Titanium Tetrachloride Binding and making Arenes from Acetylenes: the Synthesis and *X*-Ray Crystal Structure of a Titanium(IV)–Hexamethylbenzene Complex

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Concentrated solutions of $TiCl_4$ in CH_2Cl_2, *o*-$C_6H_4Cl_2$, and n-hexane reacted with hexamethylbenzene producing $[(\eta^6\text{-}C_6Me_6)TiCl_3]^+[Ti_2Cl_9]^-$, which can equally well be obtained from the same $TiCl_4$ solutions and but-2-yne.

Formation of charge-transfer complexes from $TiCl_4$ and arenes is claimed to be responsible for the coloured solution formed when $TiCl_4$ is dissolved in aromatic hydrocarbons.[1] The supposed instability/lability of the system did not encourage efforts to isolate species from such solutions. Arene complexes of titanium are rare, and only two classes are known; titanium(II) derivatives, $[(\text{arene})Ti(\mu_2\text{-}AlCl_4)_2]$,[2] and titanium(0) complexes in the form of sandwich complexes $[Ti(\text{arene})_2]$[3] or a phosphine derivative $[[(\eta^6\text{-}C_{10}H_8)Ti\{Bu^t\text{-}Si(CH_2PMe_2)_3\}]$.[4] Complexes derived from the interaction of d^0 transition metals and arenes are unknown, the closest examples being the π-arene complexes of the f-block elements[5] and of tin(II).[6]

We report the synthesis of an η^6-arene titanium(IV) complex (**1**) which is formed from the reaction of $TiCl_4$ with either hexamethylbenzene or but-2-yne (Scheme 1).

Complex (**1**)† was isolated from the reaction between $TiCl_4$ and C_6Me_6 in a molar ratio ranging from 6 to 10, using a 2 M solution of $TiCl_4$ in CH_2Cl_2, *o*-$C_6H_4Cl_2$, or n-hexane; the yield was >70% based on C_6Me_6. $TiCl_4$ was added to a solution of C_6Me_6, which suddenly became deep red and gave, in a few minutes, a yellow crystalline solid (**1**). The reaction, followed by ^1H NMR spectroscopy in CD_2Cl_2 at room temperature,

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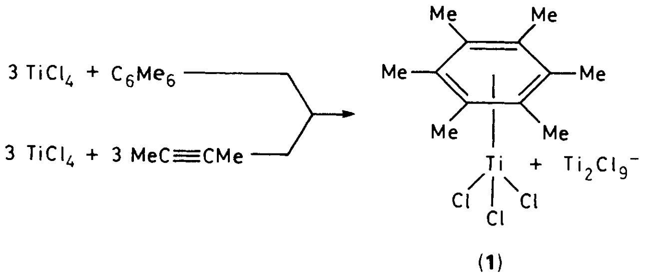
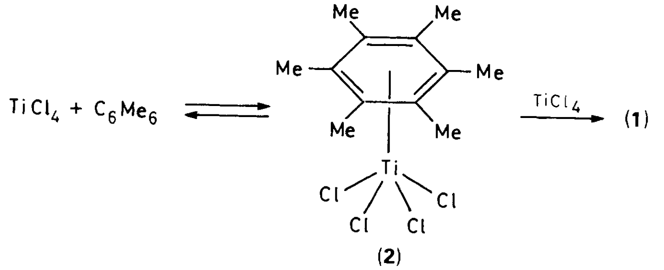
† Correct microanalytical results have been obtained.



Scheme 1



Scheme 2

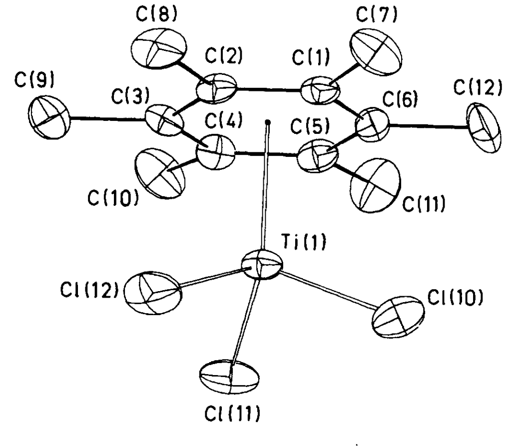


Figure 1. An ORTEP drawing of the $[(\eta^6\text{-}C_6Me_6)TiCl_3]^+$ cation. Bond distances (Å): Ti(1)–C^n, 2.059(12); Ti(1)–Cl(10), 2.182(4); Ti(1)–Cl(11), 2.168(4); Ti(1)–Cl(12), 2.186(5). Bond angles (°): Cl(11)–Ti(1)–Cl(12), 102.6(2); Cl(10)–Ti(1)–Cl(12), 102.2(2); Cl(10)–Ti(1)–Cl(11), 103.5(2); C^n–Ti(1)–Cl(12), 115.8(4); C^n–Ti(1)–Cl(11), 115.9(4); C^n–Ti(1)–Cl(10), 115.0(4). C^n refers to the centroid of C_6Me_6.

showed a broadening of the singlet at δ 2.18 and the appearance of two singlets at δ 2.82 and 2.75 of much lower intensity, when the $TiCl_4/C_6Me_6$ ratio was >1.5. The addition of a large excess of $TiCl_4$ ($TiCl_4/C_6Me_6$ >10) caused the quantitative precipitation of (**1**), while the resulting solution remained almost colourless. Complex (**1**) was also formed on reaction of 2 M solutions of $TiCl_4$ in the same solvents with but-2-yne, with a but-2-yne/$TiCl_4$ molar ratio slightly lower than 3. Complex (**1**) reacts with oxygenated solvents or water releasing hexamethylbenzene.

The easy formation of (**1**) from highly concentrated solutions of $TiCl_4$ with a high $TiCl_4/C_6Me_6$ molar ratio is, presumably, the result of the action of $TiCl_4$ on an initially formed $TiCl_4{\cdot}C_6Me_6$ adduct. The two singlets at δ 2.82 and 2.75, appearing when the reaction is followed by ^1H NMR spectroscopy, seem to support the genesis of (**1**) as in Scheme 2.

The ionization of the relatively more basic chloride in (**2**) is promoted by the excess of $TiCl_4$ forming the insoluble ionic complex (**1**). The peak at δ 2.82 is due to the Me groups in (**1**), while the other peak at δ 2.75 is probably due to complex (**2**). The formation of Ti_2Cl_9 (ref. 7) rather than $TiCl_6{}^{2-}$ (ref. 1) and $Ti_2Cl_{10}{}^{2-}$ (ref. 7) may be correlated with the rather low basicity of the Cl^- source available, as is the case for complex (**2**). We cannot exclude that in highly concentrated solutions of $TiCl_4$ an equilibrium exists between $(TiCl_4)_n$ species of different molecular complexity, one of them capable of binding C_6Me_6. It should be emphasized that the cation $[(C_6Me_6)TiCl_3]^+$ may be considered as a source for the highly acidic $[TiCl_3]^+$ form of $TiCl_4$. The trimerization of but-2-yne occurs under conditions such that we cannot prove that the reaction can be adjusted to become catalytic. Rare examples of trimerization of acetylenes by Lewis acids[8] are known, this reaction being largely confined to low-valent transition metal complexes which operate by a very different pathway.[9] In the case of the reaction in Scheme 1 we cannot invoke any metallacycle precursor ending in the trimer. The significant stability of (**1**) may be the driving force for the trimerization of but-2-yne.

The structure of $[(\eta^6\text{-}C_6Me_6)TiCl_3]^+$ is shown in Figure 1;‡ the anion $[Ti_2Cl_9]^-$ has the known structure.[7] The overall geometry of the cation can be described as a three-legged piano stool, with the Cl–Ti–Cl angles being essentially equal and averaging 102.8(3)°. The Ti–C^n (C^n = centroid of C_6Me_6) distance is significantly longer [2.059(12) Å] than in the titanium(0) arene $[Ti(\eta^6\text{-}C_6H_6)_2]$ (**3**) [1.736 Å][3d] and very close to that in $[Ti(\eta^6\text{-}C_6Me_6)(\mu_2\text{-}AlCl_4)_2]$ (**4**) (2.06 Å). Ti–C distances, ranging from 2.460(13) to 2.524(12) Å, are close to those in (**4**) ($Ti\text{–}C_{av}$, 2.50 Å).[2c]

We have found that the binding of arenes by high-valent early transition metal halides is quite a general reaction which is being actively explored in our laboratory.

We thank the Fonds National Suisse de la Recherche Scientifique (Grant. No. 2000–005536) for financial support.

Received, 4th August 1989; Com. 9/03391B

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‡ *Crystal data*: $C_{12}H_{18}Cl_3Ti{\cdot}Cl_9Ti_2$, M = 731.4, orthorhombic, space group $Pca2_1$ (from systematic absences and structure determination), a = 17.263(2), b = 8.712(1), c = 17.256(2) Å, U = 2595.2(5) Å^3, Z = 4, D_c = 1.872 g cm^{-3}, Mo-K_α radiation (λ = 0.71069 Å), μ(Mo-K_α) = 21.44 cm^{-1}. Crystal dimensions 0.40 × 0.48 × 0.51 mm. The structure was solved by the heavy-atom method (Patterson and Fourier synthesis) and refined by full-matrix least-squares. For 2252 unique observed structure amplitudes $[I > 2\sigma(I)]$ collected at room temperature on a Siemens AED diffractometer in the range $6 < 2\theta < 54°$, the R value is 0.059 (unit weights). The hydrogen atoms were put in calculated positions and introduced as fixed contributors in the final stage of refinement. All calculations were carried out using SHELX76. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

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