

Low-Valent Early Transition Metal Complexes  
Stabilized by the Chelating Tripod Phosphine Ligand  
(*t*-Butyl)Tris[(Dimethylphosphino)Methyl]Silane

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The choice of ancillary ligands can be very critical to the stability of a complex. Tertiary phosphines are effective ligands for use with a variety of metals in different oxidation states. Phosphine ligands kinetically and oxidatively stabilize transition metal complexes, and are strongly  $\sigma$ -donating and somewhat  $\pi$ -acidic in nature, making them useful with low-valent metal complexes. Chelating phosphine ligands provide enhanced stabilization over unidentate phosphines by virtue of the chelate effect. Dmpe stabilizes early first-row transition metal complexes in tetravalent, divalent, and zero-valent oxidation states [1]. Our research has extended the known chemistry of the early first-row metals through the use of a new ligand,  $\text{Bu}^t\text{Si}(\text{CH}_2\text{PMe}_2)_3$ , or "trimpsi", which is tridentate as opposed to the bidentate dmpe. The tridentate nature of trimpsi is ideally suited to occupying the three coordination sites complementary to the three halide or alkyl ligands in an octahedral complex. Trimpsi has been used to prepare new carbonyl, arene, and alkyl complexes of the early transition metals.

Zero-valent group 4 carbonyl complexes are not inherently unstable, as has long been thought [2]; in fact, carbon monoxide can be quite strongly bonded to group 4 metals, given the proper ancillary ligands. They are prepared by reductive carbonylation of phosphine metal halide precursors, such as (trimpsi) $\text{TiCl}_3$ (thf) and (trimpsi) $\text{VCl}_3$ (thf), with sodium naphthalenide [3]. The 18-electron titanium carbonyl complex, (trimpsi) $\text{Ti}(\text{CO})_4$  (Fig. 1), shows a carbonyl  $^{13}\text{C}$  NMR chemical shift of  $\delta$  276.9, which is considerably farther downfield than expected for a terminal metal carbonyl complex. The infrared stretching force constant [4] of the carbonyls ( $k = 1345 \text{ N}\cdot\text{m}^{-1}$ ) is also abnormally low for a terminal metal carbonyl. Other known examples of zero-valent group 4 carbonyls [5] have chemical shifts and force constants indicative of extraordinarily strong metal-to-ligand  $\pi$  back-bonding. These carbonyl complexes are interesting and uncommon examples of titanium(0) compounds. Unfortunately, most are only marginally stable at room temperature, and decompose over several hours even under an inert atmosphere. (Trimpsi) $\text{Ti}(\text{CO})_4$ , however, shows remarkable thermal and oxidative stability.

The extent of this  $\pi$  back-bonding [6] is so great that the carbonyl ligands take on the spectroscopic characteristics of bridging carbonyl ligands [7]. Although the metal center has only  $d^4$ , the relatively low  $Z_{\text{eff}}$  of the metal nucleus places the d orbitals at unusually high energies, promoting better  $\pi$  overlap with the ligand  $\pi^*$  orbitals. Potently electron-donating ligands, such as trimpsi, enhance the electron density on the metal center and the  $\pi$  back-bonding to the carbonyl ligands.

Group 4 and 5 metal naphthalene complexes are isolable intermediates in the reductive carbonylation of the trimpsi metal halides. The 16-electron (trimpsi) $\text{Ti}(\eta^6\text{-naphthalene})$  (Fig. 2) and the 17-electron (trimpsi) $\text{V}(\eta^6\text{-naphthalene})$  are thermally stable at room temperature, and may be isolated in the absence of carbon monoxide [8]. These are rare examples of early transition metal arene complexes [9], and are unique in that they are not prepared by transition metal vapor syntheses [10].

$(\text{trimpsi})\text{Ti}(\eta^6\text{-naphthalene})$  differs from other known bis-arene titanium(0) complexes [11] in that it is apparently paramagnetic, and NMR silent.

There are two unusual features in the molecular structure of  $(\text{trimpsi})\text{Ti}(\eta^6\text{-naphthalene})$  (Fig. 3). First, the coordinated ring of the naphthalene ligand is warped about the C1-C4 vector with a dihedral angle of  $12.4^\circ$ . This differs from  $\text{Ti}(\text{C}_6\text{H}_6)_2$  and  $\text{Ti}(\text{C}_6\text{H}_5\text{CH}_3)_2$  [12], which have planar arene rings. By comparison, the naphthalene ring in  $(\text{trimpsi})\text{V}(\eta^6\text{-naphthalene})$  is only slightly warped, with a dihedral angle of  $5.1^\circ$ . Warping of an  $\eta^6$ -arene ligand is very uncommon [13], and suggests unusual metal-to-ligand bonding. Second, the mean P-Ti-Cn-C torsion angles in  $(\text{trimpsi})\text{Ti}(\eta^6\text{-naphthalene})$  and  $(\text{trimpsi})\text{V}(\eta^6\text{-naphthalene})$  are  $13(1)^\circ$  and  $12(1)^\circ$ , respectively, which are about halfway between an eclipsed and a staggered conformation. This conformation is quite unusual; a similar twist is seen in  $\text{Cr}(\eta^6\text{-naphthalene})(\text{CO})_3$  [14], whereas  $\text{Cr}(\eta\text{-anthracene})(\text{CO})_3$  [15] and  $\text{Cr}(\eta^6\text{-phenanthrene})(\text{CO})_3$  [16] are rigorously staggered.

Like the group 4 carbonyls,  $(\text{trimpsi})\text{Ti}(\eta^6\text{-naphthalene})$  exhibits exceptionally strong back-bonding, in this case of  $\delta$  symmetry, to the naphthalene L.U.M.O. [17] from the filled  $\text{Ti } 3d_{x^2-y^2}$  orbital, enhanced by the electron-donating ability of the trimpsi ligand. The ring warps such that the carbon atoms with the greatest L.U.M.O. coefficient (C1 and C4) have the shortest metal-carbon distances. These distances are of a length comparable to the metal-carbon bond length in a titanium(II) alkyl complex [18]. This gives rise to the term "diene-diyl" bonding, commonly observed in group 4 butadiene complexes [19]. Although most metal naphthalene complexes have back-bonding to some degree, they still have planar naphthalene rings, indicating a weaker metal-to-arene  $\delta$  back-bonding than in  $(\text{trimpsi})\text{Ti}(\eta^6\text{-naphthalene})$ .

The diene-diyl bonding mode also reflects itself in a torsional "twisting" of the three phosphine coordination sites away from the typical staggered positions. When viewed as a diene-diyl ligand, the arene is formally a four-coordinate ligand; if  $(\text{trimpsi})\text{Ti}(\eta^6\text{-naphthalene})$  is considered a 3:4 piano stool complex, one sees that a trigonal prismatic geometry is adopted, similar to that observed for  $(\text{trimpsi})\text{Ti}(\text{CO})_4$ .

Early transition metal alkyl complexes are of interest as models for Ziegler-Natta [20] and Phillips [21] olefin polymerization catalysts. However, very few are stable, and those that are stable at room temperature usually have alkyl groups which are bulky,  $\beta$ -stabilized, or chelating (or any combination thereof); in addition, some have Lewis basic ligands that block open coordination sites and inhibit decomposition [22]. The stabilizing effect of the trimpsi ligand, combined with the kinetically inert  $d^3$  electronic configuration of chromium(III), allows for the synthesis of some unusual 15-electron chromium(III) complexes [23]. In particular, the complexes  $(\text{trimpsi})\text{CrEt}_3$  and  $(\text{trimpsi})\text{CrBu}^n_3$  are thermally stable at room temperature, and undergo  $\beta$ -elimination only at elevated temperatures. Although  $(\text{trimpsi})\text{CrBu}^n_3$  is paramagnetic, it is possible to observe peaks in its  $^1\text{H}$  NMR spectrum from protons on the third and fourth carbons of the *n*-butyl chains. The geometries of the *n*-butyl ligands are particularly notable in the molecular structure of  $(\text{trimpsi})\text{CrBu}^n_3$ . The *n*-butyl ligand shows mean C-C bond lengths typical of  $\text{sp}^3\text{-sp}^3$  single bonds [24]. The Cr-C-C angle and the mean C-C-C angle are similar to those of *n*-butyl groups attached to main group elements [25]. No evidence for agostic interactions

was observed. These trialkylchromium(III) complexes are themselves poor ethylene polymerization catalysts; presumably the same factors which prevent  $\beta$ -elimination also render them kinetically inert towards olefin insertion. The stability of the n-alkyl groups toward  $\beta$ -elimination suggests that they may serve as useful models for studying chain propagation mechanisms.

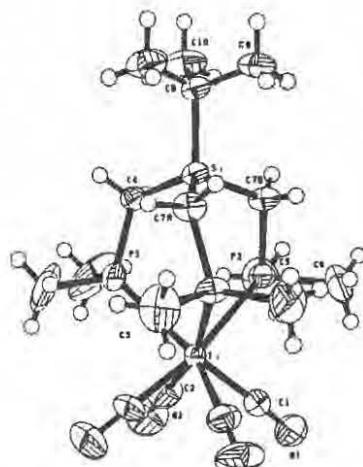


Figure 1.

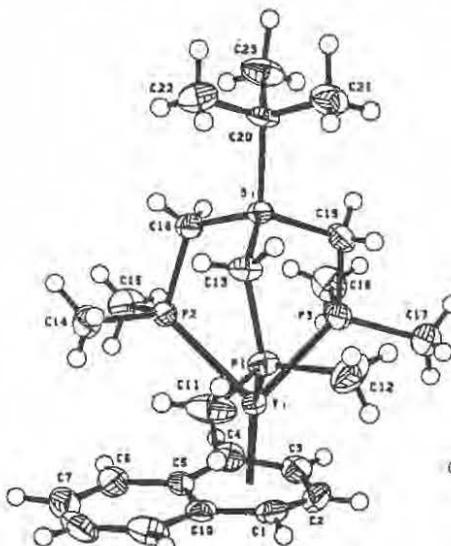


Figure 2.

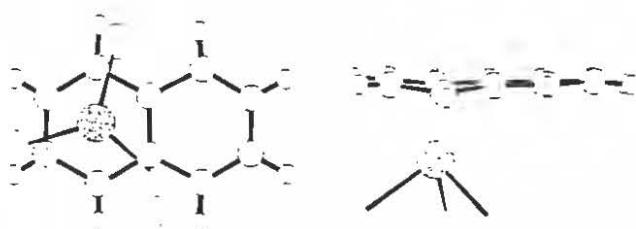


Figure 3.

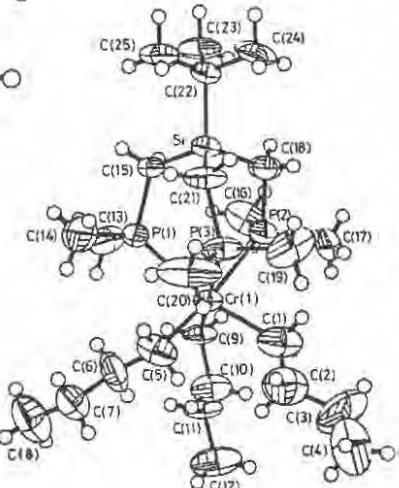


Figure 4.

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