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PREPARATION AND CHARACTERIZATION OF MONOCHLOROTRIS(4-TERT.-BUTYLPHENOXO)TITANIUM(IV)

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Abstract—Monochlorotris(4-tert.-butylphenoxo)titanium(IV) (**1**) has been prepared from titanium tetrachloride and 4-tert.-butylphenol and characterized by elemental analysis, IR, NMR and mass spectral studies. The 1 : 1 addition compounds of **1** with some aliphatic amines have also been prepared. The behaviour of this compound in the presence of strong chloride ion acceptors such as $AlCl_3$, $FeCl_3$, $SbCl_3$ and PCl_5 and $SbCl_5$ has been studied using conductance techniques.

Considerable attention has been focussed on the synthesis of sterically crowded phenoxides of transition metals because of their interesting features such as intramolecular C—H bond activities via the metallation of the tert.-butyl groups of phenoxides,[1] isolation of hydrocarbon soluble compounds in low coordination states,[2] accessibility of hydrocarbon-soluble mononuclear complexes[3] and possible η^5-phenolate bonding.[4–6] Quignard and co-workers[7] claimed that such aryloxide ligands govern both the activity and stereoselectivity by their electronic effects rather than steric effects. In an earlier communication we described the synthesis of titanium tetra-4-tert.-butylphenoxide.[8] In the present report we describe the synthesis and characterization of monochlorotris(4-tert.-butylphenoxo)titanium(IV) and its behaviour in the presence of nitrogenous bases and chloride ion acceptors.

EXPERIMENTAL

$TiCl_4$ (correct chlorine analysis) was used without further purification. 4-Tert.-butylphenol (m.p. 98°C) was recrystallized from benzene. Lewis acids and nitrogenous bases were purified by standard methods given in the literature. Titanium in the presence of aluminium was estimated after precipitation with selenious acid as TiO_2, while antimony did not interfere in the estimation of titanium as TiO_2 by the usual method.[9]

IR spectra were recorded in KBr discs using a Perkin–Elmer spectrophotometer. The ^1H NMR spectrum was obtained using a Varian EM-360 spectrometer and the mass spectrum using a Varian MAT-711 mass spectrometer. Conductance studies were carried out on an Elico conductivity bridge.

Monochlorotris(4-tert.-butylphenoxo)titanium (IV), $TiCl(OC_6H_4Bu^t\text{-}4)_3$ (**1**), was prepared by refluxing titanium(IV) chloride (1 mmol) and 4-tert.-butylphenol (3 mmol) in 1 : 3 molar ratios in dry benzene (50 cm^3) until the evolution of HCl gas ceased. The red coloured solid compound was separated by adding petroleum ether to the concentrated reaction solution. The compound was filtered, recrystallized from chloroform and finally dried *in vacuo*.

Addition compounds of the composition $TiCl(OC_6H_4Bu^t\text{-}4)_3 \cdot 2B$ (B = aliphatic amine) were prepared by adding a benzene solution of a known weight of (0.1 mol) **1** to a benzene solution of the base (0.2 mol). The contents were stirred for 2 h followed by refluxing. The adducts were isolated as solids by evaporating the solution and recrystallization from chloroform and dried *in vacuo*.

Compounds of the composition $TiCl(OC_6H_4Bu^t\text{-}4)_3 \cdot MCl_5$ (M = P, Sb) and $TiCl(OC_6H_4Bu^t\text{-}4)_3 \cdot MCl_3$ (M = Al, Fe, Sb) were prepared by reacting the components in dry benzene under reflux.

RESULTS AND DISCUSSION

Titanium(IV) chloride reacts with 4-tert.-butylphenol in a 1 : 3 stoichiometric ratio as follows:

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$$\mathrm{TiCl_4 + 3HOC_6H_4Bu^t\text{-}4 \xrightarrow[\text{reflux}]{\text{Benzene}} TiCl(OC_6H_4Bu^t\text{-}4)_3 + 3HCl.}$$

The title compound, $\mathrm{TiCl(OC_6H_4Bu^t\text{-}4)_3}$ (**1**), is a red, moisture-sensitive solid melting at 83°C. The compound is soluble in common organic solvents. Found: Ti, 8.9; Cl, 6.6; C, 67.7; H, 7.3. Calc.: Ti, 9.0; Cl, 6.7; C, 67.8; H, 7.3%. The molecular weight of the compound determined cryoscopically in nitrobenzene suggested that it exists as a monomer in this solvent and the molar conductance value of a 10^{-3} M solution in nitrobenzene ($1.67\ \Omega^{-1}\ \mathrm{cm^2\ mol^{-1}}$) suggests it is non-ionic.

In its IR spectrum, the broad band (3400–3500 $\mathrm{cm^{-1}}$) due to the hydrogen bonded —OH group in pure 4-tert.-butylphenol is missing, while the band at 1225 $\mathrm{cm^{-1}}$ assigned to ν(C—O) is significantly lowered by about 55 $\mathrm{cm^{-1}}$. This indicates the involvement of phenolic protons in the reaction as confirmed by the evolution of hydrogen chloride gas during the reaction. Bonding from the oxygen of the phenol to titanium, as evidenced from the lowering of the ν(C—O) bond, is supported by the appearance of entirely new bands in the region 490–520 $\mathrm{cm^{-1}}$, assigned to ν(Ti—O) modes. A sharp band at 385–410 $\mathrm{cm^{-1}}$ may be assigned to ν(Ti—Cl).

The proton NMR spectrum of compound **1** shows a single resonance for the tert.-butyl protons at 1.30 ppm (cf. 1.28 ppm for 4-tert.-butylphenol). The ring protons in the compound appear at H_{ortho} 7.30 and H_{meta} 6.85 ppm (cf. 7.23 and 6.75 in 4-tert.-butylphenol). The downfield shift observed in the resonances of the 4-tert.-butylphenoxo group in the compound as compared to the pure 4-tert.-butylphenol is perhaps associated with the delocalization of electrons from the aromatic nucleus to the titanium atom, thereby resulting in a slight (ArO—Ti) bonding; supported by the earlier reports of Clark and co-workers[10] on sterically congested trisphenoxide complexes of tantalum(V). Chisholm[11] reported in general that —OR ligands are better π-donors than chloride.

The mass spectrum of compound **1** gave the molecular ion peak $[\mathrm{M}]^+$ m/z 530, confirming the information given by molecular weight and IR spectral studies.

Reactions of 1 *with nitrogen bases*

Metal phenoxides, like metal alkoxides, are known to be poorer acceptors than the corresponding metal halides.[12–14] Yoshino and co-workers[15] have also reported that addition compounds of metal phenoxides are comparatively more stable than metal alkoxides. In view of these observations, reactions of **I** with nitrogenous bases have been carried out. Addition compounds of the composition $\mathrm{TiCl(OC_6H_4Bu^t\text{-}4)_3 \cdot 2B}$ were formed on reaction with different amines in benzene. The composition of these adducts was established by elemental analysis (see Table 1). These adducts are hygroscopic, non-electrolytes and exist as monomers as indicated by molecular weight determination cryoscopically in nitrobenzene.

In the IR spectra of the addition compounds, sharp bands in the regions 490–520 $\mathrm{cm^{-1}}$ and 385–410 $\mathrm{cm^{-1}}$ were assigned to ν(Ti—O) and ν(Ti—Cl) modes, respectively. Entirely new bands around 280–290 $\mathrm{cm^{-1}}$ (not present in the parent compound **1**) have been observed and may be assigned to ν(Ti—N) stretching modes.

The most impotant changes observed in the IR spectra of different amines on adduct formation with **1** are those due to ν(NH), ν(C—N) and ν(H—N—C) deformation modes. The trends in the shifts of these bands on coordination with the metal are in agreement with those reported earlier.[16–19] In view of the limited analytical data coupled with IR spectral studies, it is therefore proposed that the complexes of **I** with amines are 1:2 adducts with an octahedral arrangement around titanium.

Behaviour of I *in the presence of chloride ion acceptors*

Stabilization of the cationic complexes of the type $\mathrm{NbT_4^+}$ and $\mathrm{TaT_4^+}$ (T = Tropolone cation) by large symmetrical anions, such as $\mathrm{PF_6^-}$, $\mathrm{I^-}$, $\mathrm{Bi_2Cl_{12}^-}$ and $\mathrm{ClO_4^-}$ and those of $\mathrm{Nb(OPh)_4^+}$ and $\mathrm{Ta(OPh)_4^+}$ by $\mathrm{SbCl_6^-}$ and $\mathrm{AlCl_4^-}$, respectively,[20,21] aroused interest in studying the behaviour of **I** in the presence of some chloride ion acceptors such as pentachlorides of phosphorus and antimony and trichlorides of iron, aluminium and antimony conductometrically in $\mathrm{PhNO_2}$ at room temperature. Solutions of **1** in $\mathrm{PhNO_2}$ are very low conducting but the addition of very dilute solutions of the pentachlorides or the trichlorides in the same solvent results in a significant increase in the conductance of the solution. Conductance–composition curves (Fig. 1) reveal breaks at about 1:1 molar ratio, suggesting the formation of compounds of 1:1 stoichiometry, viz. $\mathrm{TiCl(OC_6H_4Bu^t\text{-}4)_3MCl_5}$ and $\mathrm{TiCl(OC_6H_4Bu^t\text{-}4)_3MCl_3}$, which appear to be ionic in character.

Interestingly, in a parallel experiment, in which the effect of gradual addition of the solutions of Lewis acids to pure $\mathrm{PhNO_2}$ was studied, no significant change in the conductance was observed.

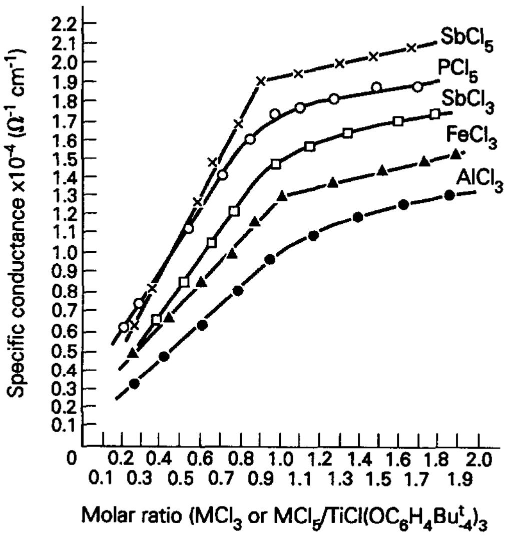

Fig. 1. Conductometric titrations of $TiCl(OC_6H_4Bu^t\text{-}4)_3$ with Lewis acids in nitrobenzene at 25±0.1°C.

These observations therefore support the formation of ionic species via the interaction of **I** with Lewis acids.

These compounds have been actually isolated in separate experiments by reacting the components in dry benzene under reflux. The stoichiometric composition of the compounds has been established by metal and halogen analyses as given in Table 2. The solid compounds obtained from the solutions are high melting. Molar conductance values of millimolar solutions of these compounds in $PhNO_2$ and CH_3CN correspond approximately to those of the 1 : 1 electrolytes reported in literature.[22] Based upon these studies, therefore, the compounds of composition $TiCl(OC_6H_4Bu^t\text{-}4)_3MCl_5$ and $TiCl(OC_6H_4Bu^t\text{-}4)_3MCl_3$ may be assumed to ionize as follows:

$$TiCl(OC_6H_4Bu^t\text{-}4)_3MCl_5 \longrightarrow Ti(OC_6H_4Bu^t\text{-}4)_3^+ + MCl_6^-$$

$$TiCl(OC_6H_4Bu^t\text{-}4)_3MCl_3 \longrightarrow Ti(OC_6H_4Bu^t\text{-}4)_3^+ + MCl_4^-.$$

The low frequency IR spectra of some of these compounds further support the formation of the cations of the type $Ti(OC_6H_4Bu^t\text{-}4)_3$. New bands (not present in the parent compound) at 358, 285 and 622, 335 cm^{-1} appear in compounds of the composition $TiCl(OC_6H_4Bu^t\text{-}4)_3PCl_5$ and $TiCl(OC_6H_4Bu^t\text{-}4)_3SbCl_5$, respectively, and may be assigned to ν(P—Cl) and ν(Sb—Cl) modes in an octahedral environment.[23] Interestingly, the band at 380 cm^{-1} due to the ν(Ti—Cl) mode present in **I**

Table 1. Analytical data and IR spectral data (cm^{-1}) for the complexes of $TiCl(OC_6H_4Bu^t\text{-}4)_3$ with aliphatic amines

Compound	% Found (Calc.) Ti	Cl	Molar conductance in $PhNO_2$ (Ω^{-1} cm^2 mol^{-1})	Molecular weight in $PhNO_2$ Found (Calc.)[a]	ν(Ti—O)	ν(Ti—Cl)	ν(Ti—N)
$TiCl(OC_6H_4Bu^t\text{-}4)_3$ · 2diethylamine	7.1 (7.0)	5.2 (5.2)	1.67	675 (677)	490	385	280
$TiCl(OC_6H_4Bu^t\text{-}4)_3$ · 2n-propylamine	7.3 (7.3)	5.4 (5.4)	1.62	652 (649)	498	392	285
$TiCl(OC_6H_4Bu^t\text{-}4)_3$ · 2sec.propylamine	7.3 (7.3)	5.4 (5.4)	1.65	(649)	502	390	288
$TiCl(OC_6H_4Bu^t\text{-}4)_3$ · 2n-butylamine	7.0 (7.0)	5.2 (5.2)	1.62	(677)	510	410	285
$TiCl(OC_6H_4Bu^t\text{-}4)_3$ · 2t-butylamine	7.1 (7.0)	5.2 (5.2)	1.63	(677)	515	406	290

[a] Molecular weight is the mean of three determinations.

Table 2. Analytical data for the complexes of $TiCl(OC_6H_4Bu^t\text{-}4)_3$ with Lewis acids

Compound	Elemental analysis % Ti Found (Calc.)	% Cl Found (Calc.)	Molar conductance (Ω^{-1} cm^2 mol^{-1}) in $PhNO_2$	CH_3CN
$TiCl(OC_6H_4Bu^t\text{-}4)_3\cdot SbCl_5$	5.8 (5.8)	25.6 (25.6)	19.5	92.3
$TiCl(OC_6H_4Bu^t\text{-}4)_3\cdot PCl_5$	6.4 (6.5)	28.8 (28.8)	20.1	95.0
$TiCl(OC_6H_4Bu^t\text{-}4)_3\cdot AlCl_3$	7.3 (7.2)	32.1 (32.0)	21.2	94.4
$TiCl(OC_6H_4Bu^t\text{-}4)_3\cdot FeCl_3$	7.0 (6.9)	30.7 (30.7)	19.1	90.5
$TiCl(OC_6H_4Bu^t\text{-}4)_3\cdot SbCl_3$	6.3 (6.3)	28.1 (28.0)	20.0	91.2

is missing in these compounds. Similarly, in the case of complexes with trichlorides of aluminium, iron and antimony, $TiCl(OC_6H_4Bu^t\text{-}4)_3MCl_3$, some new bands which were not present in **I** in the region 280–500 cm^{-1} appeared in their IR spectrum and may be considered to arise from the MCl_4^- anionic species.[24–26]

Unfortunately, all attempts to grow single crystals of any of the above isolated compounds were without success. As such, although nothing can be said conclusively, based upon the limited data available at the moment it can be suggested that compound **1** behaves as a Lewis acid in the presence of strong nucleophiles while as a chloride ion donor in the presence of strong Lewis acids.

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