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ARENETITANIUM(II) COMPLEXES OF FORMULA Ar · $TiCl_2$ · Al_2Cl_6

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Summary

The synthesis and properties of Ar · $TiCl_2$ · Al_2Cl_6 (Ar = benzene or a methylbenzene) complexes have been studied, and the results indicate an increase in stability of the arene—titanium π-bond in the order: benzene < toluene < xylenes < mesitylene < durene < hexamethylbenzene.

An exchange reaction of the aromatic ligands was observed. On the basis of conductivity measurements it was ascertained that the complexes are partially ionized in solution.

Introduction

Fischer's method [1] may be used to synthesize a homologous series of arenetitanium(II) complexes, Ar · $TiCl_2$ · Al_2Cl_6 [2,3], where Ar = benzene or a methyl derivative of benzene [2-4]. The previous studies [3,4] showed that the arene is π-bonded with titanium(II). A structure has been proposed [3] for these complexes, as in Fig. 1.

The influence of different arenes on the course of the reaction, and the magnetic properties and structure of the products was the object of this study.

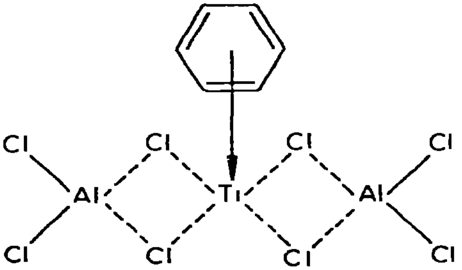

Fig. 1. The proposed structure [3] of arenetitanium(II)—aluminium chloride complexes.

Results and discussion

$Ar \cdot TiCl_2 \cdot Al_2Cl_6$ complexes with benzene, toluene, xylenes and mesitylene were obtained according to eqn. 1. Complexes with durene and hexamethylbenzene (HMB) were synthesized by the method given in ref. 4 by reduction of $TiCl_4$ with metallic aluminium in benzene in the presence of aluminium chloride and an equimolar (in ratio with $TiCl_4$) quantity of durene or HMB (eqn. 2).

$$Ar + TiCl_4 + Al + AlCl_3 \xrightarrow{Ar} Ar \cdot TiCl_2 \cdot Al_2Cl_6 \qquad (1)$$

$$Ar + TiCl_4 + Al + AlCl_3 \xrightarrow{benzene} Ar \cdot TiCl_2 \cdot Al_2Cl_6 \qquad (2)$$

Reaction time decreases with the increasing number of methyl groups in the aromatic ring of the ligand (Table 1), and the ionization potentials of the aromatic hydrocarbons decrease in the same series [5]. Thus there is a correlation between the reaction time and the ionization potential of the aromatic hydrocarbon, except for isomers; in spite of the identical ionization potentials of xylenes [5] the time of reaction varies considerably from one to another, probably because of differing steric effects.

We supposed that the complex formation proceeds in at least two stages (eqn. 3). In the first stage an intermediate solid crystalline titanium(III) complex is formed. (Synthesis of crystalline $TiCl_3 \cdot 1/3\ AlCl_3$ by reduction of $TiCl_4$ with metallic aluminium in benzene has been described [6].) In solvents with lower ionization potentials than benzene, strong interaction between an aromatic hydrocarbon molecule and titanium(III) can not be excluded. For example, complexes with the molar composition Ar/Ti = 1 are known for hexamethylbenzene [7,8]. In the second stage, the intermediate product gradually dissolves and a dark violet solution of $Ar \cdot TiCl_2 \cdot Al_2Cl_6$ complex is formed.

$$TiCl_4 \xrightarrow{Ar,Al} nAr \cdot TiCl_3 \cdot \frac{1}{3}\ AlCl_3 \xrightarrow{Al,Ar,AlCl_3} Ar \cdot TiCl_2 \cdot Al_2Cl_6 \qquad (3)$$

$(n = 0,1)$

TABLE 1

SYNTHESIS OF $Ar \cdot TiCl_2 \cdot Al_2Cl_6$ COMPLEXES

Molar ratio of $TiCl_4/Al/AlCl_3$ = 1/3/3, temperature 80°, 0.2 mole/l of $TiCl_4$ in excess of the respective arene, except where stated

Arene	Reaction time (min)	Yield (%)	Ionization potential of arene [5] (eV)
Benzene	480	93	9.56
Toluene	240	95	9.18
o-Xylene	180	97	9.04
m-Xylene	120	91	9.04
p-Xylene	300	94	9.04
Mesitylene	20	90	8.74
Durene[a]	20	89	8.53
Hexamethylbenzene[b]	20	90	8.15

[a] In benzene containing 0.2 mole/l of durene. [b] 0.1 mole/l of $TiCl_4$ in benzene containing 0.1 mole/l of hexamethylbenzene.

The shorter synthesis time with decreasing arene ionization potential can be explained by the increase of stability of the arene—titanium π-bond in the product; studies of the ^1H NMR spectra confirm this conclusion. As usual for a Ti d^2 electronic configuration, the $Ar \cdot TiCl_2 \cdot Al_2Cl_6$ (Ar = benzene, toluene) complexes are paramagnetic. The ^1H NMR spectra of these compounds reveal only broad (200 Hz) signals due to the solvent protons.

The $HMB \cdot TiCl_2 \cdot Al_2Cl_6$ complex dissolved in benzene is diamagnetic. A sharp singlet in the ^1H NMR spectrum of the complexed hexamethylbenzene is shifted 306 Hz upfield with respect to benzene used as internal reference. The ^1H NMR peak of the free HMB is shifted 301 Hz upfield from benzene. The diamagnetism of the solution of the $HMB \cdot TiCl_2 \cdot Al_2Cl_6$ complex can be explained by the d^2 spins pairing due to the formation of a stable π-bond or by the strong *d—d* titanium—titanium interaction.

On addition of 1 mole of hexamethylbenzene to the paramagnetic solution of 1 mole of $C_6H_6 \cdot TiCl_2 \cdot Al_2Cl_6$ the ^1H NMR signal becomes identical to that observed for $HMB \cdot TiCl_2 \cdot Al_2Cl_6$, confirming the irreversible character of the exchange reaction of benzene for hexamethylbenzene (eqn. 4). The product of

$$C_6H_6 \cdot TiCl_2 \cdot Al_2Cl_6 + HMB \xrightarrow{C_6H_6} HMB \cdot TiCl_2 \cdot Al_2Cl_6 + C_6H_6 \qquad (4)$$

reaction 4 can be isolated in almost quantitative yield [4]. The irreversible character of the reaction confirms that a $HMB—Ti^{II}$ π-bond is much more stable than a $C_6H_6—Ti^{II}$ π-bond. The ^1H NMR spectrum of the solution of $C_6H_6 \cdot TiCl_2 \cdot Al_2Cl_6$ containing a two-fold molar excess of HMB with respect to the complex shows only a singlet at 303 Hz upfield from benzene and of somewhat larger width at half height (2.7 Hz), in comparison with that of $HMB \cdot TiCl_2 \cdot Al_2Cl_6$ (2.2 Hz), suggesting a reversible exchange reaction between the free and complexed hexamethylbenzene (eqn. 5).

$$HMB \cdot TiCl_2 \cdot Al_2Cl_6 + HMB^{\bigstar} \overset{\text{benzene}}{\rightleftharpoons} HMB^{\bigstar} \cdot TiCl_2 \cdot Al_2Cl_6 + HMB \qquad (5)$$

Reversible exchange of complexed benzene for toluene [3] and mesitylene [4] has been previously observed, whereas the exchange for durene proceeds irreversibly [4]. These results prove the increasing stability of the π-bond between arene and titanium(II) along the methylbenzene series.

$Ar \cdot TiCl_2 \cdot Al_2Cl_6$ complexes dissolved in aromatic solvents show specific conductivity of $\approx 10^{-6}$-10^{-5} Ω^{-1} cm^{-1} (Table 2). These values are much higher than the specific conductivity of benzene [9] and are similar to the conductivity in benzene of the ionic complex $[C_6H_6Ag]^+ClO_4^-$ (36.3 10^{-6} Ω^{-1} cm^{-1}) [9].

The conductivity of solutions of $Ar \cdot TiCl_2 \cdot Al_2Cl_6$ complexes increases as the number of methyl groups in the arene ring increases. In the series of complexes with benzene, toluene, mesitylene and durene the specific conductivity is quite accurately inversely proportional to the ionization potential of the respective arene (Table 2). Due to its poor solubility in benzene, measurements for the $HMB \cdot TiCl_2 \cdot Al_2Cl_6$ complex were carried out at a lower concentration.

Thus $Ar \cdot TiCl_2 \cdot Al_2Cl_6$ complexes have a partly ionic structure:

$$\underset{(A)}{[Ar \cdot TiCl \cdot AlCl_3]^+[AlCl_4]^-} \quad \text{or} \quad \underset{(B)}{[Ar \cdot Ti]^{2+}[AlCl_4]_2^-}$$

In solution these complexes can undergo dissociation according to eqn. 6a or

TABLE 2

SPECIFIC CONDUCTIVITY OF THE SOLUTIONS OF Ar · $TiCl_2$ · Al_2Cl_6 COMPLEXES
Temperature 50°, concentration of Ti^{2+} 0.2 mole/l, except where stated.

Arene	Solvent	Specific conductivity (Ω^{-1} cm^{-1} × 10^6)	Ionization potential of arene [5] (eV)
Benzene	benzene	2.8	9.56
Toluene	toluene	19.1	9.18
Mesitylene	mesitylene	36.0	8.74
Durene	benzene	39.4	8.53
Hexamethylbenzene	benzene	39.4^a	8.15

^{a} 0.1 mole/l of HMB · $TiCl_2$ · Al_2Cl_6.

6b. The degree of dissociation of A or B increases with the decreasing ionization potential of the arene ligand.

The results obtained show that the stability of the arene—titanium(II) π-bond in the Ar · $TiCl_2$ · Al_2Cl_6 complexes increases in the series: benzene < toluene < xylenes < mesitylene < durene < HMB. The degree of dissociation

$$A \rightleftarrows [Ar \cdot TiCl \cdot AlCl_3]^+ + [AlCl_4]^- \qquad (6a)$$

$$B \rightleftarrows [Ar \cdot Ti][AlCl_4]^+ + [AlCl_4]^- \rightleftarrows [Ar \cdot Ti]^{2+} + 2[AlCl_4]^- \qquad (6b)$$

of the complexes increases in the same way. Probably with the increase of π-basicity of the arene the negative charge induced on titanium facilitates the $[AlCl_4]^-$ anion abstraction.

Experimental

All experiments were carried out under dry, deoxygenated N_2. Solvents were distilled over a sodium/potassium alloy and deoxygenated before use. ^{1}H NMR spectra were recorded on the Jeol 60 CH spectrometer. Conductivity measurements were carried out with the Radelkis OK 102/1 conductivity meter, equipped with a coupled electrode (k = 0.75 cm^{-1}).

The Ar · $TiCl_2$ · Al_2Cl_6 complexes were synthesized by the previously described method [4] under the following standard conditions: activation time of metallic aluminium with aluminium trichloride, 40 min.; temperature of activation 130-140°; molar ratio of the reactants, $TiCl_4/Al/AlCl_3$ = 1/3/3; temperature of the reaction, 80°.

For ^{1}H NMR and conductivity measurements freshly prepared solutions of the complexes were used. Their concentrations were determined by measuring the volume of hydrogen evolved during the acid hydrolysis of a sample (eqn. 7) [10].

$$Ti^2 + H^+ \rightarrow Ti^{3+} + \frac{1}{2} H_2 \qquad (7)$$

Gas chromatography revealed no isomerization of the arene in the organic layer after hydrolysis of the methylbenzene complexes.

Acknowledgement

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