

The Characterization of Early Transition Metal Alkyl Complexes  
by Solution and Solid-State NMR Spectroscopy

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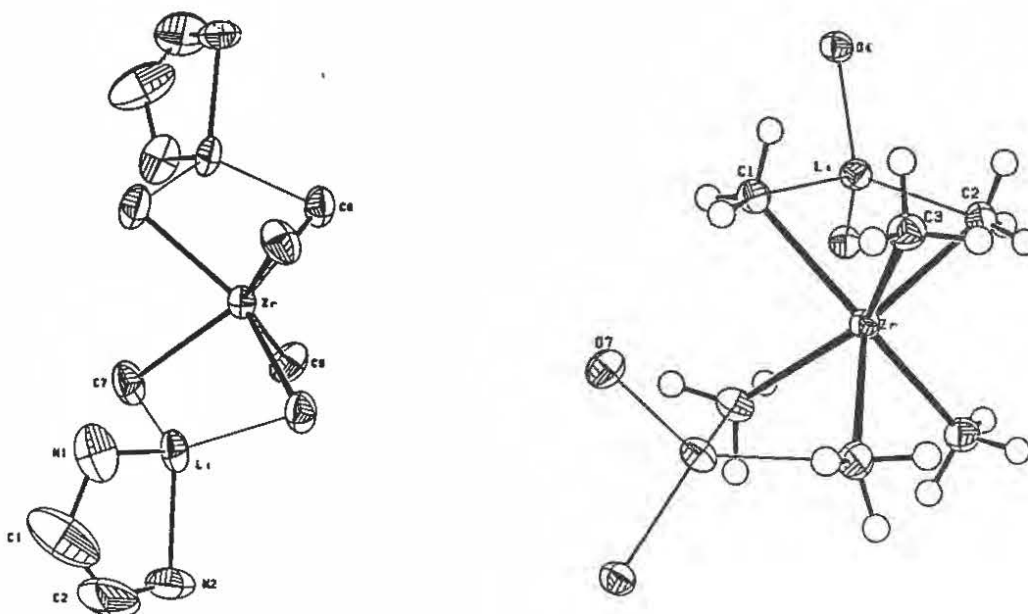
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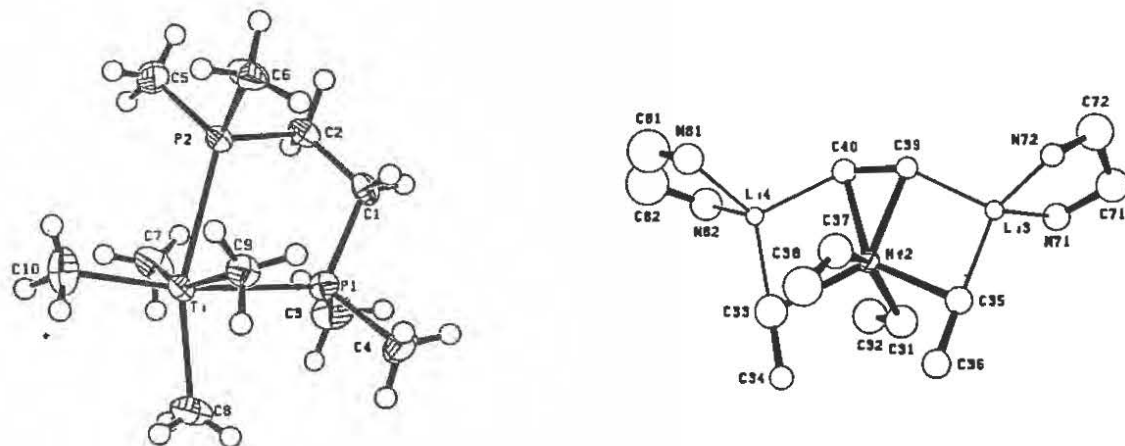
Compounds that contain early transition metals, particularly titanium, vanadium, and chromium, are used as catalysts for olefin polymerization such as in the Ziegler-Natta and Phillips processes [1]. The key intermediates in these catalysts are thought to be six-coordinate metal alkyl/olefin complexes. The synthesis and study of early transition metal alkyl complexes as models of these catalytic centers can provide insight into the mechanism of the polymerization process. The research presented here addresses two aspects of the chemistry of early transition metal alkyls: the geometry at the metal center and the ability of the metal center of the isolated complex to activate carbon-hydrogen bonds.

The hexamethyl metallates of zirconium and hafnium have been synthesized by the addition of methyllithium to  $ZrCl_4$  or  $HfCl_4$ . Single methyl environments are observed for the metal-bound methyl groups in the  $^1H$  and  $^{13}C$  NMR spectra down to  $-80^\circ C$ . The molecular structures of  $[Li(tmed)]_2[ZrMe_6]$  (tmed = N,N,N',N'-tetramethylethylenediamine) and  $[Li(diox)]_2[ZrMe_6]$  (diox = dioxane) show that the zirconium is in a trigonal prismatic environment with the lithium atoms each bridging between two methyl groups on the metal. The bond distances and angles around the zirconium are very similar in the two structures despite the fact that the tmed adduct is a monomer and the dioxane adduct is a polymer. The  $^{13}C$  solid-state NMR spectra of the two complexes show that  $[Li(diox)]_2[ZrMe_6]$  is less fluxional than  $[Li(tmed)]_2[ZrMe_6]$ .

Theoretical calculations on the geometric preferences of  $d^0$  six-coordinate metal complexes suggest that, in the absence of  $\pi$ -donor ligands, octahedral geometries are not favored due to mixing of the metal-ligand  $\sigma$ -orbitals with the  $d$  orbitals of the metal [2]. Instead, distortions away from octahedral, including trigonal prismatic structures and agostic interactions [3,4], are energetically favored for compounds of this type [5,6].  $[Li(tmed)]_2[ZrMe_6]$  is the first reported transition metal complex with six identical ligands to adopt a trigonal prismatic geometry [7].



The study of the geometries of  $d^0$  complexes was expanded to include neutral alkyl complexes of group IV metals. Six-coordinate adducts of stoichiometry  $MMe_4(P-P)$  have been made with the bidentate phosphines dmpe (1,2-bis(dimethylphosphino)ethane) and diphos (1,2-bis(dimethylphosphino)benzene) for titanium and with dippe (1,2-bis(diisopropylphosphino)ethane) and dcpe (1,2-bis(dicyclohexylphosphino)ethane) for zirconium and hafnium. Solution and solid-state NMR studies of these complexes indicate that the energy barriers for exchange of the methyl groups are very low (9-13 kcal mol<sup>-1</sup>). Crystal structure determinations of  $TiMe_4(dmpe)$ ,  $TiMe_4(diphos)$ , and  $HfMe_4(dcpe)$  show that these complexes adopt significantly distorted cis-octahedral geometries.



The reaction of ethyllithium with  $HfCl_4$  yields the anionic ethylene complex  $[Li(tmed)]_2[HfEt_4(C_2H_4)]$ . This is the first complex of a group IV metal that has an alkyl and an olefin ligand, and it serves as a model of the key intermediate in olefin polymerization catalysis. A small C-H coupling constant of 119 Hz and a long C-C distance of 1.50 Å between the two carbon atoms of the ethylene ligand suggest that this complex is best formulated as a metallacycle. GC/MS studies show that this complex is formed by  $\beta$ -hydride elimination from one of the ethyl groups and subsequent loss of ethane. Anionic homoleptic alkyl complexes have also been made with phenyl and trimethylsilylmethyl ligands.

Homoleptic alkyl complexes of vanadium(III) and chromium(II) have been made with the  $\beta$ -stabilized alkyl groups trimethylsilylmethyl and neopentyl. The low temperature <sup>1</sup>H NMR spectrum of  $[Li(thf)_2]_2[Cr_2(CH_2SiMe_3)_6]$  shows that there are three different environments for the  $CH_2SiMe_3$  groups, and suggests that agostic interactions may be present in the molecule. The addition of tmed to  $[Li(thf)_2]_2[Cr_2(CH_2SiMe_3)_6]$  yields the interesting bis-metallacycle  $[Li(tmed)]_2[Cr(K_2-CH_2SiMe_2CH_2)_2]$ .

The observation of trigonal prismatic and significantly distorted octahedral geometries for  $d^0$  alkyl complexes suggests that the intermediates of catalytic processes that involve high-valent early transition metals may not be octahedral. These results have significant mechanistic implications in terms of the proposed geometries for the intermediates in olefin polymerization processes.

## References

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