

BIS(PENTACHLOROPHENYL)THALLIUM(III) COMPOUNDS

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Summary

$(C_6Cl_5)_2TiCl$ has been prepared from $TiCl_3$ and C_6Cl_5Li . Derivatives of the type $(C_6Cl_5)_2TiX$ ($X = ClO_4, 1/2 SO_4, CH_3COO$) have been made by treatment of the $(C_6Cl_5)_2TiCl$ with silver salts. The perchlorate group in $(C_6Cl_5)_2TiClO_4$ is readily displaced by several anions to give $(C_6Cl_5)_2TiY$ ($Y = Br, I, CN$) complexes containing anions which cannot be introduced with silver salts.

Introduction

Pentachlorophenyl transition metal complexes have attracted attention because the stabilities of the metal-carbon bonds are even higher than those in analogous compounds containing the C_6F_5 group [1–3]. Among derivatives of post-transition elements, $(C_6Cl_5)_3Tl$ is fairly stable, whereas trialkyl- or triarylthallium(III) derivatives are unstable [4].

We describe below the preparations of several new bis(pentachlorophenyl)thallium(III) compounds $(C_6Cl_5)_2TiX$ ($X = Cl, Br, I, CN, CH_3COO, ClO_4, 1/2 SO_4$). The results of our studies on their Lewis acidities and their use in arylation will be reported later.

Results and discussion

(a) Preparative results

$(C_6Cl_5)_2TiCl$ (I) is conveniently prepared in ether from $TiCl_3$ and LiC_6Cl_5 in a molar ratio 1 : 2:



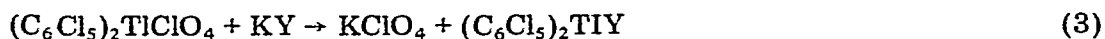
Replacement of the chlorine atom by several anions occur on treating I with the silver salts:



($X = CH_3COO, ClO_4, 1/2 SO_4$)

The reactions with silver acetate and sulphate were carried out in refluxing methanol, while THF was employed for the reaction with silver perchlorate because the increased solubility of both I and the silver salt in this solvent. Reactions with silver perchlorate carried out under apparently identical conditions gave two different solids, as shown by their IR spectra, which are discussed below.

When potassium salts of several anions $Y = \text{Br, I, CN}$, are added to a solution of II in methanol, the perchlorate anion is easily displaced and removed as the insoluble KClO_4 , and $(\text{C}_6\text{Cl}_5)_2\text{TIY}$ compounds V–VII are obtained



The analyses (Table 1) of the products are good.

All the products are unaffected by air and water. Only the iodo derivative VII is reduced to thallos iodide by an excess of KI in aqueous methanol. They also show good thermal stability, and their melting points (Table 1) are higher than those of the analogous bis(pentafluorophenyl) derivatives [5,6]. All these compounds are insoluble in most of the common organic solvents with the exception of THF and hot nitrobenzene, VII being the most soluble. This low solubility precludes molecular weight determinations.

(b) Conductivity

The conductivities of derivatives I–VI in nitrobenzene are shown in Table 2. These values clearly indicate that all the compounds except II are nonconductors in this solvent. The molar conductivity of II is somewhat low for a 1 : 1 electrolyte (for which a value of $20\text{--}30 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ would be expected [7]) and suggests the existence of the equilibrium 4 in solution



The molar conductivity of VII was measured in acetone since it is not sufficiently stable in nitrobenzene.

TABLE I
ANALYTICAL AND PHYSICAL DATA FOR $(\text{C}_6\text{Cl}_5)_2\text{TIx}$ COMPOUNDS

No.	X	Formula	M.p. ($^{\circ}\text{C}$)	Analyses found (calcd.) (%)				
				C	N	H	Cl	Tl
I	Cl	$\text{C}_{12}\text{Cl}_{11}\text{Tl}$	312–313	20.27 (19.52)			52.13 (52.81)	27.93 (27.67)
II	ClO_4	$\text{C}_{12}\text{Cl}_{11}\text{O}_4\text{Tl}$	dec. >240	18.53 (17.98)			49.02 (48.66)	25.42 (25.50)
III	AcO	$\text{C}_{14}\text{H}_3\text{Cl}_{10}\text{O}_2\text{Tl}$	204	22.10 (22.10)		0.41 (0.40)	45.75 (46.59)	26.93 (26.85)
IV	$1/2 \text{SO}_4$	$\text{C}_{24}\text{Cl}_{20}\text{O}_4\text{STl}_2$	dec. 318–320	20.02 (19.22)			47.98 (47.27)	27.01 (27.25)
V	Br	$\text{C}_{12}\text{Cl}_{10}\text{BrTl}$	dec. >228	19.01 (18.46)				26.25 (26.14)
VI	CN	$\text{C}_{13}\text{Cl}_{10}\text{NTl}$	208	22.02 (21.45)	1.84 (1.92)		49.11 (48.70)	27.37 (28.07)
VII	I	$\text{C}_{12}\text{Cl}_{10}\text{ITl}$	dec. >130 ^a	17.83 (17.37)				24.33 (24.62)

^a White needles of $\text{C}_6\text{Cl}_5\text{I}$ are formed above 130°C and then melt at 208°C .

TABLE 2
MOLAR CONDUCTIVITIES OF $(C_6Cl_5)_2TlX$ COMPOUNDS

No.	X	Solvent	$c \times 10^4$ (mol l ⁻¹)	Λ (ohm ⁻¹ cm ² mol ⁻¹)
I	Cl	Nitrobenzene	4.9	1.10
II	ClO ₄	Nitrobenzene	4.8	13.58
III	AcO	Nitrobenzene	5.0	0.02
IV	1/2SO ₄	Nitrobenzene	5.0	0.56
V	Br	Nitrobenzene	5.2	0.67
VI	CN	Nitrobenzene	5.1	3.00
VII	I	Acetone	4.8	12.50

(c) IR Spectra

The absorptions due to the pentachlorophenyl group appear in all the compounds at 1515–1505w, 1340–1330vs, 1298–1293s, 1270w, 1230–1225w, 1210–1200w, 1170–1160ms, 1080–1075m, 855–840 (one or two bands) m, 725–720w, 705w, 688–675 (one or two bands) m, 625–615w, 578–565w and 330–310w cm⁻¹. The spectrum of I shows no bands assignable to $\nu(Tl-Cl)$ above 250 cm⁻¹. The stretching vibration $\nu(Tl-Cl)$ ranges from 342 and 335 cm⁻¹ in $PhTlCl_2$ [8] down to 215 and 130 cm⁻¹ in $(C_6F_5)_2TlCl$ [9], the former compound being monomeric and the latter dimeric in the solid state. Thus the spectrum of I suggests a dimeric structure with bridging chlorine atoms. The isolation of anionic salts of the type $[X_2(C_6Cl_5)_2Tl]NR_4$ by the rupture of the bridge system [10] supports this proposal. We suggest similar structure for V and VII although the stretching vibrations $\nu(Tl-X)$ (X = Br, I) are beyond the range of our spectrophotometer.

The most significant absorptions due to the anion in the remaining compounds are shown in Table 3. We cannot locate $\nu(OCO)_{asym}$ with certainty in the spectrum of III as it is overlapped by a C_6Cl_5 absorption which occurs at about 1510 cm⁻¹. Nevertheless, the separation between $\nu(OCO)_{asym}$ and $\nu(OCO)_{sym}$ is not

TABLE 3
RELEVANT IR ABSORPTIONS DUE TO THE X ANION IN R_2TlX^a COMPOUNDS (cm⁻¹)

R_2TlCN (VI)	R_2TlOAc (III)	R_2TlClO_4 (II)	$R_2TlO_2ClO_2$ (II')	$(R_2Tl)_2SO_4$ (IV)	Assignments
2160m	see text ^b 1405s		1075s	1122s	} $\nu(C\equiv N)$ $\nu_{as}(OCO)$ $\nu_s(OCO)$
		1120– 1020vs	1025m	1090s	
		c	1000s	1075s	} ν_3^d
		638m	913w	990w	
		c	b	b	ν_1^d
			470w	470–460w	ν_4^d ν_2^d

^a R = C_6Cl_5 . ^b Overlapped by C_6Cl_5 absorptions. ^c Absent. ^d Referred to the normal modes of the tetrahedral ClO_4 or SO_4 anion [11].

much greater than 100 cm^{-1} , and this along with the conductivity in solution precludes an ionic or monodentate structure for the acetate anion. The other two possible arrangements, bidentate or bridging, cannot be distinguished by IR data alone [5,8].

The number of bands observed in the spectrum of IV indicates a C_{2v} symmetry for the sulphate anion [11], and we conclude that the anion acts as a bridging bidentate group between the two thallium atoms.

We mentioned above the isolation of two different samples of the perchlorate derivative. One of them II' shows the splitting of the ν_3 mode and the presence of ν_1 and ν_2 modes characteristic of the C_{2v} symmetry of the ClO_4 group. The spectrum of II shows the ν_3 vibration as a broad band between 1120 and 1020 cm^{-1} . Moreover, the spectrum does not contain bands due to ν_1 and ν_2 , as these modes are IR inactive for a T_d symmetry of the ClO_4 anion [12]. This ability of the perchlorate group to act both as coordinated ligand and as a free ion in the same compound is already known [13]. We can attribute this behaviour qualitatively to the interaction of several factors such as the known stability of the linear $\text{R-Tl}^+-\text{R}$ cation [14], the tendency of the thallium atom to increase its coordination number beyond three [10], and the poor donor ability of the perchlorate group.

Experimental

IR spectra were recorded on a Perkin-Elmer 457 spectrophotometer at $4000-250\text{ cm}^{-1}$ using Nujol and Fluoroluble mulls between CsI plates. Conductivities were measured with a Philips PW9501/01 conductimeter. C, H, N analyses were made with a Perkin-Elmer 240 microanalyzer. Thallium was estimated either gravimetrically as Tl_2CrO_4 or volumetrically by titration with KIO_3 . Cl was determined according to [15].

Bis(pentachlorophenyl)thallium(III) chloride (I)

Commercial hydrated thallic chloride was partially dehydrated over P_2O_5 under vacuo for several days and finally dehydrated in ether solution over molecular sieves. A freshly prepared solution of 0.02 mol of LiCl_6 [16] in diethylether was added to a solution of TlCl_3 (3.11 g ; 0.01 mol) in the same solvent at -78°C under nitrogen. The mixture was allowed to warm to room temperature and stirred overnight. It was then treated with saturated aqueous NH_4Cl . The ether layer which contained a precipitate was separated and evaporated to dryness, and the residue was dried over P_2O_5 . Recrystallization from hot nitrobenzene gave white crystals, which were repeatedly washed with warm benzene and hexane and finally dried at 140°C for several hours. Yield 65%.

Bis(pentachlorophenyl)thallium(III) perchlorate (II)

AgClO_4 (0.08 g ; 0.39 mmol) in THF (30 ml) was added dropwise to a stirred solution of I (0.29 g ; 0.39 mmol) in THF (60 ml). The AgCl was filtered off and the solution partially evaporated. Addition of benzene gave II as white crystals, which were repeatedly washed with benzene and dried under vacuum. Yield 60%.

Bis(pentachlorophenyl)thallium(III) acetate (III)

A mixture of AgOAc (0.068 g ; 0.41 mmol) and I (0.30 g ; 0.41 mmol) in

methanol (75 ml) was refluxed for 6 h. The precipitate was filtered off, the filtrate was concentrated, benzene was added and the mixture cooled to give III. Yield ca. 65%.

Di[bis(pentachlorophenyl)thallium(III)]sulphate (IV)

This was obtained as above from I (0.30 g; 0.41 mmol) and Ag_2SO_4 (0.064 g; 0.205 mmol) with 7 h refluxing. Yield 70%.

Bis(pentachlorophenyl)thallium(III) bromide (V)

A mixture of KBr (0.09 g; 0.78 mmol) and II (0.31 g; 0.39 mmol) in methanol (15 ml) was stirred at 30–40°C for 2 h. Water was added, and the precipitate was dried over P_2O_5 . Yield 55%.

Bis(pentachlorophenyl)thallium(III) cyanide (VI)

This was obtained from KCN (0.05 g; 0.78 mmol) and II (0.31 g; 0.39 mmol) as described for V. Yield ca. 55%.

Bis(pentachlorophenyl)thallium(III) iodide (VII)

A mixture of KI (0.06 g; 0.39 mmol) and II (0.31 g; 0.39 mmol) in anhydrous methanol (15 ml) at 0°C was stirred for 1 h. The yellow solution was filtered then concentrated under reduced pressure, and VII was precipitated by addition of benzene. It was recrystallized from diethyl ether-hexane. Yield ca. 30%.

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References

- 1 M.D. Rausch and F.E. Tibbetts, *J. Organometal. Chem.*, **21** (1970) 487.
- 2 J.M. Coronas and J. Sales, *J. Organometal. Chem.*, **94** (1975) 107.
- 3 R. Usón, A. Laguna and J. Pardo, *Syn. React. Inorg. Metalorg. Chem.*, **4** (1974) 499.
- 4 S. Numata, H. Kurosawa and R. Okawara, *J. Organometal. Chem.*, **102** (1975) 259.
- 5 G.B. Deacon, J.H.S. Green and R.S. Nyholm, *J. Chem. Soc.*, (1965) 3411.
- 6 G.B. Deacon and J.C. Parrot, *J. Organometal. Chem.*, **15** (1968) 11.
- 7 W.J. Geary, *Coord. Chem. Rev.*, **7** (1971) 81.
- 8 A.G. Lee, *J. Organometal. Chem.*, **22** (1970) 537.
- 9 G.B. Deacon, J.H.S. Green and W. Kynaston, *J. Chem. Soc. A*, (1967) 158.
- 10 P. Royo and R. Serrano, to be published.
- 11 K. Nakamoto, *Infrared Spectra of Inorganic and Coordination Compounds*, Wiley Interscience, New York, 1970.
- 12 B.J. Hathaway and A.E. Underhill, *J. Chem. Soc. A*, (1961) 3091.
- 13 G.A. Rodley and P.W. Smith, *J. Chem. Soc.*, (1967) 1580.
- 14 A.G. Lee, *Quart. Rev.*, **24** (1970) 310.
- 15 D.C. White, *Microchem. Acta*, (1961) 449.
- 16 M.D. Rausch, G.A. Moser and C.F. Meade, *J. Organometal. Chem.*, **51** (1973) 1.