Impact of Yb Loss/ Sublimation on Thermoelectric Properties of $Yb_{0.3}Co_{4-x}Ni_xSb_{12}$ (x=0, 0.05, 0.08 and 0.10)

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Thermoelectric materials can convert waste heat into electricity. Among them, the skutterudite materials based on $CoSb_3$ have attracted significant interest due to their tunable compositions and properties. Many studies showed that Yb-filled skutterudites ($Yb_{0.3}Co_{4-x}Ni_xSb_{12}$) contained Yb_2O_3 impurities because of high vapor pressure of Yb and its subsequent reaction with silica tube, and potentially long synthesis process. In this study we are trying to reduce the Yb sublimation and optimize synthesis of the ($Yb_{0.3}Co_{4-x}Ni_xSb_{12}$) (x=0, 0.05, 0.08 and 0.10) skutterudites. Phases with the nominal compositions ($Yb_{0.3}Co_{4-x}Ni_xSb_{12}$) (x=0, 0.05, 0.08 and 0.10) are melted at 1100 ºC for 3 hrs, quenched in air and then annealed for 48 hrs. at 650 ºC. The samples were ball milled and consolidated through spark plasma sintering. The shorter melting time at 1100 ºC decreased the Yb evaporation and yielded samples suitable for thermoelectric measurements. The element loading sequence is also important to prevent sublimation of Yb. The samples were characterized by X-Ray diffraction, scanning electron microscope. The Seebeck coefficient and electrical conductivity were measured from 300 K to 773 K. The ($Yb_{0.3}Co_{4-x}Ni_xSb_{12}$) (x=0, 0.05, 0.08 and 0.10) samples show an *n*-type behavior as the majority charge carriers are electrons whereas the pristine $CoSb_3$ (Co_4Sb_{12}) sample exhibits a *p*-type behavior since holes are dominant carriers.

Key Words: Thermoelectric, air quench and anneal, spark plasma sintering, Yb filling, sample loading.

Catching Platinum Red-Handed: Exhaustive Ligand Redistribution at a Tucked-In Iron Complex

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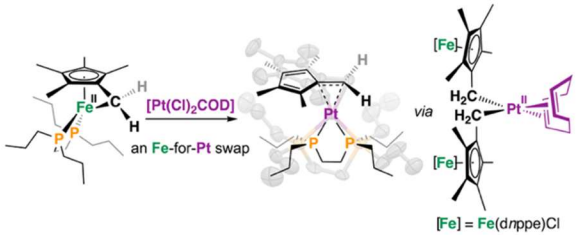

First synthesized by Thiele in the early 1900's, fulvenes are a class of conjugated organic compounds with their electronic structures intermediate of isolated olefins and cyclic conjugated systems.[1-4] Fulvenes can be generated through the deprotonation of $^{Me}Cp^-$ and precursors thereof.[5] When a transition metal is present, the species formed is referred to as a "tucked-in" complex, with early examples of a tungsten "tucked-in" complex being synthesized in 1985 by Morely and coworkers.[6] Recently, the Drover group synthesized a stable diphosphine-containing iron "tucked-in" complex which has allowed for exploration of its reactivity and functionalization.[7] The transmetalation of this iron "tucked-in" complex has been investigated with a variety of p- and d- block elements. To further elaborate upon scope, we wondered whether this transmetalation could be expanded to platinum, a 5d metal capable of two successive transmetalations. Transmetalation conventionally entails the transfer of a single ligand (e.g., aryl, hydride, or alkyl) between two centers. Herein, we demonstrate a 3d-to-5d metal-to-metal transmetalation in which the iron center of an organometallic fulvene complex is formally replaced by platinum, ultimately leaving an iron fragment devoid of ancillary ligands.[8] Representative intermediates, including two trimetallic {Fe_2Pt} complexes, were characterized by single crystal X-ray diffraction, providing direct insight into the sequence of metal−carbon bond formation and ligand reorganization underlying this transmetalation.

REFERENCES

1. Thiele, J.; Balhorn, H. *Justus Liebigs Ann. Chem*. **1906**, 348 (1−2), 1−15.
2. Thiele, J. *Ber. Dtsch. Chem. Ges.* **1900**, 33, 666−673.
3. Kawase, T.; Kurata, H. In *Cross Conjugation: Modern Dendralene, Radialene and Fulvene Chemistry*; Hopf, H., Sherburn, M. S., Eds.; Wiley-VCH: Weinheim, Germany, **2016**; 145–248.
4. Neuenschwander, M. *Pure Appl. Chem.* **1986**, 58 (1), 55−66.
5. Preethalayam, P.; Krishnan, K. S.; Thulasi, S.; Chand, S. S.; Joseph, J.; Nair, V.; Jaroschik, F.; Radhakrishnan, K. V. *Chem. Rev.* **2017**, 117
6. Cloke, F. G. N.; Green, J. C.; Green, M. L. H.; Morley, C. P. *J. Chem. Soc. Chem. Commun.* **1985**, 14, 945−946.
7. Zurakowski, J. A.; Drover, M. W. *Chem. Commun.* **2023**, 59 (76), 11349−11352
8. Almeida, A. M. D. J.; Taylor, L. J.; Dilinaer, A. D.; Drover, M. W. *Organometallics* **2026**. https://doi.org/10.1021/acs.organomet.6c00324

Boron-Directed Solid-State [2+2] Photocycloadditions

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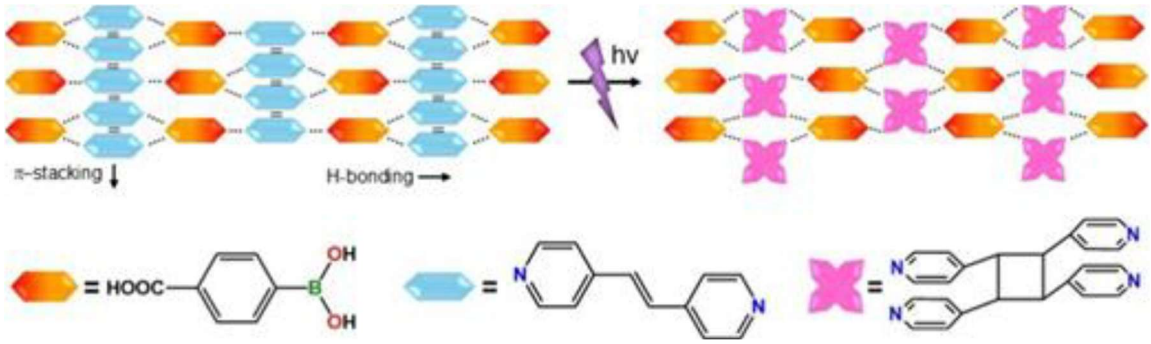
Crystal engineering offers a powerful strategy to control molecular organization and reactivity in the solid state.[1] Boron-containing compounds occupy a central role in modern chemistry, with broad applications spanning organic synthesis, materials science, optoelectronics, sensing, and medicinal chemistry. Their versatile bonding modes, tunable Lewis acidity, and ability to form reversible bonds make them attractive building blocks for functional materials. Despite their widespread utility, the potential of boronic acid derivatives to direct solid-state photoreactivity through predictable supramolecular organization remains largely underexplored.[1,2] In this work, we investigate boronic acid derivatives as supramolecular templates for directing [2+2] photocycloaddition reactions within crystalline materials. Our photochemical studies reveal highly selective solid-state transformations, including the rare single-crystal-to-single-crystal (SCSC).[3,4] This study highlights the potential of boron-driven supramolecular design as a versatile tool for steering chemical reactivity in the organic solid state.



REFERENCES

1. Campillo-Alvarado, G.; Brannan A. D.; Swenson, D. C.; MacGillivray, L. R.; Org. *Lett. 2018, 20, 5490-5492.*
2. Varughese, S.; Sinha, S. B.; Desiraju, G. R.; *Sci. China Chem. 2011, 54, 1909–1919.*
3. Vasquez-Ríos, M. G.; Campillo-Alvarado, G.; Swenson, D. C.; Höpfl, H.; MacGillivray, L. R.; *Chem. Eur. J. 2022, 28, 1-11.*
4. Barba Hernández, M.; Vasquez-Ríos, M. G.; Höpfl, H.; MacGillivray, L. R.; Cryst. Growth Des. 2025, 25, 1, 38–52.

Adsorptive Removal of Iodate Oxyanions from Water Using a Zr-based Metal–Organic Framework

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Oxyanions of various elements are common contaminants in wastewater resulting from industrial processes, mining, and power generation and other anthropogenic sources.[1] Zirconium-based metal–organic frameworks (MOFs) have been previously shown in the literature to capture a variety of oxyanions by adsorption on nodal open metal sites, typically binding in an $\eta_2\mu_2$ fashion.[2,3] Herein, the adsorption of a new class of oxyanions on Zr_6-based MOFs will be discussed, including the kinetics of adsorption, maximum uptake capacity, and characterization of the adsorption mechanism. The method of nodal binding is investigated by differential pair distribution function analysis (dPDF) and diffuse reflectance Fourier transform infrared spectroscopy (DRIFTS). Additionally, the MOF is tested for its ability for regeneration and potential for multi-cycle reuse, as well as post adsorption characterization to ensure its stability and suitability for wastewater remediation applications.[4]

REFERENCES

1. Gómez-Guzmán, J. M.; Holm, E.; Niagolova, N.; López-Gutiérrez, J. M.; Pinto-Gómez, A. R.; Abril, J. A.; García-León, M. *Chemosphere,* **2014**, 108, 76–84.
2. Howarth, A. J.; Katz, M. J.; Wang, T. C.; Platero-Prats, A. E.; Chapman, K. W.; Hupp, J. T.; Farha, O. K. *J. Am. Chem. Soc.* **2015**, *137* (23), 7488–7494.
3. Howarth, A. J.; C. Wang, T.; S. Al-Juaid, S.; G. Aziz, S.; T. Hupp, J.; K. Farha, O. *Dalton Trans.* **2016**, *45* (1), 93–97.
4. Copeman, C.; Bicalho, H. A.; Terban, M. W.; Troya, D.; Etter, M.; Frattini, P. L.; Wells, D. M.; Howarth, A. J. *Chem. Commun.* **2023**, *59* (21), 3071–3074.

Substituent-Tuned Concerted, Two-Electron Bipolar Bispyridinylidenes for Symmetric Non-Aqueous Organic Redox Flow Batteries

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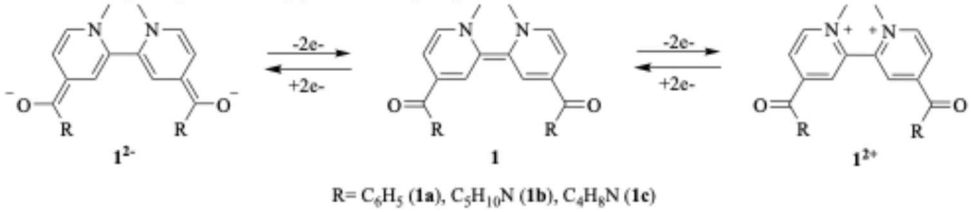
Non-aqueous organic redox flow batteries (NAORFBs) have emerged as promising candidates for grid-scale energy storage, owing to their molecular tunability, potential sustainability, and wide electrochemical windows. However, their practical implementation remains hindered by active-material crossover, limited cycling stability, and the high concentrations required to achieve competitive energy densities.[1] Symmetric redox flow batteries offer a potential solution to crossover-induced capacity loss by employing bipolar active materials that can access multiple oxidation states, enabling capacity recovery through electrolyte rebalancing.[2] While intrinsically bipolar materials based on π-conjugated frameworks offer high atom efficiency, their energy storage capabilities are often constrained by single-electron redox processes.

Concerted multi-electron redox systems offer an alternative approach to increasing energy density without relying on high active-material concentrations, which can adversely affect electrolyte viscosity and ionic conductivity. Herein, we investigate a series of [2,2′]bispyridinylidene (BPY) derivatives as intrinsic, bipolar active materials capable of concerted two-electron redox processes. Building upon previously reported [2,2′]bispyridinylidene-4,4′-dialkyl esters,[3] we systematically examine the influence of 4,4′-substituent modifications on redox behavior, solubility, electrolyte stability, and cell voltage. This work establishes molecular modification as a strategy for tuning the electrochemical and physicochemical properties of concerted two-electron bipolar materials, highlighting their potential for advancing high-energy-density symmetric NAORFBs.



Scheme 1. Redox processes of BPY derivatives: **BPYB** (**1a**), **BPYA$_6$** (**1b**), and **BPYA$_5$** (**1c**).

REFERENCES

1. Ahn, S.; Yun, A.; Ko, D.; Singh, V.; Joo, J. M.; Byon, H. R. Organic Redox Flow Batteries in Non-Aqueous Electrolyte Solutions. *Chem. Soc. Rev.* **2025**, *54* (2), 742–789. https://doi.org/10.1039/D4CS00585F
2. Tracy, J. S.; Horst, E. S.; Roytman, V. A.; Toste, F. D. Development of High-Voltage Bipolar Redox-Active Organic Molecules through the Electronic Coupling of Catholyte and Anolyte Structures. *Chem. Sci.* **2022**, *13* (36), 10806–10814. https://doi.org/10.1039/D2SC03450F
3. Al Raihan, M.; Dyker, C. A. Ester-Substituted Bispyridinylidenes: Double Concerted Two-Electron Bipolar Molecules for Symmetric Organic Redox Flow Batteries. *ACS Energy Lett.* **2023**, 3314–3322. https://doi.org/10.1021/acsenergylett.3c00969

Synthesis and Characterization of Metallopharmaceuticals Containing N-heterocyclic Carbene Ligands, Potential Anticancer Agents and the study of their Possible Mechanisms of Action

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Cancer remains one of the major public health challenges worldwide, highlighting the need for rational approaches to the design and synthesis of novel therapeutic agents. This study aimed to investigate the influence of coordination modes on the biological activity of metal complexes containing clotrimazole (CTZ) and ketoconazole (KTZ), and their corresponding N-heterocyclic carbene (NHC) derivatives as ligands. The compounds **L1** [(CTZ-Me)I] and **L2** [(KTZ-Me)I], together with the silver(I) complexes Ag(L1)(I)·H_2O (**1**), $[Ag(L1)_2]I·4CH_2Cl_2$ (**2**), $[Ag(CTZ)_2]NO_3$ (**3**), [Ag(L2)(I)] (**4**), $[Ag(L2)_2]I·2CH_2Cl_2$ (**5**), and $[Ag(KTZ)_2]NO_3$ (**6**)[1], as well as the gold(I) complexes $[Au(L1)(Cl)]·2CH_2Cl_2$ (**7**), [Au(CTZ)(Cl)] (**8**), [Au(L2)(Cl)] (**9**), and [Au(KTZ)(Cl)] (**10**)[2], were synthesized and characterized. Their structures were proposed based on the combined analysis of the characterization data. Cytotoxicity assays revealed promising activity against the MDA-MB 231 and 4TI breast cancer cell lines. DNA interaction studies suggested that DNA is unlikely to be a primary molecular target of these compounds. In contrast, studies involving bovine serum albumin (BSA) revealed predominantly electrostatic interactions with the silver(I) complexes, suggesting a potential role for this protein in their biological behavior. The gold(I) (Au(I)) complexes, in turn, exhibited significant interactions with glutathione, indicating a preferential affinity for thiol-containing biomolecules and suggesting that enzymes such as thioredoxin reductase (TrxR) may represent potential molecular targets. Furthermore, molecular docking studies suggested two potential modes of TrxR inhibition, providing additional insights into the potential mechanisms underlying the biological activity of these complexes.

REFERENCES

1. Condé, C. A. S. R., Querino, A. L. A., Silva, H., Navarro, M. Silver(I) complexes containing N-heterocyclic carbene azole drugs: Synthesis, characterization, cytotoxic activity, and their BSA interactions, Journal of Inorganic Biochemistry 246 (2023) 112303. https://doi.org/10.1016/j.jinorgbio.2023.112303
2. Condé, C. A. S. R., Bruno, K. L., Calçado, C. B., Sánchez Delgado, G. Y., Oliveira, W. X. C., Silva, H., Navarro, M. Organometallic and coordination gold(I)-azole drugs compounds: Synthesis, characterization, antitumor evaluation, and interactions with biomolecules, Journal of Inorganic Biochemistry 275 (2026) 113142. https://doi.org/10.1016/j.jinorgbio.2025.113142

Tin(II) Barium Fluorides and Chloride Fluorides Poor in Tin

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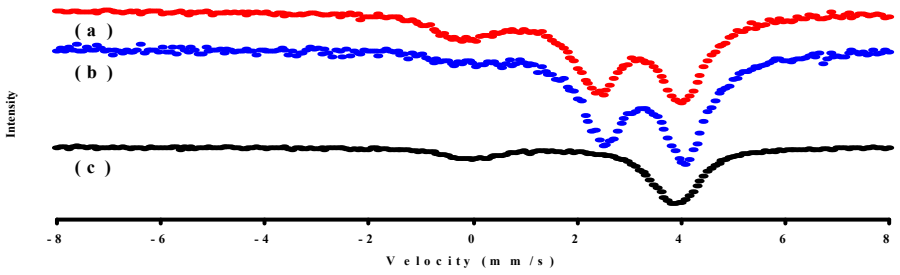
The reaction of aqueous solutions between $BaCl_2.2H_2O$ and SnF_2 results in precipitation at all molar ratios of the two reactants. In earlier works carried out in our laboratories, covalent stannous fluoride and ionic MF_2 (M = Sr, Ba or Pb) produced $MSnF_4$ and the $Pb_{1-x}Sn_xF_2$ high performance fluoride ion conductors (1,2). For reaction mixtures rich in tin, $BaSn_2F_6$ (already known) and $BaSn_2Cl_2F_4$ were obtained (3). In the current work, the reaction of SnF_2 with $BaCl_2.2H_2O$ in aqueous solution at high molar ratio (X>0.5) of barium chloride in the reaction mixture was carried out. From ca. X = 0.5 to 0.85, the new compound $BaSnClF_3{\cdot}0.8H_2O$ was obtained. For X>0.87, the $Ba_{0.85}Sn_{0.15}Cl_{1.11}F_{0.89}$ phase with the BaClF structure was formed. The latter phase is a solid solution, $Ba_{1-x}Sn_xCl_{1+y}F_{1-y}$, (0<x<0.15, -0.15<y<0.25), hence non-stoichiometric in both metals and halogens. Both compounds precipitate in the form of a fine powder. Neither could be recrystallized to form single crystals and both decompose on heating. The presentation will show the detailed study of the two compounds, using X-ray powder diffraction and ^{119}Sn Mössbauer spectroscopy, the latter for identifying the mode of tin bonding: covalent in $BaSn_2Cl_2F_4$ and in $Ba_3Sn_3Cl_4F_8{\cdot}2H_2O$, and ionic in $Ba_{0.85}Sn_{0.15}Cl_{1.11}F_{0.89}$.

REFERENCES

1. G. Dénès, J. Bratigny, D. Le Roux and A. Muntasar, *Mater. Res. Soc. Symp. Proc*. **1997**, 453, 177-182.
2. G. Dénès, G. Milova and B.D. Antonov, *Mater. Res. Soc. Symp. Proc.* **1999**, 548, 485-490.
3. Dénès, M.C. Madamba, J.M. Parris, A. Muntasar and H. Merazig, Hyp. Int. **2020**, 23, 241-268.



Ambient temperature ^{119}Sn Mössbauer spectrum of precipitated (a) $BaSn_2Cl_2F_4$, (covalent at tin), (b) $BaSnClF_3.0.8H_2O$, (covalent at tin), (c) $Ba_{1-x}Sn_xCl_{1+y}F_{1-y}$ solid solution (ionic at tin)

Reactions of Hydrazine with Main Group Lewis Acids

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Main-group chemistry is an expanding field with growing interest in providing metal-free pathways to small-molecule activation and catalysis. One subsection of the field involves exploring main-group compounds containing N–N fragments. These species offer opportunities to investigate useful nitrogen-centered reactivity, including redox chemistry[1] and azo-transfer[2]. Parent hydrazine (N_2H_4) offers a convenient route to synthesize main-group species with N–N fragments. Main-group species containing hydrazine moieties are interesting targets due to the functionalization capabilities that they offer, such as through deprotonation[3]. Understanding the reactivity of hydrazine with main-group Lewis acids may facilitate development of more convenient synthetic routes to N–N fragment containing species. Lewis acids with LUMOs derived from vacant 2p-orbitals: BF_3, Mes_2BH, $MesBH_2$, PhBBN, and C_6F_5BBN, were reacted with hydrazine, forming the mono- and bis-adducts $(NH_2NH_2)(BF_3)_2$, $Mes_2BH(NH_2NH_2)$, $MesBH_2(NH_2NH_2)$, $(PhBBN)_2(NH_2NH_2)$, and $(C_6F_5BBN)(NH_2NH_2)$. The reaction of hydrazine with $GaCl_3$ formed a polymeric species $[Cl_3GaNH_2NH_2]_n$, where gallium assumed a pseudotrigonal bipyramidal geometry, interspersed between hydrazine moieties. In contrast to these examples of Lewis acid-base adduct formation, the reaction of hydrazine with $[Et_3Si(HSiEt_3)][B(C_6F_5)_4]$ showed no evidence of silyl-hydrazine adduct formation. Instead, the hydrazinium salt $[(NH_2NH_2)_2H][B(C_6F_5)_4]$ was observed. This hydrazinium salt was also obtained separately by the reaction of hydrazine with triflic acid in the presence of $[Ph_3C][B(C_6F_5)_4]$. The reactivity of hydrazine was also explored with Lewis acids with LUMOs deriving from low-energy σ* orbitals. The phosphonium bromide $[Ph_3PBr][Br]$ was shown to form both mono- and bisadducts $[Ph_3PNHNH_2]Br$ and $[(Ph_3PNH)_2]X_2$ (X = Br, $GaCl_4$), as governed by stoichiometry. However, the species $[Et_3PBr][Br]$ showed exclusive formation of the bis-adduct $[(Et_3PNH)_2]Br_2$. Contrasting this, hydrazine was reacted with $[(C_6F_5)_3PCl]Cl$, affording the para-attacked product $(H_2NNHC_6F_4)_3PO$.[4] These results demonstrate how the electronic characteristics of main-group Lewis acids influence their reactivity with hydrazine, providing insight towards the synthesis of novel N–N fragment containing main-group targets.

REFERENCES

1. Shimizu, T.; Tanifuji, N.; Yoshikawa, H. Azo Compounds as Active Materials of Energy Storage Systems. *Angew. Chem. Int. Ed.* **2022**, *61* (36), e202206093. https://doi.org/10.1002/anie.202206093
2. Regitz, M. New Methods of Preparative Organic Chemistry. Transfer of Diazo Groups. *Angew. Chem. Int. Ed. Engl*. **1967**, *6* (9), 733–749. https://doi.org/10.1002/anie.196707331
3. Miao, L.; Yeung, J.; Yeganeh-Salman, A.; Qu, Z.; Grimme, S.; Stephan, D. W. Photolytic and Thermal Reactions of [C6H4(PPh2)2(μ-N2)] and Its Lewis Acid Adducts: N–N Bond Cleavage and Liberation of N2. *J. Am. Chem. Soc*. **2025**, *147* (6), 4720–4725. https://doi.org/10.1021/jacs.4c16123
4. Bedi, V.; Dias, A. C.; Stephan, D. W. Reactions of Hydrazine with Main Group Lewis Acids. *Dalton Trans.* **2026**, *55* (36), 13252–13261. https://doi.org/10.1039/d6dt01929c

Exploring MOF-Lipid Interfaces: Bridging Inorganic Materials with Biological Models

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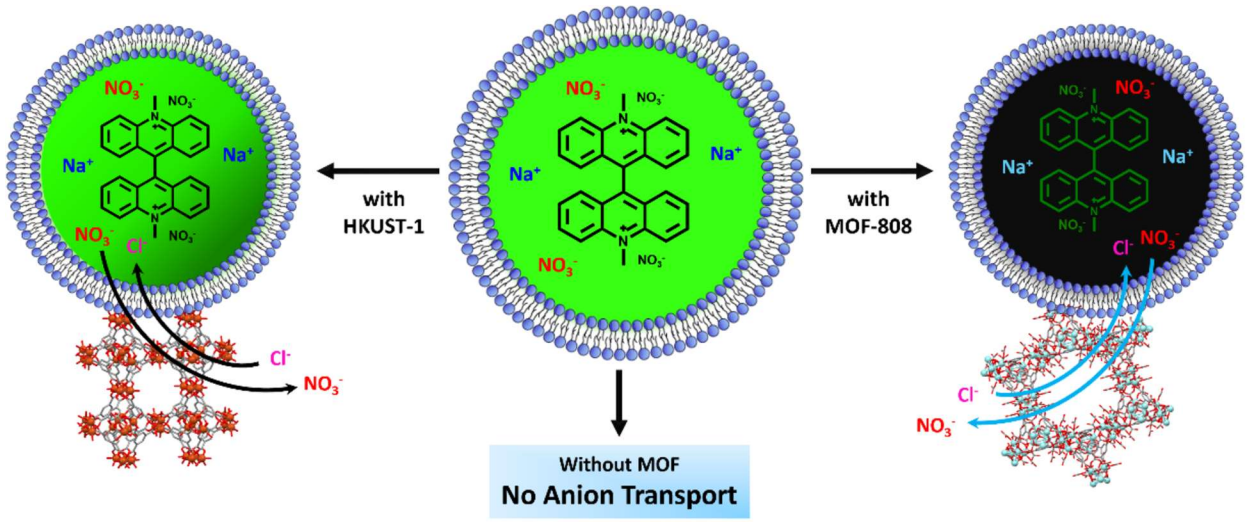
Society has seen biology (people, plants, microbes) interacting with inorganic materials regularly on the macro-scale. Here, we explore how microscopic biological models behave in the presence of inorganic constructs. Giant unilamellar vesicles (GUVs) made of phospholipids are ideal for studying cellular mechanisms due to their cell-mimicking morphology and size. Separately, metal-organic frameworks (MOFs) are actively researched owing to their unique and tunable properties, yet little is known about the interaction between MOFs and phospholipids. This study investigates the influence of the metal-phosphate interface on the formation, size distribution, and stability of GUVs with different lipid compositions. The results show that Al, Zn, Cu, Fe, Zr, and Ca metal centers of MOFs can coordinate to phospholipids on the surface of GUVs.[1] This research leads to the formation of GUV@MOF constructs that show promise for advanced biomedical applications such as bioimaging and ion transport featuring frameworks with liposomes. Building on these interactions, we investigated whether MOFs could impart additional functionality to lipid membranes by facilitating anion transport. GUVs containing $NaNO_3$ and the chloride-sensitive fluorescent probe lucigenin were formed in the presence of MOF-808 and HKUST-1. Addition of external NaCl resulted in enhanced quenching of lucigenin fluorescence in GUV@MOF-808 constructs compared GUVs immobilized to HKUST-1 and MOF-free controls. Together, these studies demonstrate how MOF-lipid interactions can be used to introduce functionality into biomimetic membranes, providing a versatile platform at the interface of inorganic materials chemistry and synthetic-cell models.



REFERENCES

1. A. Faheem, M. C. Lawrence, G. A. Bushra, M.-V. Meli and B. A. Blight, *J. Mater. Chem. B*, **2025**, *13*, 2317–2326.

Gallium Formazanate Complexes: From Gallium-68 Radiolabelling to Lewis Acidity

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Formazans are a family of compounds that contain a nitrogen-rich, π-conjugated backbone which gives rise to intense colour and redox activity, making them valuable as specialized dyes.[1,2] Their characteristic optoelectronic and redox properties can be readily tuned through modification of the substituents appended to the formazanate backbone. Given the simple synthesis of formazanate ligands along with their tunable properties, many main group formazanate complexes, including aluminum and boron, have been studied.[3,4] Herein, we report the synthesis of a series of gallium complexes bearing tetradentate formazanate ligands to expand the scope of group 13 formazanate chemistry.[5,6] The optical and redox properties of the gallium formazanate complexes were measured through UV-Vis absorption spectroscopy and cyclic voltammetry, and their stability was assessed through radiolabelling studies with gallium-68. Radiosynthesis demonstrated that a $N_2O_2^{3-}$ formazanate ligand can be radiolabelled in just 15 min at room temperature, leading to future applications as positron emission tomography (PET) imaging agents. In addition to bioimaging applications, gallium formazanate complexes with tetradentate ligands of varying charges ($N_2O_2^{2-}$, $N_2O_2^{-}$) were synthesized, and their Lewis acidity was determined via fluoride ion affinity (FIA) calculations. The FIA studies suggested that the cationic and dicationic complexes exhibited moderate and strong Lewis acidity, respectively. This work highlights the potential of this class of compounds for the production of gallium Lewis superacids and gallium-68 PET imaging agents.

REFERENCES

1. Gilroy, J. B.; Otten, E. *Chem. Soc. Rev.* **2020**, *49*, 85–113.
2. Maar, R. R. *et al. Chem. Eur. J.* **2015**, *21,* 15589-15599.
3. Barbon, S. M.; Staroverov, V. N.; Gilroy, J. B. *Angew. Chem. Int. Ed.* **2017**, *56*, 8173–8177.
4. Maar, R. R. *et al. Inorg. Chem.* **2017**, *56*, 12436–12447.
5. Chun, S. et al. Inorg. *Chem.* **2026**.
6. Chun, S. *et al*. *Dalton Trans.* **2026***, 55*, 13697–13701.

Microsolvation Effects on Frustrated Lewis Pair Reactivity: A DFT and Machine Learning Study

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Frustrated Lewis Pairs (FLPs) consist of Lewis acids (LAs) and Lewis bases (LBs) whose steric bulk inhibits the formation of classical Lewis acid-base adducts, preserving their ability to accept and donate electron pairs.[1] FLPs have been investigated for the activation of small molecules, including H_2, CO, CO_2, N_2O, NO, SO_2, H_2O, and HCOOH, as well as olefins, alkynes, and carbonyl compounds.[1,2] These systems therefore offer a metal-free platform for molecular activation and catalysis under mild conditions.[1]

Solvation plays a central role in FLP reactivity by influencing the formation of reactive Lewis acid–base encounter complexes,[3] stabilizing charge-separated species,[4] and altering the accessibility of reaction pathways.[5] Solvent molecules can also participate directly in catalysis, as demonstrated by hydrogenation systems in which the solvent acts as the Lewis base.[6] Understanding these effects therefore requires accounting for specific solute-solvent interactions. To investigate these effects, we generate a dataset of density functional theory (DFT) calculations with explicit solvent molecules, using the quantum cluster growth algorithm to sample representative solution environments around FLPs and their related reaction intermediates and transition states.[7]

To model these effects, we deploy a classical machine learning architecture that uses Extended Connectivity Fingerprints (ECFP)[8] and Tanimoto similarity thresholds to partition the dataset into structurally similar catalysts, drawing on previous applications of molecular similarity in FLP property prediction.[2] We train kernel ridge regression (KRR) models[9] on a set of 21 electronic and steric descriptors derived from DFT calculations and optimized structures, including hydride affinity, buried volume, frontier orbital energies, and Fukui reactivity indices. This framework is designed to learn nonlinear relationships between molecular descriptors and solvent-dependent reactivity, with regularization used to mitigate overfitting in a limited dataset. The resulting models relate catalyst structure, electronic properties, and local solvation descriptors to quantities relevant to catalytic performance, including FLP association energies, substrate and product binding energies, and activation barriers for small-molecule activation and subsequent substrate conversion. This approach will help identify the molecular factors underlying solvent-dependent reactivity and guide the selection of catalyst-solvent combinations with favorable activity and selectivity.

REFERENCES

1. Stephan, D. *J. Am. Chem. Soc.* **2015**, *137*, 10018
2. Ye, J. et al. *J. Phys. Chem. C* **2025**, *129*, 14346
3. Brown, L. et al. *Chem. Commun*. **2018**, *54*, 8689
4. Liu, X. et al. *ChemPhysChem* **2021**, *22*, 968
5. Privalov, T. et al. *Chem. Eur. J.* **2015**, *21*, 17708
6. Ashley, A. et al. *Angew. Chem. Int. Ed*. **2014**, *53*, 10218
7. Grimme, S. et al. *J. Chem. Theory Comput.* **2022**, *18*, 3174
8. Rogers, D. et al. *J. Chem. Inf. Model*. **2010**, *50*, 742
9. Duarte, F. et al. *Phys. Rev. Lett*. **2012**, *108*, 058301

Using Supramolecular Chemistry to Perform [2+2] Photocycloadditions in Solid-State Organic Synthesis

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Cyclobutane synthesis often involves a [2+2] photoaddition where regiochemistry can be difficult to control in intermolecular solution-based reaction. Principles of crystal engineering enable reactant alkenes to be organized in the solid state to undergo intermolecular [2+2] photodimerizations that generate desired products selectively and in near quantitative yield. Small molecules that act as supramolecular templates can be used to form cocrystals and position reactant alkenes within the 4.2 Å distance for a [2+2] photocycloaddition to occur.[1] Understanding the crystal packing of a molecule is, therefore, important to understand its solid-state reactivity. Challenging cyclobutanes in the form of polycyclobutanes (e.g., ladderanes) and cyclobutane rings fused with even larger ring systems (i.e., 5- and higher) are emerging as important building blocks in medicinal and materials chemistry, as well as the chemistry of natural products. Moreover, there is a need to develop approaches that provide ready and efficient access to such products.[2-4] In this work, we report the study of the synthesis of fused tricyclic hydrocarbon core of adjacent 4- and 6-membered rings through [2+2] photodimerizations performed in the organic solid state.[5] We approach the design of the starting alkenes by understanding the crystal packing and chemical reactivity.

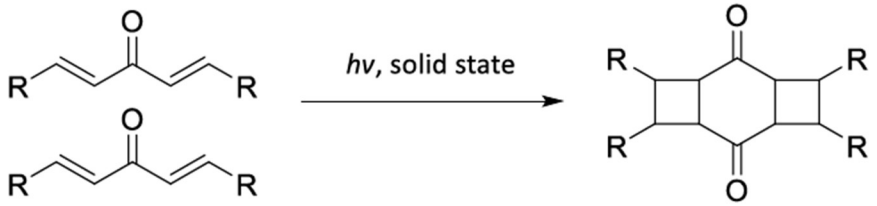

Figure 1. Reactivity to generate a fused 4-, 6-, and 4- ring system in the solid state.

REFERENCES

1. Macgillivray, L. R. *J. Org. Chem.* **2008**, *73* (9), 3311–3317.
2. Meibom, A.; Sleep, N. H.; Chamberlain, C. P.; Coleman, R. G.; Frei, R.; Hren, M. T.; Wooden, J. L. *Nature* **2002**, *419*, 705–708.
3. Epplin, R. C.; Paul, S.; Herter, L.; Salome, C.; Hancock, E. N.; Larrow, J. F.; Baum, E. W.; Dunstan, D. R.; Ginsburg-moraff, C.; Fessard, T. C.; Brown, M. K. *Nat Commun* **2022**, *13* (6056), 1–5.
4. Kolk, M. R. Van Der; Janssen, M. A. C. H.; Rutjes, F. P. J. T.; Blanco-ania, D. *ChemMedChem* **2022**, *17*, e202200020.
5. Green, B. S.; Schmidt, G. M. J. *Tetrahedron Lett.* **1970**, *11* (49), 4249–4252.

Photophysical Properties of Neutral Cyclometallating Iridium(III) Complexes

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Iridium(III) complexes are known to be photoluminescent and often have interesting photophysical properties. Varying the cyclometallating ligands of these complexes can change these photophysical properties, allowing for the synthesis of iridium(III) complexes that access the entire visible light spectrum in terms of emission colour, and are strong candidates for photocatalysis, since they can be made to access energy levels that facilitate required transitions[12,3]. A ligand that can be readily oxidized and reduced is advantageous in an iridium(III) complex because it can also participate in electron relay and provide stability to the complex during photocatalysis. Using well-established procedures for cyclometallated iridium(III) complex synthesis, we report the synthesis and characterization of multiple iridium(III) complexes that incorporate a di-imidazol-amine ancillary ligand.[4] By varying the cyclometallating ligands we accessed emission colours spanning blue, green, yellow and red across the visible light spectrum. Photophysical data was obtained for all these complexes. The di-imidazol-amine ligand provides the complexes with the potential for electron relay, and the energy tunability of the complexes make them ideal candidates for photocatalysis, specifically photocatalytic water splitting, which will be investigated further. With the hydrogen bonding sites of the ancillary ligand, these complexes will also be investigated for further photophysical tuning using complementary hydrogen bond array.

REFERENCES

1. Balónová, B.; Martir, D. R.; Clark, E. R.; Shepherd, H. J.; Zysman-Colman, E.; Blight, B. A. Influencing the Optoelectronic Properties of a Heteroleptic Iridium Complex by Second-Sphere H-Bonding Interactions. *Inorg. Chem.* **2018**, *57* (14), 8581–8587. https://doi.org/10.1021/acs.inorgchem.8b01326.
2. Balonova, B.; Jones, T. H.; True, A. E.; Hetherington, S. M.; Blight, B. A. Colour Tuneability of Heteroleptic Iridium Complexes through Second-Sphere Coordination. *RSC Advances* **2024**, *14* (46), 34288–34297. https://doi.org/10.1039/d4ra04535a.
3. Jones, T. H.; Bradshaw, C. F.; Ward, J. W.; Blight, B. A. Automation Accelerated Screening of H-Bond-Rich Iridium Photosensitisers for Hydrogen Generation. *Catal. Sci. Technol.* **2025**, *15* (8), 2459–2465. https://doi.org/10.1039/D5CY00176E.
4. Morin, G.; McCabe, C.; Turnbull, D.; Pham-Tran, V.; Légaré, M.-A. Metal-Free Catalytic Cross-Coupling of Esters and Boranes. *J. Am. Chem. Soc.* **2025**, *147* (45), 42143–42150. https://doi.org/10.1021/jacs.5c17878.

Enhanced Morphology Control and Hydrolytic Stability of HKUST-1 by Incorporation of Poly(acrylic acid)

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HKUST-1 is a copper-based metal–organic framework (MOF) with high porosity and promising catalytic and adsorption properties. However, its poor hydrolytic stability limits practical applications. Improving MOF stability under humid and biologically relevant conditions using biocompatible and greener routes remains a key challenge. Here, we report a polymer-assisted synthetic route to form octahedral HKUST-1 particles using poly(acrylic acid) (PAA) as both an acid catalyst to mediate phase transformation and a growth modulator[1]. Structural integrity and morphology were confirmed by powder X-ray diffraction and scanning electron microscopy, while porosity was evaluated using N_2 adsorption measurements. Incorporation of PAA was supported by nuclear magnetic resonance spectroscopy and pore size distribution analysis. The resulting PAA–HKUST-1 composite exhibits enhanced stability, maintaining crystallinity after exposure to air humidity for 14 days and immersion in biological buffer for 7 days. Notably, this stabilization is achieved using a hydrophilic polymer, in contrast to the more commonly reported hydrophobic polymer strategies. Ongoing work focuses on elucidating the mechanism by which PAA enhances stability and its interaction with the framework.

REFERENCES

1. Kenyon, S. S.; Van Houten, J.; Wu, W. Y.; Korzyński, M. D.; Ogata, A. F. Enhanced Morphology Control and Hydrolytic Stability of HKUST-1 by Incorporation of Poly(Acrylic Acid). *Crystal Growth & Design* **2025**, *26* (1), 1–9. https://doi.org/10.1021/acs.cgd.5c00721.

Phosphorus – Nitrogen Heterocycles from Phosphadiazonium Cations via Bond Activation

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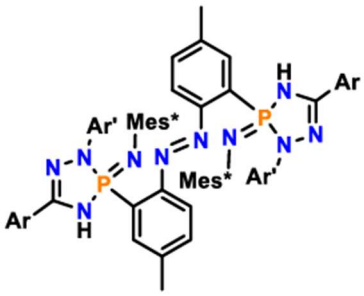
Metallomimetic chemistry of the main-group elements has attracted significant interest for small-molecule activation and catalysis, while also offering opportunities to access novel molecular architectures, including heterocycles.[1] Heterocycles that incorporate both main group elements and nitrogen are of considerable interest within the π-conjugated heterocycle community due to the unusual materials properties that they possess. Among these heterocycles, compounds containing phosphorus-nitrogen (PN) bonds are relatively rare, despite their potential use in optoelectronic materials, inorganic polymers, and for understanding structure/bonding and discovering new reactivity.[2] This rarity may stem from both elements originating from Group 15, and their compounds often acting as Lewis bases.[2] Phosphadiazonium cations ([Ar–N≡P][X] (X = OTf, $AlCl_4$, $GaCl_4$) and chloroiminophosphines (Ar–N=PCl) offer Lewis acidic P centres, despite the presence of a lone pair at phosphorus.[3] This ambiphilic character combined with the ability to access the P(III)/P(V) redox couple enables diverse reactivity, including transition-metal coordination, cyclization reaction to produce unusual heterocycles, and redox transformations yielding robust radicals.[2,4,5] These distinctive bonding and electronic properties provide a versatile platform for discovering new reactivity patterns and accessing unprecedented molecular architectures. This poster will discuss the reactivity of phosphadiazonium cations with formazanate and Schiff base ligands to access novel phosphorus-nitrogen heterocycles (*e.g.*, **1** & **2**) through bond activation.



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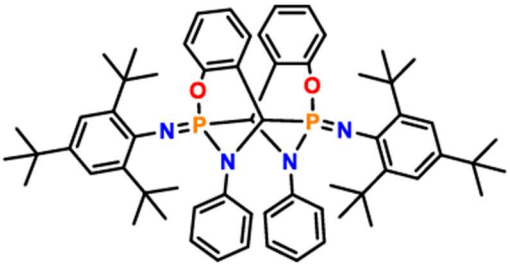

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REFERENCES

1. P. P. Power, *Nature* **2010**, *463*, 171−177.
2. S. Khan, J. B. Gilroy, *Chem. Eur. J.* **2025**, *31*, e202404420.
3. E. Niecke, M. Nieger, F. Reichert, *Angew. Chem. Int. Ed.* **1988**, *27*, 1715−1716.
4. X. Wang, Y. Chen, X. Li, L. Xu, G. Tan, *J. Am. Chem. Soc.* **2025**, *147*, 36980–36986.
5. S. K. Milkovich, F. L. Buguis, P. D. Boyle, J. B. Gilroy, *Chem. Eur. J.* **2024**, *30*, e202400569.

Programming Dual Photoreactivity in Cadmium Coordination Crystals

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A wide variety of photochemical reactions can occur in molecular crystals, with [2+2] cycloaddition among the most common.[1] These reactions are often promoted using near-UV light, creating an opportunity to introduce a second photoreactive group that responds at a different wavelength. Here, we investigate whether two distinct photochemical reactions can be incorporated into a single coordination crystal and selectively addressed with distinct wavelengths.

Azidobenzoate ligands were incorporated into pseudo-paddlewheel Cd(II) complexes containing photoreactive arylvinylpyridine ligands capable of solid-state cycloaddition. The azide provides a second photochemical pathway involving N_2 extrusion and nitrene formation. Substitution of the azidobenzoate ligand was used to tune its conjugation and shift its absorption toward shorter wavelengths, while increasing the conjugation of the arylvinylpyridine ligand shifted its absorption to longer wavelengths. Irradiation studies demonstrated dual photoreactivity within these crystals but showed that separation of absorption maxima alone was insufficient to achieve clean wavelength-selective reactivity. These results highlight both the potential and the challenges of designing molecular crystals with multiple independently addressable photochemical pathways.

REFERENCES

1. Kim, D.; Ullah, Z.; Seo, C.; Han, I.; Kim, H. Y.; Ihee, H. Photocycloaddition in Transition-Metal Complexes and Their Coordination Frameworks: Design, Reactivity, and Structural Insights. *Coordination Chemistry Reviews* **2026**, *563*, 218018. https://doi.org/10.1016/j.ccr.2026.218018.

Design and Reactivity of Piano-Stool Manganese Complexes Toward Bifunctional Homogeneous Catalysts for Dinitrogen Activation

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Activation and reduction of dinitrogen into ammonia using transition-metal catalysis remains challenging due to the high stability of the N_2 triple bond. A wide range of earth-abundant transition metals have been shown to capture and split N_2,[1,2] and a number of synthetic models have been studied in order to mimic the properties of the nitrogenase active site towards N_2 reduction[3]. Of active catalysts for N_2 reduction, very few manganese complexes are known.[4] In this work, we first investigated manganese(II) platforms, on whose one-electron reduction may generate an available coordination site for N_2 binding and activation. We then worked on the one-electron reduction of half-sandwich manganese(II) complexes supported by bifunctional diphosphine and N-Heterocyclic carbene (NHC) ligands having a pendant Lewis-acid moiety for potential N_2 activation.

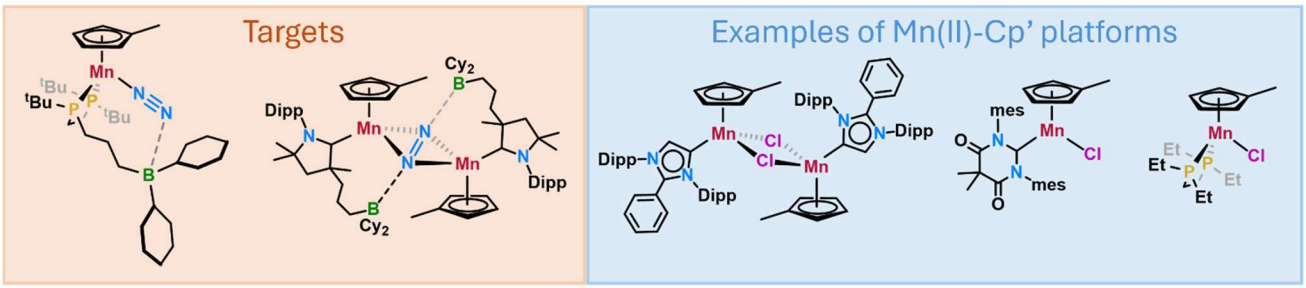

Fig. Targets with a pendant borane moiety and examples of Mn(II)-Cp' platforms synthesized

REFERENCES

1. Shima, T.; Yang, J.; Luo, G.; Luo, Y.; Hou, Z. Dinitrogen Activation and Hydrogenation by C5Me4SiMe3-Ligated Di- and Trinuclear Chromium Hydride Complexes. *J. Am. Chem. Soc.* **2020**, *142* (19), 9007–9016. https://doi.org/10.1021/jacs.0c02939
2. Reiners, M.; Baabe, D.; Münster, K.; Zaretzke, M.-K.; Freytag, M.; Jones, P. G.; Coppel, Y.; Bontemps, S.; Rosal, I. D.; Maron, L.; Walter, M. D. NH3 Formation from N2 and H2 Mediated by Molecular Tri-Iron Complexes. *Nat. Chem.* **2020**, *12* (8), 740–746. https://doi.org/10.1038/s41557-020-0483-7
3. Dean, D. R.; Bolin, J. T.; Zheng, L. Nitrogenase Metalloclusters: Structures, Organization, and Synthesis. *J. Bacteriol.* **1993**, *175* (21), 6737–6744. https://doi.org/10.1128/jb.175.21.6737-6744.1993
4. Le Dé, Q.; Valyaev, D. A.; Simonneau, A. Nitrogen Fixation by Manganese Complexes – Waiting for the Rush? *Chem. – Eur. J.* **2024**, *30* (39), e202400784. https://doi.org/10.1002/chem.202400784

Investigation of Hydrogen Bonding in two Component Cocrystals Containing Carboxylic Acids

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Cocrystallization is a strategy in crystal engineering and pharmaceutical solid-state chemistry for accessing new crystalline phases to alter various physiochemical properties through noncovalent interactions. Despite advances in crystal engineering, cocrystal formation often remains serendipitous, as the roles of functional group complementarity, intermolecular interaction hierarchies, and pKa differences in directing consistent solid-state assembly are not yet fully understood.[1] To investigate these factors, synthesis and structural characterization of two molecular cocrystals: a 1:1 cocrystal of 2-nitrobenzoic acid and *m*-toluic acid, and a multicomponent benzamide and trimesic acid cocrystal, were conducted. Powder X-ray diffraction identified phase purity of the new crystalline phases, and single crystal X-ray diffraction allowed for full structural characterization. While the 2-nitrobenzoic acid and *m*-toluic acid system forms a stoichiometric 1:1 cocrystal stabilized by carboxylic acid hydrogen bonding, crystallization of benzamide with trimesic acid preferentially forms a 2:1 cocrystal regardless of reaction stoichiometry using a 3:1 and 5:1 benzamide rich condition. These results highlight how hydrogen bond directionality and molecular conformation can supersede solution composition in determining solid-state structure, principles, which are important to rational pharmaceutical cocrystal design.

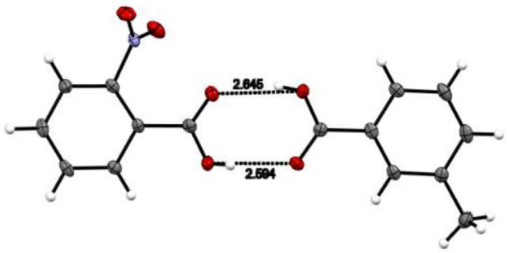

Figure 1. Molecular structure of the 1:1 cocrystal formed between 2-nitrobenzoic acid and *m*-toluic acid, highlighting the O-H···O hydrogen bonding.

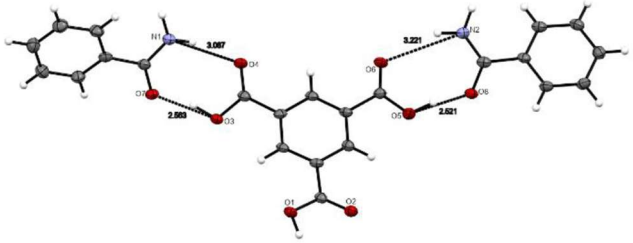

Figure 2. Molecular structure of the 2:1 benzamide and trimesic acid cocrystal showing the hydrogen bonding network between carboxylic acid groups of trimesic acid and the amide functional groups of benzamide.

REFERENCES

1. Kavanagh, O.N. et al. (2019a) 'Pharmaceutical cocrystals: From serendipity to design to application', Drug Discovery Today, 24(3), pp. 796–804. doi:10.1016/j.drudis.2018.11.023.

Hydridoaluminastibanes: A New Class of Al–Sb Bonded Main-Group Compound

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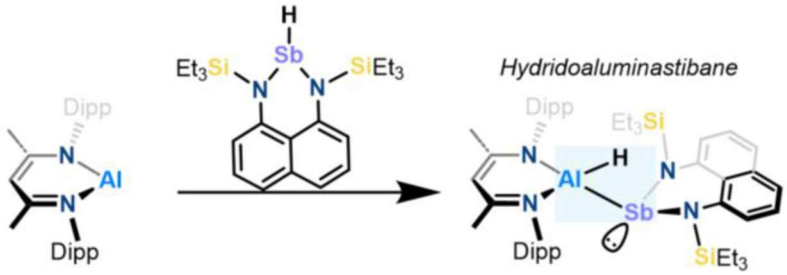
Heterometallic bonds are intriguing as differences in electronegativities of the elements and differing orbital energies/sizes display unusual reactivity. Al–Pn bonds, where Pn = Sb, Bi, are especially interesting given the significant difference between the more concentrated 3p orbitals of Al and the more diffuse 5p/6p orbitals of the heavy pnictogens, limiting effective overlap. Despite this, a diverse library of Al–Pn compounds (Pn = Sb, Bi) have been prepared. Due to their inherent instability, these compounds often feature donor/acceptor stabilization. There are a limited number of synthetic rounds to access Al–Pn covalent bonds. These include: elimination, (dehydrosilylation of acid/base protected alanes and pnictanes)[2] and oxidative addition of Pn–Pn or Pn–Cl bonds at an Al(I).[3] Overall, these demonstrate that Al–Pn bond formation is possible, while highlighting the limited strategies available. In this work, reactions of an Al(I) center with Sb–Cl, Bi–Cl and, notably, Sb–H reagents afford a family of Al(III) compounds featuring aluminum-halide and -hydride bonds. The Sb–H reaction is particularly interesting, with the simultaneous formation of Al–Sb and Al–H bonds giving the first hydridoaluminastibane, establishing a previously unknown Sb–Al–H functional group. These results introduce pnictogen hydride oxidative addition as a new strategy for Al–Sb bond formation, expanding the reactivity landscape of hydrostibination.



REFERENCES

1. Schulz, S.; Nieger, M. Reactivity of Aluminum Trialkyls R3Al, Diorganoaluminum Chlorides R2AlCl (R = Me, Et, t-Bu), and Me2AlH toward Sb(SiMe3)3: Synthesis and Structural Characterization of Al−Sb Compounds Containing σ or Dative Bonds. *Organometallics* **1999**, *18* (3), 315–319. https://doi.org/10.1021/om980824d
2. Schulz, S.; Nieger, M. [Me2AlBi(SiMe3)2]3—The First Structurally Characterized Organometallic Compound Containing a Bond between an Element of Group 13 and Bi.
3. Ganesamoorthy, C.; Bläser, D.; Wölper, C.; Schulz, S. Temperature-Dependent Electron Shuffle in Molecular Group 13/15 Intermetallic Complexes. **2014**. https://doi.org/10.1002/

Tin(II) Covalency in Alkali Metal Fluorides and Chlorides

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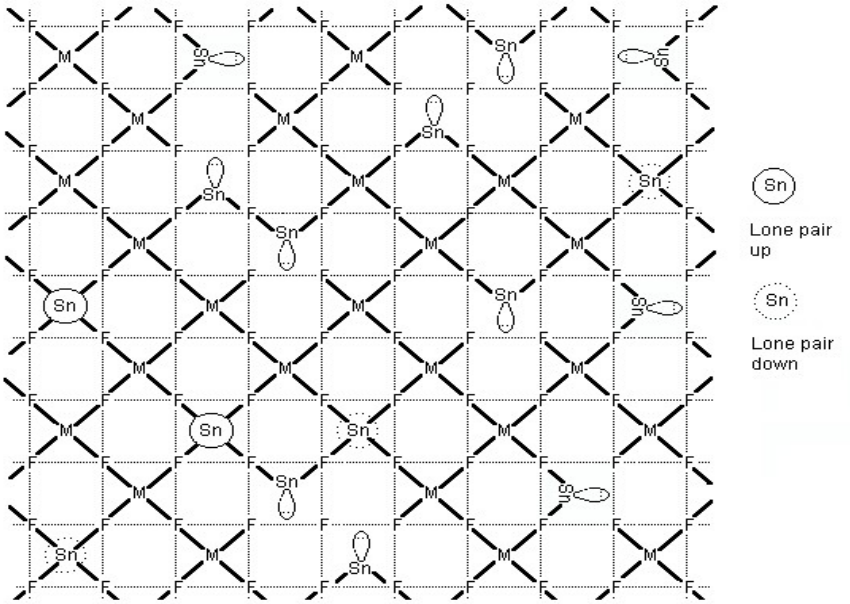
The study of the materials formed between SnF_2 and MF_2 (M = Pb or alkaline earth metal) was carried out in our laboratory and resulted in a wealth of new materials that are high performance fluoride ion conductors (1). In addition, the reaction of SnF_2 with $BaCl_2.2H_2O$ in aqueous solution was investigated. It resulted in precipitation at all molar ratios of the two reactants. This study was focused on the results obtained at low molar ratio (<0.5) of barium chloride in the reaction mixture. For the lowest barium ratios, $BaSn_2F_6$ was obtained. This compound had been prepared earlier by precipitation from aqueous solutions of barium nitrate and stannous fluoride. At higher barium chloride molar ratios, still lower than 0.5, a hitherto new compound, $BaSn_2Cl_2F_4$ was obtained. Both compounds precipitate in the form of a fine powder. Neither could be recrystallized to form single crystals and both decompose on heating. The presentation will show the detailed study of the two compounds, using X-ray powder diffraction and ^{119}Sn Mössbauer spectroscopy, the latter for identifying the mode of tin bonding.

REFERENCES

1. G. Dénès, T. Birchall, M. Sayer and M.F. Bell, *Solid State Ionics* **1984**, *13*, 213-219.
2. G. Dénès and A. Muntasar, *Hyperf. Interact*. **2004**, *153*, 121-141.



Palladium(II) Extraction and Recovery Using a Novel Non-Ionic Hydrophobic Deep Eutectic Solvent

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The development of alternative solvents capable of replacing conventional organic extraction media is an important objective in sustainable chemistry. In this context, a novel non-ionic hydrophobic deep eutectic solvent (HDES) was developed using a simple and low-impact preparation approach and investigated for the selective extraction and recovery of palladium(II) from acidic aqueous solutions. The optimal experimental conditions were established to evaluate the efficiency and selectivity of the extraction process. The results demonstrated a high Pd(II) extraction efficiency of approximately 99.8%, together with good stability and sustained performance over repeated extraction-stripping cycles. Complementary ICP-OES, FTIR, NMR, and UV-Vis analyses, together with thermal and physicochemical characterization, were used to investigate the properties of the HDES and its extraction behavior. The influence of the aqueous chemical environment and temperature, combined with spectroscopic and thermodynamic investigations, provided insights into the interactions governing Pd(II) transfer between the aqueous and hydrophobic phases. The developed HDES provides a promising alternative extraction medium to conventional organic solvents and ionic liquids for the recovery of palladium from acidic chloride media, contributing to the development of more sustainable approaches for valuable-metal separation and recycling.

REFERENCES

1. Tomasz Michałek, Volker Hessel and Marek Wojnicki, *Materials*, **2024**, *17*, 1–20.
2. M. Wang, R. Liang, L. Kou, X. Cao and D. Chen, *Environ. Sci. Nano*, **2024**, *12*, 924–935.
3. J. Wang, W. Xu, H. Liu, F. Yu and H. Wang, *Miner. Eng.*, **2021**, *163*, 106798.
4. H. Rajapakse, R. Raviadaran and D. Chandran, *Results in Engineering*, **2025**, *26*, 105188.

Chromophore Expansion Enables Molecular Solar Thermal Energy Storage in a Cd(II) Coordination Compound

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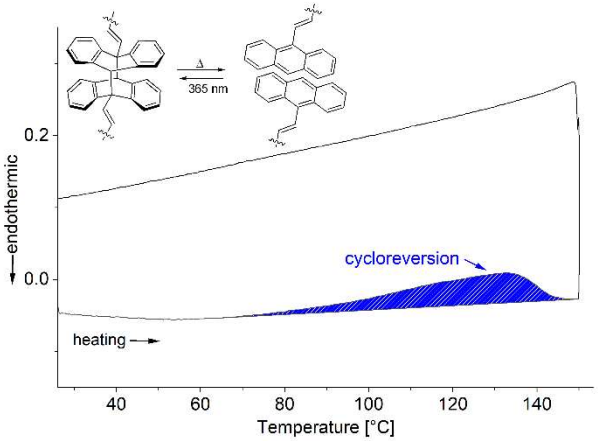

Molecular solar thermal (MOST) energy storage relies on reversible photochemical reactions that capture light energy in chemical bonds and release it as heat. Here, we demonstrate how systematic chromophore expansion enables MOST energy storage in a crystalline Cd(II) coordination compound. A family of structurally related binuclear cadmium(II) pseudo-paddlewheel complexes, $Cd_2(4\text{-IBz})_4(4\text{-ArVP})_4$ (4-IBz = 4-iodobenzoate; 4-ArVP = arylvinylpyridine), was investigated to establish the influence of chromophore size on solid-state photochemical reactivity. Expanding the aromatic system from phenyl to naphthyl to anthryl produces distinct absorption profiles, photochemical pathways, and mechanical responses while retaining a common coordination motif. Upon irradiation, the phenyl- and naphthyl-containing complexes undergo [2+2] cycloaddition, accompanied by markedly different mechanical responses. In contrast, the anthracene-containing complex undergoes single-crystal-to-single-crystal [4+4] photodimerization, forming a metastable photoproduct that releases stored energy through exothermic thermal cycloreversion. This reversible transformation can be repeated over multiple photochemical charging and thermal discharging cycles, demonstrating the potential of the coordination crystal for MOST energy storage. These findings establish chromophore expansion as an effective strategy for introducing reversible energy-storage functionality into photoresponsive coordination crystals.

REFERENCES

1. Feng, J.; Pham-Tran, V. N. P.; Mandarino, B. N.; Owens, K. R.; Protic, O. R.; Elliot, W. R.; Pallister, P. J.; Marczenko, K. M. *Mater. Chem. Front.,* **2026**, In Press.

Innovative Molecular Materials Combining Optical and Luminescent Monitoring of the Thermal Experience of their Environment

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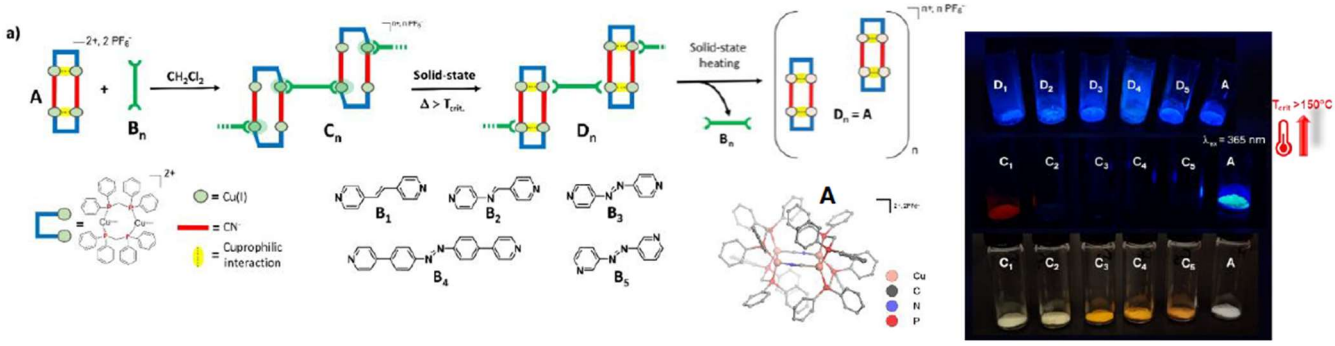
Growing attention is being directed toward molecular assemblies based on the Cu(I) ion as promising photoluminescent materials for lighting and stimuli-responsive sensing applications.[1] This interest arises from their diverse photophysical behaviors, as well as the remarkable flexibility of the coordination environment offered by Cu(I)-based derivatives. We recently reported a series of one-dimensional coordination polymers constructed from photoactive Cu_4 luminescent Cu(I) subunits[2] interconnected by N-capped ditopic linkers.[3] These materials exhibit original, irreversible yet non-destructive solid-state thermal transitions in their luminescence properties, offering attractive prospects for the design of innovative solid-state temperature sensors.

In the present contribution, we extend this approach to new systems capable of both real-time optical monitoring and a posteriori luminescent detection of threshold temperature crossing. Furthermore, the reversibility of these thermally induced transitions, enabling material reusability, will also be addressed.



REFERENCES

1. a) Yam, V. W.-W.; Au, V. K.-M.; Leung, S. Y.-L. *Chem. Rev*. **2015**, *115*, 7589; b) Czerwieniec, R.; Leitl, M. J.; Homeier, H.H.H.; Yersin, H. *Coord. Chem. Rev*. **2016**, *325*, 2; c) Kobayashi, A.; Kato, M. *Chemistry Letters* **2017**, *46*, 154; d) Lescop, C. *Acc. Chem. Res.,* **2017**, *50*, 885.
2. Lescop, C. et al. a) *Chem. Rec*. **2021**, *21*, 544; b) *Inorg. Chem. Front*., **2023**, *10*, 6976.
3. Lescop, C. et al. a) EP3820929, **2020**; b) *Adv. Opt. Mat*. **2024**, 2024, 20, 240034; c) *Inorg. Chem. Front.,* **2025**, *12*, 8460.

A Reversible System Array to Detect Saccharides from Boronic Acids and Alizarin Red

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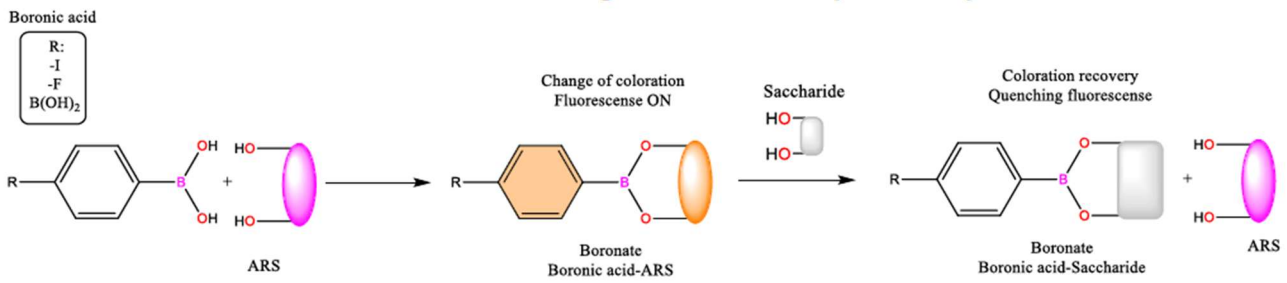
Molecular recognition is a process in which molecules identify and selectively bind to other molecules due to the complementarity of their chemical structures.[1] There are a lot of interest in the investigation of new compounds that act as molecular receptors capable of detecting and responding to various molecules in their environment. Boronic acids have been widely used to interact and detect different saccharides,[2] which play a fundamental role in multiple biological processes and have relevant industrial applications.[3] In this study, boronates (4-fluorophenylboronic acid derivatives, 4-iodophenylboronic acid and 1,4-benzenediboronic acid) were used in a system with alizarin red for the detection of saccharides (fructose, glucose and galactose). In aqueous solution at pH 7.4, alizarin red presents a purple coloration; however, upon interaction with boronic acid, a boronate is formed that changes the color of the solution to orange and generates fluorescence; subsequently, after the addition of some saccharide, the formation of a boronate complex between boronic acid and saccharide is occurs, which restores the purple color of alizarin and extinguishes the fluorescence (Scheme 1). The association constants were calculated by absorption and emission thus evaluating the formation of the compounds. A wavelength was monitored at λ = 464 nm, showing a hypsochromic shift from λ = 510 to 464 nm. Subsequently, upon formation of the new complex with the saccharides, a bathochromic shift from λ = 464 to 510 nm was recorded, demonstrating the reversibility of the system.



Scheme 1. Schematic representation of the indicator displacement sensing mechanism based on the boronic acid-Alizarin Red S system for saccharide detection.

REFERENCES

1. Samuel H. Gellman; Introduction: Molecular Recognition. Chem. Rev. 1231–1232. 1997.
2. Xin Wu, Zhao Li, John S. Fossey. Chem. Soc. Rev., 2013, 42, 8032-8038.
3. Yui Sasaki, Zhoujie Zhang and Tsuyoshi Minami. ChemComm. 2017, 53, 6561-6568.

Structural Investigation of $YbCo_3NiSb_{11}Te$ Skutterudite by Powder and Single Crystal X-ray Diffraction

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Skutterudites have a body-centered cubic crystal structure. The general formula of binary skutterudites is TX_3, where T = Co, Rh, or Ir, and the pnictogen X = P, As, or Sb. This family of materials is well known for its ability to directly convert heat into electrical energy, a property characteristic of thermoelectric materials[1]. Cobalt triantimonide (Co_4Sb_{12}) has voids that can be partially filled with rare-earth, alkaline-earth, or other suitable elements. Additionally, Co sites can be doped with Fe or Ni, while Sb sites can be doped with Te, Se, and Ge. Fillers can enhance phonon scattering through resonance and mass-fluctuation mechanisms arising from differences in atomic masses and vibrational frequencies. However, these effects are strongly influenced by the filler chemistry and the composition of the TX_3 framework. Furthermore, doping at Co sites modifies the electronic structure and lowers the thermal conductivity[2]. The flux-growth method is known for facilitating the growth of single crystals from metallic fluxes. One of the advantages of investigating single crystals is the elimination of effects caused by grain boundaries. In this work, the $YbCo_3NiSb_{11}Te$ sample was synthesized using 95 at.% Sb as the flux. The sample was encapsulated in a Canfield alumina crucible set and sealed in a silica tube under vacuum. It was kept in the furnace at various temperatures for different durations. Finally, the obtained material was taken out of the furnace at 740 °C and centrifuged immediately[3]. Phase identification was performed through powder X-ray diffraction (PXRD) on a PANalytical X'Pert Pro diffractometer with a Co-Kα radiation source (λ= 1.789 Å) and X'Celerator detector. Rietveld refinement was performed using Rietica software[4]. Single-crystal X-ray diffraction (SCXRD) was performed on a STOE IPDS II diffractometer with a Mo-Kα radiation source (λ= 0.71073 Å) over the range of $3.81 \leq 2\theta \leq 70.56°$. The crystal structure was solved and refined using SHELXL (full-matrix least squares) in the Olex2 v1.5 software[5]. The lattice parameters obtained by powder X-ray and single-crystal X-ray diffraction refinement of $YbCo_3NiSb_{11}Te$ differed by approximately 0.12%, which shows good agreement between the two approaches.

REFERENCES

1. Rogl, G. *Crystals* (2022); https://doi.org/10.3390/cryst12121843.
2. Popescu, B. *Physica B* (2026); https://doi.org/10.1016/j.physb.2026.418741.
3. P.C. Canfield, Z. Fisk. *Phil. Magos. B* (1992); 65, p. 1117.
4. Hunter B. *International Union of Crystallography Commission on Powder Diffraction Newsletter* (1998); 20, (Summer).
5. Dolomanov, O.V. *Journal of Applied Crystallography* (2009); http://dx.doi.org/10.1107/S0021889808042726

N-Heterocyclic Carbene-Functionalized Au@SiNPs and Ag@SiNPs as Active and Recyclable Hybrid Catalysts for Environmental Depollution

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Silica nanoparticles (SiNPs) have been widely used as heterogeneous supports to immobilize catalysts due to the many advantages they offer.[1,2] Furthermore, this immobilization enables easy separation, purification and reusability of the catalysts which is in agreement with green chemistry principles. Catalysts that can be used in these types of systems are metallic nanoparticles (MNPs), more specifically, gold nanoparticles (AuNPs) and its comparatively less explored homologue, silver nanoparticles (AgNPs). In fact, AuNPs and AgNPs are versatile materials with applications across numerous fields where their exceptional activity and multifunctional nature make them particularly attractive as catalysts.[3,4] However, the extremely small size of conventional AuNPs and AgNPs (typically ~ 2-5 nm) renders their recyclability challenging. To circumvent this issue, we present the covalent immobilization of AuNPs and AgNPs on SiNPs via mesoionic *N*-heterocyclic carbenes (*m*NHCs) linkers as they have established themselves as versatile ligands to stabilize MNPs due to the NHC-M bond strength that is 2 times stronger than the S-M bond leading to higher stability of the MNPs. The catalytic activities of the Au@SiNP and Ag@SiNP materials are characterized by the reduction of 4-nitrophenol, as an example of a common environmental pollutant, highlighting their use in environmental remediation. Our approach stands out as every reaction is done at the SiNP surface enabling easy separation and purification.

REFERENCES

1. Rachel ee, P.L. et al. *Front. Chem.* ***2020*****, 8,** 602.
2. Sun, W., A. Ozin, G. et al. *Chem. Catal*. **2022, 2**, 1893-1918.
3. Azizi, S., Sun, H. et al. *Cryst. Growth Des*. **2025, 25**, 2227-2266.
4. Magdy, G. et al. *Microchem. J*. **2024,196**, 109615.

A Nickel-Capped Calcium Hydride: Implications for Diene Hydrometalation

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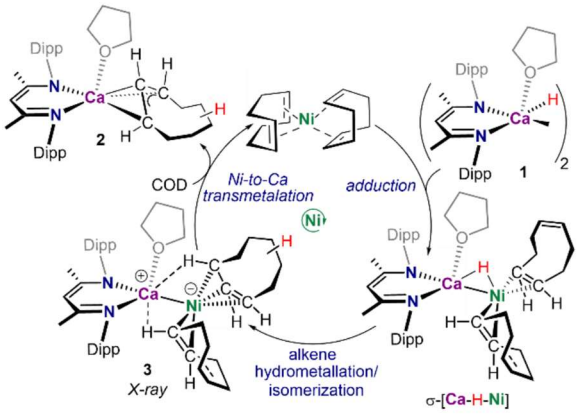
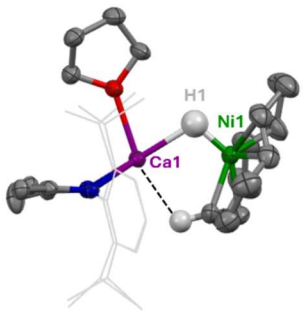
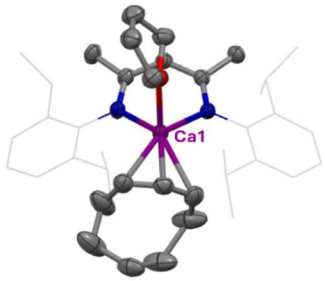
The reactivity of nickel-containing heterobimetallic hydride complexes can be leveraged for use in small molecule activation.[1] These complexes often involve complex cooperative interactions between the two metals, making it difficult to deduce their reaction mechanism. However, isolating intermediates along these pathways can reveal valuable insight into the synergistic cooperativity between the two metal centers as they work together to convert substrate to product. Generally, small molecule activation reactions result in the formation of σ-bond complex intermediates. These complexes involve electron donation from a σ-bond into the metal center, resulting in a 3c–2e interaction.[2] Heterobimetallic Ni–H–Al σ-bond complexes has been relatively well studied, however analogous complexes utilizing s-block alkali earth metals remain essentially unknown.[3] This work presents the first fully characterized Ca–H–Ni heterobimetallic σ-complex followed by a proposed mechanism showcasing the synergistic cooperation between Ni and Ca in diene hydrometallation.







REFERENCES

1. Zurakowski, J.A, Stadler, B., Drover, M. W., Crimmin M. R. *Angew. Chem. Int. Ed.*, **2025**, *64* (36)
2. Crabtree, R. H. *Angew. Chem. Int. Ed.*, **1993**, *32* (6), 789-805
3. Gawron, M.; Wolf, R. *Chem. Sci.*, **2026**, *17* (39), 18494–18517.

Completion of the 7-Halo-1,3,5-triazaadamantane Series: Organometallic Synthesis of 7-Fluoro-1,3,5-triazaadamantane

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Bridgehead-halogenated 1,3,5-triazaadamantanes (X-TAA) are rigid organic cages of C_{3v} symmetry. Unlike in the tetrahedral parent adamantane, the lowered symmetry of the TAA framework produces a permanent molecular dipole whose magnitude and direction are modulated by the bridgehead substituent. The chloro and bromo derivatives were first reported by Kuznetsov in 1985 *via* Sandmeyer chemistry[1] and were crystallographically characterized for the first time by our group.[2] While most polar molecules crystallize in nonpolar space groups, here, the rather rare polar space group R3m was adopted. The fluoro member of the series is a new molecule and has remained inaccessible under Sandmeyer conditions. We report the synthesis of 7-fluoro-1,3,5-triazaadamantane (F-TAA) by a silver-mediated organometallic route inspired by the work of Wang et al.[3] Treatment of Br-TAA with AgF in the presence of PPh_3 effects bridgehead fluorination, furnishing F-TAA, which has been isolated and characterized by ^{1}H and ^{19}F NMR spectroscopy, and successfully crystallized in the desirable R3m space group. The F-TAA unit cell is the shortest (in c-direction) of all X-TAA in R3m. Our current work targets mixed-halide cocrystals in the polar R3m space group for applications leveraging their polar structures.

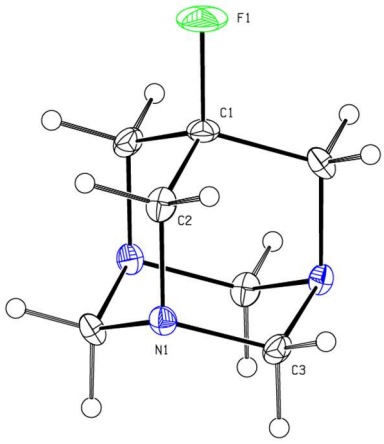

Figure 1. Crystal structure of F-TAA

REFERENCES

1. Kuznetsov, A. I.; Kosmakov, V. A.; Unkovskii, B. V. Chem. *Heterocycl. Compd.* **1985**, *21*, 697–700. https://doi.org/10.1007/BF00515076.
2. Abdur-Rashid, K.; Saha, S. K.; Mugisha, J.; Teale, S.; Wang, S.; Saber, M.; Lough, A. J.; Sargent, E. H.; Fekl, U. *Chem. Eur. J.* **2024**, *30*, e202302998. https://doi.org/10.1002/chem.202302998.
3. Wang, Z.-Y.; Freas, D. J.; Fu, G. C. *J. Am. Chem. Soc.* **2023**, *145* (46), 25093–25097. https://doi.org/10.1021/jacs.3c11042.

Accessing the Secondary Coordination Sphere for Nitrogen Activation

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Activation of dinitrogen (N_2) and concomitant functionalization is an essential industrial reaction, dominated by the Haber Bosch process, taking elemental N_2 and converting it to ammonia.[1] Due to the industrial requirement of intense temperatures and pressures, chemists have targeted viable, lower energy pathways for conversion, through use of transition metal (TM) complexes. Inspiration for activation of N_2 can be drawn from nature, with the nitrogenase enzyme being capable of room temperature ammonia generation utilizing an Fe and Mo based cofactor.[2] Model system work has often relied on understanding of reduced metal sites incorporating Mo, Fe and/or W, with low oxidation states to allow for optimal back bonding;[3] but minimal work has been done employing higher oxidation states Fe. The nitrogenase enzyme can access a variety of oxidation states, including Fe(II),[4] thus understanding how higher oxidation state Fe centres can work cooperatively with exogenous groups is essential for understanding of N_2 activation in analogous systems. Herein we present work towards activation of N_2 and hydrazine bearing an Fe(II) centre, supplemented by an outer sphere intramolecular Lewis acid to generate a “push-pull” type interaction. Computational insight complements experimental findings, demonstrating thermodynamic favourability of activating nitrogen based small molecules with different appended Lewis acids.

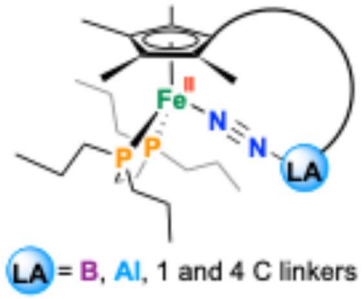

Figure 1. Generic scaffolding employing an oxidized Fe(II) centre with an appended Lewis acidic group targeting dinitrogen activation.

REFERENCES

1. Zhang, S.; Zhao, Y.; Shi, R.; Waterhouse, G. I. N.; Zhang, T. *EnergyChem* **2019**, *1* (2), 100013.
2. Hoffman, B. M.; Lukoyanov, D.; Yang, Z.-Y.; Dean, D. R.; Seefeldt, L. C. *Chem. Rev.* **2014**, *114* (8), 4041–4062.
3. Coffinet, A.; Simonneau, A.; Specklin, D. In *Encyclopedia of Inorganic and Bioinorganic Chemistry*; Scott, R. A., Ed.; Wiley, 2020; pp 1–25.
4. Wenke, B. B.; Spatzal, T.; Rees, D. C. *Angew. Chem. Int. Ed.* **2019**, *58* (12), 3894–3897.

Synthesis and Coordination Chemistry of NONO-Calix[4]arene Ligands

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Les calix[4]arènes sont des macrocycles rigides qui présentent une grande polyvalence de fonctionnalisation; cela en fait d'intéressantes plateformes pour le développement de nouveaux ligands. L'introduction de fonctions azotées permet de modifier l'environnement du centre métallique et d'envisager des applications en catalyse.

Dans le cadre de ce projet, plusieurs ligands NONO calix[4]arènes ont été préparés par l'amination d'Ullmann à partir du calix[4]arènes 1,3-bis(triflate). Un premier ligand achiral a été préparé à partir de du N,N-diméthyléthylènediamine. Un second ligand a été obtenu à partir du (1S,2S)-N,N-diméthyl-1,2-cyclohexanediamine; ce dernier étant chiral. Les produits obtenus ont été caractérisés par RMN. Ces ligands ont été utilisés dans la préparation de complexes de cuivre, de chrome et de zirconium; ceux-ci furent ensuite étudiés et identifiés par diffraction des rayons-X sur monocristal.

Ces travaux mettent en valeur la polyvalence de l'amination de Ullmann dans la préparation de ligands NONO calix[4]arènes et ouvrent la voie au développement de complexes chiraux présentant un bon nombre d'applications en catalyse stéréosélective.

REFERENCES

1. HENNRICH, G et Al. *Chem. Commun.* **2005**. 2747-2749.
2. FUJITA, J. et Al. *Appl. Phys. Lett.* **1996**. 68, 1297-1299.
3. GUTSCHE, D. C. et Al. *J. Am. Chem. Soc.* **1981.** 103, 3782-3792.
4. RAWAT, V. et Al. *Org. Biomol. Chem.* **2015**. 13, 11189.
5. NAKAMURA, Y. et Al. *J. Org. Chem.* **2011**. 76, 2168-2179.

Control of Electronic Correlation in Metal-Radical Complexes for Biomimetic Catalysis

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In coordination chemistry, non-innocent ligands are redox-active coordinating species that make formal oxidation state assignments in the complex ambiguous. An example of such a ligand is one that contains an arylnitrosyl radical anion ($ArNO^{\bullet-}$).[1–3] This research focuses on the reaction of a multidentate hydroxylamine (ArNHOH)-containing ligand with transition metal salts and the characterization of the ensuing reaction pathways. Hydroxylamines exhibit a rich amphiredox profile upon coordination to transition metals due to the nitrogen atom's ability to access a wide range of oxidation states from +III in nitro groups ($ArNO_2$) to -III in amines ($ArNH_2$).[1,3] With Fe salts, the hydroxylamine ligand disproportionates to generate an ArNH2-containing Fe complex and a (κ*N*-ArNO)-containing Fe complex. Careful examination of the ArNO complex reveals that its electronic structure is that of a low-spin Fe(III) species coordinated to an arylnitrosyl radical anion ($ArNO^{\bullet-}$). Contrary to the reaction with Cu,[3] which also exhibits κ*N* coordination of the radical, *ab initio* calculations indicate a strong correlation between the Fe and nitrosyl electrons, which is supported by a fully diamagnetic ^{1}H NMR. The properties will be discussed, especially upon counterion changes as these modify the Fe-NO interaction. Thus, the non-innocence redox the N−O bond stabilizes unusual electronic structures that cannot be described by simple oxidation state assignments. This fundamental investigation is necessary to establish a thorough understanding of the structural, electronic, and redox properties of correlated metal-radical complexes before exploring their potential as bioinspired catalysts that mimic the two-electron transformations performed by metalloenzymes such as galactose oxidase and glyoxal oxidase.

REFERENCES

1. Zsombor-Pindera, J.; Effaty, F.; Escomel, L.; Patrick, B.; Kennepohl, P.; Ottenwaelder, X. *J. Am. Chem. Soc.* **2020**, *142* (45), 19023.
2. Singh, H.; MacKay, A.; Sheibany, N.; Chen, F.; Mosser, M.; Rouet, P.-E.; Rousseau, F.; Askari, M. S.; Ottenwaelder, X. *Chem Commun* **2021**, *57*, 10403.
3. MacKay, A.; Zsombor-Pindera, J.; Effaty, F.; Sheibany, N.; Gennarini, F.; Habibian, M.; Chen, F.; Askari, M. S.; Brytskyi, M.; Kroeker, S.; Kennepohl, P.; Ottenwaelder, X. *Inorg. Chem.* **2026,** *65*, 3, 1837.

The Strength of Chalcogen Bonding Controls the Reactivity of Benzo-1,2-Chalcogenazole 2-Oxides

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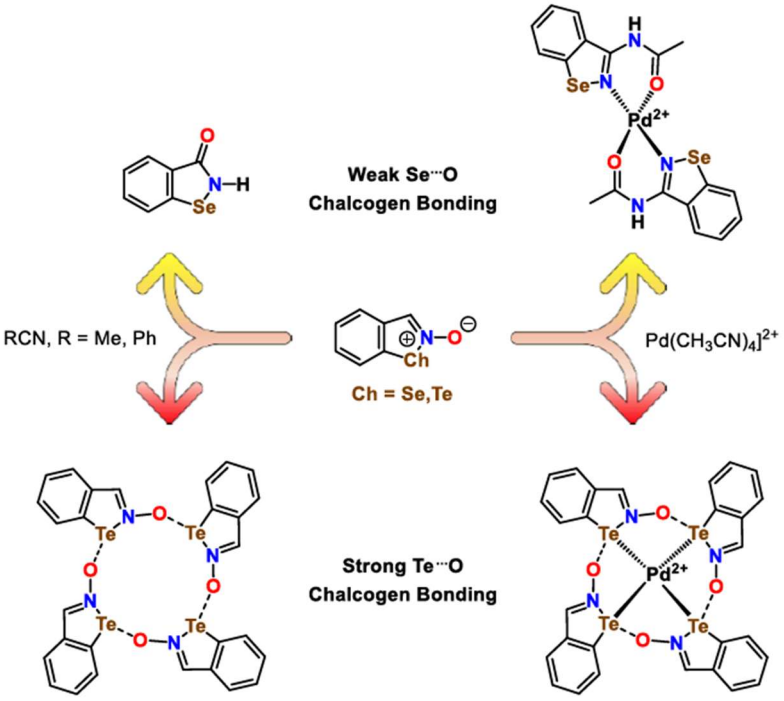
Despite being isoelectronic and isostructural, benzo-annulated iso-selena- and iso-tellurazole *N*-oxides[1] displayed remarkable differences in reactivity.[2] When exposed to $[Pd(CH_3CN)_4](BF_4)_2$, the selenium derivative quickly underwent addition to the coordinated molecule of acetonitrile; a subsequent rearrangement produced the homoleptic complex of Pd(II) with the acetamide of 3-amino-benzo-iso-chalcogenazole. The same heterocycle isomerised slowly to the corresponding iso-selenazolone upon heating in solution. In sharp contrast, the tellurium congener reacted by assembling the Pd(II) complex of its macrocyclic chalcogen-bonded tetramer and was indefinitely stable in boiling aceto- and benzonitrile. The products of these reactions were structurally authenticated by single-crystal X-ray diffraction. DFT calculations indicate that the thermodynamic drive and activation barriers for the reactions observed with the selenazole *N*-oxide are nearly the same for the tellurium compound. The implication is that while the isomerization and the addition to acetonitrile are the thermodynamically preferred processes, the strength of the Te···O chalcogen bond imposes a significant barrier that the weaker Se···O interactions cannot.



REFERENCES

1. P. C. Ho, J. Rafique, J. Lee, L. M. Lee, H. A. Jenkins, J. F. Britten, A. L. Braga and I. Vargas-Baca, *Dalton Trans.*, 2017, **46**, 6570–6579.
2. P. C. Ho, M. W. Zeng, A. M. Fox, and I. Vargas-Baca, submitted.

Tuning NCN Pincer Ligands for Hypercoordinated Organotin Monomers and Soluble Polystannanes

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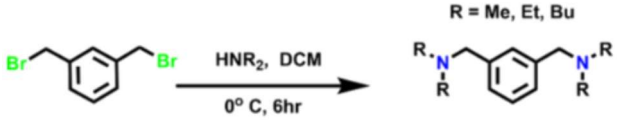
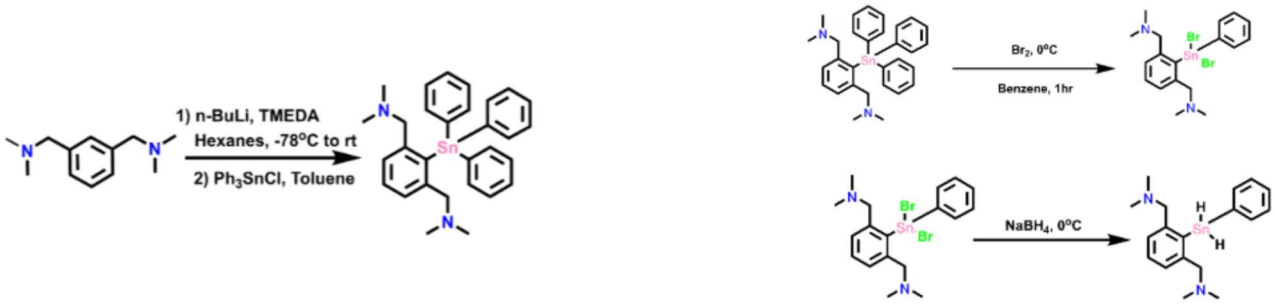
Polystannanes are organometallic polymers with σ-conjugated Sn–Sn backbones, offering potential for optical and electronic applications.[1,4] However, sensitivity to light, oxygen, and moisture, alongside poor solubility, limits their practical use.[1,2] Recent work within the Foucher group has improved stability through chelating donor ligands that enforce hypercoordinate geometries at tin centres.[2,3] However, polymerization has yielded molecular weights below 40 kDa.[2] This work investigates NCN pincer ligands bearing methyl, ethyl, and butyl substituents to address stability and solubility. Intramolecular N to Sn coordination is intended to protect the backbone, while longer nitrogen-bound alkyl groups are expected to improve solubility during polymerization and processing. The dimethyl and diethyl ligands were synthesized in 21% and 54% yields, respectively, and characterized by ^{1}H NMR spectroscopy. Initial organotin synthesis produced mixtures, as indicated by ^{119}Sn NMR spectroscopy. A revised route retaining an aryl bromine between the aminomethyl arms is being explored to control tin attachment through bromine–lithium exchange. This approach aims to produce stable, soluble polystannanes for optical and electronic materials.



Scheme 1. Original and revised synthetic routes to NCN pincer ligands bearing methyl, ethyl, and butyl substituents.



Scheme 2. Proposed synthesis of an NCN-supported organotin dihydride monomer through lithiation, tin incorporation, brominolysis, and reduction.

REFERENCES

1. Caseri, W. *Chemical Society Reviews* **2016**, *45* (19), 5187–5199.
2. D'Amaral, G. M.; Bender, D. N.; Piccolo, N.; Lough, A. J.; Gossage, R. A.; Foucher, D. A.; Wylie, R. S. *Inorganics* **2024**, *12* (4), 122.
3. Khan, A.; Foucher, D. *Coordination Chemistry Reviews* **2016**, *312*, 41–66.
4. Gon, M.; Tanaka, K. *Smart Mol.* **2025**, *4*, e20240064.

Mild Esterification of (8-(dimethylamino)naphthalen-1-yl)phosphonic acid

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Phosphorylation – the transfer of a phosphoryl (PO_3^-) group to an acceptor molecule – is a fundamental process of biochemistry, involved in the biosynthesis of DNA, RNA, and phospholipids, while also being at the core of cellular energy management, through the chemistry of adenosine triphosphate (ATP). In anthropogenic chemistry, the formation of P–O–R moieties in phosphate, phosphonate, and other moieties is of great importance, notably for the preparation of pharmaceuticals, flame retardants, and agrochemicals, as well as in biomimetic processes such as artificial gene synthesis. However, whereas biochemical P–O–R-forming reactions occur through a mild reaction between a R–OH acceptor and a stable phosphate donor under enzymatic catalysis in mild conditions, anthropogenic reactions tend to be more complicated and harsher.

This is exemplified in typical approaches to the synthesis of phosphonic esters (phosphonates). While the direct reaction of an alcohol (R–OH) with a phosphonic acid ($RP(O)(OH)_2$) would afford esterified products ($RP(O)(OR)_2$ or RP(O)(OH)OR) with elimination of water, such a process is prohibitively slow under normal synthetic conditions. As a result, phosphonic esters are usually prepared through alternative pathways such as the Michaelis-Arbuzov, Michaelis-Becker, and Atherton-Todd or Clay-Kinnear-Perren reactions. Other methods include the use of chlorinated phosphorus agents or other dehydrating or coupling reagents to facilitate esterification. Phosphonic esters can also be synthesized directly from phosphonic acids, but require elevated temperatures and strong acids or bases. Herein, we report the discovery that (8-(dimethylamino)naphthalen-1-yl)phosphonic acid can be directly esterified under mild reaction conditions. Our studies suggest a novel mechanism for esterification, which will be discussed in this presentation.

Preparation and catalytic investigation of novel (NONO)-metallocali(4)arene derivatives

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(NONO)-calix(4)arenes are an emerging class of macrocyclic compounds where two of the phenolic moieties on a regular calix(4)arene are substituted, in alternate fashion, with amines, via Ulmann-type coupling. There is perceived interest in their use as tetradentate, dianionic, intermediate hardness and highly functionalized ligand platform for the preparation of metal complexes destined for applications in homogenous catalysis. The current project aims to prepare a series of various first-row transition metal compounds, characterize them via Single crystal XRD to access structural properties. Subsequently, we aim to investigate their activity in enantioselective aza-Micheal addition, Evans-Chan-Lam coupling, PLA polymerization and insertion polymerization of acrylonitrile. Current project results are discussed, most notably the synthesis of a series of Cr(III) and binuclear Cu(II) complexes.

REFERENCES

1. Nakamura, Y.; Tanaka, S.; Serizawa, R.; Morohashi, N.; Hattori, T., *J Org Chem* **2011**, *76* (7), 2168-79.
2. Rawat, V.; Vigalok, A.; Sinha, A. K.; Sachdeva, G.; Srivastava, C. M.; Rao, G. K.; Kumar, A.; Singh, M.; Rathi, K.; Verma, V. P.; Yadav, B.; Pandey, A. K.; Vats, M., *ACS Omega* **2022,** *7* (32), 28471-28480.
3. Santoro, O.; Redshaw, C., Metallocalix[n]arenes in catalysis: A 13-year update. *Coordination Chemistry Reviews* **2021**, 448
4. Gutsche, D.; Dhawan, B.; Kwang, H.N. Muthukrishnan, R. *J. Am. Chem. Soc.* **1981***, 103* (13), 3782