An Electron-Poor Nickel Diphosphine Complex: Synthesis, Structure, and Reactivity of Ni(DFppe)$_2$

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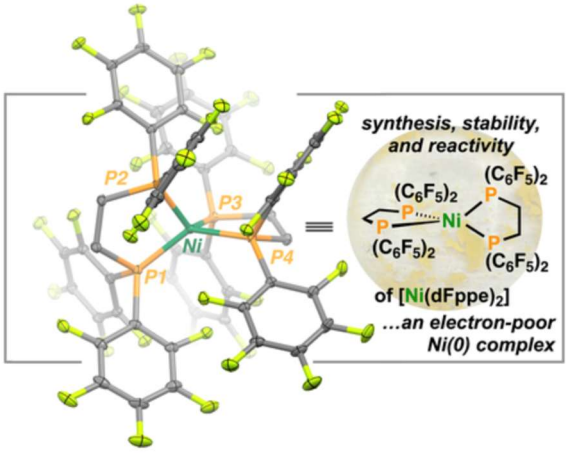
Catalysis underpins over 35% of global GDP, with catalytic processes contributing to the production of roughly 80% of all manufactured goods.[1] While most conventional catalysts contain a transition metal such as Pd, Pt, Ir, or Ru,[2] there is a growing push to employ more abundant and inexpensive first-row transition metals in pursuit of a greener and more sustainable chemical enterprise.[3,4] In this regard, air stable Ni(0) complexes have been studied as potential catalysts or precatalysts, and various strategies to stabilize Ni(0) centres have been investigated.[5–7]

Herein, we describe our effort towards the development of such a Ni(0) complex by using an electron deficient ligand 1,2-bis[bis(pentafluorophenyl)phosphino]ethane, dFppe. The target complex Ni(dFppe)$_2$ was synthesized in good yield, and characterized in both solid state and solution phase. The straightforward synthesis, easy purification, air and thermal stability, as well as reactivities of this Ni(dFppe)$_2$ complex will be discussed.



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Manganese Silene Hydride Complexes: a Novel Photochemical Synthesis, and Reactivity to Afford Vinylidene Hydride Complexes

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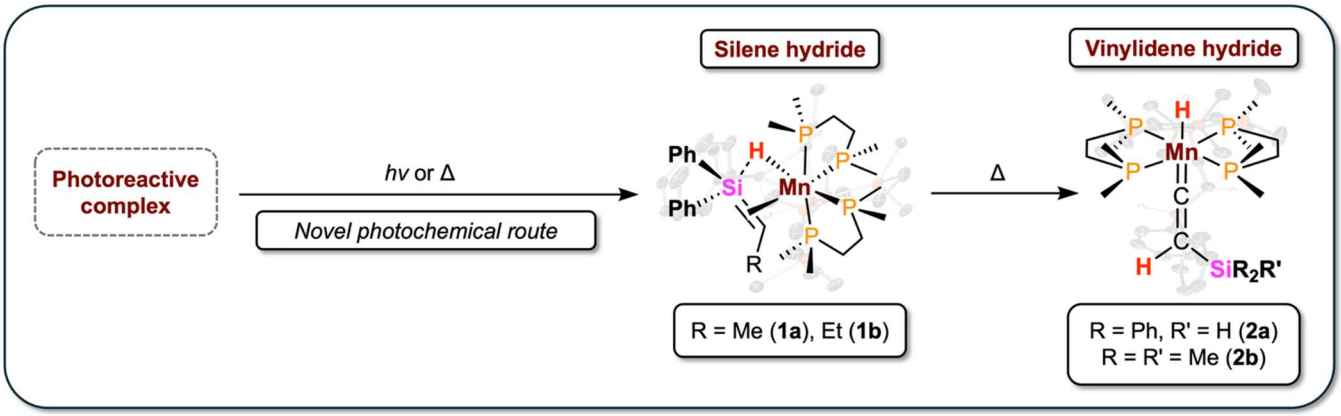
Despite potential significance in catalysis, silene complexes are poorly studied, with [(dmpe)$_2$MnH(CHR=SiR'$_2$)] (dmpe = 1,2-bis(dimethylphosphino)ethane) as the only isolated examples of first-row transition metal complexes bearing a sterically and electronically unstabilized silene ligand.[1,2] Similarly, though vinylidene complexes are considered important intermediates in various catalytic reactions, those bearing a hydride co-ligand have only been crystallographically characterized for Mo and Os.[3,4]

Manganese complexes bearing an unstabilized silene ligand and a hydride co-ligand were previously accessed in our group by reaction of a silylene hydride complex with ethylene.[1,2] Herein, we present a novel method for the synthesis of manganese silene hydride complexes (**1a, 1b**) under photochemical conditions, as well as ensuing thermal reactivity to generate the first isolated examples of first-row transition metal vinylidene hydride complexes (**2a, 2b**). Compounds **1b**, **2a**, and **2b** were spectroscopically and crystallographically characterized, and an intermediate en route to complex **1a** was identified.



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From oxide surfaces to metal–organic framework secondary building units: towards molecularly precise lanthanide sites via surface organometallic chemistry

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Surface organometallic chemistry (SOMC) is a powerful strategy for building functional solid-state materials with molecular precision. By reacting a judiciously selected molecular precursor with the surface groups of a pre-treated support material, SOMC yields well-defined surface species whose coordination environments resemble those of their molecular counterparts.[1] Critical to this method is the choice of supports as its surface is the foundation on which the active species are assembled. Oxides such as silica and alumina have historically been the supports of choice. Unfortunately, their surfaces are often amorphous and can host several types of hydroxyl groups and Lewis acidic sites, leading to a broader distribution of grafted species than intended.[2] Metal–organic frameworks (MOFs) offer a compelling alternative to oxidic materials as their secondary building units (SBUs) feature similar chemical functionalities (e.g. hydroxyl groups). Owing to the crystallinity of the framework, these hydroxyl groups serve as isolated, uniformly dispersed and structurally well-defined grafting sites that line the internal surfaces of the pores.[3] Early studies have shown that these features enable a level of precision in grafting and structural characterization methods rarely achievable on oxides.[4,5] However, the translation of SOMC principles to MOFs is still in its initial stages. The grafting of lanthanide complexes remain absent from MOF SOMC studies despite their distinctive luminescent and magnetic properties and their applications in optoelectronic, information storage, and sensing technologies.[6-8] In this presentation, I will describe our ongoing efforts to graft lanthanide(III) bis(trimethylsilyl)amide complexes, a class of canonical SOMC precursors, onto the SBU of robust Zr-based mesoporous MOFs, to advance our understanding of MOFs as SOMC supports.

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Engineering Energetic Crystals for Light-Responsive Behaviour

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The incorporation of photoresponsive molecules into energetic materials offers a potential strategy for controlling their sensitivity through light exposure. Recently, spiropyran-based photoswitches were demonstrated to reversibly modulate the impact sensitivity of conventional explosives through light exposure.[1] These findings highlight the potential for incorporating photoresponsive functionality into energetic systems.

Herein, we explore an alternative approach through the crystal engineering of candidate photoresponsive energetic materials. Organic salt formation and metalorganic coordination chemistry are investigated as routes to incorporating photoreactive functionalities into crystalline materials. Rotary crystallization is employed to obtain crystalline products suitable for structural characterization, while single-crystal X-ray diffraction is used to investigate molecular arrangements and packing interactions.

Impact sensitivity is evaluated using a BAM fall hammer to establish baseline mechanical sensitivity and support future comparisons following light exposure. Together, these investigations aim to establish relationships between crystal structure, photochemical reactivity, and energetic sensitivity, advancing the development of light-responsive energetic materials.

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