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High-valent Metal-oxo and Imido Cores in Chemistry and BiologyR. Kallol¹

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Although terminal $\text{Co}^{\text{IV}}\text{-O}$, $\text{Ni}^{\text{III}}\text{-O}$ and $\text{Cu}^{\text{III}}\text{-O}$ intermediates have been implicated as active intermediates in a number of important chemical transformations, no spectroscopic evidences for the species are available, leaving the pathway uncertain. Evidences of the presence of terminal M-O units (M = Cu(III), Ni(III) or Co(IV)) are to date limited to mass spectrometric studies in the gas phase. Theory suggests that they should be powerful oxidants, perhaps even more reactive than the related $[\text{Fe}^{\text{IV}}=\text{O}]^{2+}$ units that have been extensively studied. In this presentation, we will summarize some of our recent efforts to stabilize the elusive metal-oxo and isoelectronic metal-imido units of Cu(III), Co(IV) and Ni(III) in solution phase at low temperatures. The high-valent metal-oxo or metal-imido assignments are made on the basis of a variety of spectroscopic methods. The reactivity of the intermediates in hydrogen atom abstraction, oxo transfer reactions and dioxygen reduction reactions are also discussed.

Heptacoordinate Co(II) complex: a new architecture for photochemical hydrogen production

F. Lucarini¹

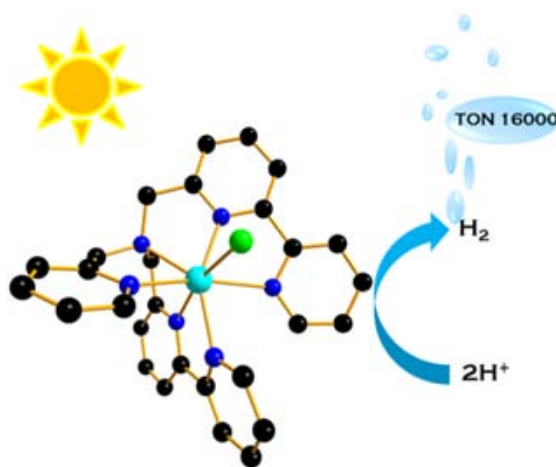
¹University of Fribourg

Hydrogen is a promising potential clean source of energy which can be produced using abundant and renewable resources (e.g. water and sunlight). Water reduction catalysts are usually based on non-precious metals among which cobalt has been the most studied because of its abundance and low price. However the development of highly active and stable catalysts that can operate in purely aqueous solutions still remains a great challenge.^[1]

The most active molecular cobalt catalysts reported in literature present a common architecture: a tetra- or pentapyridyl ligand inducing a distorted octahedral geometry, with the remaining coordination sites occupied by labile ligands (e.g. water).^[2,3]

To further investigate the effect of coordination geometry on the catalytic activity, we designed a new ligand with six coordination sites that lead to the formation of an unusual heptacoordinate Co(II) complex. Under visible light irradiation in water, this complex can efficiently catalyze the production of H₂ with a turnover number (TON) > 16000 mol H₂ (mol cat)⁻¹ and nearly 90% of H₂ evolved within the first hour of irradiation, i.e. a turnover frequency (TOF) > 4000 mol H₂ (mol cat)⁻¹ h⁻¹.^[4]

These results suggest that heptacoordinate cobalt complexes, never used so far in the field of light-driven hydrogen evolution, represent a promising alternative platform for the development of highly active and stable photocatalysts.



[1] Artero, V.; Chavarot-Kerlidou, M.; Fontecave, M. *Angew. Chem. Int. Ed.* **2011**, 50, 7238-7266.

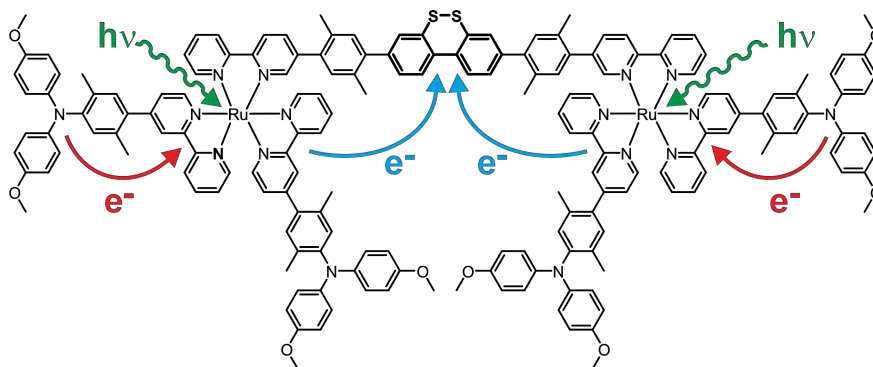
[2] Bachmann, C.; Guttentag, M.; Spingler, B.; Alberto, R. *Inorg. Chem.* **2013**, 52, 6055-6061.

[3] Singh, W. M.; Baine, T.; Kudo, S.; Tian, S. L.; Ma, X. A. N.; Zhou, H. Y.; DeYonker, N. J.; Pham, T. C.; Bollinger, J. C.; Baker, D. L.; Yan, B.; Webster, C. E.; Zhao, X. *Angew. Chem. Int. Ed.* **2012**, 51, 5941-5944.

[4] Lucarini, F.; Pastore, M.; Vasylevskiy, S.; Varisco, M.; Solari, E.; Crochet, A.; Fromm, M.K.; Zobi, F.; Ruggi, A. *Chem. Eur. J.* **2017**, DOI: 10.1002/chem.201701427.

Light-driven electron accumulation in a molecular pentad with potential inversionJ. Nomrowski¹, O. S. Wenger^{1*}¹University of Basel

Charge accumulation plays a crucial role in the greater context of artificial photosynthesis, because carbon dioxide reduction or water splitting rely on multi-electron chemistry. Due to the fact that the second reduction potential is much less negative in comparison to the first, dibenzo[1,2]dithiin is an interesting molecular unit to accumulate two electrons [1]. We expect that the potential inversion could facilitate electron accumulation compared to previously investigated systems [2, 3].



In this work, light-induced charge accumulation on dibenzo[1,2]dithiin was achieved in absence of sacrificial donors. We were able to show that after excitation of the sensitizers, the intramolecular two electron transfer from the triarylamine moieties to the dibenzo[1,2]dithiin unit indeed takes place. In presence of acid, a very long living dithiol species is formed.

[1] Gabriel B. Hall, Rudresha Kottani, Greg A. N. Felton, Takuhei Yamamoto, Dennis H. Evans, Richard S. Glass, Dennis L. Lichtenberger, *Journal of the American Chemical Society*, **2014**, 136, 4012-4018.

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[3] Yann Pellegrin, Fabrice Odobel, *Coordination Chemistry Reviews*, **2011**, 255, 2578-2593.

Gadolinium Complexes Exhibiting Ultra-fast Ligand Self-exchange in Ionic Liquids for Application in NMR Field Probes

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The technology used in Magnetic Resonance Imaging (MRI) relies on the observation of nuclear magnetic resonance (NMR) during complex choreographies of time-varying magnetic fields. Hardware imperfections as well as other external perturbances influence these field evolutions, limiting image quality and the feasibility of high-performance methods. Continuous concurrent magnetic field monitoring¹ is a method for probing the spatiotemporal magnetic field evolution in an MR system by the usage of a set of NMR field sensors. For these sensors, highly homoperfluorinated liquid compounds with short fluorine NMR relaxation times (T_1 and $T_2 < 1$ ms) are required. Effective relaxation enhancement requires a close contact between the ^{19}F atoms and a paramagnetic centre – ideally in the first coordination sphere. Herein we present that a homoperfluorinated ionic liquid in which the anions also act as ligands for the paramagnetic metal complex, offers such a possibility. The model Gd(III) complex $[\text{N}^n\text{Bu}_4][\text{Gd}(\text{Tf}_2\text{N})_4]$ ($\text{Tf}_2\text{N}^- = \text{bis}(\text{trifluoromethylsulfonyl})\text{imide}$), obtained from the reaction of its precursor $[\text{Gd}(\text{NTf}_2)_3]$ with $[\text{N}^n\text{Bu}_4](\text{NTf}_2)$, shows the extension of the coordination sphere from six to eightfold with transoid configuration of the NTf_2 ligands. Hence, the solution of the $[\text{Gd}(\text{NTf}_2)_3]$ in ionic liquids of the triflimide type $[\text{cat}^+][\text{Tf}_2\text{N}^-]$ ($\text{cat}^+ = \text{AMIm} = 1\text{-allyl-3-methylimidazolium}$, EthylMIm or PR_3R^+) is shown (by evaluation of exchange rates of the non-paramagnetic parent Yttrium compound) to yield a single ^{19}F signal, reflecting rapid ligand self-exchange, and relaxation times in the sub-millisecond range as targeted.

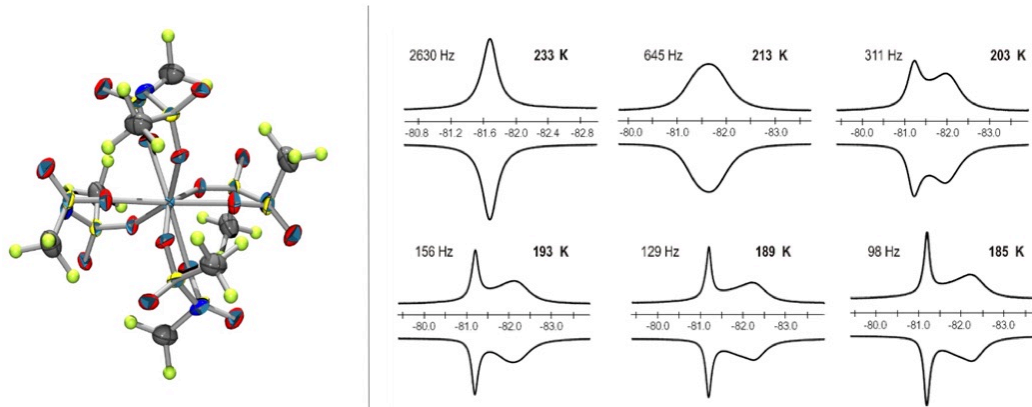


Figure 1. ORTEP of $[\text{N}^n\text{Bu}_4][\text{Gd}(\text{Tf}_2\text{N})_4]$. Cation omitted and fluorides shown as spheres for clarity. The transoid configuration is clearly visible for the $[\text{NTf}_2^-]$ ligands. Ellipsoids except for fluorides are drawn on the 30% probability level.

Figure 2. Comparison of observed (upper) with calculated (lower) ^{19}F NMR (282.39 MHz) spectra of a mixture of $[\text{Y}(\text{NTf}_2)_3]$ with $[\text{EthylMIm}][\text{NTf}_2]$ (1:1.5) in CD_2Cl_2 displaying line broadening, coalescence and splitting into two signals upon cooling.

[1] C. Barmet, N. De Zanche, B. J. Wilm and K. P. Pruessmann, *Magnetic Resonance in Medicine*, **2009**, 62, 269.

Multicoordinated Precursors for Oxide Materials' Synthesis and Other Applications

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The specific arrangement and compartmentalization of metal ions are highly interesting for research in biology as well as in materials science. In order to program the coordination of two different metal ions, functional coordinating sections in ligands can be generated by design, leading to tweezer-type complexes with new properties stemming from the combination of the different metal ions.

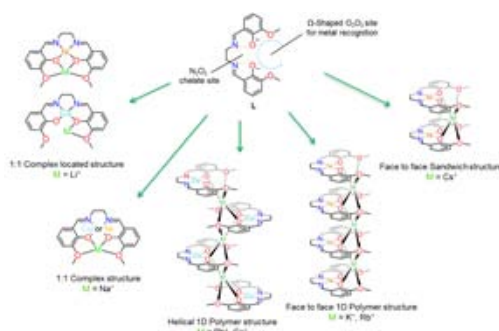
This project consists in the design of ligands with specific coordination sites to selectively bind different metal ions. The H₂L ligand [1], a Schiff base derivative, has been synthesized possessing a central coordination site made of an imine-based N₂O₂ entity used to bind to copper(II) or nickel(II) upon deprotonation. This coordination prearranges the ligand into a Ω-shape, thus generating a second recognition site, O₂O₂, composed by two phenoxy and two methoxy functions.



Structural differences influenced by alkali metal ions have been observed for copper(II) and nickel(II) compounds using single crystal X-ray diffraction.

The preorganization in these complexes allows also the synthesis of mixed oxide materials under mild conditions, controlling the stoichiometry of the final oxide material. The extreme synthesis conditions for classical solid state reactions (high pressure and/or temperature) can thus be avoided. The new mixed metal precursors are then simply combusted in air at low temperatures (ca. 300°C) to nanoscale oxide materials allowing to access new and better properties in their applications.

Further applications in mechanochemistry and for antimicrobial properties are currently investigated. One possible application is the one of optical sensing focused on the modification of the ligand for sensing applications.



Replacing activity coefficients with explicit changes in solvent chemical potentials for unravelling intermolecular association processes

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Thermodynamic laws treat solvent activity as a constant when binding equilibria occur in diluted solutions and any deviations are assumed to arise from non-ideal behaviors of the reactants and products. However a better modeling of the solvent molecules involved in solvation reactions may be beneficial to the comprehension of intermolecular association processes. In this context, Castellano and Eggers¹ developed a novel approach, in which solvent molecules were introduced as chemical partners. In the chemical potential framework, the explicit consideration of solvent contribution to the complexation equilibria results in significant deviations of the law of mass action. Stability constants, which characterize the formation of coordination complexes, are therefore significantly altered. Bearing all these elements in mind, we established theoretical and experimental methods, which aim at separately evaluating solvent effects and “pure” binding affinity accompanying the reaction of neutral tridentate ligands (**L**₁, **L**₂ and **L**₃) with neutral saturated trivalent lanthanide carriers [Ln(hfac)₃(diglyme)]. Changes in ligand lipophilicities and in metallic sizes are investigated for decrypting robust trends in binding selectivity.²

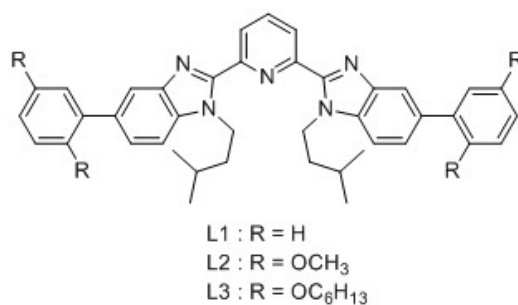


Figure 1: Chemical structures of tridentate ligands **L**₁, **L**₂, **L**₃

[1] Brian M. Castellano and Daryl K. Eggers, *J. Phys. Chem. B.*, **2013**, 117, 8180.

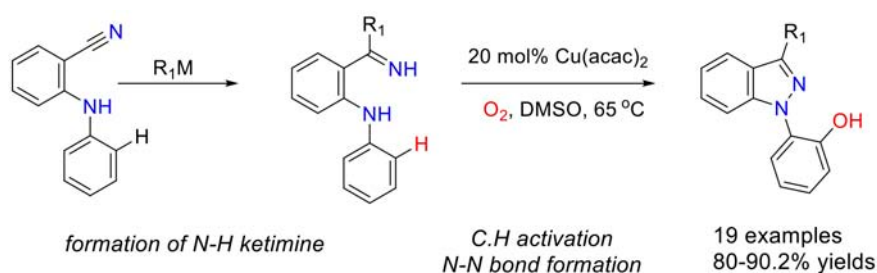
[2] Lucille Babel, Thi Nhu Y Hoang, Homayoun Nozary, Jasmina Salamanca, Laure Guénée and Claude Piguet, *Inorg. Chem.*, **2013**, 53, 3568.

A Cu-catalyzed Tandem Transformation of *ortho* C-H Hydroxylation and N-N Bond Formation: An Expedite Synthesis of 1-(*ortho*-Hydroxyaryl) 1H-Indazoles

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A facile, one-pot synthesis of 1H-indazoles featuring a Cu-catalyzed C-H *ortho* hydroxylation and N-N bond formation using pure oxygen as terminal oxidant is described. Reaction of readily available 2-arylamino benzonitriles with various organometallic reagents led to *ortho*-arylamino N-H ketimine species. Subsequent Cu-catalyzed hydroxylation at *ortho*-position of the aromatic ring followed by N-N bond formation in DMSO under pure oxygen afforded a wide variety of 1-(*ortho*-hydroxyaryl) 1H-indazoles in good to excellent yields. The efficient methodology does not require utilization of noble metal catalysts, elaborated directing groups and privileged ligands.



[1] C.-y. Chen, G. Tang, F. He, Z. Wang, H. Jing, R. Faessler, *Org. Lett.* **2016**, *18*, 1690.

Interaction of thiolato-bridged dinuclear arene ruthenium complexes with phospholipids and model membranes

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Thiolato-bridged dinuclear arene ruthenium complexes are highly cytotoxic against various cancer cell lines with IC₅₀ values of up to 30 nM [1]. A recent *in vivo* study has demonstrated that these complexes have potential as anticancer drugs, as one complex significantly prolongs the survival of tumor-bearing mice [2]. Interestingly, these complexes are very stable under physiological conditions as well as acidic and basic conditions, and they are particularly inert toward substitution. Only sulfur containing biomolecules such as cysteine and glutathione undergo catalytic oxidation in their presence [3].

Since many aspects of cellular uptake and of the tumor-inhibiting action displayed by these complexes are still largely unknown, we have studied the interactions of three trithiolato complexes with different degrees of lipophilicity $[(\eta^6\text{-}p\text{-MeC}_6\text{H}_4\text{Pr}^i)_2\text{Ru}_2(\text{R}^1)_2(\text{R}^2)]^+$ ($\text{R}^1 = \text{SC}_6\text{H}_4\text{-}m\text{-Pr}^i$:**1**; $\text{R}^2 = \text{SC}_6\text{H}_4\text{-}m\text{-Pr}^i$:**1**; $\text{R}^1 = \text{SC}_6\text{H}_4\text{-}p\text{-OMe}$:**2**; $\text{R}^2 = \text{SC}_6\text{H}_4\text{-}p\text{-OH}$:**2**; $\text{R}^1 = \text{SCH}_2\text{C}_6\text{H}_4\text{-OMe}$:**3**; $\text{R}^2 = \text{SC}_6\text{H}_4\text{-}p\text{-OH}$:**3**) and of one dithiolato complex $[(\eta^6\text{-}p\text{-MeC}_6\text{H}_4\text{Pr}^i)_2\text{Ru}_2(\text{SCH}_2\text{C}_6\text{H}_5)_2\text{Cl}_2]$:**4** with lipid membrane models in form of 1,2-dioleoyl-sn-glycero-3-phosphocholine (DOPC) vesicles, 1,2-dihexanoyl-sn-glycero-3-phosphocholine (DHPC) micelles and sodium dodecyl sulfate (SDS) micelles by nuclear magnetic resonance (NMR) spectroscopy and other techniques. 1D ¹H NMR spectra, 2D ¹H diffusion ordered spectroscopy (DOSY) spectra and T2 (spin-spin) relaxation time measurements together with electrospray ionization mass spectrometry (ESI-MS) suggest noncovalent interaction between the vesicles and the three trithiolato complexes. As expected, the strength of the interaction with the vesicles parallels the lipophilicity of the complexes. The results with the dithiolato complex **4**, on the other hand, suggest that none or only very weak interaction takes place. **1** was further studied with DOPC in presence of the lanthanide shift reagent PrCl₃ for estimating if the complex remains at the vesicle surface, is inserted between the fatty acid chains or is localized inside the DOPC vesicle.

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[2] P. Tomšík, D. Muthná, M. Řezáčová, S. Mičuda, J. Čmielová, M. Hroch, R. Endlicher, Z. Červinková, E. Rudolf, S. Hann, D. Stíbal, B. Therrien, and G. Süss-Fink, *J. Organomet. Chem.*, **2015**, 782, 42–51.

[3] F. Giannini, G. Süss-Fink, and J. Furrer, *Inorg. Chem.*, **2011**, 50, 10552–10554.

Solution grown caesium-formamidinium lead halide perovskites for detection of gamma photons

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Hybrid formamidinium (FA) lead halide perovskites (FAPbX₃, X=I or Br/I) gained considerable popularity due to their excellent performance as photovoltaic and high energy photon-detecting materials [1]. The detection of gamma photons is enabled by high electronic quality of FAPbI₃ single crystals (SCs): low noise level and dark current, high mobility-lifetime product ($1.8 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1}$), and high absorptivity of high-energy photons by Pb and I [1]. The difficulties arise from the phase instability of the desired three-dimensional (3D) FAPbI₃ cubic perovskite phase that undergoes a phase transition to non-perovskite 1D hexagonal lattice. The reason lies in the large size and spatial geometry of FA cation. The Goldschmidt tolerance factor (*GTF*) concept is a useful tool in estimation of the compositionally-dependent stability of 3D perovskites with ABX₃ general formula and idealized cubic lattice. $GTF = (r_A + r_X) / [\sqrt{2}(r_B + r_X)]$, where r_A , r_B and r_X represent the ionic radii of each lattice site constituent (in this case, $r_{FA^+} = 253 \text{ pm}$, $r_{Pb^{2+}} = 119 \text{ pm}$ and $r_I = 220 \text{ pm}$). Stable cubic perovskites typically exhibit a $GTF = 0.8-1$ ($GTF = 0.987$ for cubic FAPbI₃ at room temperature). Decreasing the *GTF* of FAPbI₃ can be obtained by replacing FA⁺ cations by smaller Cs⁺ ions, and/or by replacing I⁻ anions with smaller Br⁻ ions, likely leading to higher stability.

We will present a facile, inexpensive, solution-phase growth of cm-scale SCs of variable composition Cs_xFA_{1-x}PbI_{3-y}Br_y ($x=0-0.1$, $y=0-0.6$). Comparing to the parent cubic FAPbI₃ compound these SCs show improved phase stability with shelf life (the time before hexagonal phase impurities could be detected) of up to 20 days for quaternary Cs_xFA_{1-x}PbI₃ SCs and of more than 4 months for quinary Cs_xFA_{1-x}PbI_{3-y}Br_y SCs [2]. These SCs possess outstanding electronic quality, represented by a high carrier mobility-lifetime product (up to $1.2 \times 10^{-1} \text{ cm}^2 \text{ V}^{-1}$) and a low dark carrier density allowing the sensitive detection of gamma radiation. With stable operation up to 30 V, these novel SCs have been used in a prototype of a gamma-counting dosimeter.

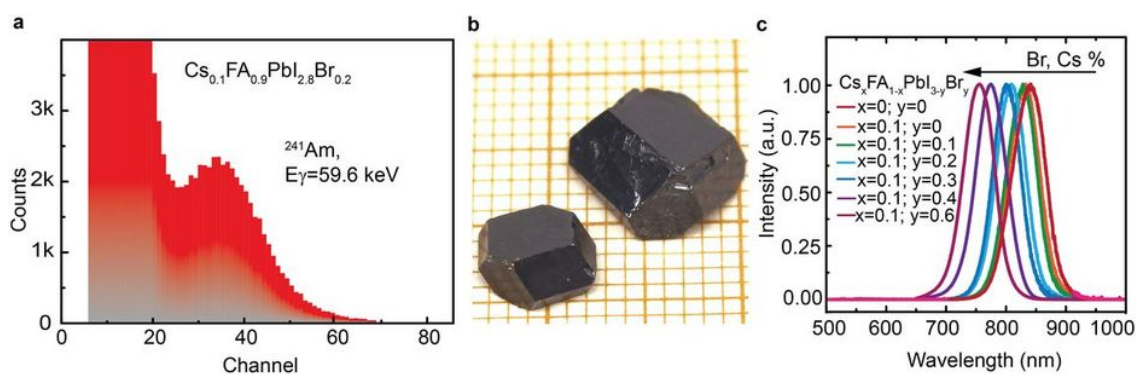


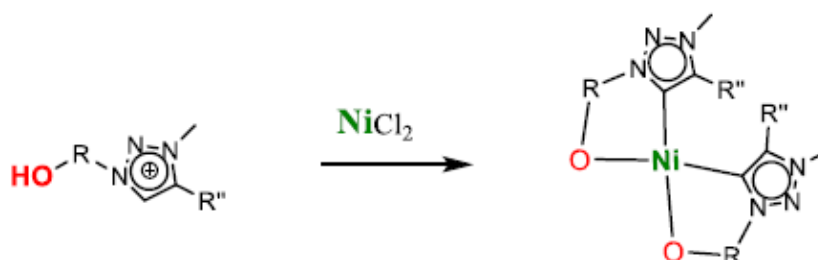
Figure 1. Energy resolved spectrum of an ²⁴¹Am source using perovskite SCs; (b) A photograph of typical 0.5-1 cm Cs_xFA_{1-x}PbI_{3-y}Br_y SCs on a millimetre-grid paper; (c) Photoluminescence spectra of ground SCs.

[1] S. Yakunin, D. N. Dirin, Y. Shynkarenko, V. Morad, I. Cherniukh, O. Nazarenko, D. Kreil, T. Nausser, M. V. Kovalenko. Nat. Photon. **2016**, 10 (9), 585-589. [2] O. Nazarenko, S. Yakunin, V. Morad, I. Cherniukh, M. V. Kovalenko. NPG Asia Mater., **2017**, 9, e373.

Nickel complexes containing oxygen-chelating mesoionic carbenes as cheap and efficient hydrosilylation catalysts.S. Bertini¹, M. Albrecht²

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Research into new and efficient catalytic systems based on Earth-abundant metals represents a significant challenge for chemistry.¹ A key prerequisite to reach this goal is the availability of suitable ligands to stabilize the metal center. This field has been considerably stimulated by the discovery of N-heterocyclic carbenes (NHCs) as ligands that impart unique properties.² Triazolylidenes are a subclass of NHCs that are excellent σ -donors and have great electronic flexibility, which allows for the stabilization of a wide variety of oxidation states of transition metals. Furthermore, their convenient synthetic modification provides access to heteroatom-functionalized NHCs for chelation. These donor-functionalized ligands have great potential for tailoring the properties of Earth-abundant metals for catalysis.



Here we will present a facile and versatile synthesis of mesoionic ligands bearing a potentially chelating hydroxide moiety on the triazole scaffold as well as a new class of nickel(II) complexes containing these O,C bidentate chelating mesoionic carbenes starting from a cheap and simple metal precursor. All these nickel complexes show high activity in hydrosilylation reactions, demonstrating the great potential of the hydroxyl group as chelating moiety for both the synthesis and the catalytic application of 3d metal complexes.

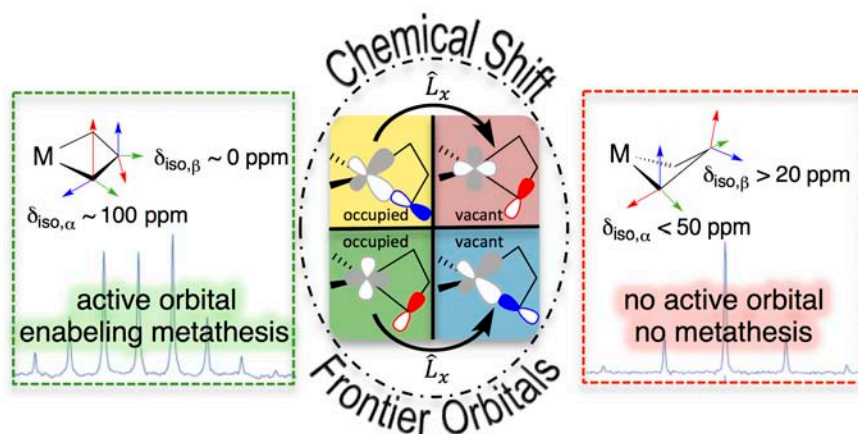
- [1] R.M. Bullock, "Catalysis without precious metals", **2011**, Wiley-VCH, Weinheim, Germany.
[2] K.H. Dötz, J. Stendel, *Chem. Rev.* **2009**, 109, 3227, F.E. Hahn, M. C. Jahnke, *Angew. Chem. Int. Ed. Engl.*, **2008**, 47, 3112, W.A Herrmann, *Angew. Chem. Int. Ed.*, **2002**, 41, 1290., J.D. Crowley, A. Lee, K. J. Kilpin, *Aust. J. Chem.*, **2011**, 64, 1118.

Metathesis Activity Encoded in Metallacyclobutane Carbon-13 NMR Chemical Shift Tensor.

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Metallacyclobutanes are an important class of organometallic intermediates, due to their role in olefin metathesis. They can have either planar or puckered rings associated with characteristic chemical and physical properties. Metathesis active metallacyclobutanes have $M-C_\alpha-C_\beta-C_\alpha'$ torsional angles close to 0° , short $M-C_\alpha$ and $M-C_\beta$ distances, long $C_\alpha-C_\beta$ bond length, and isotropic ^{13}C chemical shifts for both early d^0 and late d^4 transition metal compounds for the α - and β -carbons appearing at ca. 100 and 0 ppm, respectively. Metallacyclobutanes that do not show metathesis activity have ^{13}C chemical shifts of the α - and β -carbons at typically 40 and 30 ppm, respectively, for d^0 systems, with upfield shifts to ca. -30 ppm for the α -carbon of metallacycles with higher d^n electron counts ($n = 2$ and 6). Measurements and calculations of the chemical shift tensor combined with an orbital (natural chemical shift) analysis of the principal components ($\delta_{11} \geq \delta_{22} \geq \delta_{33}$) show that the specific chemical shift of metathesis active metallacyclobutane intermediates originates from a low-lying empty orbital on the metal of the correct symmetry to interact with a p-orbital on the α -carbon, perpendicular to the $M-C_\alpha$ axis in the metallacyclobutane plane. In the metathesis active metallacyclobutanes, the α -carbons retain some residual alkylidene character, while their β -carbon is shielded, especially in the direction perpendicular to the ring, evidencing the redistribution of electrons during the making and breaking of 2 σ - and 2 π -bonds during the metathesis process. Overall, the chemical shift tensors directly provide information of predictive value about the ability of metallacyclobutanes to function as olefin metathesis catalysts and allow distinguishing reaction intermediates from resting (off-cycle) states.

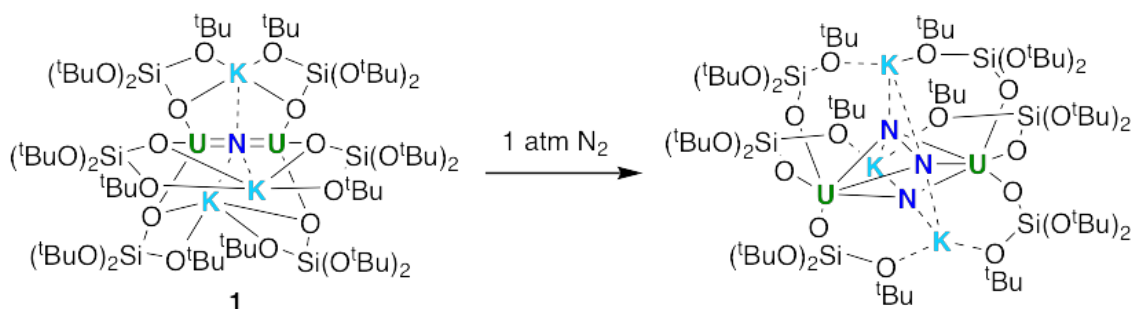


Small Molecule Activation at Multimetallic Uranium Nitrides

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¹EPF Lausanne

Uranium nitrides are attractive candidates for stoichiometric and catalytic N-transfer reactions, small molecule transformation, ^[1] and for advanced nuclear fuels. The N-C bond formation reactions are key steps in the construction of value-added chemical compounds. Recently we reported remarkable reactivity studies in f-element chemistry. Particularly desirable are the synthetic methods using cheap and available C₁ feedstock such as carbon dioxide or carbon monoxide. ^[2] *Tert*-butoxysiloxides were shown to be very effective ligands in supporting the reactivity of low valent *f* elements with small molecules. ^{[3],[4]} In particular, it was recently reported the remarkable reactivity of the previously described nitride bridged diuranium(IV) complex [Cs{[U(OSi(O^tBu)₃]₂(μ-N)}] with CO₂, CS₂, and CO, yielding to diverse N-functionalized products ^{5,6}. Moreover, very recent results show that increasing the electron density by reducing the metal centers leads to a multimetallic K₃UNU nitride bridged diuranium(III) complex, **1** (Figure 1) which shows extraordinary reactivity towards the dinitrogen molecule. We will present the reduction and further functionalization of dinitrogen in ambient condition by a uranium nitride ⁷.



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