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Reticular Design of Quantum Materials: Emergent Properties in Metal–Organic Nets

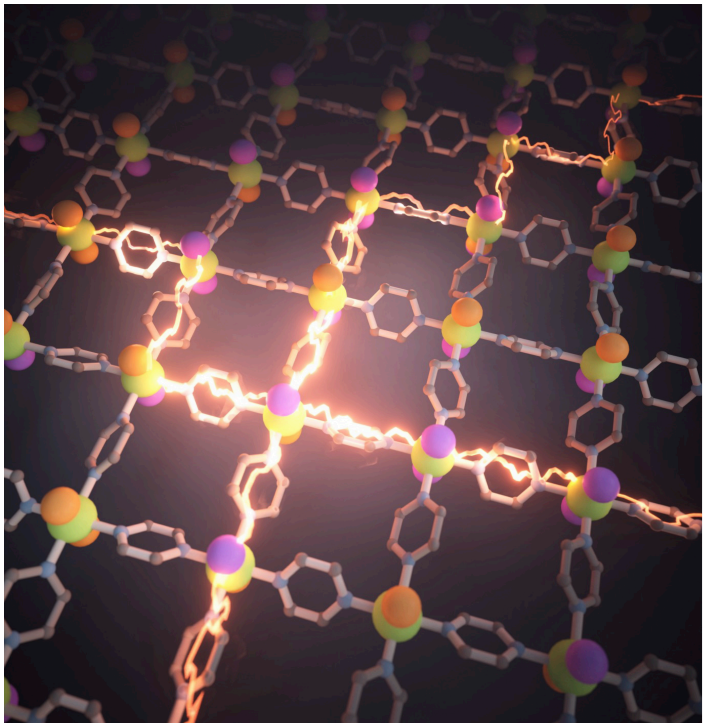
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Quantum materials exhibit exotic phenomena arising from the intricate interplay between electronic, magnetic, and lattice degrees of freedom. Traditionally, most such materials are purely inorganic and synthesized under conditions dominated by thermodynamic control. Reticular chemistry, however, provides complementary tools for quantum materials discovery, enabling the design, synthesis, and understanding of systems with unique symmetries and electronic structures.

Metal–ligand assemblies featuring variable or inseparable valence states (“non-innocence”) are widespread in coordination chemistry and offer a route to harness strong electron–electron correlations in extended networks. This strategy provides a realistic means to challenge the current state-of-the-art approaches to quantum materials.

In this lecture, I will present our recent findings in the search for genuinely new symmetries in MOFs and coordination solids, along with their emergent properties. These include metallicity, geometric frustration, valence tautomerism, and exceptionally strong magnetic correlations that give rise to high-temperature magnetic ordering.[1–9]



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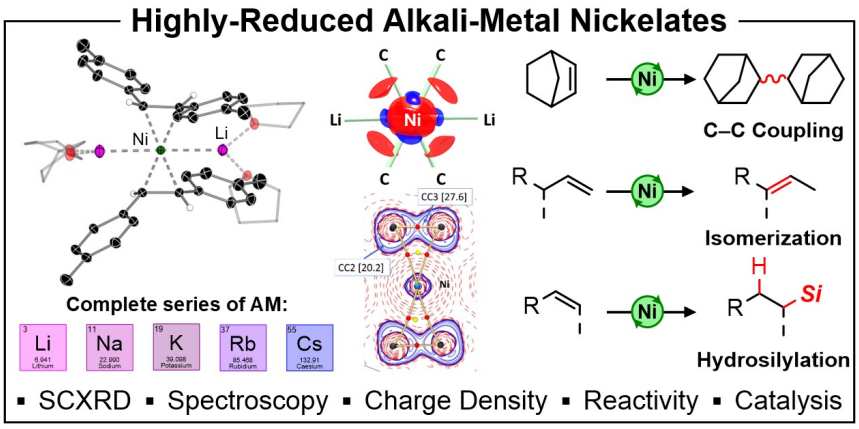
Highly Reduced Alkali-Metal Nickelates: Synthesis, Structure, and Catalytic Applications

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Low-valent nickel complexes have recently emerged as powerful reagents in challenging cross-coupling reactions and other bond forming and breaking processes.[1] These transformations typically rely on nickel's ability to adopt a range of different oxidation states and engage in reversible one and two electron reactivity.[2] While the synthesis, structure, and reactivity of low-valent Ni(I) and Ni(0) complexes are well established, examples of Ni complexes featuring formally negative oxidation states remain scarce, and in the few reported complexes, the actual oxidation state of nickel and the nature of bonding are poorly understood.[1]

In this contribution, we report a novel family of highly reduced alkali-metal nickelate complexes, $[\{(THF)_xAM\}_2Ni(^{4\text{-Me}}stb)_y]$ (where AM = alkali-metal; $^{4\text{-Me}}$stb = (*E*)-4,4-dimethylstilbene; x = 1,2; y = 2,3), which is highly electron rich. The complete alkali-metal series ranging from lithium to cesium were accessed and characterized in the solid state (except the Cs congener) and in solution. The lithium nickelate complex was studied by experimental charge density to comprehensively elucidate the structure, electronics, and bonding of this unique system. The stoichiometric and catalytic reactivity toward C−F activation, reductive norbornene coupling, hydrosilylation, and alkene isomerization were investigated and benchmarked against homometallic Ni(0) systems.[3]



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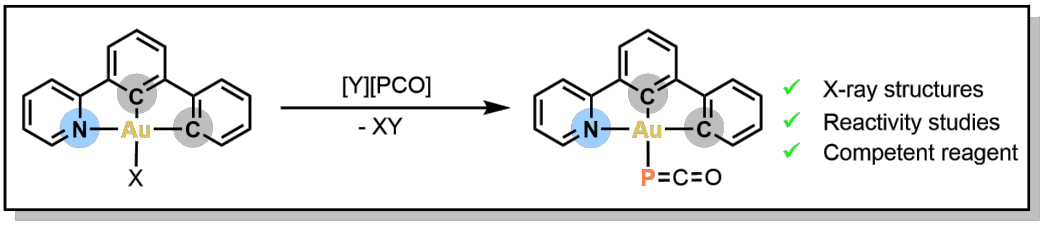
Synthesis, Isolation, and Reactivity of Gold(III) Phosphaketene Complexes

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The phosphaethynolate anion (PCO^-) was first introduced by Becker in 1992, and its ambidentate nature was subsequently demonstrated in different studies featuring salt metathesis reactions between NaPCO and different metal halides. As expected, coordination through the phosphorus atom was found to be favored by soft and polarizable elements, while hard and charge-dense Lewis acids preferred the oxygen-bound coordination[1-3]. The reductive decarbonylation of metal-phosphaketene (M−PCO) complexes was found to be a key synthetic strategy to access terminal M−P complexes,[4-6] which constitute promising platforms for phosphorus atom transfer (PAT) catalysis.

Herein, we report the characterization and reactivity of the first family of well-defined Au(III)-phosphaketene complexes supported by different tridentate (N^C^C) and (C^N^C) ligands. Our investigations revealed that the behavior of the Au(III)-PCO complexes is strongly governed by the ligand framework, which can either facilitate decarbonylation or promote PCO transfer, depending on its electronic and steric properties.



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Nitrile Activation in Platinum-Based Ligand Backbone Manipulation

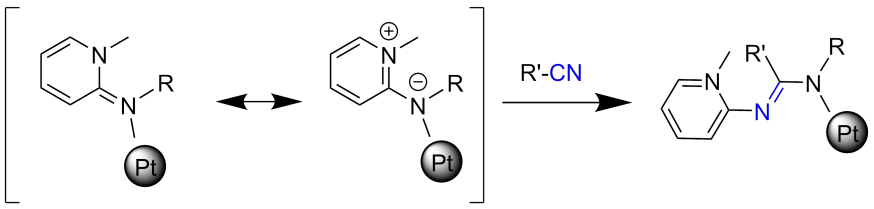
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Skeletal editing has emerged as a promising tool to access valuable derivatives by direct modification of the molecular scaffold.[1] In recent years several strategies for the insertion and deletion of carbon or nitrogen atoms have been developed.[2] Such single atom manipulations have been by far the most prominent[3,4], while the insertion of two or more atoms into an existing backbone is essentially unknown.

Here we will demonstrate the metal-mediated insertion of a -CN- fragment from small molecule nitriles into the backbone of the ligand, thus expanding the toolbox of skeletal editing methodologies. The reaction involves C–N bond breaking and both N–C and C–N bond making processes in one step. Key for this unprecedented bond activation and insertion reaction is a platinum(II) center bound to pyridinium amidate (PYA) ligands (see Figure below). These ligands are known for their electronic flexibility, which entails neutral and zwitterionic limiting resonance structures. Previous work has demonstrated a wide range of catalytic applications with these PYA ligands, including redox and polymerization processes.[5,6]

Here we will discuss the -CN- insertion in more detail, including selectivity and mechanistic aspects, as well as scope for diversification.



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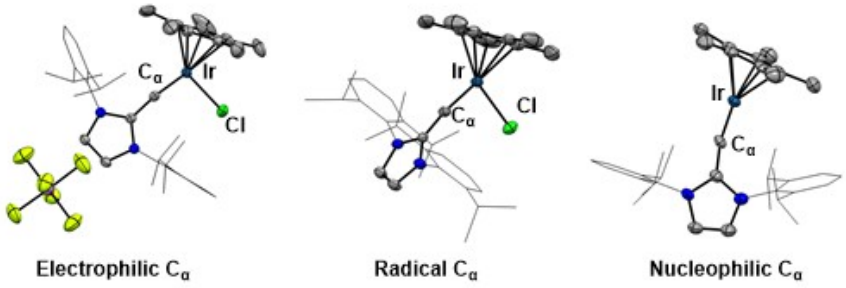
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Cp*M Complexes with the N-Heterocyclic Vinylidene Ligand IPrC

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Room-temperature stable diazoolefins provide access to a unique class of carbon-donor ligands: N-heterocyclic vinylidenes.[1] Herein, we describe Cp*M complexes with the N-heterocyclic vinylidene ligand IPrC (IPr = 1,3-bis(2,6-diisopropylphenyl)-imidazol-2-ylidene). Cationic complexes of type [Cp*IrCl(IPrC)]X (X = SbF_6, OTf) were obtained by reaction of $(Cp^*IrCl_2)_2$ with $IPrCN_2$, followed by chloride abstraction. Two-electron reduction instead of chloride abstraction gave a neutral Cp*Ir(IPrC) complex with a "pogo stick" geometry.[2] Single-electron reduction of the cationic complexes afforded Cp*IrCl(IPrC), in which the vinylidene ligand shows radical character. Combining $(Cp^*RuCl_2)_2$ with $IPrCN_2$ gave Cp^*RuCl_2(IPrC), in which the vinylidene ligand also shows radical character. Hydrogen abstraction from Et_3SiH yielded the carbene complex Cp^*RuCl_2(IPrCH). The diamagnetic complex Cp*RuCl(IPrC) was obtained by single-electron reduction of Cp^*RuCl_2(IPrC), whereas single-electron oxidation with [TEMPO]X provided ionic [Cp^*RuCl_2(IPrC)]X (X = BF_4, SbF_6) complexes. Reactions of $(Cp^*OsBr_2)_2$ with $IPrCN_2$ resulted in disproportionation and formed Cp*OsBr(IPrC) and [Cp^*OsBr_2(IPrC)]Br, while single electron reduction of [Cp^*OsBr_2(IPrC)]Br formed the meta-stable Cp^*OsBr_2(IPrC) and the vinylidene ligand also shows radical character.[3] The results underline the unique electronic properties of the vinylidene ligand IPrC in transition metal complexes.



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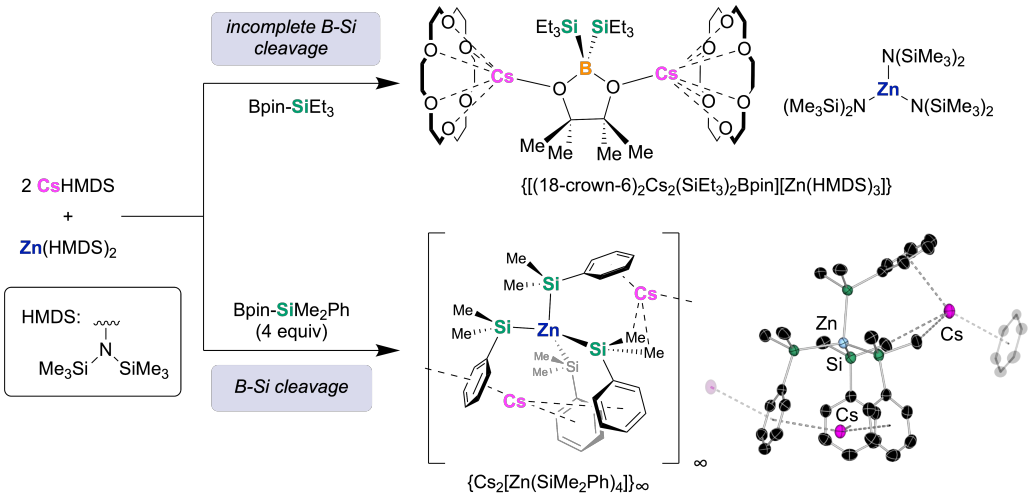
Bimetallic Silylation Reagents: Structural Investigation and Reactivity of Caesium Silylzincates

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Organosilicon compounds are fundamental building blocks in organic synthesis, playing a crucial role in the development of pharmaceuticals and agrochemicals. Silylboranes have emerged as versatile precursors for the incorporation of silicon atoms into molecular frameworks, often in combination with alkali-metal bases to generate highly reactive metal silyl reagents.[1,2] On the other hand, zinc silyl reagents typically require the use of transition-metal catalysis in order to promote these transformations.[3]

Opening new ground in this area, here we present the synthesis and reactivity of novel caesium zincate complexes bearing silyl ligands. By switching on bimetallic cooperation, these compounds exhibit unique nucleophilic profiles, allowing for the silylation of C-halogen bonds of bromo- and iodoarenes. These heterobimetallic silyl complexes are prepared by heteroleptic cleavage of the relevant silyl borane with a 2:1 mixture of Cs(HMDS) and $Zn(HMDS)_2$ (HMDS= $N(SiMe_3)_2$). Remarkably, the presence of aryl groups on the silyl substituent is key in order to favour the cleavage of the B-Si bond. This can be rationalized in terms of the formation of additional Cs-π-aryl electrostatic interactions which contribute to the overall stability of the newly generated caesium zincate, as shown in the Scheme for $[Cs_2Zn(SiMe_2Ph)_4]$.



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Beyond Steady-State in Catalysis: from Unconventional Operations to Unconventional Reactors

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The chemical industry is undergoing a fundamental shift driven by the rapid growth of variable renewable energy sources. Conventional catalytic chemical processes, designed around steady-state operation, are increasingly challenged by the intermittent nature of solar and wind power [1]. This contribution presents Casale's perspective on how unconventional operations in catalysis — and ultimately unconventional catalytic reactors — represent the most effective response to this challenge.

We first examine the techno-economics of flexible ammonia and methanol synthesis, demonstrating that adapting the synthesis loop to follow renewable energy availability — rather than buffering variability through expensive upstream storage — reduces both capital expenditure and the levelized cost of the product. In the context of rising geopolitical risk and energy price volatility, energy-independent production at a stable, predictable cost offers a compelling investment case.

We then address process electrification as the enabling technology for catalytic dynamic operation [2]. Electrification — e.g. through Joule heating, induction, microwave, and plasma — allows materials to heat and cool at rates unachievable with conventional thermal systems, enabling the catalyst to operate in a periodically forced regime. Under the right forcing conditions, the time-averaged catalytic rate can exceed the maximum achievable under any fixed static condition: a phenomenon known as dynamic catalysis. Ongoing R&D projects at Casale are exploring electrified monolith reactors, microwave-assisted catalysis, non-thermal plasma for CO_2 valorisation, and microwave-plasma torch processes for syngas generation.

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Introducing a Redox-Rich Heterometallic {Re_2Fe} Cluster with Accessible Fe Center and Catalytic Small Olefin Production

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Direct molecular-level understanding of heterogeneous catalysis remains intrinsically challenging because the active sites cannot easily be isolated and studied individually, while well-established concepts from molecular catalysis are often difficult to translate to processes on the surface.[1] Transition-metal clusters have therefore emerged as important molecular models for heterogeneous catalysts by reproducing the coordination environments around active sites in processes such as hydrogen-evolution reaction (HER)[2] and nitrogen oxide (NO_x) reduction.[3] These systems reflect not only structural features but also functional behavior of catalytic surfaces, making them highly valuable in elucidating mechanisms and potential intermediates.

Herein, we propose a new family of heterometallic clusters as a molecular framework that, instead of mimicking surface active sites only structurally, incorporates the key functional characteristics of highly reactive surfaces in heterogeneous catalysis. Our trimetallic {Re_2Fe} clusters possess one accessible and reactive Fe center together with two Re metal cores which are supported by two μ-Dipp-imido fragments (Dipp = 2,6-di*iso*propylphenyl). Direct metal-metal bonds, along with multiple terminal and bridging imido moieties, render these clusters structurally rigid over multiple redox states. Gram-scale synthesis of the cluster enabled investigation of its rich redox chemistry and the accessibility of the Fe active site through coordination of different ligands. Furthermore, preliminary studies revealed promising catalytic activity in the conversion of phosphonium ylides to olefins.

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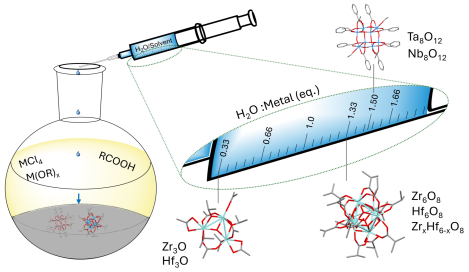
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Mechanism-Guided Precision Hydrolysis of Early Transition Metals to Access (Mixed-Metal) Oxo Clusters

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Zirconium and hafnium oxo clusters are catalysts, and building blocks for MOFs, 3D-printing and polymer composites. However,their synthesis is often a matter of trial and error, and new structures are hard to design retrosynthetically. Here, we use our recent insight in the formation mechanism of $Zr_6O_4(OH)_4(OOCR)_{12}$ oxo clusters to redesign their synthesis with higher reaction rates, more economical precursors, more sustainable solvents, and higher atom economy, all at room temperature at gram scale. We add exactly 1.33 equivalents of water for the precision hydrolysis of the metals toward Zr6-carboxylate or Hf6-carboxylate oxoclusters (carboxylate = acetate, oleate, and 2-methylbutanoate). Furthermore, we use precision hydrolysis to synthesize the elusive bimetallic Zr/Hf oxo clusters and to expand rational oxo cluster synthesis to the group 5, accessing the new $Nb_8O_{12}(OEt)_8(OBz)_8$and $Ta_8O_{12}(OEt)_8(OBz)_8$ clusters (OBz = benzoate). Precision hydrolysis allows for a rational design and an economic production of oxo clusters on a multigram scale, with potential to become the workhorse for cluster synthesis.

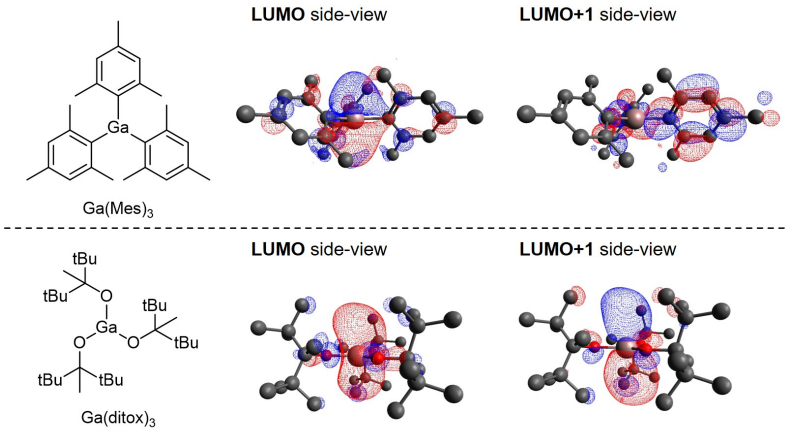


Tri-coordinated Ga Alkoxide: Surface Model of Lewis Acidic Ga Sites

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Gallium-containing metal oxides have been explored as industrially relevant catalysts for CO_x-hydrogenation and alkane dehydrogenation processes, with the help of its unique feature, such as Lewis acidity, redox properties and/or formation of metal alloys.[1,2] In particular, Lewis acidic features at the surface Ga sites are strongly dependent on the coordination environment and the geometry. However, the identification of the respective Ga surface sites remains challenging due to the presence of various Ga species on metal oxides. The investigation into the spectroscopic signatures, i.e. X-ray absorption spectroscopy (XAS) and solid-state NMR, of Ga model-complexes can be one of the powerful approaches to capture Ga surface sites by comparing Ga-containing materials.[3-6] While various Ga complexes have been reported as the surface models of Ga sites, such as tri-coordinated Ga complexes surrounded by N or C atoms[7,8] and tetra-coordinated Ga complexes surrounded by O, N or C atoms,[4-6] the synthesis of tri-coordinated Ga complexes surrounded by only O atoms has not been achieved even though such Ga complexes would be ideal models for surface Lewis acidic Ga sites on metal oxides. Herein, we synthesize a Ga tri-alkoxide complex as a monomer determined by single crystal X-ray diffraction, whose XAS feature is compared with the other tri-coordinated Ga complexes, i.e. Ga tri-aryl and Ga tri-amide, in order to explore the spectroscopic signature from different chemical environments in the same conformation. The visualized molecular orbitals using DFT calculation reveals the observed differences in XAS are derived from the contribution of pz orbital from Ga in each tri-coordinated Ga complex at LUMO or LUMO+1.



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Production of no-carrier-added ^{166}Ho for targeted radioligand therapy via neutron irradiation of enriched $^{164}Dy_2O_3$

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In the last decade, holmium microspheres containing ^{166}Ho ($t_{1/2}$=26.8 h) have been successfully employed for the treatment of several malignances, particularly liver tumors [1]. Thanks to its high-energy β^- particles ($E_{\beta^-,ave}$=667 keV), ^{166}Ho is also a potential candidate for targeted radioligand therapy. Furthermore, the versatile coordination chemistry of lanthanides enables the development of theranostic approaches based on chemically similar radiometals. In this context, our work focused on the development of an indirect production route through the neutron irradiation of enriched $^{164}Dy_2O_3$ as target material. No-carrier-added (n.c.a.) ^{166}Ho is obtained from the decay of ^{166}Dy ($t_{1/2}$=81.3 h, β^- 100%), its parent radionuclide. This approach avoids the co-production of the long-lived impurity ^{166m}Ho ($t_{1/2}$=1132 y) and enables repeated separations in a pseudo-generator configuration.

Several quartz ampoules containing 8 µg of $^{164}Dy_2O_3$ (enr. 96.8%) were irradiated at the Institut Laue-Langevin's (ILL) high-flux reactor. The production yields of the activation products were thoroughly assessed using γ-spectrometry measurements. The end-of-irradiation production yields of ^{166}Dy was 143 (9) GBq/mg using a neutron flux of 1.1×10^{15} $cm^{-2}s^{-1}$.

Extraction chromatographic (TK211/2/3) and cation exchange (Sykrogel H S 18 X-16) resins were evaluated for Dy/Ho separation. ICP-OES analysis of the collected fractions was used to assess the influence of eluent concentration, column dimensions, solution pH, and flow rate on separation performance and processing time.

The overall separation setup consisted of three columns and an additional one to enable the pseudo-generator. The TK211 extraction resin ensured rapid Dy recovery (>80% within 1 hour from loading), while removing stable holmium (^{165}Ho) and ^{166m}Ho. ^{166}Ho was isolated using Sykrogel cation exchange resin in combination with α-hydroxyisobutyric acid (α-HIBA). The TK213 extraction resin was used to remove metal contaminants, convert the product into chloride form, and elute ^{166}Ho in 1 mL volume. ^{166}Dy was recovered from the Sykrogel column using concentrated α-HIBA and loaded onto a TK212 resin to convert it into 0.5 HNO_3. This enabled recovery yields of up to 98% of ^{166}Dy, allowing ^{166}Ho ingrowth and supporting repeated generator-like processing using the Sykrogel column.

Gigabecquerel-scale production of ^{166}Ho was successfully demonstrated, yielding up to 3 GBq of n.c.a. and radionuclidically pure ^{166}Ho in approximately 1 mL of 0.1 M HCl. Ongoing optimization of the separation procedure is expected to improve activity concentration and process robustness. In parallel, the successful implementation of TK212 resin enabled the generator-based approach. Upon optimization of process reproducibility, routine production of high specific activity of ^{166}Ho could support preclinical investigations and facilitate the development of ^{166}Ho-based targeted radioligand therapy.

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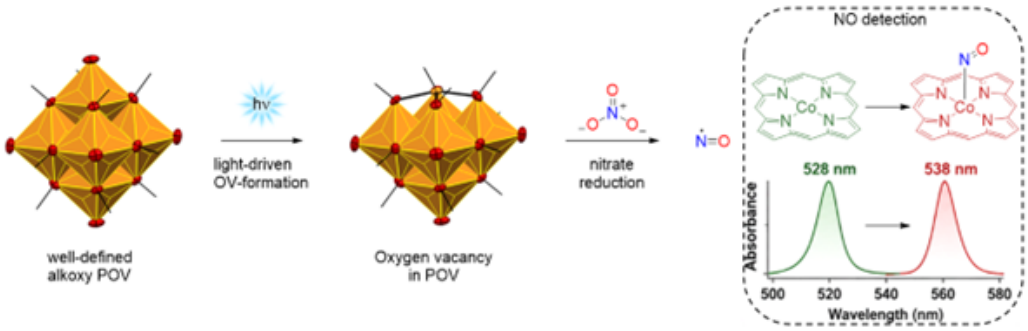
A Photochemical Nitrate-to-NO Assay Enabled by Light-Driven Oxygen Vacancy Formation in Polyoxovanadates

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Photochemical assays that couple small-molecule reactivity to direct optical readout are attractive for the chemical sensing of challenging analytes.[1] Reactive oxygen vacancies (OVs) in metal oxides are attractive motifs for such systems because of their rich small-molecule activation chemistry,[2] yet their formation and reactivity are often difficult to study directly in structurally heterogeneous materials. Polyoxovanadates (POVs) provide molecularly well-defined, soluble metal-oxide platforms for solution-state spectroscopic study of oxygen-vacancy chemistry.[3]

Herein we report a photochemical nitrate-to-NO assay based on light-driven OV generation in the POV $V_6O_7(OMe)_{12}$ (**V_6O_7**). Upon irradiation, vacancy-bearing clusters are formed in situ and subsequently reduce nitrate to NO, which is monitored in real time via a cobalt porphyrin signaling array. Solution-state spectroscopy identified key intermediates, while NO capture was tracked through a diagnostic Q-band shift in the cobalt porphyrin (528 → 538 nm upon nitrosyl-complex formation[4]). Addition of varying equivalents of $TBANO_3$ produced proportional Q-band shifts consistent with quantitative NO formation. The assay operates in the low-ppm nitrate regime and provides a direct optical readout of photochemical nitrate reduction. These results demonstrate light-driven OV formation in polyoxovanadates and establish them as molecular metal-oxide platforms for coupled photochemical reactivity and optical reporting.



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Unconventional Reactivity of BAC Carbene and PCP Carbone Ligands on Fe(II) Complexes

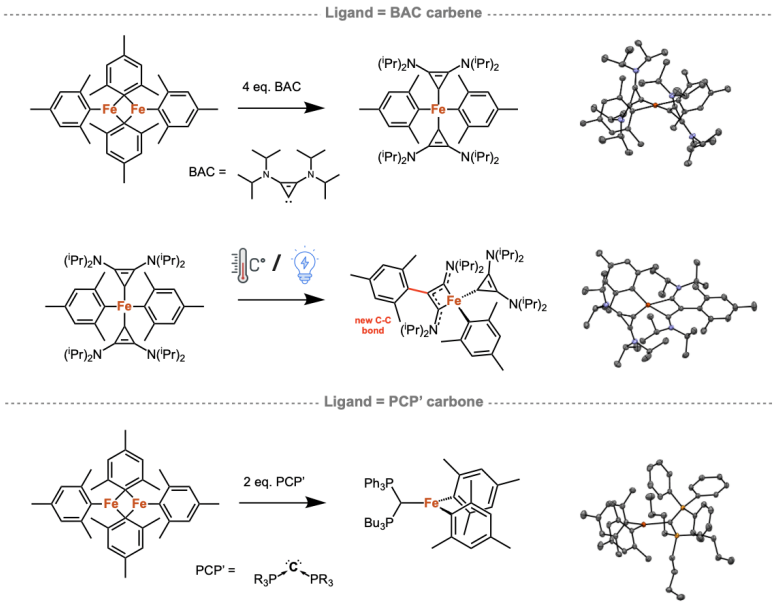
B. Berger[1], C. Copéret[1]

[1]Copéret Group, LAC, ETH Zürich

The utilization of N-heterocyclic carbenes (NHCs) and cyclic (alkyl)(amino)carbenes (CAACs) as ligands is foundational to the fields of homogeneous catalysis and organometallic chemistry. Their distinctive bonding profiles - characterized by strong σ - donation coupled with weak (in NHCs) or enhanced (in CAACs) π - accepting capabilities - are critical for electronically tuning transition metal complexes. Recently, more exotic carbon-based L-type ligands have emerged, such as bis(diisopropylamino)cyclopropenylidenes (BACs) and carbodiphosphoranes (carbones), the latter best described as featuring a central, divalent carbon(0) atom that retains two lone pairs and coordinates via double dative bonds.[1], [2] While the coordination chemistry of NHCs and CAACs is thoroughly established, transition metal complexes bearing BAC or carbone ligands remain significantly underexplored.

Motivated by this, we report the synthesis and isolation of a novel iron complex, $Fe(BAC)_2Mes_2$ (**1**), prepared via the reaction of Fe_2Mes_4 with BAC. Upon thermal (393 K) and photochemical (365 nm) activation, complex **1** undergoes a structural reorganization to yield a metallacyclobutadiene (MCBD) complex (**2**), as confirmed by single-crystal X-ray diffraction. Drawing upon recent precedents of BAC-mediated skeletal rearrangements,[3], [4] we propose a mechanism initiated by the cleavage of the cyclopropene single bond, followed by amino group migration to the α-carbon, and subsequent mesityl ligand migration to the β-carbon. This proposed pathway is currently being probed via computational studies corroborated by *in situ* EPR spectroscopy during photochemical activation. Ultimately, the formation of **2** underscores the unconventional reactivity of BAC ligands. Unraveling this mechanism will provide fundamental insights into the coordination behavior of this ligand and inform the rational design of molecular properties in future base-metal complexes.

Building upon these findings, we also present the synthesis of $Fe(PCP')Mes_2$ from the reaction of Fe_2Mes_4 with two equivalents of the carbone PCP' (where PCP' = $Ph_3P–C–P^nBu_3$). Ongoing studies are evaluating the thermal and photochemical activation pathways of this species to further elucidate the coordination motifs of carbones at iron centers.



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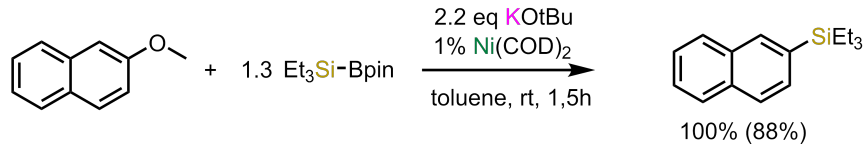
Nickel Catalysed Silylation of Aryl-Ethers: a Mechanistic Study

R. Bienenmann[1], E. Hevia[1]*

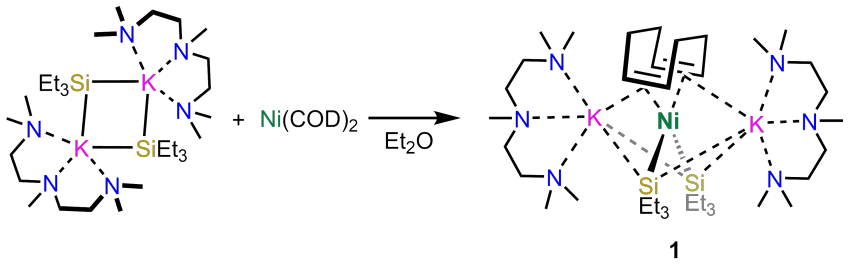
[1]Department of Chemistry, Biochemistry and Pharmaceutical Sciences, University of Bern

Aryl-ethers have a major potential as sustainable and renewable platform chemicals due to their abundance in lignin.[1] However, the bottleneck in their utilization is the cleavage and functionalization of the C–O bond which often requires harsh reaction conditions and high catalyst loadings.[2] In 2017, Martin et al. published the catalytic silylation of aryl-ethers using earth-abundant $Ni(COD)_2$ (COD = 1,5-cyclooctadiene) as catalyst under mild conditions and with low catalyst loadings (Figure 1a).[3] The remarkable efficiency of this reaction prompted us to study its mechanism, which is currently poorly understood. In this work we unveil experimentally how Et_3Si-Bpin reacts with KOtBu in two steps to form $[KSiEt_3]_2$, which we characterized both in solution as well as structurally in the solid-state. Moreover, we probed the reactivity of this $[KSiEt_3]_2$ with the $Ni(COD)_2$ pre-catalyst to reveal that it forms a highly reactive dianionic nickelate complex (**1**) with a Ni:Si ratio of 2:1, contrasting the previously hypothesized 1:1 active species (Figure 1b).[3] Stoichiometric reaction of **1** with 2-methoxynaphthalene yields the formation of both the expected 2-(triethylsilyl)naphthalene product as well as $Ni(COD)_2$, suggesting that **1** is an on-cycle species in the catalytic reaction. Based on our findings, we are able to propose a new mechanism for this relevant silylation reaction and thereby advance the understanding of nickel catalysed aryl-ether functionalization reactions.

a) Aryl-ether silylation reported by Martin et al. 2017



b) Isolated and characterized nickel silanide intermediate



1

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Synthesis and Catalytic Activity of an Anionic Zinc Dihydride Complex

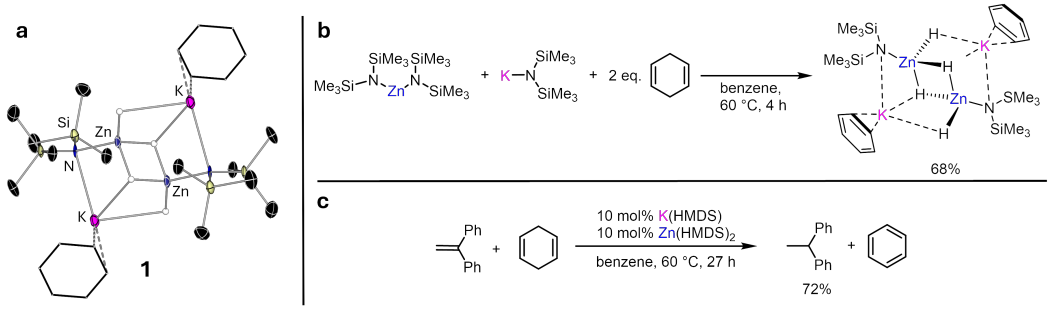
Z. Brüllhardt[1], R. Bienenmann[1], E. Hevia[1]*

[1]Department of Chemistry, Biochemistry and Pharmaceutical Sciences

Transfer hydrogenation reactions, in which a metal catalyst extracts a hydride from a hydrogen source and reduces a substrate, have traditionally been the realm of transition metals, although main group elements have shown promising reactivity in recent years. [1] Recently it has been shown that $Zn(HMDS)_2$ (HMDS = $-N(SiMe_3)_2$) with KH can catalyse hydrogenation reactions, however these reactions have a very limited scope and the active species in this transformation remains unknown. [2]

In this work we synthesize and structurally characterise a novel hydrido-zincate complex (**1)** supported by a hexamethyldisilazane ligand (Fig. 1a). This complex is formed through the deprotonation of cyclohexadiene with the relatively weak base KHMDS, generating *in situ* an available equivalent of "KH" which reacts with $Zn(HMDS)_2$ to form putative $KZN(HMDS)_2H$ intermediate. This intermediate then reacts with another equivalent of cyclohexadiene to form complex **1** (Fig. 1b). This same reaction does not proceed with Na(HMDS) which shows that the alkali metal is of critical importance.

Interestingly, zinc hydride complex **1** is an active catalyst for the transfer hydrogenation of 1,1-diphenylethylene with cyclohexadiene as the hydrogen source (Fig. 1c). As this implicates **1** as a catalytically competent complex, this provides a rare insight into the active species of a zinc catalyzed hydrogenation of alkenes.



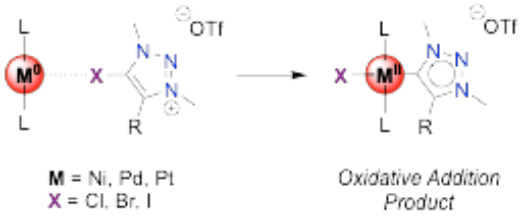
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Synthesis of Triazolylidene-Metal Complexes *via* an Unprecedented Free NHC Oxidative Addition Mechanism

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N-heterocyclic carbene (NHC)-supported metal complexes have been extensively studied in the last decades and now represent the state-of-the-art catalysts for several key synthetic applications.[1–3] Among those, 1,2,3-triazol-5-ylidene complexes demonstrated superior performances in some catalytic reactions with respect to the Arduengo-type carbene complexes, thus attracting growing interest in the field.[4,5] Therefore, accessibility to these carbene metal complexes is pivotal. Here, we will present the synthesis of metal-triazolylidene complexes *via* oxidative addition of 5-halotriazolium salts to Pt(0), Pd(0) and Ni(0) precursors. The detection of unexpected side products contradicts the conventional concerted oxidative addition pathway. Supported by trapping experiments of the intermediates and DFT investigation, we will discuss a new mechanism of oxidative addition and its scope to a wider range of polarized C–X bonds.



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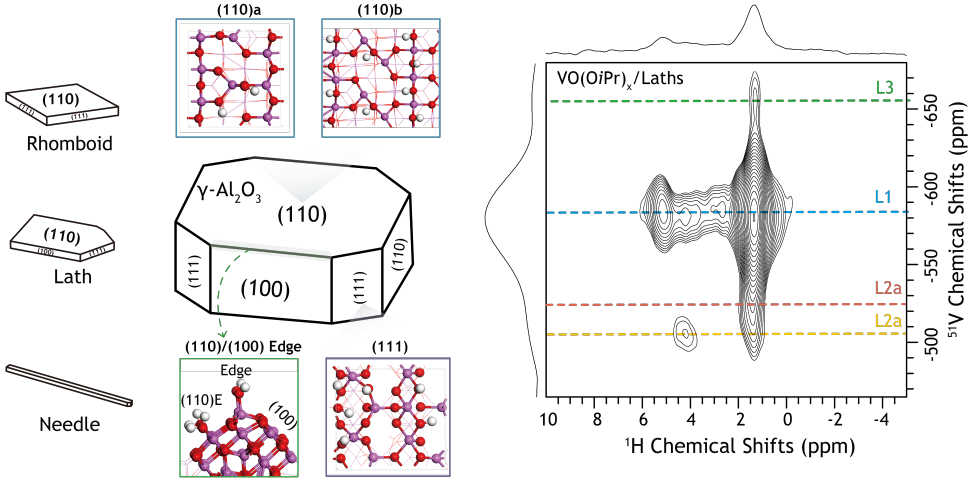
Site-Specific Speciation of Vanadium Sites on γ-Al_2O_3 Facets and Edges from ^{51}V SSNMR Spectroscopy

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γ-alumina (γ-Al_2O_3) has shown extensive applications in numerous industrial processes, owing to its thermal and mechanical stability, its tunable morphology of high surface area as well as its unique surface properties. Gaining fundamental insights into the γ-Al_2O_3 surface at the atomic and molecular levels and decoding the specific roles of surface sites in stabilizing and/or activating metal species has emerged as a pivotal objective for establishing structure-property relationships in heterogeneous catalysis. A premier example is supported vanadium on γ-Al_2O_3, which serves as one of the most prominent catalysts for the oxidative dehydrogenation (ODH) of propane.[1] The nature and local structures of surface V sites as a function of support characteristics, such as specific facets or edges of γ-Al_2O_3, have yet to be systematically investigated and remain a significant challenge.

In this work, we prepared γ-Al_2O_3 nanocrystals of distinct morphologies: Rhomboids with flat (110) and (111) facets; Laths with dominated (110) and (100) facets, as well as (111) facets; Needles with enriched (110)/(100) edges, as supports for surface study. Surface Organometallic Chemistry (SOMC) method was applied by using vanadyl isopropoxide (VO(O*i*Pr)$_3$) as a molecular precursor for grafting via protonolysis with the surface -OH groups, which are expected to be distributed on facets/edges on γ-Al_2O_3 nanocrystals. Calcination treatment was followed for the generation of surface vanadia. Multinuclear (^{1}H, ^{13}C, and ^{51}V) Solid-state Nuclear Magnetic Resonance (SSNMR) spectroscopy, leveraging high magnetic fields (up to 1.2 GHz) and fast MAS techniques, was integrated with DFT calculations to disclose the vanadium speciation (including grafted vanadium and vanadia) on γ-Al_2O_3 facets and edges.



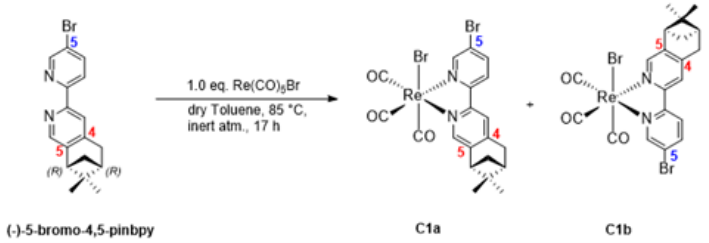
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Synthesis and diastereomers separation of chiral bromopinene-bipyridine Re(I) tricarbonyl complexes for biological studies

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In recent years, *fac*-tricarbonyl Re(I) complexes have emerged as promising compounds with anticancer and antibiotic properties[1]. Although only a limited number have demonstrated potent in vivo anticancer activity[2]. To date, the influence of the chirality of these compounds has been largely overlooked in biological studies. Nevertheless, since their mechanisms of action involve interactions with chiral biomolecular targets, such as hypoxia-inducible factors (HIFs), chirality can play a pivotal role in modulating their biological activity.



Here we focus on the synthesis of bidentate chiral ligands derived from pinene containing a bromo substituent on their bipy scaffold and their complexation with Re(I) leading to the formation of two diastereomers[3,4] with the formula *fac* -[$Re(CO)_3Br(NN)$] (Figure above). The synthesis, diastereoisomeric separation and characterization of these complexes will be presented together with an evaluation of the influence of stereoisomerism on their biological activity toward HIF-related pathways.

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A Metallosupramolecular Receptor for Squaraine Dyes Enabling Ultrafast Dark Resonance Energy Transfer

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Förster resonance energy transfer (FRET) is widely applied in imaging. Recently, dark resonance energy transfer (DRET) has emerged as a new strategy that employs non-emissive donors to achieve low background fluorescence.[1] The use of metallosupramolecular assemblies as dark donors is unprecedented.

A metal-organic cage was obtained by combining acridone-based dipyridyl ligands with Pd^{2+} ions. The cage acts as a potent receptor for squaraine dyes, with a unique selectivity profile. The cage itself is non-luminescent. Upon excitation of the acridone-based framework, ultrafast (sub-ps) DRET to the squaraine dyes was observed, resulting in bright, near-infrared emission, with pseudo-Stokes shifts of up to 440 nm.[2] Upon encapsulation of a chiral dye, chirality transfer to the host could be evidenced by circular dichroism spectroscopy.

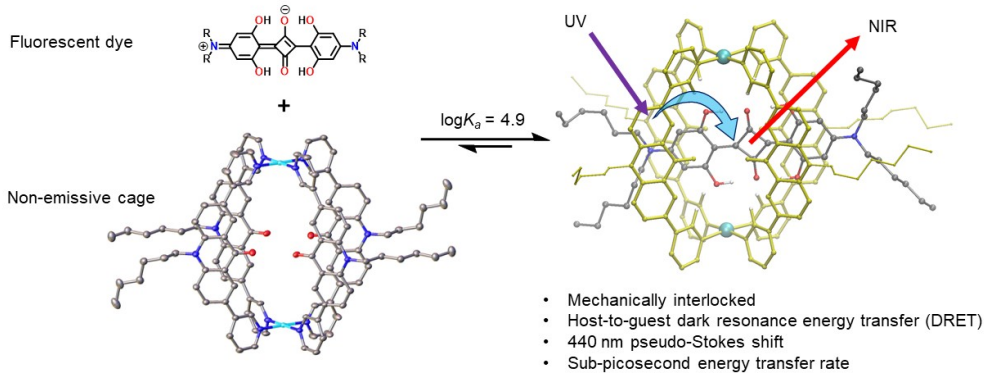


Figure 1. *A palladium-based cage encapsulates squaraine dyes in a pseudo-rotaxane-like fashion, and sensitizes the bound dye via dark resonance energy transfer.*

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Synthesis and Characterisation of Enantiopure Tricarbonyl Re(I) Anticancer Complexes for Stereocontrolled HIF Targeting

H. Chourasia[1,2], A. B. Solea[1], A. Crochet[2], C. Spack[3], B. Chapuis[2], F. Zobi[2], D. Hoogewijs[2], O. Mamula Steiner[1]*

[1]University of Applied Sciences of Western Switzerland, HEIA-FR, Pérolles 80, 1700 Fribourg, Switzerland, [2]University of Fribourg, Department of Chemistry, Chemin du Musée 9, 1700 Fribourg, Switzerland, [3]University of Fribourg, Department of Medicine/Physiology, 1700 Fribourg, Switzerland

Among transition-metal-based therapeutics, *fac*-$[Re(CO)_3]^+$ type complexes have emerged as promising anticancer agents.[1] However, the influence of stereochemistry on their biological activity remains largely unexplored. To date, only a limited number of studies[2,3] have investigated these effects using chiral ligands generating diastereomeric complexes with distinct biological activities. Preliminary studies[4] on a Re(I) tricarbonyl complex revealed also the higher uptake in hypoxic cells when compared with normoxic cells.

>In this work, we present the synthesis and the characterization, of chiral Re(I) tricarbonyl complexes based on enantiopure pinene-functionalized bipyridine and phenanthroline ligands (**Figure 1)**. This work aims to define chirality as a key design parameter for anticancer properties with a particular focus on the selective hypoxia-inducible factors (HIFs) which are key regulators for tumour progression.

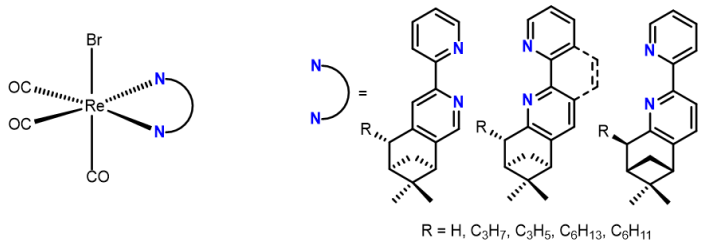


Figure 1. General representation of fac-[Re(CO)$_3$Br(NN)] complexes and their NN ligands

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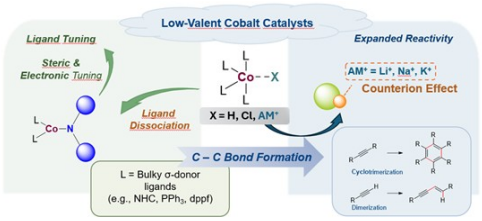
Designing Low-Valent Cobalt Complexes for Catalytic Applications

D. dejoz[1], A. Tortajada Navaro[1]*

[1]University of Fribourg

Carbon-carbon (C–C) and carbon-heteroatom bond formation remains a central transformation in organic synthesis, with broad applications in the production of pharmaceuticals, agrochemicals, and advanced materials.[1] Traditionally, these transformations rely on precious second- and third-row transition metals such as palladium, rhodium or ruthenium.[2,3] However, in recent years first-row transition metals have gained attention, due to their potential to unlock previously unexplored reaction pathways, which can open doors for new synthetic methodologies. Within this context, cobalt has previously demonstrated catalytic activity in cycloaddition reactions, particularly with alkynes and activated olefins to form complex chemical structures.[4] Despite these advances, the mechanistic pathways are still not fully understood and expanding its reactivity to less activated olefins and other small molecules remains a challenge.

Opening new avenues in cobalt catalysis, this project aims to develop a new class of more electron-rich cobalt complexes capable of promoting these catalytic reactions with non-activated olefins and other small molecules. Our strategy involves modulating the electron density at the cobalt center through two independent approaches: (1) the introduction of both bulky and strong σ-donor ligands to stabilize coordinatively unsaturated complexes while also enhancing electron density over the metal, and (2) formal reduction of cobalt center to form bimetallic cobalt-alkali metal species to access lower oxidation states, where variations in the alkali-metal counterion are expected to influence reactivity. Electronic tuning of the metal center will improve catalytic efficiency and expand the substrate scope of cobalt-mediated C–C and C–X bond-forming reactions, ultimately, providing new tools for sustainable catalysis based on abundant 3d metals.



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Xanthene-Based Iron(II) Complexes: Synthesis and Reactivity Studies

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[1]Department of Chemistry, Biochemistry and Pharmaceutical Sciences, University of Bern

Iron is an attractive metal in coordination chemistry due to its abundance, low cost, and flexible electronic structure.[1] However, this wide range of coordination environments accessible to iron often complicates the isolation and stabilization of low-coordinate iron species. Bulky amide ligands offer an effective solution by providing strong steric protection while also stabilizing electron-rich metal centers.[2] This combination enables access to unusual, controlled-iron coordination environments and catalytic reactivities that are otherwise inaccessible. However, despite this advantage, iron complexes supported by bulky amide ligands remain relatively underexplored and their structure–reactivity relationship remains poorly understood.[3]

Herein, we present the synthesis of neutral and anionic Fe(II) complexes supported by xanthene-based ligand scaffolds. A bimetallic synthetic strategy is presented which relies on the synthesis of the relevant Fe(II) complex by treating the lithiated ligand with $FeBr_2$. However, co-complexation with the relevant sodium alkyl or amide reagent was performed independently starting from the free ligand. These new compounds have been structurally characterized and their ability to undergo metalation has been investigated towards a range of organic substrates including ketones, amines and fluoroarenes. Initial findings investigating the catalytic behaviour of these iron complexes towards hydrogenation of unsaturated organic molecules will also be presented.

Metal-Organic Frameworks meet Highschool: Synthesis and Properties of Copper(II) Pyrazolate

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Coordination chemistry is an integral part of the chemistry high school curriculum in the Canton of Bern and usually covers bonding, geometry, and ligand-exchange reactions in transition metal complexes. Furthermore, the topic serves as a starting point to introduce basic concepts of quantum chemistry through the study of electronic transitions in coloured pigments[1]. Metal-organic frameworks (MOFs) are gaining increased interest as materials which can absorb small molecules, thus lending themselves to illustrate practical applications as absorbents or as sensors. Learning about MOFs allows students to bridge their pre-existing knowledge of polymerization and coordination chemistry. Moreover, MOFs demonstrate how chemistry and materials research are linked to environmental remediation and sustainability - topics to which the young generations are particularly sensitive.

However, integrating such topics into the secondary education system remains a significant challenge due to the constraints of time and resources. Nonetheless, connecting basic scientific concepts to real-world applications is a crucial aspect of education as it allows to spark the interest in STEM subjects. Practical activities can be especially effective as they are more engaging than classroom lessons and enable students to practice their practical laboratory skills alongside learning about fundamental concepts.

In this contribution, I will show a new learning unit about metal-organic frameworks for high school students and how it was implemented in the curriculum at Gymnasium Thun. Copper(II) pyrazolate MOFs were selected as a material which can be synthesized easily and rapidly in microcrystalline form without specialized laboratory equipment[2]. They have a simple structure and show remarkable colour changes upon sorption/desorption of water or ammonia, which allows students to visually monitor the exchange of guest molecules in real-time.

The original unit we designed consisted of a one-day laboratory activity during a project week at the University of Copenhagen. Given access to analytical facilities, students carried out sample preparation and characterization via Powder X-Ray Diffraction (PXRD) and single-crystal structure determination. This enabled them to evaluate reaction outcomes, discuss phase purity, and observe structural similarities between the host framework with and without guest molecules.

I will further demonstrate, how we refitted our learning unit to a modular format consisting of two 90-minute lessons, which is suitable for a standard school setting. In this version, rather than performing live measurements, students conduct the synthesis as well as colour-guided sorption experiments, and then perform digital structural analysis using the original CIF files (provided to them), ensuring that the pedagogical benefits of the unit are preserved even when time or equipment is limited.

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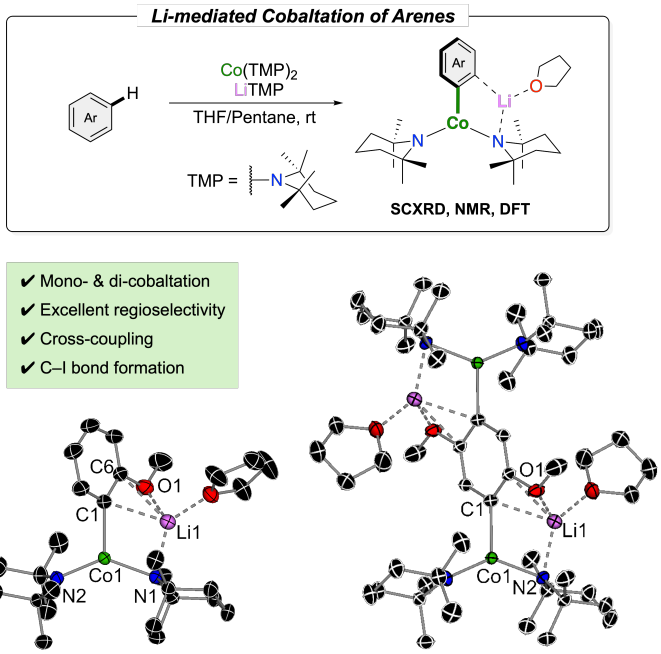
Lithium-mediated Cobaltation of Arenes and Heteroarenes

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Deprotonative metalation of arenes with alkyllithiums and lithium amides is commonly used to access functionalised aromatic compounds.[1] However, for some (hetero)arenes lacking directing groups, this method results in low chemo- and regioselectivity and requires harsh conditions.[2] To overcome these drawbacks, many heterobimetallic systems have been developed combining Li with a less electropositive metal such as Zn, Al and Mg,[3] where bimetallic cooperation leads to better functional group tolerance.

Our group recently reported the direct Co–H exchange of *N*-heterocycles with $Co(TMP)_2$ (TMP = 2,2,6,6-tetramethylpiperidide) with excellent α-to-nitrogen regioselectivity dictated by the coordination effects.[4] Building on these findings, here we combine $Co(TMP)_2$ and LiTMP and assess the potential of this heterobimetallic base in deprotonative metalation of (hetero)arenes. Isolable organometallic intermediates were characterised by XRD and NMR studies and further engaged in cross-coupling or homocoupling processes. DFT calculations were carried out to highlight the bimetallic cooperativity in these metalation reactions.



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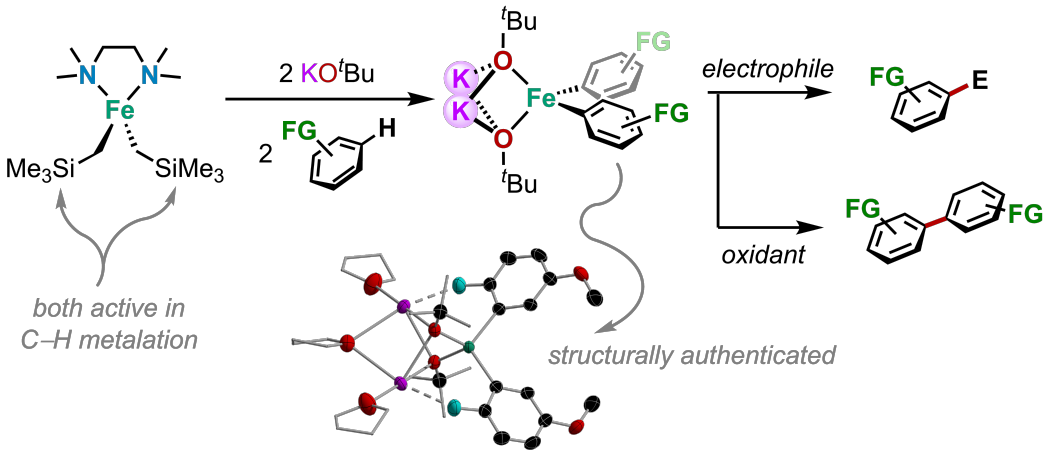
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C–H Ferration of Arenes by Iron(II) Alkyl/Potassium Alkoxide Synergism

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The functionalization of (hetero)arenes belongs to the most fundamental and widely employed transformations known to the synthetic practitioner. In this regard, the C–H metalation of arenes by polar s-block organometallics such as alkyl lithium compounds has evolved as a standard pathway for selective functionalization.[1] Groundbreaking work by Schlosser has revealed that the pairing of lithium alkyls with potassium alkoxides gives rise to mixtures with even higher basicity than their individual components.[2] Here, an extrapolation of this strategy to significantly less polar iron(II) alkyl complexes is presented. The combinaiton of the iron(II) neosyl complex [Fe(CH_2SiMe_3)$_2$(tmeda)] (tmeda: *N,N,N′,N′*-tetramethylethane-1,2-diamine) with the standard base potassium *tert*-butoxide (KO^{t}Bu) is shown to surpass their original components in C–H metalation activity. This Fe/K synergism enables the direct ferration of (hetero)aromatic substrates yielding higher-order potassium ferrates as evidenced by X-ray crystallographic studies. These are readily diversified if presented to a suitable electrophile giving high-value, functionalized arenes. Leveraging the redox flexibility of iron as a transition metal, C(aryl)–C(aryl) coupling can be achieved through oxidative treatment, a pathway that is inaccessible to conventionally employed s-block organometallics.



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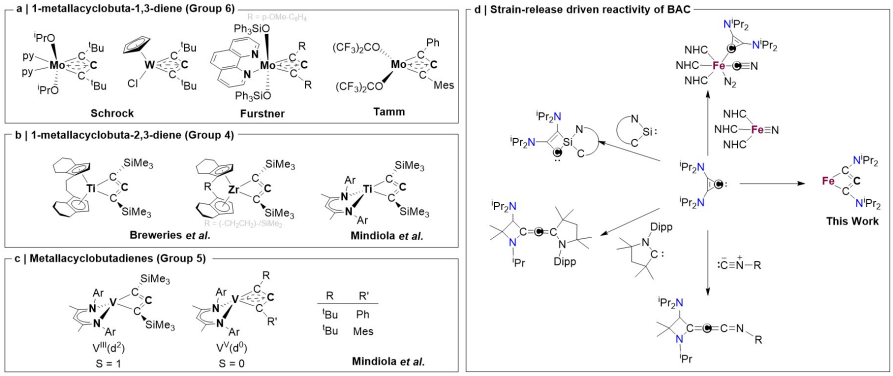
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Iron-based metallacyclobuta-2,3-diene complexes and their transformations

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Free bis(amino)cyclopropenylidene (BAC; Weiss–Yoshida reagent), introduced by Guy Bertrand[1], remains underutilized in synthesis compared with other isolable singlet carbenes (NHCs and cAAC). This disparity largely stems from the tendency of cyclopropenylidenes to undergo C_α–C_β bond rupture, a behaviour that has been exploited in carbon-atom or carbyne-transfer reactivity.[2] In this work, we now demonstrate that cyclopropenylidene reactivity can be used to access highly unusual iron four-member metallacycloallenes (1-ferracyclobuta-2,3-dienes), a rare class of species with only a few examples involving closed-shell early transition metals (Ti, Zr, V, Mo, W).[3,4]



Cyclopropenylidene activation with low-valent iron leads to metallacycloallenes accessible in three redox states. So far, we have isolated and fully characterized (single-crystal XRD, X-band EPR, ^{57}Fe Mössbauer, etc.) paramagnetic Fe metallacycloallenes in two redox states: The first species is an S = 1/2 complex formally assigned as Fe(III), whereas the second is an isostructural S = 1 congener with a formally Fe(IV) center. However, further analysis, including quantum-mechanical calculations, indicates an unconventional electronic structure that rationalizes the unexpected stability of such atom connectivities.

The electronic structure analysis of this pair of 1-ferracyclobuta-2,3-dienes was complemented by reactivity studies with redox reagents and small Lewis acids and bases. These reactions lead to the discovery of a series of unprecedented structures, including a 1-ferracyclobuta-1,3-diene and an iron complex bearing a C_6 ligand formed upon activation of a second cyclopropenylidene by the bent reactive allene fragment. Analysis of these compounds also points to the rich redox chemistry of these ligands and their unusual electronic descriptions. Together, these results expand the synthetic and mechanistic repertoire of cyclopropenylidenes, establish iron metallacycloallenes as isolable motifs across multiple redox states, and expose new opportunities for C–C bond formation driven by iron complexes.

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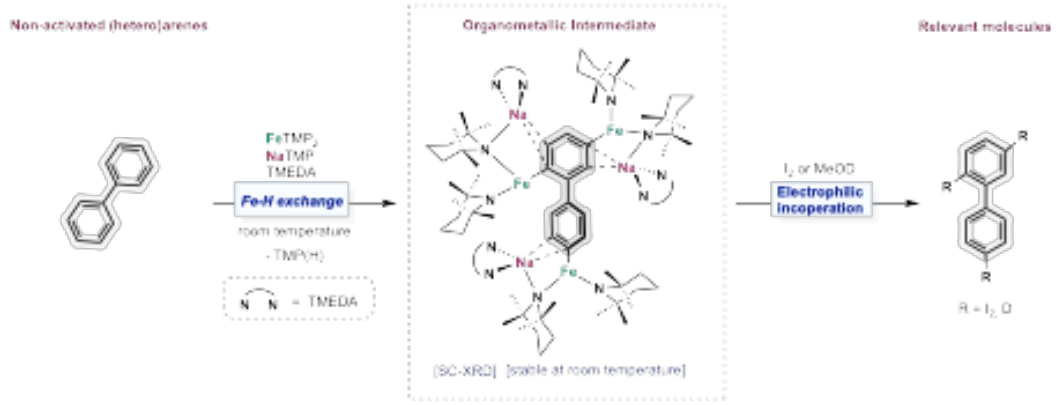
Tailoring Sodium Ferrate Complexes to Promote Poly-Metalations

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Deprotonative metalation constitutes one of the most utilized and fundamental chemical reactions, facilitating the functionalization of molecules and the generation of novel reactive species.[1,2] Traditionally these reactions are performed with monometallic organolithium (*n*BuLi) or lithium amides (LiHMDS; HMDS = $N(SiMe_3)_2$), which are highly activated due to the large polarity of their Li-N or Li-C bonds.[3] However, despite their widespread application, their high reactivity imposes challenges, including limited functional group tolerance, poor regioselectivity and the use of cryogenic due to the lack of stability of the intermediates. These factors diminish the atom economy and synthetic processes that are far from sustainability.[4] In particular, the metalation of most fundamental arenes such as benzene or other non-activated polyarenes are challenging, as the absence of functional groups results in inefficient C–H acidity.

Herein, we report the deprotonative multi-metalation of highly challenging substrates mediated by bimetallic cooperativity. By activating cooperative effects through the combination of the earth-abundant s-block metal Na and Fe in a bimetallic ate system, unique direct Fe–H exchanges on non-activated (hetero)arenes can be achieved at room temperature. With the isolation and characterization of the organometallic key intermediates, we were able to study the metalation process, observing unusual regioselectivities, which cannot be obtained with conventional single metal bases. Further functionalization allows access to valuable precursors towards more complex organic molecular scaffolds.



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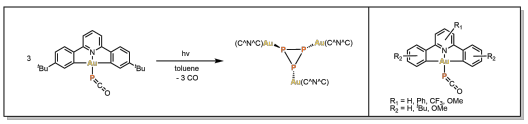
Gold(III) Phosphaketene Complexes: Synthesis and Reactivity

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In contrast to their lighter congeners, i.e. carbene and nitrene complexes, metallaphosphinidene complexes remain largely unexplored and have never been isolated. To date, only two stable organophosphinidene species have been reported, stabilized by bulky ligands and weak intramolecular interactions.[1,2] The decarbonylation of phosphaketenes (R–PCO) by heat or light provides a convenient route to both stable organophosphinidenes and transient metallaphosphinidenes.[3–5] We therefore adopted this strategy in our pursuit of a gold phosphinidene complex.

Herein, we report the synthesis of gold(III) phosphaketene complexes supported by bis-cyclometalated pincer ligands, which effectively stabilize metals in high oxidation states. Using N^C^C-type ligands, we found that although the ligand scaffold allows access to phosphaketene species, the Au–P bond is too labile, leading to rapid decomposition. In contrast, the lower *trans* effect of the C^N^C framework proved crucial for generating the first triauratriphosphirane complex via decarbonylation of the parent gold(III) phosphaketene. The structure was confirmed by single-crystal X-ray diffraction and provides strong evidence for the intermediacy of free auraphosphinidenes. Finally, ligand derivatives bearing substituents on the phenyl and pyridyl rings were prepared to further enhance phosphinidene stability and broaden the scope of its reactivity.



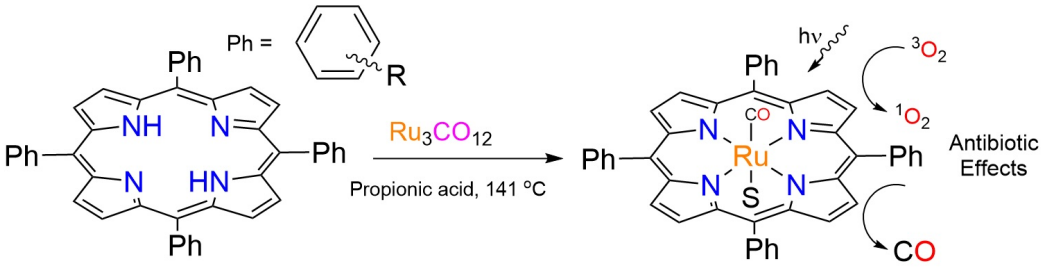
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Photodynamic antimicrobial chemotherapy, using porphyrinoids metalated to a ruthenium (II) complex for the treatment of antimicrobial resistant bacterial strains

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Porphyrinoids are a class of organic compounds that can serve as potential photosensitisers due to their strong visible absorption and tunable chemical properties, which can be further enhanced through metal coordination. This study explores the use of porphyrins in photodynamic antimicrobial chemotherapy (PACT), a light-activated strategy that generates reactive oxygen species to combat antimicrobial-resistant (AMR) bacteria. We report the synthesis and characterisation of 9 meso-substituted porphyrins as precursors for ruthenium(II) complexes. The porphyrins were prepared via acid-catalysed condensation and purified by column chromatography. Their structures and purity were confirmed using UV–Visible, FTIR, and NMR spectroscopy, yield obtained was 16-53%. These ligands were further metalated to form porphyrin-Ru (CO) complexes. Ongoing work focuses on the evaluation of their photodynamic antimicrobial activity against AMR bacterial strains. This study establishes a synthetic and structural foundation for the development of ruthenium–porphyrin photosensitisers as potential candidates for PACT applications.



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Synthetic Investigations of Metal-Oxo Cubane Complexes

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Cubic metal-oxo clusters have been a focal point of biomimetic inorganic chemistry for over a decade, since the first solution of the cuboidal Mn_4CaO_5 active site of photosystem II. While many $\{M_4O_4\}$ cubane complexes have been prepared and studied for their catalytic activity, there has been little work conducted on their formation mechanisms, leaving a gap in our understanding of these systems. This work focuses on the closing that gap and furthermore in understanding the behavior of small coordination clusters in solution. Through these studies, we aim to realize predictive strategies for the synthesis of metal-oxo cubane complexes which can be broadly applied to inorganic synthesis; a field which currently lacks a strong, predictive synthetic tool kit. Previously, we identified a $\{Co_4O_4\}$ supported by the ligand di-2-pyridyl ketone, which could be isolated in differing conformations based on synthesis conditions. These cubanes were accessible in two "types," which were determined by the anions present in the reaction solution.

In this work, we have continued our research on these cobalt-based cubanes by expansion of our synthetic conditions as well as exploring modifications to the supporting ligand. We report a new type of cubane for cobalt as well as computationally-derived mechanism of conversion for the system. The complexes have been characterized by single-crystal X-ray diffraction, powder X-ray diffraction, electrospray-ionization mass-spectrometry, Fourier-transform infrared spectroscopy, and nuclear magnetic resonance.

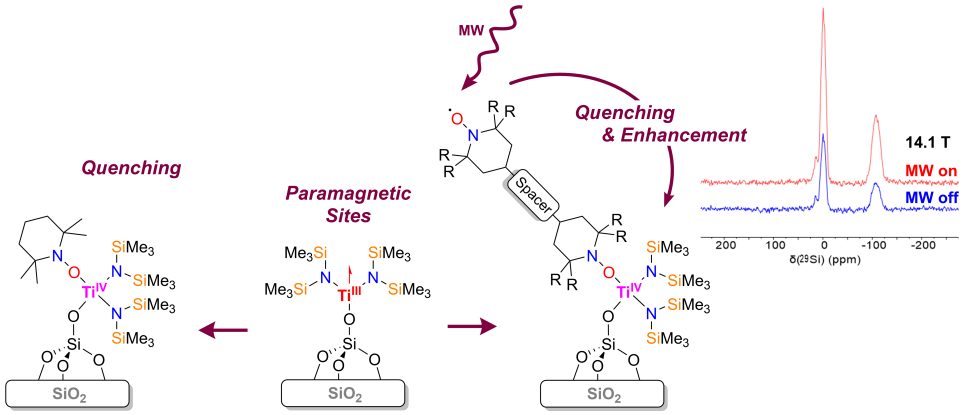
Nitroxide Radicals as NMR Probes for Paramagnetic Metal Sites

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Understanding the structure and reactivity of heterogeneous catalysts on a molecular level constitutes a major driving force in modern catalysis research, as a fundamental step towards rational catalyst design. Solid-state NMR spectroscopy (ssNMR) has been recognized as an unparalleled characterization technique on that front, providing valuable information about the electronic structure and coordination environment of supported metal sites. [1] Its application towards paramagnetic systems, however, remains challenging, despite their presence in industrially relevant heterogeneous catalytic processes, such as olefin polymerization and methane-to-methanol conversion. [2-4] In such cases, the presence of unpaired electrons at a relatively high density renders most conventional NMR approaches unsuitable, and complicates the EPR signals. In this work, we present an alternative methodology to overcome these challenges, by utilizing organic mono- and multiradicals as probe molecules for quenching the paramagnetic character of supported Ti(III) sites. In the former case, the resulting diamagnetic materials can be studied by classic ssNMR methods, while in the latter, unpaired spins are preserved on the ligand framework tethered to the metal centers, allowing signal enhancement of surface nuclei through Dynamic Nuclear Polarization (DNP) at a high magnetic field (14.1 T). This approach paves the way for significantly expanding the field of application of ssNMR, and enabling the characterization of ill-defined paramagnetic heterogeneous catalysts with the same precision as their diamagnetic counterparts.

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Comparison of different complexing agents for the separation of neighboring radiolanthanides

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Radiolanthanides are increasingly attractive for theragnostic applications in nuclear medicine, where matched radionuclide pairs enable both imaging and targeted radionuclide therapy.[1] The clinical success of ^{177}Lu-based radiopharmaceuticals followed by clinical trials of ^{161}Tb, has stimulated interest in the usage of alternative radiolanthanides in nuclear medicine. Lanthanides separation is not only critical for nuclear medicine applications but also plays an important role in industrial processes, nuclear safeguards, and environmental sciences. However, their separation remains challenging particularly for neighboring lanthanides, which exhibit very similar chemical properties, making efficient radionuclide isolation difficult.

Cation exchange chromatography remains the most effective approach for lanthanide separations and strongly depends on the choice of complexing agent.[2] While α-hydroxyisobutyric acid (α-HIBA) has been the benchmark eluent since its introduction by Choppin and co-workers in 1956, later studies by Nash and co-workers identified ligand rigidity as a critical factor influencing selectivity.[3,4] In particular, tetrahydrofuran-2,3,4,5-tetracarboxylic acid (THFTCA) and nitrilotriacetic acid (NTA) were reported as promising alternatives to α-HIBA for the separation of lighter and heavier lanthanides, respectively,[5] potentially enabling the development of improved chemical separation systems for radiolanthanides. However, THFTCA complex stability has only been investigated for a limited number of lanthanides and there are no comprehensive studies reporting the potential of THFTCA and NTA for the separation of neighboring lanthanides.

This project aims to systematically evaluate lanthanide complexation across the full series and assess the impact of ligand structure on chromatographic separation efficiency. A Design of Experiments (DoE) approach will be implemented to optimize separation parameters, identify interactions between experimental variables, and establish improved conditions for neighboring lanthanide separations relevant to radiopharmaceutical production.

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Structural and synthetic insights on alkali-metal amido nickelates

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Nickel amide complexes pose to be of great interest in modern organometallic chemistry due to their intermediacy inn homogeneous catalysis eg. Buchwald-Hartwig amination [1]. Despite being proposed as catalytic intermediates, onnly a few ezamples of isolated Ni(II/I) complexes featuring a pendant amide functionality have been reported [2], while Ni(0)-amido complexes have remained elusive to date. Recent work from our group has shown that s-block metal nnickelates cann bbe accessed by cocomplexation of Ni(0) precursors with the relevant organnolithium or Grignnard reagents [3]. Having this background, we wonndered if a similar approach could be employed to access a new family of alkalli-metal nickelates featuring amide ligands.

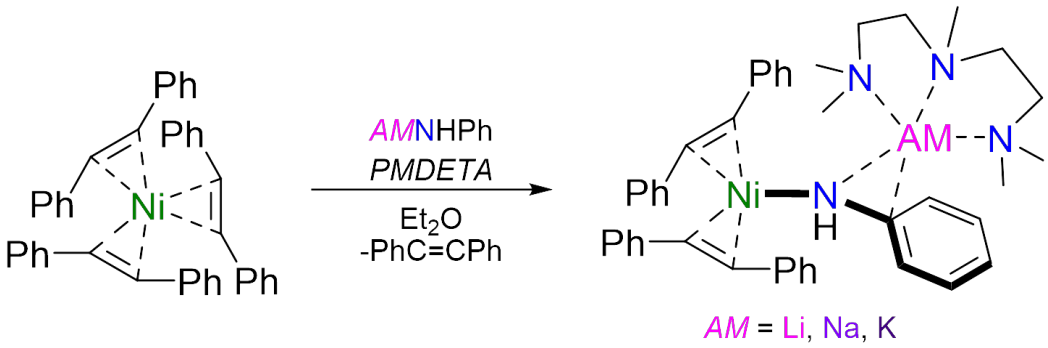


Figure 1: Schematic respresentation of the synthesis of the alkali-metal amido nickelate complexes.

In this work, we report our finndings assessing the systematic reactivity of the bench-stable Ni(0) precursor Ni(stilbene)$_3$ [4] with a range of alkali-metal amides to acces a new family of alkali-metal amido ninckelates (See Figure 1). Combinig X-Ray crystallographic analysis with NMR spectroscopic studies we provide insights into their constitutionn in solution and in solid state. Experimental studies are combinned with theoretical calculationn to advance the understanding of the bonding present in these complexes. Their reactivity towards a range of organic electrophiles under both stoichiometric and catalytic regimes will also be discussed.

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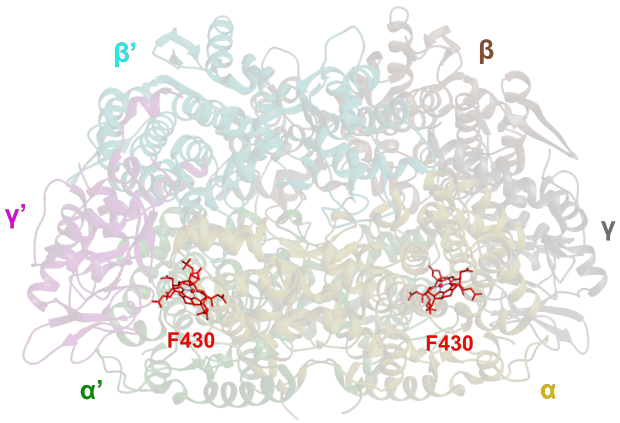
F430-Inspired Nickel Chemistry: A Platform for Radical C–H Bond Activation

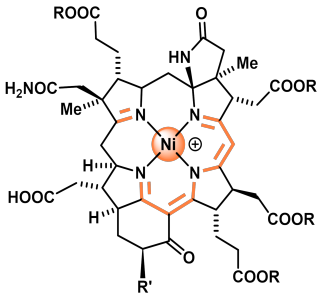
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Cofactor F430-dependent methyl-coenzyme M reductase (MCR) catalyses anaerobic oxidation of methane (AOM)[1]. In this process, methane and the heterodisulfide of coenzyme M and coenzyme B are converted in an overall endergonic reaction to methyl-coenzyme M and coenzyme B. The proposed mechanism suggests that it is a Ni(I)-induced transient thiyl radical pathway. Our group develops semi-artificial Ni-complexes derived from vitamin B_{12} as functional models of F430[2-3]. Herein, I report the development of a novel low-valent Ni complex that serves as a functional model of F430 for mechanistic studies of AOM.

(a) Structures of MCR, cofactor F430, hydrophobic analog F430M

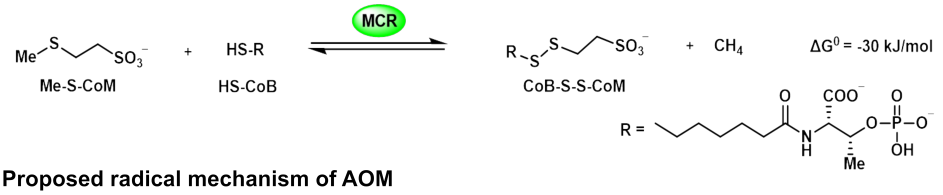




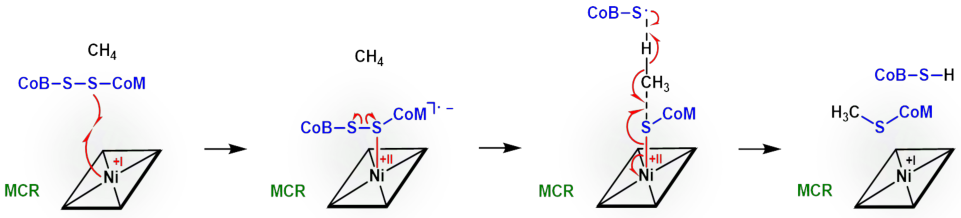
Cofactor F430 : R = H
R' = H or S-Me

Cofactor F430M : R = Me
R' = H

(b) Reaction catalyzed by MCR in methanogenic and methanotrophic archaea



(c) Proposed radical mechanism of AOM



[1] Scheller, S.; Goenrich, M.; Boecher, R.; Thauer, R. K.; Jaun, B.; *Nature* **2010**, *465* (7298), 606–608.

[2] Brenig, C.; Mosberger, L.; Blacque, O.; Kissner, R.; Zelder, F.; *Chem Commun (Camb)* **2021**, *57* (59), 7260–7263.

[3] Amini, S.; Oppelt, K.; Blacque, O.; Agrachev, M.; Jeschke, G.; Zelder, F.; *Chem Sci* **2025**, *16*, 4290-4294.