

THE NEW CHEMISTRY OF OLD PN CAGES

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Our group explores geometrically interesting molecules for functional chemistry. One area of focus is the development of molecular scaffolds from which substituents can be reliably extended with well-defined bond angles and lengths. Such molecules have applications in materials chemistry, catalysis, and in the pharmaceutical industry due to their isosterism with bioactive motifs. While this parameter space is currently dominated by hydrocarbon frameworks (*e.g.* adamantanes, aryls), we are evolving phosphorus nitrogen (PN) cages as a new family of molecular “LEGO bricks” for chemical construction. This talk will describe how we start from two well-known PN cages and two inorganic “Click” reactions to access many new classes of robust inorganic materials and molecules in a modular fashion.^[1-4] The PN scaffolds we have developed are easy to synthesize and derivatize, offer a phosphorus NMR handle, are electron-pair rich, and fill a geometric gap between the traditional organic scaffold sizes currently available. In some cases, they also exhibit exceptional stability, setting the stage for applied chemistry.

Starting from poor initial hydrophosphination catalysis with zirconium compounds of the type $(N_3N)ZrX$ ($N_3N = N(CH_2CH_2NSiMe_3)_3^{3-}$; X = anionic ligand), a family of earth abundant, highly active, and selective catalysts have been discovered and investigated. Surprisingly, photolysis is a critical factor in activity for these catalysts. The arc of catalysis moves from zirconium to iron chemistry that informs most recent discoveries in simple copper catalysts that may be the most active known. For example, bis(acetylacetonato)copper(II) is an active catalyst for the hydrophosphination of alkenes and alkynes with primary and secondary phosphines. At ambient temperature with irradiation centered at 365 nm, conversions with $Cu(acac)_2$ are remarkable with some reactions complete in minutes. This simple, inexpensive catalyst is highly effective, placing hydrophosphination in the hands of many more synthetic chemists. In both cases, the photocatalysis is hypothesized to proceed by excitation to a low-lying orbital that has significant M–P antibonding character, weakening that bond to avail faster insertion.