Mono-η-cycloheptatrienyltitanium Chemistry: Synthesis, Molecular and Electronic Structures, and Reactivity of the Complexes [Ti(η-C_7H_7)L_2X] (L = Tertiary Phosphine, O- or N-donor Ligand; X = Cl or Alkyl)†

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Bis(η-toluene)titanium reacts with cycloheptatriene in the presence of $(AlEtCl_2)_2$, at > 60 °C to form [Ti(η-C_7H_7)(η-C_7H_9)] and at room temperature [{Ti(η-C_7H_7)(thf)(μ-Cl)}$_2$] (thf = tetrahydrofuran) is also formed. The crystal structure of the latter has been determined. The dimer reacts with the ligands L_2 = $R_2PCH_2CH_2PR_2$ (R = Me or Ph), *trans*-1,2-bis(dimethylphosphino)cyclopentane, $MeOCH_2CH_2OMe$, $2PMe_3$ or $Me_2NCH_2CH_2NMe_2$, forming the compounds [Ti(η-C_7H_7)L_2Cl]. Reaction of alkyl Grignard reagents with the appropriate chloro-derivatives gives the titanium–alkyls [Ti(η-C_7H_7)L_2R] [L_2 = $Me_2PCH_2CH_2PMe_2$, R = Me or Et; L_2 = *trans*-1,2-$C_5H_8(PMe_2)_2$, R = Me]. The crystal structure of [Ti(η-C_7H_7)($Me_2PCH_2CH_2PMe_2$)Et] has been determined: there is no evidence for Ti–H–C interactions between the Ti and the hydrogens of the ethyl group. The photoelectron spectra of several Ti(η-C_7H_7) compounds are discussed in terms of the nature of the Ti(η-C_7H_7) bonding. It is proposed that the chemistry of the Ti(η-C_7H_7) system corresponds most closely to a formal description of the η-C_7H_7 group as having a −3 charge rather than the more conventional description as +1. Homogeneous mixtures of [{Ti(η-C_7H_7)(thf)(μ-Cl)}$_2$] and aluminium alkyls are shown to catalyse ethylene polymerisation.

The chemistry of the half-sandwich η-cycloheptatrienyl–transition metal system, M(η-C_7H_7), has been relatively little studied compared with the M(η-C_6H_6) and M(η-C_5H_5) systems. The most extensive studies have been made on Mo(η-C_7H_7) derivatives.[1–3] The η^7-cycloheptatrienyl ligand contributes seven electrons to a metal centre and subtends a cone angle closely similar to that of the pentamethylcyclopentadienyl ligand (see Figure 1). For transition metals with eight or more valence electrons, *e.g.* Fe, Co, and Ni, the contribution of seven electrons by the η-C_7H_7 ligand gives the fragments M(η-C_7H_7) whose electron counts are 15 (Fe), 16 (Co), or 17 (Ni) respectively. Thus the chemistry for these systems is restricted since, if the 18-electron rule is to be obeyed, these fragments are only able to add further ligands which will contribute 3 (Fe), 2 (Co), or 1 (Ni) electrons respectively. In contrast, titanium has only four valence electrons thus Ti(η-C_7H_7) is an eleven-electron system. Therefore, in principle the Ti(η-C_7H_7) group can add a further seven electrons which typically would mean three or more unidentate ligands. For example, compounds such as [Ti(η-C_7H_7)L_nX] (*n* = 2 or 3), where L are two-electron, σ-donor–π-acceptor ligands and X = halide or alkyl, can be evisaged.

As a consequence of a chance observation described below we became aware of the possibility of synthesis and study of a range of compounds of the general class [Ti(η-C_7H_7)L_nX]. Therefore, we decided to investigate compounds in this class and to compare the chemistry with that of the well established half-sandwich compounds of the later transition metals, *e.g.* [Fe(η-C_5H_5)(CO)$_2$X] (X = alkyl, acetyl, aryl, *etc.*),[4,5] and thereby evaluate more closely the functional-group properties of the η-C_7H_7 ligand, in comparison with those of the η-C_5H_5 group.

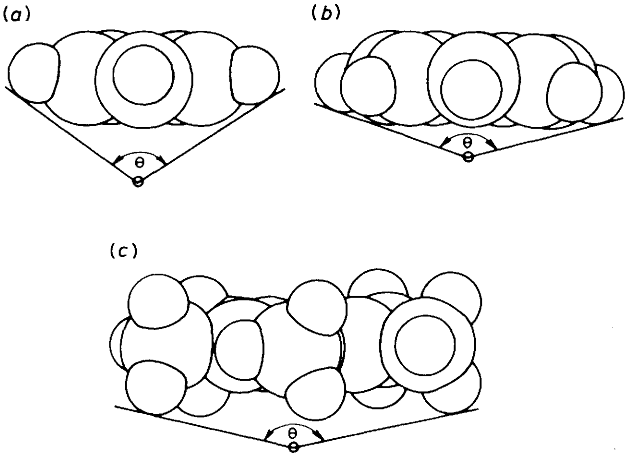

Figure 1. Comparison of the cone angles for the ligands (*a*) η-C_5H_5 (θ = 110°), (*b*) η-C_7H_7 (θ = 154°), and (*c*) η-C_5Me_5 (θ = 142°)

Some cycloheptatrienyl–titanium compounds, *e.g.* η-cycloheptatrienyl(η-cyclopentadienyl)titanium and η-cycloheptadienyl(η-cycloheptatrienyl)titanium,[6,7] have been long known. The latter have been described either as divalent[8] or as zerovalent[9] titanium compounds. Timms and Turney[10] have shown that η-cycloheptadienyl(η-cycloheptatrienyl)titanium can be made by reacting titanium atoms with cycloheptatriene.[10] The synthesis of alkyl- (and otherwise) substituted η-cycloheptatrienyl rings has been described.[11,12] Metallation reactions of η-cycloheptatrienyl(η-cyclopentadienyl)titanium have shown that the η-cycloheptatrienyl ring was attacked in preference to the η-cyclopentadienyl group.[13,14] This suggests that there is greater localisation of negative charge on the C_7 ring than on the C_5 ring, confirmed by *X*-ray photoelectron spectroscopy (x.p.s.) studies[15,16] contradicting the common formulation of the cycloheptatrienyl group as $C_7H_7^{\cdot +}$.[15–17]

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† *Supplementary data available* (No. SUP 56111, 5 pp.): thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii–xix. Structure factors are available from the editorial office.

Non-S.I. units employed: eV ≈ 1.602×10^{-19} J, Torr ≈ 133.3 Pa.

A brief report of part of the new η-cycloheptatrienyltitanium chemistry described below has appeared.[18]

Results and Discussion

Heating bis(η-toluene)titanium,[19] with ethylaluminium dichloride dimer, and a two-fold excess of cycloheptatriene at 80 °C in tetrahydrofuran (thf) for 2 h yielded dark green crystals whose ^1H n.m.r. spectrum showed them to be the well known compound, [Ti(η-C_7H_7)(η-C_7H_9)] (**1**).[7] This reaction could be carried out using 10.0 g of [Ti(η-$C_6H_5Me)_2$] giving *ca.* 82% yields of (**1**).

When [Ti(η-$C_6H_5Me)_2$] and cycloheptatriene in thf, but in the absence of $(AlEtCl_2)_2$, were heated at 110 °C for 5 h, no colour change was observed. When subsequently the mixture was treated with 0.2 mol equiv. of $(AlEtCl_2)_2$ and heated at 90 °C for 3 h, a dark green solution was formed, from which (**1**) was isolated in high yield. This suggests that the role of the $(AlEtCl_2)_2$ is probably catalytic. In subsequent syntheses $(AlEt_2Cl)_2$ was used instead of $(AlEtCl_2)_2$ since it is less active towards polymerisation of cycloheptatriene.

Table 1. Analytical (calculated values in parentheses) and spectroscopic data

Compound	Colour	Analysis (%)		^1H, ^{13}C, and ^{31}P n.m.r. data[a]
		C	H	
(**2**) [{Ti(η-C_7H_7)(thf)(μ-Cl)}$_2$]	Dark red	49.7 (53.5)	5.6[b] (6.1)	5.98 (s, 7 H, η-C_7H_7), 3.69 (br, s, 4 H, O–CH_2–), 1.86 (br, s, 4 H, O–CH_2CH_2–)[c]
(**3**) [Ti(η-C_7H_7)(dmpe)Cl]	Yellow	48.0 (47.9)	7.1 (7.0)	5.84 [t, *J*(P–H) 2.6, 7 H, η-C_7H_7], 1.21 [virtual t, *J*(P–H) 2.8, 6 H, PMe up or down], 0.65 [virtual t, *J*(P–H) 2.7, 6 H, PMe down or up], 1.51—0.31 (complex br, 4 H, P–CH_2–)[d]
(**4**) [Ti(η-C_7H_7)($PMe_3)_2$Cl]	Yellow-orange[e]			5.64 (t, 7 H, η-C_7H_7), 0.87 [d, *J*(P–H) 4, 18 H, PMe][f]
(**5**) [{Ti(η-C_7H_7)(μ-Cl)}$_2$(PMe_3)]	Purple	47.8 (48.0)	5.3 (5.4)	5.9 (s, 14 H, 2 η-C_7H_7), 0.48 [d, *J*(P–H) 6, 9 H, PMe][f]
(**6**) [Ti(η-C_7H_7)(dppe)Cl]·C_7H_8	Orange	71.3 (72.2)	6.3 (5.9)	7.7 [br s, 20 H, PPh], 5.85 (s, 7 H, η-C_7H_7), 2.05 (s, 4 H, P–CH_2–)[g]
(**7**) *trans*-1,2-$C_5H_8(PMe_2)_2$	Colourless oil[h]			1.82—1.69 (complex, 2 H, P–CH–CH_2–), 1.64—1.58 (complex, 2 H, P–CH–CH_2–CH_2–), 1.57—1.41 (complex, 4 H, –CH–CH–CH_2–), 0.925 [d, *J*(P–H) 3.5, 6 H, PMe], 0.85 [d, *J*(P–H) 3.2, 6 H, PMe].[i] ^{13}C n.m.r.: 43.4 (d, P–CH–), 29.8 (virtual t, P–CH–CH_2–), 26.7 (t, P–CH–CH_2–CH_2–), 13.8 (m, PMe), 12.6 (m, PMe).[j] ^{31}P-{H^1} n.m.r.: 42 (s)[j]
(**8**) [Ti(η-C_7H_7){*trans*-1,2-$C_5H_8(PMe_2)_2$}Cl]	Yellow	52.4 (52.7)	7.7 (7.4)	5.71 [t, *J*(P–H) 2.6, 7 H, η-C_7H_7], 1.39—0.57 (c, 20 H, all other H)[g]
(**9**) [Ti(η-C_7H_7)(dippe)Cl]	Red[k]			5.9 (s, 7 H, η-C_7H_7), 1.91 (6 lines c, 4 H, P–CH), 1.29 [dd, *J*(P–H) 7.1, 12.8, 12 H, CMe], 1.10 [d, *J*(P–H) 8.4, 4 H, CH_2], 1.05 [dd, *J*(P–H) 6.6, 11.1, 12 H, CMe][g]
(**10**) [Ti(η-C_7H_7)(tmen)Cl]	Dark red	53.5 (53.7)	7.8 (7.9)	5.8 (s, 7 H, η-C_7H_7), 2.1 (s, 12 H, NMe), 1.6 (c, 4 H, N–CH_2–)[f]
(**11**) [Ti(η-C_7H_7)(dme)Cl]	Red[l]			5.96 (br s, 7 H, η-C_7H_7), 3.00 (s, 6 H, OMe), 2.57 (br s, 4 H, O–CH_2–)[g]
(**12**) [Ti(η-C_7H_7)(dmpe)Me]	Green	54.8 (55.3)	8.1 (6.4)	5.52 [t, *J*(P–H) 3.1, 7 H, η-C_7H_7], 0.91 [t, *J*(P–H) 2.6, 12 H, PMe], 0.63 (5 lines, 4 H, P–CH_2–), −0.4 [t, *J*(P–H) 11.3, 3 H, TiMe][g]
(**13**) [Ti(η-C_7H_7)(dmpe)Et]	Dark green	56.4 (56.6)	8.6 (8.8)	5.53 [t, *J*(P–H) 2.6, 7 H, η-C_7H_7], 1.7 [t, *J*(H–H) 7.7, 3 H, Ti–CH_2CH_3], 0.9 [t, *J*(P–H) 2.5, 12 H, PMe], 0.64 (5 lines, 4 H, P–CH_2–), −0.3 [tq, *J*(H–H) 7.7, *J*(P–H) 9, 2 H, Ti–CH_2–].[g] ^{13}C n.m.r.: 87.4 (d, η-C_7H_7), 44.7 (t, Ti–CH_2–), 28.1 (t, P–CH_2–), 21.2 (q, Ti–CH_2–CH_3), 14.2 (q, PMe)[g]
(**14**) [Ti(η-C_7H_7){*trans*-1,2-$C_5H_8(PMe_2)_2$}Me]	Dark green	59.2 (59.3)	8.6 (8.7)	5.53 [t, *J*(P–H) 2.8, 7 H, η-C_7H_7], 1.32 [c, 2 H, P–CH–CH_2–CH_2–], 1.16—1.02 (c, 2 H, P–CH–CH_2–), 1.00 [d, *J*(P–H) 3.3, 6 H, PMe], 0.85—0.77 (c, 2 H, P–CH–CH_2–), 0.71 [d, *J*(P–H) 3.6, 6 H, PMe], 0.33 (br, s, 2 H, P–CH–), −0.4 [t, *J*(P–H) 11.1, 3 H, TiMe].[i] ^{13}C n.m.r.: 88.1 (d, 163, η-C_7H_7), 43.9 (br d, 137, TiMe), 28.6 (t, ring CH_2), 27.0 (t, ring CH_2), 24.1 (t, ring CH_2), 12.6 (q, PMe), 9.9 (q, PMe)[g]
(**15**) [Ti(η-C_7H_7){*trans*-1,2-$C_5H_8(PMe_2)_2$}(BH_4)]	Gold[m]			5.53 (s, 7 H, η-C_7H_7), 1.38—1.29 (c, 2 H, ring CH_2), 1.14—1.06 (c, 2 H, ring CH_2), 0.90 [d, *J*(P–H) 5.9, 6 H, PMe], 0.87—0.77 (4 H, c, –CH–CH–CH_2), 0.71 [d, *J*(P–H) 5.4, 6 H, PMe], −0.12 [br q, *J*(B–H) 55.8, 4 H, BH_4][n]

[a] Given as chemical shift (δ), multiplicity, *J* in Hz, relative intensity, assignment. Chemical shifts are relative to residual protio solvent as internal standard (^1H), internal solvent (^{13}C), and external $PO(OMe)_3$ (^{31}P). [b] Cl, 14.8 (14.4%). [c] In CD_2Cl_2. [d] In $C_6D_5CD_3$ at 100 MHz, −40 °C. [e] Not analysed due to lability, see text. [f] In C_6D_6 at 60 MHz. [g] In C_6D_6 at 300 MHz, 25 °C. [h] B.p. 50 °C, 0.02 Torr. [i] In C_6D_6 at 400 MHz. [j] In C_6D_6. [k] Characterised by ^1H n.m.r. of the crystalline sample only. [l] Thermal instability prevented microanalysis. [m] Could not be obtained free of solvent. [n] In $C_6D_5CD_3$ at 300 MHz. I.r. (mull): 1 449m, 1 580—1 690m, 2 040m, 2 090m, 2 375m, and 2 350m cm^{-1}.

Table 2. Bond distances (Å) and angles (°) for (**2**)

Ti(1)–Ti(1B)	3.883(1)	C(3)–C(4)	1.489(4)	O(1)–Ti(1)–Cl(1)	82.19(4)	C(2)–C(3)–C(4)	106.24(20)
Ti(1)–Cl(1)	2.541(1)	C(11)–C(12)	1.406(4)	O(1)–Ti(1)–Cl(1B)	80.62(4)	C(11)–C(12)–C(13)	128.89(22)
Ti(1)–Cl(1B)	2.544(1)	C(12)–C(13)	1.404(4)	Cl(1)–Ti(1)–Cl(1B)	80.42(2)	C(12)–C(13)–C(14)	128.45(22)
Ti(1)–O(1)	2.187(1)	C(13)–C(14)	1.404(3)	Ti(1)–Cl(1)–Ti(1B)	95.58(2)	C(13)–C(14)–C(15)	128.71(20)
O(1)–C(1)	1.448(2)	C(14)–C(15)	1.402(3)	O(1)–C(1)–C(2)	104.92(18)	C(14)–C(15)–C(16)	128.17(21)
O(1)–C(4)	1.439(3)	C(15)–C(16)	1.409(3)	O(1)–C(4)–C(3)	105.94(21)	C(15)–C(16)–C(17)	129.10(22)
C(1)–C(2)	1.508(3)	C(16)–C(17)	1.417(4)	C(1)–O(1)–C(4)	106.04(17)	C(16)–C(17)–C(11)	127.82(21)
C(2)–C(3)	1.506(4)	C(17)–C(11)	1.396(4)	C(1)–C(2)–C(3)	104.65(20)	C(17)–C(11)–C(12)	128.82(21)

Ti(1)–C_7(ring centroid)	1.545
Ti(1)–C(mean)	2.238(5)

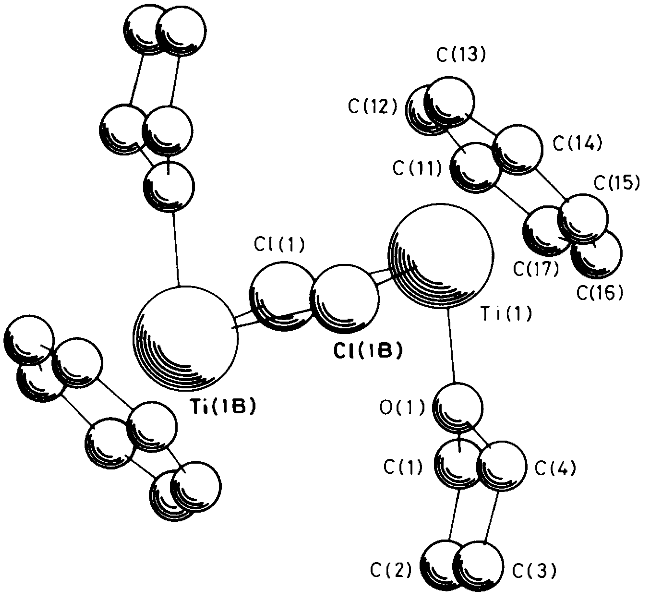


Figure 2. Crystal structure of $[\{Ti(\eta\text{-}C_7H_7)(thf)(\mu\text{-}Cl)\}_2]$ (**2**) showing the numbering scheme

Treatment of (**1**) with iodine gives purple-black TiI_4; (**1**) also reacts with $C_6H_5ICl_2$ giving a blue precipitate, which, after extraction with thf, yielded $TiCl_3(thf)_3$.

When the preparation of (**1**) was carried out at a lower temperature (60 °C) for 36 h, it was noted that fine red crystals identified as $[\{Ti(\eta\text{-}C_7H_7)(thf)(\mu\text{-}Cl)\}_2]$ (**2**) were deposited from the deep green solution. The yield was very low (5%) and the major product was (**1**). Following this observation, it was found that reactions at room temperature over a period of weeks, with the minimum quantity of solvent and $(AlEt_2Cl)_2$, together with a considerable excess of cycloheptatriene, gave improved yields of (**2**) (normally 30% and occasionally 60%): compound (**1**) was the other major product.

In a search for an alternative synthetic route to the system $[Ti(\eta\text{-}C_7H_7)L_2X]$, bis(η-toluene)titanium was treated with tropylium bromide in thf. The resulting blue-green crystals were identified as $TiBr_3(thf)_3$.

Also, using the metal-atom reactor described elsewhere,[20] titanium atoms were co-condensed with thf vapour and fine droplets of a solution of $(AlEt_2Cl)_2$ in cycloheptatriene. Compound (**2**) could be isolated from the resulting reaction mixture in *ca.* 20% yield (based on titanium).

When (**2**) was treated with an excess of cycloheptatriene and $(AlEt_2Cl)_2$ in thf at 80 °C the major product was (**1**). Thus it appears that (**2**), or a related species, *e.g.* $[Ti(\eta\text{-}C_7H_7)(thf)_2Cl]$, is an intermediate in the formation of (**1**) from $[Ti(\eta\text{-}C_6H_5Me)_2]$.

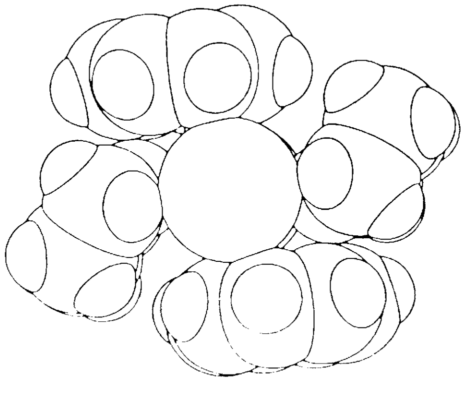


Figure 3. View of $[\{Ti(\eta\text{-}C_7H_7)(thf)(\mu\text{-}Cl)\}_2]$ along the Ti–Ti axis

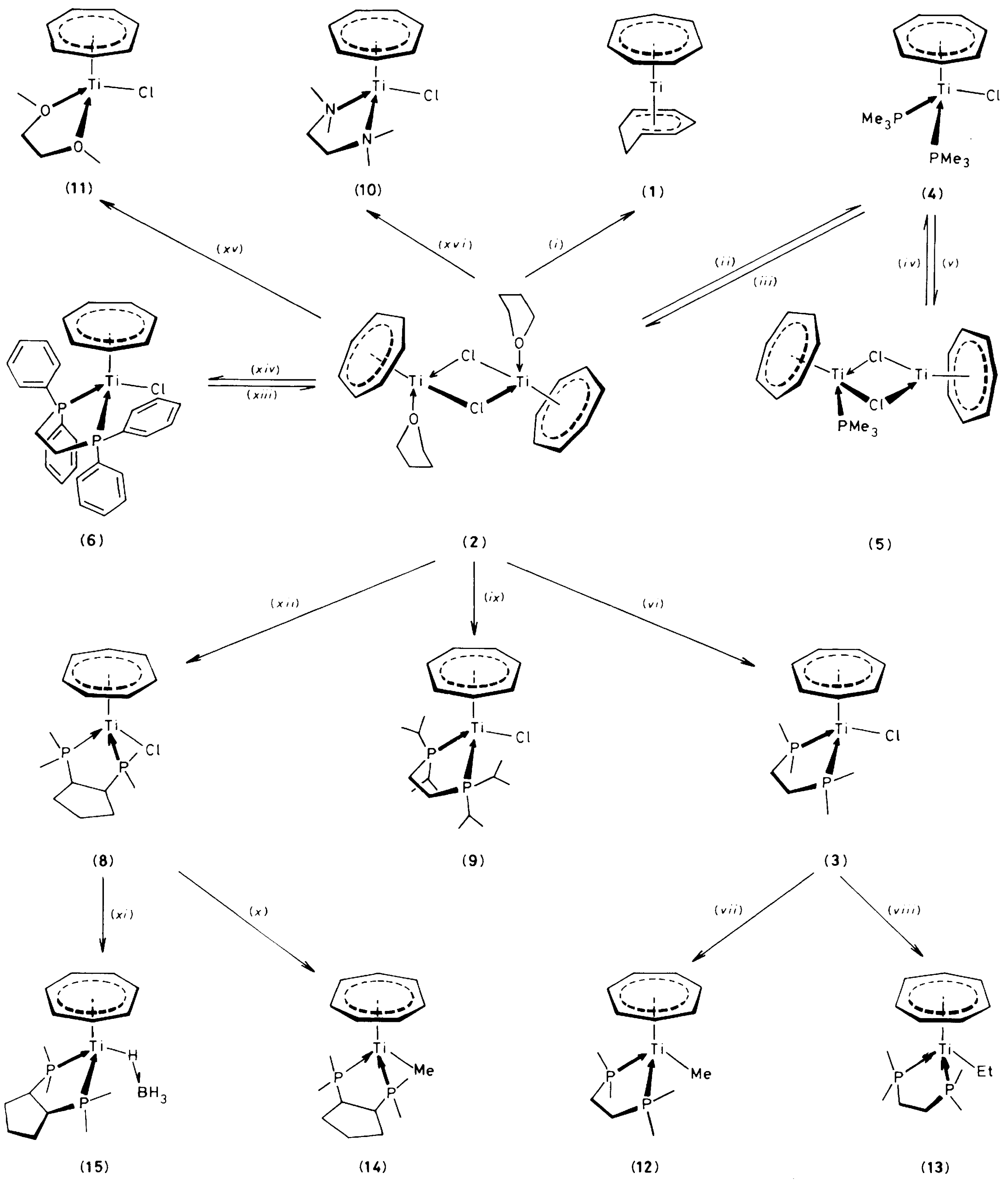
Analysis, ^1H n.m.r., and a crystal structure determination showed the red crystals of (**2**) to be the dimer $[\{Ti(\eta\text{-}C_7H_7)(thf)(\mu\text{-}Cl)\}_2]$. Analytical and spectroscopic data for all new compounds are given in Table 1. The molecule has a crystallographic centre of symmetry and is shown in Figure 2. Bond distances and angles are given in Table 2. The titanium centres are bridged by two chlorine atoms with an average Ti–Cl bond distance 2.542(2) Å, close to the value found for other bridging titanium–chlorine systems.[21,22] Each titanium centre has a 'piano-stool' geometry and the angles between the tripodal ligands are all close to 80°. The metal–metal distance of 3.883(1) Å does not suggest the presence of a metal–metal bond (*cf.* $[\{Ti(\eta\text{-}C_5H_5)_2(\mu\text{-}Cl)\}_2]$).[23] The mean distance to the ring carbon atoms is 2.238(5) Å which is slightly longer than the corresponding value of 2.194 Å for $[Ti(\eta\text{-}C_7H_7)(\eta\text{-}C_5H_5)]$.[24]

The hydrogen atoms of the cycloheptatrienyl ring are displaced by a mean distance of 0.18(5) Å out of the plane of the carbocycle, towards the metal atom. This can be accounted for in terms of the consequential improvement of overlap between the ring and metal orbitals, as discussed by Mingos and co-workers.[25] The out-of-plane angle is *ca.* 10°, which is close to the calculated value of 9° for the optimised overlap between vanadium and the cycloheptatrienyl ligand.

As noted above, the $\eta\text{-}C_5Me_5$ and $\eta\text{-}C_7H_7$ ligands have similar cone angles, but in contrast to the $\eta\text{-}C_7H_7$ ligand the methyl groups of the $\eta\text{-}C_5Me_5$ group bend away from the metal centre. In this case the metal–methyl repulsion dominates over the electronic factors.[26] Examination of computer models shows that there is steric saturation in (**2**) (Figure 3).

$[\{Ti(\eta\text{-}C_7H_7)(thf)(\mu\text{-}Cl)\}_2]$ (**2**) has a similar structure to that of the green compound $[\{Ti(\eta\text{-}C_8H_8)(thf)(\mu\text{-}Cl)\}_2]$[21] and (**2**) may also be compared to the arene compound $[\{Mo(\eta\text{-}C_6H_6)(\eta\text{-}C_3H_5)(\mu\text{-}Cl)\}_2]$.[27]

Treatment of (**2**) in toluene with 1,2-bis(dimethylphosphino)ethane (dmpe) gives yellow, air- and water-sensitive



Scheme. (*i*) Cycloheptatriene and (AlEt$_2$Cl)$_2$, in thf at 80 °C for 2 h, yield 82%; (*ii*) excess PMe$_3$ in toluene at r.t., yield *ca.* 70%; (*iii*) thf, crystallise; (*iv*) PMe$_3$ in toluene; (*v*) remove PMe$_3$ from toluene solution under reduced pressure, yield > 50%; (*vi*) dmpe in toluene at r.t., yield 75%; (*vii*) MgMeBr in thf at r.t., yield > 60%; (*viii*) MgEtBr in thf at r.t., yield 70%; (*ix*) dippe in toluene; (*x*) MgMeBr in thf, yield 73%; (*xi*) Na[BH$_4$] in thf, yield > 70%; (*xii*) *trans*-1,2-C$_5$H$_8$(PMe$_2$)$_2$ in toluene at r.t., yield 81%; (*xiii*) thf, crystallise; (*xiv*) dppe in toluene at r.t., yield 31%; (*xv*) dme in toluene, extract with toluene at 90 °C, yield 20%; (*xvi*) tmen in toluene, yield 60%

crystals of [Ti(η-C_7H_7)(dmpe)Cl] (**3**). The ^1H n.m.r. spectrum at 300 MHz has broad bands but it is possible to distinguish the methylene and methyl resonances at δ 0.82 and 0.9 respectively. It is just possible to resolve a triplet structure for the η-C_7H_7 ligand due to coupling with the ^{31}P nuclei. Variable-temperature (v.t.) ^1H n.m.r. studies (100 MHz) on [Ti(η-C_7H_7)(dmpe)Cl] over the range +50 to −40 °C showed that the coupling of the ^{31}P nuclei to the η-C_7H_7 ring is lost above about +40 °C, with a coalescence temperature of *ca.* +35 °C. The two sets of 'up' and 'down' P-methyl groups which occur as a singlet at room temperature are sharply differentiated below −40 °C and have a coalescence temperature of *ca.* −7 °C. The v.t. ^1H n.m.r. data give a value for $\Delta G^\ddagger$ of 54 ± 5 kJ mol^{-1}. The loss of ^{31}P–C_7H_7 coupling suggests that equilibration of the two sets of methyl groups occurs by a dissociative mechanism.

Addition of trimethylphosphine to (**2**) in thf followed by rapid removal of solvent under reduced pressure, gave yellow microcrystals. When these were kept under vacuum they turned into a purple solid. Subsequent addition of PMe_3 reformed the yellow compound. Attempts to recrystallise the yellow crystals from thf gave only (**2**).

In toluene, (**2**) reacted with an excess of PMe_3 and crystallisation at −80 °C gave yellow-orange crystals of [Ti(η-C_7H_7)(PMe_3)$_2$Cl] (**4**). Washing the crystals caused surface decomposition to a purple solid. For this reason elemental analyses could not be obtained.

The ^1H n.m.r. spectrum of (**4**), in the absence of an excess of PMe_3, showed a well resolved doublet at δ 0.87 (J = 4 Hz) assignable to bound trimethylphosphine and a partially resolved triplet assignable to a η-C_7H_7 ring at δ 5.64. The ^1H n.m.r. spectrum of (**4**), in the presence of an excess of trimethylphosphine, showed a singlet at δ 5.64 assignable to the η-C_7H_7 ring and a broad singlet at δ 0.9 assignable to PMe_3 rapidly exchanging between bound and unbound states. On cooling the sample to −80 °C a band assignable to unco-ordinated PMe_3 appeared as a doublet (coalescence temperature −65 °C) and the η-C_7H_7 band at δ 5.64 sharpened into a triplet with a coalescence temperature of *ca.* −70 °C. The data can be interpreted in terms of a rapid dissociative exchange of the co-ordinated and unbound PMe_3 ligands and coalescence temperature analysis provides the value $\Delta G^\ddagger$ = 45 ± 5 kJ mol^{-1} at 208 K and 46 ± 5 kJ mol^{-1} at 203 K. When a toluene solution of (**4**) was concentrated under reduced pressure to remove excess of PMe_3 it became red and a mixture of purple and yellow solids separated. Addition of further toluene followed by slow concentration under reduced pressure gave an intense purple solution and purple crystals of [{Ti(η-C_7H_7)(μ-Cl)}$_2$(PMe_3)] (**5**). These could be purified by low temperature crystallisation. Compound (**5**) is highly sensitive to oxygen and water.

The ^1H n.m.r. spectrum of (**5**) showed a singlet at δ 5.9 assignable to the η-C_7H_7 ligand, and a doublet (J = 6 Hz) at δ 0.48 assignable to a co-ordinated PMe_3 ligand. The relative intensity of the two bands was 14:9 respectively, corresponding to the formulation [{Ti(η-C_7H_7)(μ-Cl)}$_2$(PMe_3)], in agreement with elemental analysis data. A v.t. n.m.r. study in $C_6D_5CD_3$ shows that the singlet due to η-C_7H_7, at δ 6.1, gives two lines of equal intensity at δ 6.5 and 5.9 at −60 °C, broadened by solvent viscosity. These data suggest that (**5**) has the structure shown in the Scheme and undergoes rapid exchange of the PMe_3 group between the two titanium centres with no resultant coupling between C_7H_7 and ^{31}P. The compound [{Co(η-C_5Me_5)(CO)}$_2$(PMe_3)] has a related unsymmetrical structure and also undergoes exchange of the PMe_3 ligand between the cobalt centres.[28]

The trimethylphosphine ligands of (**4**) and (**5**) are highly labile, being readily displaced by solvent thf for example. Since the red dimer (**2**) is sterically crowded, it seems probable that the formation of the unsymmetrical compound (**5**) may result from steric requirements.

The difference of the $\Delta G^\ddagger$ values for the phosphine dissociation associated with ligand exchange for dmpe and $(PMe_3)_2$ compounds may be due to there being a more favourable entropy term for the intermolecular exchange of PMe_3 ligands whereas for dmpe it presumably occurs *via* an intramolecular process.

The compound [Ti(η-C_7H_7)(dppe)Cl] (**6**) [dppe = 1,2-bis(diphenylphosphino)ethane] was found to be very labile and also could not be crystallised from thf. It was obtained by mixing equimolar proportions of (**2**) and dppe in toluene.

The new diphosphine compound *trans*-1,2-$C_5H_8(PMe_2)_2$ (**7**) was prepared as a colourless oil by treatment of *trans*-1,2-bis(dichlorophosphino)cyclopentane[29] with methylmagnesium bromide in thf. The data characterising (**7**) are given in Table 1.

A stirred suspension of the red dimer (**2**) in toluene was treated with one molar equivalent of the phosphine (**7**), giving yellow crystals of [Ti(η-C_7H_7){*trans*-1,2-$C_5H_8(PMe_2)_2$}Cl] (**8**). Similarly, the bulky chelating phosphine 1,2-bis(di-isopropylphosphino)ethane (dippe)[30] and the red dimer (**2**), in toluene, gave red crystals of [Ti(η-C_7H_7)(dippe)Cl] (**9**). The ^1H n.m.r. spectrum of (**9**) shows two sets of sharp lines at δ 1.29 and 1.05, which may be assigned to the prochiral methyls of the isopropyl groups. The broad multiplet at δ 1.91 is assignable to the methine hydrogens and the singlet at δ 5.9 is assignable to the η-C_7H_7 ligand. The broadening of the methine resonance indicates that compound (**9**) is undergoing a fluxional process which affects little the methyl resonances.

In view of the evident affinity of the cycloheptatrienyl-titanium fragment to co-ordinate to the O-donor ligand, tetrahydrofuran, related O- and N-donor molecules were studied as potential ligands.

A suspension of the red dimer (**2**) in toluene reacted with dry *NNN'N'*-tetramethylethylenediamine (tmen) giving large, extremely air-sensitive, red crystals of [Ti(η-C_7H_7)(tmen)Cl] (**10**). Similarly, treatment of a suspension of the red dimer (**2**) in toluene with a large excess of 1,2-dimethoxyethane (dme) gave red crystals of [Ti(η-C_7H_7)(dme)Cl] (**11**). Compound (**11**) is exceedingly air- and water-sensitive and decomposed at room temperature. This sensitivity precluded microanalysis and the formulation of (**11**) is based primarily on the ^1H n.m.r. spectrum (Table 1).

The compounds [Ti(η-C_7H_7)(dppe)Cl], [Ti(η-C_7H_7)(dippe)Cl], [Ti(η-C_7H_7){*trans*-1,2-$C_5H_8(PMe_2)_2$}Cl], [Ti(η-C_7H_7)(tmen)Cl], and [Ti(η-C_7H_7)(dme)Cl] all show considerable line broadening in their 300-MHz ^1H n.m.r. spectra at room temperature. This may be attributed to a similar exchange process to that discussed above for (**3**).

Treatment of (**3**) in thf with methylmagnesium bromide gave dark green needles of the methyl derivative [Ti(η-C_7H_7)(dmpe)Me] (**12**). Similarly, (**3**) reacted with an excess of MgEtBr giving dark green needles of [Ti(η-C_7H_7)(dmpe)Et] (**13**). The compounds (**12**) and (**13**) are air- and water-sensitive but are thermally stable and could be sublimed at 150 °C.

The crystal structure of (**13**) has been determined, and consists of discrete molecules with the structure shown in Figure 4, together with the numbering scheme. The metal environment has a piano-stool geometry and the angles between the tripodal ligands are all close to 80°. Bond distances and angles are given in Table 3. The Ti atom has a 16-electron environment since the geometry of the ethyl ligand is normal. The Ti–C–C angle of 115.1(4)° is in the range found for other 16-and 18-electron metal-ethyl complexes.[31,32] This contrasts sharply with the distorted geometry found in [TiEtCl$_3$(dmpe)].[33] The Ti–C(1) bond length [2.211(5) Å] is longer than that found in [TiEtCl$_3$(dmpe)] and the C(1)–C(2) distance is 1.520(6) Å. The carbon atoms of the η-C_7H_7 group are coplanar within experimental error and the η-C_7H_7 ring can be described essentially as a regular heptagon with C–C bonds in the range 1.350(7)—1.441(8) Å [mean 1.392 Å] and the internal ring angles 126.9(4)—129.7(4)°, mean 128.6°. The Ti atom is 1.569 Å from the η-C_7H_7 plane and the perpendicular to the η-C_7H_7 ring from Ti meets the ring close (0.04 Å) to the centroid. The Ti–C distances [range 2.228(6)—2.263(6), mean 2.243 Å] compare well with those of the 16-electron compound (**2**) [mean 2.238 Å]. It is not possible to relate the slight variations in Ti–C bond lengths to a *trans* influence of the P atoms. The hydrogen atoms of the η-C_7H_7 group have a mean displacement of 0.14 Å out of the C_7-plane towards the metal atom. The Ti–P bond lengths of 2.673(1) and 2.636(1) Å [mean 2.655(1) Å] are in the expected range, being longer than the distances found in [$TiEtCl_3$(dmpe)].[33] The dmpe ligand dimensions are unexceptional and compare well with those found in the complexes [$TiRCl_3$(dmpe)].[34] The bonds involving H atoms are all quite normal and corresponding bond angles have a maximal deviation of *ca.* 10° from expected values.

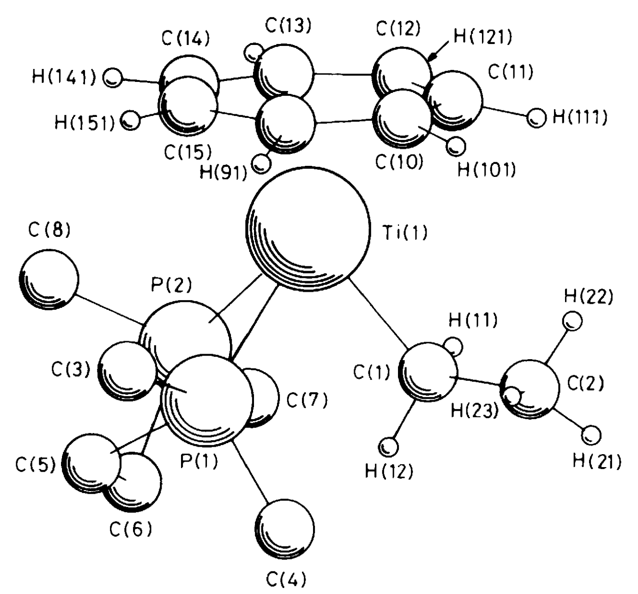


Figure 4. Crystal structure of [Ti(η-C_7H_7)(dmpe)Et] (**13**) showing the numbering scheme

The methyl derivative [Ti(η-C_7H_7){*trans*-1,2-$C_5H_8(PMe_2)_2$}-Me] (**14**) could be prepared as green dendritic flakes from (**8**) and an excess of MgMeBr. The ^1H n.m.r. spectrum of (**14**) is complicated by line broadening caused by fluxional processes but a satisfactory spectrum was obtained at 303 K and 400 MHz. The well resolved triplet at δ 5.53 [*J*(P–H) = 2.8 Hz] can be assigned to the cycloheptatrienyl group and the triplet at δ −0.4 [*J*(P–H) = 11.1 Hz], to the Ti-methyl.

Treatment of (**8**) in thf with a slight excess of Na[BH_4] gave golden brown crystals in high yield. Analytical (Table 1) and i.r. data (Table 4) suggest the formulation [Ti(η-C_7H_7){*trans*-1,2-$C_5H_8(PMe_2)_2$}(BH_4)] (**15**). The tetradeuterioborate analogue [Ti(η-C_7H_7){*trans*-1,2-$C_5H_8(PMe_2)_2$}(BD_4)] (**15-D**) was prepared using Na[BD_4]. The ^1H n.m.r. spectrum of (**15**) shows a set of four broad lines of equal intensity centred at δ −0.12 assignable to apparently equivalent hydrogens of a BH_4 group

Table 3. Bond distances (Å) and angles (°) for (**13**)

(*a*) Bond distances

Ti(1)–P(1)	2.673(1)	Ti(1)–C(9)	2.240(4)	C(10)–C(11)	1.350(7)	P(2)–C(8)	1.853(5)
Ti(1)–P(2)	2.636(1)	Ti(1)–C(10)	2.247(3)	C(11)–C(12)	1.376(7)	C(5)–C(6)	1.525(5)
P(1)–C(3)	1.837(4)	Ti(1)–C(11)	2.236(4)	C(12)–C(13)	1.372(7)	C(9)–C(10)	1.378(7)
P(1)–C(4)	1.804(7)	Ti(1)–C(12)	2.248(5)	C(13)–C(14)	1.413(7)	Ti(1)–C(15)	2.263(6)
P(1)–C(5)	1.843(3)	Ti(1)–C(13)	2.228(6)	C(14)–C(15)	1.441(8)	Ti(1)–C(1)	2.211(5)
P(2)–C(6)	1.836(5)	Ti(1)–C(14)	2.241(6)	C(15)–C(9)	1.413(8)	C(1)–C(2)	1.520(6)
P(2)–C(7)	1.827(4)						
C(9)–H(91)	1.04(6)	C(1)–H(11)	0.88(5)	C(3)–H(32)	0.98(7)	C(6)–H(61)	0.92(3)
C(10)–H(101)	1.04(7)	C(1)–H(12)	0.98(5)	C(3)–H(33)	0.80(4)	C(6)–H(62)	0.77(4)
C(11)–H(111)	0.99(5)	C(2)–H(21)	0.90(6)	C(4)–H(41)	0.96(4)	C(7)–H(71)	0.95(7)
C(12)–H(121)	0.88(6)	C(2)–H(22)	0.93(6)	C(4)–H(42)	0.94(5)	C(7)–H(72)	0.93(6)
C(13)–H(131)	0.88(6)	C(2)–H(23)	0.97(5)	C(4)–H(43)	0.88(6)	C(7)–H(73)	0.92(9)
C(14)–H(141)	0.93(4)	C(3)–H(31)	0.98(3)	C(5)–H(51)	0.84(5)	C(8)–H(81)	0.94(5)
C(15)–H(151)	0.73(6)			C(5)–H(52)	1.12(7)	C(8)–H(82)	0.84(5)

(*b*) Bond angles

Ti(1)–C(1)–C(2)	115.1(4)	C(11)–C(12)–C(13)	129.3(4)	C(1)–C(2)–H(22)	112(4)	H(42)–C(4)–H(43)	105(5)
P(1)–Ti(1)–P(2)	76.86(3)	C(12)–C(13)–C(13)	128.7(4)	C(1)–C(2)–H(23)	118(3)	H(131)–C(13)–C(12)	126(4)
P(1)–Ti(1)–C(1)	81.5(2)	C(13)–C(14)–C(15)	127.2(4)	H(21)–C(2)–H(22)	96(4)	H(131)–C(13)–C(14)	105(4)
P(2)–Ti(1)–C(1)	78.4(1)	C(14)–C(15)–C(9)	126.9(4)	H(21)–C(2)–H(23)	109(5)	H(141)–C(14)–C(13)	119(3)
Ti(1)–P(1)–C(3)	122.0(2)	C(15)–C(9)–C(10)	128.7(4)	H(22)–C(2)–H(23)	91(4)	H(141)–C(14)–C(15)	114(3)
Ti(1)–P(1)–C(4)	122.4(2)	H(91)–C(9)–C(10)	120(3)	H(31)–C(3)–P(1)	108(2)	H(151)–C(15)–C(14)	115(5)
Ti(1)–P(1)–C(5)	106.9(2)	H(91)–C(9)–C(15)	110(3)	H(32)–C(3)–P(1)	109(3)	H(151)–C(15)–C(9)	117(5)
C(3)–P(1)–C(4)	100.3(3)	H(101)–C(10)–C(9)	113(4)	H(33)–C(3)–P(1)	104(3)	H(71)–C(7)–P(2)	109(4)
C(3)–P(1)–C(5)	100.5(2)	H(101)–C(10)–C(11)	117(4)	H(31)–C(3)–H(32)	112(4)	H(72)–C(7)–P(2)	112(3)
C(4)–P(1)–C(5)	101.1(3)	H(111)–C(11)–C(10)	118(3)	H(31)–C(3)–H(33)	115(5)	H(73)–C(7)–P(2)	106(5)
P(1)–C(5)–C(6)	111.6(2)	H(111)–C(11)–C(12)	112(3)	H(32)–C(3)–H(33)	108(4)	H(71)–C(7)–H(72)	109(7)
C(5)–C(6)–P(2)	111.2(3)	H(121)–C(12)–C(11)	114(4)	H(41)–C(4)–P(1)	112(4)	H(71)–C(7)–H(73)	116(5)
C(6)–P(2)–Ti(1)	108.9(1)	H(11)–C(1)–Ti(1)	100(4)	H(42)–C(4)–P(1)	117(3)	H(72)–C(7)–H(73)	105(6)
C(6)–P(2)–C(7)	120.9(2)	H(12)–C(1)–Ti(1)	125(3)	H(43)–C(4)–P(1)	108(4)	H(81)–C(8)–P(2)	109(4)
C(6)–P(2)–C(8)	119.3(2)	H(12)–C(1)–H(11)	105(4)	H(41)–C(4)–H(42)	106(4)	H(82)–C(8)–P(2)	107(4)
C(9)–C(10)–C(11)	129.7(4)	C(1)–C(2)–H(21)	123(3)	H(41)–C(4)–H(43)	108(4)	H(81)–C(8)–H(82)	111(5)
C(10)–C(11)–C(12)	129.5(4)						

Table 4. Selected i.r. data on some metal–tetrahydroborate compounds

$M(\text{-H-})_2BH_2$[35,36]	$\text{-M-H-}BH_3$[35,36]	$[Cu(PPh_3)(\sigma\text{-}BH_4)]$[37]	**(15)**	**(15-D)**
2 400—2 600s	2 300—2 450s	2 335, 2 315s	2 350s, 2 375s	1 775, 1 780s *
1 650—2 150s	2 000s	2 050s	2 090s	1 700s
1 300—1 500s br	2 000—1 700br		2 060br	1 620br
1 100—1 200s	1 100s, 1 150w	1 060s, 1 075w	1 060s	795s *

* $\nu(B\text{-}H)/\nu(B\text{-}D) = 1.33$.

Table 5. Relative band intensities in the He-I and He-II spectra of some sandwich compounds

	a_1	e_2	e_{1a}	e_{1b}
$[Ti(\eta\text{-}C_7H_7)(\eta\text{-}C_5H_5)]$				
He-I		3.73	3.91	4.36
He-II		3.76	3.91	4.33
He-II/He-I		1.01	1.00	0.99
$[Cr(\eta\text{-}C_7H_7)(\eta\text{-}C_5H_5)]$				
He-I	0.70	3.63	4.59	5.08
He-II	1.84	3.53	4.33	4.30
He-II/He-I	2.63	0.97	0.94	0.85
$[Ti(\eta\text{-}C_8H_8)(\eta\text{-}C_5H_5)]$				
He-I	1.39	3.37	4.48	3.76
He-II	2.20	3.85	4.03	2.92
He-II/He-I	1.58	1.14	0.90	0.78
	a_1	e_2	$e_{1u} + e_{1g}$	
$[Ti(\eta\text{-}C_6H_5Me)_2]$				
		2.2	9.8	
		3.46	8.54	
		1.57	0.87	
$[Cr(\eta\text{-}C_6H_6)_2]$				
	1	4	9	
	2.3	4.5	7.2	
	2.3	1.1	0.8	

coupling to the ^{11}B ($I = \frac{3}{2}$) nucleus overlaid on a broad band due to coupling to ^{10}B ($I = 3$).

The i.r. spectra of **(15)** and **(15d)** are given in Table 4 together with comparative data from Marks *et al.*[35,36] and data for $[Cu(PPh_3)_3(HBH_3)]$.[37] Normally the BH_4 group acts as a ligand with two bridging and two terminal hydrogens $(MH_2B\overset{H}{\underset{H}{<}})$, the single bridging $M\text{-}H\text{-}BH_3$ group is rare. The bands assignable to B–H frequencies (terminal and bridging) in the i.r. spectrum of **(15)** differ from those for H_2BH_2 groups but are generally similar to those for $[Cu(PPh_3)_3(HBH_3)]$, which has been shown by *X*-ray and neutron diffraction studies to have a $M\text{-}H\text{-}BH_3$ group.[38,39] On this basis, and by electronic analogy with **(13)**, compound **(15)** is tentatively assigned the structure shown in the Scheme, which summarises this new titanium chemistry.

Catalysis Studies.—The compound $[Ti(\eta\text{-}C_5H_5)_2Cl_2]$ in conjunction with alkylaluminium compounds gives rise to moderately active Ziegler-Natta catalysts for ethylene polymerisation.[40] We were interested to test $Ti(\eta\text{-}C_7H_7)$ derivatives as precursors for homogeneous catalysts. Preliminary studies were all carried out using the red dimer, $[\{Ti(\eta\text{-}C_7H_7)(thf)(\mu\text{-}Cl)\}_2]$ **(2)**, in conjunction with a variety of alkylating agents.

The red dimer **(2)** and $(AlEt_2Cl)_2$ in dichloromethane gave a green solution which absorbed ethylene for several hours and deposited some white-brown filamentous polymer. A solution of **(2)** and $(AlEt_2Cl)_2$ in toluene when saturated with ethylene gave a green solution which absorbed further ethylene, producing filamentous polymer for a period of *ca.* 30 h. The solution was filtered and the filtrate was shown to be still active towards ethylene polymerisation. The yield of insoluble polyethylene was 0.46 g, from approximately 0.1 g of **(2)**. It was noted that when a dilute solution of $(AlEt_2Cl)_2$ was added slowly to **(2)** there was an initial precipitation of a beige solid, which ceased after addition of 2 mol equiv. of aluminium per mol of titanium. The mother-liquor was pale pink. Addition of a third equivalent of $(AlEt_2Cl)_2$ dissolved the precipitate giving a dark green solution. Further addition of $(AlEt_2Cl)_2$ developed a lime green colour. All these processes were reversed by addition of thf, ultimately reforming **(2)**.

The activity of the catalyst system was highly variable as a function of varying proportions. An excess of aluminium compound inhibited activity. The initial dark green solutions were noticeably more active than the lime green solutions containing an excess of alkylaluminium. The best but very modest[41] activity number for the catalyst was 0.11 g of polyethylene per hour per atmosphere of ethylene per mmol of catalyst. The stoicheiometry of the reaction between the red dimer and diethylaluminium chloride suggests that the first-formed product may have a Ti:Al ratio of 1:1, and that the dark green product may have a ratio 1 : 2.

Photoelectron Spectra.—In assigning oxidation states to η-cycloheptatrienyl–transition metal compounds the $\eta\text{-}C_7H_7$ group is normally given a formal charge of +1. Thus, for example, $[Ti(\eta\text{-}C_7H_7)(\eta\text{-}C_5H_5)]$ is considered to have a Ti^0 (d^4) metal centre.[9] The $[Ti(\eta\text{-}C_7H_7)]^+$ group might be expected, by analogy with *e.g.* $V(\eta\text{-}C_5H_5)$ which is also by definition d^4, to form 18-electron complexes such as $[Ti(\eta\text{-}C_7H_7)(CO)_4]^+$ {*cf.* $[V(\eta\text{-}C_5H_5)(CO)_4]$}. However, the extensive study of the $Ti(\eta\text{-}C_7H_7)$ moiety described in this paper shows it to be markedly reluctant to form any 18-electron complexes and it prefers to form 16-electron complexes with a 'piano-stool' structure which may be described as $[Ti(\eta\text{-}C_7H_7)L_2X]$ where L represents a two-electron donor ligand and X is a one-electron σ-bonded group. No complexes have been isolated with π-acceptor ligands; for example, **(2)** does not react with carbon monoxide or butadiene.

Previous photoelectron studies have provided detailed information on the electronic structure of sandwich compounds of the general type $[M(\eta^n\text{-}C_nH_n)(\eta^m\text{-}C_mH_m)]$.[17,42] The highest occupied molecular orbitals (h.o.m.o.) of $[Ti(\eta\text{-}C_7H_7)(\eta\text{-}C_5H_5)]$ comprise a degenerate pair of orbitals of e_2 symmetry, which are fully occupied, formed from a linear combination of d_{xy} and $d_{x^2-y^2}$ orbitals of the metal and the ring δ orbitals of e_2 symmetry. In a mixed sandwich compound the primary ring contributor to the e_2 orbital is the larger ring as it has the lower energy e_2 orbitals.

It has been shown from ionization-energy trends and single–triplet separations that the proportion of ring character in the e_2 orbital increases with ring size and decreases with increase in the metal atomic number across the transition series.[17,43] *X*-Ray

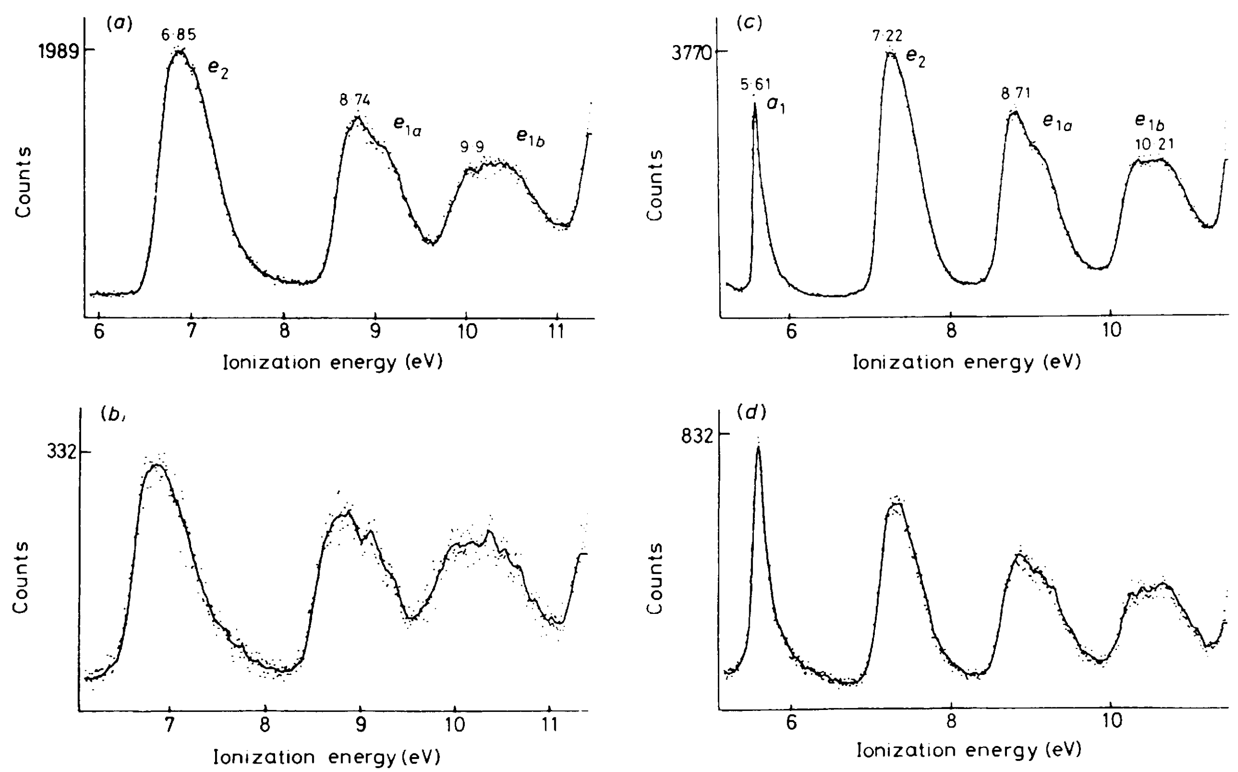


Figure 5. He-I and He-II photoelectron spectra of $[Ti(\eta\text{-}C_7H_7)(\eta\text{-}C_5H_5)]$, (*a*) and (*b*); $[Cr(\eta\text{-}C_7H_7)(\eta\text{-}C_5H_5)]$, (*c*) and (*d*)

photoelectron studies suggest that the negative charge on the C_7H_7 ring in the series of molecules $[M(\eta\text{-}C_7H_7)(\eta\text{-}C_5H_5)]$ (M = Cr, V, or Ti) follows the ordering:[15] Ti > V > Cr.

Another method of assessing the localisation of a molecular orbital is to compare the relative intensities of the photoelectron bands in the He-I and He-II spectra. This technique has been applied successfully in the study of sandwich compounds [44,45] and is based on the fact that in these cases the ionization cross section of a 3*d* electron increases relative to that of a carbon 2*p* electron on increasing the photon energy.

We decided to study the photoelectron band intensities of a series of sandwich molecules in order to gain further information on the delocalization of the e_2 orbital in C_7H_7 complexes. The compounds $[M(\eta\text{-}C_7H_7)(\eta\text{-}C_5H_5)]$ (M = Ti or Cr) are compared with their bis(arene) analogues $[Cr(\eta\text{-}C_6H_6)_2]$ and $[Ti(\eta\text{-}C_6H_5Me)_2]$, and $[Ti(\eta^8\text{-}C_8H_8)(\eta\text{-}C_5H_5)]$. The He-I photoelectron spectra of all these compounds have been reported previously.[17,46] In addition the related compound $[Ti(\eta\text{-}C_7H_7)(\eta\text{-}C_7H_9)]$ was subjected to a similar study. The results are summarised in Table 5 and some representative spectra shown in Figure 5. Only the relative values of the quoted intensities are meaningful. In fact the data are normalised to the total number of electrons occupying the e_1, e_2, and a_1 orbitals. As these numbers vary, the ratios must also be viewed relative to one another. The high He-II/He-I band intensity ratios found for ionization from the a_1 orbital in $[Cr(\eta\text{-}C_6H_6)_2]$, $[Cr(\eta\text{-}C_7H_7)(\eta\text{-}C_5H_5)]$, and $[Ti(\eta\text{-}C_8H_8)(\eta\text{-}C_5H_5)]$ show the ratio expected for a metal-localised orbital and indicate these electrons to be essentially non-bonding. Further, e.s.r. studies on $[V(\eta\text{-}C_7H_7)(\eta\text{-}C_5H_5)]$ confirm that the a_1 orbital is mainly d_{z^2} in character.[47] This non-bonding character is due to the fact that the nodal cone of the d_{z^2} orbital intersects the metal-directed lobes of the *p* orbitals of the ring close to their maximum of electron density (Figure 6). The e_2 orbitals of the $[M(\eta\text{-}C_7H_7)(\eta\text{-}C_5H_5)]$ compounds show very similar ionization cross-section ratios to the e_1 orbitals, whereas, with $[M(\eta\text{-arene})_2]$ the e_2 ionization cross-section ratios are significantly larger than the e_1 ratios.

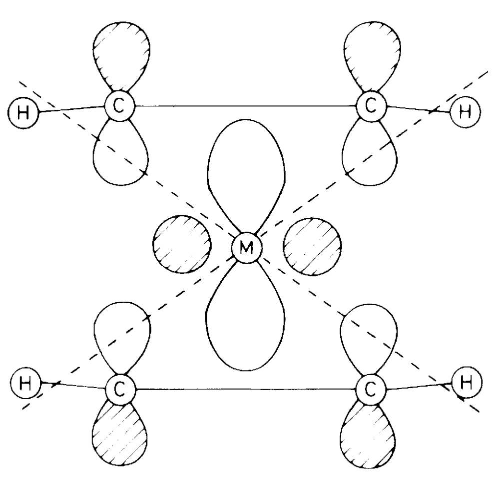


Figure 6. Diagrammatic representation of the interaction of a metal d_{z^2} orbital with a ring $a_1(\pi)$ orbital

The band intensities confirm and reinforce the previous suggestions that in a compound such as $[Ti(\eta\text{-}C_7H_7)(\eta\text{-}C_5H_5)]$ the four least tightly bound electrons (of the h.o.m.o.) are substantially localised on the $\eta\text{-}C_7H_7$ ring, and have the primary role of binding the ring to the metal. Formally three of these derive from the metal and they are therefore unavailable for further bonding with acceptor ligands or for oxidation. We would thus expect the maximum oxidation state achievable by titanium in a $Ti(\eta\text{-}C_7H_7)$ derivative to be 0. Alternatively it seems sensible to redefine the formal charge of the $\eta\text{-}C_7H_7$ ligand as −3. In which case the maximum oxidation state achievable by such compounds would be IV, and the favoured complexing of harder bases by [Ti(η-C_7H_7)]$^+$ would fit appropriately into the general pattern of titanium chemistry.

Photoelectron Spectrum of [Ti(η-C_7H_7)(η-C_7H_9)].—The photoelectron spectrum of [Ti(η-C_7H_7)(η-C_7H_9)] is shown in Figure 7 and the data are summarised in Table 6. It may be assigned by comparison with that of [Ti(η-C_7H_7)(η-C_5H_5)] and by consideration of the molecular orbitals (m.o.s) of the cycloheptadienyl ligand. The bands at 6.65 and 10.0 eV correlate with the e_2 (6.85) and e_{1b} (9.9) ionizations of [Ti(η-C_7H_7)(η-C_5H_5)] and may be given corresponding assignments. In place of the e_{1a} ionization (8.74 eV) of [Ti(η-C_7H_7)(η-C_5H_5)] there are two less intense bands at 7.32 and 9.06 eV. These may be assigned to e_{1a}^+ and e_{1a}^- ionizations: the correlation of π-orbitals of the dienyl systems of C_5H_5 and C_7H_9 are shown in Figure 8.

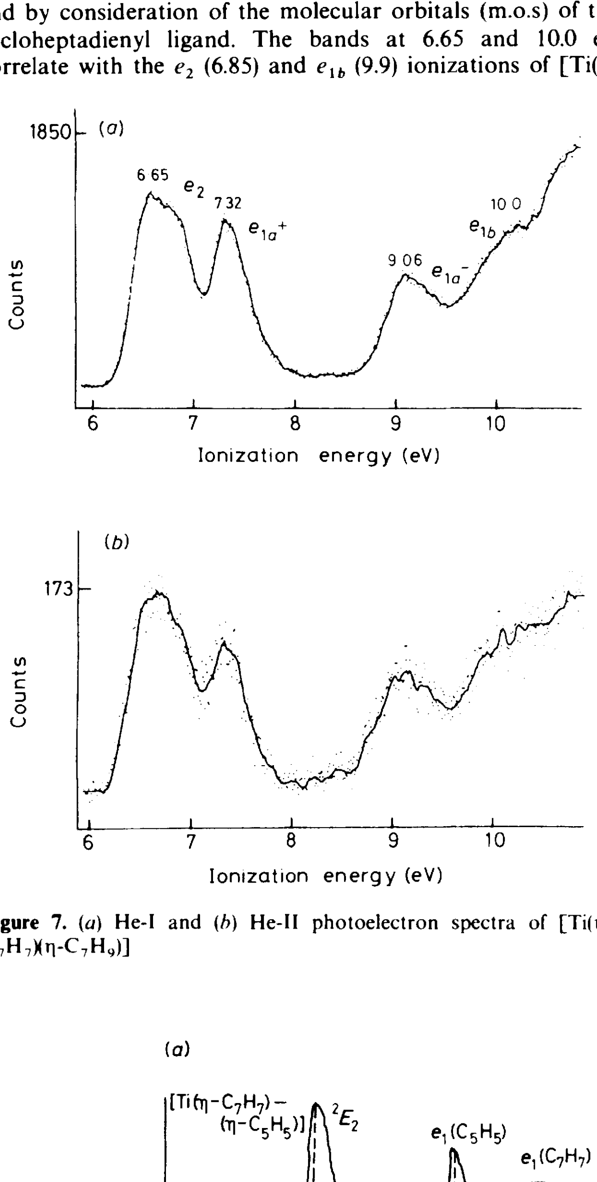


Figure 7. (*a*) He-I and (*b*) He-II photoelectron spectra of [Ti(η^5-C_7H_7)(η-C_7H_9)]

The loss of degeneracy in the open dienyl system might also be expected to produce differential back bonding from the titanium to the e_{2a}^+ and e_{2a}^- components of the C_7H_9 ring. It is interesting in this context that the e_2 ionization of [Ti(η-C_7H_7)(η-C_7H_9)] has a broader band than [Ti(η-C_7H_7)(η-C_5H_5)], and clearly shows an incipient splitting.

Bonding in the Compounds [Ti(η-C_7H_7)L_2X].—The orbital structure of a piano-stool molecule of the general type [M(η-C_nH_n)L_3] has been described by Hoffmann and co-workers.[48] These molecules are generally assumed to have three-fold symmetry (C_{3v}) so that the orbitals are classified as a_1 and *e*. A generalised m.o. scheme is shown in Figure 9. Many such compounds are known to have an 18-electron configuration, *e.g.* [Cr(η^6-C_6H_6)(CO)$_3$] and [Fe(η-C_5H_5)(CO)$_3$]$^+$. In these cases the a_1 orbital is filled whereas for 16-electron compounds such as the titanium ones dealt with here, the a_1 orbital is the lowest unoccupied molecular orbital (l.u.m.o.). We see, therefore, that the stability and occupancy of this a_1 orbital holds the key to the electron number of these complexes and their reactivity.

Table 6. Ionization energies and band intensities in the He-I and He-II spectra of [Ti(η-C_7H_7)(η-C_7H_9)]*

	Assignment			
	e_2	e_{1a}^+	e_{1a}	e_{1b}
Ionization energy	6.65	7.32	9.06	10.0
He-I	3.5	1.9	2.4	4.2
He-II	3.8	1.8	3.4	3.0
He-II/He-I	1.1	0.9	1.4	0.7

* Bands e_{1a}^-, e_{1b}, and the main C–H ionization band overlap extensively so intensity data on this molecule are less reliable than for other sandwich compounds.

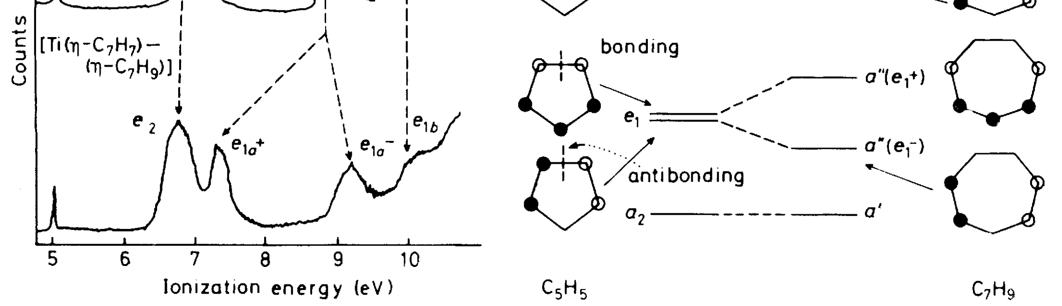


Figure 8. (*a*) He-I photoelectron spectra of [Ti(η-C_7H_7)(η-C_5H_5)] and [Ti(η-C_7H_7)(C_7H_9)]. (*b*) Correlation between the π orbitals of the C_5H_5 ring and the C_7H_9 ring

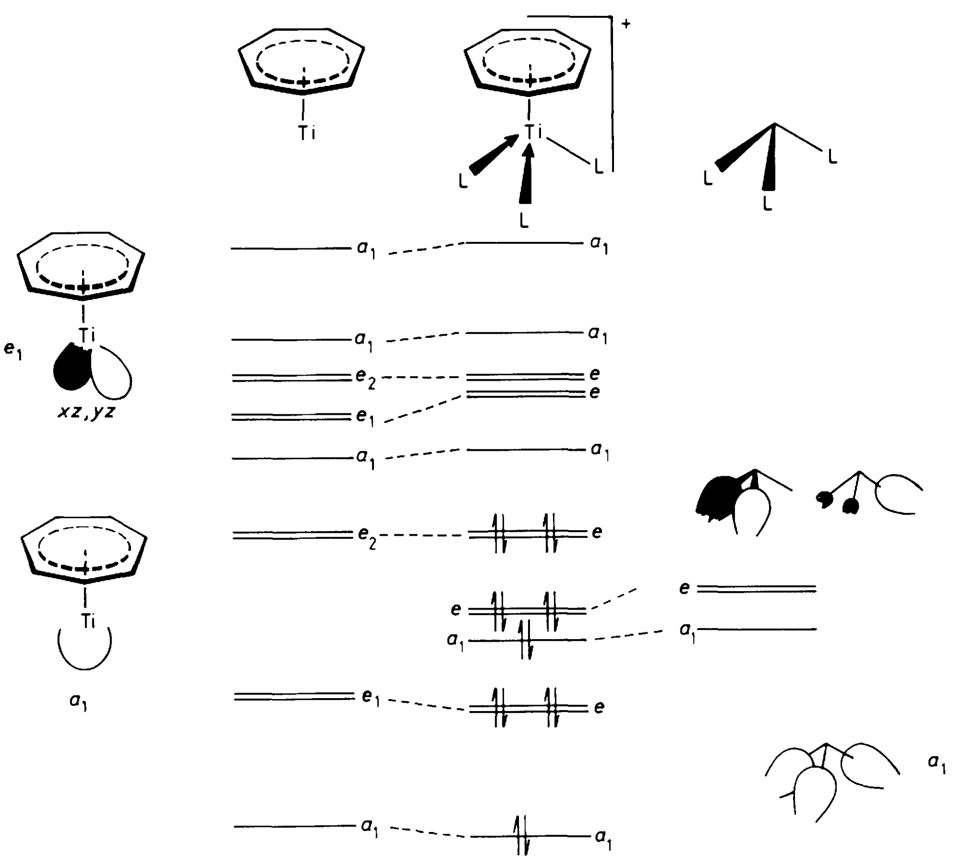


Figure 9. Qualitative interaction diagram showing the symmetry-allowed interactions between a Ti(η-C_7H_7) unit and three σ-donor ligands

The symmetry-allowed metal-localised components of the a_1 orbital are the d_{z^2}, s, and p_z orbitals. The contributing ligand orbitals can be both σ and η in character. The in-phase contribution of all the donor functions is of a_1 symmetry, as is the in-phase combination of the π-acceptor functions. As discussed above the ring a_1 σ orbital makes very little contribution to this a_1 orbital. The angle the nodal cone of the d_{z^2} orbital makes with the z axis is 54° 44′.[49] In the compound (**2**) the angle between the ligands and the metal–ring axis is *ca.* 42°, thus there will be a small interaction, which would be expected to destabilise the a_1 orbital slightly. The most stable piano-stool compounds with an 18-electron count are those with strong π-acceptor ligands, most notably carbonyl complexes such as [Mn(η-C_5H_5)(CO)$_3$], [V(η-C_7H_7)(CO)$_3$], and [Cr(η-C_6H_6)(CO)$_3$]. In these cases we expect stabilisation of the a_1 orbital by back donation to the CO group. Photoelectron studies (assuming Koopmans' theorem)[44,50] indicate that the a_1 and e orbitals are close in energy, the ionization energies being *ca.* 7 eV. In contrast, in the [M(η-arene)(PR$_3$)$_3$] compounds ionization energies are much lower, *ca.* 5.5 eV;[51] thus phosphine ligands are less able to stabilise the a_1 orbital. These compounds act as strong bases, being capable of protonation at the metal centre.[52]

The identity of the metal concerned is particularly important to the energy of the a_1 orbital since it may be assumed to be largely d_{z^2} in character. There is an increase in binding energy across the transition series following the increase in nuclear charge, thus the d-orbital energy will be highest for titanium. The factors influencing the stability of the a_1 orbital are summarized below.

Stabilized by	Destabilized by	Unaffected by
π-Acceptor ligands (*e.g.* CO)	π-Donor ligands (*e.g.* Cl⁻)	Ring a_1 contributions
Metals late in the transition series (*e.g.* Fe)	Metals early in the transition series (*e.g.* Ti)	

All factors mitigate against molecules of the type [Ti(η-C_7H_7)L_2X] co-ordinating a further Lewis base. The absence of d electrons in the a_1 orbital and the extensive delocalization of the e electrons onto the C_7H_7 ring also deter co-ordination by π-acceptor ligands.

The role of the ligand σ-donor orbitals is important when considering the spatial orientation of the a_1 orbital. The interaction of the in-phase ligand donor functions with the metal d_{z^2} and p_z orbitals will result in a bonding m.o. of mainly ligand character directed towards the ligands. The antibonding combination will consequently be directed towards the ring and be mostly of metal character. The combination of the high energy and unfavourable localisation of this a_1 orbital may well account for the absence of an agostic ethyl in [Ti(η-C_7H_7)(dme)Et]. In a related manner, the unusual σ-co-ordination of the BH_4 group in (**15**) is accounted for.

The crystal structures of compounds (**1**), (**2**), and (**13**) show a distinct shortening in the average distance between the carbon atoms of the C_7 ring and the metal. The values are respectively 2.194(5), 2.238(5), and 2.243(6) Å, and these may be compared with the average Ti–C distances in η-cyclopentadienyl complexes of 2.32—2.40 Å. For compound (**2**) this difference is

Table 7. Selected least-squares best planes for (**2**) and (**13**). In the equations, X, Y, and Z represent fractional co-ordinates with respect to the crystallographic axes. Values are the displacement (Å) of the specified atom from the plane

(*a*) Compound (**2**)

Plane 1: Ring C(11)—C(17)

Equation: $1.842\,91X + 14.476\,55Y + 4.285\,22Z = 4.173$

C(11)	−0.011	H(11)	−0.168
C(12)	0.011	H(12)	−0.206
C(13)	0.004	H(13)	−0.219
C(14)	−0.013	H(14)	−0.256
C(15)	0.003	H(15)	−0.165
C(16)	0.008	H(16)	−0.157
C(17)	−0.003	H(17)	−0.109
Ti(1)	−1.545		

(*b*) Compound (**13**)

Plane 1: Ring C(9)—C(15)

Equation: $-7.917\,46X + 2.484\,38Y + 4.613\,29Z = 0.237$

C(9)	0.011	H(91)	0.306
C(10)	−0.003	H(101)	0.171
C(11)	0.007	H(111)	0.222
C(12)	−0.016	H(121)	0.128
C(13)	0.012	H(131)	0.062
C(14)	0.005	H(141)	0.015
C(15)	−0.016	H(151)	0.101
Ti(1)	1.569		

Plane 2: C(1), P(1), P(2)

Equation: $7.939\,47X + 2.369\,65Y - 4.531\,73Z = -3.447$

C(1)	0.000	Ti(1)	1.674
P(1)	0.000	C(2)	0.014

16 standard deviations shorter than for TiC_5 and must be regarded as significant. It can be explained to occur as a result of improved overlap between the e_2 ring orbital and the δ-symmetry metal-localised orbital if the ring is closer to the metal. The C_7H_7–Ti distance in (**1**) has been discussed previously as a function of the strength of the e_2 interaction.

Experimental

All manipulations of solvents and air-sensitive materials were carried out with rigorous exclusion of moisture and oxygen. Argon was purified by passage through 4A molecular sieves and Fluka BTS catalyst. Glass reaction vessels were heated to *ca.* 300 °C under vacuum prior to use. Hydrocarbon solvents and thf were collected after prolonged refluxing over molten Na, K, or an alloy of the two; dichloromethane was conventionally dried, then stored over activated 4A molecular sieves. Solvents for n.m.r. studies were stored over Na/K alloy or molecular sieves, where appropriate.

Hydrogen-1 n.m.r. spectra were determined on JNM PMX-60 (60 MHz), Bruker WH300 (300 MHz), or Bruker 400 instruments (400 MHz). Carbon-13 n.m.r. spectra were determined using Bruker 300 (75.4 MHz) or AM 250 instruments (62.8 MHz). Variable-temperature ^1H n.m.r. spectra were run on a JEOl FX 100 instrument. Infrared spectra were determined on a Pye-Unicam SP 2000 spectrometer. Photoelectron spectra were determined on a PES Laboratories 0078 instrument.

η-Cycloheptadienyl(η-cycloheptatrienyl)titanium, (**1**).—Bis(η-toluene)titanium[19] (5 g, 21.5 mmol) in thf (200 cm^3) was treated with cycloheptatriene (7 cm^3, 67 mmol). A solution of diethylaluminium chloride (1.0 mol dm^{-3}, 15 cm^3, 15 mmol) was then added and the mixture heated at 70 °C for 7 h to ensure complete reaction. The solvent was partially removed under reduced pressure to a volume of 40 cm^3. After being warmed to dissolve some material the solution was filtered. On cooling it to −80 °C, dark green crystals separated which were washed with light petroleum (40 cm^3, b.p. 40—60 °C). The washings were combined with the mother-liquor, and this was cooled to give a second crop of crystals. The combined yield was 4.1 g, 82%.

Experiment to show the Catalytic Role of Ethylaluminium Dichloride in the Above Reaction.—Deep red-purple bis(η-toluene)titanium (1.4 g, 6.0 mmol) in thf (40 cm^3) was treated with cycloheptatriene (2 cm^3, 18 mmol) in thf (15 cm^3). The mixture was heated in a sealed ampoule at 110 °C for 5 h and no colour change was observed. The ampoule was opened and a solution of $(AlEtCl_2)_2$ in toluene (1 cm^3 of a 1.3 mol dm^{-3} solution) was added. The mixture was heated at 90 °C for 3 h giving a dark green solution. The volatile components were removed under reduced pressure to give an oily solid. This was extracted with light petroleum (b.p. 40—60 °C; 20 cm^3), and the extract filtered, concentrated under reduced pressure, and cooled to −80 °C. Green crystals were obtained which were shown to be $[Ti(\eta\text{-}C_7H_7)(\eta\text{-}C_7H_9)]$ by their i.r. spectra.

Reaction of η-Cycloheptadienyl(η-cycloheptatrienyl)titanium with Iodine.—$[Ti(\eta\text{-}C_7H_7)(\eta\text{-}C_7H_9)]$ (1.0 g, 4.3 mmol) in toluene (50 cm^3) at −80 °C was treated with an excess of iodine (0.5 g) in toluene (30 cm^3) giving a dark solution and some dark solid. The solid was isolated by filtration (−20 °C) and washed with cold light petroleum (b.p. 40—60 °C; 2 × 30 cm^3). The solid was extracted into a mixture of toluene and light petroleum and cooling separated purple-black crystals of tetraiodotitanium.

Reaction of η-Cycloheptadienyl(η-cycloheptatrienyl)titanium with $C_6H_5ICl_2$.—$[Ti(\eta\text{-}C_7H_7)(\eta\text{-}C_7H_9)]$ (0.3 g, 1.3 mmol) in thf (40 cm^3) was treated with $C_6H_5ICl_2$ (0.35 g, 1.3 mmol) in thf (40 cm^3). No immediate reaction was observed, but after 3 h the solution developed a blue tinge. After 24 h a light blue-grey material was deposited. The solid was identified as slightly impure $TiCl_3(thf)_3$.

Bis[(μ-chloro)(η-cycloheptatrienyl)(tetrahydrofuran)-titanium], (**2**).—*Method A.* Diethylaluminium chloride dimer in toluene (1.0 mol dm^{-3} in Al, 25 cm^3) and thf (40 cm^3) at room temperature was treated with cycloheptatriene (10 cm^3, 95 mmol) and then bis(η-toluene)titanium (8.7 g, 37 mmol). The mixture was stirred for 1 h and then filtered. The filtrate was stored for three weeks at room temperature during which time there was slow deposition of large red crystals. After this time further diethylaluminium chloride solution (16 cm^3) and cycloheptatriene (10 cm^3) was added and deposition of red crystals continued over the following two weeks. The mother-liquor was decanted off and the resulting crystals were washed with toluene (2 × 10 cm^3) and dried *in vacuo*. The yield was 2.55 g, 27%. The decanted mother-liquor produced more red dimer (*ca.* 1 g) during two months.

Method B. Titanium atoms (1.08 g, 22 mmol), vapourised from an electron-gun furnace were co-condensed with thf vapour (40 cm^3) and simultaneously with an atomised spray of a mixture of cycloheptatriene and diethylaluminium chloride (5:2 v/v, 40 cm^3) over 4 h. The apparatus is described elsewhere.[20] A dark red matrix was formed, which upon warming to room temperature (r.t.) turned salmon pink. The product was washed from the reaction wall with thf (300 cm^3). The volatile components were removed under reduced pressure, giving red crystals and a dark oil. This was washed with light petroleum (b.p. 100—120 °C, 15 cm^3), then with toluene (40 cm^3), and finally with thf (10 cm^3). The residue was extracted with thf (3 × 50 cm^3) and concentration under reduced pressure and cooling of the extract (to −30 °C) gave red crystals. The yield was 0.43 g, 7%. A further *ca.* 1 g of the compound crystallised out of the collected washings over a period of weeks.

[1,2-*Bis*(*dimethylphosphino*)*ethane*]*chloro*(η-*cycloheptatrienyl*)*titanium*, (**3**).—A stirred suspension of the red dimer (0.8 g, 3.24 mmol) in toluene (20 cm^3), was treated with a solution of 1,2-bis(dimethylphosphino)ethane (0.4 cm^3) in toluene (10 cm^3). The initially red mixture rapidly became yellow, and precipitation of yellow crystals followed. The mixture was stirred for 1.5 h. The volatile components were removed under reduced pressure giving a yellow solid which was extracted with hot toluene (80 °C, 90 cm^3), the extract was filtered, then cooled to −20 °C giving fine yellow crystals (0.72 g) which were washed with cold toluene (−78 °C). The mother-liquor was concentrated to 20 cm^3, then cooled giving large yellow needles, which were washed and collected. The combined yield was 0.78 g, 75%.

Reaction of [{Ti(η-C$_7$H$_7$)(thf)(μ-Cl)}$_2$] (**2**) *with* PMe$_3$ *in Toluene*: *Chloro*(η-*cycloheptatrienyl*)*bis*(*trimethylphosphine*)*titanium*, (**4**).—A stirred suspension of (**2**) (0.7 g, 2.8 mmol), in toluene (30 cm^3) was cooled under reduced pressure to 77 K, and PMe$_3$ vapour (*ca.* 1 g) was condensed onto the frozen solution. As the mixture warmed the solution became yellow, and eventually orange. Upon concentration under reduced pressure the solution became red. After filtration, the yellow colour was restored by the introduction of a small amount of PMe$_3$ vapour. Cooling of the solution to −80 °C resulted in the formation of yellow-orange crystals which were isolated and washed with cold toluene. Upon drying *in vacuo* the crystals turned dark red, yield *ca.* 70%. The product was characterised by ^{1}H n.m.r. spectroscopy (see text).

(*Trimethylphosphine*)*bis*[*chloro*(η-*cycloheptatrienyl*)*titanium*], (**5**).—A suspension of the red dimer (0.5 g, 1.0 mmol) in toluene (50 cm^3) was cooled and an excess of PMe$_3$ vapour (*ca.* 1 g) was condensed into the Schlenk vessel under reduced pressure. On warming, the solution became orange and nearly all the solid dissolved. The solution was filtered, then the volatile components were removed under reduced pressure to give, in the first instance, a red solution, then a mixture of purple and yellow solids. More toluene was added (50 cm^3) and all the solids dissolved. The solution was concentrated under reduced pressure at 50 °C whereupon it developed an intense purple colour, and a purple solid separated slowly. A further quantity of toluene (50 cm^3) was added and half of it removed under reduced pressure. An equal volume of light petroleum (b.p. 40—60 °C) was added to the concentrate, and the solution was filtered and cooled to −80 °C giving purple needles. These were recrystallised from a mixture of light petroleum (b.p. 40—60 °C) and toluene: yield 0.23 g, 60%.

[1,2-*Bis*(*diphenylphosphino*)*ethane*]*chloro*(η-*cycloheptatrienyl*)*titanium*, (**6**).—A recrystallised sample of 1,2-bis(diphenylphosphino)ethane (1.22 g, 0.31 mmol) was mixed with (**2**) (0.72 g, 0.5 mmol). Toluene (50 cm^3) was added and the mixture was stirred overnight to give an orange powder. The solvent was removed under reduced pressure, and the resulting orange solid was extracted with hot toluene (90 °C, 100 cm^3). The extract was filtered and the filtrate was cooled to −20 °C. Orange crystals separated which were twice recrystallised from hot toluene (90 °C). The compound crystallises with a molecule of toluene. The yield was 0.61 g, 31%.

trans-1,2-*Bis*(*dimethylphosphino*)*cyclopentane*, (**7**).—*trans*-1,2-Bis(dichlorophosphino)cyclopentane (13.2 g, 48.5 mmol), prepared as described previously,[29] in thf (80 cm^3) was treated slowly with a solution of MgMeBr (180 mmol) in thf (1.0 mol dm^{-3}). A white precipitate was formed immediately and became thicker as the addition continued. After the addition was completed the mixture was stirred for several hours and then hydrolysed by slow addition of a saturated solution of NH$_4$Cl (40 cm^3). Light petroleum (b.p. 30—40 °C; 40 cm^3) was added and the organic layer was separated. The aqueous phase was washed twice more with light petroleum (b.p. 30—40 °C; 2 × 40 cm^3). The combined organic fractions were dried over MgSO$_4$, then the more volatile components were removed under reduced pressure to leave 10 cm^3 of a yellow oil which was twice distilled under reduced pressure. The first distillation was at 0.05 Torr (60 °C) and the second was at 0.02 Torr (50 °C), giving a colourless oil. The yield was 5.1 g, 54%.

[trans-1,2-*Bis*(*dimethylphosphino*)*cyclopentane*]*chloro*(η-*cycloheptatrienyl*)*titanium*, (**8**).—A suspension of the red dimer (2.6 g, 102 mmol) in toluene (40 cm^3) was treated with *trans*-1,2-C$_5$H$_8$(PMe$_2$)$_2$ (2 g, 10 mmol) in toluene (30 cm^3). After stirring for 1 h yellow crystals separated. The volatile components were removed under reduced pressure to give a yellow solid. Some of this was extracted in toluene (80 cm^3), the solution was filtered and concentrated (to 60 cm^3). The concentrate was cooled to −20 °C, to give small yellow crystals. These were recrystallised from toluene giving rectangular crystals; yield 3.0 g, 81%.

[1,2-*Bis*(*di-isopropylphosphino*)*ethane*]*chloro*(η-*cycloheptatrienyl*)*titanium*, (**9**).—A solution of the red dimer (0.15 g, 0.3 mmol) in toluene (50 cm^3) was filtered into a Schlenk vessel containing 1,2-bis(di-isopropylphosphino)ethane (0.5 cm^3) giving an orange-red solution. The volatile components were removed under reduced pressure and the red residue was extracted into toluene (15 cm^3). A similar volume of light petroleum (b.p. 30—40 °C) was added, and the solution was cooled to −20 °C. The resulting dark red crystals were isolated and washed with a small quantity of light petroleum (b.p. 40—60 °C) and dried *in vacuo*; yield 0.05 g, 20%.

Chloro(η-*cycloheptatrienyl*)(NNN′N′-*tetramethylethylenediamine*)*titanium*, (**10**).—A suspension of the red dimer (0.6 g, 1.2 mmol) was stirred overnight in toluene (40 cm^3) to break up the larger crystals. The suspension was cooled to 77 K under reduced pressure and tmen (*ca.* 3 cm^3) was condensed onto the frozen solution. As the mixture warmed up, many bright red crystals were formed. The mixture was stirred for several hours to ensure complete reaction. The volatile components were removed under reduced pressure to give a red crystalline powder. This was extracted with hot toluene (70 cm^3, 50 °C) and the filtered extract was cooled to −20 °C giving red crystals; yield 0.4 g, 60%.

Chloro(η-*cycloheptatrienyl*)(1,2-*dimethoxyethane*)*titanium*, (**11**).—A suspension of (**2**) (0.6 g, 1.2 mmol) was stirred overnight in toluene (40 cm^3) to break up the large crystals. The mixture was cooled to 77 K under reduced pressure. 1,2-Dimethoxyethane (8 cm^3) was distilled into the reaction vessel under reduced pressure. The mixture was stirred and a red solid separated. The volatile components were removed under reduced pressure and the residual solid was extracted in warm toluene (60 cm^3, 90 °C) which dissolved about half the material. Cooling of the extract to −20 °C produced dark red crystals. These were twice more recrystallised from toluene. The compounds slowly decomposed during the final removal of solvent under reduced pressure.

[1,2-*Bis(dimethylphosphino)ethane*](η-*cycloheptatrienyl*)*methyltitanium*, (**12**).—[Ti(η-C_7H_7)(dmpe)Cl] (0.2 g, 0.6 mmol) in thf (20 cm^3) was treated with MgMeBr (1 cm^3 of a *ca.* 2 mol dm^{-3} solution) in thf. The solution became dark green and the volatile components were removed under reduced pressure to give a green solid. This was twice extracted into light petroleum (b.p. 40—60 °C; 40 cm^3) and the combined extracts were cooled to −80 °C, giving fine green needles which were washed with cold light petroleum (b.p. 40—60 °C); yield 70%.

[1,2-*Bis(dimethylphosphino)ethane*](η-*cycloheptatrienyl*)*ethyltitanium*, (**13**).—The compound [Ti(η-C_7H_7)(dmpe)Cl] (0.5 g), partially dissolved in thf (20 cm^3), was treated with an excess of MgEtBr in thf (30 cm^3 of a 2 mol dm^{-3} solution) giving a green solution. The volatile components were removed under reduced pressure to give a green oil which was extracted into light petroleum (b.p. 40—60 °C; 60 cm^3) and cooling of the extract to −20 °C caused large green crystals to separate. These were recrystallised from light petroleum (b.p. 30—40 °C); yield 0.44 g, 70%.

trans-[1,2-*Bis(dimethylphosphino)cyclopentane*](η-*cycloheptatrienyl*)*methyltitanium*, (**14**).—The compound [Ti(η-C_7H_7){*trans*-1,2-$C_5H_8(PMe_2)_2$}Cl] (1.3 g, 3.6 mmol) in thf (45 cm^3) was treated with an excess of MgMeBr in thf (20 cm^3 of a 0.1 mol dm^{-3} solution). The mixture became dark green. The volatile components were removed under reduced pressure giving copious green crystals. The solid was extracted with toluene (2 × 30 cm^3) and light petroleum (b.p. 40—60 °C, 170 cm^3) was added to the extract. Upon cooling it to −80 °C light green crystals formed. These were recrystallised from light petroleum (b.p. 40—60 °C, 100 cm^3) to give large green dendritic crystals; yield 0.89 g, 73%.

Reaction Mixture from [{Ti(η-C_7H_7)(thf)(μ-Cl)}$_2$] *and Diethylaluminium Chloride in* CH_2Cl_2.—A suspension of [{Ti(η-C_7H_7)(thf)(μ-Cl)}$_2$] (0.15 g, 0.25 mmol) in dichloromethane (40 cm^3) was treated with diethylaluminium chloride to give a lime green solution and some brown oily solid. The

Table 8. Final atomic fractional co-ordinates for (**2**)

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Ti(1)	0.535 79(4)	0.108 53(2)	0.016 28(3)	H(2)	0.082(4)	0.092(2)	−0.155(2)
Cl(1)	0.290 57(6)	0.006 49(2)	0.072 63(5)	H(3)	−0.028(3)	0.112(1)	−0.436(3)
O(1)	0.358 6(2)	0.098 42(8)	−0.199 8(1)	H(4)	0.022(4)	0.030 4(9)	−0.372(3)
C(1)	0.142 1(3)	0.113 9(1)	−0.233 9(2)	H(5)	0.270(4)	0.107(1)	−0.537(2)
C(2)	0.078 3(4)	0.080 6(1)	−0.382 1(2)	H(6)	0.309(4)	0.027 2(8)	−0.470(3)
C(3)	0.271 3(5)	0.078 4(2)	−0.448 3(3)	H(7)	0.473(4)	0.157 4(7)	−0.347(3)
C(4)	0.438 0(4)	0.104 5(2)	−0.334 0(2)	H(8)	0.567(3)	0.077(2)	−0.324(3)
C(11)	0.422 6(4)	0.179 1(1)	0.184 5(3)	H(11)	0.295(2)	0.174(2)	0.221(3)
C(12)	0.594 1(4)	0.138 9(1)	0.251 5(2)	H(12)	0.560(4)	0.106(1)	0.327(2)
C(13)	0.783 2(4)	0.128 3(1)	0.204 5(2)	H(13)	0.865(4)	0.088(1)	0.254(3)
C(14)	0.848 6(3)	0.156 0(1)	0.078 9(3)	H(14)	0.967(3)	0.132(1)	0.053(3)
C(15)	0.743 5(4)	0.202 4(1)	−0.028 9(3)	H(15)	0.805(4)	0.209(2)	−0.115(2)
C(16)	0.543 6(4)	0.231 1(1)	−0.038 7(3)	H(16)	0.497(4)	0.253(1)	−0.132(2)
C(17)	0.399 1(4)	0.220 6(1)	0.056 4(3)	H(17)	0.266(2)	0.241(1)	0.021(3)
H(1)	0.128(4)	0.168 9(6)	−0.237(3)				

Table 9. Final atomic fractional co-ordinates for (**13**)

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Ti(1)	−0.054 8(1)	−0.1338	0.225 3(1)	H(31)	−0.098 8(50)	0.017 3(13)	0.369 3(46)
P(1)	−0.255 0(1)	−0.0590	0.282 9(1)	H(32)	−0.305 0(77)	0.031 1(20)	0.276 1(70)
P(2)	−0.369 8(1)	−0.1582	0.030 0(1)	H(33)	−0.192 2(67)	0.013 8(15)	0.189 3(52)
C(1)	−0.159 1(6)	−0.177 9(1)	0.388 7(5)	H(41)	−0.228 4(70)	−0.054 6(18)	0.557 1(60)
C(2)	−0.057 1(10)	−0.171 8(2)	0.567 7(6)	H(42)	−0.379 9(58)	−0.090 1(17)	0.474 2(51)
C(3)	−0.203 2(7)	0.010 4(1)	0.276 3(6)	H(43)	−0.398 5(70)	−0.034 5(20)	0.447 6(60)
C(4)	−0.323 1(7)	−0.059 9(2)	0.458 2(7)	H(51)	−0.545 3(64)	−0.044 6(16)	0.139 0(55)
C(5)	−0.467 3(5)	−0.062 2(1)	0.118 7(6)	H(52)	−0.425 5(75)	−0.049 4(18)	0.016 1(61)
C(6)	−0.530 5(5)	−0.118 2(1)	0.081 9(6)	H(61)	−0.637 1(49)	−0.120 3(14)	0.000 6(46)
C(7)	−0.457 8(7)	−0.223 7(2)	0.030 2(8)	H(62)	−0.530 6(52)	−0.130 2(13)	0.161 5(44)
C(8)	−0.425 9(7)	−0.147 0(2)	−0.187 4(5)	H(71)	−0.580 4(102)	−0.222 5(25)	−0.022 7(81)
C(9)	0.145 5(6)	−0.070 6(2)	0.265 4(7)	H(72)	−0.436 5(89)	−0.236 5(21)	0.134 4(71)
C(10)	0.220 3(5)	−0.111 0(2)	0.369 0(6)	H(73)	−0.395 9(101)	−0.245 1(26)	−0.014 9(84)
C(11)	0.218 4(5)	−0.162 7(2)	0.340 0(6)	H(81)	−0.541 4(79)	−0.154 2(19)	−0.237 5(67)
C(12)	0.146 5(6)	−0.189 4(2)	0.197 2(8)	H(82)	−0.404 8(72)	−0.115 6(20)	−0.200 6(63)
C(13)	0.049 8(6)	−0.170 8(2)	0.047 4(7)	H(91)	0.124 1(77)	−0.035 0(20)	0.311 8(64)
C(14)	0.006 0(6)	−0.118 7(2)	−0.001 3(6)	H(101)	0.264 8(98)	−0.099 6(27)	0.489 1(85)
C(15)	0.052 0(7)	−0.072 7(2)	0.097 9(9)	H(111)	0.253 8(65)	−0.186 5(19)	0.434 6(58)
H(11)	−0.150 1(61)	−0.209 9(18)	0.355 4(50)	H(121)	0.147 1(87)	−0.224 4(25)	0.210 6(73)
H(12)	−0.283 5(64)	−0.172 8(17)	0.369 6(57)	H(131)	0.012 3(95)	−0.188 9(23)	−0.042 6(74)
H(21)	−0.073 3(83)	−0.192 5(21)	0.644 7(62)	H(141)	−0.059 6(67)	−0.112 0(18)	−0.108 1(61)
H(22)	0.060 9(79)	−0.179 4(19)	0.591 7(70)	H(151)	0.007 5(100)	−0.048 9(24)	0.059 7(79)
H(23)	−0.029 4(75)	−0.136 9(21)	0.610 7(64)				

solution started to take up ethylene after a few minutes giving a brown solid over the course of 24 h. The solid was isolated and washed with acetone in air; the yield of solid (78% organic) was 0.3 g.

Reaction Mixture from [{Ti(η-C_7H_7)(thf)(μ-Cl)}$_2$] *and Diethylaluminium Chloride in Toluene.*—A suspension of [{Ti(η-C_7H_7)(thf)(μ-Cl)}$_2$] (0.15 g, 0.25 mmol) in toluene (80 cm^3), under an atmosphere of ethylene, was treated with a solution of diethylaluminium chloride in toluene (1 mol dm^{-3}) to give a dark green solution with some oily solid. There was a steady uptake of ethylene for 32 h to give a grey-brown filamentous solid. The green solution which was very air sensitive was filtered and still found to be an active catalyst. The grey solid was washed in air with acetone to give a white plastic. Yield 0.46 g (99.9% organic).

Titration of [{Ti(η-C_7H_7)(thf)(μ-Cl)}$_2$] *against Diethylaluminium Chloride.*—A solution of the red dimer was treated with a dilute solution of diethylaluminium chloride to give the following changes. As the solution was first added a green-brown precipitate was formed, which was produced until only a pale pink solution remained; at this point 2 mmol of $(AlEt_2Cl)_2$ had been added. Further addition caused the precipitate to redissolve giving a green solution, and this process was complete after the addition of a further 1 mmol of aluminium compound. Although the concentration of the original titanium compound was uncertain, it is reasonable to suppose that the solution contained 1 mmol.

Best Activity Number for the Catalyst.—A catalytic solution was made up of [{Ti(η-C_7H_7)(thf)(μ-Cl)}$_2$] (*ca.* 0.07 g, 0.3 mmol) in toluene (40 cm^3), and a dilute solution of diethylaluminium chloride. The solution took up ethylene for 32 h giving 1.4 g of polyethylene which after washing analysed as 99% pure. Assuming a steady uptake, the activity of the catalyst is 0.11 (gram atom)$^{-1}$ h^{-1} $mmol^{-1}$.

Crystal Data for (**2**).—$C_{22}H_{30}Cl_2O_2Ti_2$, $M = 493.19$, monoclinic, space group $P2_1/n$ (no. 14), $a = 6.630(3)$, $b = 17.729(3)$, $c = 9.370(1)$ Å, $\beta = 98.82°$, $U = 1\,088$ Å^3, $Z = 2$, $D_c = 1.51$ g cm^{-3}, $F(000) = 936$.

Data were measured ($2\theta_{max.} = 60°$) on an Enraf-Nonius CAD4 diffractometer using Mo-K_α radiation ($\mu = 9.89$ cm^{-1}) and ω–2θ scans. 2 603 Independent reflections [$I > 3\sigma(I)$] were used in the refinement, and an absorption correction was not applied. The structure was solved by a combination of direct methods and electron-density difference maps, and was refined by a least-squares method, using a large-block approximation to the normal matrix. All atoms were refined anisotropically, except for the hydrogens, which were refined using two common thermal parameters, one for the η-C_7H_7 ligand and one for the thf. 'Soft' restraints were applied to maintain C–H bond lengths equal to their mean. A Hughes[53] weighting scheme was used to calculate weights for the 372 most intense reflections. The R value converged to 0.028 ($R' = 0.038$) in the final refinement of 175 parameters.

Crystal Data for (**13**).—$C_{15}H_{28}P_2Ti$, $M = 318.24$, monoclinic, space group $P2_1/n$ (no. 14), $a = 8.138(1)$, $b = 25.657(4)$, $c = 8.791(5)$ Å, $\beta = 109.65(3)°$, $U = 1\,728.5$ Å^3, $Z = 4$, $D_c = 1.22$ g cm^{-3}, $F(000) = 680$.

The data were measured ($2\theta_{max.} = 60°$) on an Enraf-Nonius CAD4 diffractometer using Mo-K_α radiation and ω–2θ scans. 2 108 Independent reflections with $I > 3\sigma(I)$ were used in the refinement, and an absorption correction was not applied. The structure was solved by a combination of Patterson and difference-electron density methods and refined by least squares with a large-block approximation to the normal matrix. All atoms, except the hydrogens, were refined anisotropically. The hydrogens were located from a difference map and were refined isotropically. The weighting scheme was a three-term Chebyshev polynomial with coefficients 382, 525, and 152.[54] The final R value was 0.039 ($R' = 0.049$).

Details of least-squares planes for (**2**) and (**13**) are in Table 7; final atomic co-ordinates are in Tables 8 and 9 respectively.

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References

1 E. F. Ashworth, M. L. H. Green, and J. Knight, *J. Chem. Soc., Chem. Commun.*, 1974, 5.

2 E. F. Ashworth, J. C. Green, M. L. H. Green, J. Knight, R. B. A. Pardy, and N. J. Wainwright, *J. Chem. Soc., Dalton Trans.*, 1977, 1693.

3 M. Bochmann, M. Green, H. P. Kirsch, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1977, 714; M. Green, H. P. Kirsch, F. G. A. Stone, and A. J. Welch, *ibid.*, p. 1755.

4 T. S. Piper, F. A. Cotton, and G. Wilkinson, *J. Inorg. Nucl. Chem.*, 1955, **1**, 165.

5 'Comprehensive Organometallic Chemistry,' eds. G. Wilkinson, F. G. A. Stone, and E. W. Abel, Pergamon Press, Oxford, 1982, ch. 4, pp. 331—399; S. G. Davies, 'Organotransition Metal Chemistry: Applications to Organic Synthesis,' Pergamon Press, Oxford, 1982, chs. 2, 4, 5.

6 H. O. Van Oven and H. S. De Liefde Meijer, *J. Organomet. Chem.*, 1971, **31**, 71.

7 H. O. Van Oven and H. J. De Liefde Meijer, *J. Organomet. Chem.*, 1970, **23**, 159.

8 M. Bottrill, P. D. Gavens, and J. McMeeking, in 'Comprehensive Organometallic Chemistry,' eds. G. Wilkinson, F. G. A. Stone, and E. W. Abel, Pergamon Press, Oxford, 1982, vol. 3, p. 292.

9 S. Datta, M. B. Fischer, and S. S. Wreford, *J. Organomet. Chem.*, 1980, **188**, 353.

10 P. L. Timms and T. W. Turney, *J. Chem. Soc., Dalton Trans.*, 1976, 2021.

11 H. T. Verkouw and H. O. Van Oven, *J. Organomet. Chem.*, 1973, **59**, 259.

12 H. T. Verkouw, M. E. E. Veldman, C. J. Groeneboom, H. O. Van Oven, and H. J. De Liefde Meijer, *J. Organomet. Chem.*, 1975, **102**, 49.

13 C. J. Groeneboom, H. J. De Liefde Meijer, and F. Jellinek, *Recl. Trav. Chim. Pays-Bas.*, 1974, **93**, 6.

14 C. J. Groeneboom, H. J. De Liefde Meijer, and F. Jellinek, *J. Organomet. Chem.*, 1974, **69**, 235.

15 C. J. Groeneboom, G. Sawatsky, H. J. De Liefde Meijer, and F. Jellinek, *J. Organomet. Chem.*, 1974, **76**, C4.

16 C. J. Groeneboom and F. Jellinek, *J. Organomet. Chem.*, 1974, **80**, 229.

17 S. Evans, J. C. Green, S. E. Jackson, and B. Higginson, *J. Chem. Soc., Dalton Trans.*, 1974, 304.

18 M. L. H. Green, N. J. Hazel, P. D. Grebenik, V. S. B. Mtetwa, and K. Prout, *J. Chem. Soc., Chem. Commun.*, 1983, 356.

19 M. T. Anthony, M. L. H. Green, and D. Young, *J. Chem. Soc., Dalton Trans.*, 1975, 1412.

20 F. G. N. Cloke and M. L. H. Green, *J. Chem. Soc., Dalton Trans.*, 1981, 1938.

21 H. R. Van Der Wal, F. Overzet, H. O. Van Oven, J. L. De Boer, H. J. De Liefde Meijer, and F. Jellinek, *J. Organomet. Chem.*, 1975, **92**, 329.

22 R. Jungst, D. Sekutowski, J. Davies, M. Luty, and G. Stucky, *Inorg. Chem.*, 1977, **16**, 1645.

23 R. S. P. Coutts, P. C. Wailes, and R. C. Martin, *J. Organomet. Chem.*, 1973, **47**, 375.

24 J. D. Zeinstra and J. J. de Boer, *J. Organomet. Chem.*, 1973, **54**, 201.

25 M. Elian, M. M. L. Chen, D. M. P. Mingos, and R. Hoffmann, *Inorg. Chem.*, 1977, **15**, 1148.

26 T. C. MacKenzie, R. D. Sanner, and J. E. Bercaw, *J. Organomet. Chem.*, 1975, **102**, 457.

27 M. L. H. Green and W. Silverthorn, *J. Chem. Soc., Dalton Trans.*, 1973, 301.

28 O. N. Kirchner, P. D. Grebenik, and J. C. Green, unpublished work.

29 D. L. Allen, V. C. Gibson, M. L. H. Green, J. F. Skinner, J. Bashkin, and P. D. Grebenik, *J. Chem. Soc., Chem. Commun.*, 1983, 895.

30 V. C. Gibson and M. L. H. Green, unpublished work.

31 K. Prout, T. S. Cameron, R. A. Forder, S. R. Critchley, B. Denton, and G. V. Rees, *Acta Crystallogr., Sect. B*, 1974, **30**, 2290.

32 A. L. Carruthers, T. T. Bowman, P. L. Gans, and A. T. McPhail, *J. Chem. Soc., Chem. Commun.*, 1973, 415.

33 Z. Dawoodi, M. L. H. Green, V. S. B. Mtetwa, and K. Prout, *J. Chem. Soc., Chem. Commun.*, 1982, 802.

34 Z. Dawoodi, M. L. H. Green, V. S. B. Mtetwa, and K. Prout, *J. Chem. Soc., Chem. Commun.*, 1982, 1410.

35 T. J. Marks, W. J. Kennelly, J. R. Kolb, and L. A. Shimp, *Inorg. Chem.*, 1972, **11**, 2540.

36 T. J. Marks and J. R. Kolb, *Chem. Rev.*, 1977, **77**, 272.

37 J. C. Bommer and K. W. Morse, *J. Chem. Soc., Chem. Commun.*, 1977, 137.

38 C. Kutal, P. A. Grutsch, J. L. Atwood, and R. D. Rogers, *Inorg. Chem.*, 1978, **17**, 3558.

39 F. Takusagawa, A. Fumagalli, T. Koetzle, S. G. Shore, T. Schmitkons, A. V. Frabei, K. W. Morse, C. Y. Wei, and R. Bau, *J. Am. Chem. Soc.*, 1981, **103**, 5165.

40 H. Sinn and W. Kaminsky, *Adv. Organomet. Chem.*, 1980, **18**, 99.

41 M. Bottrill, P. D. Gavens, J. W. Kelland, and J. McMeeking, in 'Comprehensive Organometallic Chemistry,' eds. G. Wilkinson, F. G. A. Stone, and E. W. Abel, Pergamon Press, Oxford, 1982, vol. 3, p. 433.

42 C. J. Groeneboom, H. J. De Liefde Meijer, and F. Jellinek, *J. Organomet. Chem.*, 1975, **97**, 73.

43 D. W. Clack and K. D. Warren, *Inorg. Chim. Acta*, 1978, **30**, 251.

44 M. F. Guest, I. H. Hillier, B. R. Higginson, and D. R. Lloyd, *Mol. Phys.*, 1975, **29**, 113.

45 J. C. Green, *Struct. Bonding (Berlin)*, 1981, **43**, 37; C. Cauletti, J. C. Green, M. R. Kelly, P. Powell, J. van Tilborg, J. Robbins, and J. Smart, *J. Electron. Spectrosc.*, 1980, **19**, 327.

46 S. Evans, J. C. Green, and S. E. Jackson, *J. Chem. Soc., Faraday Trans. 2*, 1972, 249.

47 F. G. N. Cloke, A. N. Dix, J. C. Green, R. N. Perutz, and E. A. Seddon, *Organometallics*, 1983, **2**, 1150.

48 T. A. Albright, P. Hoffman, and R. Hoffmann, *J. Am. Chem. Soc.*, 1977, **99**, 7546.

49 M. F. Rettig, C. D. Stout, A. Klug, and P. Farnham, *J. Am. Chem. Soc.*, 1970, **92**, 5100.

50 D. L. Lichtenberger and R. F. Fenske, *J. Am. Chem. Soc.*, 1976, **98**, 50.

51 S. E. Jackson, D.Phil. Thesis, University of Oxford, 1973.

52 M. L. H. Green, L. C. Mitchard, and W. Silverthorn, *J. Chem. Soc., Dalton Trans.*, 1974, 1361.

53 E. W. Hughes, *J. Am. Chem. Soc.*, 1941, **63**, 1737.

54 J. R. Carruthers and D. J. Watkin, *Acta Crystallogr., Sect. A*, 1979, **35**, 698.

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