The Oxidation Chemistry of Low Valent Phosphorus

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Abstract: The Oxidation Chemistry of Low Valent Phosphorus

The “main group” of the periodic table refers to elements within the s- and p-block. These elements display an incredible variety of properties and thus have many uses industrially, such as components within electronics or in the production of polymers, to name a few.1 Our research group has been interested in the development of new configurations and bonding motifs for some main group elements within the p-block.2 Specifically, we are interested in the synthesis of molecules containing elements in low oxidation states or valence states, which are electron rich and can undergo a variety of further reactivities and chemistry, such as: transition metal coordination, insertion chemistry, and oxidation reactions.3 Despite their reactivity and increased electron density, these molecules require configurations that allow them to be relatively stable so that they can be easily handled for further chemistry and modification. One of these molecules that our research group has reported is called a “triphosphonium cation” which refers to a dicoordinate (low valent) phosphorus atom (in the +1 oxidation state) coordinated and stabilized by a chelating diphosphine ligand.4 Recently, we have found one of these triphosphonium molecules, [P(dppe)]Br, to be very useful in the generation of other phosphorus molecules containing a low oxidation state phosphorus centre.5

The focus of my project is exploring new ligands to react with this triphosphonium molecule to generate new or useful phosphorus-containing molecules. I have been successful in employing tetrathiocine ligands in oxidative addition reactions, as an alternative and more convenient method to generate a diphosphane molecule, which had been previously shown to generate stable radical molecules.6 These investigations were performed using air and moisture free techniques during the synthesis and characterization of these compounds. Multinuclear Nuclear Magnetic Resonance (NMR) spectroscopy was used to characterize the compounds as well as provide mechanistic insight to the reaction. X-ray crystallography was also employed to identify the bonding and connectivity of these new molecules. Future applications of these results can include ligands for transition metals, and trithiaphosphite applications for industrial uses such as lubricants and oils.


