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Synthesis, spectroscopic studies and reactivity of η^6-arene derivatives of titanium(IV) ☆

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Abstract

Halide abstraction from TiX_4 by AlX_3 in the presence of some aromatic hydrocarbons afforded the η^6-arene complexes of titanium(IV) of formula $[TiX_3(\eta^6\text{-arene})]AlX_4$ (arene = 1,3,5-$Me_3C_6H_3$, X = Cl, Br; arene = 1,2,4,5-$Me_4C_6H_2$, X = Cl; arene = Me_6C_6, X = Cl, Br, I). The corresponding chloro complexes of 1,4-$Me_2C_6H_4$, 1,2,3-$Me_3C_6H_3$ and 1,2,4-$Me_3C_6H_3$ were characterized in solution by ^{13}C NMR spectroscopy. Arene displacement from $[TiCl_3(\eta^6\text{-arene})][AlCl_4]$ occurs with THF or TlCp ($Cp = C_5H_5^-$) to afford $TiCl_4(THF)_2$ or $CpTiCl_3$, respectively. The titanium(IV)–arene complexes efficiently promote the hydrogen–deuterium exchange of the ring protons between C_6D_6 and $C_6H_{6-n}Me_n$.

Keywords: Titanium complexes; Arene complexes

1. Introduction

Several η^6-arene complexes of low-valent metals are known in the literature, further to the pioneering work in this field by Fischer and co-workers [1]. On the other hand, η^6-arene complexes of main group, d and f transition elements in their usual oxidation states are relatively rare [2] and important work in this area has been carried out by Cotton and co-workers.

The paucity of data concerning arene derivatives of titanium(IV) has recently been noted [3] in a paper concerning the preparation of $[MCp^*Me_2(\eta^6\text{-arene})][BMe(C_6F_5)_3]$ complexes, M = Ti, Zr, Hf; $Cp^* = C_5Me_5$. Some years ago, Krauss et al. [4] showed that the deeply coloured solutions of $TiCl_4$ in aromatic hydrocarbons contain aromatic-to-titanium charge transfer complexes and, in the case of the $TiCl_4$/hexamethylbenzene system, they isolated a compound of analytical composition $3TiCl_4 \cdot Me_6C_6$ [4b]. Crystallographic work by Floriani and co-workers [5] clarified the nature of this product and established that the reaction of $TiCl_4$ with either Me_6C_6 or butyne-2 leads to the ionic arene derivative of titanium(IV) of composition $[TiCl_3(\eta^6\text{-}Me_6C_6)]Ti_2Cl_9$. Presumably, equilibrium (1) operates in aromatic hydrocarbon solution, thus allowing the isolation of the arene complexes only in the case of the more stable, fully substituted methyl derivative. We therefore reckoned that, if the counteranion of the η^6-arene complex could be replaced by another one not involving a component of the equilibrium, the formation of these compounds could become possible also with other methyl substituted aromatic hydrocarbons and with halides other than the chloride. In this paper we establish that stable arene complexes of titanium(IV) of general formula $[TiX_3(\eta^6\text{-arene})]AlX_4$ can be isolated.

$$3TiCl_4 + \text{arene} \rightleftharpoons [TiCl_3(\eta^6\text{-arene})]Ti_2Cl_9 \quad (1)$$

In view of the renewed interest in organometallic complexes of titanium(IV) and zirconium(IV) as initiators of olefin polymerization [6], these results may promote further work in this area. Furthermore the tetrachloroaluminato arene complexes reported in this paper have been found to promote the ring proton exchange between the titanium-coordinated arene and C_6D_6.

2. Experimental

Unless otherwise stated, all operations were carried out in an atmosphere of prepurified argon. The reaction

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☆ Dedicated to Professor Frank Albert Cotton on the occasion of his 65th birthday, in recognition of his outstanding contributions to inorganic chemistry.

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vessels were oven dried before use. Solvents were dried by conventional methods.

IR spectra were recorded with a Perkin-Elmer model FT 1725X instrument on solutions or nujol mulls of the compounds prepared under rigorous exclusion of moisture and oxygen. NMR spectra (^{1}H: 200 MHz, ^{13}C: 50.3 MHz, reference TMS; ^{27}Al: 52.1 MHz, reference $[Al(H_2O)_6]Cl_3$) were recorded with a Varian Gemini 200 spectrometer at room temperature.

The liquid aromatic hydrocarbons (C. Erba, Fluka or Aldrich) were distilled from sodium; 1,2,4,5-$Me_4C_6H_2$ (Fluka) and Me_6C_6 (Aldrich) were used as received; C_6D_6 was distilled from sodium and CD_2Cl_2 was stirred over P_4O_{10} and then evaporated under reduced pressure in a trap cooled with liquid nitrogen.

Titanium tetrachloride (C. Erba) was distilled at atmospheric pressure and stored at ~4 °C under argon in vessels free of silicon grease. Titanium tetrabromide, $TiBr_4$, and titanium tetraiodide, TiI_4, were prepared from $TiCl_4$ and the corresponding hydrogen halide in pentane or in heptane as solvent, respectively [7]. Aluminium trichloride, $AlCl_3$ (C. Erba), and aluminium tribromide, $AlBr_3$ (Fluka), were commercial products sublimed in vacuo prior to use. Aluminium triiodide, AlI_3, was prepared according to a literature procedure [8].

2.1. *Synthesis of $[TiX_3(\eta^6\text{-arene})]AlX_4$ (arene = 1,3,5-$Me_3C_6H_3$, X = Cl, Br; arene = 1,2,4,5-$Me_4C_6H_2$, X = Cl; arene = Me_6C_6, X = Cl, Br, I*

2.1.1. *Arene = 1,3,5-$Me_3C_6H_3$, X = Cl*

A red–orange suspension of $AlCl_3$ (2.92 g, 21.90 mmol) in 1,3,5-$Me_3C_6H_3$ (30 ml) was treated with $TiCl_4$ (4.15 g, 21.87 mmol) at 27 °C. A red–orange solution formed instantaneously with droplets of a deep red liquid. On addition of heptane (50 ml), the immediate precipitation of a deep yellow solid was observed; the solid was filtered off, washed with heptane (2×25 ml) and dried in vacuo at room temperature affording 8.71 g (90% yield) of $[TiCl_3(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)]AlCl_4$. *Anal.* Found: Al, 5.8; Cl, 55.8; Ti, 10.3. Calc. for $C_9H_{12}AlCl_7Ti$: Al, 6.1; Cl, 56.0; Ti, 10.8%. IR spectrum (nujol mull): 3057w, 3045w, 1569m, 1309m, 1262w, 1170w, 1092w, 1032m, 878ms, 660w, 493vs and 457vs cm^{-1}. ^{13}C NMR (C_6D_6) δ (ppm): 154.67 (s), 134.22 (t, $J_{CD}=26.5$ Hz), 24.72 (s). ^{27}Al NMR (C_6D_6) δ (ppm): 97.34 ($w_{1/2}\cong 900$ Hz). The ^{27}Al NMR spectrum of $AlCl_3$ in C_6D_6 has a single resonance at 89.97 ppm ($w_{1/2}\cong 1000$ Hz).

The tetrabromoaluminato derivative $[TiBr_3(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)]AlBr_4$ was obtained similarly: orange, 77% yield. *Anal.* Found: Al, 4.0; Br, 73.6; Ti, 6.6. Calc. for $C_9H_{12}AlBr_7Ti$: Al, 3.6; Cl, 74.1; Ti, 6.3%. IR spectrum (nujol mull): 3056w, 3046w, 1571m, 1309m, 1258w, 1167w, 1090w, 1034m, 873ms, 662w, 395vs cm^{-1}. ^{27}Al NMR (C_6D_6) δ (ppm): 92.42 ($w_{1/2}\cong 910$ Hz). The ^{27}Al NMR spectrum of $AlBr_3$ in C_6D_6 has a single resonance at 75.21 ppm ($w_{1/2}\cong 1000$ Hz).

2.1.2. *Arene = 1,2,4,5-$Me_4C_6H_2$, X = Cl*

A yellow suspension of $AlCl_3$ (1.2 g, 9.00 mmol) in toluene (30 ml) was treated with $TiCl_4$ (1.73 g, 9.12 mmol) at 27 °C to obtain a red–orange solution. Addition of 1,2,4,5-$Me_4C_6H_2$ (1.22 g, 9.09 mmol) caused the immediate formation of a biphasic liquid system which consisted of a pale yellow upper layer and a deep red lower one. The upper layer was removed via cannula and the lower one was treated with heptane (50 ml), thus causing the formation of a deep yellow, microcrystalline solid which was filtered off, washed with heptane and dried in vacuo affording 2.74 g (66% yield) of $[TiCl_3(\eta^6\text{-}1,2,4,5\text{-}Me_4C_6H_2)]AlCl_4$. *Anal.* Found: Al, 5.8; Cl, 53.6; Ti, 10.2. Calc. for $C_{10}H_{14}AlCl_7Ti$: Al, 5.9; Cl, 54.3; Ti, 10.5%. IR spectrum (nujol mull): 3017 vw, 1488m, 1259w, 1031m, 1013w, 917w, 676w, 492vs and 451vs cm^{-1}. ^{1}H NMR spectrum (CD_2Cl_2) δ (ppm): 8.13 (s, 2H), 2.82 (s, 12H). ^{13}C NMR (C_6D_6) δ (ppm): 150.52 (s); 139.02 (t, $J_{CD}=25$ Hz); 22.48 (s). The ^{13}C NMR spectrum in CD_2Cl_2 is given in Table 1.

2.1.3. *Arene = Me_6C_6, X = Cl*

A suspension of $AlCl_3$ (4.36 g, 32.70 mmol) in toluene (50 ml) was treated with $TiCl_4$ (6.22 g, 32.79 mmol) at 27 °C. Addition of Me_6C_6 (5.46 g, 33.65 mmol) caused the formation of a bright yellow solid. After 5 h stirring at 27 °C, the suspension was filtered and the bright yellow solid was washed with toluene (2×25 ml) and heptane (2×25 ml) and dried in vacuo at room temperature affording 14.01 g (88% yield) of $[TiCl_3(\eta^6\text{-}Me_6C_6)]AlCl_4$. *Anal.* Found: Al, 5.7; Cl, 50.8; Ti, 9.5. Calc. for $C_{12}H_{18}AlCl_7Ti$: Al, 5.6; Cl, 51.2; Ti, 9.9%. IR spectrum (nujol mull): 1290 m, 1070m, 1013w, 988w, 796w, 498vs, 443vs cm^{-1}. ^{1}H NMR spectrum (CD_2Cl_2) δ (ppm): 2.8[illegible] (s). The ^{13}C NMR spectrum in CD_2Cl_2 is in Table 1.

The following compounds were obtained similarly.

$[TiBr_3(\eta^6\text{-}Me_6C_6)]AlBr_4$: orange, 75% yield. *Anal.* Found: Al, 2.9; Br, 69.4; Ti, 6.4. Calc. for $C_{12}H_{18}AlBr_7Ti$: Al, 3.4; Br, 70.2; Ti, 6.0%. IR spectrum (nujol mull): 1287m, 1072m, 1013w, 985w, 796w and 392vs cm^{-1}. ^{1}H NMR spectrum (CD_2Cl_2) δ (ppm): 2.83. The ^{13}C NMR spectrum in CD_2Cl_2 is in Table 1.

$[TiI_3(\eta^6\text{-}Me_6C_6)]AlI_4\cdot C_7H_8$: deep red, 55% yield. *Anal.* Found: Al, 2.1; I, 73.1; Ti, 4.4. Calc. for $C_{19}H_{26}AlI_7Ti$: Al, 2.2; I, 73.0; Ti, 3.9%. IR spectrum (nujol mull): 1287m, 1070m, 1015w, 985w and 796w cm^{-1}. ^{1}H NMR spectrum (CD_2Cl_2) δ (ppm): 2.90.

When the reaction was repeated with 1,2,3- or 1,2,4-$Me_3C_6H_3$, intractable oils were obtained on addition of $TiCl_4$ to a red–orange suspension of $AlCl_3$ (see Section 3).

Table 1
^{13}C NMR spectra of $[TiX_3(\eta^6\text{-arene})]AlX_4$ complexes in CD_2Cl_2

Arene	X	δ (ppm)		Δδ^a (ppm)
		Bonded arene	Free arene	
1,2,4,5-$Me_4C_6H_2$	Cl	151.51	134.04	+17.47
		140.03	131.46	+8.57
		23.24	19.33	+3.91
Me_6C_6	Cl	151.09	132.23	+18.86
		22.37	17.07	+5.3
Me_6C_6	Br	150.20	132.23	+17.97
		23.33	17.07	+6.26

[a] Δδ = (chemical shift of the complexed arene) − (chemical shift of the free arene).

2.2. NMR study of the $TiCl_4/AlCl_3$/arene system in C_6D_6; arene = toluene, 1,4-$Me_2C_6H_4$, 1,2,3-$Me_3C_6H_3$, 1,2,4-$Me_3C_6H_3$, 1,3,5-$Me_3C_6H_3$, 1,2,4,5-$Me_4C_6H_2$

To deuterated benzene (1 ml) the arene and $TiCl_4$ were added in a 1:1 molar ratio to obtain solutions whose colour depends on the nature of the arene (orange to dark red). The solution was treated with $AlCl_3$ ($AlCl_3/TiCl_4$ molar ratio = 1) which caused the instantaneous formation of a biphasic liquid system consisting of a pale yellow upper layer and a deep red lower one. The lower layer was examined by ^1H and ^{13}C NMR spectroscopy. The ^{13}C NMR data are in Table 2.

In the case of 1,3,5-$Me_3C_6H_3$ or 1,2,4,5-$Me_4C_6H_2$, both the proton and the ^{13}C NMR spectra obtained according to this procedure were superimposable to those obtained by treating the preformed complexes $[TiCl_3(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)]AlCl_4$ or $[TiCl_3(\eta^6\text{-}1,2,4,5\text{-}Me_4C_6H_2)]AlCl_4$ with C_6D_6.

2.3. Hydrogen/deuterium exchange between C_6D_6 and $[TiCl_3(\eta^6\text{-arene})]AlCl_4$ (arene = 1,3,5-$Me_3C_6H_3$, 1,2,4,5-$Me_4C_6H_2$)

The arene derivative $[TiCl_3(\eta^6\text{-}1,2,4,5\text{-}Me_4C_6H_2)]AlCl_4$ (0.28 g, 0.61 mmol) was treated at room temperature with C_6D_6 (1 ml). The original yellow solid dissolved quickly giving a red biphasic liquid system. After overnight stirring, the volatiles were removed in vacuo and collected at low temperature. A ^1H NMR spectrum of the distillate showed the presence of a resonance centred at 7.2 ppm due to partially deuterated C_6D_6. The yellow residue was dissolved in CD_2Cl_2 and examined by NMR spectroscopy. ^1H spectrum: 2.82 ppm, without ring proton resonance. The ^{13}C spectrum showed the resonances due to the ring and methyl carbon atoms (151.49 (s), 140.13 (t, $J_{CD} = 25$ Hz), 23.18 (s)) of titanium-complexed 1,2,4,5-$Me_4C_6H_2$.

In the case of 1,3,5-$Me_3C_6H_3$, after evaporation of the volatiles, the distillate was treated with a known amount of ferrocene as internal standard and found by ^1H NMR to contain ring protons (resonance centred at 7.2 ppm) in a 2.8 ratio to titanium.

2.4. Reaction of $[TiCl_3(\eta^6\text{-}Me_6C_6)]AlCl_4$ with THF

Solid $[TiCl_3(\eta^6\text{-}Me_6C_6)]AlCl_4$ (2.21 g, 4.55 mmol) was added to THF (50 ml) cooled at ~ −120 °C. A yellow solution was obtained at room temperature. The volume was reduced to ~20 ml and the resulting suspension was cooled to −30 °C affording yellow crystals which were recovered by decantation and dried in vacuo at room temperature affording 0.87 g of $TiCl_4(THF)_2$ [9] (IR and elemental analysis). The solvent was evaporated to dryness and the pale yellow residue was partially dissolved in heptane (50 ml). The suspension was filtered and the solid was dried in vacuo affording 0.43 g of $TiCl_4(THF)_2$ [9] (total yield 86%). The solution was evaporated to ~20 ml and on cooling to about −30 °C colourless crystals were obtained which were decanted and dried in vacuo affording 0.843 g (67% yield) of $AlCl_3(THF)_2$ [10] (IR and elemental analysis). The solution was treated with a water/$CDCl_3$ mixture and the organic layer was found to contain THF and hexamethylbenzene by ^1H NMR.

2.5. Reaction of $[TiCl_3(\eta^6\text{-}Me_6C_6)]AlCl_4$ with thallium cyclopentadienide

A suspension of $[TiCl_3(\eta^6\text{-}Me_6C_6)]AlCl_4$ (2.48 g, 5.1 mmol) in toluene (50 ml) was treated with TlCp (1.375 g, 5.1 mmol). After 15 h stirring at room temperature, a black precipitate was filtered, the volume of the solution was reduced to ~30 ml and heptane (30 ml) was added. The orange solid which formed was filtered off, washed with heptane (2 ml) and dried in vacuo affording 0.94 g (84% yield) of $CpTiCl_3$ [11] (^1H NMR and elemental analysis).

2.6. Reaction of $[TiCl_3(\eta^6\text{-}Me_6C_6)]AlCl_4$ with $CoCp_2$

A yellow suspension of $[TiCl_3(\eta^6\text{-}Me_6C_6)]AlCl_4$ (1.23 g, 2.53 mmol) in toluene (50 ml) was treated with

Table 2
^{13}C NMR spectra of [TiX$_3$(η^6-arene)]AlX$_4$ complexes in C_6D_6

Arene	X	δ (ppm)		Δδ [a] (ppm)
		Bonded arene	Free arene	
Toluene [b]	Cl	137.70	137.86	−0.16
		129.40	129.34	+0.06
		128.91	128.54	+0.37
		125.68	125.69	−0.01
		21.37	21.41	−0.04
1,4-$Me_2C_6H_4$ [b]	Cl	150.27	134.64	+15.63
		136.51 (t, J_{CD} = 24.5 Hz)	129.24	+7.27
		23.77	20.97	+2.8
1,2,3-$Me_3C_6H_3$ [b]	Cl	153.03	136.13	+16.90
		152.72	134.75	+17.97
		134.40 (t, J_{CD} = 27.6 Hz)	127.98	+6.42
		132.79 (t, J_{CD} = 27.2 Hz)	125.59	+7.20
		23.61	20.44	+3.17
		18.88	15.10	+3.78
1,2,4-$Me_3C_6H_3$ [b]	Cl	153.57	136.05	+17.52
		151.25	135.03	+16.22
		149.78	133.16	+16.62
		138.09 (t, J_{CD} = 26.6 Hz)	130.77	+7.32
		137.38 (t, J_{CD} = 27.2 Hz)	129.83	+7.55
		133.93 (t, J_{CD} = 26.7 Hz)	126.80	+7.13
		24.12	20.96	+3.16
		22.82	19.57	+3.25
		21.35	19.17	+2.18
1,3,5-$Me_3C_6H_3$	Cl	154.67	137.49	+17.18
		134.22 (t, J_{CD} = 26.5 Hz)	127.33	+6.89
		24.72	21.24	+3.48
1,2,4,5-$Me_4C_6H_2$	Cl	150.52	133.52	+17.0
		139.02 (t, J_{CD} = 25 Hz)	131.46	+7.56
		22.48	19.15	+3.33

[a] Δδ = (chemical shift of the complexed arene) − (chemical shift of the free arene).

[b] Compound not isolated; obtained in solution by mixing equimolar quantities of $TiCl_4$, $AlCl_3$ and the parent arene in C_6D_6 (see Section 2).

$CoCp_2$ (0.498 g, 2.63 mmol). A brown violet solid formed which was filtered, washed with heptane (2×5 ml) and dried in vacuo at room temperature (0.99 g). The solid was treated with THF (30 ml) to obtain a pale brown solid in an almost colourless solution. The solid was filtered, washed with THF (2×5 ml) and dried in vacuo affording $CoCp_2[TiCl_4(THF)_2]$ [7] (1.14 g, 86% yield) (IR and elemental analysis).

The solution was dried in vacuo at room temperature and the residue was dissolved in heptane (50 ml); upon cooling at ~ −30 °C, colourless microcrystals of $AlCl_3(THF)_2$ [10] (0.50 g, 71%) (Al and Cl analysis) were collected by filtration and drying in vacuo.

3. Results and discussion

Solutions of TiX_4 in arene promptly react at room temperature with AlX_3 giving the solid products of Eq. (2).

$$TiX_4 + AlX_3 + \text{arene} \longrightarrow [TiX_3(\eta^6\text{-arene})]AlX_4 \qquad (2)$$

arene = 1,3,5-$Me_3C_6H_3$, X = Cl, Br; arene = 1,2,4,5-$Me_4C_6H_2$, X = Cl; arene = Me_6C_6, X = Cl, Br, I.

The reactions were carried out in the neat arene (1,3,5-$Me_3C_6H_3$) or in toluene in the other cases. Biphasic liquid systems were obtained with 1,3,5-$Me_3C_6H_3$ and 1,2,4,5-$Me_4C_6H_2$ from which microcrystalline, thermally stable solids almost insoluble in aliphatic hydrocarbons were obtained by addition of heptane. With hexamethylbenzene, the complexes separated out from the crude reaction mixtures as yellow (X = Cl) to orange (X = Br) to deep red (X = I) solids. Both [TiX$_3$(η^6-1,3,5-$Me_3C_6H_3$)]AlX$_4$ and [TiI$_3$(η^6-Me_6C_6)]AlI$_4$ react with halogenated hydrocarbons, the other compounds being stable in dichloromethane solution for days under rigorous exclusion of moisture.

Solutions of TiX_4 in neat arene (vide infra) in the presence of AlX_3 were found to develop intense red–brown colours. We believe that, under these conditions, equilibrium (1) is followed by equilibrium (3) in the presence of $AlCl_3$, the stability of the arene complexes increasing as the methyl substitution increases.

$$[TiCl_3(\eta^6\text{-arene})][Ti_2Cl_9] + 3AlCl_3 + 2\text{arene} \rightleftharpoons 3[TiCl_3(\eta^6\text{-arene})]AlCl_4 \qquad (3)$$

The solid state IR spectra in nujol emulsion (KBr disks) of the chloride derivatives isolated as microcrystalline solids show, in addition to the typical absorption of coordinated arenes [12], two strong absorptions in the 500–440 cm^{-1} range which have been assigned to the Al–Cl and to the Ti–Cl stretching vibrations [13], respectively. In the case of $[TiBr_3(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)]AlBr_4$ and $[TiBr_3(\eta^6\text{-}Me_6C_6)]AlBr_4$, a strong band at about 395 cm^{-1} is attributed to the Al–Br stretching vibration [13].

The ^1H NMR spectra of $[TiCl_3(\eta^6\text{-}1,2,4,5\text{-}Me_4C_6H_2)]AlCl_4$ in CD_2Cl_2 show singlets at $\delta = 8.13$ and 2.82 ppm; in the same solvent, the aromatic hydrocarbon has a ring proton resonance at 6.96 ppm and a methyl proton resonance at 2.26 ppm which represents a downfield shift of 1.17 and 0.56 ppm upon complexation to titanium(IV). The ^1H NMR spectrum of $[TiCl_3(\eta^6\text{-}Me_6C_6)]AlCl_4$ in CD_2Cl_2 has singlets at δ 2.80 (X = Cl) and 2.83 (X = Br) ppm due to the methyl protons which are shifted downfield by 0.5 ppm with respect to the uncomplexed hydrocarbon. The ^{13}C NMR spectrum of the 1,2,4,5-tetramethyl derivative is characterized by three singlets at δ 151.51 (quaternary aromatic carbon atoms), 140.03 (aromatic *C*H carbons) and 23.24 (*C*H_3 groups) ppm. The hexamethyl compounds, on the other hand, show singlets at δ 151.09 (X = Cl) or 150.20 (X = Br) and at δ 22.37 (X = Cl) or 23.33 (X = Br) ppm, see Table 1. Thus, complexation of the aromatic hydrocarbon to titanium(IV) is characterized by downfield shifts of both the ^1H and ^{13}C NMR parameters, in CD_2Cl_2 as solvent. Particularly relevant are the downfield shifts of the ^{13}C resonances upon complexation, which amount to about 18 ppm for the ring carbon atoms bonded to a methyl group, i.e. for the quaternary carbon atoms.

Due to the low stability of the less substituted methyl derivatives in dichloromethane, and to the unsuccessful attempts to isolate the corresponding complexes (intractable oils were frequently observed), it was decided to verify the phenomenon of arene complexation to titanium(IV) by studying the ^1H and ^{13}C NMR spectra of the $TiCl_4$/arene/$AlCl_3$ systems in C_6D_6. The $1,4\text{-}Me_2C_6H_4$ and the tri- and tetramethyl derivatives give rise to a double liquid layer with aromatic hydrocarbons in general (with the parent hydrocarbon in the case of the $1,3,5\text{-}Me_3C_6H_3$ complex, with toluene in the case of the $1,2,4,5\text{-}Me_4C_6H_2$ derivative and with C_6D_6 in both cases). We therefore examined the lower more dense liquid layer obtained by treating $[TiCl_3(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)]AlCl_4$ or $[TiCl_3(\eta^6\text{-}1,2,4,5\text{-}Me_4C_6H_2)]AlCl_4$ with C_6D_6. The ^1H NMR spectra thus obtained show signals around 7 ppm (the position is almost independent of the arene) and at about 2 ppm with a relative intensity of the aliphatic and the aromatic protons much higher than expected (about 5 versus 3 in the case of the trimethyl- and about 8 versus 6 in the case of the tetramethyl derivative). Moreover, the ^{13}C NMR spectra show, in addition to the singlets at ~150 and ~20 ppm (see Table 2), triplets centred at 134.22 ppm (26.5 Hz being the separation of the components of the triplet) for the trimethyl compound and at 139.02 ppm (separation, 25 Hz) in the case of the tetramethyl compound; moreover, a singlet is detectable at 128.4 ppm in the spectra of both arene derivatives (Fig. 1).

As 25 Hz is a typical value of $J(^2H\text{–}^{13}C)$, the triplets observed in the spectra of the arene derivatives could be easily attributed to coupling within the aromatic C–D bonds. Thus, we had established that a rapid H/D exchange reaction of the ring protons occurs upon contact of the η^6-arene complex with C_6D_6. It should be noted that the molar ratio between C_6D_6 and the complexed arene in these systems is about 100.

The ^{13}C NMR data of Table 2 confirm that complexation to titanium(IV) occurs with the methyl substituted arenes containing at least two methyl groups. As a matter of fact, $\Delta\delta$ values for the ^{13}C resonances ranging from 15.6 to 17.5 ppm have been observed for the dimethyl-, trimethyl- and tetramethyl-substituted aromatic hydrocarbons in the presence of $AlCl_3/TiCl_4$, see Table 2. This compares well with the ^{13}C NMR

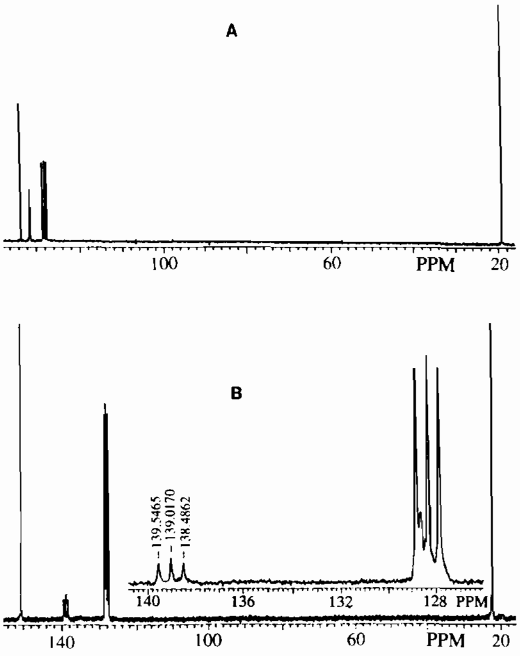


Fig.1. ^{13}C NMR spectra (50.3 MHz, C_6D_6) of: (A) $1,2,4,5\text{-}Me_4C_6H_2$; (B) $[TiCl_3(\eta^6\text{-}1,2,4,5\text{-}Me_4C_6H_2)]AlCl_4$.

data obtained in CD_2Cl_2 solution, for the preformed titanium(IV) complexes of 1,2,4,5-tetramethylbenzene and hexamethylbenzene, as reported in Table 1.

As mentioned above, the downfield shifts of the signals of the coordinated arene with respect to the free arene are particularly large for the signals of the quaternary aromatic carbon atoms (15–17 ppm). This is consistent with the results obtained in the case of $[V(CO)_4(\eta^6\text{-arene})]^+$ [14], $[NbL(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)_2]^+$ [15] and iridium(I) [16] cations; on the other hand, an opposite trend was obtained with *neutral* arene derivatives of chromium(0) [17], the ^1H and ^{13}C NMR signals of the complexed arenes being shifted upfield with respect to the free arene. It appears that the dominating factor in determining the proton and the carbon chemical shifts in the cationic species is the positive charge on the cation which effectively deshields both the proton and the carbon atoms of the metal-bonded aromatic hydrocarbon.

The ^{13}C NMR spectra were of paramount importance in detecting the phenomenon of arene complexation to titanium(IV) as monitored by the downfield shift of the ^{13}C resonance of both ring and methyl carbon atoms, see Table 2. As can be seen from the data of Table 2, all aromatic hydrocarbons, except toluene, undergo, in the presence of $TiCl_4$, a downfield shift of the resonances with respect to the uncomplexed aromatic hydrocarbon. This could be explained by assuming that a small fraction of titanium(IV) is complexed to toluene and that, in addition, free toluene and complexed toluene are in rapid equilibrium, on the NMR time scale, between themselves and with free C_6D_6 and complexed C_6D_6. On the other hand, this is not probably a reasonable interpretation of the NMR data because no H/D exchange was observed when $TiCl_4$ and $AlCl_3$ were treated with equimolar amounts of toluene in C_6D_6. Thus, the absence of both significant chemical shift displacement with respect to the free arene and H/D exchange suggests that no complexation of toluene or C_6D_6 occurs in the $TiCl_4/AlCl_3$ system to any significant extent.

In order to establish on a more quantitative basis the extent of the H/D exchange we treated the preformed complexes $[TiCl_3(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)]AlCl_4$ or $[TiCl_3(\eta^6\text{-}1,2,4,5\text{-}Me_3C_6H_3)AlCl_4$ with C_6D_6. After 10 min stirring at room temperature, the volatiles were removed. The ^1H NMR spectrum of the distillate in both cases showed the presence of aromatic protons; in the case of the trimethyl derivative, by using ferrocene as internal standard, 2.8 moles of aromatic protons were observed with respect to the titanium complex, thus showing that the H/D exchange was complete, within experimental error. Moreover, in the case of the tetramethyl derivative, the ^1H NMR spectrum of the yellow solution obtained by dissolving the titanium-containing residue in CD_2Cl_2 did not produce any resonance due to aromatic protons thus confirming the substantially quantitative, fast H/D exchange.

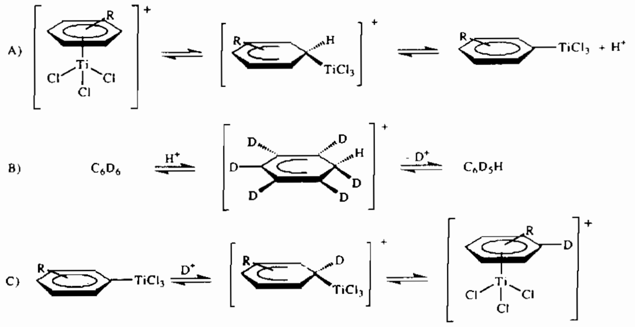
The literature reports the use of Lewis acid catalysts for the deuteration of aromatic and some aliphatic compounds [18]. Deuterated benzene is often used as a deuterium source in the presence of alkylaluminium halides, $SbCl_5$, $NbCl_5$, $AlCl_3$ or BBr_3 [18c]. The ^{27}Al NMR data on the 1,3,5-trimethylbenzene derivatives exclude the presence in our systems of free $AlCl_3$ or $AlBr_3$ in any detectable amount, see Section 2.

The mechanism proposed [18c] for the deuteration of aromatics in the presence of C_6D_6/Et_2AlCl/water involves an electrophilic process with HCl, the latter acting as the co-catalyst. The other possibility [18c] involves the formation of radical cations as intermediates: interconversion of π- and σ-bonded aromatic species to the Lewis acid may lead to isotopic exchange.

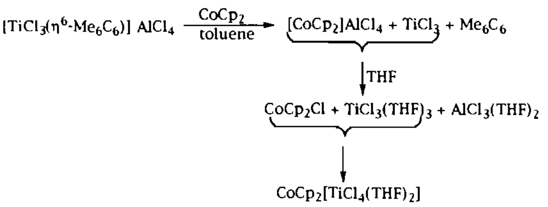
A possible mechanism of the H/D exchange in our case may be described as in Scheme 1. The formation of the σ-aryl complex, see sequence (A), is considered as the possible source of H^+. σ-aryl complexes of titanium(IV) of formula $ArTiCl_3$ are usually unstable at room temperature, but the pentafluorophenyl derivative $(C_6F_5)TiCl_3$ shows a melting point of 118 °C [19]. According to sequence (B), the deuterium cation D^+ may be generated followed by the formation of the deuterated arene derivatives of titanium(IV) through the sequence (C). On the other hand, we cannot exclude that a role in the H/D exchange in our systems is played by minor amounts of HCl produced by adventitious water.

The formation of the σ and π titanium(IV) complexes appears to be an essential requisite for the H/D exchange to occur, since, as mentioned earlier, no H/D exchange was observed for those aromatic hydrocarbons (C_6H_6, toluene) which do not appear to form complexes with titanium(IV) on the basis of the ^{13}C NMR data.

A word of comment for the experimental observation that some of the titanium(IV) η^6-arene complexes form a liquid biphasic system with aromatic hydrocarbons. This is believed to be a phenomenon of 'liquid clathrate' [20] formation discussed in an earlier publication [1z].



Scheme 1.



Scheme 2.

The formation of the titanium(IV) arene complexes is a very fast process probably being complete within the time of mixing the reagents. These findings may be relevant to the general problem of charge transfer complexes in the TiX_4/aromatic hydrocarbon systems [4,21].

The $[TiCl_3(\eta^6\text{-}Me_6C_6)]AlCl_4$ derivative has been used to study the reactivity of this class of compounds. It has been observed that the arene ligand is readily displaced in reactions with Lewis bases such as THF or Cp^- or in the presence of mild reducing agents such as cobaltocene. As a matter of fact, $[TiCl_3(\eta^6\text{-}Me_6C_6)]AlCl_4$ promptly reacts with THF to give the THF adducts of $TiCl_4$ and $AlCl_3$ (Eq. (4)) or with TlCp in toluene suspension to give $CpTiCl_3$ (Eq. (5)).

$$[TiCl_3(\eta^6\text{-}Me_6C_6)]AlCl_4 + 7THF \longrightarrow TiCl_4(THF)_2 + AlCl_3(THF)_2 + Me_6C_6 \quad (4)$$

$$[TiCl_3(\eta^6\text{-}Me_6C_6)]AlCl_4 + TlCp \longrightarrow CpTiCl_3 + \text{'}TlAlCl_4\text{'} + Me_6C_6 \quad (5)$$

By reaction with $CoCp_2$ in toluene, an insoluble brown–violet compound is readily formed which, upon reaction with THF affords high yields of $CoCp_2[TiCl_4(THF)_2]$. By taking into consideration that $AlCl_3(THF)_2$ has been found as a reaction product and that $CoCp_2[TiCl_4(THF)_2]$ may originate from either $CoCp_2$ with $TiCl_4(THF)_2$ or from $CoCp_2Cl$ and $TiCl_3(THF)_3$ [7], the titanium(III) compound may be considered as the results of the reaction sequence described in Scheme 2.

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