

Oxidative Addition of E-H Bonds by Low-Symmetry Phosphorous Compounds

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The activation of Earth-abundant small molecules such as CO₂, N₂, and H₂O has been a topic of immense interest across numerous scientific disciplines. Small molecules present potential for application as renewable energy sources (H₂, CH₄, NH₃)^{1,2} as well as versatile chemical feedstocks for an array of valuable organic functionalities such as alcohols, carboxylic acids, and amines.³ However, the aforementioned small molecule examples are often very stable, including strong element-hydrogen bonds which present a challenge to activate.⁴

Although main group elements have been utilized in tandem with transition metals for E-H bond cleavage⁵⁻⁷, transition metal-free systems have also been successful in the activation of small molecules. Singlet carbenes have been shown to cleave dihydrogen and N-H bonds.⁸ Similarly, silylenes and germylenes have demonstrated cleavage of an N-H bond of ammonia.⁹ Such compounds highlight the competency of main group elements towards some of the challenging transformations required for efficient activation of small molecules.

Arduengo and coworkers were recently able to synthesize a stable, planar phosphorane complex featuring T-shaped geometry around the phosphorous center, a significant deviation from the trigonal pyramidal geometry typically associated with phosphorous in a 3+ formal oxidation state.¹⁰ Interested in probing the potential for reactivity with this unusual geometry, Radosevich treated Arduengo's phosphorane with excess ammonia-borane (see Figure 1), furnishing, in good yield, a five-coordinate phosphorous dihydride.¹¹

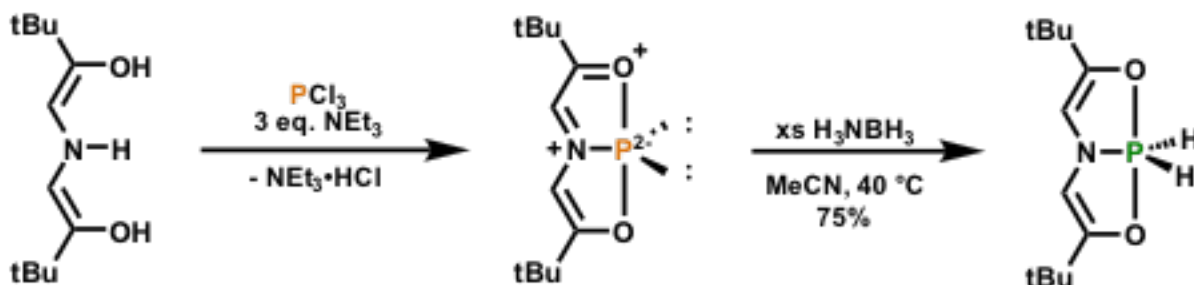


Figure 1: Formation of planar phosphorane followed by P(V) dihydride

Work has since been expanded to the cleavage of N-H bonds in ammonia and primary alkyl amines. Such reactions often proceed quickly and in quantitative yield¹², though performance is significantly diminished for aryl amines bearing steric bulk at positions ortho to the nitrogen. DFT studies (M062X, 6-311++G(2d,2p)), as well as kinetic data and Eyring analysis, suggest an electrophilic stepwise oxidative addition of N-H bonds to the phosphorous center of the phosphorane. Though subsequent reductive elimination has not yet been observed using this system, exchange of amines has been demonstrated at high temperatures, as well as catalytic transfer hydrogenation from ammonia-borane to generate diphenyl hydrazine from azobenzene.

Similar reactivity with phosphorous-containing molecules has been shown by the Goicoechea group¹³. Treatment of a “pincer” phosphorous compound bearing an *N,N*-bis(3,5-di-tert-butyl-2-phenoxy)amide ligand with ammonia or primary amines afforded oxidative addition products analogous to those observed by Radosevich. Similarly, exposure to one equivalent of H₂O resulted in the formation of the corresponding P(V) hydrido hydroxyl species, signifying the third example of a main group element cleaving the O-H bond in water under mild conditions and in equimolar amounts. Heating this P(V) species in the presence of another equivalent of P(III) starting material resulted in activation of the second O-H bond to form an oxygen bridged

third example of a main group element cleaving the O-H bond in water under mild conditions and in equimolar amounts. Heating this P(V) species in the presence of another equivalent of P(III) starting material resulted in activation of the second O-H bond to form an oxygen bridged dimeric species, the first main group compound known to show controlled, sequential breaking of both O-H bonds in a water molecule (See Figure 2).

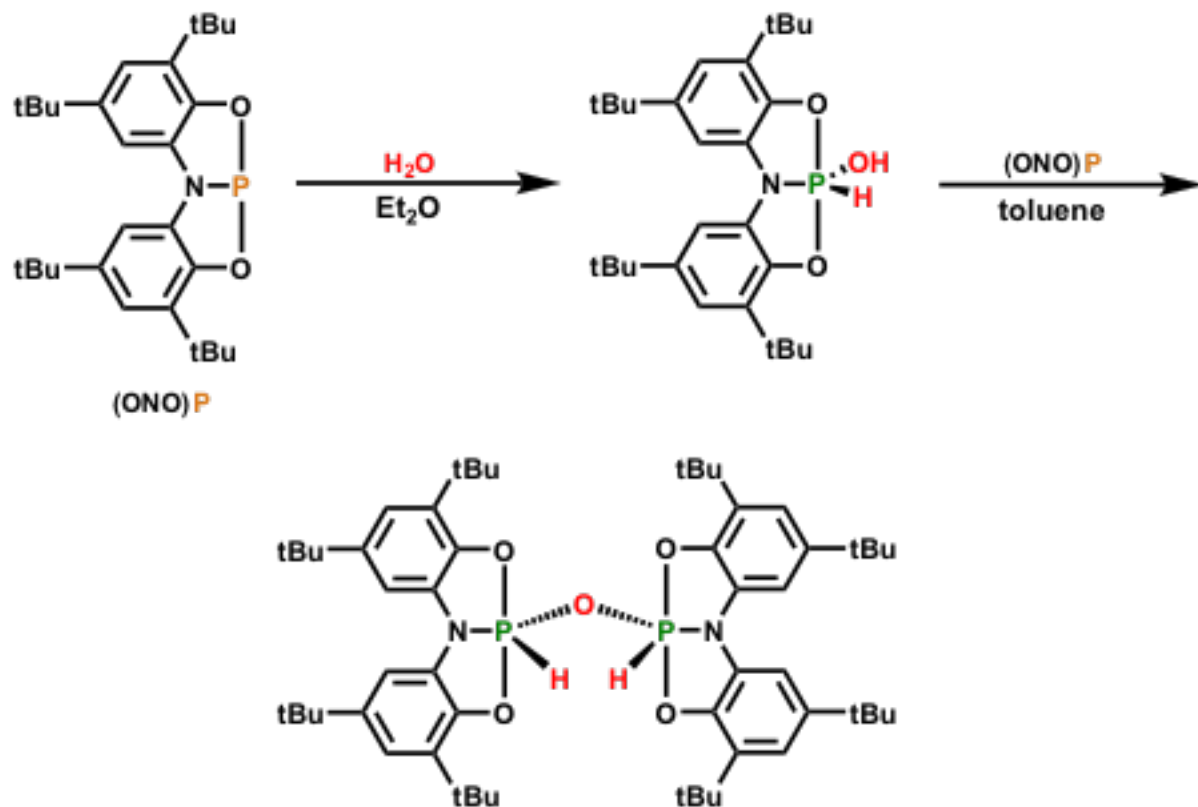


Figure 2: Complete splitting of H₂O by a main group element

While catalytic examples of E-H activation are still few, very promising reactivity has been exhibited by low symmetry phosphorous compounds which have potential to cycle between the P(III) and P(V) oxidation states. Continued effort is directed at the synthesis of similar low-symmetry phosphorous-centered compounds and the development of new catalytic applications for such systems.

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