

Evidence for Carbon–Hydrogen–Titanium Interactions: Synthesis and Crystal Structures of the Agostic Alkyls $[\text{TiCl}_3(\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2)\text{R}]$ ($\text{R} = \text{Et}$ or Me)^{*}

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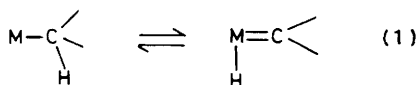
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The compounds $[\text{TiCl}_3(\text{dmpe})\text{R}]$ ($\text{R} = \text{Me}$, CH_2D , or Et ; $\text{dmpe} = \text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2$) have been prepared. An X-ray crystal structure determination of $[\text{TiCl}_3(\text{dmpe})\text{Et}]$ shows that the Ti–C–C angle of the Ti–Et moiety is $86.3(6)^\circ$. Variable-temperature n.m.r. studies show the molecule to be fluxional at room temperature. At -90°C the n.m.r. spectra correspond to the structure found in the crystal and $J(\text{C}-\text{H})$ for the ethyl CH_2 hydrogens is 150.2 Hz. It is concluded that the ethyl group is bonded by a $\overline{\text{Ti}-\text{CH}_2\text{CH}_2-\text{H}}$ system. The crystal structure of $[\text{TiCl}_3(\text{dmpe})\text{Me}]$ has been determined from X-ray and neutron diffraction data. The data show the methyl group to be distorted such that it is tilted with respect to the Ti–C vector and one hydrogen atom closely approaches the Ti centre giving an angle for Ti–C–H of $93.5(2)^\circ$ (neutron data). Variable-temperature n.m.r. studies show that $[\text{TiCl}_3(\text{dmpe})\text{R}]$ ($\text{R} = \text{CH}_3$ or CH_2D) are fluxional but provide no evidence for differentiation of the C–H moiety of the methyl group.

The reversible 1,2-hydrogen shift process in certain transition metal–alkyl compounds (α -elimination), equation (1), is now



well established.^{1–3} The forward reaction amounts to the oxidative-addition of a C–H unit to the metal centre and the formation of the alkylidene–hydride causes a formal increase in the electron number of the metal by two and the reduction of the d^n number of the metal centre by two. The formal oxidative-addition of the α -C–H bond can, therefore, only take place if the metal centre has at least two electrons available, *i.e.* $n = 2$ or more for d^n . There must also be an appropriate empty orbital on the metal centre.

We were interested to examine transition metal–alkyls in which the metal centre had an appropriate empty orbital but with a d^0 configuration. We wondered if there would be evidence for interaction between the α -C–H group and the empty metal orbital giving rise to distortions akin, for example, to those found to occur in certain tantalum–alkylidene compounds.⁴ For these reasons we set out to determine the structure of a transition metal–alkyl compound which had an electron number for the metal of 16 or less and which was d^0 . Since it was necessary to locate hydrogen atoms near the transition metal a metal with a low atomic number was preferred. Also, in order to decrease the likelihood of disorder in the crystal low molecular symmetry was desired. Examination

of the literature in the light of these constraints led us to select the compounds $[\text{TiCl}_3(\text{dmpe})\text{R}]$ [$\text{R} = \text{Et}$ (2) or Me (3); $\text{dmpe} = \text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2$]. The synthesis and characterisation of these compounds is described below. Preliminary reports of a part of these studies have appeared.^{5,6}

Results

The long-known⁷ compound TiCl_3Et (1) is an extremely air- and moisture-sensitive liquid which decomposes steadily at room temperature. Hydrocarbon solutions at room temperature decompose more slowly. Compound (1) may be distilled *in vacuo* but the vapour is photosensitive. Treatment of (1) with 1,2-bis(dimethylphosphino)ethane (dmpe) gave black-red crystals of $[\text{TiCl}_3(\text{dmpe})\text{Et}]$ (2). Compound (2) is also extremely air- and moisture-sensitive but it is considerably more thermally stable than (1) and the solid can be kept at room temperature. Solutions of (2) in toluene decompose steadily at room temperature yielding a dull-red insoluble powder. Crystals of $[\text{TiCl}_3(\text{dmpe})\text{Et}]$ suitable for X-ray diffraction were prepared by slow crystallisation at -5°C from toluene. It was essential to remove any traces of TiO_2 formed by contact with the glass.

The complex $[\text{TiCl}_3(\text{dmpe})\text{Me}]$ (3) was prepared by treatment of a light petroleum (b.p. $40\text{--}60^\circ\text{C}$) solution of TiCl_3Me ⁸ with dmpe at -15°C . The orange-red precipitate was recrystallized from toluene as red-black crystals. These were extremely air- and moisture-sensitive but less thermally sensitive than the ethyl analogue (2). Solutions may be allowed to stand at room temperature for several days before decomposition becomes substantial. The decomposition product was a red powder identical in appearance and behaviour to that obtained from thermal decomposition of (2).

Crystal Structures of (2) and (3).—The molecular structures of (2) and (3) were determined from X-ray data at room temperature [(3X)] and neutron data at 20 K for (3) [(3N)].

* [1,2-Bis(dimethylphosphino)ethane]trichloro-(ethyl- C^α , H^β)titanium and -(methyl)titanium.

Supplementary data available (No. SUP 56535, 6 pp.): thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii–xx. Structure factors are available from the editorial office.

Table 1. Selected interatomic distances (Å) and interbond angles (°)

	(2) X-Ray	(3X) X-Ray	(3N) Neutron	(2) X-Ray	(3X) X-Ray	(3N) Neutron
Ti-Cl(1)	2.408(3)	2.294(1)	2.312(2)	74.8(3)	80.0(2)	76.36(6)
Ti-Cl(2)	2.313(3)	2.310(1)	2.324(2)	149.6(3)	154.6(2)	150.91(8)
Ti-Cl(3)	2.303(3)	2.305(1)	2.311(2)	117.0(4)	115.9(2)	114.91(7)
Ti-P(1)	2.560(3)	2.585(1)	2.589(2)	117.4(3)	117.9(2)	117.57(7)
Ti-P(2)	2.570(3)	2.582(1)	2.591(2)	114.8(4)	111.5(2)	111.71(7)
Ti-C(1)	2.151(9)	2.149(5)	2.122(2)	104.0(5)	103.2(3)	103.69(7)
Ti-C(2)	2.524(10)			100.4(7)	104.1(3)	103.30(7)
P(1)-C(3)	1.804(10)	1.805(5)	1.821(2)	100.7(6)	102.5(3)	104.13(8)
P(1)-C(4)	1.827(9)	1.811(6)	1.821(2)		111.2(4)	109.82(8)
P(1)-C(5)	1.84(1)	1.815(6)	1.837(2)		109.6(4)	108.05(7)
P(2)-C(6)		1.831(6)	1.833(2)		104.3(4)	103.99(8)
P(2)-C(61)	1.84(2)				102.5(4)	105.74(7)
P(2)-C(62)	1.83(1)			103.9(6)	106.8(5)	103.74(8)
P(2)-C(7)	1.83(1)	1.807(7)	1.815(2)		111.5(2)	111.46(7)
P(2)-C(8)	1.83(3)	1.798(7)	1.814(2)	115.4(5)	115.1(3)	115.25(7)
C(5)-C(6)		1.485(9)	1.535(1)	115.4(5)	115.3(4)	115.52(8)
C(5)-C(61)	1.54(3)				2.03(3)	2.447(3)
C(5)-C(62)	1.54(3)			2.73(8)	2.56(4)	2.803(3)
C(1)-C(2)	1.467(15)			2.77(7)	2.68(3)	2.737(3)
Cl(1)-Ti-Cl(2)	92.0(1)	93.30(5)	93.54(6)		1.00(2)	1.095(3)
Cl(1)-Ti-Cl(3)	93.5(1)	95.56(6)	95.46(7)		0.93(2)	1.082(2)
Cl(1)-Ti-P(1)	156.8(1)	168.59(6)	169.45(9)		0.90(2)	1.090(3)
Cl(1)-Ti-P(2)	82.1(1)	94.18(6)	94.93(7)			
Cl(1)-Ti-C(1)	128.4(3)	111.2(2)	114.03(8)	Ti...H(23)	2.22(10)	
Cl(2)-Ti-Cl(3)	173.0(1)	168.27(6)	168.23(8)	C(2)-H(23)	1.04(2)	
Cl(2)-Ti-P(1)	85.9(1)	83.95(4)	83.79(6)	Ti-C(1)-C(2)	86.3(6)	
Cl(2)-Ti-P(2)	87.6(1)	87.11(5)	87.95(7)	Ti-C(1)-H(11)		70(2)
Cl(2)-Ti-C(1)	90.4(3)	92.0(2)	92.76(7)	Ti-C(1)-H(12)		105(4)
Cl(3)-Ti-P(1)	87.3(3)	85.86(5)	85.99(6)	Ti-C(1)-H(13)		117(3)
Cl(3)-Ti-P(2)	88.9(1)	84.59(6)	83.74(6)	H(11)-C(1)-H(12)		104(4)
Cl(3)-Ti-C(1)	89.6(3)	92.0(2)	90.49(7)	H(11)-C(1)-H(13)		146(4)
P(1)-Ti-P(2)	74.75(9)	74.66(4)	74.82(6)	H(12)-C(1)-H(13)	100(8)	106(5)

For (3N): neutron only

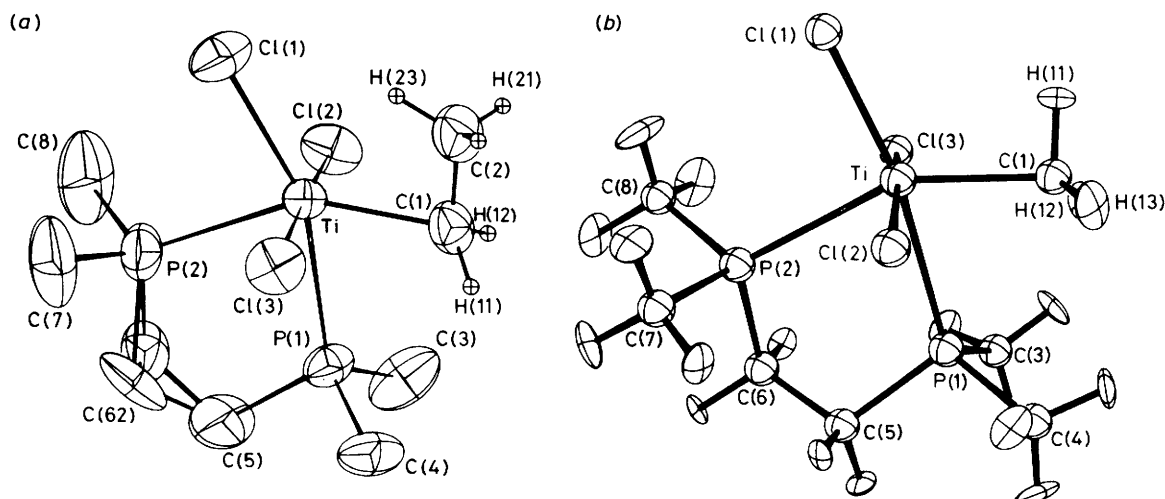
C(3)-H(31)	1.086(2)	C(4)-H(43)	1.088(2)	C(7)-H(71)	1.089(2)	C(8)-H(83)	1.087(3)
C(3)-H(32)	1.085(3)	C(5)-H(51)	1.098(2)	C(7)-H(72)	1.093(3)	H(11)...Cl(1)	3.322(3)
C(3)-H(33)	1.091(3)	C(5)-H(52)	1.098(2)	C(7)-H(73)	1.090(3)	H(11)...Cl(3)	3.237(3)
C(4)-H(41)	1.086(3)	C(6)-H(61)	1.102(2)	C(8)-H(81)	1.086(3)	H(12)...Cl(3)	3.110(3)
C(4)-H(42)	1.089(3)	C(6)-H(62)	1.099(2)	C(8)-H(82)	1.085(3)	H(13)...Cl(2)	2.967(3)

dmpe methyl, average angles

P-C-H	109.8(7)
H-C-H	109.2(5)

dmpe methylene, average angles

P-C-H	108.6(16)
C-C-H	111.4(10)
H-C-H	107.7(9)

**Figure 1.** The molecular structures of (a) (2), and (b) (3N) with the atom numbering. Thermal ellipsoids represent the 50% probability surface

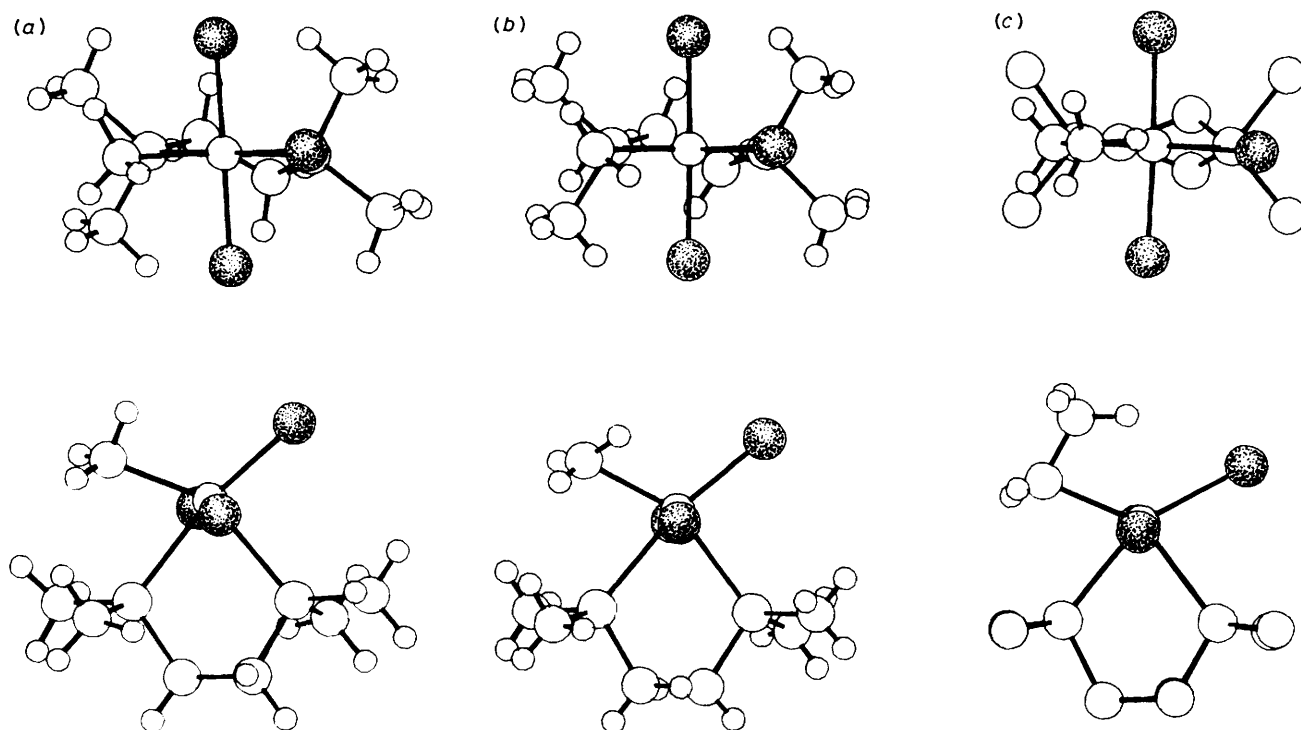


Figure 2. The molecular structures of (a) (3N), (b) (3X), and (c) (2) each projected onto and perpendicular to the P(1),Ti(1),P(2) plane to illustrate their similarity and their principal chemical features; Cl atoms are shaded

Compounds (2) and (3N) are shown with the atom numbering schemes and thermal ellipsoids in Figure 1. In Figure 2, (2), (3X), and (3N) are arranged to show structural comparisons. Selected interatomic distances and interbond angles with estimated standard deviations are given in Table 1. In general, bond lengths observed in (3N) are slightly longer than in (3X) which reflects the lesser thermal motion at 20 K. In both (2) and (3) the titanium centre has a distorted formally octahedral stereochemistry with the chelating dmpe ligand, the alkyl group, and one chlorine atom forming a plane, the second and third chlorine atoms at the two apices.

The dmpe ligand in (2) is disordered at C(5) and C(6). A similar disorder in (3) is not obvious but the short C(5)–C(6) bond [1.485(9) Å] in (3X) contrasts with the more normal value of 1.535(1) Å in (3N) and is indicative of some disorder at room temperature. Comparison of the dmpe ligands in Figure 2 shows how the disorder in (2) and to a lesser extent in (3X) increases the apparent symmetry of the dmpe ligand. The dimensions of the dmpe ligands are otherwise unexceptional. In both (2) and (3) the Ti–P(1) bond *trans* to Cl(1) is not significantly different in length from Ti–P(2) *trans* to the alkyl group, but the Ti–P bonds found here (mean 2.579 Å) are rather shorter than those observed in the 16-electron complex [Ti(η -C₇H₇)(dmpe)Et] (mean 2.665 Å)⁹ and [Ti(CO)₂(PF₃)(dmpe)₂] (mean 2.609 Å).¹⁰

In each of (2), (3X), and (3N) the axial Ti–Cl(2) and Ti–Cl(3) bond distances agree quite well. The observed bond lengths [2.303(3)–2.324(2) Å] are similar to the Ti–Cl bond lengths in octahedral titanium complexes (mean 2.324 Å)¹¹ but markedly shorter than those found in the 16-electron bent titanocenes (2.362 Å)¹¹ and longer than those in [TiCl₂(μ -O)(η -C₅H₅)₂] [2.239(2) Å]¹² and TiCl₄ (2.170 Å, from electron diffraction).¹³ The equatorial Ti–Cl(1) bond length in (3X) and (3N) is the same or very slightly shorter than the axial bond lengths, but in (2) it is exceptionally long, 2.408(3) Å.

The most interesting aspects of these structures concern the alkyl groups. In contrast to the 16- and 18-electron metal ethyls

where M–C–C angles in the range 108–126° have been reported,^{11,14} the Ti–C(1)–C(2) angle in (2) is 86.3(6)° and indicates clearly that there is a severe distortion with the result that the methyl group C(2) is drawn towards the titanium centre. There is no evidence from the structure that the unusual disposition of the ethyl group arises from intermolecular interactions. The ethyl hydrogen atoms are clearly resolved. The H(23) atom of the methyl group is located 2.22(10) Å from the metal. There are other examples where hydrogen atoms of formally saturated C–H systems closely approach a metal centre.¹⁵ H(23) is 0.17 Å out of the P(1),P(2),C(1),Cl(1) plane. The ethyl C(1)–C(2) bond length of 1.467 Å is rather shorter than the average C–C bond length, 1.541 Å, in metal ethyls.^{11,14} The Ti–C(1) distance [2.151(9) Å] is in the expected range for Ti–C bond lengths. The molecule represents a step along the reaction co-ordinate towards β -elimination to form the ethylene–hydride cation and a chloride anion, with a shortening of C(1)–C(2) towards the ethylenic C–C bond length, a substantial Ti...H(23) interaction, and a lengthening of Ti–Cl(1) prior to expulsion as the anion.

The Ti–C(1) bond length to the methyl group in (3) measured by X-ray methods [(3X), 2.149(5) Å] is in good agreement with (2) [2.151(9) Å]. The hydrogen atoms at C(1) in (3X) are clearly resolved and indicate the methyl group to be grossly distorted such that one of the hydrogen atoms is in close proximity to the metal atom. A Ti–C(1)–H(11) angle of 70(2)° was indicated with a Ti...H(11) distance of 2.03(3) Å, shorter than that in (2). The neutron determination confirms the existence of a C–H...Ti interaction but there are substantial and significant differences in the methyl groups in (3X) and (3N). The Ti–C(1) bond distance in (3N) of 2.122(2) Å is significantly shorter than that found in (3X) of 2.149(5) Å, and in opposition to the general trend that (3N) gives longer bond lengths than (3X). The C(1)–Ti–X (X = P or Cl) angles also show marked differences (Table 1). In the neutron determination, the CH₃ group is a regular trigonal pyramid [in contrast to the distorted flattened

Table 2. N.m.r. data

Compound	Nucleus	$\theta/^\circ\text{C}$	Data and assignments ^a
[TiCl ₃ (dmpe)Me] (3)	¹ H	-90	2.29 [t, 3 H, <i>J</i> (P-H) 7.7, TiCH ₃], 2.19 [m, 2 H, CH ₂], 2.03 [m, 2 H, CH ₂], 1.61 [d, 6 H, <i>J</i> (P-H) 10.0, 2PCH ₃], 1.42 [d, 6 H, <i>J</i> (P-H) 10.30, 2PCH ₃] ^b
		35	2.19 [t, 3 H, <i>J</i> (P-H) 8.0, TiCH ₃], 2.15 [d, 4 H, <i>J</i> (P-H) 11.9, 2CH ₂], 1.59 [d, 12 H, <i>J</i> (P-H) 10.0, 4PCH ₃] ^b
	¹³ C	-90	87.52 [d of q, <i>J</i> (C-H) 129.5, <i>J</i> (P-C) 32.4, TiCH ₃], 26.65 [t of 4 line m, <i>J</i> (C-H) 136.6, CH ₂], 22.98 [t of 4 line m, <i>J</i> (C-H) 122.6, CH ₂], 13.26 [q of 4 line m, <i>J</i> (C-H) 132.0, 4PCH ₃] ^c
		35	82.59 [s, br, TiCH ₃], 26.64 [t, <i>J</i> (C-H) 130.5, 2PCH ₂], 14.01 [q, <i>J</i> (C-H) 131.0, 4PCH ₃] ^c
	³¹ P- ¹ H	-70	28.14 [s, 1 P, dmpe], 26.72 [s, 1 P, dmpe] ^c
		10	28.5 [s, br, 2 P, dmpe] ^c
[TiCl ₃ (dmpe)(CH ₂ D)] (3D)	¹ H	20	2.17 [d, 4 H, <i>J</i> (P-H) 12.0, 2CH ₂], 1.89 [s, br, 2 H, TiCH ₂ D], 1.54 [d, 12 H, <i>J</i> (P-H) 9.8, 4PCH ₃] ^d
		35	81.85 [m, br, TiCH ₂ D], 26.53 [s, br, 2PCH ₂], 13.91 [d, <i>J</i> (P-C) 16.6, 4PCH ₃] ^b
[TiCl ₃ (dmpe)Et] (2)	¹³ C	-92	87.14 [t, br, <i>J</i> (C-H) 130.5, TiC], 26.50 [t, br, <i>J</i> (C-H) 139.4, PCH ₂], 22.78 [t, br, <i>J</i> (C-H) 139.4, PCH ₂], 13.16 [q, br, <i>J</i> (C-H) 130.5, 4PCH ₃] ^b
		35	81.85 [m, br, TiCH ₂ D], 26.53 [s, br, 2PCH ₂], 13.91 [d, <i>J</i> (P-C) 16.6, 4PCH ₃] ^b
[TiCl ₃ (dmpe)Et] (2)	¹ H	-90	2.70 [d of t, 3 H, <i>J</i> (H-H) 7.8, <i>J</i> (P-H) 6.56, TiCH ₂ CH ₃], 2.53 [ddq, 2 H, <i>J</i> (H-H) 7.8, <i>J</i> (P-H) 12.1, <i>J</i> (P-H) unresolved, TiCH ₂], 2.29 [12-line m, 2 H, PCH ₂], 2.15 [12-line m, 2 H, PCH ₂], 1.68 [d, 6 H, <i>J</i> (P-H) 10.3, 2PCH ₃], 1.53 [d, 6 H, <i>J</i> (P-H) 10.0, 2PCH ₃] ^b
		0	2.65 [m, 5 H, TiC ₂ H ₅], 2.24 [s, vbr, 4 H, 2PCH ₂], 1.64 [s, vbr, 12 H, 4PCH ₃] ^b
	40	2.76 [second-order 7-line m, 2 H, TiCH ₂], 2.57 [second-order 8-line m, 3 H, TiCH ₂ CH ₃], 2.24 [complex doublet, 4 H, <i>J</i> (P-H) 11.5, 2PCH ₂], 1.66 [d, 12 H, <i>J</i> (P-H) 9.8, 4PCH ₃] ^b	
	¹³ C	-60	81.04 [tdd, <i>J</i> (C-H) 150.2, <i>J</i> (P-C) 31.8, <i>J</i> (P-C) 3.1, TiCH ₂], 27.77 [tdd, <i>J</i> (C-H) 128.9, <i>J</i> (P-C) 14.5, <i>J</i> (P-C) 19.5, PCH ₂], 23.08 [tdd, <i>J</i> (C-H) 136.4, <i>J</i> (P-C) 22.8, <i>J</i> (P-C) 12.4, PCH ₂], 14.15 [qd, <i>J</i> (C-H) 130.8, <i>J</i> (P-C) 23.5, 2PCH ₃], 13.80 [q of d, <i>J</i> (C-H) 130.8, <i>J</i> (P-C) 21.3, 2PCH ₃], 3.81 [qdd, <i>J</i> (C-H) 126.8, <i>J</i> (P-C) 11.7, <i>J</i> (P-C) 1.5, Ti-CH ₂ CH ₃] ^c
		0	85.16 [t, br, <i>J</i> (C-H) 147.3, TiCH ₂], 28.11 [t, br, <i>J</i> (C-H) ca. 129, PCH ₂], 23.58 [t, br, <i>J</i> (C-H) ca. 138, PCH ₂], 13.91 [qd, <i>J</i> (C-H) 131.8, <i>J</i> (P-C) 21.9, 4PCH ₃], 5.76 [q, br, <i>J</i> (C-H) 125.7, TiCH ₂ CH ₃] ^e
	³¹ P- ¹ H	-70	30.3 [d, 1 P, <i>J</i> (P-P) 3, dmpe], 23.6 [d, 1 P, <i>J</i> (P-P) 3, dmpe] ^c
20		28.4 [s, vbr, 2 P, dmpe] ^c	

^a Given as: chemical shift (δ) [multiplicity, relative intensity, *J* in Hz, assignment]. ^b 400-MHz Spectra in CD₂Cl₂. ^c In CD₂Cl₂. ^d In C₄D₈O at 300 MHz. ^e In CD₂Cl₂ at 300 MHz.

pyramid in (3X)] which is tilted such that the Ti-C(1)-H(11) angle is 93.5(2)°, as compared with Ti-C(1)-H(12) [118.4(2)°] and Ti-C(1)-H(13) [112.9(2)°]. In all other respects the methyl group appears normal, with C-H distances and H-C-H angles in typical ranges with no unusual values associated with H(11) except for Ti-C(1)-H(11). The neutron analysis shows Ti...H(11) 2.447(3) Å, which is shorter than Ti...H(12) [2.803(3) Å] and Ti...H(13) [2.737(3) Å]. The interligand distances H(11)...Cl(1) [3.322(3) Å] and H(11)...Cl(3) [3.237(3) Å] are both longer than H(12)...Cl(3) [3.110(3) Å] and H(13)...Cl(2) [2.967(3) Å].

It appears that in the X-ray study of (3X) the position of H(11) is subject to appreciable error, well beyond the least-squares derived e.s.d. [angle Ti-C(1)-H(11) differs by more than 7 σ between (3X) and (3N)]. Ibers¹⁶ has noted the difficulties sometimes experienced in properly locating hydrogen atoms in X-ray work; these difficulties stem from the fact that peaks due to hydrogen atoms are typically near the noise level of the electron-density maps. However the discrepancy may be due to an asymmetric distribution of electron density about the hydrogen nucleus so that the centroid of the electron density does not coincide with the nuclear position. Thus, neutron data may be required to accurately and unambiguously locate hydrogen nuclei.

N.M.R. Studies.—The ¹H n.m.r. spectrum of (2) at -90 °C may be assigned in a straightforward manner. N.m.r. data and assignments are given in Table 2. The ³¹P n.m.r. spectrum at -70 °C indicates the two phosphorus nuclei to have different chemical shifts. The ¹³C n.m.r. spectrum at -60 °C shows there to be two pairs of inequivalent PMe₂ groups and two different CH₂ groups.

Table 3. Temperature variation of chemical shifts of Ti-CH₂CH₃ in the ¹H n.m.r. spectra of (2)

$\theta/^\circ\text{C}$	$\delta(\text{CH}_3)/\text{p.p.m.}$	$\delta(\text{CH}_2)/\text{p.p.m.}$
-90	2.70	2.53
-70	2.70	2.55
-50	2.70	2.58
-30	2.67	2.61
0	2.65	2.65
20	2.61	2.69
40	2.57	2.76

These data strongly suggest that the structure of (2) in solution at -90 °C is the same as that derived from the crystal structure determination. Variable-temperature n.m.r. data show that (2) undergoes fluxional processes at room temperature. As the temperature is raised, two dominant changes are seen in the ¹H n.m.r. spectrum. The chemical shift of the band assigned to the TiCH₂ group moves towards that of the band assigned to the methyl of TiEt. At -30 °C, the CH₃ band also begins to move toward that of the CH₂ group. At ca. 0 °C, the two signals superimpose (at 2.65 p.p.m.). As the temperature is raised to 40 °C, the two signals have 'passed through' each other and at higher temperatures move to 2.76 (Ti-CH₂) and 2.57 p.p.m. (CH₃). At this temperature the Ti-CH₂ band is a seven-line multiplet, and that for the CH₃ group is a complex, partly resolved eight-line multiplet. On cooling the original spectrum returns unchanged. Variable-temperature chemical shift data for the Ti-C₂H₅ hydrogens are given in Table 3.

The bands assignable to the PCH₂ and PCH₃ groups of (2) also shift with varying temperature. At -90 °C there are two multiplets at 2.29 and 2.15 p.p.m. (PCH₂) and two doublets at 1.68 and 1.53 p.p.m. (PCH₃). At 0 °C both the signals become

very broad and are close to coalescence and at 20 °C they begin to sharpen. At 40 °C the signals are well resolved doublets at 2.24 (2PCH₂) and 1.66 p.p.m. (4PCH₃). Thus the PCH₂ groups become equivalent.

The ¹³C n.m.r. at 0 °C shows a quartet of doublets at 13.91 p.p.m. due to the four equivalent PCH₃ carbon nuclei split successively by their three protons and only one phosphorus nucleus. At 20 °C the ³¹P n.m.r. spectrum shows only a single very broad resonance and the phosphorus nuclei have become equivalent. The equivalence of the two CH₂PMe₂ groups presumably arises from rapid intramolecular interchange of the ethyl group from the low-temperature equatorial site to an axial position, *via* a 'turnstile' mechanism.

The value of $J(\text{C-H})$ at -60 °C for the TiCH₂ group is 150.2 Hz and this lies within the range expected for an *sp*²-hybridised CH₂ group rather than *sp*³. $J(\text{C-H})$ for the CH₃ group (of TiEt) is 126.8 Hz. The high value of $J(\text{C-H})$ for the CH₂ group, which is close to that for *sp*² C-H, can be correlated with the acute Ti-C-C angle at the CH₂ group. The value of $J(\text{C-H})$ of 126.8 Hz for the CH₃ group is consistent with the expected value for $J(\text{C-H})_{\text{av}}$ for an agostic ethyl group.¹⁵

The ¹³C n.m.r. spectrum of (2) at 0 °C shows a broad triplet at 85.16 p.p.m. due to the α -carbon of the Ti-C₂H₅ group coupled to two protons. The $J(\text{C-H})$ value at 147.3 Hz is the same, within experimental error, as at -60 °C. There is also a broad quartet at 5.76 p.p.m. due to the β -carbon of the Ti-C₂H₅ ethyl group. The value of $J(\text{C-H})$ at 0 °C (125.7 Hz) is close to that at -60 °C. These data suggest that the agostic ethyl group is still present at 0 °C. Finally, the change of chemical shift with temperature of the Ti-C₂H₅ hydrogens may be ascribed to the changing equilibrium concentrations of isomers with the isomers involved presumably being those where the ethyl group lies in the TiP₂ plane (equatorial) or normal to it (axial). There may also be an equilibrium between the agostic ethyl structure and an isomer of (2) with a normal Ti-C₂H₅ group.

The ¹H n.m.r. spectrum of (3) in CD₂Cl₂ at -90 °C shows a 1:2:1 triplet at 2.29 p.p.m. assignable to the TiCH₃ hydrogens coupled to two apparently equivalent ³¹P nuclei. There are two complex unresolved multiplets at 2.19 and 2.03 p.p.m. due to two inequivalent PCH₂ groups; and two sets of doublets at 1.61 and 1.42 p.p.m. due to two inequivalent sets of PCH₃ groups. The ¹³C n.m.r. spectrum of (3) in CD₂Cl₂ at -90 °C shows a doublet of quartets at 87.52 p.p.m. assignable to the Ti-CH₃ carbon nucleus coupled to three hydrogens and one phosphorus nucleus. In contrast to the observation of a binomial triplet for the Ti-C₂H₅ group in the ¹H n.m.r. spectrum, the low-temperature (-70 °C) ³¹P-¹H n.m.r. spectrum shows the presence of two inequivalent phosphorus nuclei at 28.14 and 26.72 p.p.m. We conclude that the magnitudes of $J(\text{P-H})$ for the Ti-C₂H₅ group are fortuitously coincident and that the structure of (3) at low temperature corresponds to that found in the crystal. On warming from -90 °C the ¹H n.m.r. spectrum steadily changes over the temperature range -90 to 35 °C, the triplet resonance for the Ti-CH₃ group moves from 2.29 to 2.19 p.p.m. The triplet is due to the TiCH₃ resonance coupled to two apparently equivalent phosphorus nuclei. This triplet is superimposed on a doublet at 2.15 p.p.m. assignable to two equivalent sets of PCH₂ protons. There is a doublet at 1.59 p.p.m. assignable to four equivalent sets of PCH₃ protons. Thus the four PCH₃ groups become chemically equivalent at the higher temperature limit, presumably *via* a turnstile mechanism involving the Ti-CH₃ group and the chlorine ligands, as proposed for (2). Rapid inversion of the PCH₂CH₂P backbone is also presumably taking place at this temperature, although this is not a requirement imposed by the spectrum as long as the methyl group occupies all four remaining octahedral available sites in the course of its dynamic behaviour. The ³¹P-¹H n.m.r. spectrum at 10 °C shows a single broad resonance at 28.5 p.p.m.

The broad nature of this signal presumably is due to its not having fully sharpened following coalescence. The deuterio-methyl analogue of (3), [TiCl₃(dmpe)(CH₂D)] (3D) was prepared using Zn(CH₂D)₂. The data for (3D) correspond closely to those of (3). The ¹³C n.m.r. spectrum provided the value for the ¹³C-¹H coupling constant of the methyl group of 130.5 Hz; this is closely similar to that for the C-methyl group of (3).

The compound [TiCl₃(dmpe)Me] was treated with a large excess of KH in toluene at room temperature. After 3 d the solution had changed from blood-red to an intense orange colour. Reddish crystals (30%) were obtained and a crystal structure determination showed them to be [TiCl₂(dmpe)₂] (4). During our work on (4) we discovered that the compound had been prepared independently,¹⁷ and so we discontinued our study.

Discussion

The distortions observed in the compounds (2) and (3) were the first reported for simple transition metal-alkyl groups.^{5,6} There are, however, a number of compounds for which there is clear evidence for bonding between a transition metal and carbon-hydrogen bonds. These have been reviewed recently.¹⁵ In most of the previous examples of M-H-C interactions the C-H group is part of a polyene system which is π -bonding to the metal centre.

It is quite new to think in terms of alkyl groups in transition metal-alkyl compounds acting as bidentate ligands, which formally donate three electrons to the metal centre. In order to emphasise this relatively recently recognised but probably quite widespread mode of bonding between saturated hydrocarbon groups and transition metal centres, the term agostic* has been introduced to describe the M-H-C(saturated) bond.¹⁵

Ab initio molecular orbital (m.o.) calculations on an analogue of (2), [TiEt(PH₃)₂Cl₂H] have provided support for an agostic C-H-M interaction.¹⁸ Calculated values of 89° for Ti-C-C, a short Ti-H ^{β} distance (2.23 Å) and a long C-H ^{β} (1.11 Å) bond were found in the fully optimized geometry.¹⁸ Analysis of the ligand effects suggested a donor interaction from the C-H ^{β} bond to a vacant Ti *d* orbital.

Consideration of the bonding in titanium-methyl derivatives akin to (3) has been given by Eisenstein and Jean¹⁹ and Morokuma and co-workers.²⁰ Eisenstein and Jean adopt a description somewhat analogous to that proposed for the distortions in tantalum-alkylidene groups²¹ whereby there is overlap between the Ti-CH₃ *p* orbital and a low-lying Ti *d* orbital. The consequential tilting of the methyl group does not involve direct Ti-H interaction and the local geometry of the CH₃ fragment is not significantly perturbed from C_{3v} in agreement with the observed geometry.

Ab initio m.o. calculations²⁰ on the compound [TiMe(PH₃)₂X₂Y] give a distorted Ti-C-H angle of 100°, as compared to the observed angle of 93.5(2)°, in (3N). This theoretical analysis attributes the distortion of the methyl group to direct interaction between the filled CH bonding orbital and an unoccupied Ti *d* orbital.²⁰

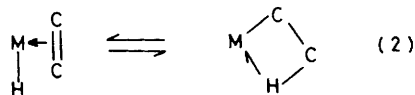
The description given by Eisenstein and Jean¹⁹ for distortions of the methyl group in [TiMeH₃]²⁻ can apply also to (2) whereby distortion of the α -carbon of the ethyl group would result in close approach of the methyl group to the metal. However, distortions at an α -carbon cannot account for the M-H-C interactions observed in compounds such as [Mo{Et₂-

* The term agostic is derived from the Greek word 'agostos' which may be translated as to clasp, to draw towards, to hold to oneself. We wish to acknowledge the advice of Mr J. Griffin, Balliol College, Oxford, who suggested the word.

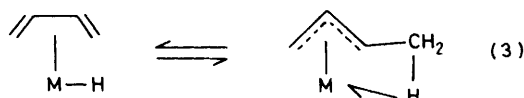
$B(pz)_2\{2-PhC_2H_4(CO)_2\}$ ($pz = \text{pyrazolyl}$).²² We prefer to think of the close approach of the C–H bond of ethyl compounds to a transition metal as arising from a M–H–C bonding interaction.

The intermolecular oxidative-addition of β -C–H groups of metal alkyls giving the metal–olefin–hydride compound is a classic reaction of metal alkyls. In the ethyl compound (2) it appears as if the ethyl group models a stage about half-way along the reaction co-ordinate for a β -elimination reaction to form the titanium–ethylene–hydride complex, $[TiH(dmpe)(\eta-C_2H_4)Cl_3]$. However, this compound would not be expected to be stable since the d^0 titanium centre cannot formally back-donate electrons to the ethylene ligand, as required in the conventional description of the metal–olefin bond. It might therefore have been expected that these distorted alkyls would only be observed when the metal centre had both an electron count less than 18 and a d^0 configuration.

However, the agostic M–H–C structure can be preferred to the 18-electron polyene-hydride alternative¹⁵ even when the metal centre has suitable d^n electrons, *i.e.* even for $n > 2$, the equilibrium (2) can lie to the right-hand side.



Brookhart,^{23a} Ittel,^{23b} and co-workers have shown that there can be an equilibrium between metal–diene–hydride systems and M–enyl–H groups: *viz.* equilibrium (3) where the ground-



state structure^{23c,d} has the agostic, carbon–hydrogen–metal bond. The equilibrium (2) between 18-electron metal–ethylene–hydride compounds and the 18-electron $M-C_2H_4-H$ system was first found in the compound $[Co(C_2H_4-H)(\eta-C_5Me_5)(\eta-C_2H_4)]BF_4$.²⁴ More recently the analogous cation $[Co(C_2H_4-H)(\eta-C_5Me_5)\{P(p-MeC_6H_4)_3\}]^+$ has been shown to have an agostic ethyl group by crystal structure determination.²⁵ In the latter compound the Co–C–C angle of the Co–ethyl group is $74.5(2)^\circ$; also, the C–C distance of the agostic ethyl is $1.480(5) \text{ \AA}$ (compared to 1.54 \AA for normal C–C single bonds) and the conformation about the C–C bond is eclipsed. Matrix isolation studies suggest the presence of an agostic ethyl group in the compound $[W(\eta-C_5H_5)(CO)_2Et]$.²⁶ We note, however, that $[Fe(\eta-C_5Me_5)(PMe_3)(\eta-C_2H_4)H]$ is an ethylene–hydride compound and is not agostic. There is a rapid equilibrium between the Fe–H and two hydrogens of the $\eta-C_2H_4$ group.²⁷ The crystal structure determination of $[Ti(dmpe)_2XY]$ ($X = Cl, Y = Me; X:Y = 1.3:7$) has indicated there to be a distorted methyl group.¹⁷

Agostic M–H–C systems normally exhibit characteristic features in their n.m.r. spectra and, as first demonstrated by Calvert and Shapley,²⁸ may be detected by comparison of their n.m.r. spectra with those of partially deuterated analogues. We note, however, that although the neutron diffraction data for (3) provide clear evidence for a highly distorted Ti–C₂H₅ group, the n.m.r. data for (3) and (3D) do not show significant variation of chemical shifts or any change in the values of $J(C-H)_{av}$ on deuteration.

The neutron diffraction data show that the distortion of the methyl group may be described as a tilting of a methyl group about the normal to the Ti,C(1),H(11) plane. The H–C–H angles are all normal and, more importantly, the three C–H

distances are the same within experimental error (Table 1). Neutron diffraction data on other agostic C–H hydrogens show that there is a lengthening of the C–H bond.¹⁵ In all previous cases where both neutron diffraction data and appropriate n.m.r. data, including partial deuteration, have been obtained on compounds with agostic C–H groups, the presence of the agostic hydrogen is indicated by the n.m.r. data. The lengthening of the C–H(agostic) bond is necessary for the detection of the agostic hydrogen by the Shapley experiment²⁸ since lengthening of the C–H(agostic) bond would cause a significant change in the C–H stretching frequency compared to those of the two normal C–H bonds of the agostic methyl group. Different C–H force constants for C–H groups which undergo fast exchange on the n.m.r. time-scale are required for a difference in the zero-point energy differences between H and D in the agostic bonds relative to terminal bonds. This changes the relative residence times of the agostic and normal hydrogens in the bridge position for the n.m.r. experiment. We conclude that since the three C–H distances of the Ti–CH₃ group of (3) are the same the C–H bond strengths will be closely similar. The closely similar n.m.r. data for (3) and (3D) can be understood in this way.

The averaged value of $J(C-H)$ for the agostic methyl group of (2) is 126.8 Hz. This is comparable with $J(C-H)_{av}$ found for other methyl groups with agostic hydrogens.¹⁵ It therefore seems that the C–H(agostic) of (2) will be found to be longer than the other two C–H bonds. This in turn means that the C–H–Ti interaction in (2) would be stronger than for (3). Elementary ring-strain arguments predict that the four-membered ring in (2) would be preferred to a three-membered ring in (2) involving an agostic α -hydrogen.

The compounds $[TiCl_3(dmpe)R]$ have, at first sight, a 12-electron count, but the presence of the M–H–C bridge raises this to 14 electrons. (A simple procedure for counting electrons in two-electron, three-centre bridging hydrogen systems has been discussed elsewhere.^{29,*})

It has been proposed that agostic interactions play a role in the bonding of intermediates formed during the polymerisation of ethylene by Ziegler–Natta catalysts.¹⁵ An early suggestion was that an α -agostic M–H–C interaction could assist in the crucial carbon–carbon bond-forming step.¹⁵ Recently, Schmidt and Brookhart have proposed that metal– β -agostic alkyls are involved in ethylene polymerisation catalysis where the factors which favour an agostic alkyl structure over an ethylene–hydride structure will facilitate alkyl-to-olefin migration in $M(\eta\text{-olefin})(\text{alkyl})$ compounds and lead to carbon–carbon bond formation.³⁰

Strong support for this proposal arises from the observation that the agostic-ethyl compounds $[Co(C_2H_4-H)(\eta-C_5H_5)-L]^+ A^-$ [$L = P(OMe)_3$ or $P(p-MeC_6H_4)_3$] are catalysts for ethylene polymerisation.^{25,30} A clear implication of the correlation between the partial migration of the hydrogen in the agostic-ethyl structure and the migration of an alkyl group to co-ordinated olefin is that this description is evocative of the alkyl-migration (Cossee) mechanism for Ziegler–Natta catalysis.³¹ The fact that the fragment $Ti(dmpe)Cl_3$ can interact with both an α -hydrogen of (3) and a β -hydrogen of (2) suggests that the stereoelectronic properties of a metal centre which favour β -interactions also favour α -hydrogen interactions. Thus, whilst the correlation between β -agostic-alkyl interactions and low-energy alkyl-to-ethylene migration provides an elegant basis for support for the Cossee mechanism, the involvement of α -hydrogen interactions,¹⁵ although less compelling, cannot be excluded.

* In this paper the Figures 6(f) and 6(e) should be interchanged when referred to in the text.

Experimental

All reactions and manipulations were carried out in an inert atmosphere or *in vacuo*. Light petroleum (b.p. > 80 °C) and toluene were dried by refluxing over potassium metal under dinitrogen. Light petroleum (b.p. 30–40 and 40–60 °C) was dried over sodium–potassium alloy. Solvents were distilled immediately prior to use.

Dichloromethane was dried by refluxing over CaH₂ and stored over molecular sieves (type 4A) for prolonged periods. N.m.r. spectra were obtained on either JNM-PMX, Bruker R32 (90 MHz), and 300 MHz or 400 MHz Bruker instruments. Spectra were calibrated using solvent peaks as internal standards. All chemical shifts are given in p.p.m. relative to δ(SiMe₄) = 0 p.p.m. Coupling constants (*J*) are in Hz.

Trichloro(ethyl)titanium.—The procedure previously described⁷ was employed with small modifications. Tetraethyl-lead (7.13 g, 0.022 mol) in a Schlenk vessel (250 cm³) equipped with a magnetic stirrer was attached to a vacuum manifold, cooled to –196 °C and evacuated. Light petroleum (50 cm³, b.p. 40–60 °C) was then distilled *in vacuo* into this reaction vessel, followed by TiCl₄ (8.39 g, 0.044 mol). The cooled mixture was evacuated for a few minutes and then allowed to warm gradually to room temperature (r.t.). On melting, contact between the reagents gave rise to a deep red-brown colouration and a thick brown precipitate. The mixture was stirred rapidly for 1 h after it had reached r.t. It was then filtered to give a deep red filtrate which was cooled to –78 °C. After 1 h a mass of purple-black crystals precipitated. The supernatant solution was discarded by decantation and the residual solid was redissolved in light petroleum (15 cm³, 40–60 °C). The solution was cooled to –78 °C giving purple crystals which were collected and stored at –80 °C.

Trichloro(methyl)titanium.—The published procedure⁸ was used with some modifications. ZnMe₂ (2.80 g, 0.029 mol) was placed in a Schlenk vessel (150 cm³) equipped with a magnetic stirrer bar. The vessel was attached directly to a vacuum manifold, cooled to –196 °C and evacuated. 2-Methylbutane (25 cm³) was then distilled *in vacuo* into this vessel followed by TiCl₄ (10.62 g, 0.056 mol). On melting, contact between the reagents gave rise to an initial red-brown colouration which dissipated as the mixture was allowed to warm gradually to r.t. to give an orange-yellow solution containing a finely divided white suspension of ZnCl₂. The mixture was stirred rapidly for 1 h after reaching room temperature, filtered, and the filtrate was cooled to –78 °C. A solid purple-black crystalline crust formed over 1–2 h which was then isolated by decantation. The solid was recrystallised twice from 2-methylbutane and then dried *in vacuo* at –78 °C for several hours. Yield 4.69 g, ca. 50%. The compound was stored at –78 °C under argon.

[1,2-Bis(dimethylphosphino)ethane]trichloro(ethyl)titanium.—The quantity of TiCl₃Et used was assessed by difference weighing of the storage vessel before and after removal of this compound. A red solution of TiCl₃Et (1.983 g, 1.1 mmol) in light petroleum (25 cm³, b.p. 40–60 °C) was stirred rapidly at –15 °C under argon. A solution of dmpe (1.42 g, 9.5 mmol) in the same solvent (15 cm³) was added dropwise. A chocolate brown precipitate formed on contact, and the addition was carefully continued over 2 h until the red colour had considerably diminished and no further precipitate was formed. The mixture was stirred at r.t. for 15 min, allowed to settle, and the solution separated by filtration. The brown solid was washed with light petroleum (2 × 30 cm³, b.p. 30–40 °C) and dried *in vacuo*. The residue was extracted at r.t. with toluene (3 × 30 cm³) and the extract was concentrated under reduced pressure giving red-black crystals. The solution was cooled to

Table 4. Crystal data

	(2)	(3), X-Ray	(3), Neutron
Formula	C ₈ H ₂₁ Cl ₃ P ₂ Ti	C ₇ H ₁₉ Cl ₃ P ₂ Ti	C ₇ H ₁₉ Cl ₃ P ₂ Ti
<i>M</i>	333.5	319.5	319.5
<i>T</i> /K	293–296	293–296	20
	Monoclinic	Orthorhombic	Orthorhombic
<i>a</i> /Å	7.827(4)	13.242(2)	12.921(3)
<i>b</i> /Å	16.411(6)	14.041(4)	13.667(2)
<i>c</i> /Å	12.019(6)	16.522(2)	16.719(4)
β/°	93.24(4)		
<i>U</i> /Å ³	541.4	3 071.9	2 952.4
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> <i>b</i> <i>ca</i>	<i>P</i> <i>b</i> <i>ca</i>
<i>Z</i>	4	8	8
<i>D</i> _c /Mg m ^{–3}	1.436	1.382	1.438
<i>F</i> (000)	688	1 312	
λ/Å	0.7107	0.7107	1.1604
μ/cm ^{–1}	12.49	12.53	1.406
Crystal size (mm)	0.6 × 0.3 × 0.3	0.6 × 0.3 × 0.15	2.4 × 2.4 × 4.8

–30 °C and further red-black crystals separated. These were collected and dried *in vacuo*. Yield 1.60 g, ca. 44%.

[1,2-Bis(dimethylphosphino)ethane]trichloro(methyl)titanium.—A yellow solution of TiCl₃Me (0.42 g, 2.5 mmol) in light petroleum (15 cm³, b.p. 40–60 °C) was cooled to –15 °C and stirred rapidly. The ligand dmpe (0.37 g, 2.5 mmol) in light petroleum (15 cm³, b.p. 40–60 °C) was added dropwise giving an orange-red precipitate. The addition was carefully continued over 2 h until no further precipitate formed. The mixture was warmed to r.t. and stirred for a further 15 min. It was then filtered and the residue washed with light petroleum (2 × 20 cm³, b.p. 40–60 °C) and dried *in vacuo*. The resulting reddish brown powder was extracted with toluene (10–15 cm³) giving an intense blood-red solution which was concentrated until red crystals formed. It was then cooled to –30 °C giving deep red-black crystals, which were isolated and dried. Yield 0.48 g, 60%. A molecular weight determination (isobestic in CH₂Cl₂) for this complex in CH₂Cl₂ gave a value of 346 (calc. 320).

Reaction between [TiCl₃(dmpe)Me] and Potassium Hydride.—The compound [TiCl₃(dmpe)Me] (0.005 g, 0.16 mmol) in toluene (50 cm³) was treated with an excess of a slurry of potassium hydride (ca. 1.0 g) in light petroleum (50 cm³, b.p. 40–60 °C). The mixture was stirred at r.t. for 3 d and the solution changed from blood-red to an intense orange. It was then filtered and reduced in volume gradually, under reduced pressure, to 2 cm³, and small orange-red crystals formed. Light petroleum (50 cm³, b.p. 40–60 °C) was added to the mixture to complete dissolution. The solution was slowly cooled to –25 °C and after 3 d red crystals precipitated. These were recrystallised from light petroleum (b.p. 40–60 °C). Yield 0.020 g, 30%.

Structure Analysis.—The very air-sensitive dark red prismatic crystals of (2) and (3) were mounted in glass capillary tubes under an argon atmosphere. The crystal data are given in Table 4.

X-Ray measurements were made on an Enraf-Nonius CAD-4 diffractometer at Oxford. For (2) the intensities of 1 762 unique reflections with *I* > 3σ(*I*) were obtained from 5 604 observations (2θ < 60°) with an internal *R* of 0.06 and for (3) the intensities of 2 193 unique reflections with *I* > 3σ(*I*) were obtained from 5 313 observations (2θ < 60°) with an internal *R* of 0.12. The data for (2) and (3) were corrected for Lorentz and polarization effects but only those for (3) were corrected for absorption.³²

Both structures were determined by heavy-atom Patterson

Table 5. Atomic co-ordinates with standard deviations in parentheses

(a) For (2)

Atom	X/a	Y/b	Z/c	Atom	X/a	Y/b	Z/c
Ti	0.044 7(2)	0.171 8(1)	0.217 1(1)	C(5)	0.428 2(16)	0.054 7(7)	0.140 1(14)
Cl(1)	-0.161 6(3)	0.142 4(2)	0.352 8(2)	C(61)	0.321 8(22)	-0.010 2(8)	0.197 0(16)
Cl(2)	-0.104 0(3)	0.095 0(1)	0.082 4(2)	C(62)	0.403 7(24)	0.028 2(16)	0.260 7(13)
Cl(3)	0.222 6(3)	0.242 1(2)	0.342 5(2)	C(7)	0.255 5(19)	0.040 2(8)	0.438 8(11)
P(1)	0.306 9(3)	0.147 6(1)	0.103 4(2)	C(8)	0.035 2(20)	-0.050 7(7)	0.283 9(12)
P(2)	0.176 9(4)	0.038 0(2)	0.292 6(2)	H(11)	0.158 1(71)	0.304 5(53)	0.099 3(84)
C(1)	0.050 1(13)	0.273 4(5)	0.104 2(8)	H(12)	0.027 2(130)	0.259 1(62)	0.023 6(29)
C(2)	-0.103 1(14)	0.302 6(6)	0.156 9(2)	H(21)	-0.183 2(105)	0.301 4(62)	0.088 4(52)
C(3)	0.268 8(15)	0.133 0(7)	-0.044 6(8)	H(22)	-0.074 5(127)	0.355 8(33)	0.193 1(76)
C(4)	0.477 3(12)	0.223 8(6)	0.114 4(9)	H(23)	-0.143 1(122)	0.272 3(55)	0.226 6(52)

(b) For (3X)

Ti	0.436 1(1)	0.202 17(5)	0.656 37(5)	H(31)	0.389 5(36)	-0.115 7(26)	0.705 8(32)
Cl(1)	0.488 0(1)	0.344 1(1)	0.601 6(1)	H(32)	0.482 4(30)	-0.050 2(39)	0.719 9(30)
Cl(2)	0.305 8(1)	0.271 9(1)	0.728 0(1)	H(33)	0.448 4(42)	-0.068 5(41)	0.633 9(17)
Cl(3)	0.542 2(1)	0.108 4(1)	0.579 7(1)	H(41)	0.257 4(42)	0.089 0(31)	0.810 6(40)
P(1)	0.348 9(1)	0.044 7(1)	0.697 3(1)	H(42)	0.354 5(34)	0.046 1(48)	0.834 4(33)
P(2)	0.306 1(1)	0.168 7(1)	0.543 5(1)	H(43)	0.259 0(42)	-0.018 7(30)	0.810 5(39)
C(1)	0.517 8(4)	0.170 2(4)	0.765 4(4)	H(51)	0.183 3(29)	0.064 8(31)	0.645 1(35)
C(3)	0.424 2(4)	-0.061 8(3)	0.687 3(4)	H(52)	0.215 3(39)	-0.041 6(19)	0.641 8(33)
C(4)	0.298 8(5)	0.035 3(5)	0.799 0(4)	H(61)	0.306 0(34)	-0.003 2(31)	0.547 9(38)
C(5)	0.238 5(4)	0.021 4(4)	0.635 3(4)	H(62)	0.194 9(27)	0.054 7(41)	0.520 6(33)
C(6)	0.257 3(5)	0.046 9(4)	0.549 4(4)	H(71)	0.228 7(55)	0.295 6(39)	0.521 3(44)
C(7)	0.194 5(7)	0.242 7(6)	0.545 9(5)	H(72)	0.160 0(49)	0.219 7(48)	0.499 7(29)
C(8)	0.354 7(9)	0.174 2(8)	0.441 9(4)	H(73)	0.158 8(51)	0.239 5(58)	0.595 9(26)
H(11)	0.562 9(22)	0.202 2(22)	0.725 0(17)	H(81)	0.416 4(36)	0.144 7(58)	0.429 7(52)
H(12)	0.534 3(37)	0.106 1(16)	0.761 5(32)	H(82)	0.379 1(61)	0.236 1(28)	0.431 2(52)
H(13)	0.484 6(29)	0.176 2(30)	0.812 5(17)	H(83)	0.294 9(35)	0.176 2(63)	0.410 4(42)

(c) For (3N)

Ti	0.440 2(1)	0.200 4(1)	0.656 7(1)	H(31)	0.382 2(2)	-0.133 4(2)	0.705 2(2)
Cl(1)	0.497 62(6)	0.347 76(4)	0.605 31(4)	H(32)	0.498 1(2)	-0.065 0(2)	0.715 8(2)
Cl(2)	0.308 96(5)	0.272 80(4)	0.731 01(4)	H(33)	0.442 6(2)	-0.081 0(2)	0.619 8(1)
Cl(3)	0.545 65(6)	0.103 92(5)	0.577 63(4)	H(41)	0.251 6(2)	0.091 9(2)	0.812 2(2)
P(1)	0.348 16(9)	0.039 13(8)	0.695 91(7)	H(42)	0.363 7(2)	0.023 9(2)	0.839 2(1)
P(2)	0.305 5(1)	0.170 06(8)	0.544 65(7)	H(43)	0.252 4(2)	-0.037 2(2)	0.803 0(2)
C(1)	0.520 86(8)	0.153 99(7)	0.760 61(6)	H(51)	0.171 4(2)	0.061 8(2)	0.655 8(1)
C(3)	0.425 73(8)	-0.070 98(7)	0.683 19(6)	H(52)	0.209 5(2)	-0.060 7(1)	0.638 9(1)
C(4)	0.299 04(8)	0.028 76(7)	0.797 63(6)	H(61)	0.320 3(2)	-0.002 8(2)	0.520 7(1)
C(5)	0.234 41(8)	0.015 82(7)	0.632 79(6)	H(62)	0.189 9(2)	0.037 0(2)	0.507 3(1)
C(6)	0.258 53(8)	0.043 50(7)	0.545 81(5)	H(71)	0.209 0(2)	0.320 3(2)	0.549 2(2)
C(7)	0.188 47(8)	0.243 03(7)	0.551 44(6)	H(72)	0.135 9(2)	0.225 9(2)	0.502 2(2)
C(8)	0.350 9(1)	0.191 79(8)	0.443 54(6)	H(73)	0.149 8(2)	0.229 3(2)	0.608 3(2)
H(11)	0.585 7(2)	0.204 0(2)	0.750 4(2)	H(81)	0.413 6(2)	0.141 8(2)	0.429 5(2)
H(12)	0.550 1(2)	0.079 9(2)	0.762 6(2)	H(82)	0.379 3(2)	0.266 3(2)	0.439 4(2)
H(13)	0.481 1(2)	0.173 5(2)	0.815 9(2)	H(83)	0.288 8(2)	0.181 2(2)	0.400 5(1)

and electron-density methods and refined first isotropically then anisotropically by full-matrix least-squares methods. For (2) inspection of the electron-density maps, bond lengths, and thermal parameters during the refinement process indicated that C(5) and C(6) of the dmpe backbone were disordered. C(6) was successfully resolved on two sites with 50% occupancy, but C(5) was found to be best represented by a single atom site with very large thermal parameters. Within the chelate ring P-C was constrained to 1.83(3) and C-C to 1.54(3) Å.³³ The dmpe hydrogen atoms were not found but those of the ethyl group were located from the difference electron-density syntheses and their positional parameters refined with fixed isotropic thermal parameters. The refinement converged at R 0.056, R' = 0.066 (unit weights), max. (shift/e.s.d.) < 0.01. The final difference electron-density map had no major feature except a peak of $0.55 \text{ e } \text{Å}^{-3}$ very near to C(5). For (3) the refinement proceeded smoothly first with isotropic then anisotropic temperature parameters to R 0.058, when all hydrogen atoms were located from the difference-electron density synthesis. Those bonded to

C(1), the most prominent, were refined freely with isotropic temperature factors and the rest had C-H constrained to 0.95(2) Å and a fixed common isotropic temperature factor. The final refinement, which converged at R 0.040, R' 0.038 (unit weights), max. (shift/e.s.d.) < 0.01, included an empirical extinction parameter. The maximum peak height on the final difference-electron density map was $0.15 \text{ e } \text{Å}^{-3}$. X-Ray scattering factors were taken from ref. 34.

The neutron diffraction measurements on (3) were obtained at the Brookhaven High Flux Beam Reactor with the crystal at a temperature of 20 K using a Displex closed-cycle helium refrigerator mounted on a single-crystal diffractometer.^{35,36} A total of 6 437 observations (hkl , hkl) corrected for Lorentz factors and absorption (based on azimuthal scans for three reflections) were merged to give 4 434 unique data (internal R 0.042, R' 0.032) of which 2 757 with $I > 3\sigma(I)$ were used in the final refinement. The positional parameters of the hydrogen atoms were obtained initially from a Fourier map using phases derived from the non-hydrogen atom co-ordinates of the r.t. X-

ray analysis. In the final cycles of least-squares, which included a secondary extinction correction, all atoms were refined with anisotropic temperature factors. Scattering lengths were obtained from Koester³⁷ and were not refined as variables. The refinement converged at $R(F)$ 0.036, $R'(F^2)$ 0.056, with weights of $w = [\sigma_c^2(F^2) + (0.02 F^2)^2]^{-1}$, where $\sigma_c(F^2)$ is derived from counting statistics.

For each analysis the final atomic parameters are presented in Table 5. All the X-ray analysis calculations were carried out at Oxford on the inhouse VAX 11/750 computer using the Oxford CRYSTALS program suite.³⁸ The neutron analysis was performed at the Brookhaven and Argonne National Laboratories.

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