VIII-B Coordination Chemistry of Sterically Hindered Ligands and Multidentate Ligands, and Activation of Small Molecules

This project is focused on the design and synthesis of new ligands that are capable of supporting novel structural features and reactivity. Currently, we are investigating multidentate ligands based on aryloxide, thiolate, and amidinate. In addition, we set out to study metal complexes with sterically hindered arylthiolate ligands. Our recent efforts have been directed toward activation of small molecules.

VIII-B-1 Synthesis of a Vanadium(III) Tris(arylthiolato) Complex and Its Reactions with Azide and Azo Compounds; Formation of a Sulfenamide Complex *via* Cleavage of an Azo N=N Bond

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Thiolate complexes continue to attract considerable attention due to their unique chemical properties and structural diversity. Since thiolate groups meet the electronic and steric requirements necessary to stabilize a wide variety of metal complexes, they have been used as auxiliary ligands. On the other hand, thiolate complexes are known to undergo chemistry at the sulfur center, including oxidation/reduction and protonation/deprotonation, a complement to traditional chemistry for these complexes centered on the metal. In this study, we report the synthesis of a mononuclear vanadium(III) complex having the $[SC_6H_3\text{-}2,6\text{-}(SiMe_3)_2]^-$ (= $[SAr]^-$) ligands.

The tris(arylthiolate) vanadium(III) complex (**1**) has been synthesized in good yield. This complex is found to undergo CH activation across a V–S bond in the presence of TMEDA to give a cyclometalated species along with free arylthiol. Complex **1** behaves as a two-electron reductant toward Ad-N_3, yielding an imide complex. Treatment of **1** with azobenzene produces an imide-sulfenamide compound, in which an azo N=N bond cleavage takes place concomitant with formation of a V=N and an S–N bond. These results suggests that the reaction proceeds through a cooperative activation sequence involving both vanadium and sulfur centers.

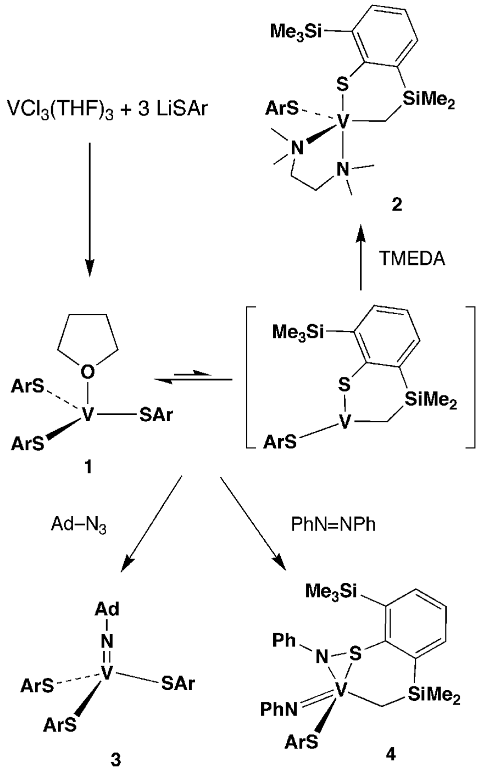

Figure 1.

VIII-B-2 Titanium and Zirconium Complexes of Preorganized Tripodal Triaryloxide Ligands

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Multidentate ligands play an important role in coordination chemistry and catalyst design. An attractive multidentate ligand is a trianionic tetradentate ligand of the tripodal $[X_3E]$ type (X = N, O, S; E = N, P), which had led to atrane molecules with unique structures and patterns of reactivity. The degree of interaction between the metal center and the neutral E atom can exert a profound influence on the reactivity of the resulting complexes. In this context, a tri(2-oxyphenyl)methane-derived system $[O_3]^{3-}$ appears practically attractive. This ligand can coordinate to a metal in two forms, which differ mainly as a result of the relative stereochemistry at the methine carbon. Furthermore, intramolecular metalation of the somewhat acidic methine linkage in the $[O_3]$ complexes is expected to occur quite readily, resulting in formation of 5-carbametalatranes

([O_3C] complexes). In this study, tri(2-oxy-3,5-di-*tert*-butylphenyl)methane has been used to prepare titanium and zirconium complexes of the general formula [O_3] MX (M = Ti, X = NEt_2, Cl, CH_2Ph; M = Zr, X = CH_2Ph). The tripodal [O_3] ligand in titanium complexes adopt the *syn*- and the *anti*-conformation, while the *syn* complex of zirconium undergoes facile C–H activation to give a 5-carbametalatrane [O_3C]Zr(THF)$_3$. Reactivity studies with these group 4 metal complexes are ongoing.

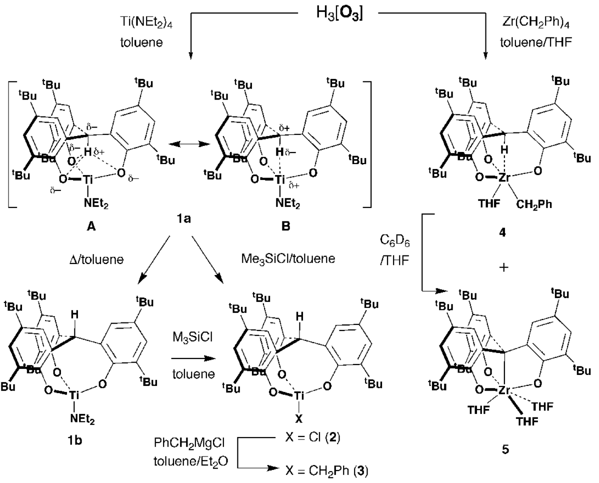

Figure 1.