The Synthesis and Characterization of Early Transition-metal Complexes with Terminal Nitrido Complexes

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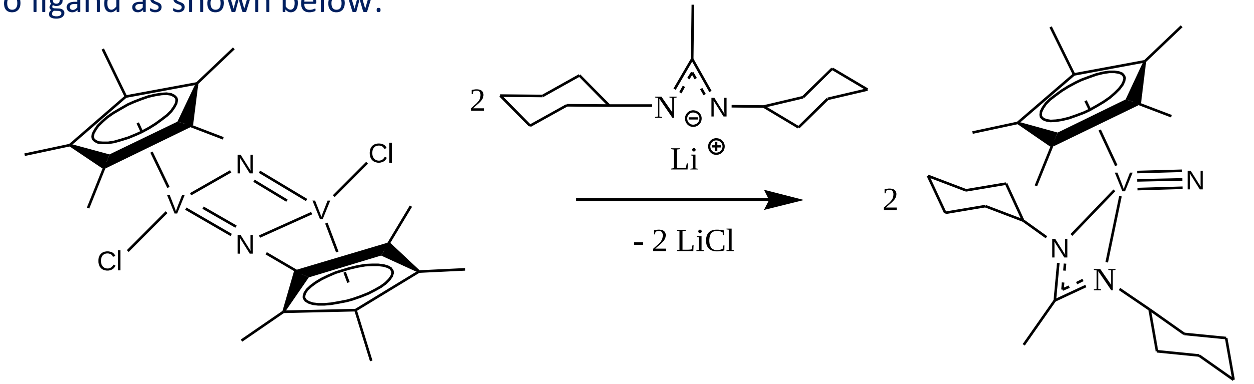
Complexes of early transition-metals with terminal nitrido ligands have great potential to act as nitrogen-atom transfer reagents towards a variety of important organic substrate molecules. However, the highly reactive [M≡N] moiety has a strong tendency to oligomerize via the formation of metal nitride bridges . We are seeking to prepare new complexes with terminal nitrido ligands by employing combinations of sterically demanding ancillary ligands to prevent such oligomerization. For instance, the reaction of $[Cp^{*}V(\mu_2\text{-}N)Cl]_2$ with two equivalents of lithium bis(cyclohexyl)methylamidinate was expected to form a monomeric complex with a terminal nitrido ligand as shown below:



However, this reaction unexpectedly yielded the dinuclear complex shown opposite with a single symmetric linear V=N=V bridge. We are seeking to understand the mechanism and rationale for the formation of this product by exchanging the chloride ligands of $[Cp^{*}V(\mu_2\text{-}N)Cl]_2$ with a series of mono- and di-dentate ligands of different steric demands.