Frustrated Lewis Pair reactivities of phosphino-phosphenium cations

([1]*Department of Chemistry, University of Toronto*) ○Hyehwang Kim,[1] Douglas W. Stephan[1]

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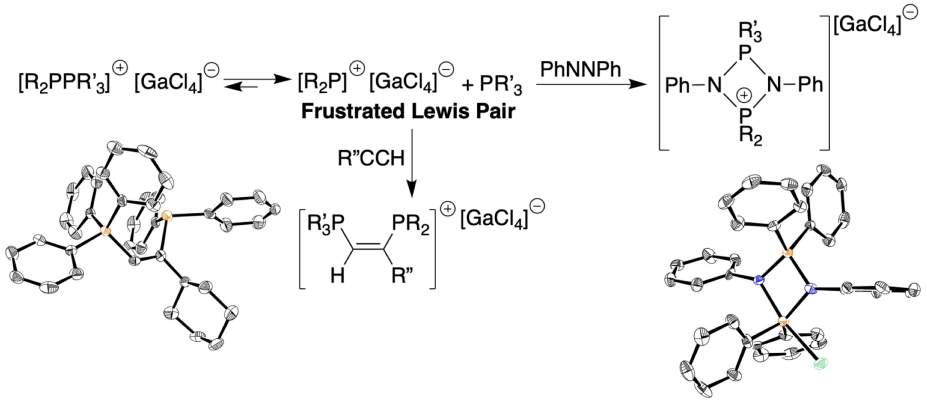
The field of frustrated Lewis pair (FLP) chemistry began in 2006 with the Stephan group's landmark report on reversible H_2 activation by a main group compound.[1] Since then, the field has grown immensely by showing how main group compounds can activate small molecules such as CO_2 and CO.[2] FLPs are principally based on Lewis acids and bases that are sterically precluded from adduct formation. Recently, FLP chemistry has also been demonstrated from equilibrium access to the free Lewis acid and base, thus showing that it is not necessary for the Lewis acid and base to be sterically "frustrated".[3]

With this in mind, we present our work on the FLP chemistry of phosphino-phosphenium cations (PPCs) of the forms $[R_2PClPR'_2]^+$ and $[R_3PPR'_2]^+$. Intrigued by reports of these cations undergoing phosphine exchange,[4] we proposed that the labile dative bond in phosphino-phosphenium cations would provide access to the Lewis basic phosphine and Lewis acidic phosphenium moieties in FLP chemistry. In the first part of this presentation, we report the reactions of PPCs with terminal alkynes which resulted in FLP addition products. This methodology was adapted for the synthesis of several dissymmetric *cis*-olefin-linked bidentate phosphines, thus avoiding the conventional use of radicals, transition metals, or pyrophoric lithium reagents. In the second part, we report the cleavage of N=N double bonds in azobenzene using PPCs as FLPs, and the functionalization of the resulting four-membered phosphorus-nitrogen heterocycles.



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