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Molecular Analogs of Metal-oxide Supported Catalysts
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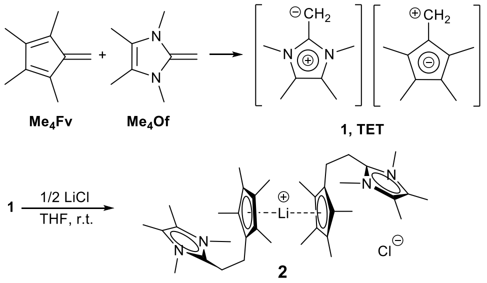
Overview. Work in our laboratory has addressed the development titantium and cerium complexes as metalloligand electron reservoirs for multi-electron reactions. This program has identified the need to develop masked low-valent precursors to develop the requisite synthetic chemistry. Therefore, the development of δ accepting ligands to stabilize low-valent precursors was pursued.

Year 1 Results. To-date, the synthesis of a zwitterionic, neutral ligand: 2,3,4,5-tetramethylcyclopentadienyl-1-ethelene-bridged-2,3,4,5-tetramethylimidazolium (TET) (Scheme 1) has been established. The coordination chemistry and solution NMR (^{13}C and DOSY) of the system demonstrates that the formation of the C–C bond of the ethylene bridge is dependent on the addition of a Lewis acid (*i.e.* Li^+ or Ti^{3+}). Reaction with trivalent titantium or lithium leads to the complexation of the neutral zwitterionic ligand via the cyclopentadienyl anion with a pendant imidazolium cation. Reduction of the trivalent (TET)$TiCl_3$, leads to the formation of a formally tetravalent titanium dimeric 'tuck-in, tuck-over' complex. The formation of the dimeric 'tuck-in, tuck-over' complex implies that coordination and reduction of the tethered imidazolium occurs under reducing conditions and opens the coordination chemistry of imidazolium cations in the support of low-valent complexes. We are currently investigating the potential of the TET ligand to stabilize low-valent *d*- and *f*-block ions.

Career Development. The ACS-PRF has supported the stipend and materials and supplies for partial support of a postdoctoral fellow in the La Pierre group. These resources have facilitated the rapid development of a reactive ligand and derived organometallic complexes. These initial studies and related work will be submitted for publication soon.



Scheme 1. Synthesis of TET and complexation with LiCl.