

Coordinately and Electronically
Unsaturated Organometallic Complexes

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Because of their industrial importance and intriguing nature, Ziegler-Natta catalysts have been studied for over 30 years. Active catalysts for ethylene and propylene polymerization are limited, almost exclusively, to the metals titanium, vanadium, and chromium [1]. Low-valent, early transition metal alkyl complexes are of fundamental importance to the study of olefin polymerization catalysis, yet such species are relatively rare [2].

Recently, electronically unsaturated titanium alkyls have been shown to possess "agostic" hydrogen interactions [3]. Facile olefin insertion may be related to the peculiar electronic nature of the metal-carbon interaction in such distorted alkyl complexes [4]. As part of our effort to model olefin polymerization catalysts, we have prepared a series of coordinately and electronically unsaturated organometallic compounds. We have employed sterically demanding ligands to allow isolation of complexes with low coordination numbers and electron counts.

The reaction of divalent transition metal halides with the bulky chelating phosphine 1,2-bis(diisopropylphosphino)ethane, dippe, gives a series of coordinately unsaturated complexes of stoichiometry $\text{MX}_2(\text{dippe})$ for $\text{M} = \text{V}, \text{Cr}, \text{Mn}, \text{Fe},$ and Co [5]. Both the vanadium(II) and chromium(II) complexes readily form adducts with tetrahydrofuran or acetonitrile. The base-free chromium species exists as a dimer, $[\text{CrCl}_2(\text{dippe})]_2$, in the solid state that consists of two square-planar chromium centers arranged in pairs via asymmetric chloride bridges (Figure 1). The manganese, iron, and cobalt complexes are all tetrahedral

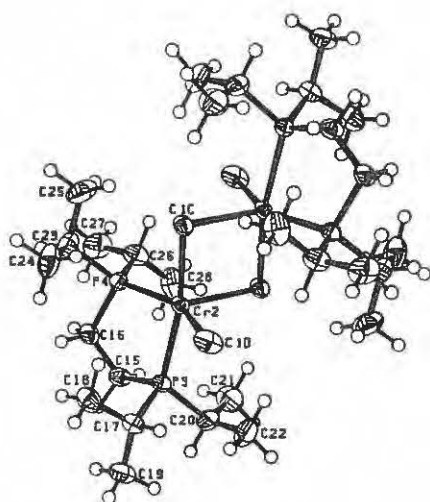


Figure 1

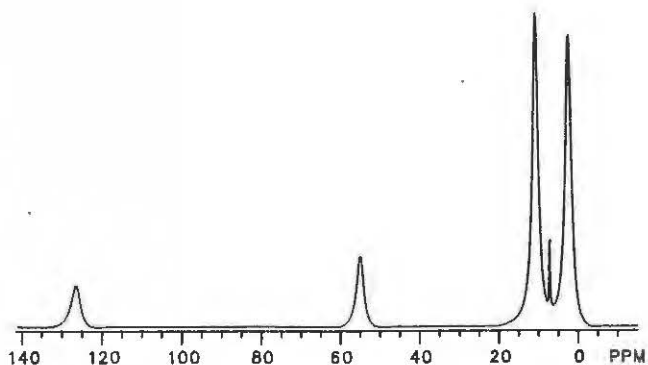


Figure 2

monomers, as confirmed by the X-ray crystal structure of $\text{FeCl}_2(\text{dippe})$. NMR and EPR studies show that all of the four-coordinate species exist in high-spin electronic configurations. The ^1H NMR spectrum of $\text{FeCl}_2(\text{dippe})$ is shown in Figure 2. The $\text{MX}_2(\text{dippe})$ complexes serve as excellent starting materials for the preparation of low electron-count organometallic derivatives of these elements.

Alkylation of $\text{MX}_2(\text{dippe})$ adducts gives rise to organometallic derivatives. For example, the 14-electron complexes $\text{FeR}_2(\text{dippe})$ have been prepared for a variety of β -stabilized alkyl groups, including CH_2CMe_3 , CH_2SiMe_3 , CH_2Ph , and CH_2 -*p*- $\text{C}_6\text{H}_4\text{Me}$ [6]. An X-ray structure reveals that $\text{Fe}(\text{CH}_2$ -*p*- $\text{C}_6\text{H}_4\text{Me})_2(\text{dippe})$ adopts a tetrahedral structure (Figure 3). In contrast, the 12-electron $\text{CrR}_2(\text{dippe})$ complexes adopt nearly square-planar structures in the solid state. The structure of $\text{Cr}(\text{CH}_2\text{CMe}_3)_2(\text{dippe})$ is shown in Figure 4. The preference of Cr(II) for square-planar geometry is electronic in origin and reflects enhanced stabilization energy upon half-filling the four low-lying orbitals which are characteristic of square-planar ligand arrays [7].

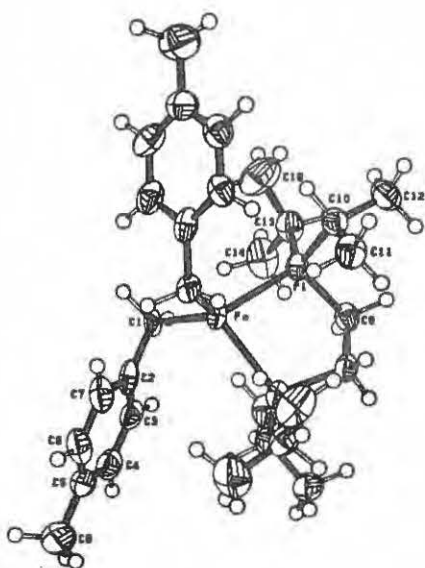


Figure 3

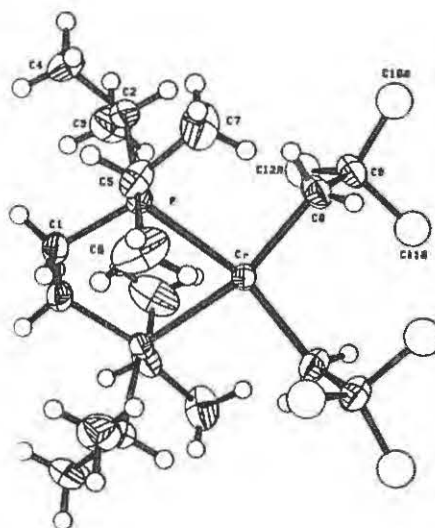


Figure 4

The $\text{FeR}_2(\text{dippe})$ complexes react with carbon monoxide to yield $\text{Fe}(\text{CO})_3^-(\text{dippe})$ and ketone, R_2CO . When mono-alkyl derivatives, $\text{FeRX}(\text{dippe})$, are carbonylated, however, the acyl complexes $\text{Fe}[\eta^2\text{-C}(\text{O})\text{R}]\text{X}(\text{CO})(\text{dippe})$ and $\text{Fe}[\eta^1\text{-C}(\text{O})\text{R}]\text{X}(\text{CO})_2(\text{dippe})$ can be isolated [8]. The Fe(II) alkyls show no reaction with ethylene while the $\text{CrR}_2(\text{dippe})$ complexes react to yield small amounts of polyethylene.

Since real Ziegler-Natta catalysts are most often based on Ti(III), dippe adducts of trivalent metals have also been prepared. Reaction of dippe with the trivalent chlorides $\text{MCl}_3(\text{thf})_3$ (where $\text{M} = \text{Ti}, \text{V}, \text{Cr}$) results in the formation of either dimeric adducts, $[\text{MCl}_3(\text{dippe})]_2$, or monomeric adducts of stoichiometry $\text{MCl}_3(\text{dippe})(\text{thf})$. For example, the X-ray structure of $[\text{TiCl}_3(\text{dippe})]_2$ reveals a chloride-bridged dimer with octahedral geometry around each Ti center. The monomeric chromium derivative $\text{CrCl}_3(\text{dippe})(\text{thf})$ can be alkylated with AlMe_3 to yield $\text{CrMeCl}_2(\text{dippe})(\text{thf})$ which polymerizes ethylene under mild conditions.

References

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