

A Titanium–Methyl Group containing a Covalent Bridging Hydrogen System: X-Ray Crystal Structure of $\text{Ti}(\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2)\text{MeCl}_3$

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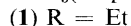
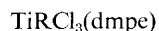
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The X-ray crystal structure of $\text{Ti}(\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2)\text{MeCl}_3$ shows that a Ti–C–H angle and the corresponding Ti–H distance of the Ti–Me moiety are $70(2)^\circ$ and $2.03(4) \text{ \AA}$, respectively; the bonding of the Ti–H–C(methyl) system is described in terms of a two-electron three-centred covalent bond and it is proposed that such distorted transition metal– α -hydrogen interactions will occur quite widely.

A continuing study of factors which lead to reversible 1,2-hydrogen shift equilibria in transition metal alkyl systems¹ led us to propose² that when a methyl group is attached to a d^0 metal centre which has a less than 18-electron environment (an electronically unsaturated centre) then one of the C–H bonds of the methyl group might distort towards the metal centre.

We have previously shown that a β -C–H moiety of the ethyl group in $\text{TiEtCl}_3(\text{dmpe})$ (**1**) can bond to the titanium centre *via* a bridging hydrogen system, causing distortion of the Ti–C–C angle to 86° .³ We now report the X-ray crystal structure of the methyl analogue, $\text{TiMeCl}_3(\text{dmpe})$ (**2**).



This was prepared, by addition of dmpe (1 equiv.) to TiMeCl_3 in light petroleum (b.p. $40\text{--}60^\circ\text{C}$) at -15°C , as extremely sensitive red-black crystals. The variable temperature ^1H n.m.r. spectrum of (**2**) shows it to be a fluxional molecule similar to (**1**);³ the spectra will be discussed in detail elsewhere.

Crystal data: $\text{C}_7\text{H}_{19}\text{Cl}_3\text{P}_2\text{Ti}$, $M = 319.5$, orthorhombic, space group $Pbca$, $a = 13.242(2)$, $b = 14.041(4)$, $c = 16.522(2) \text{ \AA}$, $U = 3071.7 \text{ \AA}^3$, $Z = 8$, $D_c = 1.382 \text{ g cm}^{-3}$; $\mu(\text{Mo-K}\alpha) = 12.53 \text{ cm}^{-1}$; data were collected on an Enraf-Nonius CAD4F diffractometer using graphite monochromated $\text{Mo-K}\alpha$ radiation up to $2\theta = 60^\circ$. The structure was solved by Patterson and Fourier methods and refined isotropically and then anisotropically by full-matrix least-squares using 2193 absorption-corrected independent reflexions with $I > 3\sigma(I)$. All the hydrogens were located from a difference map. The hydrogens of C(1), which were the most prominent in the difference map,

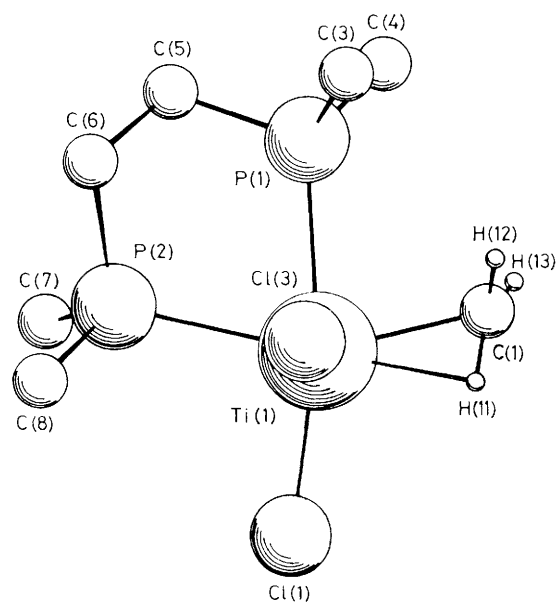


Figure 1. Crystal structure of (**2**) showing the plane containing the $\text{P}_2\text{TiCH}(11)$ atoms; for clarity, the hydrogens of the dmpe ligand are omitted: the Cl(2) atom (not shown) is located symmetrically in the Cl(3)–Ti axis below the plane. Selected distances and angles are: Ti–Cl(1), 2.294(1), Ti–Cl(2), 2.310(1), Ti–Cl(3), 2.305(1), Ti–C(1), 2.149(5), Ti–H(11), 2.03(4), Ti–H(12), 2.56(5), Ti–H(13), 2.68(4), C(1)–H(11), 1.00(2), C(1)–H(12), 0.93(2), C(1)–H(13), 0.90(2) Å; Ti–C(1)–H(11), $70(2)^\circ$, Ti–C(1)–H(12), $105(4)^\circ$, Ti–C(1)–H(13), $117(3)^\circ$, H(11)–C(1)–H(12), $104(4)^\circ$, H(11)–C(1)–H(13), $146(4)^\circ$, H(12)–C(1)–H(13), $106(5)^\circ$.

were refined isotropically and the rest of the hydrogens were assigned fixed isotropic temperature factors and their positional parameters refined with slack constraints;⁵ the C-H bond lengths were constrained at the values observed on the difference map, with an allowed estimated standard deviation of 0.02 Å. The refinement has converged to an R value of 3.99% (R_w 3.82 %).†

The molecular structure is shown in Figure 1 together with important dimensions. The titanium centre adopts a distorted octahedral stereochemistry which is largely similar to that in (3),³ and in particular the C(1) atom in both complexes is deflected away from Cl(1), although to a lesser extent in the present case. The C(1) methyl group has a low thermal motion and clearly resolved hydrogens, but it displays a severe distortion such that one of the hydrogen atoms is in close proximity to the metal atom. The Ti-H(11) distance of 2.03(4) Å lies well within the sum of the van der Waals radii and is shorter than that in (1) (2.29 Å). The Ti-C(1)-H(11) angle of 70(2)° reflects the severity of the distortion required to bring H(11) to its observed position. We conclude that a direct Ti-H-C interaction is present which can be described in terms of a two-electron three-centred bond.

The geometry of (2) provides the first evidence for a highly distorted transition metal- α -hydrogen interaction in a metal-alkyl system, and may be regarded as a model for the transition state of the 1,2-hydrogen shift (α -elimination) process. The distortion of the Ti-Me group in (2) may be compared with those in the alkylidene systems M-CHR where the M-C-H angle lies in the region 78–85°.⁶

Evidence for π -interactions between a transition metal and α -C-H systems has been obtained from ¹H n.m.r. data⁷ and e.s.r. data.⁸ There is also considerable evidence for direct bonding of β and other aliphatic C-H hydrogens to metal centres.^{3,9–11}

Taken together these data show that when a transition metal centre has a vacant orbital of suitable energy and direction, then C-H groups, even of aliphatic systems can act essentially as 'lone pairs' which can donate to suitable empty metal orbitals. Suitable metal centres are likely to be found for \leq 16-electron transition metal-alkyl compounds.

When the 'half-arrow' convention¹² is used to represent the formal 'lone pair' donation then the Ti-methyl group of (2) (Figure 2) is seen to act formally as a three-electron donor to the titanium. Also, the bidentate nature of the methyl group in (2) is emphasised and this provides a means whereby a metal centre can govern the stereochemistry of an aliphatic alkyl ligand. The above observations are relevant to our earlier proposal that the carbon-carbon bond-forming step in Ziegler-

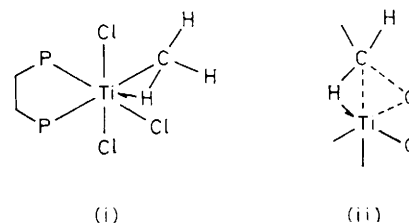


Figure 2. (i) A formal representation of the bonding in (2). (ii) A representation of a transition state for the carbon-carbon bond-forming step in the olefin insertion reaction involving interaction of an α hydrogen with the metal centre.

Natta olefin polymerisation is assisted by migration of an α -hydrogen from the growing polymer chain to the metal.¹³ Most of the principles of this proposal are still valid even if the α -hydrogen migration to the metal centre is only partial rather than complete [see Figure 2 (ii)].

We thank the Petroleum Research Fund administered by the American Chemical Society for partial support. We also thank the S.E.R.C. for a post-doctoral fellowship (to Z.D.) and the British Council for a research studentship (to V.S.B.M.).

Received, 13th September 1982; Com. 1083

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.