

The First Tris(n-butyl) Transition Metal Complex. Synthesis and Structures of the Fifteen Electron Chromium(III) Alkyls $[\text{Bu}^t\text{Si}(\text{CH}_2\text{PMe}_2)_3]\text{CrMe}_3$ and $[\text{Bu}^t\text{Si}(\text{CH}_2\text{PMe}_2)_3]\text{CrBu}^n_3$

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Reaction of the phosphine adduct $[\text{Bu}^t\text{Si}(\text{CH}_2\text{PMe}_2)_3]\text{CrCl}_3$ with alkyl-lithium reagents gives the first octahedral chromium(III) trialkyls $[\text{Bu}^t\text{Si}(\text{CH}_2\text{PMe}_2)_3]\text{CrR}_3$ ($\text{R} = \text{Me}, \text{Bu}^n$); both compounds have been crystallographically characterized and the n-butyl compound is found to be remarkably resistant to β -elimination.

The transfer of a hydrogen atom from the β -carbon of an alkyl group to a transition metal is a facile process in most instances;^{1,2} however, there are exceptions: for example, in CrBu^t_4 ,³ the bulky t-butyl groups prevent the changes in bond distances and angles necessary for β -elimination, and in $\text{MnBu}^t_2(\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2)$,⁴ the high-spin d^5 electronic configuration prevents β -elimination since no acceptor orbitals are present on the metal centre. We now describe the

preparation of some 15-electron chromium(III) alkyls including the first tris(n-butyl) complex of a transition metal; this complex is remarkably stable toward β -elimination.

Alkylation of the octahedral tripod phosphine complex $(\text{trimp})\text{CrCl}_3$,⁵ [$\text{trimp} = \text{Bu}^t\text{Si}(\text{CH}_2\text{PMe}_2)_3$] with 3 equiv. of MeLi in diethyl ether or Bu^nLi in pentane, followed by crystallization from toluene or pentane gives the 15-electron chromium(III) alkyls, $(\text{trimp})\text{CrMe}_3$ (**1**) and $(\text{trimp})\text{CrBu}^n_3$

(2).† The *n*-butyl complex was originally prepared during attempts to synthesize a chromium hydride under conditions that successfully convert $\text{CrCl}_2(\text{dmpe})_2$ into $\text{CrH}_4(\text{dmpe})_2$, ($\text{dmpe} = \text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2$);⁶ we found instead that (2) may be obtained in high yield even if the alkylation step is performed under 5 atm of H_2 .⁷ The dark red complexes (1) and (2) possess three unpaired electrons, $\mu = 3.5 \mu_B$, and exhibit shifted and broadened ^1H n.m.r. spectra consistent with the paramagnetism. The protons of the Cr–Me group in (1) were not observed, and only the γ - CH_2 and terminal CH_3 protons of the Cr–Buⁿ group in (2) were located; evidently the α - and β -hydrogen atoms experience large contact shifts. The e.s.r. spectrum of (1) in a frozen toluene glass at 77 K shows broad features at $g_{\parallel} = 1.93$ and $g_{\perp} = 3.43$, characteristic of an axially symmetric d^3 system. Both (1) and (2) catalyse the polymerization of ethylene at 5 atm and 25°C.

The molecular structures of (1) and (2) are shown in Figures 1 and 2.‡ Both molecules adopt *fac*-octahedron co-ordination geometries with the average Cr–C distances [2.12(2) Å in (1); 2.13(1) Å in (2)] being virtually identical. The average Cr–P distances [2.51(1) Å in (1); 2.589(3) Å in (2)] are significantly different, evidently due to the larger steric demand of *n*-butyl groups. The Cr–C and Cr–P distances may be compared with those in other chromium(III) complexes: shorter and longer Cr–C bond lengths are found in $\text{Cp}_2\text{Cr}_2\text{Me}_2\text{Cl}_2$ [2.073(3) Å]⁸ and $\text{Li}_3\text{CrMe}_6 \cdot 3\text{C}_4\text{H}_8\text{O}_2$ [2.30(1) Å],⁹ respectively, while significantly shorter Cr–P bonds are seen in $[\text{MeC}(\text{CH}_2\text{PMe}_2)_3]\text{CrCl}_3$ [2.458(2) Å].¹⁰ The only other crystallographically characterized methyl chromium phosphine complex, $\text{CrMe}_2(\text{dmpe})_2$, has Cr–C and Cr–P distances of 2.168(4) and 2.345(1) Å.¹¹

† Selected data for (1): M.p. 200°C (decomp.); i.r. (Nujol): 2780 ($\nu_{\text{C-H}}$), 480 ($\nu_{\text{Cr-C}}$), 465 cm^{-1} ($\nu_{\text{Cr-C}}$); ^1H n.m.r. (C_7D_8 , 300 MHz, 25°C): δ 0.51 (s, w_1 120 Hz, Bu^tSi), –9.53 (s, w_1 850 Hz, PMe_2), –29.0 (s, w_1 1500 Hz, SiCH_2P). For (2): M.p. 95°C (decomp.); i.r. (Nujol): 2770, 2700, 2630 ($\nu_{\text{C-H}}$), 415 cm^{-1} ($\nu_{\text{Cr-C}}$); ^1H n.m.r. (C_6D_6 , 300 MHz, 25°C): δ 8.27 (s, w_1 340 Hz, $\text{CrCH}_2\text{CH}_2\text{CH}_2\text{Me}$), 4.78 (s, w_1 580 Hz, $\text{CrCH}_2\text{CH}_2\text{CH}_2\text{Me}$), 0.52 (s, w_1 155 Hz, Bu^tSi), –9.26 (s, w_1 1500 Hz, PMe_2), –25.6 (s, w_1 2000 Hz, SiCH_2P). Satisfactory elemental analyses (C, H, Cr) were obtained for both compounds.

‡ Crystal data for (1): $\text{C}_{16}\text{H}_{42}\text{CrP}_3\text{Si}$, $M = 407.52$, orthorhombic, space group $Pnma$, $a = 18.365(6)$, $b = 13.153(3)$, $c = 20.053(7)$ Å, $U = 4844(3)$ Å³; $Z = 8$, $D_c = 1.118$ g/cm³; $\mu_c(\text{Mo-K}\alpha) = 7.00$ cm⁻¹, $R = 0.075$, $R_w = 0.073$ for 1479 unique data with $I > 2.58\sigma(I)$. For (2): $\text{C}_{25}\text{H}_{60}\text{CrP}_3\text{Si}$, $M = 533.76$, monoclinic, space group $P2_1/n$, $a = 13.510(5)$, $b = 15.728(4)$, $c = 15.737(5)$ Å, $\beta = 91.79(3)^\circ$, $U = 3342(2)$ Å³, $Z = 4$, $D_c = 1.061$ g/cm³; $\mu_c(\text{Mo-K}\alpha) = 5.20$ cm⁻¹, $R = 0.065$, $R_w = 0.063$ for 2098 unique data with $I > 2.58\sigma(I)$. Data were collected on a Syntex $P2_1$ diffractometer, using graphite-crystal monochromated Mo- $K\alpha$ radiation ($\lambda = 0.71073$ Å), and ω – 2θ scans. For (1), the structure was solved by direct methods (MULTAN) in the centric space group. A group isotropic thermal parameter was refined for the disordered carbon atoms C(3), C(7A), C(7B), C(14), C(17A), and C(17B), independent isotropic thermal coefficients were varied for C(9) and C(19), and the remaining non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included as fixed contributors in 'idealized' positions (for methyl groups, staggered with respect to the substituents on the attached sp^3 atom) with C–H = 0.95 Å, and a group isotropic thermal parameter was refined. For (2), the intensity data were corrected empirically for absorption effects, and the structure was solved by Patterson methods (SHELXS-86). All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were treated as above. The *n*-butyl groups showed large thermal motion, but all attempts to locate two or more discrete positions for any of these groups were unsuccessful.

Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

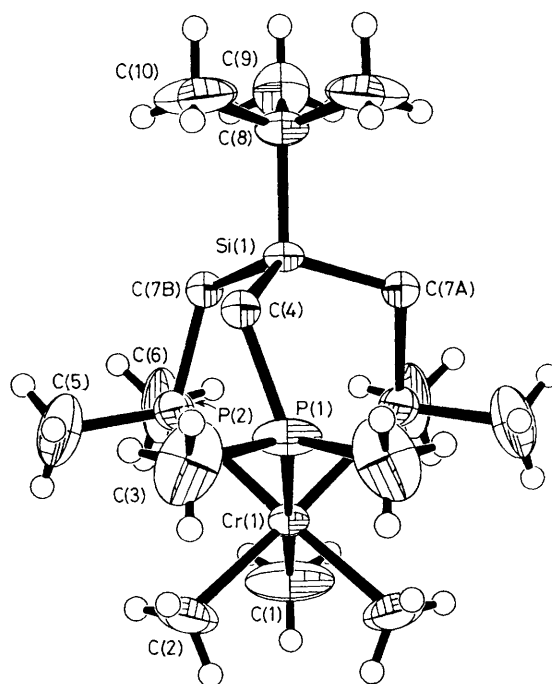


Figure 1. Molecular structure of (trimpsi) CrMe_3 (1). Important bond distances (Å) and angles ($^\circ$): Cr(1)–C(1) 2.09(2), Cr(1)–C(2) 2.14(1), Cr(1)–P(1) 2.521(6), Cr(1)–P(2) 2.504(4), Cr(1) \cdots Si(1) 3.975(5); C(1)–Cr(1)–C(2) 88.3(6), C(2)–Cr(1)–C(2') 90.2(6), P(1)–Cr(1)–P(2) 85.8(1), P(2)–Cr(1)–P(2') 85.4(2), C(1)–Cr(1)–P(1) 179.0(6), C(1)–Cr(1)–P(2) 93.4(4), C(2)–Cr(1)–P(1) 92.4(4), C(2)–Cr(1)–P(2) 92.2(4), C(2)–Cr(1)–P(2') 177.1(4). The other independent molecule in the unit cell has essentially identical metric parameters.

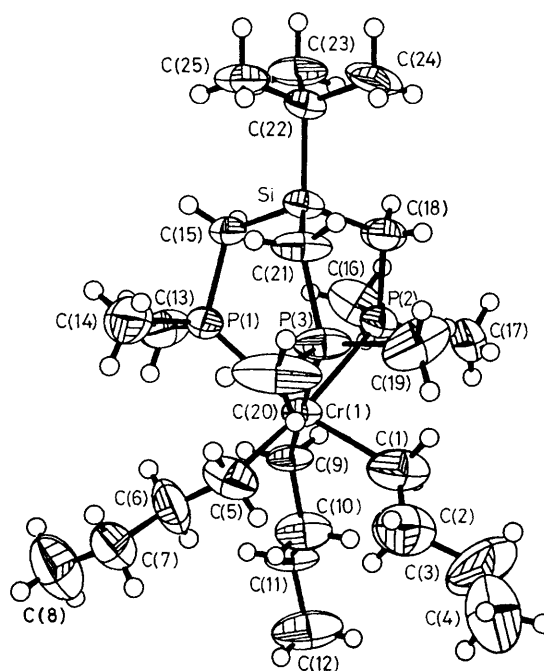


Figure 2. Molecular structure of (trimpsi) CrBu_3 (2). Important bond distances (Å) and angles ($^\circ$): Cr(1)–C(1) 2.17(1), Cr(1)–C(5) 2.10(1), Cr(1)–C(9) 2.137(8), Cr(1)–P(1) 2.596(3), Cr(1)–P(2) 2.582(3), Cr(1)–P(3) 2.557(3), C(9)–C(10) 1.49(1), C(10)–C(11) 1.51(1), C(11)–C(12) 1.48(1), Cr(1) \cdots Si 4.019(3); C(1)–Cr(1)–C(5) 98.9(4), C(1)–Cr(1)–C(9) 92.4(4), C(5)–Cr(1)–C(9) 95.4(4), Cr(1)–C(1)–C(2) 127(1), Cr(1)–C(5)–C(6) 125.7(9), Cr(1)–C(9)–C(10) 119.2(6).

The average C–Cr–C angles of 88.9(6)° in (1) and 95.6(4)° in (2) reflect the larger steric demands of n-butyl groups vs. methyl groups. The geometries of the n-butyl ligands in (2) are of most interest in these structures: the group showing the least thermal motion, C(9) through C(12), has C_α–C_β, C_β–C_γ, and C_γ–C_δ distances of 1.49(1) Å that are typical of sp³–sp³ single bonds.¹² The Cr–C_α–C_β angle of 119.2(6)° and the C–C–C angles of 116.7(8)° are similar to those of n-butyl groups attached to main group elements.¹³ The hydrogen atoms could not be located; however, we do not consider the i.r. bands in the 2700 cm⁻¹ region low enough in energy to be suggestive of agostic interactions.¹⁴

The thermal stabilities of both compounds are remarkable, especially given their electron counts of fifteen. In the solid state the methyl compound decomposes at ca. 200 °C while the n-butyl compound can be heated to 95 °C before thermolysis occurs. Analysis of the gaseous products by gas chromatography and mass spectroscopy shows the presence of methane from (1), and butane and butenes in a ratio of 1.5 : 1 from (2). The high barrier for β-elimination undoubtedly arises in part from the kinetically inert d³ electronic configuration and the chelating nature of the tripod phosphine ligand which inhibits dissociative equilibria on entropic grounds. Understanding the barriers to β-elimination is an important aspect of the elucidation of the mechanism of alkene polymerization catalysis.¹⁵ One important class of alkene polymerization catalysts, the Phillips' catalysts, are chromium-based,¹⁶ and accordingly a study of the mechanistic aspects of β-elimination in (trimps)CrBuⁿ₃ is currently under way.

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