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Reluctant formation of a titanium(IV) arene complex

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A new high-valent hexaethylbenzene complex of titanium is formed in the reaction of hexaethylbenzene with $TiCl_4$, when $AlCl_3$ is used.

High-valent transition metal arene complexes are still scarce. In spite of recent discoveries in the field, it is not well understood, how they form, especially the ionic complex $[\eta^6\text{-}C_6Me_6TiCl_3]^+[Ti_2Cl_9]^-$, which can be obtained from $TiCl_4$ and hexamethylbenzene, has been a mystery (equation 1).[1–3]

$$C_6Me_6 + 3TiCl_4 \rightleftharpoons [\eta^6\text{-}C_6Me_6TiCl_3]^+[Ti_2Cl_9]^- \qquad (1)$$

In the past, it has been shown that less substituted arenes, even pentamethylbenzene, which is lacking only one methyl group, as compared with hexamethylbenzene, do not form stable arene complexes in the same way as hexamethylbenzene does.[4]

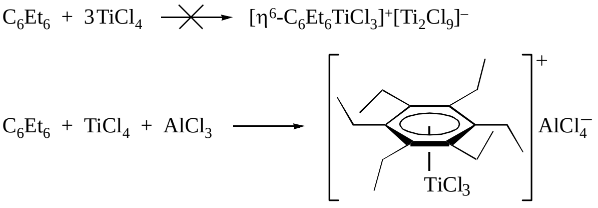
We have previously shown that, assuming an equilibrium exists between $TiCl_4$ and the free arene on the one side and the arene complex on the other side, the number of alkyl substituents plays an important role in the stability of the arene complex. Six methyl groups are necessary to form a stable complex in the reaction with $TiCl_4$. This phenomenon is unprecedented in low-valent transition metal arene chemistry. According to *ab initio* calculations, every methyl group contributes 5–6 kcal mol^{-1} to the binding energy of the arene to the $TiCl_3^+$ fragment.[5] In the case of pentamethylbenzene this is enough to shift the equilibrium completely to the reactant side. In fact, indications of an arene complex could be only obtained by using neat $TiCl_4$ as the solvent.

We reacted hexaethylbenzene with $TiCl_4$ in dichloromethane and did not observe the formation of an arene complex as would be indicated by substantial shifts in the ^1H and ^{13}C NMR spectra. Instead, we observed the signal of the free arene. The brown colour of the solution indicated the presence of charge-transfer complexes. Even in neat $TiCl_4$ as a solvent,[4] we could not observe the formation of a stable arene complex (Scheme 1).

This result was very puzzling, especially in light of the low-valent transition metal arene chemistry, where hexamethylbenzene and hexaethylbenzene can be used interchangeably.[6]

Following the procedure of Calderazzo *et al.*,[7] the reaction was then repeated in benzene or toluene as a solvent and $AlCl_3$ was added to remove the chloride ion from $TiCl_4$, in order to form the cationic titanium species, and an arene complex could be obtained (Scheme 1).[†]

The obtained complex was clearly identified by NMR spectroscopy, where it exhibits shifts in the ^1H and ^{13}C NMR spectra to more positive values compared to the free arene, which clearly indicate the complexation of the arene to the $TiCl_3^+$ centre.



Scheme 1

Ab initio molecular orbital calculations revealed that hexaethylbenzene should have essentially the same binding energy to the $TiCl_3^+$ fragment as hexamethylbenzene (83.98 *vs.* 84.94 kcal mol^{-1}).[‡,8,9] The calculated geometry around the titanium atom is virtually identical to that of the hexamethylbenzene complex (Figure 1). There are no close Ti–H and Ti–C (other than ring carbons) distances (from possible agostic interactions), and the ethyl groups are rotated so that they are pointing up and down in an alternating fashion. The Cl atoms are located beneath the ring C atoms that have an ethyl group pointing up.

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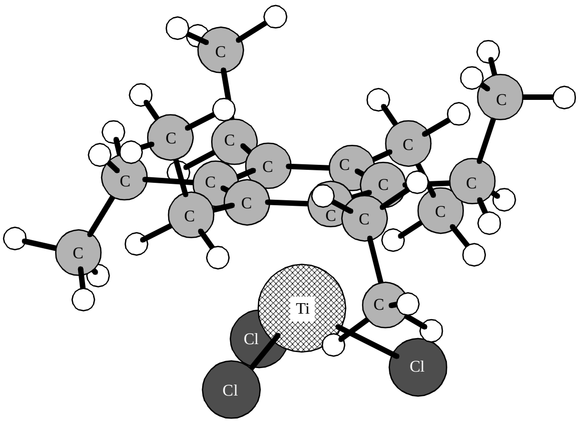

Figure 1 Calculated structure of the cation hexaethylbenzene trichlorotitanium(IV). All Ti–C distances are between 2.56 and 2.57 Å and all Ti–Cl distances are 2.18 Å.

[†] *General experimental details*: All manipulations were performed in a dry argon atmosphere and using standard Schlenk glassware. Solvents were dried according to standard procedures. All chemicals were obtained from Acros. To a solution of $AlCl_3$ (0.65 g, 4.87 mmol) in benzene (10.0 ml), hexaethylbenzene (1.00 g, 4.06 mmol) was added followed by the addition of 0.67 ml (6.06 mmol) of $TiCl_4$. The colour of the solution went from pale-yellow to dark red-brown after the addition of $TiCl_4$.

The solution was left stirring for 3 h and the product was filtered off and washed with benzene (10 ml). This produced 1.97 g of product (90.8% yield based on hexaethylbenzene). After recrystallization from dichloromethane, 1.31 g of purified product was obtained (60.4% based on hexaethylbenzene).

^1H NMR (300 MHz, CD_2Cl_2) δ: 1.47 (t, 12H, $CH_2\mathit{Me}$, J 7 Hz), 3.11 (q, 18H, $C\mathit{H_2}Me$, J 7 Hz). ^{13}C NMR (75.4 MHz, CD_2Cl_2) δ: 14.91 ($CH_2\mathit{Me}$), 27.00 ($\mathit{C}H_2Me$), 155.74 (ring carbons). Found (%): C, 36.93; H, 5.21. Calc. for $C_{18}H_{30}AlCl_7Ti$ (%): C, 37.97; H, 5.31.

[‡] All calculations were done using the program GAMESS.[8] The basis set used was a combination of an effective core potential basis set for titanium by Hay and Wadt and of a double-zeta basis set by Dunning and Hay (see ref. 10). The basis was augmented with d functions (Cl: $\zeta = 0.619$ and C: $\zeta = 0.72$). No symmetry was implied in the calculations. The structures were optimised at the Hartree-Fock level and then, single point frozen core MP2 energy calculations were performed for each structure. The formation energy was obtained from the difference of the energies of optimised hexaethylbenzene and $TiCl_3^+$ and the energy of the titanium complex. The binding energy is the negative of the formation energy.

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