem.* **2007**, DOI 10.1007/s00775-006-0195-5

Support from the Swiss National Foundation (200020-113728/1 to E.F.) is gratefully acknowledged.

Cu(II) coordination in self-assembling copolymer architectures: Nanovesicles and micelles

Cornelia G. Palivan*, Alessandro Napoli, Wolfgang Meier

Chemistry Department, University of Basel, Klingelbergstr. 80, 4056, Basel Switzerland

One of the most powerful approaches in obtaining well-defined scaffolds for three-dimensional (3D) cell culture, DNA-based structures and metal nanostructured materials is the use of self-assembly mechanisms¹. The presence of metals in these systems changes dramatically their physical and chemical properties leading to composite materials with new behavior and therefore larger technological applications.

In this study we were interested to establish if metal coordination in self-assembling systems is depending on the resulting morphologies and how far is this related to the molecular parameters and environment. Using EPR and UV-Vis spectroscopy we investigated the coordination sites for Cu(II) in PEG/PPS block copolymers², which form either micelles or nanovesicles, when diluted in polar solvents.

In water, when PEG/PPS copolymer system is forming nanovesicles, the Cu(II) paramagnetic species indicate that the metal is only coordinated to PEG. When PEG/PPS system auto-assembles in spherical micelles both polymer domains are accessible for the metal: the major paramagnetic species is a Cu(II)-PEG species, while the minor one are specific for Cu(II)-PPS coordination. The detailed analysis of the spin Hamiltonian parameters together with the electronic spectra let us to establish the various Cu(II) species formed when PEG/PPS block copolymers were assembled in different morphologies and to have an insight into the role of these architectures in forming metal composite nanosystems.

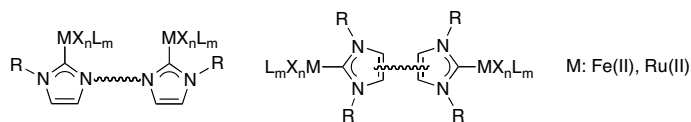
[1] M. Antonietti, S. Foerster, *Adv. Materials* **2003**, 15(16), 1323.[2] A. Napoli, H. Bermudez, J.A. Hubbell, *Langmuir* **2005**, 21(20), 9149.**Bimetallic Redox Switches Comprising N-Heterocyclic Carbene Spacers**

László Mercs, Martin Albrecht*

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

Molecular switches represent an attractive class of functional entities [1]. As active sites, transition metals are particularly useful since they typically change oxidation states reversibly. Multistage switching may be accessible by connecting two active sites with a spacer that allows for a certain degree of electronic communication, for example via π delocalization [2].

Recently, we have shown that the bonding of N-heterocyclic carbenes (NHCs) to Fe(II) centers reveals substantial metal-to-carbene π backbonding [3]. Hence this type of ligand may be a suitable spacer for interconnecting two redox-active metal centers (see Figure).



We will present our progress in using bifunctional NHC ligands as spacers in binuclear iron and ruthenium complexes. Specifically, we will focus on the quality of different carbene spacers, which has been probed by measuring the spectroscopic and electrochemical characteristics of the bimetallic systems.

[1] W. Kaim, G. K. Lahiri, *Angew. Chem. Int. Ed.* **2007**, 46, 1778.[2] B. S. Brunshwig, C. Creutz, N. Sutin, *Chem. Soc. Rev.* **2002**, 31, 168.[3] L. Mercs, G. Labat, A. Neels, A. Ehlers, M. Albrecht, *Organometallics* **2006**, 25, 5648.**Diversity in the coordination chemistry of silver(I): Chains, poly-catenanes, helices and chiral metallacycle motifs**Katharina M. Fromm¹, Markus Meuwly², Jorge Sague¹

1) Department of Chemistry/University of Fribourg, Chemin du Musée 9, CH-1700 Fribourg, Switzerland

2) Dept of Chemistry, University of Basel, Switzerland

Silver metallosupramolecular chemistry is a topic of current interest for materials in industrial and biological applications. Silver(I) salts are readily available and inexpensive, however, the flexible coordination sphere of this metal ion results in unpredictable outcomes of the complexation reactions.

In order to gain an insight into this particular subject, we have synthesized a series of silver(I) complexes with different ditopic ligands [1, 2].

The analysis of the crystal structures of these complexes and the results of DFT calculations at the B3LYP/6-311++G** level, reveal the complexity and the subtle interplay of the supramolecular forces, which drive the crystallization processes of these complexes.

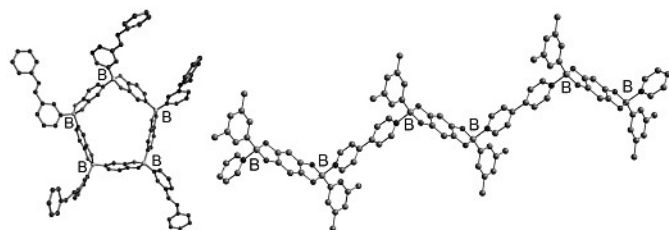
The obtention of different topologies in the solid state may be overcome by a conscious choice of the ligand and the counter ion, and reaction parameters like concentration, temperature and time of reaction [3].

[1] Fromm, Katharina M.; Doimeadios, Jorge L. Sague; Robin, Adeline Y., *Chemical Communications (Cambridge, United Kingdom)* **2005**, 36, 4548.[2] Fromm, Katharina M.; Gueneau, Estelle D.; Robin, Adeline Y.; Maudez, William; Sague, Jorge; Bergougnant, Remi., *Zeitschrift fuer Anorganische und Allgemeine Chemie* **2005**, 631(10), 1725.[3] Sague, J.L. and Fromm, K.M., *Crystal Growth & Design* **2006**, 6(7), 1566.**Boronic Acids as Building Blocks in Supramolecular Chemistry**

Nicolas Christinat, Rosario Scopelliti and Kay Severin*

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

The synthesis of supramolecular structures by self-assembly has received considerable attention over the last years. Many of the reported structures have been obtained using transition metal-ligand interactions. As an alternative, boronic acids can be employed as building blocks for the construction of complex assemblies [1]. In particular, boronic acids are very convenient reagents, as they easily form cyclic esters with diols and are able to bind to N-donor ligands. Moreover, the side chain of boronic acids can be easily functionalized, thus increasing the scope of possible reactions with these building blocks. We now demonstrate that complex structures such as macrocycles, dendritic nanostructures and coordination polymers can be assembled in a single step by using in parallel two or more independent condensation reactions involving boronic acids [2,3].

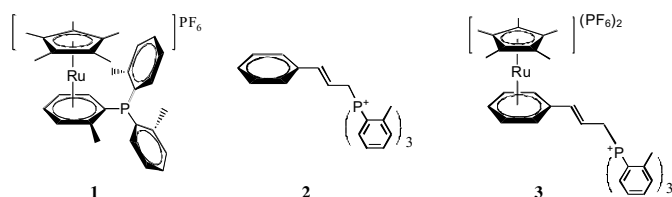
[1] H. Höpfl, *Struct. Bonding* **2002**, 103, 1-56.[2] N. Christinat, R. Scopelliti, K. Severin, *Chem. Commun.* **2004**, 10, 1158-1159.[3] N. Christinat, R. Scopelliti, K. Severin, *J. Org. Chem.* **2007**, 72, 2192-2200.

Reactions of Ru(Cp*) Complexes with P(o-tolyl)₃

Helen Caldwell, Sheila Isseponi, Paul S. Pregosin*

ETH Hönggerberg, Wolfgang-Pauli Strasse 10, CH-8093 Zürich, Switzerland

Reaction of [RuCp*(CH₃CN)₃]PF₆ with P(o-tolyl)₃ affords [RuCp*{(η⁶-o-tolyl)P(o-tolyl)₂}]PF₆, **1**, in which the P atom is not coordinated to the metal. The solid state structure of **1** has been determined. Reaction of the Ru(IV) dication [RuCp*(η³-PhCHCHCH₂)(DMF)₂][PF₆]₂ with P(o-tolyl)₃ gives a mixture of the phosphonium salt PhCH=CHCH₂P(o-tolyl)₃, **2**, and the dication [RuCp*(η⁶-PhCH=CHCH₂P(o-tolyl)₃][PF₆]₂, **3**. The former is the result of attack of the P atom on the allyl ligand. The latter product is formed by complexation of **2** via the phenyl group of the former allyl ligand.



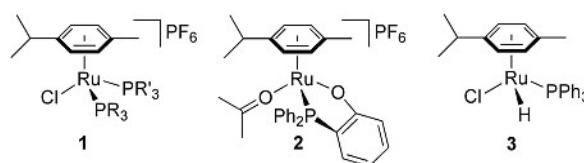
The reasons for this unusual chemistry will be discussed.

Catalytic activity of bis-phosphine ruthenium(II)-arene compounds: chemoselective hydrogenation and mechanistic insights¹

Adrian B. Chaplin and Paul J. Dyson

Ecole Polytechnique Fédérale de Lausanne, EPFL-BCH, CH-1015, Lausanne, Switzerland

Half sandwich ruthenium(II)-η⁶-arene complexes are an important and widely used class of organometallic compound, which exhibit a diverse range of coordination chemistry and show considerable potential as catalysts for a variety of organic transformations.² Following earlier work in our group, involving prescreening for catalytic activity,³ we report here the activity of the air and moisture stable bis-phosphine ruthenium(II)-arene complexes (**1**, R/R' = Ph or *p*-tol) for the chemoselective reduction of aldehydes in the presence of olefinic bonds. Mechanistic studies including comparisons with a structural analogue (**2**), reactions of an isolated hydride complex (**3**), base poisoning experiments and a computational analysis, help rationalize the preferential hydrogenation of C=O bonds, which is suggested to proceed via an ionic outer-sphere mechanism.



[1] A. B. Chaplin and P. J. Dyson, *Submitted*.

[2] J. Gimeno, V. Cardiero and P. Crochet, *Comprehensive Organometallic Chemistry III*, Eds. D. M. P. Mingos, R. H. Crabtree and M. Bruce, Elsevier, Oxford, 2007, Vol. 6, 465.

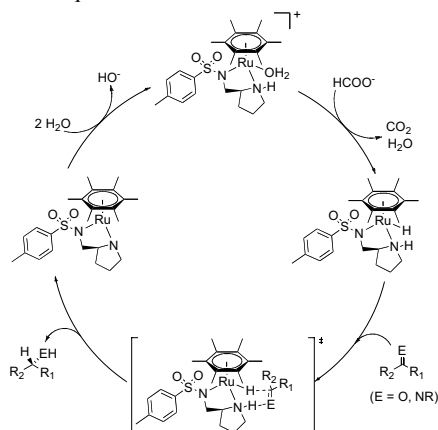
[3] A. B. Chaplin and P. J. Dyson, *Organometallics* 2007, 26, 2447.

Water-Soluble Arene Ruthenium Catalysts for Asymmetric Transfer Hydrogenation of α-Aryl Ketones and Imines in Aqueous Solution

Jérôme Canivet and Georg Süß-Fink*

Institut de Chimie, Université de Neuchâtel, CH-2007 Neuchâtel
e-mail: georg.suess-fink@unine.ch

A new family of cationic arene ruthenium complexes containing chiral *N,N*-chelating ligands is presented. The air-stable water-soluble tetrafluoroborate salts catalyze the enantioselective transfer hydrogenation of prochiral ketones and imines in aqueous solution.



The scope and the mechanism of this reaction as well as the synthesis and characterization of the catalytically active complexes will be discussed.¹

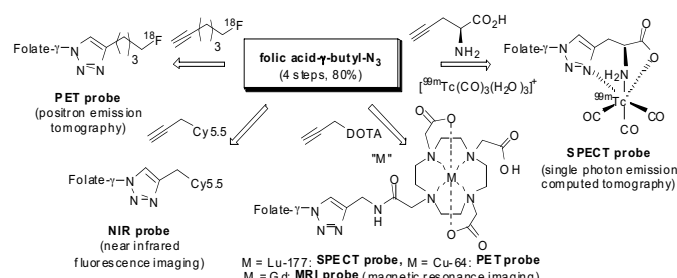
[1] J. Canivet, G. Süß-Fink, *Green Chemistry* 2007, in the press

Convenient access to molecular imaging probes by "click chemistry"

Thomas L. Mindt, Tobias Ross, Thomas Müggler, Roger Schibli

Department of Chemistry and Applied Biosciences and Animal Imaging Centre ETH/University of Zurich, ETH Zurich, Wolfgang Pauli Strasse 10, 8093 Zürich, Switzerland

We have recently shown that "click chemistry" (the Cu(I)-catalyzed cycloaddition of terminal alkynes and azides) [1] can be employed for the efficient synthesis of triazole-based metal chelates while simultaneously attaching them to (bio)molecules. [2] Application of our click approach enables the rapid parallel development of tracers for a variety of imaging modalities. For example, starting from a common azido folic acid precursor, tumor targeting SPECT-, PET-, MRI- and NIR tracers were obtained in high yields by reaction with different alkyne-functionalized imaging probes or precursors thereof. Specific targeting of the tumor associated folate receptor was achieved with all new click imaging tracers. First comparative in vitro and in vivo data obtained by different imaging techniques will be presented.



[1] V. Rostovtsev et al. *Angew. Chem.-Int. Ed.* 2002, 41, 2596; C. Tornøe et al. *J. Org. Chem.* 2002, 67, 3057

[2] T. L. Mindt et al. *J. Am. Chem. Soc.* 2006, 128, 15096

Assembly of Metallomacrocycles from Ditopic 2,2':6',2''-Terpyridine Ligands with Flexible SpacersEdwin C. Constable, Kate Harris, Catherine E. Housecroft, Markus Neuburger and Silvia Schaffner

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

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

Examples will be presented of metallomacrocycles of various sizes and nuclearities formed from the reactions of such ditopic ligands containing a flexible oligo- or poly(ethylene glycol) spacer with various cobalt salts.

Also presented will be a novel exchange reaction resulting from the reaction of these or 4'-alkoxy-2,2':6',2''-terpyridine ligands with cobalt(II) ions in the presence of alcohols.

- [1] S. Schmatloch, A. M. J. van den Berg, H. Hofmeier and U. S. Schubert, *Designed Monomers and Polymers*, **2004**, 7, 191-201.
- [2] E. C. Constable, C. E. Housecroft, M. Neuburger, S. Schaffner and C. B. Smith, *Dalton Trans.*, **2005**, 2259-2267.

Serendipitous Nanoparticle Synthesis From Microwave Assisted Chemistry of Iron(III) and 2,2'-BipyridineEdwin Constable, Emma Dunphy, Catherine Housecroft and Amina Wirth[†]University of Basel, Spitalstrasse 51, 4056, Basel, Switzerland
[†]Technical University of Northwest Switzerland, Muttenz, Switzerland

TiO₂ is a useful photoanode in dye sensitised solar cells.¹ It is a wide band gap semiconductor, however, and low absorption in the visible spectrum make pursuing alternative materials favourable in water-splitting chemistry. One such alternative is the use of hematite and recent studies have indicated that Si-doped thin films of Fe₂O₃ demonstrate improved activity.^{2,3} Here we report the synthesis and characterisation of 2,2'-bipyridine coated iron oxide nanoparticles. Their photophysical and electrochemical properties will be reported and preliminary application in photoelectrodes discussed.

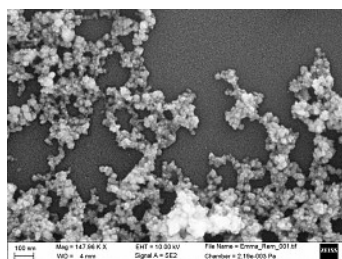


Figure 1 – SEM image of 2,2'-bipyridine coated iron oxide nanoparticles

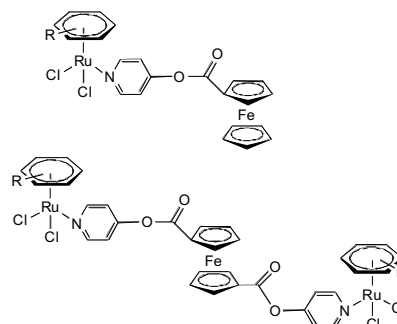
- [1] Grätzel M., *Nature*, **1991**, 335, 737.
- [2] Hoffmann M., Martin S., Choi W., Bahnemann D., *Chem. Rev.*, **1995**, 95, 69
- [3] Cesar I., Kay A., Martinez J., Grätzel M., *J. Am. Chem. Soc.*, **2006**, 128, 4582

Ferrocenoyl Pyridine Arene Ruthenium Complexes: Synthesis, Electrochemistry and Anti-Tumor ActivityMathieu Auzias, Georg Süss-Fink*

Institut de Chimie, Université de Neuchâtel, CH-2009 Neuchâtel

e-mail: georg.suess-fink@unine.ch

Ferrocenoyl pyridine arene ruthenium complexes of the general formula Ru(η⁶-arene)Cl₂(NC₅H₄OOC-C₅H₄FeC₅H₅) and [Ru(η⁶-arene)Cl₂]₂(NC₅H₄OOC-C₅H₄FeC₅H₄-COOC₅H₄N) have been synthesized from the corresponding arene ruthenium dichloride dimer and the ferrocenoyl-substituted pyridine derivatives.



The electrochemical behavior as well as the anti-tumor activities (against A2780 human ovarian) of these complexes have been studied in collaboration with Prof P. Štěpnička (Prague) and Prof. P. J. Dyson (Lausanne).

The synthesis and characterisation of a hydrogenase mimic covalently linked to a Ru (II)-based sensitizerElaine A. Medlycott, Edwin C. Constable, Egbert Figgemeier, Catherine E. Housecroft.

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

The elucidation of the structure and nature of the active site of hydrogenase enzymes has captured the interest of bioinorganic chemists.[1] Both Ni-Fe and Fe-Fe clusters are found in nature depending on the catalytic process, but it is the hydrogenase enzymes incorporating Fe-Fe clusters which are involved in the biological production of hydrogen. The synthesis of hydrogenase mimics may provide a means to exploit such systems for the efficient production of hydrogen. Of particular interest, is the introduction of a photosensitizer into such a system in order to develop light-driven catalysts.[2] Ruthenium(II) polypyridine complexes are the prototypical photosensitizer of choice.

Herein, we report the synthesis of a surface-bound [Ru(tpy)]²⁺-based photosensitizer covalently linked to an Fe-Fe cluster. The spectroscopic and electrochemical properties of the multicomponent system on the surface will be discussed in the context of photocatalysed H₂ production.

- [1] a) J.W. Peters, W. N. Lanzilotta, B. J. Lemon, L. C. Seefeldt, *Science*, **1998**, 282, 1853; b) Y. Nicolet, C. Piras, P. Legrand, C. E. Hatchikian, J. C. Fontecilla-Camps, *Structure*, **1999**, 7, 13.
- [2] a) S. Ott, M. Kritikos, B. Åkermark, L. Sun., *Angew. Chem. Int. Ed.* **2003**, 42, 3285; b) S. Ott, M. Borgström, M. Kritikos, R. Lomoth, J. Bergquist, B. Åkermark, L. Hammarström, L. Sun., *Inorg. Chem.*, **2004**, 43, 4683.

Photocatalytic Energy Storage: An artificial biomimetic Model of Photosystem I

Benjamin Probst, Roger Alberto

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

Chromophores of the type $[\text{Re}^{\text{I}}\text{X}(\text{CO})_3\text{diimine}]$ combined with *her* (hydrogen evolution reaction) catalysts of the type $[\text{Co}^{\text{III}}(\text{dmgH})_2\text{YZ}]$ provide functional biomimetics of PSI.^[1-3] TOF's up to 30 h⁻¹ in Rhenium were measured for H₂ production, confirming our proposed catalytic scheme as shown below. Mechanistic studies to provide a better understanding of the complex kinetics and to determine rate limiting steps as well as back reactions will be presented. New molecular assemblies are investigated to address inner- vs. outersphere electron transfer processes.

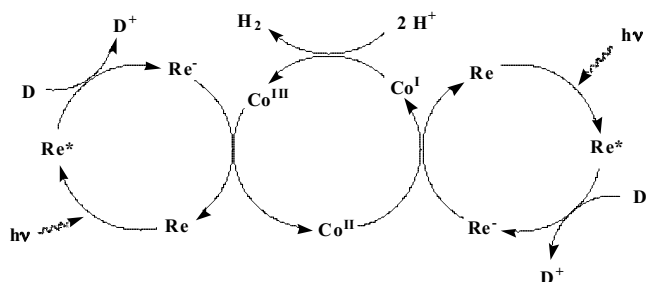


Figure 1 Schematic of the photocatalysed reductive halfreaction. D = triethanolamine, Re = $[\text{Re}^{\text{I}}\text{X}(\text{CO})_3\text{diimine}]$, Co = $[\text{Co}^{\text{III}}(\text{dmgH})_2\text{YZ}]$.

- [1] P. Kurz *et al.*, *Eur. J. Inorg. Chem.* **2006**, 15, 2966.
[2] M. Razavet, V. Artero, M. Fontecave, *Inorg. Chem.* **2005**, 44, 4786.
[3] J. Hawecker, J. M. Lehn, R. Ziessel, *Nouv. J. Chim.* **1983**, 7, 271.

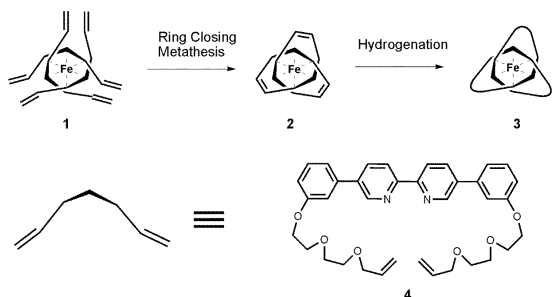
On Sokolov's approach to a Molecular Knot using Ring Closing Metathesis

Pirmin Rösel, Christopher Smith, Catherine E. Housecroft, Edwin C. Constable*

Department of Chemistry, Spitalstrasse 51, 4056 Basel, Switzerland

We all meet knots in daily life and most of us are fascinated from its unique topology. More importantly, knots are also found in proteins and DNA and hence play an important role in nature [1].

An early approach towards a molecular knot is Sokolov's application of an octahedral tris(chelate) template [2].



We synthesised the homoleptic iron(II)-complex **1** which has terminal alkene functionalities. NMR spectroscopic and ESI-MS measurements confirm the successful trifold intramolecular Ring Closing Metathesis. Our present efforts are concentrated in separation and characterisation of **3** and its isomers.

- [1] *Molecular Catenanes and Knots*; Sauvage, J.-P., Dietrich-Buchecker C. Eds.; Wiley: New York, **1999** and ref. herein.
[2] V. I. Sokolov, *Russ. Chem. Rev.* **1973**, 42, 452.

A novel family of Cu(I) complexes incorporating 2,2'-bipyridine ligands for sensitizer applications in solar cells

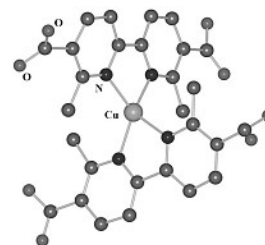
Ana Hernandez Redondo, Edwin C. Constable, Catherine E. Housecroft, Markus Neuburger, Silvia Schaffner

Department of Chemistry, University of Basel, Spitalstrasse 51,
CH-4056 Basel, Switzerland

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

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

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



- [1] A. Hagfeldt and M. Grätzel, *Acc. Chem. Res.* **2000**, 33, 269-277.
[2] M. Grätzel *et al.*, *J. Am. Chem. Soc.* **1993**, 115, 6382-6390.

¹⁴N-NMR studies related to the solvent exchange reaction on $[\text{Ln}(\text{CH}_3\text{CN})_9][\text{Al}(\text{OC}(\text{CF}_3)_3)_4]$

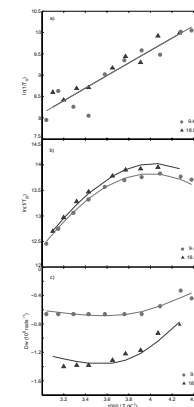
Gabriella Bodizs, Lothar Helm

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

Solvent exchange reactions in aqueous or non-aqueous solutions are the simplest chemical reactions on metal cations: a solvent molecule situated in the first coordination shell of the ion is replaced by another one, generally entering from the second shell. [1, 2]

The knowledge of the mechanism and the rate constant of the solvent exchange reactions are fundamental, since these reactions represent an important step in complex formation reactions on metal ions. Thus, homoleptic metal complexes with labile uncharged ligands, like CH₃CN, are essential synthetic precursors which can be used to produce a wide range of compounds under non-aqueous conditions.

Here we present results of the ¹⁴N-NMR variable temperature measurements related to the acetonitrile exchange reaction on homoleptic lanthanide complexes.



Temperature dependence of ¹⁴N-NMR relaxation rates and the reduced chemical shifts at 9.4 and 18.8 T for the Gd complex.

- [1] F. A. Dunand, L. Helm, *Adv. Inorg. Chem.* **2003**, 54, 1.
[2] L. Helm, A. E. Merbach, *Chem. Rev.* **2005**, 105, 1923

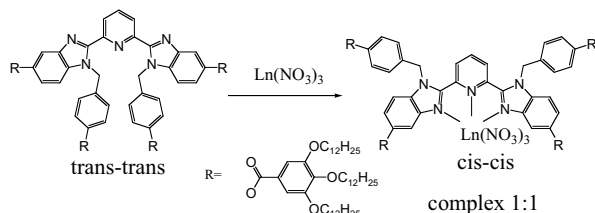
Thermotropic Lanthanidomesogens at Low Temperature

L. Guénée, H. Nozary, G. Bernardinelli, F. Gummy, A. Aebischer, J.-C. Bünzli, B. Donnio, D. Guillon, C. Piguet* and A. Escande

Department of Inorganic, Analytical and Applied Chemistry, University of Geneva, Geneva, 1211, Switzerland

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

The 2,6-bis-[5-(3,4,5-tris-dodecyloxy-benzoyloxy)-1-[4-(3,4,5-tris-dodecyloxy-benzoyloxy)-benzyl]-1H-benzimidazol-2-yl] pyridine was syn-



thesized and studied for its complexation with $\text{Ln}(\text{NO}_3)_3$ ($\text{Ln}=\text{La-Lu}$).

Scheme 1: Assembly of mesomorphic lanthanide complexes from dodecatenar receptors

Low-temperature first-order melting processes ($-43^\circ\text{C} \leq T_m \leq -25^\circ\text{C}$) produce unprecedented room-temperature luminescent lanthanidomesogens.[1]

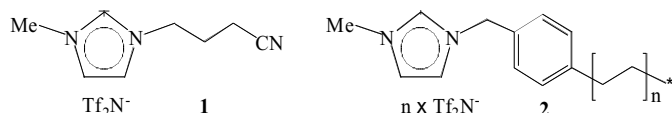
[1] A. Escande, L. Guénée, H. Nozary, G. Bernardinelli, F. Gummy, A. Aebischer, J.-C. Bünzli, B. Donnio, D. Guillon and C. Piguet*, *submitted*, 2007

Nanocatalysis: designed nanoparticles that operate in ionic liquids

Xue Yang,^{a,b} Zhaofu Fei,^a Dongbing Zhao,^a Wee Han Ang,^a Yongdan Li,^b Paul J. Dyson^a

a: Swiss Federal Institute of Technology, EPFL-BCH Lausanne 1015-Lausanne, Switzerland. b: School of Chemical Engineering, Tianjing University, Tianjing 300072, China

Palladium nanoparticles [NPs] have been found to act as catalyst reservoirs in many C-C coupling reactions [1]. Using ionic liquids (ILs) as solvent, Pd NPs have been prepared, isolated and characterized by Transmission Electron Microscopy (TEM) [2].



Dissolving PdCl_2 in IL **1** containing an ionic polymer **2**, followed by reduction with NaBH_4 , affords Pd NPs with an average size of 2.5 nm. The Pd NPs were found to be highly active catalyst precursors in Suzuki C-C coupling reactions. For substrates such as 4-iodobenzonitrile and 1-iodo-4-nitrobenzene, within 8 hours at 100°C a yield of 99% can be obtained. The use of the ionic polymer **2** has three major advantages: 1. stabilization of the Pd NPs; 2. preventing the palladium NPs from leaching; 3. improved recycling of the ionic liquids solvent [3].

- [1] B. F. G. Hohnson, *Topics in Catalysis* **2003**, 24, 147.
 [2] Z. Fei, T. J. Geldbach, D. Zhao, P. J. Dyson. *Chem. Eur. J.* **2006**, 12, 2122.
 [3] Z. Fei, D. Zhao, D. Pieraccini, W. H. Ang, T. J. Geldbach, R. Scopelliti, C. Chiappe, P. J. Dyson. *Organometallics* **2007**, 26, 1588.

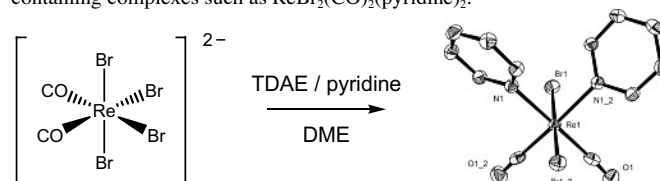
Synthesis and reactivity of 17-e⁻ “[Re^(II)(CO)₂]²⁺” based complexes

Lukas Kromer, Bernhard Spingler, Roger Alberto

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

Rhenium carbonyl complexes are of interest for several research fields such as radiopharmaceutical and photo chemistry. We introduced several complexes with the $[\text{Re}^{\text{II}}(\text{CO})_2]^+$ moiety and studied their applicability to both of the above mentioned fields [1]. A “[$\text{Re}^{\text{II}}(\text{CO})_2$]” intermediate is postulated in photochemical CO_2 reduction [2] which encouraged us to closer look at the rare chemistry of $\text{Re}(\text{II})$. $\text{Re}(\text{II})$ complexes are paramagnetic 17-e⁻ species. A reasonable reactive synthon is lacking and most of the known $\text{Re}(\text{II})$ -carbonyl complexes are stabilized by phosphines or are electrochemically generated [3, 4].

We investigated a new pathway to synthesise reactive $\text{Re}(\text{II})$ complexes with exclusively monodentate ligands such as bromide and/or pyridine. We will present synthetic and physico-chemical studies about new $[\text{Re}^{\text{II}}(\text{CO})_2]$ containing complexes such as $\text{ReBr}_2(\text{CO})_2(\text{pyridine})_2$.



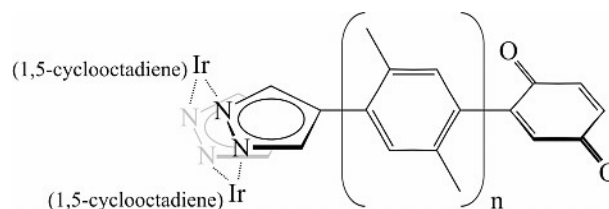
- [1] L. Kromer, B. Spingler, R. Alberto, *J. Organomet. Chem.* **2007**, 692, 1372.
 [2] J. Hawecker, J.-M. Lehn, R. Ziessel, *Helv. Chim. Acta* **1986**, 69, 1990.
 [3] A. Bond, R. Colton, D. Humphrey, P. Mahon, G. Snook, V. Tedesco, J. Walter, *Organometallics* **1998**, 17, 2997.
 [4] E. Schelter, J. Bera, J. Bacsá, J. Galán-Mascarós, K. Dunbar, *Inorg. Chem.* **2003**, 42, 4256.

High Driving Force Dyads for Light-triggered Electron Tunneling

Mathieu E. Walther, Oliver S. Wenger*

Université de Genève, Département de Chimie Minérale, Analytique et Appliquée, 30 quai Ernest-Ansermet, 1211 Genève 4

Pyrazolyl-bridged binuclear iridium(I) complexes are extremely powerful photoreductants [1]. We are synthesizing and characterizing a series of dyads in which electron donors of this type are covalently linked to acceptors such as 1,4-benzoquinone. The two redox partners are held at fixed distance relative to one another by rigid *p*-xylene-based bridges of variable length.



The energy levels of these particular linkers are nearly length-independent, thereby allowing for rigorous experimental testing of the superexchange theory [2] for the biologically relevant process of long-distance electron tunneling. Contrary to many previously investigated systems, these high driving force dyads also permit investigation of photoinduced charge-separation in media with low dielectric constants and studies at cryogenic temperatures.

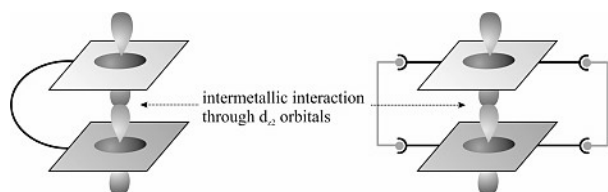
- [1] K. A. Beveridge, G. W. Bushnell, K. R. Dixon, D. T. Eadie, S. R. Stobart, J. L. Atwood, M. J. Zaworotko, *J. Am. Chem. Soc.* **1982**, 104, 920.
 [2] H. M. McConnell, *J. Chem. Phys.* **1961**, 35, 508.

Metal-metal Interactions in Platinum and Gold Complexes

Jonathan Freys, David Hanss, Oliver S. Wenger*

Université de Genève, Département de Chimie Minérale, Analytique et Appliquée, 30 quai Ernest-Ansermet, 1211 Genève 4

Dimeric coordination compounds having face-to-face square-planar d^8 metal centers are among the photophysically and photochemically most interesting coordination compounds [1]. Weak noncovalent intermetallic interactions are often responsible for their unusual properties. We investigate these interactions in newly synthesized coordination compounds that are designed such as to induce short d^8 - d^8 contacts. This includes both the use of noncovalent and covalent linkers between platinum(II) and gold(III) centers.



Materials of this type may be of interest in the contexts of multi-electron redox chemistry, chemical sensing, and supramolecular chemistry.

[1] D. M. Roundhill, *Photochemistry and Photophysics of Metal Complexes*, Plenum Press, New York & London, 1994.

The synthesis and characterisation of a porphyrin functionalized with 2,2':6',2''-terpyridine ligands

Paulina Chwalisz, Edwin C. Constable, Catherine E. Housecroft.

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

Porphyrins have been extensively studied for the last fifty years and there are many actual and potential applications making such systems very attractive synthetic targets. They may be applied as electrochemical sensors or in the area of alternative energy sources. More recently, they have been studied for applications in photodynamic therapy.[1]

Herein, we present the synthetic route employed to obtain porphyrin functionalized 2,2':6',2''-terpyridine (tpy) ligands and their metal complexes. Introducing the tpy component offers a means to coordinate a range of metals in a pseudo-octahedral geometry in addition to the porphyrin N_4 donor site.

The synthetic strategy for the preparation of terpyridine-based porphyrins is based on Lindsey's procedure [2], in which catalytic amounts of a Lewis acid ($Et_2O \cdot BF_3$) are used. The condensation reaction between pyrrole and 4'-phenylcarbonyl-2,2':6',2''-terpyridine carried out in dichloromethane is employed for the synthesis of the target ligand.

[1] Pandey, R. K.; Zheng, G. *Porphyrins as Photosensitizers in Photodynamic Therapy*, in *The Porphyrin Handbook*, Kadish, K. M.; Smith, K. M.; Guillard, R., editors; Academic Press: San Diego, CA, 2000; Vol. 6, Chapter 43, pp. 157- 230.

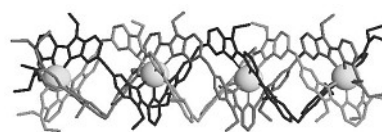
[2] Lindsey, J. S. *Synthesis of meso-Substituted Porphyrins*, in *The Porphyrin Handbook*, Kadish, K. M.; Smith, K. M.; Guillard, R., editors; Academic Press: San Diego, CA, 2000; Vol. 1, Chapter 2, pp. 45-118.

Synthesis and properties of the first linear tetrametallic triple-stranded lanthanides helicate and rational modeling of free energy changes accompanying self-assembly process

K.Zeckert, J.Hamacek, J.-M.Senegas, C.Piguet*, N.Dalla Favera

Departement of Inorganic, Analytical and Applied Chemistry, University of Geneva, Geneva 1211, Switzerland

In order to address long range intermetallic interactions, the segmental tetraridant ligand L^4 has been designed for Ln(III) complexation. This ligand consists of two different coordination units. Reaction with stoichiometric quantities of $Ln(CF_3SO_3)_3 \cdot xH_2O$ in solution in the millimolar range, leads to the formation of the major tetrametallic complex $[Ln_4(L^4)_3]^{12+}$. The X-ray crystal structure shows the three ligand strands wrapped about a pseudo-threefold axis defined by the four aligned metal ions (1). The luminescent properties in acetonitrile points that the structure is maintained in solution.



The experimental macroscopic formation constants ($\log \beta^{LnL}$) were rationalized by the application of a simple *extended site-binding* model, based on (i) an absolute affinity for each nine-coordinate lanthanide occupying terminal or central sites, (ii) intermetallic and interligand interaction and (iii) entropic correction for intramolecular cyclization.

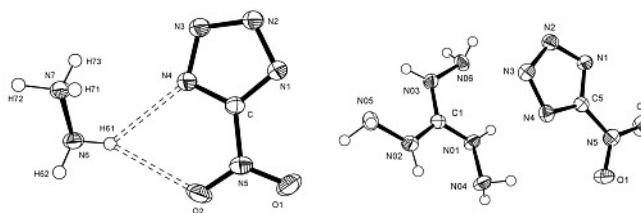
[1] K.Zeckert, J.Hamacek, J.-M.Senegas, N.Dalla Favera, S.Floquet, G. Bernardinelli, C.Piguet, *Angew.Chem.Int. Ed.* 2005, 44, 1-6.

Energetic, Nitrogen-rich Salts of 5-nitrotetrazolate

T.M. Klapötke, P. Mayer, J.M. Welch

University of Munich, Butenandtstr. 5-13 (D), D-81377 Munich, Germany

A new family of energetic salts based on 5-nitrotetrazole (ammonium, hydrazinium, guanidinium, aminoguanidinium, diaminoguanidinium and triaminoguanidinium) were synthesized and studied. Each compound was identified by FAB+ and FAB- mass spectrometry, infrared and Raman spectroscopy and X-ray crystallography. The bulk composition of each material was confirmed by elemental analysis and sensitivities to impact, friction and sparks as well as thermal stabilities were also assessed. The heat of combustion of each compound was determined experimentally using bomb calorimetry and predicted using quantum chemical calculations and the Jenkins' approximation of lattice enthalpy. The performance of each substance was then subsequently predicted using the EXPLO5² code. Candidates showing low sensitivity, good thermal stability and reasonable expected performance were synthesized on a 5g scale for further testing.



[1] H.D.B. Jenkins, D. Tudela, L. Glasser, *Inorg. Chem.* 2002, 41, 2364.

[2] M. Sucecka, EXPLO5 version 5.02, 2005.

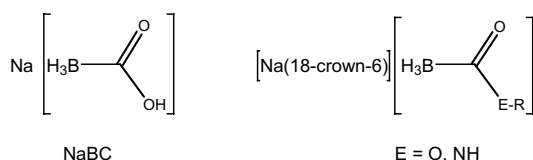
Derivatives of Sodium Boranocarbonate as new CO-releasing molecules

Tamil Selvi Pitchumony, Bernhard Spingler and Roger Alberto

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

Carbon monoxide is fast emerging as an important biological signaling molecule despite its inherent toxicity. Recent investigations have brought to limelight the various physiological effects of CO which includes vasorelaxation and inhibition of transplant rejection, among others.^[1] This led to the tantalising concept of using CO for therapeutic purposes wherein compounds that transport and deliver this gas to a target tissue would clearly facilitate both the clinical feasibility and the specificity of CO therapy.

Sodium boranocarbonate Na[H₃BCO₂H] (NaBC) is the first water-soluble and non-heavy metal containing CO-releasing molecule.^[2] In order to tune the rate of CO release, we modified the NaBC molecule and synthesised various derivatives which release CO under physiological conditions. The synthesis, structure and CO releasing properties of the various derivatives of NaBC will be presented. The biological studies carried out with some of the compounds will also be presented.



[1] R. Motterlini, B. E. Mann, T. R. Johnson, J. E. Clark, R. Foresti and C. Green, *Curr. Pharma. Design*, **2003**, *9*, 2525.

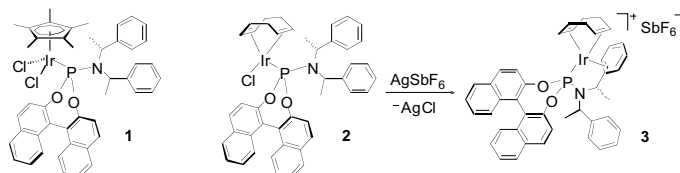
[2] R. Alberto, Motterlini, P. Sawle, S. Bains, J. Hammad, R. Foresti, and C. Green, *FASEB J.*, **2005**, *19*, 284.

 η^2 -Interactions in Chiral Iridium Phosphoramidite Complexes

Tina Osswald, Igor S. Mikhel, Antonio Mezzetti*

Dept. of Chemistry and Applied Biosciences, ETH Zürich, CH-8093 Zürich

In the last years, metal complexes containing monodentate chiral phosphoramidite ligands (P*) have found increasing application in asymmetric catalysis thanks to their excellent asymmetric induction in enantioselective reactions [1]. Our group has recently prepared ruthenium complexes that display an η^2 -interaction between the metal and one aryl group of the amine moiety of the binaphthol-based phosphoramidite [2]. We are studying analogous interactions for Ir(I) and Ir(III) complexes starting from the newly prepared [IrCl₂(Cp*)(P*)] (1) and [IrCl(cod)(P*)] (2).



Chloride abstraction from 2 with AgSbF₆ gives [Ir(cod)(P*)]SbF₆, in which the η^2 -interaction was observed by 2D NMR studies. The analogous reaction of 1 is under investigation.

[1] Kezuka, S., Takeuchi, R. S. *Synthesis* **2006**, 3349.

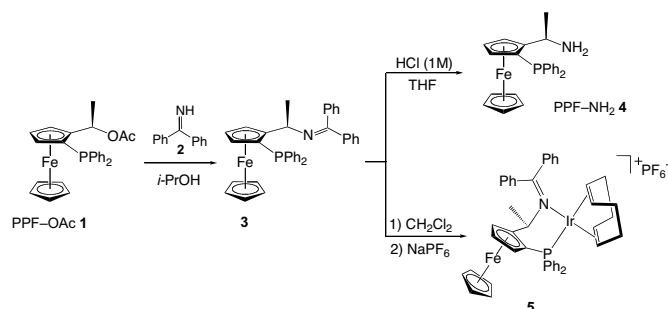
[2] Huber, D., Kumar, P. G. A., Pregosin, P. S., Mikhel, I. S., Mezzetti, A. *Helv. Chim. Acta*. **2006**, *89*, 1696.

Benzophenone Imine as Synthron for Chiral Ferrocenylamine

Francesco Camponovo, Antonio Togni*

Dept. of Chemistry and Applied Biosciences, ETH Zurich, 8093 Zurich

All chiral ferrocenyl P[^]N ligands incorporating an imine moiety that have been reported to date have been prepared by condensation of primary amines with aldehydes or ketones [1]. We report here the direct synthesis of a new chiral ferrocenyl P[^]N ligand (3) from PPF-OAc (1) and benzophenone imine (2), which acts as ammonia equivalent after deprotection to give amine (4) in 70 % overall yield.



The phosphine imine 3 can also be used as chiral P[^]N ligand. The Ir(I) complex [Ir(3)(COD)]PF₆ (5) was prepared and characterized by single crystal X-ray diffraction. Complex 5 will be tested in the asymmetric transfer hydrogenation of ketones and olefins.

[1] T. Hayashi, C. Hayashi, Y. Uozumi, *Tetrahedron Asymmetry* **1995**, *6*, 2503.

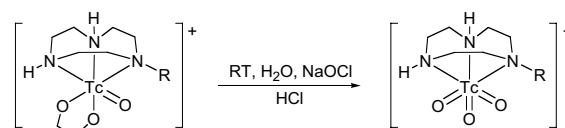
Syntheses of [^{99m}Tc^{VII}O₃]⁺ complexes from [^{99m}Tc^VO]³⁺ precursors

H. Braband, Y. Tooyama and R. Alberto

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

The labelling of small biomolecules with ^{99m}Tc under retention of bioactivity is the major challenge in modern radiopharmacy. Consequently, great interest persists for the synthesis of new stable metal cores which can easily be conjugated to targeting molecules. We aim at using the “[⁹⁹TcO₃]⁺” core and present the first example of accessing rare types of Tc(VII) complexes.

Recently, the water stable complex [TcO₃(tacn)]⁺ (tacn = 1,4,7-triazacyclononane) was prepared by oxidation of the Tc(V) ethylene glycolato complex [TcO(OCH₂CH₂O)(tacn)]⁺ [1]. Following this “Tc(V) → Tc(VII)” approach, further water-stable “[⁹⁹TcO₃]⁺” based complexes with tacn derivatives (e.g. 1-benzyl-1,4,7-triazacyclononane and N-(4-benzylcarboxylic acid)-1,4,7-triazacyclononane) were synthesised by the oxidation of the corresponding Tc(V) complexes with hypochlorite [OCl] as oxidant and fully characterized. The pendent groups are designed for covalent coupling to biomolecules.



R = H, benzyl, benzylcarboxylic acid

Since the “[⁹⁹TcO₃]⁺” core is small, its high potential for radiopharmaceutical application is obvious. Studies with ^{99m}Tc evidenced for the first time the existence of “[^{99m}TcO₃]⁺” complexes at tracer level. Its syntheses and reactivities will be presented.

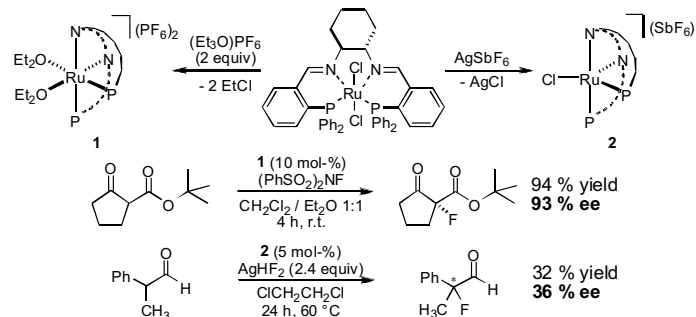
[1] H. Braband, U. Abram, *Inorg. Chem.* **2006**, *45*, 6589.

Catalytic Enantioselective Fluorinations with Ru/PNNP Complexes

Martin Althaus, Antonio Togni*, Antonio Mezzetti*

Dept of Chemistry and Applied Biosciences, ETH Zürich, CH-8093 Zürich

As the demand for bioactive compounds containing a C–F stereocenter steadily increases, methods for enantioselective fluorinations are eagerly being sought. We have recently found out that the dicationic ruthenium complex **1** catalyzes the fluorination of β -ketoesters with NFSI, giving up to 93 % ee.¹ An interesting feature of the reaction is that oxygen-containing additives strongly influence both activity and enantioselectivity.



To gain mechanistic insight, we identified adducts of the 1,3-dicarbonyl compounds with the Ru/PNNP fragment and studied their reaction with NFSI. More recently, we discovered that **2** catalyzes the α -fluorination of 2-phenyl-2-alkylacetaldehydes with AgHF_2 . Under these conditions, 2-phenylpropionaldehyde is fluorinated with 36 % ee, whereas primary aldehydes or 2,2-dialkylacetaldehydes do not react. We are still investigating the scope and mechanism of this transformation.

[1] Althaus, M.; Becker, C.; Togni, A.; Mezzetti, A., to be published.

Palladium-Catalyzed Asymmetric Allylic Alkylation with Artificial Metalloenzymes

Julien M. Pierron, Christophe G. Malan, Thomas R. Ward*

Institut de Chimie, Université de Neuchâtel
Rue Emile Argand 11, Case Postale 158 CH-2009 Neuchâtel SUISSE
Fax +41 (0)32 718 25 11
E-mail: thomas.ward@unine.ch

In the past few years our group has developed efficient artificial metalloenzymes for hydrogenation- and transfer hydrogenation reactions using the biotin-avidin technology. [1]

Recently we have focused our efforts on more challenging reactions.

The palladium-catalyzed asymmetric allylic alkylation has been demonstrated to be an extremely powerful method in organic synthesis which, to the best of our knowledge, has no equivalent in the enzymatic kingdom. [2] Our efforts to implement an artificial allylic alkylase based on the biotin avidin technology will be disclosed.

[1] Ward, T. R., *Chem. Eur. J.* **2005**, *11*, 3798-3804.[2] Trost, B. M. et al. **2006**, *39*, 747-760.Ultrafast Dynamics in Rhenium(I) Carbonyl-Bipyridine Complexes $[\text{Re}(\text{L})(\text{CO})_3(\text{bpy})]^{m+}$ (L = Cl, I, n = 0; L = 4-Et-pyridine, n = 1) probed by femtosecond fluorescence up-conversionAmal El Nahhas¹, Andrea Cannizzo¹, Ana Maria Blanco-Rodríguez², Jakub Šebera³, Stanislav Zális³, Antonín Vlček, Jr.^{2,3}, Christian Bressler¹, Majed Chergui¹

¹ Laboratoire de Spectroscopie Ultrarapide, ISIC, FSB-BSP, Ecole Polytechnique Fédérale de Lausanne, CH-1015 Lausanne-Dorigny, Switzerland

² School of Biological and Chemical Sciences, Queen Mary, University of London, Mile End Road, London E1 4NS, United Kingdom

³ J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, Dolejškova 3, CZ-182 23 Prague, Czech Republic

Controlling the singlet and triplet metal-to-ligand charge transfer (MLCT) excited states of transition metal complexes is key to their efficient use in photonic and energy conversion applications.

Femtosecond-resolved fluorescence spectra of the complexes $[\text{Re}(\text{L})(\text{CO})_3(\text{bpy})]^{m+}$ (L = Cl, I, n = 0; L = 4-Et-pyridine, n = 1) were investigated in acetonitrile using spectrally broad-band up-conversion technique. A time zero Stokes-shifted ¹MLCT fluorescence is observed, for all investigated complexes, upon excitation. The fluorescence exhibits biexponential decay, while its maximum shifts slightly to lower energies. The measured decay times are 80, 400 fs; 150, 830 fs; and 146 fs, 1.2 ps, for L=Cl, Etpy and I, respectively. Phosphorescence from the triplet ³MLCT state rises with kinetics identical to the faster fluorescence decay component, which corresponds to intersystem crossing (ISC). We attribute the slower decay to a process that repopulates the ground state, bypassing the phosphorescent triplet.

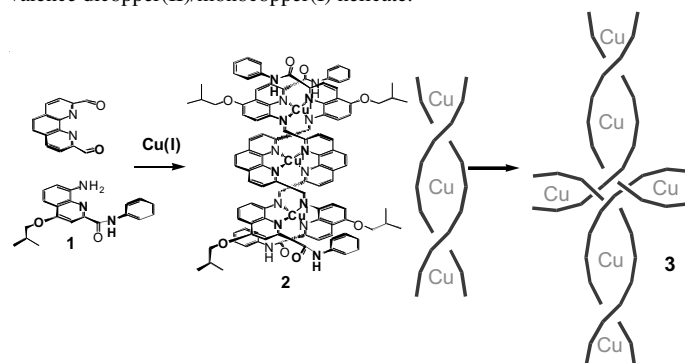
Dynamic Rearrangement and Mixed Valence Properties of a Tricopper Helicate

Victoria E. Campbell[†], Nicolas Delsuc[‡], Ivan Huc[‡], and Jonathan R. Nitschke[†]

[†]Department of Organic Chemistry, University of Geneva, 30 quai Ernest-Ansermet, 1211 Genève 4, Switzerland

[‡]Institut Européen de Chimie et Biologie, 2 Rue Robert Escarpit, 33607 Pessac Cedex, France

Tricopper(I) helicate **2** was made via subcomponent self-assembly [1], reacting phenanthroline-2,9-dicarbaldehyde, and aminoquinoline **1**, with copper(I) oxide. Helicate **2** can easily undergo a solvent dependent dynamic rearrangement giving the cross-like six copper(I) complex **3**. Furthermore, the outer copper(I) ions of helicate **2**, can be selectively oxidized by the addition of a base followed by exposure of the helicate to air, giving mixed valence dicopper(II)/monocopper(I) helicate.

[1] Nitschke J. R., *Acc. Chem. Res.*, **2007**, *40*, 103.

Histidine versus cysteine coordination of metal ions in the metallothionein *Musa acuminata* MT3

Augusto C. S. Cabral, Eva Freisinger

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

Metallothioneins (MTs) constitute a wide family of ubiquitous proteins, present in all animal phyla examined so far as well as in certain fungi, plants and cyanobacteria. As the main characteristic, MTs are generally small proteins (~7kDa) featuring a high percentage of sulphur in form of cysteine thiolate groups as well as a relatively large metal ion content [1].

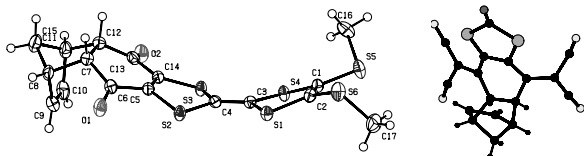
M. acuminata MT3 consists of a total of 65 amino acids, among these 10 cysteine and 1 histidine residue. The predominant part of metal ions, if not all, is bound in form of metal-thiolate clusters [1]. However, there are also examples of histidine containing MTs, in which participation of this residue in metal ion coordination has been shown [2].

In order to evaluate the role of histidine in the cluster formation of *M. acuminata* MT3, the H46C-MT3 mutant, in which the histidine residue has been exchanged for cysteine, was constructed and over-expressed in *E. coli*. Metal ion-to-protein ratios obtained by F-AAS measurements and protein quantifications based on SH-contents, ESI-MS data, as well as metal ion titration experiments followed by UV-VIS spectroscopy all showed that both, wild-type MT3 as well as the H46C-MT3 mutant, have the ability to coordinate a total of four divalent metal ions. Additionally, clear indications for histidine participation in metal ion coordination will be presented.

- [1] P. González-Duarte, in: J. A. McCleverty, T. J. Meyer (Eds.), *Comprehensive Coordination Chemistry II*, Elsevier Ltd., Amsterdam 2004, Vol. 8, pp. 213.
 [2] C. A. Blindauer, M. D. Harrison, J. A. Parkinson, A. K. Robinson, J. S. Cavet, N. J. Robinson, P. J. Sadler, *Proc. Natl. Acad. Sci. U.S.A.* **2001**, *98*, 9593.

Precursors of Fused D-A dyad involving TTF and TCNQ moietiesXavier Guégano^a, Shi-Xia Liu^a, Antonia Neels^b, Silvio Decurtins^{*a}^aDepartement für Chemie und Biochemie, Universität Bern, Freiestrasse 3, CH-3012 Bern, Switzerland^bInstitut de Microtechnique, Université de Neuchâtel, Rue Jaquet-Droz 1, CH-2002 Neuchâtel, Switzerland

Fused Donor-Acceptor systems are being explored within the wide fields of nonlinear optics, solvatochromism among others [1]. Recently, Hudhomme et al. [2] reported a system incorporating the well-known redox-active unit TTF and moderate acceptor *p*-benzoquinone. In order to improve the acceptor ability, the conversion of the quinone into a stronger acceptor unit as TCNQ is under investigation in our group. To reach the unprecedented fused TTF-TCNQ derivative, the compounds below have been designed and synthesized.



Herein, we will describe the synthetic pathway, crystal structure and properties of these derivatives.

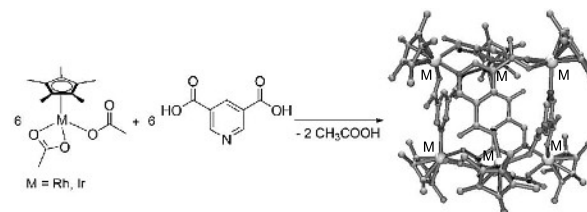
- [1] Bendikov, M.; Wudl, F.; Perepichka, D.F. *Chem. Rev.* **2004**, *104*, 4891
 [2] Dumur, F.; Gautier, N.; Gallego-Planas, N.; Sahin, Y.; Levillain, E.; Mercier, N.; Hudhomme, P.; Masino, M.; Girlando, A.; Lloveras, V.; Vidal-Gancedo, J.; Rovira, C. *J. Org. Chem.* **2004**, *69*, 2164

Self-Assembly of Coordination Cages with Organometallic Half-Sandwich Complexes

Sebastian Mirtschin, Elvira Krasniqi, Rosario Scopelliti, Kay Severin

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

Organometallic half-sandwich complexes of the late transition metals are versatile building blocks for the construction of supramolecular architectures [1]. So far, most efforts have focused on macrocyclic complexes but recent results show that coordination cages can be assembled as well [2].



We will describe the synthesis, the host-guest chemistry, and the adaptive behavior of novel (cyclopentadienyl)Rh and Ir complexes, which were obtained with the trifunctional ligand pyridine-3,5-dicarboxylic acid. The cages act as potent and selective exo-receptors for potassium ions.

- [1] K. Severin, *Chem. Comm.* **2006**, 3859-3867.
 [2] T. Brasey, R. Scopelliti, K. Severin, *Chem. Comm.* **2006**, 3308-3310.

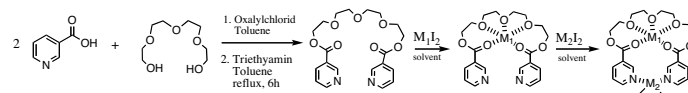
Mixed Metal Compounds for Nano Oxide Materials

Fabienne Gschwind, Katharina M. Fromm*

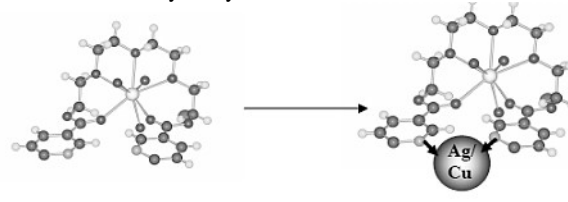
University of Fribourg, Chemin du Musée 9, CH-1700 Fribourg, Switzerland

Complexes of alkaline and earth alkaline metal ions may provide precursors for the synthesis of high Tc superconductors. Previous work has dealt with the synthesis of alkali and alkaline earth metal compounds, aiming among other properties also at the volatility of the products and their capacity of forming oxides [1]. We propose to make single source precursors with functional cyclic and open polyether molecules.

We developed a ligand system which allows the coordination to different metal ion types by different ligating atoms.



With alkaline earth metal ions such as calcium, the ligand wraps around the metal ion, yielding a complex in which the nitrogen atoms are oriented such as to accommodate very likely another metal ion such as transition metals.



- [1] K. M. Fromm, *Dalton Transactions*, **2006**, (43), 5103-5112.

Investigation of the structural rearrangement of the *btuB* riboswitch RNA induced by different B₁₂ derivatives

Sofia Gallo and Roland K. O. Sigel

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

Michael Oberhuber and Bernhard Kräutler

Institute of Organic Chemistry, Leopold-Franzens University Innsbruck, Innrain 52a, A-6020 Innsbruck, Austria

The B₁₂-responding *btuB* riboswitch RNA of *E. coli* was shown to specifically bind coenzyme B₁₂ (AdoCbl) and to undergo a structural rearrangement of the RNA, resulting in an altered gene expression. [1-3]

Our studies focus on the structural changes that are induced to this RNA sequence upon binding to different B₁₂ derivatives and which part of the B₁₂ molecule is recognized by the riboswitch. We performed spontaneous self-cleavage experiments with AdoCbl, vitamin B₁₂ (VitB₁₂), adenosyl Factor A (AdoFactA) and adenosyl cobinamide (AdoCobi) and determined the K_D values to be 90 nM for AdoCbl, 337 nM for AdoFactA, 313 μM for VitB₁₂ and 705 μM for AdoCobi. All four derivatives induce the same overall structural changes in the 202 nt long riboswitch. Accordingly, the corrin moiety is the determinant for the structural rearrangement of the *btuB* riboswitch, irrespective of the differing affinities of the tested B₁₂-derivatives.

- [1] M. Mandal, R. R. Breaker, *Nat. Rev. Mol. Cell Bio.* **2004**, 5, 451-463.
 [2] X. Nou, R. J. Kadner, *P. Natl. Acad. Sci.* **2000**, 97, 7190-7195.
 [3] A. Nahvi, N. Sudarsan, M. S. Ebert, X. Zou, K. L. Brown, R. R. Breaker, *Chem. Biol.* **2002**, 9, 1043-1049.

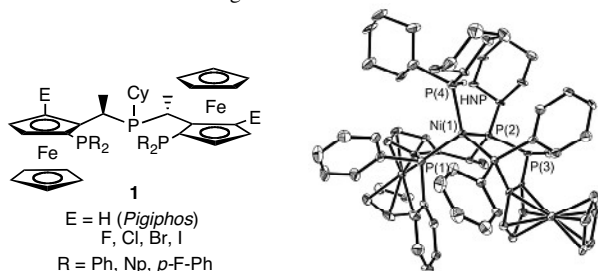
Support by the University of Zürich (*Forschungskredit* to S.G.), by the Swiss National Science Foundation (*SNF-Förderungsprofessur*, R.K.O.S.), by the Austrian National Science Foundation (FWF, P-13695) and by the European Commission (HPRN-CT-2002-00195, B.K.) is gratefully acknowledged.

Tridentate Ferrocenyl Ligands in Catalytic Hydrophosphination of Methacrylonitrile

Pietro Butti, Antonio Togni*

Department of Chemistry and Applied Biosciences, ETH Zurich, Wolfgang-Pauli Strasse 10, 8093 Zurich, Switzerland

Very few catalytic enantioselective syntheses of chiral phosphines have been described in the literature [1]. Our group recently reported that a dicationic [Ni(L)(1)] (L = Solv., R-CN) complexes catalyzes intermolecular hydrophosphination reactions in good yield and high enantiomeric excess [2]. We show now that the selectivity of the hydrophosphination of methacrylonitrile is influenced by the systematic modification of 1 at different positions of the ferrocene ligand.



Coordination chemistry studies indicate that a Ni(II) precatalyst is required for catalytic activity. Indeed, [Ni(O)(HPCy₂)] does not undergo P-H activation and is not a catalyst of the hydrophosphination reaction.

- [1] See, e.g.: (a) Scriban, C.; Kovacic, I.; Glueck, D.S. *Organometallics* **2005**, 24, 4871-4874. For a review, see: (b) Baillie, C.; Xiao, *J. Curr. Org. Chem.* **2003**, 7, 477-514.
 [2] Sadow, A. D.; Togni, A. *J. Am. Chem. Soc.*; **2005**; 127(48); 17012-17024.

Direct syntheses of ^{99m}Tc^{VI} complexes with the [TcO₃]⁺ core from [TcO₄]⁻

Y. Tooyama, H. Braband and R. Alberto

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

Beside the well developed [Tc(CO)₃]⁺ core, we are exploring chemistry with the even smaller [TcO₃]⁺ moiety. Complexes with this core would be very small and, thus, affect the biological properties of targeting agents the least. Before aiming at using this core in labelling chemistry, the properties and synthetic approaches to model complexes have to be studied.

The [TcO₃]⁺ core has to be stabilized preferentially with tripodal ligands. Principally, two synthetic routes to complexes [L³TcO₃] are possible. First, by oxidation of a lower valent complex or, secondly, by direct activation of [^{99m}TcO₄]⁻. The second route is uncommon even for other transition elements but proved to be very useful for technetium. The reaction of [^{99m}TcO₄]⁻ with benzoyl chloride gives the mixed anhydride [O₃Tc(O₂C-Ph)] (1) which can be used for direct reaction with a variety of tripodal ligands.

The reaction of (1) with Hbpza (bis-(pyrazole-1-yl)acetate)¹ produced rapidly [TcO₃(bpza)] (2) in good yield. The synthetic approach is general and can be extended to many other ligand types. The stabilities and approaches for identical complexes with ^{99m}Tc will be presented.

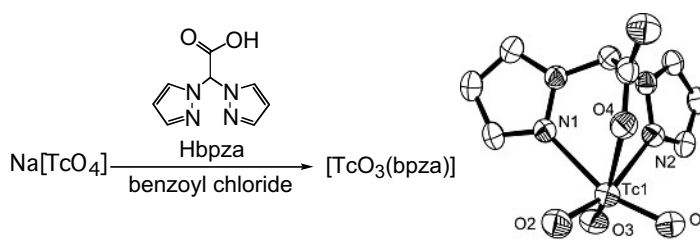


Fig.1 Ortep drawing of (2)

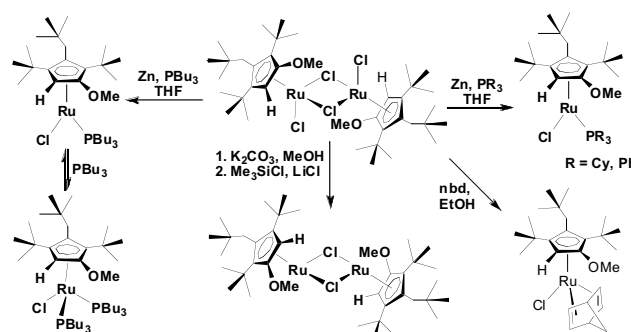
- [1] N. Burzlaff, I et al *J.Organomet.* **2001**, 626, 16-23

A Novel Cyclopentadienyl Ligand: Increased Steric Hindrance Leading to Stabilization of Unusual Coordinatively Unsaturated Complexes

Barnali Dutta, Euro Solari, Rosario Scopelliti, Kay Severin*

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

We have recently reported the one-pot synthesis of Ru(III) complex with very distinct and sterically hindered cyclopentadienyl ligands through a Ru-mediated coupling reaction of *tert*-butylacetylene and alcohol. [1] They have been found to be versatile starting materials for the preparation of Ru(II) half-sandwich complexes. Importantly, it is possible to stabilize coordinatively unsaturated complexes, which are not accessible with the standard Cp* ligand.



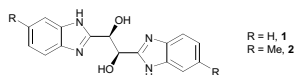
- [1] S. Gauthier, E. Solari, B. Dutta, R. Scopelliti and K. Severin, *Chem. Commun.* **2007**, DOI: 10.1039/b618712a

Getting more out of mass spectrometry: the pseudoisotope approach

Sarah Norman, Alexandra Spyratou, Carlos da Silva, Xavier Melich, Claire Deville, Philippe Perrotet and Alan F. Williams

Département de Chimie minérale, analytique et appliquée, Université de Genève, 30 quai Ernest Ansermet, CH 1211 Genève 4.

Electrospray mass spectrometry is established as a powerful technique for studying self-assembled complexes in solution.[1,2] However, it is sometimes difficult to identify exactly the nuclearity since a complex of formula $[M_nL_q]^{z+}$ will give a peak at the same m/z value whatever the value of n . Isotopic splittings can allow the resolution of this question, but not all elements have suitable isotopes, and when the complexes are highly charged the resolution of the instrument may be insufficient.



Ligands such as **1** and **2** differ only in the presence of methyl groups far from the coordination site and will show identical coordination behaviour, differing only in molecular weight: they may be regarded as *pseudoisotopic*.

Mixtures of pseudoisotopic ligands may be used to establish unambiguously the nuclearity of complexes formed in self-assembly reactions. As with true isotopes they may be used to study exchange reactions: the scrambling of pseudoisotopic ligands offers a simple way of establishing the lability of multinuclear complexes, with some surprising results. Examples of the use of this method will be given.

- [1] C. Piguet, G. Bernardinelli, and G. Hopfgartner, *Chem. Rev.*, **1997**, 97, 2005.
 [2] A. Marquis-Rigault, A. Dupont-Gervais, A. V. Dorsselaer, and J.-M. Lehn, *Chem. Eur. J.*, **1996**, 2, 1395.

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

Maria Casapu¹, Jan-Dierk Grunwaldt¹, Marek Maciejewski¹, Stephan Eckhoff², Ulrich Göbel², Meike Wittrock², Alfons Baiker¹

¹Department of Chemistry and Applied Biosciences, ETH-Zurich, Hönggerberg, CH-8093 Zurich, Switzerland

²Umicore AG & Co. KG, Rodenbacher Chaussee 4, D-63403 Hanau-Wolfgang, Germany

In order to decrease fuel consumption, lean-burn engines with direct fuel injection have been introduced however this approach requires new catalyst concepts for NO_x -reduction. The most promising strategy to reduce NO_x -emissions is the use of the NO_x storage-reduction (NSR) catalyst. The NSR catalysts contain noble metals (Pt, Rh) and a storage component (Ba, K) deposited on carrier oxides with a high surface area, such as Al_2O_3 or CeO_2 . The NSR performance of such catalysts is high but deactivation can be caused by exposure to high temperatures during operation.

Our study presents a detailed investigation on the processes occurring during ageing of Pt/Ba/CeO₂ and Pt/Ba/Al₂O₃ NO_x storage-reduction catalysts. During ageing Ba-support mixed oxides are formed. We investigated their stability in the presence of H₂O, NO₂ and CO₂. BaCeO₃ could be decomposed in the presence of NO₂/H₂O at 300–500°C. BaAl₂O₄ was decomposed in this atmosphere only at lower temperatures. Also in a CO₂ containing atmosphere BaCeO₃ is decomposed recovering the active NO_x storage phase of BaCO₃. This process was not observed for BaAl₂O₄. The instability of the undesired mixed oxides could be utilized for the regeneration of thermally aged catalysts as recent tests at an engine bench have shown [1]. Finally, we investigated the fate of Pt during ageing.

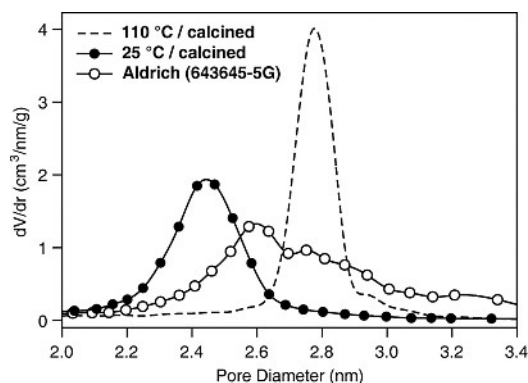
- [1] M. Casapu, J.-D. Grunwaldt, M. Maciejewski, M. Wittrock, U. Göbel, S. Eckhoff, A. Baiker, *Top. Catal.* in press (2007).

Convenient Room Temperature Synthesis of High Quality Mesoporous Silica MCM-41

Hanna Salmio, Dominik Brühwiler*

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

The original synthesis of MCM-41 (a mesoporous molecular sieve featuring a hexagonal array of one-dimensional channels) dates back to 1992 [1]. In the following years, synthesis procedures were further developed, resulting in optimized materials for applications as diverse as catalysis, drug delivery, and sensing. We present a simplified synthetic pathway requiring no complex procedures and no special lab equipment. Batches of up to 25 g were obtained by this method and further scale up is feasible. Materials prepared by this convenient synthesis have excellent properties and compare favorably to commercially available MCM-41 products.



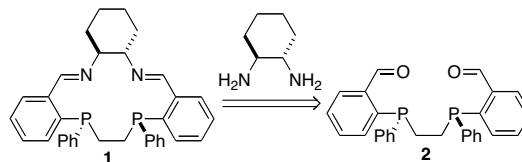
- [1] C. T. Kresge et al., *Nature* **1992**, 359, 710.

Ru / PNNP Complexes with Cyclic PNNP Ligands

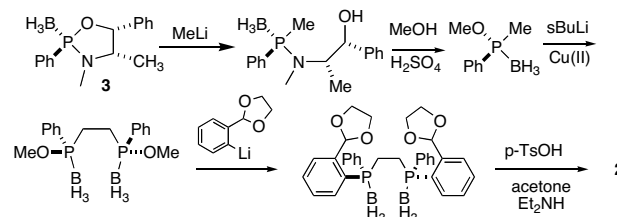
Marco Ranocchiaro and Antonio Mezzetti*

Dept of Chemistry and Applied Biosciences, ETH Zürich, CH-8093 Zürich

We have used Ru/PNNP complexes as catalysts for atom-transfer reactions such as the epoxidation, cyclopropanation, and aziridination of olefins and for the fluorination and Michael addition of β -ketoesters.¹ We report here recent progress toward the synthesis of the macrocyclic PNNP ligand (**1**) that is expected to form more rigid and selective catalysts. We plan to prepare **1** from diamino cyclohexane and diphosphine **2**:



Up to now, we obtained diphosphine **2** from oxazaphospholidine borane **3** according to Jugé's method:²



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

- [2] Kaloun, E. B.; Merdès, R.; Genet, J.-P.; Uziel, J.; Jugé, S. *J. Organomet. Chem.* **1997**, 529, 455.