

Preparation of Titanium Pentamethylcyclopentadienyl Trialkyls and Crystal Structure of Tribenzylpentamethylcyclopentadienyltitanium, showing Some Evidence of a $\text{CH}_2 \cdots \text{Ti}$ Interaction

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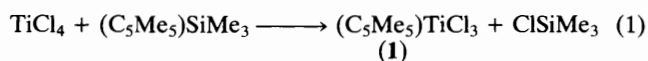
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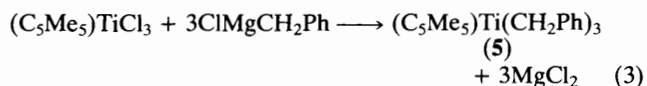
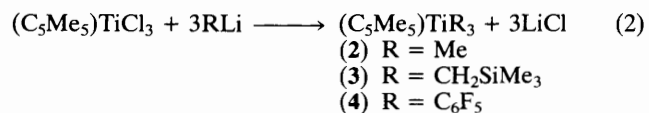
Titanium pentamethylcyclopentadienyl trialkyls $(\eta^5\text{-C}_5\text{Me}_5)\text{TiR}_3$ (R = Me, CH_2SiMe_3 , C_6F_5 , and CH_2Ph) are easily obtained by conventional alkylation of the trichloro analogue; the structure of the tribenzyl derivative, determined by X-ray methods, shows some evidence of a $\text{CH}_2 \cdots \text{Ti}$ interaction.

Monocyclopentadienyl complexes of the early transition metals are being intensively studied¹ owing to the fact that a single cyclopentadienyl ring, especially the pentamethylated ligand, imparts sufficient stability to the complex while at the same time leaving co-ordination vacancies in the metal suitable for interactions with additional ligands. We report here the high-yield synthesis of some titanium monopentamethylcyclopentadienyl trialkyls, which should be formally twelve electron species.

The trichloro-derivative (1) can be prepared in practically quantitative yield according to reaction (1).



Compound (1) can be in turn easily alkylated in a conventional way using stoichiometric amounts of the corresponding organolithium or Grignard reagents in diethyl ether or hexane, equations (2) and (3).



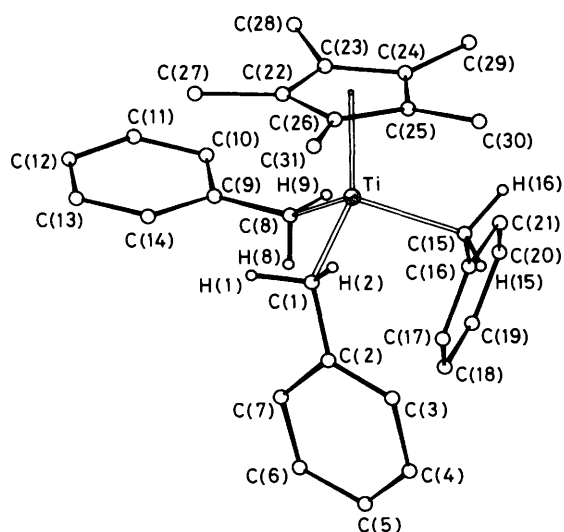


Figure 1. View of the structure of $(\eta^5\text{-C}_5\text{Me}_5)\text{Ti}(\text{CH}_2\text{Ph})_3$ with the atomic numbering scheme. Selected bond distances (Å) and angles ($^\circ$): Ti-C(1) 2.156(10), Ti-C(8) 2.081(10), Ti-C(15) 2.140(10); C(1)-Ti-C(8) 104.2(4), C(8)-Ti-C(15) 103.8(4), C(1)-Ti-C(15) 103.2(4), Ti-C(1)-C(2) 114.0(7), Ti-C(8)-C(9) 139.0(7), Ti-C(15)-C(16) 113.9(6).

Compounds (2)–(5) were analytically and spectroscopically characterized[†] and in view of the lack of structural data on monocyclopentadienyl triorgano-derivatives of the group 4 elements and of the high formal electronic deficiency of the titanium atom, an X-ray analysis of (5) was undertaken.‡ The structure of (5), depicted in Figure 1, is a ‘three-legged piano stool’ with the three ‘legs’ symmetrically placed; the three $\text{C}_\alpha\text{-Ti-C}_\alpha$ angles are about 104° and the plane through the three α -carbon atoms is almost parallel to the plane of the C_5Me_5 ligand [dihedral angle: $2.6(4)^\circ$]. Two of the benzyl ligands are positioned with their phenyl rings pointing downwards with respect to the cyclopentadienyl ring, as expected, while the third one surprisingly has its phenyl ring

pointing upwards, being disposed almost parallel to the cyclopentadienyl ring [dihedral angle: $7.0(4)^\circ$]. The Ti-C(8) distance [2.081(10) Å] is shorter than those to C(1) and C(15) [2.156(10) and 2.140(10) Å] involving the other benzyl ligands and the Ti-C(8)-C(9) angle $139.0(7)^\circ$ is, to our knowledge, unprecedentedly large for an expected tetrahedral angle.

This situation is in striking contrast with that found for the analogous $(\text{C}_5\text{Me}_5)\text{Th}(\text{CH}_2\text{Ph})_3$, where the three benzyl groups have their phenyl rings pointing in the opposite direction to the C_5Me_5 ring but a ‘benzallyl’ type distortion of the benzyl groups is found;² this same kind of distortion is also present in $\text{Ti}(\text{CH}_2\text{Ph})_4$.³ Our example is, however, similar to that reported for $(\text{C}_5\text{Me}_5)\text{Ta}(\text{CHPh})(\text{CH}_2\text{Ph})_2$, a three-legged piano stool complex in which the phenyl ring of the benzylidene ligand points toward the C_5Me_5 ring allowing in this way the benzylic hydrogen atom to interact with the metal.⁴ Thus, in our case the CH_2 hydrogens of the ‘anomalous’ benzyl ligand are situated at 2.32 and 2.37 Å from Ti, distances which are much shorter than those involving the CH_2 hydrogen atoms of the ‘normal’ benzyl groups (2.57–2.66 Å) and moreover are of the same order as those reported in other cases where a C-H-Ti interaction is present.^{5,6} Thus, the structural features of (5), rather than being a consequence of the packing forces in the crystal may indicate the existence of a double ‘agostic’⁷ C-H₂ ··· Ti interaction by means of which the Ti atom alleviates its electronic deficiency.

To the best of our knowledge compound (5) is the first case in which such a double interaction C-H₂ ··· M is postulated;§ such a possibility has already been theoretically discussed in $\text{H}_5\text{TiCH}_3^{2-}$ model systems.⁸

Our system is also fluxional as shown by the ^1H n.m.r. spectra in which a single peak for the six benzylic protons is seen even at -70°C ; this case would nevertheless not be uncommon within C-H ··· M interactions.⁷

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† *N.m.r. data*: (2), ^1H (C_6D_6) δ 1.74 (s, 15H, C_5Me_5) and 0.99 (s, 9H, Me); ^{13}C (C_6D_6) δ 122.3 (C_5Me_5), 61.2 (Me), and 12.0 (C_5Me_5); (3) ^1H (C_6D_6) δ 1.86 (s, 15H, C_5Me_5), 1.37 (s, 6H, CH_2), and 0.28 (s, 27H, SiMe₃); ^{13}C (C_6D_6) δ 122.6 (C_5Me_5), 84.4 (CH_2), 12.9 (C_5Me_5), and 2.95 (SiMe₃); (4) ^1H (C_6D_6) δ 1.79 (s, C_5Me_5); ^{13}C (tetrahydrofuran) δ 142.9, 130.3, and 129.7 (C_6F_5), 126.6 (C_5Me_5), and 14.5 (C_5Me_5); (5) ^1H (C_6D_6) δ 7.26–6.94 (m, Ph), 2.73 (s, 6H, CH_2), and 1.61 (s, 15H, C_5Me_5); ^{13}C (CDCl_3) (assignments confirmed by ^{13}C - ^1H coupled spectra) δ 150.0 ($\beta\text{-CH}_2\text{Ph}$), 128.2 (*o*-Ph), 126.7 (*m*-Ph), 123.9 (C_5Me_5), 122.3 (*p*-Ph), 94.0 (CH_2), and 11.9 (C_5Me_5).

‡ *Crystal data* for (5): $\text{C}_{31}\text{H}_{36}\text{Ti}$, $M = 456.53$, orthorhombic, space group $Pbca$, $a = 16.589(6)$, $b = 22.898(8)$, $c = 13.556(7)$ Å, $U = 5149(4)$ Å³, $Z = 8$, $D_c = 1.178$ g cm⁻³, $F(000) = 1952$, $\lambda = 0.71073$ Å, $\mu(\text{Mo-K}_\alpha) = 3.42$ cm⁻¹. The intensities of 4083 independent reflections were collected on a Siemens AED diffractometer (with θ in the range $2.5\text{--}24^\circ$) using the $\theta\text{-}2\theta$ scan technique and niobium-filtered Mo-K α radiation. The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares on the basis of 1604 observed reflections [$I \geq 2\sigma(I)$] with anisotropic thermal parameters for the non hydrogen atoms excepting those of the phenyl rings. All hydrogen atoms, clearly localized from a ΔF map, were not refined but introduced in the final structure factor calculations. Final R and R_w values of 0.064 and 0.081. 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, 1986.

§ Since submission of this work a neutron diffraction study providing evidence of a C-H₂ ··· Th interaction has appeared; see ref. 9.