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The effect of solubility on the stability of titanium(IV) arene complexes derived from hexasubstituted arenes and $TiCl_4$

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Abstract

The investigation of new titanium(IV) hexaalkylarene complexes gave new insight into the stability of high-valent metal arene complexes. In contrast to low-valent transition metal arene complexes these complexes are in equilibrium with the free arenes. The stability of the complexes was shown to depend strongly on both the donor ability of the arene *and* on their solubility. This is unprecedented in transition metal arene chemistry. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

While the chemistry of low-valent transition metal arene complexes is well established, high-valent transition metal arene complexes, especially those with the transition metal in its highest oxidation state and a d^0 electron configuration, remain elusive.

Early studies were mostly focussed on solutions of early transition metal halides with arenes [1,2]. Only a few examples of d^0 transition metal arene complexes exist, due, in part, to the inherent low stability of these complexes caused by the lack of d-electrons and the resulting inability for back-donation in the metal–arene bonding [2–7].

The system hexamethylbenzene–$TiCl_4$ stands out as a special case. In the early 1960s, Krauss and coworkers obtained a compound composed of three equivalents of $TiCl_4$ and one equivalent of hexamethylbenzene [2,3], the structure of which was reported as $[\eta^6\text{-}(C_6Me_6)TiCl_3]^+[Ti_2Cl_9]^-$ (**1**) [4,5]. In the description of the formation of **1**, there is a proposed equilibrium between hexamethylbenzene and $TiCl_4$, and **1**.

Overall, two $TiCl_4$ molecules abstract a chloride ion from another $TiCl_4$ to form the ionic arene complex [4,5]. The formation of **1** was exceptional, since no other arene formed a complex like **1**. The explanation for this behavior lies in the donor abilities of the arene. We have shown that each methyl group contributes ca. 5–6 kcal mol^{-1} to the overall binding energy of the $TiCl_3^+$ fragment to the arene if all substituents are included in the calculation [6]. This finding explained the observations of Kochi and coworkers, who had indications for an ionic arene complex formed from pentamethylbenzene in neat $TiCl_4$, but could not characterize the compound further due to its low stability [7]. Thus removal of one methyl group from hexamethylbenzene can shift the equilibrium in the formation of a complex such as **1** completely to the side of the reactants away from the arene complex.

Calderazzo and coworkers overcame the lack of binding energy for less methylated benzenes by using stronger chloride abstracting reagents such as $AlCl_3$ and $GaCl_3$ [8].

In our own studies, we found that hexa*ethyl*benzene, which has been used interchangeably with hexa*methyl*benzene in low-valent transition metal arene chemistry, does *not* form an arene complex such as **1**, even with neat $TiCl_4$ as the solvent. The lack of binding energy

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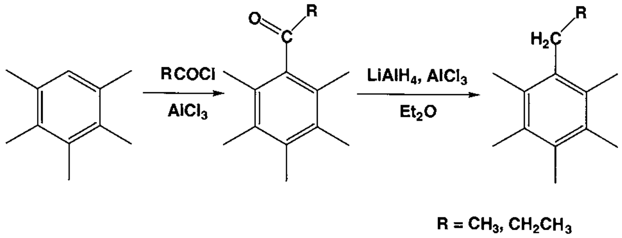
does not explain the inability of hexa*ethyl*benzene to form an arene complex similar to **1**, since it is virtually the same as for hexa*methyl*benzene. However, with $AlCl_3$ as a chloride-abstracting reagent, an arene complex can be formed [9]. In our opinion, this significant difference between the two hexaalkylbenzenes in the reaction with $TiCl_4$ is due to the much higher solubility of the hexa*ethyl*- versus hexa*methyl*benzene compound. Sterically, hexa*ethyl*benzene, although more demanding, is flexible enough to accommodate am ML_3 fragment comfortably [10].

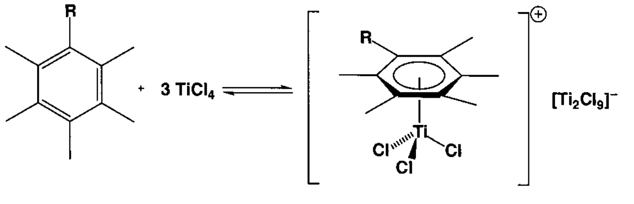
2. Results and discussion

In order to gage solubility effects on the stability of the ionic arene complexes of type **1** (inspired by the introduction of the ethyltetramethylcyclopentadienyl ligand in Cp* chemistry [11]) we synthesized alkylpentamethylbenzenes, which would afford more soluble arene complexes. Ethylpentamethylbenzene and pentamethylpropylbenzene were chosen and synthesized by Friedel–Crafts acylation and subsequent reduction of the ketones (Scheme 1) [12].

Ethylpentamethylbenzene and pentamethylpropylbenzene react with a ca. 10 fold excess of $TiCl_4$ to form the ionic arene complexes **2a** and **2b** (Fig. 1). The equilibrium nature of these reactions is much more apparent in these cases than in the case of **1**. The result is that the yields of solid complex in both cases were slightly below 50%, although high concentrations of all reactants were used. Cooling of the remaining solutions yields more of the solid complex, which is consistent with an equilibrium that has negative enthalpy *and* negative entropy terms and therefore favors the complexes at low temperature. When the yellow solids obtained in these reactions are dissolved in CD_2Cl_2 for NMR analysis, only the signal of the free arene can be initially observed. The solution itself exhibits a brown color, which is consistent with the presence of neutral charge-transfer complexes.



Scheme 1.



2a: R=CH_2CH_3
2b: R=$CH_2CH_2CH_3$

Fig. 1. Formation of **2a** and **2b**.

After adding an approximately fivefold excess of $TiCl_4$ to the NMR solution, the signal for the complexed arene appears together with the signal for the free arene in ^1H- and ^{13}C-NMR. A portion of the arene complex precipitates out of the solution after the addition of $TiCl_4$, since the dissolution equilibrium of the arene complex is also involved (Eq. (1)). It was clear that in no case could we see completely the conversion of all arene to complexed arene (with or without precipitation).

$$\begin{tikzcd}
[\eta^6\text{-}(C_6EtMe_5)TiCl_3]^+[Ti_2Cl_9]^-_{solid} \arrow[r, shift left] & [\eta^6\text{-}(C_6EtMe_5)TiCl_3]^+[Ti_2Cl_9]^-_{solution} \arrow[l, shift left] \arrow[d, shift left] \\
& C_6EtMe_{5\,(solution)} + 3\ TiCl_{4\,(solution)} \arrow[u, shift left]
\end{tikzcd} \tag{1}$$

The ratio of free arene and complexed arene in solution is approximately 1:1, in spite of the excess of $TiCl_4$. The higher solubility of **2a** enabled us to obtain a ^{13}C-NMR spectrum, which was impossible in the case of the highly insoluble $[\eta^6\text{-}(C_6Me_6)TiCl_3]^+[Ti_2Cl_9]^-$ (**1**). The signals of **2a** and **2b** exhibit significant shifts to higher ppm values compared to the free arenes, which results from the lack of backbonding in these complexes (Table 1).

Coordination of the $TiCl_3^+$ fragment removes electron density from the ring carbon atoms, and consequently from the attached alkyl groups. For comparison, we also synthesized the complex $[\eta^6\text{-}(C_6Me_5Et)TiCl_3]^+[AlCl_4]^-$ (**3a**), a compound that is not in equilibrium with the free arene. These results correspond nicely to the shifts observed for the known complex $[\eta^6\text{-}(C_6Me_6)TiCl_3]^+[AlCl_4]^-$, which indicates that the cation $[\eta^6\text{-(arene)}TiCl_3]^+$ is present in solution. Furthermore, the signals for the cation complexes **2a** and **3a** are almost identical, with the main difference being that free arene is present in the solution of **2a**, i.e. an equilibrium concentration of the arene. The shift to lower ppm values for the methyl carbon atom of the ethyl group is consistent with a similar observation for the complex $[\eta^6\text{-}(C_6Et_6)TiCl_3]^+[AlCl_4]^-$ [9]. The equilibrium between the arene and the arene complex is slow on the NMR timescale.

The structure of **2a** in the solid state was determined by X-ray diffraction and confirmed that **2a** has the same composition as **1** (arene·$3TiCl_4$) (Tables 2 and 3).

Table 1
NMR signals of the arene complexes **2a** and **2b** compared with the signals of the free arenes

	Group	Free arene (ppm)	Complex (ppm)	Δδ (ppm)
2a ^{1}H-NMR	CH_3(ethyl)	1.12 (t)	1.39 (t)	0.27
	CH_2(ethyl)	2.72 (q)	3.12 (q)	0.40
	Ring methyls	2.25, 2.22	2.79, 2.83	0.54, 0.61
3a ^{1}H-NMR	CH_3(ethyl)	1.12 (t)	1.39 (t)	0.27
	CH_2(ethyl)	2.72 (q)	3.12 (q)	0.40
	Ring methyls	2.25, 2.22	2.79, 2.85	0.54, 0.63
2b ^{1}H-NMR	CH_3(propyl)	0.96 (t)	1.20 (t)	0.24
	CH_3–CH_2–	1.42 (m)	1.74 (m)	0.32
	Ring methyls	2.15, 2.17	2.79, 2.82, 2.83	0.64, 0.65, 0.66
2a ^{13}C-NMR	CH_3(ethyl)	14.30	12.80	-1.50
	CH_2	23.73	28.92	5.48
	Ring carbons	131.28, 132.20, 132.34, 137.76	150.98, 151.03, 151.40, 153.41	19.70, 18.83, 19.06, 15.65
2b ^{13}C-NMR	CH_3(propyl) [a]	14.71	14.95	0.24
	$CH_2\mathit{C}H_2CH_3$	23.68	22.60	-1.08
	Ring methyls [b]	16.48, 16.91	21.61, 22.22, 22.35	5.13, 5.31, 5.44
	$\mathit{C}H_2CH_2CH_3$	33.12	37.56	4.44

[a] The signal for the free arene and the complexed arene seem to have the same shift, because of the distance to the ring.

[b] In the free arene, two of the methyl groups have the same resonance but split up in the complexed arene.

Two crystallographically independent formula units are found in the asymmetric unit.

All important distances and angles around the titanium atom of the cation of **2a** show no significant differences compared to the structure of $[\eta^6\text{-}(C_6Me_6)TiCl_3]^+[Ti_2Cl_9]^-$ (**1**) [4,5] (Figs. 2 and 3, Table 3). The two crystallographically independent cations of **2a** have a three-legged piano-stool geometry. All Ti–C distances to the ring carbon atoms are in the range of 2.489(3)–2.543(3) Å. The Ti–Cl distances and Cl–Ti–Cl angles are very similar within the two independent units and between the independent units. The distances and angles indicate a local (non-crystallographic) symmetry of almost C_{3v} for the $TiCl_3$ fragment. The main difference between the two crystallographically independent units is in the rotation of the arene ligand in the cation relative to the chlorine atoms. The structure of the anions is best described as two distorted face-sharing octahedra.

3. Experimental

3.1. General methods

All reactions involving the synthesis of the titanium arene complexes and their handling were performed using standard Schlenk techniques. Chemicals were obtained from Acros unless specified otherwise and used without further purification. Hexane and dichloromethane were distilled over calcium hydride and stored over molecular sieves. Toluene was dried and distilled over Na and stored over molecular sieves. NMR solvents were stored over molecular sieves.

3.2. Preparation of acetylpentamethylbenzene

1.69 g acetyl chloride (21.5 mmol) in a suspension of 3.06 g $AlCl_3$ (22.9 mmol) in 12 ml CH_2Cl_2 was treated with a solution of 2.00 g pentamethylbenzene (13.5 mmol) in 6 ml of CH_2Cl_2 at 0°C. Argon was then introduced into the reaction flask periodically to drive off the HCl. After 4 h stirring, 15 ml ice cold water was added slowly, followed by 16 ml concentrated HCl with stirring. The organic layer was separated and washed with 100 ml of 0.5% Na_2CO_3 solution to remove acid traces. The organic layer was then dried over anhydrous Na_2CO_3, and the CH_2Cl_2 was removed in vacuo and 2.33 g (12.2 mmol) of the product was isolated (90.7% yield).

^{1}H-NMR (300 MHz, $CDCl_3$) δ: 2.12, 2.18, 2.22 (s, 15H, C–CH_3), 2.45 (s, 3H, CO–CH_3). ^{13}C-NMR (75.4 MHz, $CDCl_3$) δ: 15.91, 16.64, 17.05 (ring methyl groups); 33.11 (CO–CH$_3$); 126.94, 133.04, 135.31, 140.85 (ring carbons); 210.07 (CO–CH_3). GC/MS: m/z 190 (M^+). M.p. 91.6°C.

3.3. Preparation of pentamethylpropionylbenzene

2.0 g of propionyl chloride (21.6 mmol) in a suspension of 3.06 g $AlCl_3$ (22.9 mmol) in 12 ml CH_2Cl_2 was treated with a solution of 2.00 g pentamethylbenzene (13.5 mmol) in 6 ml CH_2Cl_2 at 0°C. Argon was introduced into the reaction flask periodically to drive off the HCl. After 4 h stirring, 15 ml ice cold water was added slowly, followed by 16 ml concentrated HCl with stirring. The organic layer was separated and washed with 100 ml 0.5% Na_2CO_3 solution to remove acid traces. The organic layer was dried with anhydrous Na_2CO_3, and the CH_2Cl_2 was removed in vacuo and

2.53 g (12.4 mmol) of the product were obtained (92.1% yield). ^{1}H-NMR (300 MHz, CDCl$_3$) δ: 1.21 (t, $J = 8$ Hz, CO–CH$_2$CH_3); 2.10, 2.19, 2.24 (s, 15H, ring methyls), 2.70 (q, $J = 8$ Hz, 2H, CO–CH_2). ^{13}C-NMR (75.4 MHz, CDCl$_3$) δ: 7.45 (CO–CH$_2$$CH_3$); 15.84, 16.56, 17.10 (ring methyl groups); 38.66 (–CO–CH$_2$), 127.19, 132.93, 135.19, 140.72 (ring carbons); 212.61 (CO–CH$_3$). GC/MS: m/z 204 (M$^+$). M.p. 92.8°C.

Table 2
Crystallographic information for **2a**

Crystal data	
Empirical formula	$C_{13}H_{20}Cl_{12}Ti_3$
Crystal habit, color	Irregular block, yellow
Crystal size (mm)	0.38 × 0.31 × 0.17
Crystal system	Orthorhombic
Space group	$Pca2_1$
Unit cell dimensions	
a (Å)	17.2163(3)
b (Å)	17.5664(5)
c (Å)	17.6534(5)
Volume (Å^3)	5338.9(2)
Z	8
Formula weight	745.39
Density (calculated) (Mg m^{-3})	1.855
Absorption coefficient (mm^{-1})	2.080
F(000)	2944
Data collection	
Diffractometer	Siemens SMART Platform CCD
Wavelength (Å)	0.71073
Temperature (K)	173(2)
θ range for data collection (°)	1.16–27.53
Index ranges	$0 \le h \le 22$, $0 \le k \le 22$, $-22 \le l \le 22$
Reflections collected	47517
Independent reflections	12179 ($R_{\text{int}} = 0.0363$)
Solution and refinement	
System used	SHELXTL-V5.0 [d]
Solution	Direct methods
Refinement method	Full-matrix least-squares on F^2
Weighting scheme	$w = [\sigma^2(F_o^2)+(AP)^2+(BP)]^{-1}$, where $P = (F_o^2+2F_c^2))/3$, $A = 0.0209$ and $B = 1.177$
Absorption correction	SADABS [d]
Maximum and minimum transmission	1.000 and 0.819
Absolute structure parameter	−0.02(2)
Data/restraints/parameters	12177/1/505
R indices ($I > 2\sigma(I) = 10317$)	$R_1 = 0.0314$ [a], $wR_2 = 0.0545$ [b]
R indices (all data)	$R_1 = 0.0460$ [a], $wR_2 = 0.0596$ [b]
Goodness-of-fit on F^2	1.042 [c]
Largest diff. peak and hole (e Å^{-3})	0.345 and −0.359

[a] $R_1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$.

[b] $wR_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

[c] S = goodness of fit = $\Sigma[w(F_o^2 - F_c^2)^2]/(n-p)^{1/2}$ where n is the number of reflections and p is the number of refined parameters.

[d] SHELXTL-PLUS V5.0, Siemens Industrial Automation, Inc., Madison, WI.

Table 3
Selected distances (Å) and angles (°) for **2a**

Ti(1)–C(1)	2.491(3)	Ti(2)–C(14)	2.507(3)
Ti(1)–C(2)	2.529(3)	Ti(2)–C(15)	2.517(3)
Ti(1)–C(3)	2.512(3)	Ti(2)–C(16)	2.543(3)
Ti(1)–C(4)	2.525(3)	Ti(2)–C(17)	2.526(3)
Ti(1)–C(5)	2.518(3)	Ti(2)–C(18)	2.489(3)
Ti(1)–C(6)	2.495(3)	Ti(2)–C(19)	2.532(3)
Ti(1)–Cl(1)	2.1803(10)	Ti(2)–Cl(4)	2.1857(11)
Ti(1)–Cl(2)	2.1853(11)	Ti(2)–Cl(5)	2.1831(11)
Ti(1)–Cl(3)	2.1910(11)	Ti(2)–Cl(6)	2.1901(11)
Cl(1)–Ti(1)–Cl(2)	102.87(4)	Cl(4)–Ti(2)–Cl(5)	102.50(4)
Cl(1)–Ti(1)–Cl(3)	102.07(4)	Cl(4)–Ti(2)–Cl(6)	102.69(5)
Cl(2)–Ti(1)–Cl(3)	103.50(4)	Cl(5)–Ti(2)–Cl(6)	103.23(5)

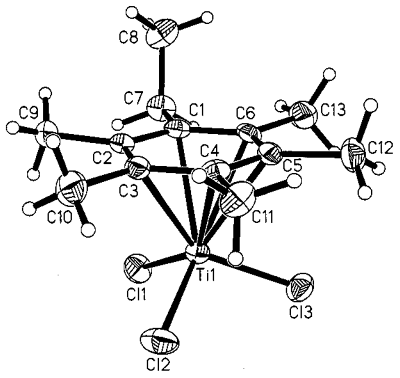


Fig. 2. Thermal ellipsoid plot of the first of the independent cations in **2a**.

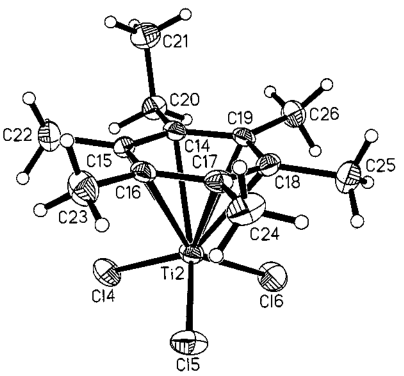


Fig. 3. Thermal ellipsoid plot of the second of the independent cations in **2a**.

3.4. Preparation of ethylpentamethylbenzene

An 8 ml ethyl ether solution of 0.93 g AlCl$_3$ (6.97 mmol) was added dropwise to a suspension of 0.53 g LiAlH$_4$ (13.97 mmol) in 14 ml of ether. 5 min later, a solution containing 1.06 g of acetylpentamethylbenzene (5.57 mmol) and 0.74 g AlCl$_3$ (5.55 mmol) in 14 ml ether was introduced at a rate such as to produce gentle reflux. After 2 h stirring at room temperature, 12 ml of ice cold water were added slowly and then 8 ml of 6 N sulfuric acid. After separating the organic layer, the aqueous layer was extracted three times with ether. The combined ether extracts were dried over anhydrous Na_2CO_3, and the ether was removed in vacuo. The yield was 0.86 g (4.88 mmol; 87.6%). Anal. Found: C, 88.38; H, 11.32. Calc. for $C_{13}H_{20}$: C, 88.56; H, 11.44%.

^{1}H-NMR (300 MHz, $CDCl_3$) δ: 1.11 (t, $J = 8$ Hz, $CH_2C\mathit{H}_3$); 2.25, 2.23 (s, 15H, ring methyls), 2.72 (q, $J = 8$ Hz, 2H, $C\mathit{H}_2$). ^{13}C-NMR (75.4 MHz, $CDCl_3$) δ: 14.03 ($CH_2\mathit{C}H_3$); 16.02, 16.66, 16.71 (ring methyl groups); 33.48 ($\mathit{C}H_2$), 131.28, 132.20, 132.34, 137.76 (ring carbons); GC/MS: *m*/*z* 176 (M^+). M.p. 66.0°C.

3.5. Preparation of pentamethylpropylbenzene

An 8 ml ethyl ether solution of 0.93 g $AlCl_3$ (6.97 mmol) was added dropwise to a suspension of 0.53 g $LiAlH_4$ (13.97 mmol) in 14 ml of ether. 5 min later, a solution containing 1.14 g pentamethylpropionylbenzene (5.58 mmol) and 0.74 g $AlCl_3$ (5.55 mmol) in 14 ml ether was introduced at a rate such as to produce gentle reflux.

After 2 h stirring at room temperature, 12 ml of ice cold water were added slowly and then 8 ml of 6 N sulfuric acid. After separating the organic layer, the aqueous layer was extracted three times with ether. The combined ether extracts were dried over anhydrous Na_2CO_3, and the ether was removed in vacuo to isolate the product. The yield was 0.91 g (4.78 mmol; 85.6%). Anal. Found: C, 88.26; H, 11.81. Calc. for $C_{14}H_{22}$: C, 88.35; H, 11.65%.

^{1}H-NMR (300 MHz, $CDCl_3$) δ: 0.96 (t, $J = 7$ Hz, 3H, $CH_2CH_2C\mathit{H}_3$); 1.43 (m, 2H $CH_2C\mathit{H}_2CH_3$); 2.15, 2.17 (s, 15H, ring methyls), 2.56 (m, 2H, $C\mathit{H}_2CH_2CH_3$). ^{13}C-NMR (75.4 MHz, $CDCl_3$) δ: 14.66 ($CH_2{-}CH_2\mathit{C}H_3$); 16.31, 16.74, 16.77 (ring methyl groups); 23.22 ($-CH_2\mathit{C}H_2CH_3$); 32.92 ($-\mathit{C}H_2CH_2CH_3$); 131.56, 132.26, 132.34, 136.55 (ring carbons); 212.61 ($\mathit{C}O{-}CH_3$). GC/MS: *m*/*z* 190 (M^+). M.p. 52.2°C.

*3.6. Synthesis of (η^6-C_6Me_5Et)$TiCl_3$]$^+$[Ti_2Cl_9]$^-$ (**2a**)*

All operations were carried out in an atomosphere of argon. The reaction vessels were oven dried before use.

To a Schlenk flask containing a solution of 0.40 g ethylpentamethylbenzene (2.27 mmol) in 15 ml CH_2Cl_2, 2.5 ml $TiCl_4$ (4.76 g, 24.6 mmol) were added. The reaction solution turned from colorless to red–brown upon addition of $TiCl_4$, and a yellow solid precipitated out. The reaction mixture was allowed to stir at room temperature for 1 day. After filtration, the solid product was washed with hexane and dried in vacuo at room temperature. The yield for the titanium ethylpentamethylbenzene complex was 0.73 g (0.98 mmol, 43.2%). Anal. Found: C, 20.66; H, 2.96. Calc. for $C_{13}H_{20}Cl_{12}Ti_3$: C, 20.95; H, 2.70%. The yield of these complexes can be improved by evaporating CH_2Cl_2 from the filtrate and by cooling the filtrate as well.

Crystals suitable for X-ray analysis were prepared from a solution of the titanium(IV) arene complex in CH_2Cl_2 that contained an excess of $TiCl_4$. The solution was kept in a Schlenk tube under argon at room temperature. A small amount of argon was kept running into the Schlenk tube through a needle in a rubber septum for a while to help evaporate some solvent. Then a rubber cap was used to seal the Schlenk tube. Large yellow column-shaped single crystals of **2a** were formed over a period of 4 days.

*3.7. Synthesis of (η^6-C_6Me_5Pr)$TiCl_3$]$^+$[Ti_2Cl_9]$^-$ (**2b**)*

In an analogous procedure, to a Schlenk flask containing a solution of 0.43 g pentamethylpropylbenzene (2.26 mmol) in 15 ml, 2.5 ml $TiCl_4$ (4.76 g, 24.6 mmol) were added. The reaction solution turned from colorless to red–brown upon addition of $TiCl_4$, and a yellow solid was precipitated out. After filtration, the solid product was washed with hexane and dried in vacuo at room temperature. The yield was 0.72 g of the titanium pentamethylpropylbenzene complex (0.95 mmol, 42.0%).

3.8. Synthesis of (η^6-C_6Me_5Et)$TiCl_3$]$^+$[$AlCl_4$]$^-$

A suspension of 0.59 g $AlCl_3$ (4.42 mmol) in 15 ml toluene was treated with 0.84 g $TiCl_4$ (4.43 mmol). Addition of 0.80 g ethylpentamethylbenzene (4.53 mmol) caused the formation of a bright yellow solid. After 24 h stirring at room temperature, the suspension was filtered and the bright yellow solid was washed with hexane and dried in vacuo affording 1.01 g (2.02 mmol, 45.7% yield) of [(η^6-C_6Me_5Et)$TiCl_3$]$^+$[$AlCl_4$]$^-$. Anal. Found: C, 30.22; H, 4.30. Calc. for $C_{13}H_{20}AlCl_7Ti$: C, 31.27; H, 4.04%.

4. Conclusion

We have investigated the formation of high-valent d^0 titanium arene complexes in order to shed light into the 'uniqueness' of the complex [η^6-(C_6Me_6)$TiCl_3$]$^+$ [Ti_2Cl_9]$^-$ (**1**), which is formed in a reaction of hexamethylbenzene with titanium tetrachloride. Before our investigations no other arene was observed to form this type of product. Our investigations show that the uniqueness of **1** is in part due to the donor abilities of hexamethylbenzene, and to a large extent due to its low solubility. By utilizing substituted pentamethylbenzenes we increased the solubility of the ionic arene complexes and could show that they form, like hexamethylbenzene, stable arene complexes of the kind [η^6-(arene)-$TiCl_3$]$^+$[Ti_2Cl_9]$^-$. At the same time, these complexes are more soluble and we could observe that the equilibrium of the reaction lies more on the side of the reactants compared to the hexamethylbenzene complex.

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