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Synthesis and Applications of Donor Flexible Thioamide Ligands

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Pyridinium amidates (PYAs) are nitrogen-based, donor-flexible ligands characterized by the ability to adapt to diverse electronic environments by displaying both neutral (L-type) and anionic (X-type) metal bonding contributions.¹ PYA complexes have exhibited exceptional catalytic performance in transition metal-catalyzed reactions, including transfer hydrogenation,² alcohol oxidation,³ ketone arylation,⁴ and water oxidation.⁵ Here, we expanded this family of donor-flexible ligands to include thioamides, which we consider advantageous due to the combination of hard and soft donor atoms, offering a diverse range of coordination modes and electronic properties for a broad range of metals. We will present the first pyridinium thioamidate (PYT) complex synthesis and the specific properties induced by the PYT using spectroscopy, cyclic voltammetry, and X-ray diffraction (XRD), offering a detailed comparison to analogous PYA systems. Our results indicate that PYTs serve as robust ligands that exhibit strong donor properties and show potential for application in transition-metal-catalyzed processes.

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Wide variability in the kinetic and thermodynamic stability of Pd₆L_x-type coordination cages

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Several novel and reported octahedral [Pd₆L₁₂]¹²⁺ and [Pd₆L₈]¹²⁺-type coordination cages were synthesized (Figure 1a). Both, their thermodynamic and kinetic stability were investigated by subjecting cage solutions to different concentrations of pyridine in DMSO or acetonitrile. The cage degradation was monitored by ¹H NMR. Thermodynamic stability was quantified using Dpy₅₀ values, the number of equivalents of pyridine at which 50 % of the cages are remain intact at equilibrium. For kinetic stability, the half-lives (*t*_{1/2}) were determined for various pyridine concentrations. The thermodynamic stability of the cages varies by nearly two orders of magnitude and the kinetic stability over four orders of magnitude (Figure 1b). The stability of the cages was primarily governed by the nature of the donor group, topicity playing a subordinate role. Additionally, we show that kinetically trapped imidazole-based cages can be enriched by precipitation and crystallized. Notably, we report for the first time the crystal structure of a [Pd₈L₁₆]¹⁶⁺-type cage.

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Tailoring Sodium Ferrate Complexes to promote Arene MetalationsJ. Kuziola¹, E. Hevia^{1*}¹Department of Chemistry, Biochemistry and Pharmaceutical Sciences, University of Bern

Deprotonative metalation constitutes one of the most utilized and important chemical reactions, facilitating the functionalization of molecules and the generation of novel reactive species.^{1,2} Traditionally these reactions are performed with monometallic organolithium or lithium amides, which are highly activated due to the large polarity of their Li-N or Li-C bonds.³ However, their high reactivity imposes challenges, which 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 challenging due to the lack of acidity based on the absence of functional groups.

Herein, we report the deprotonative mono- and multi-metalation of highly challenging substrates mediated by bimetallic cooperativity. The combination of alkali metal sodium and the earth abundant iron in a bimetallic ate system allows a unique ability to promote direct Fe-H exchange on non-activated arenes at ambient conditions. 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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The supramolecular chemistry of gold(I) cyclic trinuclear complexes: from nano onions to extended networks based on B-N linkages

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Coinage-metal-based cyclic trinuclear complexes (CTCs)[1] are a class of trimeric structures with the general formula M_3L_3 , where M = Cu(I), Ag(I), or Au(I). Gold(I) CTCs are especially interesting due to their tunable π -acidity/basicity,[2] their ability to form strong intermolecular aurophilic interactions that drive self-assembly[3], and their capacity to form excimer/excplex species and engage in diverse host-guest interactions.

While studies have predominantly focused on the self-assembly of gold(I) CTCs via columnar stacking through metallophilic interactions, their behavior in aqueous environments, relevant for soft-matter applications, and their incorporation into extended architectures via dynamic, reversible linkages such as B–N bonds remain largely unexplored. Embedding gold(I) CTCs into supramolecular frameworks opens new possibilities for the development of functional materials with unique and versatile properties.

We are investigating the supramolecular potential of gold(I) CTCs in two complementary directions. Firstly, the self-assembly of an amphiphilic $Au_3(\text{pyrazolate})_3$ complex in water leads to the formation of "nano onions" (Figure 1A).[4] We have investigated the influence of the metal center and of the position and number of the amphiphilic side chains on the self-assembly. The nanostructures were characterized using cryo- and transmission electron microscopy, dynamic light scattering, and energy-dispersive X-ray spectroscopy.

In a parallel approach, we employed pyridine-functionalized $Au_3(\text{pyrazolate})_3$ complexes as modular building blocks for the formation of coordination polymers with boronic esters via B–N dative bonds. These interactions yield 1D and 2D porous crystalline networks, with channels and cavities visible from their single-crystal packing (Figure 1B). These are the first examples of B–N-based supramolecular structures incorporating gold(I) CTCs, demonstrating the compatibility of metallophilic and dative interactions and offering new directions for the application of these complexes in supramolecular chemistry.

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Polyoxometalate-Loaded Carboxymethyl Chitosan Nanoparticles with Anticancer Activity

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Polyoxometalates (POMs) have emerged over the last half a century as promising biomedical agents ([1], [2], [3]), due to their ability to interact with biomolecules and the tunability of their properties ([1], [2], [4], [5], [6]) In this study, a small series of polyoxometalates and carboxymethyl chitosan nanoparticles are explored for their anticancer activity through extended viability assays, in which the cell viability is investigated for one or two days post 24 h of treatment. Cytotoxicity based on tungsten nuclearity and structure-type is investigated. Among the tested species, $[\text{NaP}_5\text{W}_{30}\text{O}_{110}]^{14-}$ exhibited significantly higher cytotoxicity towards the PC-3 prostate cancer cells, with an IC_{50} value ca. 5 times lower (per mole of tungsten) than smaller tungstates ($[\text{WO}_4]^{2-}$, $[\text{PW}_9\text{O}_{34}]^{9-}$, and $[\text{PW}_{12}\text{O}_{40}]^{3-}$). $[\text{Co}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2]^{10-}$ showed generally reduced cytotoxicity, suggesting that the heteroatom influences the activity.

Encapsulation of POMs in 100-250 nm carboxymethyl chitosan nanoparticles ([7], [8]), characterized by cryo-TEM, DLS, and other spectroscopic techniques, typically enhances cytotoxicity compared to the pristine POM. Interestingly, a simple CMC/POM mixture was also found to enhance the activity. Additionally, a CMC- $[\text{Co}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2]^{10-}$ nanoparticle formulation showed selective toxicity towards HeLa cervical cancer cells over non-malignant MRC-5 cells in the extended viability assay. These findings highlight the potential of POM/CMC nanosystems for targeted anticancer therapies.

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Electronic structure distortions in chromium chelates impair redox kinetics in flow batteries

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Aminopolycarboxylate chelates are emerging as a promising class of electrolyte materials for aqueous redox flow batteries, offering tunable redox potentials, solubility, and pH stability through careful selection of ligands and transition metal ions. Despite their potential, the impact of molecular structure modifications on the electronic and electrochemical properties of these chelates remains underexplored. Here, we examine how introducing a hydroxyl group, often employed to enhance solubility, on the backbone of the reference chelate CrPDTA significantly changes the thermodynamics and kinetics of its redox process. We correlate changes in molecular and electronic structures with different electrochemical responses resulting from the hydroxyl addition and show that the introduction of this functional group leads to a distortion in the octahedral coordination of chromium. This distortion leads to increased anisotropy in spin density, weaker metal–ligand orbital overlap, and a non-integral change in chromium oxidation state, collectively resulting in significantly slower electron transfer kinetics. Our findings underscore the importance of maintaining a stable hexacoordinate geometry across operational pH ranges and caution against ligand modifications that compromise the octahedral structure. These insights inform future design strategies for high-performance APC-based negative electrolytes in redox flow batteries.

Jonathan R. Thurston, Keith P. White, Max Kudisch, Luis Kitsu Iglesias, Julia Lorenzetti, Francesco Bernasconi, Michael F. Toney, Michael P. Marshak, David Reber, *Batteries & Supercaps*, **2025**, e202500250

Exploiting Synergic Reactivities of S-Block Metal Nickelates for Bimetallic CatalysisE. Hevia¹

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Heterobimetallic nickelates derived from Ni(0)-olefin complexes and polar organometallics were widely studied during the spawn of low-valent organonickel chemistry but remained dormant in the literature for several decades.¹ We have recently demonstrated that nickelates are key intermediates in the Ni-catalysed cross-coupling of aryl ethers, prompting a renewed experimental and theoretical interest into these unique heterobimetallic complexes.²

In this talk, the synthesis and structures of homoleptic s-block metal nickelates which can be readily accessed from Ni(0) olefin complexes and a variety of s-block metal organometallics will be discussed.³ Structural and Mechanistic insights and applications of these nickelates in catalytic cross-coupling reactions and C-C bond cleavage will also be discussed.^{4,5}

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Catalytic and stoichiometric stepwise conversion of side-on bound dinitrogen to ammonia mediated by a uranium complex

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Catalytic conversion of dinitrogen (N₂) to ammonia (NH₃) with side-on bound molecular complexes and associated mechanistic studies of their stepwise reduction are relevant to gaining a better understanding of the mechanism of both the industrial (Haber-Bosch) and the biological (nitrogenase) processes, as molecular catalytic N₂ to NH₃ conversion currently exclusively involves reduction and protonation of terminal or bridging end-on bound metal-N₂ complexes. In that regard, low-valent multimetallic complexes of uranium are of great interest due to their ability to bind and transform chemically inert small molecules such as dinitrogen^[1a], however, advanced synthetic techniques required to access and to stabilise these species renders their isolation challenging. Recently, we reported a rare triply reduced N₂³⁻ moiety reported by stabilisation in a diuranium aryloxide complex, which upon further reduction results in dinitrogen cleavage and gives the U₄N₄ cubane and the U₆N₆ edge-shared cubane clusters – unprecedented high nitrogen-content species and molecular models for the binary uranium nitride UN_x that produce quantitative ammonia upon protonation with acid.^[1b]

More recently, here, using a uranium triamidoamine complex [$\{U^{IV}(\text{Tren}^{\text{DMBS}})\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-N}_2)$] (Tren^{DMBS} = {N(CH₂CH₂NSiMe₂^tBu)₃}³⁻), catalytic N₂ to NH₃ conversion involving side-on bound N₂ binding was identified for the first time.^[2] Stoichiometric reactions reveal stepwise reduction of N₂ from free-N₂ to bridging side-on bound forms and subsequently to bridging nitrides, uniquely accessing four different states of side-on bound N₂ for the same molecular system. This reveals the roles of N₂, N₂²⁻, N₂³⁻, N₂⁴⁻, and N³⁻ in the catalytic conversion of N₂ to NH₃ when involving side-on bridging N₂. The recognition that side-on bound N₂ can be catalytically activated and converted into NH₃ through polymetallic cooperativity provides conceptual homogeneous-heterogeneous links, to e.g. Haber-Bosch processes, and offers new vistas for the elaboration of molecular catalytic transformations involving N₂ and likely other small molecules.

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A Gold(III)-Azide Platform for Nitrene Transfer and C–H Functionalization

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The development of transition metal complexes capable of stabilizing high-energy intermediates is central to advancing selective group-transfer reactions. Traditional gold nitrene transfer involves substrate activation and formation of α -imino gold carbenes as key intermediates, with discrete gold-nitrene species remaining elusive.^[1-3]

Here, we report a structurally characterized Au(III) complex supported by a tridentate (N[^]C[^]C) ligand and bearing an azido moiety, which serves as a direct precursor to a gold-bound nitrene. Upon photochemical activation,^[4-6] the azide undergoes dinitrogen extrusion to generate a reactive Au(III)-nitrene species that engages in C-H insertion into aldehydes, yielding isolable Au(III)-amido intermediates. These complexes represent the first examples of direct nitrene transfer to aldehydes with gold(III). Furthermore, catalytic amidation is achieved under mild conditions, with mechanistic and kinetic studies providing strong support for the proposed pathway. Beyond C-H amidation, the azido complex facilitates nitrene transfer to phosphines and displays additional reactivity, including C-H metalation and click reactions, highlighting its modular and substrate-dependent versatility.

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Boron-to-Gold Transmetalation: A Unifying Platform for Gold(III) Cyclometalation

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Despite their widespread application in catalysis, material science and biomedical research,¹ the development of gold(III) complexes remains limited by challenges associated with their synthesis. The use of bidentate and tridentate ligands is crucial to prevent the facile reduction to gold(I) or decomposition to elemental gold(0). However, most of the existing protocols to access both, mono and bis-cycloaurated complexes rely on harsh conditions and/or require the use of toxic reagents (e.g. Hg or Sn).² On the other hand, organoborane compounds have been efficiently used in stoichiometric and catalytic transmetalation reactions to gold(III),³ making them an appealing class of functional groups to direct the cyclometalation step.

In this work, we have developed a novel and environmentally-friendly approach to access gold(III) complexes via boron-mediated transmetalation.⁴ A late-stage functionalization strategy allows the incorporation of boronic ester groups onto a wide array of (N[^]C) and (N[^]C[^]C) ligands. The X-ray diffraction analysis of the *B(OR)*₂-functionalized ligands reveals the presence of a B-N dative bond, crucial in stabilizing the substrates while promoting the transmetalation. The desired transformation could be achieved under remarkably mild conditions with a broad functional group tolerance, affording mono- and bis-cyclometalated gold(III) complexes in moderate to very good yields. Furthermore, the expansion of this method to the synthesis of (C[^]N[^]C)Au(III) complexes has been successfully achieved.

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Noncovalent Immobilization of Open-Shell Organometallic Complexes on Carbon Nanotubes

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The immobilization of open-shell transition metal complexes bearing unpaired electrons on carbon nanomaterials holds promise for a range of applications across spintronics, catalysis, and chemical sensing.^[1] Such hybrid systems combine the synthetic tunability of molecular complexes with the favorable optoelectronic properties of carbon-based nanostructures. However, existing approaches often disrupt either the structural integrity of the complex or the desirable properties of the carbon material. This challenge is exacerbated for complexes containing unpaired electrons, whose extreme sensitivity to ambient conditions typically limits their practical use.^[2-4] New approaches are therefore needed to both identify open-shell metal complexes exhibiting environmental stability and efficiently heterogenize them on carbon nanomaterials.

Herein, we present the non-covalent functionalization of carbon nanotubes with open-shell transition metal complexes.^[5] The complexes feature primarily ligand-centered radicals and are air- and moisture-stable, allowing for spectroscopic and electrochemical characterization under ambient conditions. Comprehensive solid-state characterization confirmed the structural integrity of the complex in the composite, with no disruption to the carbon nanotube framework and retention of its favorable optoelectronic properties. Electrochemical studies established that the material maintains stability over prolonged redox cycling, reversibly accessing three distinct redox states. This property was leveraged in preliminary electrochemical sensing studies of cyanide anions.^[6] Taken together, these results establish a modular sensing platform integrating environmentally stable open-shell complexes and conductive carbon supports.

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Structure and Bonding of Solvent-Free Neopentyl Sodium and its Applications for the Metalation of non-Activated Substrates

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From as far back as the 1940s, alkyl sodium reagents have been examined for their powerful basicity, with the ability to deprotonate non-activated aromatic and vinylic C-H bonds. Pioneering work by the likes of Morton and Finnegan demonstrated how pentyl sodium could be synthesised in situ from pentyl chloride and sodium metal to react with alkyl substituted benzene derivatives and various olefins to afford organosodium intermediates which could subsequently be trapped with simple electrophilic quenches.^[1] These studies however often required very long reaction times due to the very poor solubility of the sodiated species and the nature of the organosodium intermediates found in these complex mixtures remained unknown. With an increase in understanding of organolithium reagents as powerful bases these organosodiums were left behind as mere curiosities.

Our group has recently been highlighting the potential of alkyl sodium reagents. We have shown how the alkyl sodium reagent $\text{NaCH}_2\text{SiMe}_3$ can have its solubility and thus reactivity tuned with the addition of Lewis donors such as PMDETA ($\text{N,N,N',N'',N'''}\text{-pentamethyldiethylenetriamine}$), forming a hydrocarbon soluble alkyl sodium reagent used in benzylic metalations.^{[2][3]} In this communication, we report on the synthesis and characterisation in the solid and solution states of a highly basic alkyl sodium complex, neopentyl sodium, combined with in-depth bonding analysis. The enhanced solubility of this reagent adds to its ability to metalate stoichiometric quantities of nonactivated substrates such as benzene or simple cyclic olefins with the addition of the Lewis donor PMDETA, an electrophilic quench was subsequently carried out to demonstrate the high efficiency of the sodiations carried out under these conditions. The sodiated intermediates could be isolated and characterised using a combination of X-ray crystallography and ^1H NMR DOSY (Diffusion Ordered Spectroscopy), revealing some rare examples of aryl- and vinyl sodium complexes, further expanding our understanding on the constitution of these reaction intermediates, advancing our understanding of how these systems operate in solution.

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Evidence of Transient Iron Carbide Species in Apparent σ -Bond Metathesis ReactionB. Berger¹, C. Copéret^{1*}¹D-CHAB, ETH Zürich, Vladimir-Prelog-Weg 2/10, Zürich, Switzerland

Terminal molecular Iron carbides remain unknown in the literature, despite their possible involvement as transient intermediates in the corresponding Fischer-Tropsch process.^[1] A promising strategy to prepare and probe the elusive reactivity of such species, is to use carbon atom transfer (CAT) reagents as ligands for iron complexes.^{[2],[3]} Herein, we report the synthesis and isolation of a novel iron complex FeBAC□Mes□ **1**, prepared from the reaction of Fe□Mes□ with bis(diisopropylamino)cyclopropenylidene (BAC).^[4] Upon thermal (393 K) and photochemical (365 nm) activation, complex **1** reorganizes into a metallacyclobutadiene (MCBD) complex **2** as evidenced by single crystal X-Ray diffraction. Drawing parallels with analogous molybdenum-based MCBD complexes,^[5] we propose that this rearrangement probably proceeds via an initial carbon atom transfer forming a transient iron carbido intermediate arising from the BAC ligand. Although the putative iron carbide intermediate could not be isolated so far —likely due to its high reactivity—, the formation of this iron-based MCBD complex notably involves the activation and formation of carbon-carbon σ -bonds.^[6]

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Toward predicting silver ion binding in proteins

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Silver ions and nanoparticles are known to possess antimicrobial properties.^[1] Yet the Gram-negative bacteria *Salmonella Typhimurium* “learned” how to tolerate larger amounts of silver by expressing a silver efflux system Sil, encoded on a transferable plasmid pMG101.^[2] This silver efflux system is quite similar to the copper efflux system Cus, except for one specific protein, SilE, which is proposed to act like a silver sponge.^[2,3] SilE is a small periplasmic protein composed of 143 amino acids and containing many histidine (His, H) and methionine (Met, M) residues, organized mainly in tetrapeptide (and one tripeptide) entities, which could be expected to bind silver(I) ions.^[4] In previous model studies in our group, Chabert *et al.* highlighted that each HX_nM (n=1,2) peptide was able to coordinate to one silver(I) ion.^[4] Furthermore, we demonstrated that the nature of the amino acid “X” influences the association constant log(K_{ass}).^[4,5]

Based on these observations and in order to gain a more basic understanding of silver ion binding in peptides and proteins, the HQAMAEAHRRM peptide (B2) and its mutant forms were synthesized and studied for their interactions with Ag⁺, revealing differences and similarities in coordination and folding. My research aims are to determine what initiates the α -helix and drives cooperative Ag⁺ binding. Some first trends will be presented.

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Nickel bidentate N-N-PYA complexes for cross electrophile couplingsL. Burri¹, M. Albrecht^{2*}

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Cross electrophile coupling (XEC) is becoming an increasingly popular method to form biaryl products. The use of two electrophiles instead of the conventional use of an organometallic reagent considerably widens the pool of available coupling partners that furthermore do not suffer from stability issues.^{1,2} Current XEC catalysts typically are based on nickel complexes. Screening of different ligand variations revealed that (N-N') ligands such as bipyridine variations impart highest activity.³

Our group recently used (N-N') ligands with the pyridinium amidate (PYA) motive with great success for palladium α -arylation of ketones.⁴ PYA ligands are unique in the sense that they offer donor flexibility, which is able to impact catalysis. In addition, PYA ligands are also easy to functionalize and therefore provide an interesting target to expand the range of ligands for XEC catalyst development. We will present a series of new nickel(II) (N-N')-PYA complexes and will discuss their ability to catalyze cross electrophile coupling of aryl iodides with aryl bromide.

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Dark resonance energy transfer in palladium-based rotaxanesD. W. Chen¹, K. Severin^{1*}

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Förster resonance energy transfer (FRET) is widely applied in imaging, and has been studied in mechanically interlocked systems. Dark resonance energy transfer (DRET) is a recently developed strategy that uses non-emissive FRET donors to achieve large Stokes shifts and low background fluorescence.¹

A palladium-based coordination cage was prepared by self-assembly, and was found to encapsulate several squaraine dyes with micromolar affinity. Bulky substituents on the dye prevent unthreading at room temperature, making the assembly mechanically locked as a rotaxane. The cage is non-emissive, but can act as a dark donor and transfer energy to the squaraine via FRET, enabling a 390 nm Stokes shift.

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Structure and Catalytic Properties of Homo- and Heterometallic Iron(II)-based Di(2-pyridyl)ketone Oxoclusters

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Electrochemical water splitting is essential for reducing our dependence on fossil fuels¹ through green hydrogen production and requires designing new, low-cost 3d transition metal-based catalysts for the sluggish oxygen evolution reaction (OER)^{2,3}. We report on the synthesis, characterization, and OER performance of new types of homo- and heterometallic iron(II)-based di(2-pyridyl)ketone oxoclusters, **1**-[Fe₄(dpy-C{OH}O)₄(OAc)₃(H₂O)]ClO₄ and **2**-[Fe₂Ni₂(dpy-C{OH}O)₄(OAc)₃]ClO₄ (dpy = di(2-pyridyl)diol), referred to as **1**-{Fe₄O₄} and **2**-{Fe₂Ni₂O₄}⁴. The heterometallic oxocluster is the first sought-after molecular cut-out of the key active {H₂O-Fe₂Ni₂(OR)₂-OH₂} motif, bridging molecular and heterogeneous OER catalysts as a model to understand the key synergisms in NiFe oxide-based materials. The precise positions of Fe(II) and Ni(II) cations within the **2**-{Fe₂Ni₂O₄} oxocluster, along with the detailed structural and electronic features, were elucidated with a variety of methods, including extended advanced X-ray absorption spectroscopy and total neutron scattering techniques, accompanied by time-dependent density functional theory (TD-DFT) calculations. (Spectro)electrochemical analyses showed that **2**-{Fe₂Ni₂O₄} exhibits synergisms between Fe(II) and Ni(II) centers, tuning the redox potentials of both metals and the molecular stability of the mixed-valent {(Fe^{III})₂Ni₂O₄} pre-catalyst species. **2**-{Fe₂Ni₂O₄} displays a maximum j_{cat} of 1.75 mA/cm² for the OER and a Faradaic efficiency of 84.8% under turnover conditions. Although the oxocluster experienced notable degradation during OER, significant metal (oxy)hydroxide formation could be excluded. **2**-{Fe₂Ni₂O₄} is introduced as a new molecular platform for in-depth studies of NiFe synergism, along with ligand engineering or polymer matrix strategies.

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Au(III)-Catalysed Amidation of Aldehydes via Nitrene Transfer

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The development of transition metal complexes capable of stabilizing high-energy intermediates is central to advancing selective group-transfer reactions. Traditional gold nitrene transfer involves substrate activation and formation of α -imino gold carbenes as key intermediates, with discrete gold-nitrene species remaining elusive.^[1-3]

Here, we report a structurally characterized Au(III) complex supported by a tridentate (N[^]C[^]C) ligand and bearing an azido moiety, which serves as a direct precursor to a gold-bound nitrene. Upon photochemical activation,^[4-6] the azide undergoes dinitrogen extrusion to generate a reactive Au(III)-nitrene species that engages in C-H insertion into aldehydes, yielding isolable Au(III)-amido intermediates. These complexes represent the first examples of direct nitrene transfer to aldehydes with gold(III). Furthermore, catalytic amidation is achieved under mild conditions, with mechanistic and kinetic studies providing strong support for the proposed pathway. Beyond C-H amidation, the azido complex facilitates nitrene transfer to phosphines and displays additional reactivity, including C-H metalation and click reactions, highlighting its modular and substrate-dependent versatility.

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NHC Metal Peptide Conjugates for Abiotic Catalysis

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N-heterocyclic carbene (NHC) ligands have fundamentally transformed homogeneous catalysis, with impact in particular on catalysis with first row transition metals and precious platinum group metals. Considering these advances, it is remarkable that only few attempts have been demonstrated to incorporate NHCs into artificial metalloenzymes.^{1–4} We therefore sought to develop non-canonical amino-acids (ncAAs) for site-specific incorporation into a peptide chain. For example, we have demonstrated the introduction of the NHC-like ncAA Hum into a small peptide to produce a minimalistic iridium peptide conjugate for hydrogenation reactions as a miniaturized prototype of an artificial hydrogenase.⁵ Here, we will present our latest advances in developing NHC precursor ncAAs and their scope in binding a diverse set of transition metals for new-to-nature catalysis.

Figure Non-canonical amino-acids with a NHC-like side-chain which can be site-specifically included into a peptide sequence through Solid Phase Peptide Synthesis (SPPS).

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Stronger B-N dative bonds in supramolecular self-assemblyJ. Gome¹, K. Severin^{1*}¹EPFL SB ISIC LCS

Supramolecular self-assembly relies on reversible interactions to allow for error correction and the generation of a single, well-defined architecture. Thus far, much of the work in this field has focussed on metal-ligand coordination bonds or reversible imine bonds to produce such structures. One class of assembly that has been less studied are those formed by dynamic B-N dative bonds.

B-N dative bonds have previously been used to form networks and polymers, usually employing a boronic ester as the Lewis acid^[1]. Here, we use poly-Lewis acidic alkylboranes in a bid to strengthen the B-N bond and stabilising the architectures. It is also hoped that a stronger B-N bond will favour the formation of discrete architectures of which there are relatively few examples.

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From N2-methylated Triazoles to β -diketiminato-like Complexes: A Route via Selective Triazolium Ring Cleavage

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1,2,3-substituted triazoliums are a prominent class of ligand precursor in carbene chemistry, serving as versatile NHC precursors and being applied to a myriad of catalytic reactions.¹ Typically, methylation of 1,2,3-triazoles proceeds exclusively at the N3-position.

Here we demonstrate for the first time that it is possible to selectively methylate 1,2,3-triazoles at the N2 position, in contrast to this central dogma of triazolium chemistry. Even more striking, our investigations reveal “hidden” reactivity in the corresponding 1,2,4-triazolium. Metalation with various metal precursors leads to cyclic N–N bond cleavage and complexes that are analogous in structure to common β -diketiminates.^{2,3} This unique pathway broadens the synthetic scope of triazolium chemistry and opens opportunities for novel metal complexes and their catalytic transformations.

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Accessing one-pot Synthesis of Dihydropyridine Derivatives through a Nucleophilic Organosodium Compound

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The availability and high reactivity of organolithium compounds combined with the great solubility in hydrocarbon solvents enabled their widespread use in organic synthesis.¹ Trying to find more sustainable alternatives, the much more earth-abundant and highly reactive sodium congeners have recently been found to be a powerful alternative.² Yet, the advantages of those compounds are undermined by their low solubility in hydrocarbon solvents and the challenge in handling. Previous work in our group has shown that N-donor PMDETA can be used to solubilize organosodium compounds, which increases their reactivity and opens new roads for C-H formation or deuteration reactions.³⁻⁵

Advancing the work in this field, we report the use of organosodium compounds for the formation of C-C bonds through nucleophilic attack on pyridines. This enables the formation of dihydropyridines, which are relevant in biological chemistry or in transfer hydrogenation.⁶⁻⁷ We show how those reactions can be performed in a one-pot process, starting from the in-situ formation of benzyl sodium, followed by the addition of pyridine. Further, we investigate the different reactivities of the benzyl sodium compound by systematically changing pyridine to 3- and 4-picoline, where we show that changing the substrate leads to a change in reactivity. Lastly, we explore how the addition of the boron compound $B(CH_2SiMe_3)_3$ affects the selectivity of the reaction.

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Synthesis and Application of Carborane Derivatives in RadiochemistryE. Liu^{1,2}, C. Berton^{1,2*}, J. Holland^{3,4*}¹University of Zurich, ²Department of Chemistry, ³University of Zurich, ⁴Department of Chemistry

Polyhedral boron clusters are fascinating boron-rich compounds featuring icosahedral geometry and delocalization of electron density. These clusters have garnered significant attention due to their exceptional stability, versatile functionalization capabilities, and potential applications in medical science. Supramolecular chemistry offers innovative approaches for developing radiopharmaceuticals through controlled host-guest interactions. We aim to design and synthesize a novel host-guest complex incorporating a polyhedral boron cluster as a specialized guest molecule.

In this study, we explore the synthesis, characterization of ⁶⁸Ga-DFO carborane and explore its host-guest interactions with cucurbit[7]uril (CB[7]). The molecular recognition process was systematically examined through comprehensive NMR spectroscopy and radiolabeling studies. The radiosynthesis of the ⁶⁸Ga-DFO complex was successfully achieved under mild conditions. Notably, we report the unprecedented observation of CB[7] dissolution in organic solvents. Functionalization of CB[7] opens new avenues for expanding the scope of supramolecular chemistry involving CB[7]-carborane systems. Our findings provide valuable insights into the development of novel radiopharmaceutical platforms based on host-guest chemistry.

Probing the Metal-Binding Site of Hydrolytic Metalloenzymes through Genetic Code Expansion

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The advent of genetic code expansion (GCE) has enabled researchers to go beyond the 20 canonical amino acids by incorporating diverse non-canonical amino acids (ncAAs). This allowed for the introduction of non-biological mechanisms^{1,2}, enhancing catalytic activities³, and creation of novel artificial metalloenzymes.⁴ Notably, structural analogs of histidine have been employed to replace histidine ligands in copper and iron-dependent proteins, augmenting their electronic properties.^{5,6} These works demonstrated the power of ncAAs to directly engineer the primary coordination sphere of metalloenzymes, — a challenging task due to the limitations of canonical metal-binding residues. Inspired by this approach, we sought to leverage ncAA-based mutagenesis to probe the metal-binding sites of hydrolytic metalloenzymes, which harness transition-metal cofactors (e.g. Zn^{2+} , Co^{2+}) as Lewis acids to lower the pK_a of metal-bound water, facilitating the generation of a catalytic hydroxide nucleophile.⁷ Stabilization of the metal cofactor and electronic charge in these complexes is crucial to preserve the enzyme's catalytic activity, as evidenced by forcing a negative charge accumulation on a histidine side chain in a Zn^{2+} -dependent carbonic anhydrase.⁸

Prompted by this finding, we theorized that the polarization of the N-H bond on the non-coordinating nitrogen of the imidazole moiety in a metal-coordinating histidine could destabilize the coordination environment. To probe this hypothesis, we replaced a N^π -coordinating histidine with a N^π -methylated histidine analog within the primary coordination sphere of a metal-dependent phosphotriesterase from *P. diminuta*. Upon this substitution, we compared the kinetic behavior of the N^π -methylated histidine variants with the wild-type enzymes to elucidate the effects of the N^π -methylated histidine coordination. Through these assays, we observed a universal decrease in pK_a for all of the N^π -methylated histidine-containing variants. Additionally, we observed catalytic improvement at low and neutral pH values. A comparison of the impacts with highly homologous Zn- and Co-dependent variants are described for substrates with different rate-limiting step(s).

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Investigations of the Formation of Cobalt-Based Metal-Oxo CubanesW. R. Marks¹, K. F. Würzer^{1*}, G. R. Patzke^{1*}¹Universität Zürich, Chemistry

Coordination complexes are ubiquitous in inorganic chemistry for the study of reaction mechanisms, magnetism, and as models for larger biomolecules. The study of these complexes is often solely focused on the application of the formed complex, while formation and speciation are merely observed. In this work, a family of metal-oxo cuboids which demonstrate unusual polymorphic ligand coordination are reported. These cobalt-based cubane complexes (of the general formula $\{\text{Co}_4\text{L}_4\}^{4+}$; L = di-2-pyridyl ketone) demonstrate structure control via both coordinating and non-coordinating anions. Elucidating the structure directing role of traditionally non-coordinating anions in the synthesis of these cubane complexes is explored through single-crystal X-ray diffraction, Raman, FT-IR, and paramagnetic NMR. Previously two polymorphs of cobalt-based cubanes were reported by our group, accessible through the application of perchlorate or nitrate salts in cubane synthesis. This work presents a third polymorph of cubane arising from expanded synthetic parameter screening. The goal of this project is to demonstrate that non-coordinating anions play a nontrivial role in coordination cluster formation, as well as to study cobalt cubane-cluster formation to better understand the mechanism of their assembly.

Tailoring Na/Zn Bimetallic Combinations for Dihydrogen Activation and Unsaturated Substrate Hydrogenation

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The hydrogenation of unsaturated substrates via molecular hydrogen activation is one of the most extensively utilized chemical reactions.¹ Although H₂ activation is typically induced by precious transition metals, growing societal emphasis on sustainability has driven efforts for alternatives to these often expensive, toxic, and scarce elements.² Recently main group metal systems have shown great promise using s-block metal amides,³ and zinc complexes.⁴ While these studies give high conversions, they often require harsh conditions, i.e. high temperatures, pressures, and long reaction times. Thus, efficient precious metal-free hydrogenation of unsaturated substrates via H₂ activation at ambient conditions would provide a break through in this field.

Herein, we report the synthesis and characterisation of a novel well-defined sodium dihydride zincate species: NaZnH₂(TMP)(TMEDA) (TMEDA= tetramethylethylene diamine), accessed through activation of H₂ by the combination of Zn(TMP)₂ and NaTMP (TMP = 2,2,6,6-tetramethylpiperidine) at ambient pressure and temperature. Both metal species show a synergistic effect for this process, being unable to activate and transfer H₂ efficiently on their own. Our studies have shown that both hydrides are active, as seen through hydrogenation of a model imine substrate at room temperature. These investigations are being extended towards other unsaturated substrates, examining the role of the alkali metal and the amide ligand.

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Potassium Alkoxide Powered Ferraion of Iodoarenes using an Fe(II) Alkyl ComplexM. Misteli¹, N. Jin^{1*}, E. Hevia^{1*}¹Departement für Chemie, Biochemie und Pharmazie, Universität Bern

Metal-halogen exchange reactions are amongst the most widely used and powerful methods for the selective functionalisation of organic molecules. Typically these reactions are performed by highly polar organometallic reagents such as organolithium and Grignard reagents.^[1] On the contrary, organoiron complexes have shown no applications in this type of transformation. Recently our group has explored the reactivity of Fe(II) amide complexes for the regioselective functionalisation of aromatic molecules via direct Fe–H exchange as well as demonstrating the potential of Fe(II) aryl complexes to engage in Fe catalysed C–C cross coupling reactions.^[3–5] Breaking new ground in this area, this presentation highlights the potential organoiron reagent [Fe(CH₂SiMe₃)₂(TMEDA)] (TMEDA = *N,N,N',N'*-tetramethylethylenediamine) with iodoarenes such as 2-iodoanisole (see Figure) to promote direct Fe–I exchange on the addition of potassium *tert*-butoxide. By isolation and characterisation of key reaction intermediates, new mechanistic insights have been accomplished, indicating that bimetallic cooperation between the K and Fe(II) centres is key in order to enable this unique reactivity.

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Functionalised arene ruthenium complexes for photodynamic therapy

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Photodynamic therapy (PDT) is used to treat a variety of diseases and several types of cancer. It requires three elements: a photosensitiser (PS), oxygen, and light. When the PS is exposed to light, it becomes activated from a ground to an excited state. As it returns to the ground state, it releases energy, which is transferred to oxygen to generate reactive oxygen species (ROS), like singlet oxygen and free radicals. These ROS activate an immune response, damage tumour vasculature, and induce tumour cell death.^[1]

However, PDT can be limited by different factors, one of which is hypoxia, a low concentration of oxygen that limits PDT efficiency. Therefore, we designed hybrid PDT agents, composed of arene ruthenium complexes (1, 2 or 4 units) at the periphery of porphyrin-based PS (monopyridyl, dipyrindyl, tetrapyrindyl porphyrins), which are also coordinated to anthracenyl-containing ligands (**L**₁-**L**₄) (see Figure 1). Anthracenyl moiety possesses the ability to trap singlet oxygen ¹O₂ in the form of endoperoxides, and transport oxygen to cancer sites.^[2,3]

Figure 1. Hybrid arene ruthenium PDT agents to treat colon cancer.

The new PDT agents merge the chemotherapeutic action of ruthenium complexes with the possibility of transporting oxygen, and to operate under light to treat cancer. They show cytotoxicity and phototoxicity in the lower nanomolar range under blue, green, and red light, against the human colon cancer cell line HCT116, with the most active compounds being the disubstituted derivatives with IC₅₀ values as low as 3 nM concentrations (blue light, 420 nm, 20 J/cm²).

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Development of an Organic-compatible pH Meter and its Use for Overpotential Determination

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Determination of $-\log a(\text{H}^+)$, or pH, is essential for understanding any proton-coupled electron transfer (PCET) reactions, i.e., those involving transfer of both electrons and protons, as the equilibrium potential of these reactions in a certain given proton environment scales with the pH of such environment as dictated by the Nernst equation. As a result, overpotential applied during constant potential electrolysis could only be determined with knowledge of the pH of the system at which electrocatalysis is being carried out. [1]

While pH determination is relatively easy in protic solvents, in aprotic solvents it is plagued by multiple issues, including but not limited to homoconjugation or other acid-base interaction between species, sensitivity to ionic strength of solution and to protic impurities (e.g. water). An *in-situ* determination of pH is therefore critically needed for better understanding and characterisation of catalytic PCET reactions, e.g. CO₂ reduction. While pH measurements via use of RHE have been proposed, especially in the context of catalytic hydrogen evolution, they either require *a priori* knowledge of the homoconjugation constants [2] or continuous H₂ bubbling [3], which not only poses safety issue but also limits its use for reactions involving gaseous substrates, e.g. CO₂ or NO_x.

We herein report the use of a dynamic Pd-H electrode, generated *operando*, as a proxy for RHE. [4] Furthermore, by referencing to electron-only pseudo-reference, e.g. $\text{Fc}^{+/0}$, and calibrating with a set of buffers with well-defined pH values, an organic pH meter that can also be used in presence of gaseous substrates was constructed. pH of composite electrolytes used in CO₂RR was then re-evaluated, highlighting importance of accurate pH determination in benchmarking catalysts performance.

Scheme 1 Dynamic Pd-H electrode in contact with an aprotic organic solvent

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Salen-derived heterometallic complexes

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Salen is one of the most studied ligands in chemistry, notably for its straightforward synthesis and its ability to coordinate a variety of metal ions.¹ This Schiff base compound has a N₂O₂ chelate site allowing the coordination of one metal ion. Salen is an interesting ligand in that it can be functionalized providing a panoply of new ligand structures, offering numerous sites for metal coordination. In our study, we aim at synthesizing multi-metallic complexes with two or three different metal ions. To achieve this goal, salen-type ligands were designed with different sites of coordination in order to bind multiple metal ions. The combination of different metal ions can provide enhanced chemical and biological properties, broadening their range of applications.² Depending on the functionalization and the nature of the metal ions, the obtained complexes were either used as mixed metal oxides precursors or as fluorimetric and colorimetric sensors. Furthermore, the antibacterial properties of these complexes were tested on *Staphylococcus aureus*, providing insight into the potential enhancement of bioactivity by metal ion combinations. The design of salen-type ligands having distinct sites of coordination able to bind different metal ions are a key aspect of our investigation. The preliminary findings of this study will be presented.

Figure 1. General representation of salen-type ligand.

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Metal- vs Ligand-Bound Hydride Storage on Iridium–PYA ComplexesS. Reuge¹, M. Albrecht^{1*}

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Our group recently reported a highly active catalyst towards formic acid dehydrogenation.¹ The complex bears a O-functionalized pyridinium-amidate (PYA) moiety, which exhibits a unique donor flexibility, known to impart high catalytic activity (Fig. 1a).² Further modifications of this complex enabled us to observe unique reactivity, namely the reversible storage of a hydride on the PYA moiety upon reaction with formate (Fig. 1b).³ Similar to nature's NAD⁺/NADH hydride storage and transfer system, the complex reversibly dearomatizes upon addition of the hydride.⁴

The hydride-bearing complex exhibits remarkable stability in air and moisture, however reacts towards electrophiles such as acids and carbonyl compounds. This property enabled efficient hydrogenation catalysis and deuterium isotope labeling without notable scrambling in the presence of air and moisture.

In this work we will interrogate the reactivity of the Ir-PYA complexes towards different hydride sources in order to establish factors that distinguish hydride storage on the ligand through dearomatization, or on the iridium as classic metal-hydride species. Moreover, stability and reactivity features emerging from the different hydride storage modes will be presented.

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Direct Access to Bridged Ni(I)-Imido Complexes from Amines: Synthetic Pathways and Prospects for Catalytic Nitrene Transfer

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Through the atom-economical transfer of nitrene units, nickel imido complexes enable the transformation of small molecules—including olefins, carbon monoxide, and isocyanides—into valuable nitrogen-containing products such as aziridines, isocyanates, and carbodiimides.¹⁻⁴ The formation of most metal imido systems, however, typically requires pre-activated nitrene precursors, such as organic azides.¹⁻⁶ Their synthesis introduces additional steps, ultimately reducing the overall atom economy. A catalytic approach that generates reactive nitrene equivalents directly from amines would address this limitation by streamlining synthesis, minimizing additional transformations, and enabling late-stage functionalization. Despite this promise, direct access to reactive metal-imido species from amines remains rare, particularly for nickel.^{7,8} Here, we describe the development of two synthetic routes to bridged Ni(I)-imido complexes derived directly from anilines. These complexes serve as a platform to investigate reactivity with various acceptor molecules and explore the potential for catalytic C–N bond formation using unactivated nitrogen sources. Additionally, we show that applying these synthetic methods to arylphosphanes leads to divergent reactivity, yielding three distinct organophosphorus-containing nickel complexes.

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Synthesis of POM - Cubane Hybrids and their catalytic performanceA. Schultz¹, G. Patzke^{2*}¹Aaron A. Schultz, ²Greta R. Patzke

Polyoxometalates (POMs) have a wide variety of applications due to their structural diversity, tunability and redox stability and therefore are of high interest in many different research areas. To improve the desired properties of the POMs, hybrid materials with covalent and non-covalent bonds can be synthesized. Herein, the formation of POM hybrids derived from a combination of POMs with different metal oxo-clusters are described. Mainly the negatively charged full-Keggin type POM {Co(II)W₁₂O₄₀}, with {Na}, {K} and {NH₄} as counterions, was used as a starting material and combined with the positively charged {Co(II)₄O₄} cubane [Co(II)₄(dpy{OH}O)₄(OAc)₂(H₂O)₂](BF₄)₂ (Co₄O₄-dpk). Different counterions for the cubane formation were tested in combination with the POM and influenced the crystallization process. The cubane was replaced with the mononuclear {Co(III)(dpk-OH)₂} complex to investigate the influence of the cubane structure on catalytic properties of the resulting salt. Replacing the starting POM with an unsaturated Keggin type POM {BiW₉O₃₄} was investigated for the same reason. The structures were determined using SC-XRD and PXRD Raman and FT-IR spectroscopy. The redox reactions and stability of the compounds were studied by cyclic voltammetry.

Active Sites in Supported Tungsten Oxide Olefin Metathesis Catalysts Elucidated Through Probe Molecule-Enhanced ^{183}W -NMR Spectroscopy

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Olefin metathesis over supported metal oxides is a cornerstone of large-scale petrochemical processes, most notably in the triolefin process for propene production [1]. Silica-supported tungsten oxide catalysts are favored for their stability but require significantly higher operating temperatures than supported molybdenum or rhenium oxides. This is attributed to larger energetic barriers for forming the requisite metal-alkylidene active sites. The local chemical environment of metal-oxo and dioxo sites in precatalysts is believed to critically affects their ability to form active sites [2,3].

Metal NMR has been shown to be a highly sensitive probe of the local structural environment. However, ^{183}W NMR spectroscopy is highly challenging due to the low gyromagnetic ratio and natural abundance of the nucleus, as well as its large chemical shift range. Especially in the solid state, there are few reported examples, all of which use molecular or cluster samples with high tungsten weight loadings [4].

We show that by adsorbing highly NMR-active phosphine probe molecules to the tungsten sites of metathesis catalysts, we can enhance their ^{183}W NMR signatures through ^{31}P detection. Additionally, the associated passivation of the Lewis acidic sites enables us to employ Dynamic Nuclear Polarization Surface Enhanced Spectroscopy (DNP-SENS). The ^{183}W NMR signatures recorded in this fashion can be combined with DFT calculations to refine structural models of the catalysts, enabling us to characterize their active sites in unprecedented detail.

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An Experimental Evaluation of the Hydricity of Hydrosilanes

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Hydrosilanes are versatile reagents for hydride transfer reactions and key building blocks in silicon polymer chemistry. The ability of these reagents to reduce various functional groups under mild conditions has made their use ubiquitous in organic synthesis [1] as well as in the direct reduction of small molecules such as CO₂ [2].

Despite their widespread use in these reactions, the thermodynamic hydricity (the propensity of the silane to transfer a hydride, H⁻) has so far only been obtained using calculations and experimental values are missing from literature [3]. Here, I will present our efforts to experimentally evaluate the hydricity of hydrosilanes via their cationic silylium (R₃Si⁺) counterparts [4].

Silylium ions have been known and used in the past decades, however their high reactivity has hampered the measurement of basic physical properties such as their reduction potentials [5]. With a careful selection of experimental parameters, we were able to measure such values for three sterically encumbered triarylsilyliums. On the basis of this data, we were able to estimate the hydricity of the corresponding triarylhydrosilanes. In one case, we could confirm the hydricity value using an independent approach via hydride-exchange reactions. Our findings suggest that calculated hydricities are underestimated relative to the experimental values.

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Exploring Iron-Sulfur Clusters in Metallothioneins

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Iron-sulfur cluster proteins are ubiquitously found in all life forms, exhibiting diverse functions as electron carriers, enzymatic catalysts, and gene regulators. Typically, these proteins bind [2Fe-2S], [3Fe-4S], or [4Fe-4S] core units via cysteine side chains, although additional coordination by histidine has also been observed.

Similarly to that, metallothioneins are also a widespread group of proteins with various functions. They play a role in homeostasis of Zn^{II} or Cu^I, detoxification of Cd^{II} or Hg^{II}, and fighting oxidative stress. For plant MTs, the subfamilies MT1-3 share various characteristics, such as a structural motif consisting of two cysteine-rich domains linked by a Cys-free amino acid sequence. Ordered secondary structures in apo-MTs are rarely observed, as the protein conformation is largely dictated by metal coordination, which, similar to iron-sulfur cluster proteins, involves cysteine thiolate ligands.

Until now, research on MTs has predominantly focused on the formation of clusters involving d¹⁰ metal ions such as Zn^{II} or Cd^{II}. Although there are a few reports on metal-sulfur cluster formations, these too have primarily involved cadmium or zinc. There have been only rare reports on iron coordinating to metallothioneins. A former PhD student from the Freisinger group recently found an iron-sulfur cluster during the heterologous expression of MT3 in *E. coli*. This finding raises new questions about potential functions within this protein family.

The initial objective of my PhD project is hence to investigate this novel complex, starting with a detailed examination of MT3 from *Malus domestica* (mal_MT3). To characterize this new cluster, I will optimize established methodologies for iron-sulfur proteins for application to the metallothionein protein family. In this poster, I am showing the results of our initial *in vitro* studies, which demonstrate the formation pathway of the iron-sulfur cluster.

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Synthesis, Structure, and Reactivity of Novel Heterobimetallic Ni(0) Amide Complexes

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Nickel amide complexes pose to be of great interest in modern organometallic chemistry due to their intermediacy in homogeneous catalysis eg. Buchwald-Hartwig amination^[1-2]. Despite being proposed as intermediates, only a few examples of isolated Ni(II/I) complexes featuring a pendant amide functionality have been reported^[3-5], while Ni(0)-amido complexes have remained elusive to date. Building on recent work from our group which has shown that s-block metal nickelates can be accessed by co-complexation of Ni(0) complexes with the relevant organolithium^[6] or Grignard reagent,^[7] we pondered if a similar approach could be employed to access a new family of alkali-metal nickelates containing amide ligands.

Figure 1: *left*) Schematic representation of the synthesis of the alkali-metal amido nickelate complexes; *right*) Solid state molecular structure of $[\text{Ni}(\text{Ar}^{\text{stb}})_2\text{NHPH}][\text{Li}(\text{THF})_3]$.

In this work, we report our findings assessing the systematic co-complexation of the commercially available Ni(0) precursors $\text{Ni}(\text{Ar}^{\text{stb}})_3$ ^[8-9] with a range of alkali metal amides (see Figure 1). By trapping and structurally defining key intermediates, new insights have been gained into their constitution and stability. Their reactivity towards a range of organic electrophiles has also been investigated under both stoichiometric and catalytic regimes.

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A Biomimetic Model of Anaerobic Oxidation of Methane

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Abstract: Cofactor F430-dependent methyl-coenzyme M reductase (MCR) catalyses the endergonic conversion of the heterodisulfide adduct of coenzymes M and B with methane to methyl-coenzyme M and coenzyme B. In a radical mechanism, the Ni(I)-induced formation of a transient thiyl radical of coenzyme B from the heterodisulfide has been proposed. Our group develops semi-artificial Ni-complexes derived from vitamin B₁₂ as functional models of F430^[1-3]. Herein, I introduce the synthesis and electrochemistry of a new seco-corrin **Ni-1**⁺ (Scheme 1A) and discuss electrochemical model reactions reminiscent of the anaerobic oxidation of methane with F430.

Scheme 1. A: Anaerobic oxidation of methane and structures of coenzyme F430 & its biomimetic model **Ni-1**⁺. B: Proposed radical mechanism of AOM catalysed by F430-dependent MCR.^[3-4]

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Controlled Chalcogenide Binding on Transition Metal Phosphide SurfacesG. P. Wasser¹, M. F. Delley^{1*}¹University Basel, Mattenstrasse 22, 4002 Basel

Most of today's state-of-the-art catalysis relies on noble metals. To achieve more sustainable processes, these scarce materials need to be replaced with catalysts based on earth-abundant elements. Past research has established transition metal phosphides as promising catalysts for hydroprocessing reactions as well as for water splitting.^[1-2] Further catalytic improvements were achieved by incorporating different chalcogenides into the transition metal phosphides.^[3-4] However, only little information is known about how the addition of the chalcogenides influences the catalysis, because the doping with these chalcogenides into the transition metal phosphides is often not well defined. Herein, we report a method that allows for the controlled addition of selenium to a cobalt phosphide surface using molecular Se-transfer reagents. The doping with multiple different chalcogenides allowed us to probe the interaction between different binding sites. Together with our data recently reported for controlled sulfur addition onto cobalt phosphide,^[5] our results provide key insight into the identity, accessibility, and relative binding strength of binding sites of different chalcogenides on a cobalt phosphide surface. With this more detailed picture of the surface sites, we open new avenues for more rationally designed transition metal phosphide modification to improve their catalytic capabilities.

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A Synthetic Pathway to 8Fe-8S Clusters, Using Stepwise Interconversions, Demonstrates Biomimetic Control of Topology

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Iron-sulfur clusters are molecular metallocofactors responsible for electron transport and storage, while also serving as catalytic active sites in many enzymes [1]. Smaller ([Fe₂S₂] to [Fe₄S₄]) clusters are mostly formed on apoenzymes from simple precursors, but higher-nuclearity clusters, that is [Fe₈S₈], often require an intricate cooperation of multiple gene products that act as scaffolds, maturases and transferases for their assembly [2]. The biogenetic pathway of the nitrogenase active site metalloenzyme, termed the iron-molybdenum cofactor (*FeMo-co*) is unparalleled in this aspect and while still not completely known, several intermediate structures and roles of gene products on this pathway have been elucidated in recent years [2-4]. Synthetic mimics of many of these structures have been prepared, allowing for spectroscopic identification and rationalization of inherent properties, yet they diverge from their biogenic counterparts in their mechanism of formation [5,6]. In this work, a [Fe₈S₈(SAr)₄] iron-sulfur cluster coined “interlocked” double-cubane (*ildc*) is presented, which mimics the nitrogenase K-cluster – a proposed precursor to *FeMo-co* [3] – not only in its structure, but also in its genesis [7]. Starting from an [Fe₂S₂] rhomb, and parallel to the biosynthetic pathway, a coherent cyclic synthetic network of [Fe₂S₂], [Fe₄S₄] and [Fe₈S₈] clusters with increasing nuclearity and complexity is reported. Apart from serving to better understand control of topology in both biological and artificial syntheses, characterization of all intermediate products, and particularly the [Fe₈S₈] clusters, lends insight on how their electronic structures are affected by changes in binding and redox state.

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Ambiphilic Reactivity of Iridium Complexes with N-Heterocyclic Vinylidene Ligands

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Room-temperature stable diazoolefins provide access to a unique class of carbon-donor ligands: *N*-heterocyclic vinylidenes. Herein, we describe iridium complexes with terminal *N*-heterocyclic vinylidene ligands. Cationic complexes of type [Cp*IrClL]X (X = SbF₆, OTf; L = *N*-heterocyclic vinylidene) were obtained by reaction of (Cp*IrCl₂)₂ with an *N*-heterocyclic diazoolefin, followed by chloride abstraction. Reduction instead of chloride abstraction gave a neutral Cp*IrL complex with a “pogo stick” geometry. Crystallographic analyses of the complexes revealed very short iridium-carbon bonds, suggesting partial carbyne character. The vinylidene ligands display ambiphilic reactivity. The cationic complex forms covalent adducts with halides and pseudohalides, whereas the neutral complex reacts with electrophiles. These transformations generate rare carbon-donor species, including anionic *N*-heterocyclic olefins with pronounced carbene character or a side-on bound alkylidene ketene.

Tuning Cobalt Oxo Cubanes: Effects of Counterions, and Solvents on Cluster Formation and Stability

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Transition metal oxo clusters are highly valued for applications as single molecule magnets, as water oxidation catalysts, and as photoluminescent materials.^[1] This project focuses on the structural tunability of cobalt-based transition metal oxo cubanes, inspired by nature's oxygen-evolving complex in photosystem II. A detailed analysis of these cobalt oxo clusters led to the discovery of three distinct types of cubanes, each differing in the structural arrangement of the ligand di(2-pyridyl) ketone.^[2] Adjustments in reaction conditions, such as the use of different counterions like ClO_4^- , significantly impact the structural composition and can influence the catalytic performance of the resulting complexes.^[3] This study includes a systematic screening of reaction parameters, revealing how subtle changes in conditions - such as the choice of anions, and solvents - affect product formation and structural diversity. This sheds light on the mechanistic intricacies of these complex systems.

To further understand the stability and behaviour of the cubanes in solution, paramagnetic NMR spectroscopy was employed in deuterated solvents. The recorded T_1 -relaxation times enabled the assignment of paramagnetic signals to the di(2-pyridyl) ketone ligands for these fascinating compounds.

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Production of high specific activity, radionuclidically pure ^{166}Ho for Targeted Radionuclide Therapy

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Targeted Radionuclide Therapy (TRT) is effective against small metastases, owing to advances in targeting agents and novel radionuclides. Radiolanthanides, in particular, show promise due to their favorable nuclear decay properties and well-established chelation chemistry, although separation of lanthanides themselves remains challenging due to their similar chemical behavior. Notably, ^{166}Ho ($t_{1/2}=26.8(12)\text{h}$, $\beta^-=100\%$, $E_{\beta\text{-av}}=665\text{ keV}$) [1] is a medically relevant radioisotope that has been employed in the treatment of various cancers [2]. The β^- particles emitted by ^{166}Ho travel approximately 2-3 mm in tissue, enabling the therapeutic cross-fire effect. However, all current clinical studies have used the carrier-added form of ^{166}Ho , which contains the long-lived metastable radionuclide impurity $^{166\text{m}}\text{Ho}$ ($t_{1/2}=1133\text{ y}$) [2]. To address this issue, the present study focuses on developing an efficient production method for obtaining ^{166}Ho for TRT with high specific activity, i.e., in non-carrier added (n.c.a.) form and free of $^{166\text{m}}\text{Ho}$, using enriched dysprosium oxide targets.

At the Institut Laue-Langevin (ILL), several ampoules each containing few micrograms of $^{164}\text{Dy}_2\text{O}_3$ (enr. 96.8 %) were irradiated to produce the ^{166}Ho parent radionuclide ^{166}Dy ($t_{1/2}=81.5\text{ h}$) via two subsequent neutron capture reactions. The products of these irradiations helped in designing bench experiments to develop a purification method in view of a future large-scale ^{166}Ho production and determination of co-produced side products relevant for the personnel dose and waste management. Liquid chromatography using column separation was adopted as a purification methodology. Different types of resins were evaluated: extraction resins (LN and TK211) and cation exchange resins (Sykam, AG MP-50). In this context, we thoroughly investigated relevant parameters affecting the separation, namely: eluent flow rate, pH, complexing agent concentration (α -hydroxyisobutyric acid (α -HIBA)), and column dimensions to optimize separation efficiency. The separation performance was analyzed from the separated samples using inductively coupled plasma optical emission spectrometry (ICP-OES). Peak tailing was observed in all cases, but particularly when using cation exchange resin leading to significant presence of holmium in the dysprosium fractions. To minimize holmium impurity by reducing peak tailing, ethylamine was tested as resin conditioning solution for the cation exchange. The preliminary results indicated that pairing ion exchange resin Sykam with α -HIBA exhibits superior performance compared to the other ones investigated regarding recovery yields and separation resolution. Nonetheless, future work will focus on improving the separation resolution by testing methylamine and ammonium acetate for resin regeneration, ultimately aiming at establishing a quick, efficient, and reproducible separation system for routine production. Achieving radionuclidically pure ^{166}Ho in high specific activity enables its candidacy for clinical applications in TRT.

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Probing Polypropylene Ziegler-Natta Catalyst Surface Sites Using ^{15}N -Labeled PyridineU. Yildirim¹, A. Yakimov^{1*}, C. Copéret^{1*}¹Department of Chemistry and Applied Biosciences, ETH Zürich, CH-8093 Zürich, Switzerland

Polypropylene and polyethylene account for over 50% of global non-fiber plastic production, with heterogeneous Ziegler-Natta (ZN) catalysts playing a crucial role in their synthesis.^{1,2} However, understanding the atomistic structure-activity relationships of these catalysts remains challenging due to their complex preparation and low titanium loading. ^{15}N solid-state nuclear magnetic resonance (ssNMR) of adsorbed pyridine can be used to assess the type and strength of Lewis and Brønsted acid sites.³ Here, this approach is applied to ZN supports, precatalysts, and activated catalysts to identify key surface species. To define the ^{15}N chemical shift ranges relevant to these systems and assess sensitivity, we synthesized a series of well-defined molecular model Ti(III) and Ti(IV) complexes bearing pyridine ligands as spectroscopic references. A clear correlation was established between the ^{15}N ssNMR chemical shifts of these models and those of industrial ZN precatalysts treated with ^{15}N -labeled pyridine. Specifically, a fully chlorinated titanium Lewis acid site was identified, which correlates with enhanced catalytic activity. In contrast, two distinct magnesium Lewis acid sites were also observed, with the presence of one correlating with reduced activity. These results provide new insights into the local environments of active species and represent a step forward in understanding the surface chemistry of ZN catalysts.

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