η-Cycloheptatrienyltitanium Chemistry: Halogeno-, Tertiary Phosphine, and Alkyl Derivatives: Crystal Structures of $[Ti(\eta-C_7H_7)(C_4H_8O)(\mu-Cl)]_2$ and $Ti(\eta-C_7H_7)(Me_2PCH_2CH_2PMe_2)Et$

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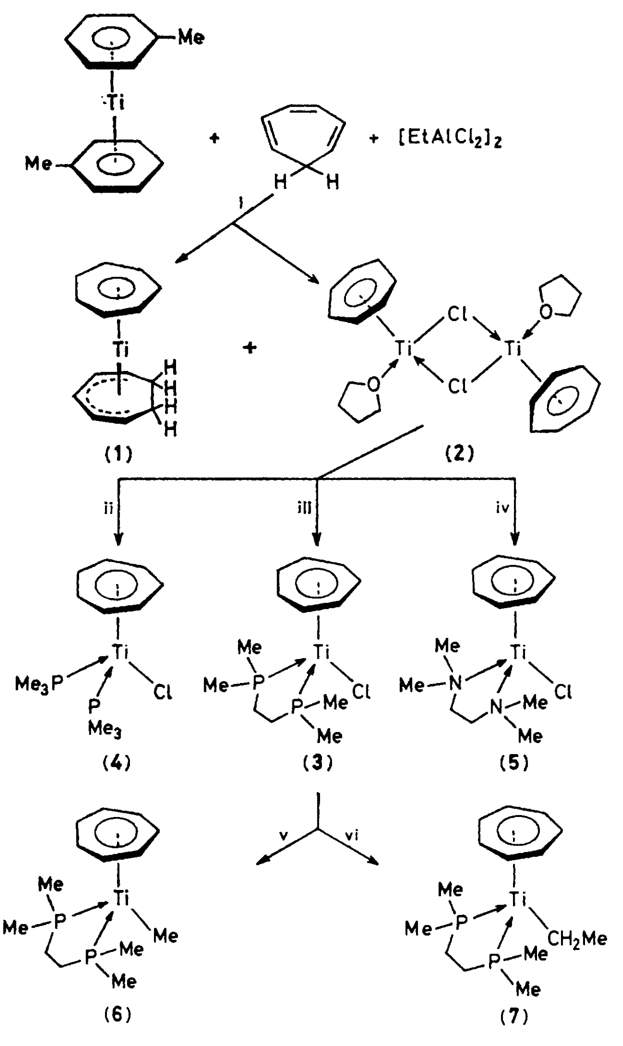
The new binuclear compound $[Ti(\eta-C_7H_7)(C_4H_8O)(\mu-Cl)]_2$ reacts with bis-1,2-(dimethylphosphino)ethane giving $[Ti(\eta-C_7H_7)(Me_2PCH_2CH_2PMe_2)Cl]$ from which the alkyl derivatives $[Ti(\eta-C_7H_7)(Me_2PCH_2CH_2PMe_2)R]$ (R = Me or Et) may be prepared; the crystal structures of $[Ti(\eta-C_7H_7)(C_4H_8O)(\mu-Cl)]_2$ and $[Ti(\eta-C_7H_7)(Me_2PCH_2CH_2PMe_2)Et]$ have been determined.

The compound $[Ti(\eta-C_7H_7)(\eta-C_7H_9)]$ (**1**) has been long known.[1,2] We have found that heating $[Ti(\eta-C_6H_5Me)_2]$[3,4] with cycloheptatriene in the presence of $(AlEt_2Cl)_2$ gives high yields of (**1**). In a typical experiment 12 g of $[Ti(\eta-C_6H_5Me)_2]$ were converted into 10 g of $[Ti(\eta-C_7H_7)(\eta-C_7H_9)]$.

In contrast, the reaction of $[Ti(\eta-C_6H_5Me)_2]$ in tetrahydrofuran with 1 equivalent of $(AlEtCl_2)_2$ and excess of cycloheptatriene at room temperature deposited red crystals of the binuclear compound $[Ti(\eta-C_7H_7)(C_4H_8O)(\mu-Cl)]_2$ (**2**) in 20% yield. The crystal structure of (**2**) has been determined.

Crystal data: $C_{22}H_{30}Cl_2O_2Ti_2$ $M = 493.19$, monoclinic, space group $P2_1/n$, $a = 6.630(3)$, $b = 17.729(3)$, $c = 9.370(1)$ Å, $\beta = 98.82(3)°$, $U = 1088$ Å^3, $Z = 2$, $D_c = 1.51$ g cm^{-1}. Data were measured ($2\theta_{max} = 60°$) on an Enraf–Nonius



Scheme 1. *Reagents and conditions* (all reactions at room temperature): i, 15 days; ii, excess of PMe_3 in toluene for 2 h (>80% yield); iii, dmpe in toluene for 2 h (>80%); iv, $Me_2NCH_2CH_2NMe_2$ in toluene for 2 h (>80%); v, MeMgCl in tetrahydrofuran (thf) for 12 h (>70%); vi, EtMgCl in thf for 12 h (>70%).

CAD4 diffractometer using Mo-K_α radiation and ω-2θ scans. 2603 independent reflections with $I > 3\sigma(I)$ were used in the refinement [μ(Mo-K_α) = 9.89 cm^{-1}: an absorption correction was not applied]. The structure was solved by a combination of direct methods and Fourier difference maps, and was refined by least squares using a large-block approximation to the normal matrix. All atoms were refined anisotropically except for hydrogens, which were refined using two common temperature factors, one for the C_7H_7 ligand and one for the thf ligand. 'Soft' constraints were applied to maintain C–H bond lengths equal to their mean. The current *R*-value is 0.028 (R_w = 0.038).† The molecule has a crystallographic centre of symmetry. The hydrogen atoms of the η-C_7H_7 group have a mean displacement of 0.18(5) Å out of the C_7-plane towards the metal atom.

Treatment of $[Ti(\eta\text{-}C_7H_7)(C_4H_8O)(\mu\text{-}Cl)]_2$ with bis-1,2-(dimethylphosphino)ethane (dmpe) gives the compound $[Ti(\eta\text{-}C_7H_7)(Me_2PCH_2CH_2PMe_2)Cl]$ (**3**) as air-sensitive golden crystals.‡ Similarly, (**2**) reacts with PMe_3 and $Me_2NCH_2CH_2NMe_2$ giving the compounds $Ti(\eta\text{-}C_7H_7)L_2Cl$, where L_2 = $(PMe_3)_2$ (**4**) and $(Me_2NCH_2)_2$ (**5**).‡ The compound (**2**) reacts with methylmagnesium bromide giving dark green crystals of the highly sensitive methyl compound $[Ti(\eta\text{-}C_7H_7)(Me_2PCH_2CH_2PMe_2)Me]$ (**6**).‡

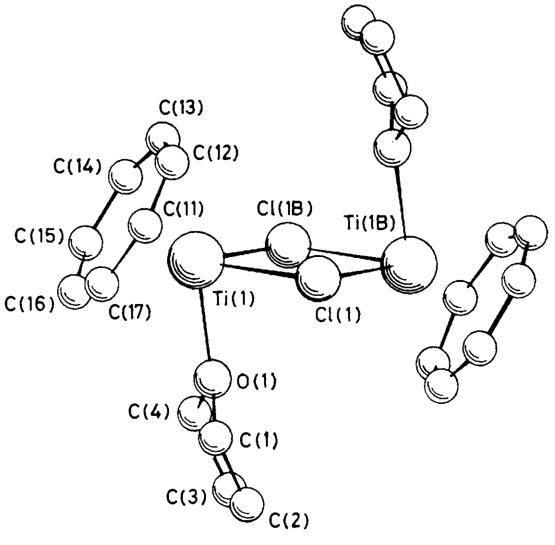


Figure 1. Molecular structure of (**2**). Hydrogens are omitted for clarity. Atoms with serial B are related by the symmetry operator $1-x, -y, -z$. Key parameters are Ti(1)–Ti(1B) 3.883(1), Ti(1)–Cl(1) 2.541(1), Ti(1)–Cl(1B) 2.544(1), Ti(1)–O(1) 2.187(1), Ti(1)–ring centroid 1.545, Ti(1)–C(average) 2.238(5) Å; O(1)–Ti(1)–Cl(1) 82.19(4), O(1)–Ti(1)–Cl(1B) 80.62(4), Cl(1)–Ti(1)–Cl(1B) 80.42(2), Ti(1)–Cl(1)–Ti(1B) 99.58(2)°.

The ethyl compound $[Ti(\eta\text{-}C_7H_7)(Me_2PCH_2CH_2PMe_2)Et]$ (**7**) is similarly prepared from (**2**) and ethylmagnesium chloride and the crystal structure of (**7**) has been determined in order to find whether there was a direct bonding interaction between the titanium atom and the β-C–H system of the ethyl group similar to that found for $Ti(dmpe)EtCl_3$.[5]

Crystal data: $C_{15}H_{28}P_2Ti$, M = 318.24, monoclinic, space group $P2_1/c$, a = 8.138(1), b = 25.657(4), c = 8.791(5) Å, β = 109.65(3), U = 1728.5 Å^3, Z = 4, D_c = 1.223 g cm^{-3}. Data were measured ($2\theta_{max}$ = 60°) on an Enraf–Nonius CAD4 diffractometer using Mo-K_α radiation and ω-2θ scans. 2108 independent reflections with $I > 3\sigma(I)$ were used in the refinement (an absorption correction was applied). The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares. All atoms were refined anisotropically except for hydrogens, which were refined isotropically. The hydrogens were located from a difference map. The current R value is 0.039 (R_w = 0.049).†

The structure of (**7**) shows that there is no interaction between any hydrogen of the ethyl group and the titanium centre. The absence of a bridging C–H–Ti bond in (**7**) may be understood in terms of the location of the LUMO which would act as the potential acceptor metal orbital. This would be the a_1 orbital of essentially d_{z^2} character and thus not well orientated for bonding to an alkyl hydrogen. This is the same reason why $Ti(\eta\text{-}C_6H_6)_2$, a 16-electron compound, does not readily form adducts with, for example, trimethylphosphine.

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

‡ ^1H N.m.r. spectra (C_6D_6): (**3**), δ 5.64 (7H, s, C_7H_7), 0.9 (12H, s, 4 × Me), and 0.82 (4H, s, 2 × CH_2); (**4**), δ 5.64 (7H, s, C_7H_7) and 0.87 (18H, d, J_{PH} 4 Hz, 6 × Me); (**5**), δ 5.84 (7H, s, C_7H_7), 2.1 (12H, s, 4 × Me), and 1.6 (4H, m, 2 × CH_2); (**6**), δ 5.52 (7H, t, J_{PH} 3.1 Hz, C_7H_7), 0.91 (12H, t, J_{PH} 2.6 Hz, 4 × Me), 0.63 (4H, 5-line m, 2 × CH_2), and −0.45 (3H, t, J_{PH} 11.3 Hz, TiMe).

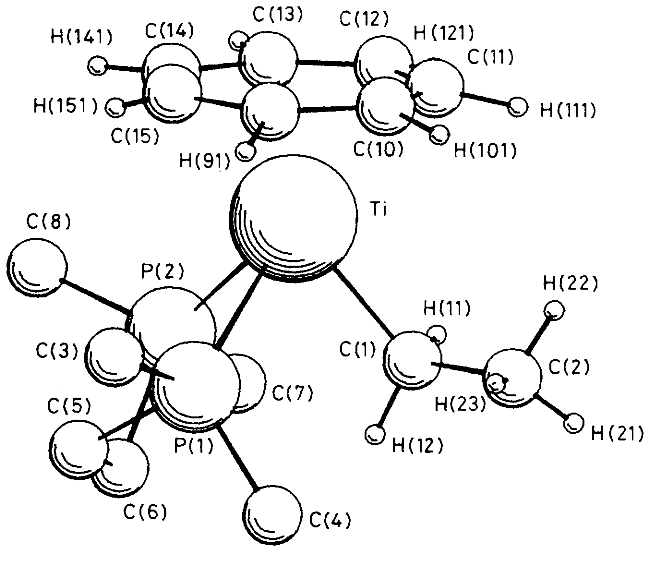

Figure 2. Molecular structure of (**7**). Hydrogens of the dmpe ligand are omitted for clarity. Key parameters are Ti–C(1) 2.211(5), Ti–C(ring)(average) 2.243(5), Ti–C(2) 3.170(6), Ti–P(1) 2.673(1), Ti–P(2) 2.636(1), Ti–H(22) 3.255(6) Å. The angle Ti–C(1)–C(2) is 115.1(4)° and this can be contrasted with the similar angle in $TiCl_3Et$(dmpe) of 85.9(6)°.[5]

The π-C_7H_7 radical has a degenerate set of M.O.s of δ-symmetry with respect to the ring–metal axis (defined as the z-axis) which are occupied by one electron. These δ-orbitals are of suitable symmetry to overlap with the d_{xy} and $d_{x^2-y^2}$ orbitals of the titanium. In these compounds (**1**)—(**7**) the titanium centres have three electrons essentially located in these d-orbitals and their interaction with the ring δ-orbitals will give rise to a pair of occupied bonding e_2 orbitals. We may consider two extreme cases depending on the relative energies of the ligand and metal d-orbitals when the occupied e_2 orbitals are essentially either metal or η-C_7-ring in character. If the e_2 electrons are mainly of metal character the titanium will be formally d^4, *i.e.* zerovalent. If the e_2 electrons are mainly of ring character then the metal is essentially d^0, *i.e.* tetravalent.

The simplicity of the synthesis and thermal stability of the compounds (**2**)—(**7**) strongly suggest that there can be an extensive chemistry of the sixteen-electron Ti(η-C_7H_7)L_2 moiety. Indeed the Ti(η-C_7H_7)L_2 system may be compared to the well known eighteen-electron Fe(η-C_5H_5)L_2 group for which an interesting and very substantial chemistry has been discovered. By implication many formally low-valent half-sandwich compounds containing the Ti(η-C_7H_7) system can be expected.

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