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Synthesis and reactivity of titanium(II) arene complexes

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Abstract

The synthesis of the arene derivatives of titanium(II), Ti(η^6-arene)[(μ-X)$_2$(AlX$_2$)]$_2$ (X = Br, I) from reaction of TiX$_4$, AlX$_3$, and Al with the parent arene is described, and their reactions are reported. Treatment of Ti(η^6-arene)[(μ-X)$_2$(AlX$_2$)]$_2$ with carbon monoxide at low temperature has given the dicarbonyl derivatives {Ti(η^6-arene)(CO)$_2$[(μ-X)$_2$(AlX$_2$)]} AlX$_4$ (X = Br, I). The room temperature, AlX$_3$-mediated carbonylation of toluene, which is in competition with the formation of titanium(II) carbonyl complexes, has been studied. Treatment of Ti(η^6-arene)[(μ-X)$_2$(AlX$_2$)]$_2$ (X = Cl, Br), with TlCp (Cp = η^5-cyclopentadienyl) and carbon monoxide at room temperature and atmospheric pressure has given TiCp$_2$(CO)$_2$ in good yields.

Introduction

The most recent work on the chemistry of low-valent derivatives of group 4 elements relates to (unsubstituted or alkylated) cyclopentadienyl complexes containing CO [1], CO$_2$ [2], CS$_2$ [2,3], phosphines [1a,4], nitriles [5], isonitriles [1d,4e,5], or alkynes p6[as additional ligands. For the oxidation states II or lower, group 4 metal derivatives not containing cyclopentadienyl ligands are still quite rare, the known compounds being restricted to carbonyl [7], tertiary phosphine [7], and bis-arene [8] complexes. Recently the unstable Ti(CO)$_6$ has been reported [7e] to be formed at low temperature from titanium vapour, and the [Zr(CO)$_6$]$^{2-}$ anion synthesised [7f].

The use of Al/AlX$_3$/reducing system in aromatic hydrocarbons, originally introduced by Fischer and Hafner [9] in connection with the structure elucidation of Hein's chromium derivatives and for the preparation of vanadium(0) bis-arene complexes [10], was subsequently extended to many other transition elements [11],

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[*] Dedicated to Professor Ernst Otto Fischer on the occasion of his 70th birthday on November 10th, 1988.

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including 4*f* [12] and 5*f* [13] cations. Several years ago, the Fischer–Hafner method was applied to titanium, and use of the $TiX_4/AlX_3/Al$/arene system led to the isolation of the titanium(II) arene derivatives, $Ti(\eta^6\text{-arene})[(\mu\text{-}X)_2(AlX_2)]_2$ [14]. Most of this work was carried out on the chloro complexes [14a–e,14h,14j], and the benzene and hexamethylbenzene derivatives were studied by X-ray diffraction methods [14h,14j]. At the beginning of this work, the bromo and the iodo derivatives had apparently not been isolated, although there was spectroscopic evidence of their existence in solution [14f].

The energies of the titanium–halogen bonds, Ti–X, are expected to decrease in the sequence $X = Cl > Br > I$, presumably leading to lower stability and higher reactivity on going from the lighter to the heavier halide ligand.

In the framework of our studies concerning the ligand effect on the reactivity of group 4 metal complexes [15], it was decided to study the reduction of $TiBr_4$ and TiI_4 with Al/AlX_3 in the presence of arenes and to attempt the isolation of the derivatives $Ti(\eta^6\text{-arene})[(\mu\text{-}X)_2(AlX_2)]_2$ with X = Br or I. We now report that these attempts were successful and that carbonyl derivatives of titanium(II) can be obtained by using these halogeno-η^6-arene complexes, especially the bromo derivatives, as starting materials. Some of the results were outlined in a preliminary communication [16].

Experimental

Unless otherwise stated, all operations were carried out under prepurified argon. Reaction vessels were oven-dried before use. Solvents were dried by conventional methods.

Infrared spectra were recorded on a Perkin–Elmer Model 283 spectrophotometer equipped with grating; solutions or Nujol mulls of the compounds, prepared with rigorous exclusion of moisture and oxygen, were used. In the case of the dicarbonyl $\{Ti(\eta^6\text{-arene})(CO)_2[(\mu\text{-}X)_2(AlX_2)]\}AlX_4$ derivatives, the Nujol mulls were prepared at −40 °C under a carbon monoxide atmosphere. UV-VIS spectra were measured on a Perkin–Elmer Lambda 15 spectrophotometer. GLC analyses were performed with a Dani 8400 instrument fitted with a Carbowax 20M column. GC-MS analyses were performed with a Dani 3800 gas-chromatograph coupled to a HP 5970 mass spectrometer.

Titanium tetrabromide and titanium tetraiodide were prepared from $TiCl_4$ and the corresponding hydrogen halide in n-heptane as solvent [16]. Aluminium trichloride (C. Erba), and aluminium tribromide (Fluka), were commercial products sublimed in vacuo prior to use. Aluminium triiodide [17], thallium(I) cyclopentadienide, TlCp [18], and the chloroaluminato derivatives, $Ti(\eta^6\text{-arene})[(\mu\text{-}Cl)_2(AlCl_2)]_2$, (arene = benzene, toluene, *p*-xylene and mesitylene) [14a,b], were prepared by published procedures.

Preparation of $Ti(\eta^6\text{-arene})[(\mu\text{-}X)_2(AlX)]_2$ (1: X = Br; arene = benzene, toluene, p-xylene and mesitylene; X = I, arene = benzene, toluene, and p-xylene)

Only the preparation of $Ti(\eta^6\text{-toluene})[(\mu\text{-}Br)_2(AlBr_2)]_2$ is described in detail, the other preparations being performed similarly. Reaction conditions, yields, and analytical data are shown in Tables 1 and 2.

Table 1

Preparation of Ti(η^6-arene)[(μ-X)$_2$(AlX)$_2$)]$_2$, reaction conditions and yields

$TiBr_4$ (mmol)	$AlBr_3$ (mmol)	Al (mmol)	Arene (ml)	Reflux period [a] (h)	Yield (%)
5.9	11.9	35.1	benzene(50)	5	51
8.2	17.6	50.0	toluene(75)	2.5	76
10.4	19.1	64.3	*p*-xylene(100)	1.5	76
5.1	11.6	34.3	mesitylene(30)	1	49
TiI_4 (mmol)	AlI_3 (mmol)				
2.6	4.9	16.0	benzene(30)	–	30
6.4	8.8	38.1	toluene(50)	–	40
9.0	17.3	61.0	*p*-xylene(100)	–	11
13.0	17.4	78.0	mesitylene(100)	–	[b]

[a] The mixture was stirred overnight (15 h) at room temperature in each case. [b] Not isolated, see Result and discussion.

A suspension of aluminium powder (1.35 g; 50.0 mmol) in toluene (75 ml) was treated with $AlBr_3$ (4.7 g; 17.6 mmol) and $TiBr_4$ (3.0 g; 8.2 mmol). The initially orange oily mixture became a dichroic green-violet suspension after 15 h stirring at room temperature. The suspension was refluxed for 2.5 h then filtered at room temperature, and the solution was reduced in volume to 15 ml then treated with n-heptane (50 ml), which induced separation of a black-violet solid. This was filtered off and dried in vacuo at room temperature (5.21 g; 76% yield).

Reaction ot Ti(η^6-arene)[(μ-X)$_2$(AlX$_2$)]$_2$ with CO at low temperature: synthesis of {Ti(η^6-arene)(CO)$_2$[(μ-X)$_2$(AlX$_2$)]} AlX$_4$ · arene (arene = benzene, toluene, p-xylene, mesitylene; X = Br, I)

Only the preparation of {Ti(η^6-toluene)(CO)$_2$[(μ-Br)$_2$(AlBr$_2$)]} AlBr$_4$ · toluene is described in detail, the other preparations being carried out similarly. As indicated in Table 3, some of the compounds (X = Cl) could not be obtained pure owing to the formation of untractable oils (see Results and discussion), and were identified spectroscopically (see Table 4).

Table 2

Ti(η^6-arene)[(μ-X)$_2$(AlX$_2$)]$_2$, analytical data [a]

Arene	Formula	X (%) [b]	Al (%) [c]	Ti (%) [c]
Benzene	$C_6H_6Al_2Br_8Ti$	76.2(78.0)	6.8(6.6)	5.7(5.8)
Toluene	$C_7H_8Al_2Br_8Ti$	75.3(76.7)	7.2(6.5)	5.5(5.7)
p-Xylene	$C_8H_{10}Al_2Br_8Ti$	75.1(75.4)		
Mesitylene	$C_9H_{12}Al_2Br_8Ti$	73.8(74.2)		
Benzene	$C_6H_6Al_2I_8Ti$	85.6(84.9)		
Toluene	$C_7H_8Al_2I_8Ti$	84.0(84.0)		
p-Xylene	$C_8H_{10}Al_2I_8Ti$	83.2(83.0)		
Mesitylene	$C_9H_{12}Al_2I_8Ti$	[d]		

[a] Calculated values in parentheses. [b] Determined by the Volhard method. [c] Calculated from the experimentally determined sum of oxides and the halide content. [d] Not isolated, see Results and discussion.

Table 3

{Ti(η^6-Arene)(CO)$_2$[(μ-X)$_2$(AlX$_2$)]}(AlX$_4$)·Arene [a] derivatives: analytical data [b] and yields

Arene	Formula	Yield (%) [c]	CO (%) [d]	Arene (%) [e]	X (%)
Benzene	$C_{14}H_{12}Al_2Br_8O_2Ti$	41	5.6(5.9)	–	68.5(67.0)
Toluene	$C_{16}H_{16}Al_2Br_8O_2Ti$	82	4.9(5.7)	18.9(18.8)	65.3(65.1)
p-Xylene	$C_{18}H_{20}Al_2Br_8O_2Ti$	62	5.5(5.5)	20.8(21.0)	63.2(63.3)
Mesitylene	$C_{20}H_{24}Al_2Br_8O_2Ti$	57	5.1(5.4)	23.5(23.2)	62.5(61.6)
Benzene	$C_{14}H_{12}Al_2I_8O_2Ti$	7.5	4.0(4.2)	–	74.6(76.4)
Toluene	$C_{16}H_{16}Al_2I_8O_2Ti$	11	4.3(4.1)	–	74.1(74.8)
p-Xylene	$C_{18}H_{20}Al_2I_8O_2Ti$	10	3.9(4.0)	–	72.2(73.3)
Mesitylene	$C_{20}H_{24}Al_2I_8O_2Ti$	9	3.8(4.0)	–	74.4(71.8)

[a] The chloro derivatives could not be isolated pure, and were identified spectroscopically (IR room temperature, see Table 4). [b] Calculated values in parentheses. [c] With respect to the starting TiX$_4$. [d] By decomposition with diiodine in toluene under strictly anhydrous conditions. [e] Determined by GLC or ^{1}H NMR analysis (ferrocene as internal standard) of a CCl$_4$ solution of the free arene after decomposition of the complex with deoxygenated water and extraction of the free arene with CCl$_4$.

A solution of Ti(η^6-toluene)[(μ-Br)$_2$(AlBr$_2$)]$_2$ prepared as described above from 12.4 mmol of TiBr$_4$, was cooled to −15 °C then treated with carbon monoxide at atmospheric pressure. There was a fast CO absorption up to a CO/Ti molar ratio of ca. 2 with precipitation of a brown solid *. When the CO uptake became negligible (ca. 2 h), the suspension was filtered, and the brown solid collected on a pre-cooled filter (about −78 °C). It was washed with cold n-pentane (3 × 10 ml) and dried at about −30 °C in a CO stream (10.0 g; 82% yield based on TiBr$_4$ initially taken). The compound loses CO at room temperature and, much more slowly, at temperatures as low as −20 °C under a CO atmosphere. Analytical and spectral data are given in Tables 3 and 4.

The stability of the carbonyl derivatives of titanium(II) under carbon monoxide was checked gas-volumetrically as follows.

(a) A toluene solution of Ti(η^6-toluene)[(μ-Br)$_2$(AlBr$_2$)]$_2$ (25 ml, 3.08 mmol) was treated with CO at 20.2 °C and 755 mmHg total pressure. A fast CO gas absorption took place until a final CO/Ti molar ratio of 1.47 was reached (210 min). The mixture was treated immediately with an excess of diiodine (introduced as a solid in a thin-walled glass container which was broken by stirring), and the CO evolved was found to correspond to 98% of the absorbed amount.

(b) Under the same conditions, 3.08 mmol of Ti(η^6-toluene)[(μ-Br)$_2$(AlBr$_2$)]$_2$ were carbonylated and, after 16 h stirring at 20.2 °C, an excess of diiodine was added. The CO evolved was found to correspond to 89% of the absorbed amount. In a parallel experiment, after 16 h stirring at 20.2 °C under CO atmosphere, the mixture was hydrolyzed and the toluene layer was dried over MgSO$_4$, then shown (IR) to contain *p*-tolualdehyde (11% yield with respect to titanium).

(c) A toluene solution of Ti(η^6-toluene)[(μ-Br)$_2$(AlBr$_2$)]$_2$ prepared as described above from 36.1 mmol of TiBr$_4$, was treated at 20 °C with CO for 24 h and then kept at 50 °C for 4 h. The dark-brown reaction mixture was then evaporated to

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* For arene = *p*-xylene, mesitylene, X = Br and arene = toluene, X = I, the final CO/Ti molar ratios were 1.6, 1.7 and 0.5, respectively.

Table 4

$(Ti(\eta^6\text{-arene})(CO)_2[(\mu\text{-}X)_2(AlX_2)])(AlX_4)\cdot$Arene derivatives; infrared spectra in the carbonyl stretching region [a]

X	arene	$\nu(CO)$ (cm^{-1})
Cl [b]	Benzene	2105; 2084
	Toluene	2096; 2076
	p-Xylene	2095; 2075
	Mesitylene	2097; 2075
Br	Toluene	2089; 2061
	p-Xylene	2083; 2064
	Mesitylene	2067; 2042
I	Toluene	2079; 2057
	p-Xylene	2071; 2053
	Mesitylene	2063; 2049

[a] Nujol mulls prepared at ca. −40 °C under a CO atmosphere. The intensity of the bands is vs-s in order of decreasing wavenumber value. [b] Impure product. See Table 3 and Results and discussion.

dryness in vacuo and the residue carefully treated with dry Et_2O (100 ml). The brown suspension formed was treated at room temperature with H_2O (100 ml) and the brown aqueous solution separated and extracted with Et_2O (2 × 20 ml). The combined ether extracts were washed with water and dried over $MgSO_4$. After distillation of Et_2O at atmospheric pressure, the yellow orange liquid residue was distilled and the fraction of b.p. 39–41 °C/0.1 mmHg collected. The colourless liquid (2.97 g; 68% yield) was found to have properties identical with those of an authentic sample of *p*-tolualdehyde (IR, ^1H NMR and GC-MS).

When the (a), (b) and (c) runs were performed with the chloride derivatives, $(\eta^6\text{-toluene})[(\mu\text{-}Cl)_2(AlCl_2)]_2$, the following results were obtained:

(a) 98% of the absorbed CO was evolved at the end of the carbonylation upon treatment with a I_2/toluene solution;

(b) 96% of the absorbed CO was evolved upon treatment with a I_2/toluene solution after 16 h stirring under carbon monoxide at room temperature;

(c) No significant amount of *p*-tolualdehyde was formed after 16 h at room temperature and 5 h at 50 °C, followed by treatment with water.

Carbonylation of $Ti(\eta^6\text{-}HMB)[(\mu\text{-}X)_2(AlX_2)]_2$ (HMB = hexamethylbenzene) in toluene

A toluene (100 ml) solution of $Ti(\eta^6\text{-toluene})[(\mu\text{-}Br)_2(AlBr_2)]_2$, prepared as described above from 9.6 mmol of $TiBr_4$ was treated with HMB dissolved in toluene (10 ml). The formation of a precipitate after a few minutes denoted the occurrence of the arene exchange reaction. The mixture was cooled to −25 °C and treated with CO for 15 h. The solid was collected on a pre-cooled filter (about −78 °C), washed with cold n-pentane, and dried at ca. −30 °C in a CO stream to give $\{Ti(\eta^6\text{-}HMB)(CO)_2[(\mu\text{-}X)_2(AlX_2)]\}\ AlX_4\cdot 1.1$ toluene (7.2 g; 71% yield with respect to $TiBr_4$). IR spectrum (Nujol mull): 2066m, 2038m cm^{-1}. Anal. Found: Al, 5.1; Br, 60.0, CO, 5.3, Ti, 4.5; $C_{21.7}H_{26.8}Al_2Br_8O_2Ti$ calcd.: Al, 5.1, Br, 60.3, CO, 5.3, Ti, 4.5. The HMB/toluene ratio in the compound was determined as follows: a weighed amount of the compound was treated with ice-water and the organic substances extracted with CCl_4. ^1H NMR analysis of the CCl_4 solution revealed a HMB/toluene molar ratio of 1/1.1.

Carbonylation of toluene in the presence of AlX_3 (X = Cl, Br, I)

X = Cl. A suspension of $AlCl_3$ (1.95 g; 14.6 mmol) in toluene (50 ml) was treated with CO. After 15 h stirring at 20.4 ° C and 762 mmHg of total pressure, 1.4 mmol of CO were absorbed, corresponding to a CO/Al molar ratio of 0.1. On hydrolysis, free aldehyde ($\tilde{\nu}$(CO) 1706 cm^{-1} in toluene) was found in the organic layer.

X = Br. A sealed thin-walled glass vial containing $AlBr_3$ (1.59 g; 6.0 mmol) was broken by mechanical stirring in toluene (20 ml) presaturated with CO, and the mixture was treated with CO at 20.4 ° C and 762 mmHg total pressure. The initially yellow colour of the solution changed to red brown during the absorption of CO. After 12 h stirring the CO/Al molar ratio was 0.91. The solution was filtered and reduced in volume to 5 ml in vacuo at room temperature, and n-heptane was added. The yellow solid that separated was filtered off and dried in vacuo to give 1.48 g (64% yield) of $AlBr_3$(*p*-tolualdehyde) in the form of a yellow-orange solid, extremely sensitive to moisture. Anal. Found: Al, 7.3, Br, 62.0; $C_8H_8AlBr_3O$ calcd.: Al, 7.0; Br, 62.0%. IR spectrum (Nujol mull): 3080w, 1950w, 1625w, 1586vs, 1551s, 1050w, 1420m-w, 1335w, 1320m, 1260m, 1240m-s, 1175s, 855m, 815s, 790m-w, 765m, 670m, 655m, 620m-w, 590m, 500m-w, 480m-w and 435m-s cm^{-1}. On exposure to moisture, the absorptions at 1586vs and 1551s were quickly replaced by the absorption of the free aldehyde at 1701 cm^{-1}. ^1H NMR spectrum (C_6D_6, δ values in ppm relative to TMS as internal standard): 8.7 (s, 1 H), 6.7 (m, 4 H), 1.9 (s, 3 H).

In a separate run, the toluene solution obtained by carbonylation of toluene in the presence of 1.71 g (6.4 mmol) of $AlBr_3$ was dried in vacuo at room temperature and the orange residue hydrolized at 0 ° C. The aqueous layer was extracted several times with Et_2O, and the combined ethereal extracts were dried over $MgSO_4$. After distillation of the ether at atmospheric pressure, the residue was distilled and the fraction of b.p. 39–41 ° C/10^{-1} mmHg (0.52 g, 70% yield) was collected, and identified as *p*-tolualdehyde (IR, ^1H NMR, and GC-MS).

X = I. A solution of AlI_3 (1.43 g; 3.5 mmol) in toluene (50 ml) did not absorb CO during 21 h at 19.3 ° C and 761 mmHg total pressure.

Reaction of {Ti(η^6-toluene)$(CO)_2$[(μ-Br)$_2$($AlBr_2$)]} $AlBr_4$ · toluene with TlCp

A suspension of TlCp (0.54 g; 2.0 mmol) in toluene (30 ml) was treated at −50 ° C under argon with a sample of {Ti(η^6-toluene)$(CO)_2$[(μ-Br)$_2$($AlBr_2$)]}$AlBr_4$ · toluene (0.96 g; 1.0 mmol) which had been kept in the freezer at about −30 ° C for 11 d. No gas evolution was noticed as the reaction mixture was being warmed to room temperature, and after 2 h a brown suspension was obtained. An IR spectrum of the solution in the carbonyl stretching region showed two absorptions at 1966 and 1881 cm^{-1} typical [19] of $TiCp_2(CO)_2$. No other carbonyl absorptions were observed. Treatment of the filtered solution with an excess of diiodine in toluene at 25.4 ° C caused the evolution of 1.41 mmol of CO, corresponding to a 70% carbonylation yield to $TiCp_2(CO)_2$.

Reaction of Ti(η^6-arene)[(μ-X)$_2$(AlX_2)]$_2$ with thallium cyclopentadienide and CO. Preparation of $TiCp_2(CO)_2$

The carbonylation of the Ti(η^6-arene)[(μ-X)$_2$(AlX_2)]$_2$ in the presence of thallium cyclopentadienide was monitored by measuring the gas absorbed at 23.2 ° C. Experi-

Table 5

Reaction of Ti(η^6-arene)[(μ-X)$_2$(AlX$_2$)]$_2$ with TlCp under CO [a]

Arene/X	Ti (mmol)	TlCp (mmol)	Solvent (ml)	CO/Ti (absorbed)	CO/Ti [b] (evolved)	Cp$_2$Ti(CO)$_2$ [c] (yield, %)
Benzene/Cl	1.5	3.3	30	0.9	0.7	32
Toluene/Cl	1.6	3.2	34	1.4	1.2	59
p-Xylene/Cl	1.9	3.8	39	1.4	1.2	59
Mesitylene/Cl	0.3	1	15	0.8	0.8	42
Toluene/Br	1.2	2.4	25	1.0	0.6	27
Toluene/I	0.5	1	10	0.5	0.4	18

[a] Arene as solvent, T 23.2 °C. [b] By treatment of the arene solution with diiodine in pyridine. [c] Compound identified spectroscopically. Yields with respect to titanium introduced, based on the mols of CO evolved by decomposition with diiodine.

mental conditions and other data are shown in Table 5. When the gas absorption had ceased (ca. 30 min), an infrared spectrum of the solution in the carbonyl stretching region showed the two absorptions at 1967s and 1883vs cm^{-1} due to TiCp$_2$(CO)$_2$. The amount of TiCp$_2$(CO)$_2$ in solution was determined by measuring the volume of CO evolved after decomposition with a solution of I$_2$ in pyridine.

The yield of isolated product was established in separate experiments. A solution of Ti(η^6-toluene)[(μ-Cl)$_2$(AlCl$_2$)]$_2$ was obtained as described in the literature [14a] from TiCl$_4$ (20.5 mmol), Al powder (123.0 mmol), and AlCl$_3$ (40.9 mmol) in toluene (50 ml). After filtration to remove the residual aluminium, the solution was rapidly added (about 2 min) to a suspension of TlCp (10.9 g, 40.5 mmol) in 100 ml of toluene and the mixture was kept under carbon monoxide at room temperature. Formation of an oil was observed, as a vigorous absorption of CO took place and continued for about 1 h. The upper layer was separated and the solvent removed under reduced pressure at room temperature; the residue was treated with 150 ml of boiling n-hexane and the solution was filtered while still hot. The oil was extracted with n-hexane (2 × 30 ml) and the extracts were combined with the main n-hexane solution. The solution was concentrated to small volume and cooled to -78 °C, then the red-brown TiCp$_2$(CO)$_2$ which crystallized out was filtered off and dried in vacuo (2.04 g; 42% yield).

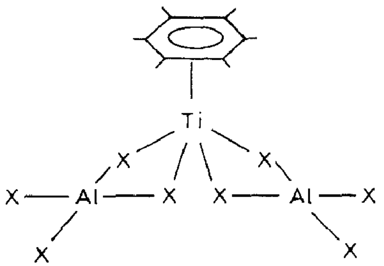
When a similar procedure was carried out with a solution of the bromo derivative Ti(η^6-toluene)[(μ-Br)$_2$(AlBr$_2$)]$_2$ in the parent hydrocarbon, a 28% yield of crystalline TiCp$_2$(CO)$_2$ was obtained.

Results and discussion

The aluminium powder reduction of TiX$_4$ (X = Br, I) in arene as solvent in the presence of AlX$_3$ affords the tetrahaloaluminates Ti(η^6-arene)[(μ-X)$_2$(AlX$_2$)]$_2$ **1** in good (X = Br) or low to moderate (X = I) yields, according to eq. 1. In order to obtain pure crystalline products the stoichiometric amount of AlX$_3$ is required: if

$$3\ \mathrm{TiX_4} + 2\ \mathrm{Al} + 4\ \mathrm{AlX_3} + 3\ \mathrm{arene} \xrightarrow[\mathrm{X = Br, I}]{\mathrm{arene}} 3\ \mathrm{Ti}(\eta^6\text{-arene})\left[(\mu\text{-X})_2(\mathrm{AlX_2})\right]_2 \qquad (1)$$

an excess of the arene-soluble AlX$_3$ is used, oily or impure products were formed. An excess of Al powder is necessary in order to achieve better yields of Ti(η^6-arene)[(μ-X)$_2$(AlX$_2$)]$_2$ (X = Br, I).



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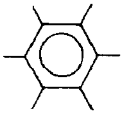


= benzene , toluene , *p*-xylene , mesitylene

The tetrahaloaluminates of titanium(II) and dark crystalline solids, sensitive to oxygen and moisture, and rapidly decomposed by Lewis bases such as THF or Et_2O [14a]. The iodide derivatives, $Ti(\eta^6\text{-arene})[(\mu\text{-I})_2(AlI_2)]_2$, must be prepared at room temperature, since under refluxing (in benzene or toluene) low yields are obtained. The bromo and the iodo complexes, like the chloro derivatives, are soluble in the parent aromatic hydrocarbon, and give strongly coloured solutions. Owing to the similarity of the electronic spectra of the bromo and the iodo derivatives to those of the chloro complexes (Table 6), for which the structural data in the solid state are available [14h,j], the halide-bridged structure **1** is assumed for all the compounds. Electronic spectral data for some of the titanium(II) complexes were reported earlier by Mach and coworkers [14f], who examined the spectra for two arene ligands (benzene and hexamethylbenzene) in benzene as solvent. Our data complement theirs and, furthermore, we report spectral data determined in the parent hydrocarbon to avoid possible complications arising from arene exchange. When comparison is possible, our data agree with those reported in the literature [14f] in respect of wavelengths and molar extinction coefficients. The spectra are characterized by three main absorptions, the lowest wavelength band being attributed [14f] to the superposition of a charge transfer and a *d–d* electronic transition. The most

Table 6

$Ti(\eta^6\text{-arene})[(\mu\text{-X})_2(AlX_2)]_2$: UV-VIS spectra

Arene/X	Solvent	λ (nm) [a]
Benzene/Cl	Benzene	395(630), 559(100), 912(30)
Toluene/Cl	Toluene	395(1560), 548(105), 806(35)
p-Xylene/Cl	*p*-Xylene	393(660), 527(160) [b]
Mesitylene/Cl	Mesitylene	390(400), 548(90) [b]
Toluene/Cl	Toluene	395(1560), 548(105), 806(35)
Toluene/Br	Toluene	398(810), 567(140), 804(50)
Toluene/I	Toluene	408 [c], 573 [c], 810 [c]

[a] Molar extinction coefficient (M^{-1} cm^{-1}) in parentheses. [b] The absorption around 800 nm is too weak to be determined with sufficient accuracy. [c] Spectrum measured on the crude reaction mixture after filtration from aluminum. Molar extinction coefficients not given because concentration is uncertain.

significant wavelength shift arises from change of the halide, in the sequence I > Br > Cl, in agreement with the relative position of these ligands in the spectrochemical series.

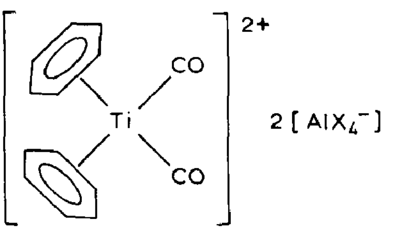
Having found reliable methods for the synthesis of the bromo and the iodo derivatives, we thought it of interest to investigate the reactivity of these systems towards carbon monoxide. In view of the decreasing stability of the titanium–halide bond [20] in the sequence Cl > Br > I, it was expected that the bromo and the iodo complexes would undergo substitution reactions much more readily than the corresponding chloro complexes.

Solutions of the halo derivatives **1** in the parent aromatic hydrocarbon as solvent react with carbon monoxide at atmospheric pressure at temperatures of ca. −20 °C to give red to brown solids of analytical composition $Ti(arene)_2(CO)_2(AlX_4)_2$ **2** (X = Br, I). The carbonyl derivatives are sparingly soluble in the reaction medium, and extremely reactive towards oxygen, moisture, Lewis bases, and halogenated compounds, and decompose when kept at room temperature (vide infra).

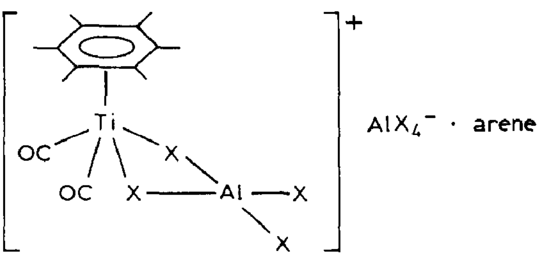
In the case of the chloride derivatives, solutions of $Ti(\eta^6\text{-arene})[(\mu\text{-Cl})_2(AlCl_2)]_2$ were treated with CO at low temperature: oils were obtained in most cases, but in other cases solid products were obtained after several hours stirring at room temperature; however, their analytical data were not satisfactory, and they were characterized only spectroscopically by their IR spectra in the carbonyl stretching region (see Table 4).

The data in Table 4 show that the positions of the CO stretching vibrations depend on the nature of both the halide and the arene ligands. As regards the effect of the arene, the observed wavenumber decreases with increasing methyl substitution, in agreement with what was expected on the basis of the increase in the donor ability of the arene ligand. A more general observation is that the wavenumber value of the CO stretching vibrations is particularly high (2105 + 2040 cm^{-1}), especially in view of the relatively low oxidation state of the metal (for comparison, $TiCp_2(CO)_2$ shows two absorptions at 1975 and 1897 cm^{-1}). This observation argues in favour of a weaker π-contribution to the Ti–CO bond in these arene systems.

As far as the identity of compound **2** is concerned, two suggestions can be advanced in the light of the available data, namely $[Ti(\eta^6\text{-arene})_2(CO)_2]AlX_4]_2$ (**2A**), and $\{Ti(\eta^6\text{-arene})(CO)_2[(\mu\text{-X})_2(AlX_2)]\}AlX_4 \cdot$ arene (**2B**). Structure **2A** involves the still unknown $[Ti(\eta^6\text{-arene})_2(CO)_2]^{2+}$ cation, isoelectronic with $[VCp_2(CO)_2]^{2+}$ [21] and coordinatively similar to titanocene dicarbonyl, $TiCp_2(CO)_2$. However, since the IR data (Table 4) in the carbonyl stretching region depend on the nature of the halide ligand, the latter presumably interacts with both



(**2A**)

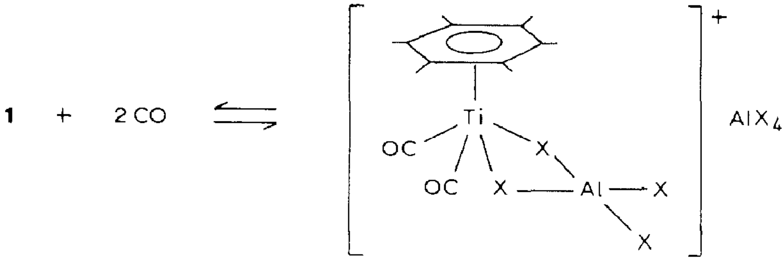


(**2B**)

titanium and aluminum, and this favours formulation **2B**. A μ-isocarbonyl arrangement such as $(\eta^6\text{-arene})TiX_2[(\mu\text{-CO})AlX_3]_2$ must be excluded, among reasons, in the light of the knowledge [22] that this type of bonding gives rise to CO stretching vibrations between 1700 and 1600 cm^{-1}. If the formulation **2B** is correct, the presence of lattice arene is required by the analytical data. This is substantiated by the finding that carbonylating of a suspension of $Ti(\eta^6\text{-HMB})[(\mu\text{-Br})_2(AlBr_2)]_2$ in toluene yielded a compound containing both hexamethylbenzene and toluene in the molar ratio ca. 1/1. Since hexamethylbenzene is assumed, for electronic reasons to be better able than toluene to coordinate to titanium but less able for steric reasons to occupying lattice vacancies, this finding is in agreement with the general assumption of a 1/1 relationship between coordinated and clathrated arenes in this class of compounds [14h].

The high wavenumber values of the CO stretching vibrations in our compounds have already been noted. They are in the range usually [23] associated with the coordinated CO undergoing nucleophilic attack. The possibility therefore existed of a titanium-mediated electrophilic attack of CO on the coordinated arene to give $C_6H_{5-n}R_nCHO$. On the other hand, the $AlCl_3/CO/HX$ system is well known [24] to induce the CO insertion into the aromatic C–H bond of toluene with formation of *p*-tolualdehyde. In order to gain a better insight into this problem, we undertook the study of the reaction of $Ti(\eta^6\text{-toluene})[(\mu\text{-X})_2(AlX_2)]_2$ with CO at room temperature or above.

Then $Ti(\eta^6\text{-toluene})[(\mu\text{-Br})_2(AlBr_2)]_2$ was exposed to a CO atmosphere at room temperature in a gas volumetric apparatus, a fast CO absorption took place up to a CO/Ti molar ratio of about 1.5. The lower CO/Ti molar ratio observed in the room temperature reaction relative to that (ca. 2) observed in the reaction carried out at lower temperature, can be accounted for by assuming that an equilibrium such as that indicated in equation 2 is established, the formation of the carbonyl derivative being obviously favoured by lower temperatures.



(2)

The reasons for this interpretation are as follows. On several occasions it had been observed qualitatively that, when exposed to moisture, the toluene carbonyl complexes, in the solid state or in suspension, gave rise to the corresponding aromatic aldehyde. We therefore decided to undertake a series of experiments aimed at confirming the formation of both the carbonyl derivatives of titanium(II) and *p*-tolualdehyde, using $Ti(\eta^6\text{-toluene})[(\mu\text{-Br})_2(AlBr_2)]_2$ as the reference substrate.

Treatment of a solution of $Ti(\eta^6\text{-toluene})[(\mu\text{-Br})_2(AlBr_2)]_2$ with CO at atmospheric pressure at 20.2 °C, followed by addition of I_2 immediately after the CO absorption had ceased, caused the evolution of gas corresponding to 98% of the absorbed amount. In another experiment, in which the reaction time was increased to 16 h, other experimental conditions being essentially the same, 89% of the absorbed CO was evolved on treatment with I_2, and the balance was found to be present in *p*-tolualdehyde (11% with respect to titanium by IR determination). The yield of *p*-tolualdehyde was 62% (isolated product) when $Ti(\eta^6\text{-toluene})[(\mu\text{-}Br)_2(AlBr_2)]_2$ was kept under a CO atmosphere for 24 h at 20 °C and then 4 h at 50 °C. In a parallel experiment, no CO evolution was observed upon I_2 addition, showing that the toluene in the complex had been completely and slowly converted into *p*-tolualdehyde. These facts show that a smaller amount of CO is absorbed in the carbonylations of the titanium(II) derivative at room temperature which is not attributable to the formation of *p*-tolualdehyde. Although we have observed that a toluene suspension of $\{Ti(\eta^6\text{-toluene})(CO)_2[(\mu\text{-}Br)_2(AlBr_2)]_2AlBr_4$ is completely decomposed upon addition of *p*-tolualdehyde (in agreement with the low stability of the carbonyl-arene complexes in the presence of Lewis bases), this decomposition mechanism does not operate under our experimental conditions, since *p*-tolualdehyde actually forms a $AlBr_3$ adduct, vide infra.

No *p*-tolualdehyde was formed when the chloride derivative $Ti(\eta^6\text{-toluene})[(\mu\text{-}Cl)_2(AlCl_2)]_2$ was treated with CO either at room temperature or at 50 °C. In view of the observed increase in wavelength of the CO stretching vibrations on going from bromide to chloride, the failure to form *p*-tolualdehyde in the chloride system strongly suggests that titanium does not play any important role in the carbonylation of the arene. We therefore undertook some carbonylation experiments in the presence of AlX_3 alone in toluene as solvent. The amount of CO absorbed with time in carbonylation reactions carried out at 20.4 °C is shown in the plot of Fig. 1. It is noteworthy that the rate of carbonylation of toluene to *p*-tolualdehyde was much higher for $AlBr_3$ than for the slightly soluble $AlCl_3$. On the other hand, no carbonylation was observed in the presence of AlI_3. Thus, $AlBr_3$ appears to represent the best compromise between electronic properties and solubility. The much lower conversion into *p*-tolualdehyde observed in the room temperature experiments with $Ti(\eta^6\text{-toluene})[(\mu\text{-}Br)_2(AlBr_2)]_2$, together with the other experimental observations, led us to conclude that aldehyde formation in the carbonylation of the titanium(II) derivative is a subsequent reaction due to the presence of some AlX_3 released in solution.

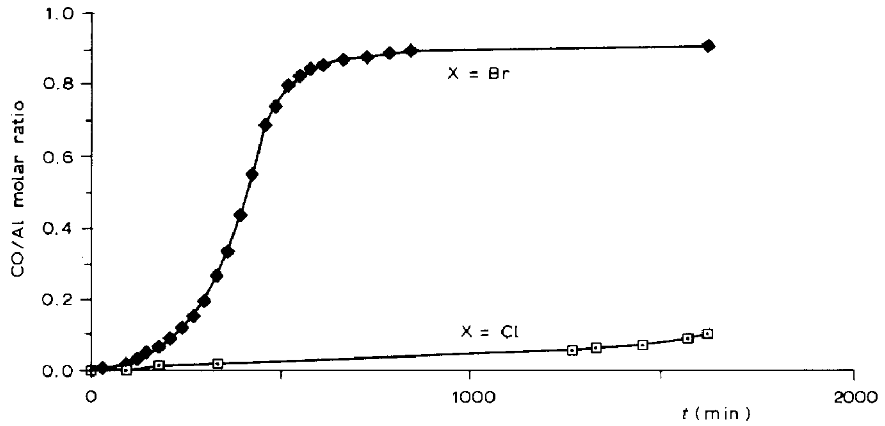


Fig. 1. Carbonylation of toluene in the presence of AlX_3. Solvent: toluene; [AlX_3] 0.3 *M*; Temperature 20.4 °C; P(CO) + *P*(solvent) 1 atm.

During the carbonylation of toluene in the presence of $AlBr_3$, the *p*-tolualdehyde complex $AlBr_3(CH_3C_6H_5CHO)$ was formed, as shown in eq. 3 and could be isolated as a moisture-sensitive orange microcrystalline solid, which was characterized analytically by observation of the IR absorptions at 1580 and 1550 cm^{-1} attributable to the aluminium-coordinated aldehyde carbonyl group. The aldehyde could be released from the $AlBr_3$ complex by hydrolysis.

$$AlBr_3 + CO + C_6H_5CH_3 \rightarrow AlBr_3(CH_3C_6H_5CHO) \qquad (3)$$

It is noteworthy that although carbonylation of arenes to give aromatic aldehydes catalysed by aluminium chloride in the presence of HCl and CuCl (the Gattermann–Koch reaction) has been known since 1897 [24] to the best of our knowledge there has been no work on the carbonylation of toluene to *p*-tolualdehyde by use of the system $AlBr_3$/CO/toluene. It has been shown [25] that copper(I) salts are not essential for the $AlCl_3$-mediated carbonylation of benzene and toluene. The presence of small amounts of HBr in our system (arising from hydrolysis of $AlBr_3$ by adventitious moisture) cannot be excluded but, it is noteworthy that the conditions in our toluene carbonylation are milder than those used in a typical Gattermann–Koch reaction [26], and the addition of HBr as a separate component of the reaction mixture is not required.

In order to permit better characterization of the dicarbonyl derivative **2** and to permit study of its reactivity, the compound $\{Ti(\eta^6\text{-toluene})(CO)_2[(\mu\text{-Br})_2(AlBr_2)]$ $AlBr_4 \cdot$ toluene was treated with TlCp in toluene under argon. Immediate reaction took place without gas evolution, and $TiCp_2(CO)_2$ was formed in good yield (see eq. 4). These observations show that the formation of $TiCp_2(CO)_2$ is to be regarded as a substitution reaction, but the two CO groups originally present in **2** are retained within the coordination sphere of the metal.

$$\mathbf{2} + 2\,TlCp \rightarrow TiCp_2(CO)_2 \qquad (4)$$

The availability of the arenetitanium(II) derivatives prompted us to attempt a direct synthesis of titanocene dicarbonyl from TiX_4, see eq. 5. The reaction was

$$TiX_4 \xrightarrow[(2)\ TlCp,\ CO]{(1)\ Al,\ AlX_3,\ arene} TiCp_2(CO)_2 \qquad (5)$$

studied for different arene and halide ligands and it was found that, independent of the nature of the arene or the halide, the reactions are very fast (CO absorption becomes negligible after ca. 20 min at room temperature). The best yields were obtained for arene = toluene and halide = Cl (Table 5). On a preparative scale, the yields of recrystallized $TiCp_2(CO)_2$, vary from 18 to 59%. We think that this synthesis may be competitive with other preparations of $TiCp_2(CO)_2$ described in the literature [13,27], because of its use of low cost and readily available materials.

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