

π -Bonded Cationic Ligands as Catalysts and Precursors

Richard A. Kemp, Department of Chemistry and Chemical Biology, University of New Mexico

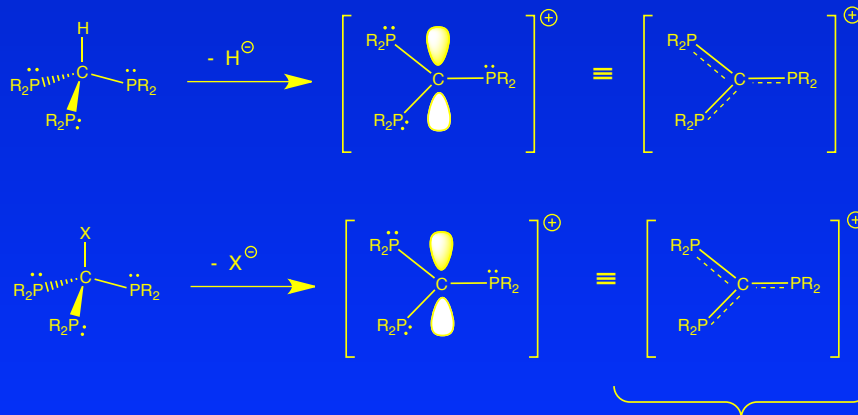
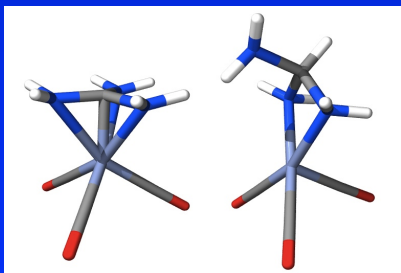


Ligands are integral components of the synthetic chemist's toolkit. All commonly-used π -ligands are either neutral or anionic in charge. To our knowledge, the only cationic ligands that directly react with metal species do so in a σ -fashion, with examples being $[\text{NO}]^+$, $[(\text{R}_2\text{N})_2\text{P}]^+$, and triazolium cations $[\text{C}_2\text{N}_3\text{R}_4]^+$. We are interested in a class of as-yet unprepared ligands - 6 π -electron containing **cationic** ligands - that should π -bond to metals much like well-known neutral and anionic analogues. Target molecules will rely on $p\pi$ - $p\pi$ bonding to stabilize the cationic Group 14 center. As examples, DFT calculations have shown a net attraction between species such as $[(\text{R}_2\text{N})_3\text{C}]^+$ or $[(\text{R}_2\text{P})_3\text{C}]^+$ and metal fragments, with the planar central C cation symmetrically-bound to a $\text{M}(\text{CO})_3$ moiety. The synthesis of the cationic precursors by hydride abstraction has been challenging, as we are seeing fragmentation of the precursor $(\text{R}_2\text{P})_3\text{CH}$ species under highly acidic conditions rather than hydride removal. We are now preparing precursors with better leaving groups, such as halides. As well, we are also preparing derivatives of $(\text{R}_2\text{P})_3\text{CH}$ in which the P(III) atoms have been protected. In order to examine the fundamental stability of these cationic complexes, we are examining $[(\text{R}_2\text{P})_3\text{CH}]\text{M}(\text{CO})_3$ complexes and their cationic $\{[(\text{R}_2\text{P})_3\text{C}]\text{M}(\text{CO})_3\}^+$ species derived from hydride removal. In order to validate our initial hypothesis we are also examining heavier Group 14 analogues such as Ge and Sn in order to take advantage of weaker E-X and E-H bonds.

Routes Using $(\text{R}_2\text{P})_3\text{CX}$ as Examples

X-ray Structures of $[(\text{Ph}_2\text{P})_3\text{CH}]\text{W}(\text{CO})_3(\text{EtCN})$ and $\text{GeCl}_2(\text{Ph}_2\text{P}-\text{PPh}_2)$

Density Functional Theory (DFT) Comparison of the Structures of $\{[(\text{H}_2\text{N})_3\text{C}]\text{Cr}(\text{CO})_3\}^+$ and $\{[(\text{H}_2\text{N})_3\text{CH}]\text{Cr}(\text{CO})_3\}$ Indicating Symmetric π -Bonding of Cationic Ligand



π -Bonding Cationic Ligands

