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CATIONIC COMPLEXES OF TITANIUM(III) WITH HEXAMETHYLBENZENE

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Summary

The preparation and properties of titanium(III) cationic complexes with hexamethylbenzene are described.

Hexamethylbenzene was found to form monometallic cationic complexes $[(HMBTiCl_2)^+]$ as well as trimetallic cationic clusters $[(HMB_3Ti_3Cl_6)^+]$. Composition of the latter however remains uncertain.

The ability of HMB to form complexes with titanium(III) appears to be unique in the series of polymethylbenzenes.

Introduction

Only a few examples of titanium(III) complexes with aromatic hydrocarbons have been reported in the literature. Fischer and Rohrscheid [1] described the preparation of the paramagnetic trimetallic cationic complexes $(HMB_3Ti_3Cl_6)^+$ by careful hydrolysis of the interaction product from $TiCl_4$, hexamethylbenzene (HMB), Al and $AlCl_3$. Hydrolysis of the solid material obtained by reduction of $TiCl_4$ with $(C_2H_5)_3Al_2Cl_3$ in benzene containing HMB was reported to yield a diamagnetic crystalline complex $HMBTiCl_2OH$ [2]. It is worth noting the fact that neither the IR nor ^{1}H NMR spectra revealed the presence of the [—OH] group in this compound [2].

Previously [3] we have suggested that the titanium(III) species containing the complexed molecule of polymethylbenzene and $AlCl_3$ are formed as intermediates in the course of the reduction of $TiCl_4$ by Al carried out in benzene containing polymethylbenzene and $AlCl_3$ in equimolar amounts to $TiCl_4$. Further reduction of this intermediate leads to the titanium(II) complexes $ArTiCl_2Al_2Cl_6$ (Ar-polymethylbenzene) [3,4]. We now report the preparation and some properties of the titanium(III) hexamethylbenzene cationic complex $(HMBTiCl_2)AlCl_4$ (I) which may be regarded as an intermediate in the synthesis of titanium(II) arene complexes.

Results and discussion

Reaction of $TiCl_4$ with at least twofold excess of $(C_2H_5)_2AlCl$ at 70°C in benzene containing HMB in equimolar amount to $TiCl_4$ yields the black crystalline complex $(HMBTiCl_2)AlCl_4$ (I) (eq. 1).

$$TiCl_4 + HMB \xrightarrow[\text{benzene, }70^\circ\text{C, 3 h}]{(C_2H_5)_2AlCl} (HMBTiCl_2)AlCl_4 \tag{1}$$

Complex I and its derivatives have been characterized by their analytical composition, chemical behaviour, conductometric measurements (Table 1), IR, ESR and electronic spectra.

The infrared spectrum of solid I in nujol, apart from bands assignable to complexed HMB [1,2] contains a single strong absorption at 492 cm^{-1} characteristic of the Al—Cl stretching frequency in $(AlCl_4^-)$ [5].

The complex is insoluble in nonpolar organic solvents. Upon treatment with alcohols, acetone, DMSO or pyridine at low temperature it dissolves forming blue-violet deeply coloured solutions. The visible region electronic spectra of such solutions in pyridine, methanol or DMSO are composed of a strong band at 18700 cm^{-1} and shoulder at 15000 cm^{-1}. The latter most probably corresponds to *d-d* transition in the d^1 system while the former is of arene ligand to metal charge-transfer origin. It is worth noting that upon extended exposure to air this spectrum gradually collapses into low intensity broad unsymmetrical absorption at around 20000 cm^{-1}. Precipitation of pure HMB occurs simultaneously from methanolic solution. The initial colour changes to light red or light brown.

Solutions of I are paramagnetic. In the ESR spectrum of I in pyridine a single sharp resonance accompanied by a set of weak satellites is observed at $g = 1.96$. Such a spectrum is characteristic of the titanium(III) species. The satellites arise from titanium isotopes with odd nuclear spin number [6].

Conductivity measurements performed with a pyridine solution of I show that the complex in solution dissociates with formation of $(HMBTiCl_2)^+$ cation (eq. 2).

TABLE 1

ANALYTICAL DATA AND PHYSICAL PROPERTIES OF TITANIUM(III) CATIONIC COMPLEXES WITH HEXAMETHYLBENZENE

Compound	Colour	Analysis found (calcd.) (%)			HMB/Ti found [a] (mol/mol)	Λ_M [b] (ohm^{-1} cm^2 mol^{-1})
		Ti	Al	Cl		
$(HMBTiCl_2)AlCl_4$	black	10.65 (10.65)	5.37 (6.00)	47.60 (47.28)	0.95	42.5 [c]
$(HMBTiCl_2)PF_6$	black	10.21 (11.24)		15.82 (16.64)	1.02	
$(HMB_3Ti_3Cl_6)Cl \cdot CHCl_3$	violet	13.51 (14.48)		34.73 (35.72)	0.98	60
$(HMB_3Ti_3Cl_6)PF_6$	black-violet	13.43 (14.54)		20.34 (21.65)	0.97	90

[a] By GLC upon hydrolysis with aq. H_2SO_4 and extraction with benzene. [b] In methanol at 25°C for ca. 10^{-3} *M* solutions. [c] In pyridine.

$$(HMBTiCl_2)AlCl_4 \overset{S}{\rightleftharpoons} (HMBTiCl_2)^+ + Cl^- + AlCl_3 \cdot S \qquad (2)$$

The possibility of such dissociation and cationic character of titanium(III) hexamethylbenzene complex were further confirmed by isolation of the complex $(HMBTiCl_2)PF_6$ (II) by exchange of the anion in I for the hexafluorophosphate anion (eq. 3).

$$(HMBTiCl_2)AlCl_4 + KPF_6 \xrightarrow[-70^\circ C]{CH_3OH} (HMBTiCl_2)PF_6 \qquad (3)$$

In the IR spectrum of $(HMBTiCl_2)PF_6$ an absorption at 492 cm^{-1} is no longer present. New bands occur at 865(sh) and 845s cm^{-1} (P—F stretching [1]) and at 555m cm^{-1} (P—F bending [1]). The visible region electronic spectra of II in polar solvents are virtually identical with that of $(HMBTiCl_2)AlCl_4$ solutions.

Reaction of $(HMBTiCl_2)AlCl_4$ with water at low temperature produced $(HMB_3Ti_3Cl_6)Cl \cdot CHCl_3$ (III) which subsequently was converted into its analog $(HMB_3Ti_3Cl_6)PF_6$ (IV). The latter, by comparison of its IR spectrum, molar conductivity and elemental composition, was found to be identical with the compound previously described by Fischer [1]. Electronic spectra of II and IV in methanol were quite similar to those of complexes I and II. This indicates the usefulness of visible region electronic spectra for detection of titanium(III) hexamethylbenzene complexes.

Despite our efforts we failed to isolate $(HMBTiCl_2OH)$ previously reported [2] to be the sole product prepared according to the procedure analogous to the one employed in this work.

Solid material identical to III also results from hydrolysis of titanium(II) complex $HMBTiCl_2Al_2Cl_6$. During the latter reaction evolution of hydrogen is observed. The amount of evolved hydrogen corresponds with oxidation of titanium(II) to titanium(III) (eq. 4).

$$Ti^{+2} + H^+ \rightarrow Ti^{+3} + 0.5\ H_2 \qquad (4)$$

It is worth noting that the cation in III or IV might contain tricoordinate oxygen bonded simultaneously to three titanium centers i.e. its composition is $(HMB_3Ti_3Cl_6O)^+$ (V) instead of $(HMB_3Ti_3Cl_6)^+$. Neither our results nor the data reported by Fischer rule out this possibility. It can nevertheless be concluded that hexamethylbenzene may form with titanium(III) monometallic as well as trimetallic cationic complexes. One of them, namely $(HMBTiCl_2)AlCl_4$ (I), may be regarded as an intermediate in the synthesis of titanium(II) arene complexes.

All our attempts to isolate complexes analogous to I or III with 1,2,4,5-tetramethylbenzene (TMB) were unsuccessful. The product obtained similarly to I has no definite analytical composition. Hydrolysis of $TMBTiCl_2Al_2Cl_6$ [3,4] gives a blue-violet solution which quickly changes its colour to red-brown. Such behaviour is typical of the decomposition of initially formed cationic species. Most probably this reflects greater thermal stability of the titanium(III) hexamethylbenzene complex as compared with the titanium(III) tetramethylbenzene complex.

Experimental

General

All experiments were carried out under dry deoxygenated argon. Solvents were dried and deoxygenated prior to use by known procedures.

Titanium tetrachloride (Fluka AG) was purified by distillation. Diethylaluminium chloride prepared by a known procedure was used without further purification. Potassium hexafluorophosphate (BDH) was used as supplied. Hexamethylbenzene was obtained by alumina catalysed high temperature alkylation of phenol with methanol. The crude product was purified by crystallization from benzene/ethanol and dried in vacuo.

The IR spectra of solids in Nujol mulls were recorded on a Perkin—Elmer model 577 grating spectrophotometer, ESR on a Jeol JES-ME, 3X and electronic spectra on a Specord UV-VIS apparatus. Conductivity measurements were carried out on a Radelkis OK 102/1 conductivity meter equipped with a coupled electrode ($k = 0.705$ cm^{-1}).

The HMB/Ti molar ratio was established by decomposition of the weighed samples with hot H_2SO_4/water solution (1 : 1 by volume) and subsequent extraction of the aqueous layer with benzene. HMB was found to be the sole organic product thus liberated. The amount of HMB was determined by GLC using cyclododecane as internal standard.

Preparation of [(HMBTiCl$_2$)AlCl$_4$]

To a stirred solution of HMB (1.62 g, 10 mmol) and $(C_2H_5)_2AlCl$ (4.68 g, 30 mmol) in 15 cc benzene a solution of $TiCl_4$ (1.90 g, 10 mmol) in 5 cc benzene was added dropwise at room temperature over 15 min. Deposition of a black precipitate and evolution of gas (ethane and ethylene) was observed during the process. Upon addition of $TiCl_4$ the reaction mixture was heated to 70°C and stirred for 3 h. The black precipitate formed was then filtered, washed several times with benzene and dried in vacuo. Yield: 3.9 g of $(HMBTiCl_2)AlCl_4$ (86.5%). IR (Nujol): ν(Al—Cl) 492 cm^{-1}. HMB/Ti molar ratio 0.95.

A similar reaction with 1,2,4,5-tetramethylbenzene does not yield a product with definite analytical composition.

Preparation of (HMBTiCl$_2$)PF$_6$

To a cold (—70°C), stirred solution of $(HMBTiCl_2)AlCl_4$ (0.92 g, 2 mmol) in 50 cc methanol a solution of KPF_6 (0.38 g, 2.07 mmol) in 20 cc methanol was added. It was found necessary to dissolve complexes at low temperature in order to prevent their thermal decomposition due to heat of solvation [1]. The reaction mixture was stirred for 15 min until a black crystalline precipitate started to appear. Precipitation was completed by twofold dilution of the reaction mixture with diethyl ether. The precipitate was collected on a filter, washed with ether and dried. Yield: 0.63 g $(HMBTiCl_2)PF_6$ (75%). IR (Nujol): ν(P—F) 865(sh) and 845s cm^{-1}, γ(P—F) 555m cm^{-1}. HMB/Ti molar ratio 1.02.

Preparation of (HMB$_3$Ti$_3$Cl$_6$)Cl · CHCl$_3$

To a vigorously stirred solid $(HMBTiCl_2)AlCl_4$ (0.4 g, 0.9 mmol) 20 cc of a chilled mixture of H_2O and $CHCl_3$ (1 : 1 by volume) was added at —2°C. The dark blue-violet reaction mixture formed was stirred for 1 h. The layers were then separated and the aqueous layer was additionally extracted with $CHCl_3$. The combined extracts were dried over Na_2SO_4 and evaporated to dryness. Yield: 0.14 g $(HMB_3Ti_3Cl_6)Cl \cdot CHCl_3$. HMB/Ti molar ratio 0.98. IR (nujol): γ(C—Cl) 750s cm^{-1}.

Reactions of $ArTiCl_2Al_2Cl_6$ (Ar-hexamethylbenzene or 1,2,4,5-tetramethylbenzene) were carried out similarly. Evolution of hydrogen was observed in these cases.

Preparation of $(HMB_3Ti_3Cl_6)PF_6$

$(HMB_3Ti_3Cl_6)PF_6$ was prepared from III (0.7 g) and KPF_6 (0.2 g) according to the procedure described by Fischer [1]. Yield: 0.48 g (62%). HMB/Ti molar ratio 0.97.

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References

1 E.O. Fischer and F. Rohrscheid, J. Organometal. Chem., 6 (1966) 53.
2 H. Weber, W. Ring, U. Hochmuth und W. Franke, Liebigs Ann., 681 (1965) 10.
3 R. Gieżyński, S. Dzierzgowski and S. Pasynkiewicz, J. Organometal. Chem., 87 (1975) 295.
4 S. Pasynkiewicz, R. Gieżyński and S. Dzierzgowski, J. Organometal. Chem., 54 (1973) 203.
5 L. Kazicyna and S. Pasynkiewicz, Dokl. Akad. Nauk SSSR, 141 (1961) 624.
6 T. Dzhabiev and A. Shilov, Zhurn. Strukt. Khim., 6 (1965) 302.