New Organometallic Derivatives of Titanium(II) containing π-Acids as Ligands

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The titanium(II) derivatives $Ti(\eta^6\text{-arene})[(\mu\text{-}X)_2(AlX_2)]_2$, (X = Br or I) in the parent aromatic hydrocarbon react with CO at atmospheric pressure to give thermally unstable complexes of proposed structure $Ti[(\eta^6\text{-arene})(CO)_2(\mu\text{-}X)_2\text{-}(AlX_2)]AlX_4$ and with C_2Ph_2 to give tetra-substituted cyclobutadiene derivatives $Ti(\eta^4\text{-}C_4Ph_4)[(\mu\text{-}X)_2(AlX_2)]_2$ (X = Br).

Low-valent titanium is a subject of current investigation.[1] The chloro-derivatives of titanium(II) of general formula $Ti(\eta^6\text{-arene})[(\mu\text{-}Cl)_2(AlCl_2)]_2$ have been widely studied;[2] on the other hand, the bromo analogues have only been identified spectroscopically, while the attempted isolation[3] of the iodo derivatives was unsuccessful. The expected decrease[4] of the titanium–halogen bond strength along the Cl > Br > I sequence presumably has made the study of the Br and I systems difficult. However, the presence of weaker ligands around titanium may induce their easier displacement in favour of species typically stabilizing low oxidation states. We now report the successful isolation of titanium(II) organometallic derivatives using the halogeno-η^6-arene complexes, especially the bromo-derivatives, as starting material.

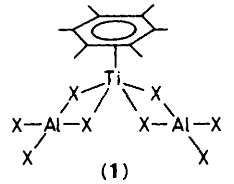
Solutions of the bromo- and iodo-derivatives $Ti(\eta^6\text{-arene})[(\mu\text{-}X)_2(AlX_2)]_2$,† (X = Br or I) (**1**) in the parent aromatic hydrocarbon (arene = benzene, toluene, 1,4-$C_6H_4Me_2$, or 1,3,5-$C_6H_3Me_3$) react with CO at atmospheric pressure at temperatures around −20 °C to give red to brown products of analytical composition $Ti(arene)_2(CO)_2{\cdot}2AlX_4$ (**2**), sparingly soluble in the reaction medium.‡ The molar ratio of absorbed CO to titanium was close to 2. The carbonyl derivatives decompose quickly at room temperature even in the solid state under a CO atmosphere, slow decomposition occurring at −40 °C. They are extremely sensitive to both oxygen and moisture. I.r. data (Table 1) show that the positions of the carbonyl absorptions are affected by the nature of both the arene ligand and the halide. Two main structural proposals are possible on the basis of the observed data, namely $[Ti(\eta^6\text{-arene})_2(CO)_2]^{2+}(AlX_4^-)_2$ (**2A**) and $[Ti(\eta^6\text{-arene})(CO)_2\text{-}(\mu\text{-}X)_2(AlX_2)]^+AlX_4^- \cdot$ arene (**2B**). Structure (**2A**) includes the $[Ti(\eta^6\text{-arene})_2(CO)_2]^{2+}$ cation, isoelectronic with the well known[5] $[V(\eta^5\text{-}C_5H_5)_2(CO)_2]^+$ cation. However, the fact that the CO i.r. absorptions are affected by the nature of the halide suggests that the halide interacts with both titanium and aluminium, thus favouring formulation (**2B**). The presence of lattice arene in formulation (**2B**) is substantiated by the observation that carbonylation of a toluene solution of $Ti(\eta^6\text{-toluene})[(\mu\text{-}Br)_2(AlBr_2)]_2$ in the presence of hexamethylbenzene (20 mol. equiv.) yielded a solid compound containing both hexamethylbenzene and toluene in the ratio *ca.* 1:1 with respect to titanium, thus suggesting that toluene is occupying the lattice vacancies.[2f,g]

The dicarbonyl complex (**2**) (arene = toluene, X = Br) reacts with $Tl(\eta^5\text{-}C_5H_5)$, [Tl(cp)] or with $C_6H_{11}NC$, or with $Ph_2PCH_2CH_2PPh_2$ (diphos) in the parent aromatic hydrocarbon at *ca.* −20 °C *under argon* to give $Ti(cp)_2(CO)_2$ (70% yield), or $Ti(arene)_2(C_6H_{11}NC)_2{\cdot}2AlBr_4$ ($\tilde{\nu}_{NC}$ 2274 and 2214 cm^{-1}, toluene solution, 15% yield) or $Ti(arene)_2(diphos){\cdot}2AlBr_4$ (58% yield), respectively. For the latter two compounds, structures similar to (**2B**) are proposed with the two carbonyl groups replaced by $C_6H_{11}NC$ or diphos. Finally, solutions of the η^6-toluene complex (**1**) react with C_2Ph_2 to give the soluble, diamagnetic, cyclobutadiene derivatives $Ti(\eta^4\text{-}C_4Ph_4){\cdot}2AlX_4$ (X = Cl or Br) (**3**). Structure assignment as $Ti(\eta^4\text{-}C_4Ph_4)[(\mu\text{-}X)_2(AlX_2)]_2$ is based on the typical[6] band at 1393 cm^{-1} due to co-ordinated tetra-substituted cyclobutadiene and on the reaction with $K_2(cot)$ (cot = cyclooctatetraene) leading (59% yield) to $Ti(\eta^4\text{-}C_4Ph_4)(cot)$[7] and with Tl(cp) giving (96% yield) the known[8] $(cp)_2\overline{Ti{-}CPh{=}CPh{-}CPh{=}}CPh$.

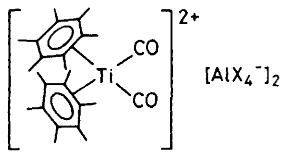
Table 1. Carbonyl stretching vibrations of the titanium(II) complexes, $Ti(arene)_2(CO)_2{\cdot}2AlX_4$.[a]

Arene	X	$\tilde{\nu}_{CO}/cm^{-1}$	
Toluene	Br	2089	2061
1,4-$C_6H_4Me_2$	Br	2083	2064
1,3,5-$C_6H_3Me_3$	Br	2067	2042
Toluene	I	2079	2057
1,4-$C_6H_4Me_2$	I	2071	2053
1,3,5-$C_6H_3Me_3$	I	2063	2049

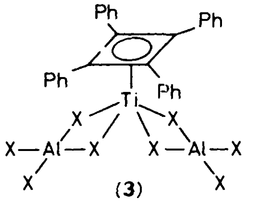
[a] Nujol mull. The intensity of the bands is vs,s in the order of decreasing $\tilde{\nu}$.



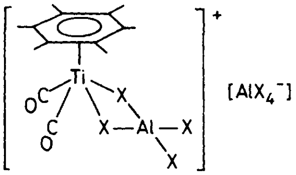
(**1**)



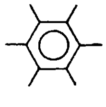
(**2A**)



(**3**)



(**2B**)



= C_6H_6, C_6H_5Me, 1,4-$C_6H_4Me_2$, or 1,3,5-$C_6H_3Me_3$

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† The η^6-arene titanium(II) complexes were isolated as microcrystalline violet to black solids from the reaction of TiX_4 with the strictly stoicheiometric amount of AlX_3 in the presence of an excess of Al as reducing agent at room temperature (X = I), or at room temperature followed by 2—4 h reflux (X = Br). The molecular structure of these compounds, which was not established, is assumed to be the same as that of the chloro derivative, as determined by *X*-ray diffraction studies.[2f,g] All the compounds reported in this paper gave satisfactory analyses (metal and halogen or metal and CO).

‡ The same reaction of the chloro-η^6-arene derivatives led to intractable oily products.

By reaction of (**1**) (X = Br) with 3 equiv. of but-2-yne (C_2Me_2), a mixture of $Ti(\eta^4\text{-}C_4Me_4)[(\mu\text{-}Br)_2(AlBr_2)]_2$ and $Ti(\eta^6\text{-}C_6Me_6)[(\mu\text{-}Br)_2(AlBr_2)]_2$ was obtained after 2 h stirring at room temperature; when the reaction time was prolonged to 15 h pure $Ti(\eta^6\text{-}C_6Me_6)[(\mu\text{-}Br)_2(AlBr_2)]_2$ was isolated in 87% yield.

The relevance of these observations for the preparation of low valent titanium complexes is under investigation.

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