Inorganic and Coordination Chemistry

Reactions of Cp'2CeH: Breaking C-H and C-O Bonds and Making C-C Bonds

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The net reaction of the monomeric lanthanidehydride, bis[1,2,4-(Me3C)3C5H2]2CeH abbreviated as Cp'2CeH, and methylaldehydes is Cp'2CeX and CH4. The mechanism of this metathesis reaction does not proceed through a one-step metathesis transition state; rather, the reaction proceeds buy way of a two-step process in which the first step is an α-CH bond activation generating H2 and the intermediate, Cp'2Ce(η-CH2X), that evolves into the products as H2 traps the methylene fragment. Isolation of the intermediate, when X = OMe in the reaction between CH3OMe and the hydride, followed by its rearrangement to Cp'2CeOMe and CH4 supports the two-step mechanistic postulate that involves successive CH and CO bond breaking steps. When the ethers contain α- and β-CH bonds, for example in diethyl ether, the α- and β-CH activation steps are of comparable energy, but only the β-activation intermediate leads to the final product. The net reaction with CH3OSiMe3 yields Cp'2CeOMe and HSiMe3, is a SiO bond splitting reaction that does proceed by way of a metathesis transition state that involves five-coordinate silicon. In contrast, the net reaction between Cp'2CeH and CH2OMe yields Cp'2Ce(η-CH2OMe), which rearranges to Cp'2CeOMe, Cp'2CeOCH2Me (a Wittig rearrangement product), isobutene and isobutane. Evidence for this C-O bond breaking and C-C bond making reaction will be presented. The mechanistic principles developed from these studies are applicable to those metals that cannot undergo oxidative addition-reductive elimination steps and therefore of general utility.


Inorganic and Coordination Chemistry

What is alumina? A molecular point of view

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While alumina is often just considered as a way to support active phases (active sites and nanoparticles), alumina, for instance, readily activates the C-H bond of methane at low temperatures (e.g. 25-100 °C).[1] Moreover, it is often a key component to obtain catalytic activity for heterogeneous catalysts including for the so-called single-site catalysts.[2] Thus, one might ask what is so special about alumina and more precisely what are the surface sites that allow activation of C-H bond and metal centers. Here will be described the key structural features of this support, which are essential for generating active sites, by a combined experimental and computational approach. [3]


Inorganic and Coordination Chemistry

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

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

In this context, the sensitisation of lanthanne luminescence in the green (1B), red, (Eu) even infra-red (Yb) has been achieved by a two-photon antenna effect, a third order NLO phenomenon. Optimisation of the molecular two-photon cross-section involving a new sensitisation process, design of Ln-based nanoparticles as well as applications in bio-imaging using confocal biphotonic microscopy will be presented.

Inorganic and Coordination Chemistry

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

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

Inorganic and Coordination Chemistry

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

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

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


Inorganic and Coordination Chemistry

Development of Biopolymeric Drug Carriers for Targeted Delivery of Polyoxometalates

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

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

Inorganic and Coordination Chemistry

NEW FUNCTIONALIZED η⁷–ARENE RUTHENIUM COMPLEXES FOR BIOLOGICAL APPLICATIONS

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Recently, it was shown that ruthenium possesses several favorable chemical properties, suggesting that it may be a strong candidate to replace platinum and to form a basis for anticancer drug design [1-4]. Besides the rich synthetic chemistry, ruthenium possesses the ability under physiological conditions to adopt a large range of oxidation states (Ru³⁺, Ru⁴⁺ and Ru⁶⁺), an important feature for metal-based anticancer drugs. In addition, ruthenium compounds are generally less toxic than platinum compounds and it is believed that remarkable anticancer activity of ruthenium resides in its ability to mimic iron in binding to several biomolecules, including serum transferrin and albumin.

Like other classes of ruthenium compounds, organometallic ruthenium complexes bearing η⁷-arene ligands have been intensively studied as potential anticancer drugs candidates. In this contribution, we report the synthesis and characterization of new functionalized η⁷-arene ruthenium complexes which were designed in order to improve their cytotoxicity, selectivity against cancer cells, but also to facilitate their uptake by cancer cells.


Inorganic and Coordination Chemistry

17 e⁻ Rhenium CO-Releasing Molecules on a Cobalamin Scaffold

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Cyanocobalamin (B₁₂) offers a biocompatible scaffold for CO-releasing 17-electrons dicarbonyl complexes based on the cis-trans-[Re(CO)₂Br]⁺ core. A Co–C=N-Re conjugate is produced in a short time and high yield from the reaction of [Et₂N₃][Re₂Br₂(CO)₉] with B₁₂ [1-2]. These B₁₂-Re(CO)₉ derivatives are characterized by an improved stability in aqueous aerobic media over the metal complex alone, and afford effective therapeutic protection against ischemia-reperfusion injury in cultured cardiomyocytes. The non-toxicity of the resulting metal fragment after CO release, is attributed to the oxidation of the metal and formation in solution of the ReO₅⁻ anion which is among the least toxic of all of the rare metals inorganic compounds.


Inorganic and Coordination Chemistry

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

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


Inorganic and Coordination Chemistry

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

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Vitamin B₁₂ is essential for humans and plays a key role in cell division. Since fast proliferating cells such as cancer cells are strong consumers of B₁₂, catalytically inactive surrogates offer potential medical applications. [1] Most studies with Cbs investigated the coordination chemistry at the ζζ⁻(“upper”) side of the corrin macrocycle. Rather little is known about the impact of structural changes at the αα⁻(“lower”) side of the molecule. [2] We are interested in the development of B₁₂ derivatives with tuneable coordination and redox properties for physico-chemical studies and biological applications. For this purpose, we modified the ζζ⁻ side chain of B₁₂ with different peptide structures. [3] A linear relationship between the “base-on” stability and the reduction potential of cobalt was demonstrated. We also showed that these B₁₂ derivatives are useful for the identification of related natural counterparts. [4] The biological behavior of this class of compounds in enzymatic reactions as well as B12-dependent bacteria growth tests will be discussed.

Inorganic and Coordination Chemistry

A Molecular Pentafold Knot


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


Inorganic and Coordination Chemistry

Metal cluster and functional analysis of plant Metallothioneins

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

Following previous investigations on the MT2 from Cicera arietinum, which implicated increased metal ion incorporation into the metal-thiolate cluster in the presence of sulfide ions [2], we analyzed this feature further with different techniques, e.g. UV, CD, MCD, F-AAS, ESI-MS, and colorimetric assays. Owing to their high metal ion binding capacity, a functional role of the plant MTs in metal ion homeostasis and heavy metal detoxification was assumed and yeast complementation assays were performed. The protection system of this model organism against toxic metal ion concentrations was knocked out and replaced by plasmid DNA encoding the MT2 and, therefore, TD-DFT calculations were carried out. The calculations showed that the LUMO only extended over the 4'-pyridyl-2,2':6',2''-terpyridine unit and, therefore, the N-substitution has little effect on the electronic and spectroscopic properties of the complexes. The latter are being tested for stability and water-splitting activity.


Inorganic and Coordination Chemistry

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

Federico Giannini a,b, Julien Furrer a,b, Bruno Therrien b, Georg Süß-Fink a

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

In this regard, we have synthesized various thiophenolato-bridged dinuclear aren ruthenium complexes of the general formula [(p-cymene)Ru(SPh)] with IC50 values being in the submicromolar range, and analyzed their interaction with amino acids, nucleotides, glutathione and peptides under physiological conditions.3,4 The aim of this initial screening by NMR spectroscopy is to provide the basis for subsequently understanding and characterizing the possible mode of action of these organometallic species with cellular targets in cancer cells and blood plasma at a molecular level. The results presented provide a first insight into their mode of action, and may provide guidance for synthesizing future optimized ruthenium-based drugs.


Inorganic and Coordination Chemistry

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

Edwin C. Constable, Michael Devereux, Emma L. Dunphy, Catherine E. Housecroft, Jennifer A. Rudd and Jennifer A. Zampese

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We have investigated the effects of attaching different substituents, R, to the pyridyl N-position of 4'-pyridyl-2,2':6',2''-terpyridine (L) on the electronic and spectroscopic properties of the [RuL2(H2O)]1 complexes. Experimentally, anion exchange has a negligible effect on the electronic and spectroscopic properties and, therefore, TD-DFT calculations were carried out. The calculations showed that the LUMO only extended over the 4'-pyridyl-2,2':6',2''-terpyridine unit and, therefore, the N-substitution has little effect on the electronic and spectroscopic properties of the complexes. The latter are being tested for stability and water-splitting activity.

Inorganic and Coordination Chemistry

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

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

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

Inorganic and Coordination Chemistry

**New iridium(III) blue emitters**

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Light Emitting Electrochemical Cells (LEECs) are electroluminescent devices with an emissive organic layer, like Organic Light Emitting Diodes (OLEDs). Up to today, OLEDs are used in a wide range of applications including digital screens and for room lighting. Compared to an OLED, a LEEC has a significantly simplified architecture. Two electrodes sandwich the emissive layer containing the light emitting molecules. But in LEECs the emitting molecules need to be ionic, unlike in OLEDs. While the OLEDs need a perfect encapsulation to prevent the degradation of the electron-injecting layers, air-stable electrodes like gold or silver can be used with LEECs. Four new iridium(III) complexes have been prepared, which all show a blue emission with quantum yields up to 100%.

Inorganic and Coordination Chemistry

**PCsp3P and PCsp3P Palladium (II) Hydride Pincer Complexes: Small Structural Difference – Large Effect on Reactivity**

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Switzerland

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

Inorganic and Coordination Chemistry

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

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

Inorganic and Coordination Chemistry

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

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

Inorganic and Coordination Chemistry

**PCsp3P and PCsp3P Palladium (II) Hydride Pincer Complexes: Small Structural Difference – Large Effect on Reactivity**

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

**IC 21**

**[Fe]-Hydrogenase Models Featuring Acylmethylypyridinyl Ligand**

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[Fe]-hydrogenase (Hmd) catalyzes the reversible reduction of methylenetetrahydrofolate to H2 and formate in a wide pressure range, has shown in Figure 1.[1,2]

Herein we present two model complexes which reproduce the main structural features of the active site of [Fe]-hydrogenase.1,4

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**IC 22**

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

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Recent publications reported that the olivine phase of LiMnPO4 is one of the best alternative cathode materials for Li-Ion Batteries (LIB). The layered rock salt oxides LiCoO2, LiNiO2, and LiMnO2 have been reported that the structure is deformed at overcharging and the transition metal is dissolved into the commercial electrolyte upon cycling. Therefore, it has been researched to replace those layered structures by polyanionic olivine LiMPO4 (M = transition metal) structure due to the excellent cyclability, thermal and chemical stability, low cost and low environmental impact.[3]

Despite of its high theoretical capacity (170 mAh/g), high operating voltage (4.1 V vs. Li) and good capacity retention, LiMnP04 suffers from low intrinsic electronic/ionic conductivity. Particularly, at high current densities the electrochemical performance is poor caused by the slow Li diffusion kinetics within the grains. Reducing the particle size has been found to be one of the effective ways to increase the rate performance because nanoparticles reduce the diffusion path length for Li+ and increase the contact area with conductive additives.[4]

We synthesized nanoparticles of LiMnP04 via thermal decomposition method using surfactant. Specific surface area measured by nitrogen adsorption method is 99 m2/g, corresponding to 17 nm of particle size.

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

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**IC 23**

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

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As an energy carrier, hydrogen holds the potential to provide clean, safe and affordable energy in an easily usable form. Formic acid is an excellent source of hydrogen, having many advantages including weight and safety issues. A viable H2 storage system, based on the selective homogeneous catalytic decomposition of formic acid into H2 and CO2, in a wide pressure range, has been proposed.2,3 The catalytically active species are formed in situ from RuCl3 and TPPTS in aqueous solution.[4]

Heterogeneous catalysts could be advantageous for recycling, especially for dilute formic acid solutions, or for small, mobile and portable applications. Several approaches have been used to immobilize/solidify the homogeneous Ru/TPPTS3,4. We will present our recent results concerning the immobilization/solidification of the ruthenium complexes on silica supports, for hydrogen production from formic acid. These catalysts offer the advantage of high catalytic activity and easy catalyst separation/recycling in dilute HCOOH.

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

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**IC 24**

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

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Ruthenium cyclopentadienyl complexes such as Cp*RuCl(cod) and Cp*RuCl2(PPh3)2 are active catalysts for the ‘click’ reaction between azides and alkynes. We show that those complexes are also able to catalyze the transformation of benzyl azide into hydrobenzamide. The catalyst precursor [Cp*RuCl2] (Cp* = 9-Me2-1-methoxy-2,4-di-tert-butyl-3-norbcypentadienyl) was found to be particularly active and selective. The transformation has been extended to other benzyl azides and the mechanism has been studied as well. In the presence of water, benzyl azides are converted to aldehydes.

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Inorganic and Coordination Chemistry

Intercluster Compounds for Nanosized Materials

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The term “intercluster compound” refers to assemblies that are constituted of at least two different, large, inorganic building blocks [1, 2]. A few intercluster compounds already exist and it has been possible to determine their crystal structures by single crystal X-ray diffraction. These results deliver insights into the arrangement of large building units in the solid state material and the underlying intermolecular forces [3, 4]. These first results show that intercluster compounds are very promising for the study of structural and physical properties of nanosized particles. They also open a wide range for new applications (lithography techniques, electronic or optical devices, study of quantum effects and also of orbital bands). Since only a few compounds have been studied, there is a huge potential for new discovery in this field. We would like to present new building blocks [5] and their corresponding intercluster compounds.


Inorganic and Coordination Chemistry

Copper-containing Gallium Defect Spinels

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Although impressive progress in oxide nanomaterials synthesis has been reported,[1] many compounds still require the development of individual preparative pathways. This applies for metal-doped defect spinels of the γ-Ga2O3 type that are far less explored than CuGa2O4 or CuGaO2.[2–3]. However, by applying state-of-the-art microwave-hydrothermal (MW-HT) techniques, we synthesized hierarchically nanostructured γ-Ga2O3:Cu2+ materials. The implementation of Cu2+ ions into nanoscale γ-Ga2O3 matrices is completed within less than 30 minutes of reaction time, resulting in products with homogeneous distribution of Cu2+ and high surface areas. Therefore, the γ-Ga2O3:Cu2+ materials are promising for catalytic processes, such as methanol synthesis, water splitting or the photocatalytic degradation of organic compounds.

Representative SEM and TEM images of MW-HT synthesized γ-Ga2O3:Cu2+.

We thus report on the analytical characterization and catalytic behavior of the obtained γ-Ga2O3:Cu2+ spinels.


Inorganic and Coordination Chemistry

Folding properties of metallothionein Ec-1 from wheat (Triticum aestivum) investigated by intrinsic tryptophan fluorescence

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

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Inorganic and Coordination Chemistry

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

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1University of Basel, Department of Chemistry, CH-4056 Basel Switzerland
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During the past decade, artificial metalloenzymes based on biotin-avidin technology have been extensively investigated in the Ward group.[1] These artificial metalloenzymes rely on the localization of a catalytically active organometallic moiety within a chiral protein scaffold. In order to develop a new generation of artificial metalloenzyme, we transferred our knowledge of the biotin-streptavidin technology to a sulfonamide-human carbonic anhydrase II system. This protein offers new interesting characteristics including a deeper binding pocket and a monomeric structure allowing a much more straightforward in silico modeling of the new artificial metalloenzyme.[2–3]

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

Inorganic and Coordination Chemistry

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

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Methods for the preparation of cubane-type \([\text{Re}_2(\text{CO})_6(\mu_2-\text{OH})_2] \) \(^1\) and incomplete cubane-type \([\text{Re}_2(\text{CO})_6(\mu_2-\text{OH})(\mu-\text{OH})] \) \(^2\) clusters were described in the early 90’s. \(^1\) Especially trinuclear incomplete clusters of type 2 are of high interest due to their rich coordination chemistry. Thus, trinuclear Re(I) cluster 2 acts as a novel tripodal ligand for a wide range of divalent metals (Cu, Mn, Zn, Co) forming the “double-cubane” structure type 4. \(^2\) By replacing OH with SR these Re(I) clusters are thought to have similar redox-chemical properties as Fe-S-cluster, therefore mercapto analogues like \([\text{Re}_2(\text{CO})_6(\mu_2-SH)(\mu-\text{SH})] \) \(^3\) are prepared for the Fe-S-cluster mimic. Further, different trinuclear Rhenium mercapto cubane-types \([\text{Re}_3(\text{CO})_9(\mu_2-SR)(\mu-\text{SR})] \) \(^3\) were prepared in order to extend the coordination number of the tripodal ligand forming the sixfold-coordinated complex 5. These clusters were synthesized using \([\text{ReBr}_3(\text{CO})_11] \) \(^3\) as starting material and the condition mentioned in the scheme below. 1 to 5 were structural characterized and electrochemical investigated.

[Diagram of clusters]


[References]

Inorganic and Coordination Chemistry

Synthesis and Studies of New Iridium Hydride Complexes

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Caticnic iridium complexes incorporating chiral P,N– and heterocyclic car-bene–ligands have proven to be highly effective catalysts for the enantiose-
lective hydrogenation of unfunctionalised olefins\(^1\). For this reason, the chemistry of iridium hydride complexes, which are intermediates in hydro-
genation reactions, continues to be of considerable interest\(^2\).

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

\[^{1}\] S. J. Roseblade, A. Pfaltz, Accounts of Chemical Research 2007, 40, 1402.

Inorganic and Coordination Chemistry

Iridium(III) Complexes for Light Emitting Electrochemical Cells

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


Inorganic and Coordination Chemistry

Reaction of NO\(^+\) with O\(_2\) in Cold Hydrocarbons

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

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

We conclude that the autooxidation of NO\(^+\) proceeds via ONOO\(^-\), not \(\text{N}_2\text{O}_2\).

Within recent years, nanocontainers have attracted increasing interest due to their ability to enclose guest molecules inside their empty core. Because of this potential, hollow nanoparticles may find numerous applications such as drug carriers, reactors, confined reaction vessels, building blocks for photonic crystals or multienzyme biocatalysis. The microemulsion approach for the production of nanocontainers is a relatively new method enabling dissolution of any substance. Subsequent reaction between reagents on the boundary phase between a micelle and the surrounding phase leads to the formation of a nanocontainer. The aim of this study is to encapsulate an antimicrobial silver coordination polymer inside inorganic nanocapsules. We have successfully synthesized hollow spheres of a well-defined porous shape with an outer diameter of 41±5 nm and with a wall thickness of 11±2 nm (Fig. 1).

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


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**Sodium phosphacyanate as building block for heterocyclic compounds**

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The reaction of NaNH with carbon monoxide gives the phosphor analogue compound of sodium cyanate, namely Sodium phosphacyanate NaO-C≡P. In a different route carbon monoxide is replaced by ethylene carbonate, which is readily handleable. The phosphacyanate anion is a small molecule, which contains a phosphorus-carbon triple bond and is therefore a very versatile building block in organophosphorus chemistry. Among others NaOCP can act as a nucleophile. Depending on their electronic character, electrophiles attack the phosphacyanate anion either at the phosphorus or the oxygen atom. Furthermore we found that the phosphacyanate anion undergoes cycloadditions. Nevertheless NaOCP has not been widely investigated as a starting material. Exploring the chemistry of NaOCP we tested its reactivity towards an acid chloride. Surprisingly in the reaction with 2,4,6-trimethylbenzoyl chloride the five-membered heterocyclic compound 1 is formed.

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

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

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

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Inorganic and Coordination Chemistry

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

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Poly(bipyridine)-ruthenium(II) complexes with carbonylate anchoring groups have been extensively studied because of their exceptional photophysical properties: they can be used as tuneable pigments in dye-sensitised solar cells (DSSCs). Complexes with carbonylate anchoring groups bind strongly to the titanium dioxide surface of solar cells. Most complexes have used 4,4'-dicarboxy-2,2'-bipyridine as the anchoring ligand because this ligand facilitates photoinduced electron transfer from the excited ruthenium centre to the surface, which is very important for the efficiency of DSSC.[3]

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

2IC 37
3IC 38
4IC 39
5IC 40

We report here heteroaromatic (HetAr) substituted bpy-ligands (see scheme). Homoleptic [Cu(6-HetAr-bpy)][PF6] complexes show unusual behaviour in solution and have been studied by NMR spectroscopy. Their incorporation into DSSC devices is also described.

Inorganic and Coordination Chemistry

**IC 41**

**Mg^{2+}** binding sites in the κζ region of group II intron Sc.ai5y

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Magnesium ions are crucial cofactors of group II intron ribozymes, which need them not only for folding and charge compensation, but also to catalyze self-splicing [1]. The group II intron core structure contains the κζ region of domain I (D1κζ), which interacts with the conserved domain 5 (D5) both through a tetraloop receptor (ζ) and a three-way junction (κ). The ζ interaction is known to depend upon di- or multivalent metal ions [2], while there is no information yet on κ.

We are investigating the structure of the isolated D1κζ of *S. cerevisiae* group II intron Sc.ai5y by NMR spectroscopy. Upon addition of Mg^{2+} we observe large changes in both κ and ζ that allow us to characterize the location and thermodynamics of Mg^{2+} binding.

Financial support by a Marie Curie Intra European Fellowship (RNABC, 226794 to DD) and in the form of access to the Bio-NMR Research Infrastructure (FP7/2007-2013, grant agreement 261863) within the 7th European Community Framework Programme as well as by the Swiss National Science Foundation (200021-124834 to RKOS) is gratefully acknowledged.


Inorganic and Coordination Chemistry

**IC 42**

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


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*S. cerevisiae* (Sc.) ai5y is a multi-domain RNA (~900 nts) belonging to the class of group II intron ribozymes, whose folding and splicing activities are influenced by metal ions. We designed a derivative of this large ribozyme, named D135-L14, which is labeled by the Cy3-Cy5 fluorophores pair and preserves the dynamics and the catalytic activity of the parent ribozyme [1]. FRET of the labeled RNA has been investigated both in bulk experiments and at the single molecule (sm) level by TIRF microscopy. Particularly, smFRET time trajectories revealed a new paradigm folding for this construct, characterised by three FRET states whose distribution depends on the type and concentration of metal ions in the system [1,2]. In order to assign each FRET state to a specific intermediate in the folding process, different mutated D135-L14 have now been made and analysed by smFRET.

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


Inorganic and Coordination Chemistry

**IC 43**

**Molecular computing**

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Certain compounds can work as so-called molecular switches. Inherent properties of molecules such as conformation, isomerisation, redox properties, pH sensitivity, photoinduced electron transfer and photophysics form the basis of the input and outputs, desirable in a molecular computational device. Our group has reported molecular switching properties of ruthenium(II) terpyridine metal complexes with pendant pyridine units which can exist in different protonation states, each displaying different photophysical characteristics. By observing the change in luminescence 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.


Inorganic and Coordination Chemistry

**IC 44**

**Luminescent Carbene Platinum(II) Arylacetylide Complexes**

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

![Structure of the complexes](image)

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

Inorganic and Coordination Chemistry

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

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

\[
R = \text{OMe, Br, NO}_2
\]

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


Inorganic and Coordination Chemistry

NMR structural investigation of the κ-ζ region of the group II intron ribozyme ScaI5

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Group II introns are large self-splicing RNAs that need monovalent and divalent metal ions for folding and activity [1]. They perform the splicing by catalysis. The so called κ-ζ region of domain 1 (D1), together with domain 5, represents the minimal required structure for activity. Despite the biological importance of these RNAs, only little structural information on their tertiary architecture is known so far [3]. We are investigating by NMR the 3D structure of the κ-ζ region of D1 of ScaI5 group II intron from yeast mitochondria. This RNA contains structural features associated with high mobility. The presence of Mg\(^{2+}\) proved to be essential to partially overcome the mobility. NMR experiments run in different experimental conditions and at different magnetic fields allowed the attributions of most of the \(^1\)H, \(^{13}\)C and \(^{15}\)N NMR resonances. The NMR structure of the κ-ζ region and its Mg\(^{2+}\) binding properties will be presented.


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

Inorganic and Coordination Chemistry

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

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

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

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

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

The multicomponent reaction of diboronic acids with a catechol and a tripyridyl linker results in the formation trigonal prismatic cages. The cages are able to encapsulate polyaromatic molecules such as triphenylene or coronene. The compounds are close structural analogues of coordination cages described by the group of Fujita.


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The isolation and characterization (including structural aspects) of these new complexes (arene)Ru2(SR)2Cl2 and their properties with respect to their [(arene)Ru2(SR)3]Cl counterparts as well as a simple synthetic strategy for the synthesis of mixed complexes of the type [(arene)Ru2(SR)2(SR′)]+ will be presented.


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The values of the rate constants k1 and k2 describe the decay in phosphate buffer.


We report ruthenium nanoparticles (~4 nm) intercalated in hectorite to be a highly efficient (conversion 100%, turnover frequency 177 h⁻¹) and highly selective (selectivity > 99%) reusable catalyst for the hydrogenation of FA to give THFA under mild conditions (methanol solution, 40 °C, 20 bar H₂). After a total turnover number of 1423, the hectorite-supported ruthenium nanoparticles are deactivated but can be recycled and regenerated.

Inorganic and Coordination Chemistry

IC 57

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

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The use of carbon dioxide - formic acid cycle for hydrogen storage and delivery is advantageous for environmental reasons [1]. The formic acid decarboxylation reaction should be selective, to produce only CO₂ and H₂ (no CO). The hydrogen production should take place under mild conditions, and in aqueous solution; since water obviously preferred to the organic solvents, as reaction medium.

Efficient catalysts have already been developed for this reaction [2], using highly negatively charged hydrophilic sulfonated phosphine ligands with Ru(II). In this contribution we will present our new results, the application of the tricationic phosphine ligand (IC 3), studying the electronic effect of the ligand on the catalytic decarboxylation reaction.

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


Inorganic and Coordination Chemistry

IC 58

Sustainable Copper Based Materials for OLED Like Devices

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

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


Inorganic and Coordination Chemistry

IC 59

Investigations on the Interaction between the btuB Riboswitch and Fluorescent B₃H₆ Derivatives

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Certain natural occurring RNA sequences serve as genetic control elements via specific binding to a variety of metabolites and a subsequent structural change [1]. These so called riboswitches are located in the 5′-untranslated region of bacterial messenger RNAs. The btuB riboswitch of E. coli binds to coenzyme B₁₂ and its derivatives with high selectivity [2, 3]. To investigate the structural changes, we use FRET ( Förster Resonance Energy Transfer) by labeling cobalamin and the RNA with one fluorophore each (dye-plexes for optimization of light emitting device properties.

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


Inorganic and Coordination Chemistry

IC 60

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

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Homogeneous hydrogenations of polar C=O and C≡N functional groups attract increasing interest in both industry and academia. Most of the transition metal based catalysts enabling reduction of these types of functional groups are based on noble metals like Ru, Rh, Ir [1]. Therefore, in recent years an extensive search for non-precious, low-toxicity metals, such as Mo and W has been initiated. Bullock and co-workers have reported Mo and W complexes that showed catalytic activity in the hydrogenation of ketones, [2] but the TOF values achieved were quite low. Recently our group has developed complexes of the type Mo(NO)(P₂P(Cl))₂H(P₂P = bidentate ligand) which showed hydrogenation activities in the presence of acids towards imines up to TOFs of 121 h⁻¹.

Our approach to molybdenum and tungsten nitrosyl catalysts has been developed further using tridentate phosphine ligands. The investigations of their hydrogenation catalyses of simple imines, ketones will be reported.

Inorganic and Coordination Chemistry

**IC 61**

**Mg**²⁺ dependent folding of the * btuB* riboswitch

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Riboswitches are small conserved sequences in the 5'-untranslated region of bacterial mRNA that follows a structural change upon binding to certain metabolites and thereby altering the gene expression [1]. The 202 nt long * btuB* riboswitch of *E. coli* undergoes a structural rearrangement on interaction with coenzyme B₁₂ and some of its derivatives [2]. Although being one of the earliest reported riboswitches, the folding of the * btuB* riboswitch and its interaction with coenzyme B₁₂ is not well understood.

The structure of riboswitch’s unliganded state is vital to its ability to bind ligand productively. Here, we report the requirement of Mg²⁺ for the formation of a competent unliganded state of the * btuB* riboswitch giving insights into different domains of the riboswitch involved in the structural change. Moreover, the Mg²⁺ binding sites could be mapped on the structure of the * btuB* riboswitch with the help of Tb³⁺.

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Inorganic and Coordination Chemistry

**IC 62**

**The cyclic analog of the wheat metallothionein γ-Ec-1 domain**

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The seed-specific metallothionein (MT) Ec-1 from common bread wheat is considered to function as a Zn²⁺ reservoir for the germination process. It has been shown to contain two metal binding domains, i.e. γ- and β-Ec-1, coordinating two and four Zn²⁺ ions, respectively. The two metal ions in γ-Ec-1 are arranged in a Zn₄Cys₈ cluster. Circular proteins have several advantages compared to their linear analogs, e.g. conformational and entropic stabilization, enhanced resistance to chemical and heat denaturation, and *in vivo* stabilization against proteolytic cleavage [2]. Cyclization of MTs is expected to reduce conformational flexibility and might influence the metal binding properties and specificities as well as help to facilitate crystallization. Additionally, γ-Ec-1 shows surprising similarities to the cyclotides, the largest group of naturally occurring cyclic peptides, which make comparative studies very interesting. Cyclotides are also rich in Cys residues and contain potential metal-binding sites [3]. The cyclic analog of γ-Ec-1 was prepared *in vitro* from a precursor protein obtained with a modified pTWIN2 vector in *E. coli* and identified by mass spectrometry.


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Inorganic and Coordination Chemistry

**IC 63**

**Lead bromide and iodide in ionic liquids**

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

Ionic liquids are very polar with certain anions being highly coordinating and thus can break the coordination network of the lead halides [2]. Being conductive, ionic liquids are also ideal alternative to the pure inorganic salts such as KI, which are often used as component for conducting materials. We have investigated the interactions of lead bromide and iodide in a series of imidazolium-based ionic liquids. In ionic liquids with bulky anions such as BF₄⁻, BF₂⁻ and TCN, the solubility of lead bromide and iodide are very limited. However, in ionic liquids with bromide and iodide anions, lead bromide and iodide can form stable complexes with melting points significantly decreased. Physical properties such as refractive index and conductivity of the obtained lead bromide and lead iodide-ionic liquids composite have been also investigated.


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Inorganic and Coordination Chemistry

**IC 64**

**fac-[TeO₃(tacn)]⁺: A Versatile Precursor for the Labeling of Pharamcophores, Amino Acids and Carbohydrates via cycloaddition strategies**

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One of the most sensitive methods for non-invasive imaging is the detection of γ-radiation where technetium-99m (⁹⁹mTc) plays a prominent role. The site specific conjugation of ⁹⁹mTc to a targeting vector, in a manner in which the product retains the affinity of the parent, is challenging. To address this issue, one can take advantage of the rich coordination chemistry of technetium. In this context complexes containing the Te⁶⁺ core, fac-[TeO₃(tacn)]⁺, came into focus of recent research, because they react with alkenes undergoing metal-mediated [3+2] cycloaddition reactions [1]. This reactivity can be used as a creative route to preparing novel molecular imaging probes. We developed a synthesis for the water stable complex [TeO₃(tacn)]⁺ that is suitable for clinical translation. Furthermore, to explore the potential and general utility of the [3+2] cycloaddition reactions as bioconjugation strategy, three classes of vectors were attached to the core. 4-Nitro-imidazole as a new hypoxia imaging agent, histidine to create a new non-natural amino acid that can be incorporated into peptides and radiolabeled and a simple sugar derivative, because of the interest in preparing ⁹⁹mTc labelled carbohydrates. In addition to the synthetic work the first biodistribution studies of [⁹⁹mTcO₃(tacn)] and the small [3+2] cycloadduct [⁹⁹mTcNO₂(Imi)(tacn)] were completed, suggesting that these complexes are stable *in vivo*.

Inorganic and Coordination Chemistry

**Hydrogenation of carbon dioxide for hydrogen storage**

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Renewable energy sources are of interest due to the environmental problems resulting from increasing CO$_2$ emission. A new and viable way for hydrogen storage was recently proposed based on the formic acid – carbon dioxide system.

Formic acid can be used as a hydrogen carrier via the selective decomposition of HCOOH into CO$_2$ and H$_2$\textsuperscript{[1-2]}. To achieve a carbon dioxide neutral system, the CO$_2$ must be recycled via direct hydrogenation. As the delivery of H$_2$ is performed in aqueous - and acidic - solution it is important to find a catalyst for CO$_2$ reduction that is active under the same conditions. At the moment a large number of catalytic systems are known to be active under neutral or basic conditions, which require the presence of a buffer, an amine or a base.

Preliminary studies performed with a water soluble rhenium complex, [ReCl$_5$(PTA)$_3$]$^{\text+i/2}$\textsuperscript{[3]} have shown certain catalytic activity in the hydrogenation of CO$_2$ in aqueous solution in the absence of amines or other additives. The rate of CO$_2$ hydrogenation was found to be strongly dependent on the pH of the solution.

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Inorganic and Coordination Chemistry

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

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

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

A distinct zinc and cadmium binding site in the mixed M\textsuperscript{II}/Cys\textsubscript{6} metal cluster of the γ-Ec-1 metallothionein

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

The γ-domain of the E\textsubscript{c}-1 MT from bread wheat contains a M\textsuperscript{II}/Cys\textsubscript{6} cluster, and we recently determined the solution structures of the Zn\textsuperscript{II} as well as the Cd\textsuperscript{II}/E\textsubscript{c}-1 form by NMR spectroscopy [1]. Upon exposure of Cd\textsuperscript{II} to the fully metallated Zn\textsubscript{2}Cd\textsubscript{II} form, we observed formation of a mixed Zn\textsuperscript{II}/Cd\textsuperscript{II} species, triggering the hypothesis of a certain metal ion specificity of the two metal binding sites. The finding was confirmed by a number of spectroscopic measurements, including UV-vis, CD, MCD as well as multi-nuclear, multi-dimensional NMR, providing information upon the selective character of the metal binding sites. In addition, presence of a ZnCd\textsubscript{2}E\textsubscript{c}-1 species was confirmed with ESI-MS.

Financial support from the Swiss National Science Foundation is gratefully acknowledged (SNSF-Professorship PP002-119096/1 to EF).


Inorganic and Coordination Chemistry

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

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

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

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

Inorganic and Coordination Chemistry

**IC 73**

**Rhenium Based Metal-Ligand Bifunctional Catalysis**

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There is growing interest in developing new metal ligand bifunctional catalysts for hydrogenations and transfer hydrogenations. The catalytically active species of these catalysts are expected to contain an acidic, as well as a hydridic hydrogen atom, which can be transferred to double bonds of various preferably polar organic substances. We prepared rhenium complexes isoelectronic to the well-known Shvo ruthenium system $\text{[(2,3,4,5-P$_3$-C$_6$H$_4$_CO)$_2$Ru]$\text{NO}(\text{py})$][1] by replacing the RuCO unit with a ReNO fragment. Such complexes of the type $\text{Re(NO)}(\text{L})(\text{H})(\text{C$_2$H$_5$OH})\text{L}=\text{PrPr$_5$}$, PCI$_3$[2] possess reasonable catalytic activity in transfer hydrogenations of aromatic and aliphatic ketones as well as imines applying 2-propanol as a hydrogen donor. For ketones TOF values up to 380 TON/h and for arylimines TOF values up to 60 TON/h were achieved.

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


Inorganic and Coordination Chemistry

**IC 74**

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

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

The subsequent addition of Ag$^+$ encouraged the self-organisation of discrete triple-helicates as a result of the soft d$^0$ metal interacting with the thiol groups while showing no preference for the tridentate binding site intended for the lanthanide.

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

Reference:


Inorganic and Coordination Chemistry

**IC 75**

**Rhenium Complex Catalyzed Homogeneous Hydrogenations**

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Highly active and selective catalysts are available to hydrogenate various unsaturated substrates and make it a method of choice for environmentally benign and enantioselective reductions. The element rhenium being border to precious metals may have preserved at least some of the precious metal’s character, like for instance the preference for interaction with H$_2$ and olefins. The chemical properties made us believe that appropriate rhenium complexes could be also efficient hydrogenation catalysts. We therefore targeted the development of new rhenium nitrosyl complexes on the basis of their isoelectronic relationship to ruthenium carbonyl or phosphine rhodium halide fragments, which comprise essential building blocks of effective hydrogenation catalysts.

Reference:


Inorganic and Coordination Chemistry

**IC 76**

**Functionalized Triazacyclononane Derivatives as Potential Multimeric Ligands for the fac-[TcO$_3$]$^{3-}$-core**

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Recently our group has demonstrated the use of 1,4,7-triazacyclononane (tacn) and its derivatives, tacn-R (R= bz, bz-COOH), to stabilize the fac-[TcO$_3$]$^{3-}$core, even in water [1]. To further extend this array and to develop this chemistry further for radiopharmaceutical applications, derivatives that offer the possibility for conjugation to biomolecules via amide bond formation were scrutinized. Hence, 1,4,7-triazacyclononane-N$_x$.N’$.N''$-triacetic acid (NOTA) and N-benzyl-2-(1,4,7-triazan-1-yl)acetamide (tacn-BA) were selected as viable candidates for our evaluation. NOTA, with three pendent acyl functionalitites, is a potential multimeric ligand, which can bind up to three moieties (e.g small peptides) to target a receptor. Thus this ligand could help to develop target specific radiopharmaceuticals with higher receptor binding constants. Talcn-BA on the other hand is a model for a monomeric ligand bearing a biomolecule conjugated via an amide bond.

We report a comparative study of the coordination properties of these two tacn derivatives and their ability to stabilize the fac-[TcO$_3$]$^{3-}$core. Therefore a synthesis for [TcO$_3$(NOTA)]$^{3-}$ (1), the first negatively charged complex containing the fac-[TcO$_3$]$^{3-}$ moiety and [TcO$_3$(tacn-BA)]$^{3-}$ (2) had to be developed.

Reference:


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

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**Scheme 2.** Click synthesis of the modified ligand.
Since lateral intermolecular cohesion is strongly affected by simple methyl substitution in [Ln(L)$_3$(NO$_3$)$_3$], we developed four different ligands, in which both the location and the number of additional methyl groups were systematically varied. Three lanthanides (La, Eu, Lu) were selected for preparing the associated nitrate complexes [Ln(L)$_3$(NO$_3$)$_3$]. As these complexes undergo dimerization processes in solution, the corresponding thermodynamic parameters will be used for tentatively rationalizing the liquid-crystals properties variations.

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


Antoine Gomila, Alan F. Williams
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The design of new discrete objects requires the consideration of different elements of symmetry inherent in the clusters considered. For example, the use of bis(bidentate) ligands with an Mn$^{2+}$ axis, can lead, in the presence of vapor deposition techniques, which use single source precursors, but some of them have problems: sensitivity to air, decomposition to undesired side-products and difficulty to scale them up for use in industrial production.

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


Inorganic and Coordination Chemistry

Preparation of discrete buildings with new bis(bipyridine) ligands

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The design of new discrete objects requires the consideration of different elements of symmetry inherent in the clusters considered. For example, the use of bis(bidentate) ligands with an Mn$^{2+}$ axis, can lead, in the presence of vapor deposition techniques, which use single source precursors, but some of them have problems: sensitivity to air, decomposition to undesired side-products and difficulty to scale them up for use in industrial production.

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Inorganic and Coordination Chemistry

Precursors for mixed metal oxides

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Mixed metal oxides are very important ingredients for material science. In particular case they are considered for their superconducting properties (for example YBa$_2$Cu$_3$O$_7$).

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

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


Inorganic and Coordination Chemistry

New ways of LiCoO$_2$ preparation

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

\[
\text{Li}_2\text{CO}_3 + \text{CoO} \rightarrow 600^\circ\text{C, O}_2 \text{ for 24h} \rightarrow \text{L-T-LiCoO}_2 \\
\text{800-900^\circ\text{C, O}_2 \text{ for 12h}} \rightarrow \text{HT-LiCoO}_2
\]

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

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

Inorganic and Coordination Chemistry

Synthesis of New Silver Compounds with Nicotinic acid Derivatives

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


Inorganic and Coordination Chemistry

Heterophosphorous phenol

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


Inorganic and Coordination Chemistry

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

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Metal-organic frameworks (MOFs) have recently emerged as a novel class of crystalline porous polymers with unique properties.[1] MOFs feature high chemical versatility that allows them to undergo post-synthetic modification (PSM) with organic molecules. We present here vapor-phase PSM (VP-PSM) of amino-functionalized MOFs such as IRMOF-3, NH₂-MIXMOF-5, and NH₂-UoO-66 with anhydrides and aldehydes under static vacuum without solvent to favor the diffusion of the reagents in the vapor phase within the pores. Acetic anhydride smoothly reacted at 100 °C overnight with all NH₂-functionalized MOFs to quantitatively give the corresponding amides. Aldehydes reacted with IRMOF-3 and NH₂-MIXMOF-5 giving the products with full conversion (Figure 1).

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


Inorganic and Coordination Chemistry

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

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The research of our group is focused on the design and self-assembly processes of new polynuclear complexes, which may find applications in medical imaging, (supra) molecular sensors, and nanomaterials. The lanthanide based systems are of interest due to their similar thermodynamic behavior, but different luminescent and paramagnetic properties. One of the developed concepts deals with tetranuclear assemblies with three-dimensional arrangements of lanthanide cations. These tetrahedral compounds are formed by the self-assembly of Ln(III) and tripodal ligands bearing three coordinating strands attached to a short spacer. [1] The nanomeric complexes within this family may have particular properties depending on subtle structural modifications of the ligand structure. Consequently, we can generate compact tetranuclear complexes or cage-containing assemblies with host-guest interactions. The self-organization and different properties of these unusual complexes will be discussed in this contribution.

Inorganic and Coordination Chemistry

“Noyori” Asymmetric Transfer Hydrogenation of Imines – a Study of Several Unexpected Influential Parameters
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Asymmetric transfer hydrogenation (ATH) is a reliable way of reducing prochiral ketones and imines to afford optically enriched chiral alcohols and amines.

Noyori-type complexes consisting of a Ru(II) atom, a chiral diamine ligand and a η⁶-arene are able to catalyze the ATH with high enantioselectivities, at promising reaction rates, and under mild conditions.

For this study, a model catalytic complex [RuCl₂(S,S-TsDPEN)(p-cymene)] was chosen and used to reduce a prochiral imine (1-methyl-3,4-dihydrosquinoine) to the corresponding amine. An azotrope mixture of formic acid and triethylamine served as a hydrogen donor for the reduction.

CO₂ is formed as a by-product during the reaction and is reportedly [1] able to form a complex with the catalyst. The aim of this study was to evaluate the influence of CO₂ on both reaction rate and enantioselectivity of ATH.

It was found that under the conditions favoring the formation of the CO₂-catalyst complex, reaction rates notably decreased. Thus, the influence of CO₂ as a by-product of the reaction was found to be of major importance and should be taken into consideration.

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


Inorganic and Coordination Chemistry

DFT Calculations in the Asymmetric Transfer Hydrogenation of Imines and Ketones Catalyzed by Noyori Ru(II) Complexes
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Asymmetric transfer hydrogenation (ATH) of imines and ketones using chiral Ru(II)Cl₂{η⁶-p-cymene}[N-tosyldiphenylethylene diamine] is an excellent and now well-established method for preparing optically pure compounds.

As it has been shown, the reaction mechanism is not a trivial issue. In the case of ketones, the mechanism was described in depth by Noyori et al., employing extensive density functional theory (DFT) calculations. However, recent experimental evidence suggests that the ATH of imines proceeds via a different, ionic pathway: We set out to investigate both mechanisms computationally using methods which Noyori used in his work, although calculating the full molecules instead of simplified structures. The results fully supported the ionic mechanism for imines and the original (Noyori) mechanism for ketones.

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

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


Inorganic and Coordination Chemistry

Nitrous Oxide Activation by Dinuclear Ru Complexes
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Nitrous oxide’s role in ozone depletion and its greenhouse effect has stimulated a lot of interest in activation of this kinetically inert molecule. In addition, N₂O is an appealing oxidant due to its thermodynamic potency and environmentally friendly nature (the only by product in oxygen atom transfer reactions is N₂).

Recently, we discovered that dinuclear Ru complexes are able to activate N₂O at room temperature (see picture). NMR spectroscopic and crystallographic analyses show that the Ru complexes mediate a rupture of the N−O bond to give Ru–dinitrogen complexes along with autoxidation products.
Chemical Lithiation for New and Better Performing Electrode Materials: A Review

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