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Synthesis and Reactivity of Phosphorus Compounds with a Tridentate Ligand

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The activation of small molecules such as ammonia and hydrogen gas has attracted increasing attention from the point of view of the sustainable energy resources. Few main group organic compounds exhibit reversible redox cycles that are characteristic of transition metal complex catalysts. Recently geometrically constrained trivalent phosphorus compounds have been shown to cleave the bonds of amines, alcohols and ammonia borane to yield pentacoordinate phosphorus compounds.¹ Furthermore, the first reported planar “T-shaped” phosphorus system by Arduengo has been shown to undergo catalytic transfer hydrogenation between ammonia borane and azobenzene (Figure).¹ Thus, the chemistry of the structurally unique phosphorus species could be applied as organic catalysts enabling such transformations without expensive and toxic metals.

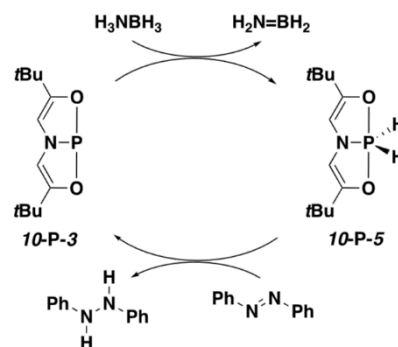
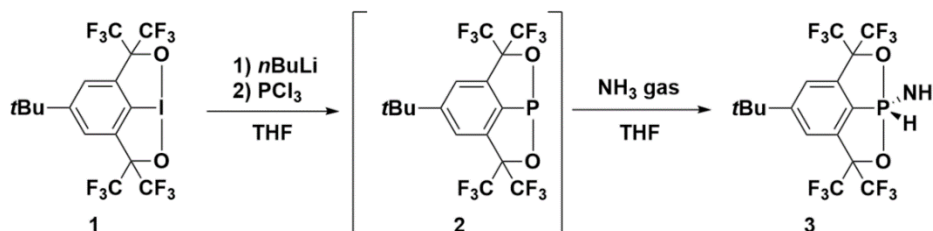


Figure. Catalytic hydrogenation

Computational studies have indicated the activations of small molecules proceed via a nucleophilic attack on the central phosphorus atom with an empty orbital and thus unusual electrophilicity of the constrained phosphorus is the key of the reactions.² In this work, we have investigated the synthesis and reactivity of a novel T-shaped phosphorus compounds with a rigid tridentate ligand bearing electron-withdrawing trifluoromethyl groups, which were expected to react with a variety of small molecules.

The lithiation of **1** with 3 equivalent of *n*BuLi followed by the installation of phosphorus atom with PCl₃ resulted in the formation of the geometrically constrained phosphorus compound **2** according to its ³¹P NMR spectrum although the isolation of **2** have not been successful yet due to its instability (Scheme). The reaction of **2** generated *in situ* with ammonia at room temperature cleaved the N-H bond to afford the pentacoordinated species **3**. The structure of **3** was confirmed by its NMR spectrum and X-ray crystallographic analysis. Further investigation of the reactivity of **2** with other small molecules is in progress.



Scheme. Synthesis and reaction of the geometrically constrained phosphorus compound **2**

Ref.

(1) N. L. Dunn, M. Ha, A. T. Radosevich, *J. Am. Chem. Soc.* **2012**, *134*, 11330–11333.

(2) S. M. McCarthy, Y.-C. Lin, D. Devarajan, J. W. Chang, H. P. Yennawar, R. M. Rioux, D. H. Ess, A. T. Radosevich, *J. Am. Chem. Soc.* **2014**, *136*, 4640–4650.