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THE SYNTHESIS OF TITANIUM(II) COMPLEXES CONTAINING METHYLBENZENE LIGANDS

S. PASYNKIEWICZ, R. GIEŻYŃSKI and S. DZIERZGOWSKI

Institute of Organic Chemistry and Technology, Technical University (Politechnika), Warsaw (Poland)

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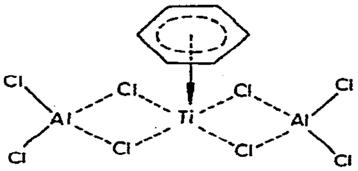
SUMMARY

A new method for the preparation of titanium(II) complexes of the type $Ar \cdot TiCl_2 \cdot Al_2Cl_6$ (where Ar is tetra-, penta- or hexa-methylbenzene) is described. The present work supports the π nature of the bond between the titanium atom and the aromatic ligand as postulated elsewhere.

Titanium(II) and aluminium chloride complexes with aromatic hydrocarbons having the formula $Ar \cdot TiCl_2 \cdot Al_2Cl_6$ (where Ar is benzene, toluene or mesitylene) have been prepared by treating titanium tetrachloride with metallic aluminium and aluminium chloride in the respective aromatic hydrocarbons[1-3].

Martin and Vohwinkel[2,3] have suggested structure (I) for these complexes, based on their chemical and catalytic properties.



(I)

The aromatic hydrocarbon molecule is bonded through a π-bond to the titanium atom while the aluminium chloride molecules are chlorine-bridged with the titanium dichloride. The benzene complex was found to be active as a catalyst in the cyclotrimerization of butadiene[3].

Complexes of tetra-, penta- or hexa-methylbenzenes have not been described hitherto. We now describe the preparation of complexes of the type $Ar \cdot TiCl_2 \cdot Al_2Cl_6$ in which Ar depicts benzene (Bz), mesitylene, 1,2,4,5-tetramethylbenzene (TMB) or hexamethylbenzene (HMB).

All these complexes are crystalline violet solids, soluble in aromatic but insoluble in aliphatic hydrocarbons.

The titanium(II) benzene, toluene and mesitylene complexes are readily obtained by reaction (1).

$$Bz + TiCl_4 + Al + AlCl_3 \xrightarrow{\text{benzene}} Bz \cdot TiCl_2 \cdot Al_2Cl_6 \tag{1}$$

The titanium(II) tetramethylbenzene and the hexamethylbenzene complexes may be prepared by either of the two following routes: (a) Direct synthesis by reduction of

$$HMB + TiCl_4 + Al + AlCl_3 \xrightarrow{\text{benzene}} HMB \cdot TiCl_2 \cdot Al_2Cl_6 \tag{2}$$

titanium tetrachloride with metallic aluminium in the presence of aluminium chloride in benzene containing an equimolar (in relation to $TiCl_4$) amount of the respective polymethylbenzene (eqn. 2) or (b) Ligand exchange reactions between the benzene

$$Bz \cdot TiCl_2 \cdot Al_2Cl_6 + HMB \xrightarrow{\text{benzene}} HMB \cdot TiCl_2 \cdot Al_2Cl_6 + Bz \tag{3}$$

complex and tetra- or hexa-methylbenzene in benzene solution (eqn. 3).

With tetramethylbenzene and higher homologues, reaction (3) proceeds quantitatively but with trimethylbenzenes direct synthesis and ligand exchange reactions result in a mixture of complexes containing both benzene and mesitylene[2].

The rate of direct synthesis depends on the number of the methyl groups attached to the benzene ring. The time required for complete reaction decreases as the degree of substitution of the hydrocarbon increases. For example, using methods (1) and (2) above, the time required for the preparation of the benzene and hexamethylbenzene complexes was 8 h and 20 min respectively.

The quantitative yield obtained in reaction (3) and the formation of a complex of formula $HMB \cdot TiCl_2 \cdot Al_2Cl_6$ confirm the existence of a π-bond between the titanium atom and the aromatic ligand.

EXPERIMENTAL

Direct synthesis

Aluminium metal powder, 2 g (73 mmoles), and freshly sublimed aluminium chloride, 2.7 g (20 mmoles), were mixed under nitrogen and stirred with heating at 130–140° for 30 min. The mixture was then cooled and 1.55 g (10 mmoles) of 1,2,4,5-tetramethylbenzene in 80 cm^3 of dry deoxygenated benzene added. The contents were heated up to the boiling point of the solvent and 1.99 g (10 mmoles) of $TiCl_4$ in 5 cm^3 of benzene was added dropwise over 15 min. The mixture was heated for another 20 min with stirring, then cooled and filtered under a nitrogen atmosphere. Benzene was separated from the dark violet filtrate by evaporation *in vacuo* and 4.2 g of crude product isolated, the yield being 82% based on the $TiCl_4$ used. The crude product was recrystallized from a benzene-n-hexane mixture to give dark violet crystals. This crystalline product was hydrolysed with 10% H_2SO_4 and the hydrolyzate subsequently extracted with n-hexane. Gas chromatographic analysis of the organic layer revealed the presence of only 1,2,4,5-tetramethylbenzene. The amount of TMB was ca. 1 mole of TMB per mole of the complex. (Found: Ti/Al/Cl = 1/2.01/7.99.)

A similar procedure led to the formation of dark violet crystals of the complex $HMB \cdot TiCl_2 \cdot Al_2Cl_6$ in 90% yield. (Found: Ti/Al/Cl = 1/2.04/8.01.)

In a similar manner, a benzene solution of the mesitylene complex was prepared, but in spite of repeated attempts a pure mesitylene complex could not be separated by crystallization. The organic hydrolyzate of the complex contained benzene as well as mesitylene.

Synthesis by ligand exchange

To a solution of 10 mmoles of $Bz \cdot TiCl_2 \cdot Al_2Cl_6$ in 80 cm^3 of benzene, prepared according to the procedure given by Martin and Vohwinkel[2,3], 1.62 g (10 mmoles) of hexamethylbenzene in 10 cm^3 of benzene was added at room temperature. After the reagents had been mixed together dark violet crystals appeared within 10 min. These were filtered, washed with n-hexane and dried *in vacuo* to give 4.3 g (73%) of the complex. Hydrolysis of the crystalline complex with 10% H_2SO_4 and extraction with n-hexane yielded pure hexamethylbenzene in the organic layer (HMB/Ti = 1/1). Benzene was not present during this analysis. (Found: Ti/Al/Cl = 1/2.06/8.07.)

All the complexes were found to be highly sensitive to moisture and air especially when in solution. For this reason, adequate precautions are vital during their preparation and storage.

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