PREPARATION AND PROPERTIES OF STABLE MONO-, TRIS-, TETRAKIS- OR HEXAKIS(PENTAHALOPHENYL)THALLIATE(III) COMPLEXES

R. USÓN, A. LAGUNA and J.A. ABAD

Department of Inorganic Chemistry, University of Zaragoza (Spain)

(Received February 4th, 1980)

Summary

Reaction of TlR_2X, TlX_3 and $[TlX_4]^-$ with RLi (R = C_6F_5 or C_6Cl_5) leads to derivatives containing anions of the types $[TlR_4]^-$, $[TlR_2R'_2]^-$ or $[TlR_6]^{3-}$. Reactions of $TlCl_3$ with $[TlR_4]^-$ lead to $[(\mu\text{-}Cl)(TlR_2Cl)_2]^-$ (R = C_6F_5) or $[TlRCl_3]^-$ (R = C_6Cl_5) while addition of X^- (X = Br^- or SCN^-) to $Tl(C_6Cl_5)_3$ gives $[Tl(C_6Cl_5)_3X]^-$. All the novel anions were isolated as salts of bulky cations (Me_4N, Bu_4N, PPN or Ph_3BzP).
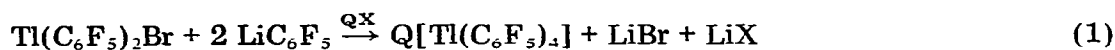
Introduction

Organothallium complexes containing the C_6F_5 group have received some attention in recent years [1—5], but, in spite of their higher thermal stability [6], only a few derivatives containing the C_6Cl_5 group have been reported, $Tl(C_6Cl_5)_3$ [7], $Tl(C_6Cl_5)_3L$ (L = amine) [7] and $Tl(C_6Cl_5)_2X$ (X = halogen) [6]. Few anionic derivatives of the general formulae [3,8,9] $[TlRX_3]^-$, $[TlRX_4]^{2-}$, $[TlR_3X]^-$ and only a single tetraalkylthalliate(III), $Li[TlMe_4]$ [10], have been described. No organothalliate(III) with a coordination number higher than 5 has previously been reported. We describe below the preparation of anionic arylthallium derivatives, some of which, viz $[TlR_4]^-$, $[TlR_2R'_2]^-$ and $[TlR_6]^{3-}$, do not contain any ancillary ligand. Some of the results were the subject of a preliminary communication [11].
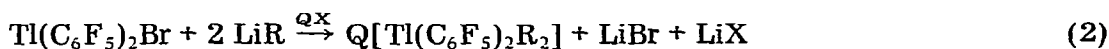
Results and discussion

Tetraaryl derivatives ·

Mixed or homoleptic tetraarylthalliate have been obtained by the following processes (eqn. 1—4)

$$Tl(C_6F_5)_2Br + 2\ LiC_6F_5 \xrightarrow{QX} Q[Tl(C_6F_5)_4] + LiBr + LiX \tag{1}$$

X = Cl, Br; Q = Et_4N, Bu_4N, Ph_3BzP

$$Tl(C_6F_5)_2Br + 2 LiR \xrightarrow{QX} Q[Tl(C_6F_5)_2R_2] + LiBr + LiX \tag{2}$$

$$R = C_6H_5, C_6Cl_5; Q = Bu_4N, Ph_3P=N=PPh_3$$

$$TlCl_3 + 4 LiC_6F_5 \xrightarrow{QX} Q[Tl(C_6F_5)_4] + 3 LiCl + LiX \tag{3}$$

$$X = Cl, Br; Q = Bu_4N, Ph_3BzP$$

$$Q[TlX_4] + 4 LiR \rightarrow Q[TlR_4] + 4 LiX \tag{4}$$

$$R = C_6F_5, C_6Cl_5; Q = Me_4N, Et_4N, Bu_4N$$

All the tetraarylthalliates (I—VII, see Table 1), isolated as salts of bulky cations, are white air- and moisture-stable crystals. They are soluble (less so for those containing C_6Cl_5) in polar solvents, such as acetone and nitromethane, and the conductivities of the solutions are those expected for 1 : 1 electrolytes (see Table 1).

TABLE 1

ANALYTICAL DATA FOR COMPLEXES I—XV

	Complex	Analysis found (calcd.) (%)				Λ_M	m.p. (°C)
		C	H	N	Tl		
I	$Et_4N[Tl(C_6F_5)_4]$	38.43 (38.32)	1.93 (2.01)	1.32 (1.40)	20.01 (20.37)	117 [a]	132(d)
II	$Bu_4N[Tl(C_6F_5)_4]$	43.57 (43.08)	3.20 (3.25)	1.35 (1.26)	18.30 (18.33)	99 [a]	127(d)
III	$Ph_3BzP[Tl(C_6F_5)_4]$	48.93 (48.40)	2.11 (1.81)		16.52 (16.67)	100 [a]	128
IV	$Me_4N[Tl(C_6Cl_5)_4]$	27.16 (26.36)	1.04 (0.95)	1.56 (1.10)	16.24 (16.02)	98 [a]	205(d)
V	$Bu_4N[Tl(C_6Cl_5)_4]$	34.01 (33.27)	2.63 (2.51)	1.17 (0.97)	15.06 (14.15)	91 [a]	196(d)
VI	$Bu_4N[Tl(C_6F_5)_2(C_6Cl_5)_2]$	38.49 (37.96)	2.89 (2.87)	1.04 (1.11)	16.85 (16.14)	85 [a]	142(d)
VII	$PPN[Tl(C_6F_5)_2(C_6H_5)_2]$	58.41 (58.53)	3.06 (3.27)	1.51 (1.14)	16.37 (16.60)	86 [a]	94
VIII	$[Bu_4N]_3[Tl(C_6F_5)_6]$	51.44 (52.16)	5.46 (5.63)	2.54 (2.17)	11.29 (10.57)	288 [b]	63
IX	$Bu_4N[Tl(C_6F_5)_3Cl]$	40.52 (41.52)	3.44 (3.69)	1.26 (1.42)	20.36 (20.78)	97 [a]	83
X	$Bu_4N[Tl(C_6Cl_5)_3Br]$	31.06 (32.04)	2.65 (2.85)	1.14 (1.10)	15.85 (16.03)	90 [a]	145
XI	$Ph_3BzP[Tl(C_6Cl_5)_3NCS]$	39.21 (38.75)	1.68 (1.63)	0.98 (1.03)	15.28 (14.98)	92 [a]	182(d)
XII	$Ph_3BzP[Tl(C_6F_5)Cl_3]$	45.25 (44.79)	2.64 (2.66)		24.62 (24.59)	127 [a]	127
XIII	$Bu_4N[Tl(C_6Cl_5)Cl_3]$	32.71 (32.93)	3.63 (3.77)	1.82 (1.75)	24.57 (25.47)	120 [a]	121(d)
XIV	$Bu_4N[(\mu\text{-Cl})\{Tl(C_6F_5)_2Cl\}_2]$	33.16 (33.70)	2.51 (2.55)	1.07 (0.98)	28.97 (28.67)	114 [a]	152
XV	$Bu_4N[(\mu\text{-Cl})\{Tl(C_6F_5)_3\}_2]$	37.20 (36.98)	2.34 (2.15)	0.73 (0.83)	24.29 (24.20)	83 [a]	107

[a] In acetone. [b] In nitromethane.

*Hexaaryl derivative*

If reaction 1 is carried out in 1 : 6 molar ratio and [Bu$_4$N]X is added in 1 : 3 molar ratio a precipitate is obtained which after recrystallization from dichloromethane-hexane is identified as (Bu$_4$N)$_3$[Tl(C$_6$F$_5$)$_6$] (VIII). It is less stable than the tetraarylderivatives and decomposes when exposed to IR radiation. The proposed formula is confirmed by elemental analysis (see Table 1) and by conductance studies; the plot of its equivalent conductance versus $\sqrt{c}$ gives a straight line with tangent 1134, indicating a 1 : 3 electrolyte.

It was not possible to prepare pentacoordinated species by adjusting the LiR and/or QX ratios, and the reaction in every case gave the hexaaryl derivative, though in lower yields.

Other anionic aryl derivatives (IX—XV)

Ether solutions of thallium(III) chloride react with Q[Tl(C$_6$F$_5$)$_4$] (see eqn. (5)) with precipitation of Q[{Tl(C$_6$F$_5$)$_2$Cl}$_2$Cl] (XIV), and the compound Q[Tl(C$_6$F$_5$)$_3$Cl] (IX) (Q = Bu$_4$N) can be isolated from the solution.

$$TlCl_3 + Q[Tl(C_6F_5)_4] \xrightarrow{\text{OEt}_2} Q[\{Tl(C_6F_5)_2Cl\}_2] + Q[Tl(C_6F_5)_3Cl] \qquad (5)$$
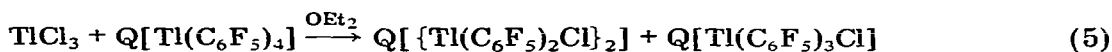
A similar reaction of Q[Tl(C$_6$Cl$_5$)$_4$] in dichloromethane proceeds according to eqn. 6 to give a mixture of tris(pentachlorophenyl)thallium(III) and the

$$TlCl_3 + Q[Tl(C_6Cl_5)_4] \xrightarrow{CH_2Cl_2} Tl(C_6Cl_5)_3 + Q[Tl(C_6Cl_5)Cl_3] \qquad (6)$$
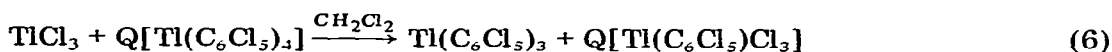
anionic complex (XIII).

A derivative of the general formula Q{Tl(C$_6$F$_5$)Cl$_3$] can be prepared by treating Q[TlCl$_4$] with Tl(C$_6$F$_5$)$_2$Cl in CH$_2$Cl$_2$ solution.

Another example of the substitution of halogen atoms by aryl groups is that shown in eqn. 7 (Q = Bu$_4$N)

$$Q[Tl(C_6F_5)_4] + Tl(C_6F_5)_2Cl \rightarrow Q[(C_6F_5)_3Tl\text{—}Cl\text{—}Tl(C_6F_5)_3] \qquad (7)$$
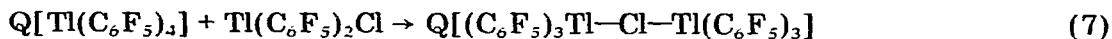
This gives a binuclear single-bridged complex. With Tl(C$_6$F$_5$)$_2$NCS this reaction takes a similar course, giving an oil whose IR spectrum is that expected for Q[(C$_6$F$_5$)$_3$Tl—NCS—Tl(C$_6$F$_5$)$_3$], though the complex could not be crystallized.

Finally, the addition of halide or pseudohalide to Tl(C$_6$Cl$_5$)$_3$ leads, to anionic derivatives of the type Q[Tl(C$_6$Cl$_5$)$_3$X]:

$$Tl(C_6Cl_5)_3 + QX \rightarrow Q[Tl(C_6Cl_5)_3X] \qquad (8)$$

X = Br, SCN; Q = Bu$_4$N, Ph$_3$BzP

IR spectra

All the pentafluorophenylthalliate(III) complexes show the vibrations characteristic of the C$_6$F$_5$ group. In compounds of the type C$_6$F$_5$X no band has hitherto been assigned to the pure stretching C—X, though in the 800—750 cm^{-1} region there is an X-sensitive absorption which is assignable [13—15] to a mode involving predominantly C—X stretching and which can be related to the symmetry of the compound, as has been reported for Tl [14], Pd and Pt [16,17] complexes.

This X-sensitive absorption appears as a single band (t_{1u} or t_2, respectively)

TABLE 2

INFRARED SPECTRA

	ν(Tl—C)^a (cm^{-1})	ν(Tl—Cl) (cm^{-1})
Et$_4$N[Tl(C$_6$F$_5$)$_4$]	762vs	
Bu$_4$N[Tl(C$_6$F$_5$)$_4$]	765s	
Ph$_3$BzP[Tl(C$_6$F$_5$)$_4$]	765s	
Bu$_4$N[Tl(C$_6$F$_5$)$_2$(C$_6$Cl$_5$)$_2$]	760m, 754m	
PPN[Tl(C$_6$F$_5$)$_2$(C$_6$H$_5$)$_2$]	778m, 770m	
[Bu$_4$N]$_3$[Tl(C$_6$F$_5$)$_6$]	764m	
Bu$_4$N[Tl(C$_6$F$_5$)$_3$Cl]	790m, 770m	250m
Ph$_3$BzP[Tl(C$_6$F$_5$)Cl$_3$]	b	295s, 280s
Bu$_4$N[(μ-Cl){Tl(C$_6$F$_5$)$_2$Cl}$_2$]	790s, 778m	255m, 201m
Bu$_4$N[(μ-Cl){Tl(C$_6$F$_5$)$_3$}$_2$]	775s, 768s (sh)	205m
Me$_4$N[Tl(C$_6$Cl$_5$)$_4$]	828s	
Bu$_4$N[Tl(C$_6$Cl$_5$)$_4$]	829s	
Bu$_4$N[Tl(C$_6$F$_5$)$_2$(C$_6$Cl$_5$)$_2$]	828s (br)	
Bu$_4$N[Tl(C$_6$Cl$_5$)$_3$Br]	835m, 828m	
Ph$_3$BzP[Tl(C$_6$Cl$_5$)$_3$NCS]	938vs (br)	
Bu$_4$N[Tl(C$_6$Cl$_5$)Cl$_3$]	825m	298vs, 285s (sh)

^{a} See text. ^{b} Probably masked by absorptions due to the cation.

in complexes containing [Tl(C$_6$F$_5$)$_6$]$^{3-}$ (O_h) or [Tl(C$_6$F$_5$)$_4$]$^-$ (T_d) and is split if the symmetry is lowered so that two bands (a_1 and e) are observed for [Tl-(C$_6$F$_5$)$_3$Cl]$^-$ and [(μ-Cl){Tl(C$_6$F$_5$)$_3$}$_2$]$^-$ (C_{3v}), two (a_1 and b_1) for [Tl(C$_6$F$_5$)$_2$R$_2$]$^-$ (C_{2v}) and two (a' and a'') for [(μ-Cl){Tl(C$_6$F$_5$)$_2$Cl}$_2$] (C_s). The single band expected for [Tl(C$_6$F$_5$)Cl$_3$]$^-$ is masked by the vibrations of the cation (Ph$_3$BzP) which fall in the same region.

The pentachlorophenyl derivatives show the expected vibrations [18] along with one or two bands at about 830 cm^{-1} which were previously observed for Hg [19], Au [20] and Tl [7] derivatives and which must be analogous to the absorptions of C$_6$F$_5$X derivatives considered above. These absorptions are sensitive (though less so than in the case of the C$_6$F$_5$ complexes) to the change of the central cation, the geometries and the nature of the various ligands present. The absorptions expected for [Tl(C$_6$Cl$_5$)$_3$Br]$^-$ (C_{3v}), [Tl(C$_6$Cl$_5$)$_3$NCS]$^-$ (C_{3v}) and [Tl(C$_6$F$_5$)$_2$(C$_6$Cl$_5$)$_2$]$^-$ (C_{2v}) are only observed in the first case, whilst the other two complexes exhibit a single assymetric band.

[Tl(C$_6$Cl$_5$)$_4$]$^-$ and [Tl(C$_6$Cl$_5$)Cl$_3$]$^-$ show a single band, as expected. The vibrations due to ν(Tl—Cl)$_{terminal}$ are observed at 300—250 cm^{-1} (Table 1) whilst those due to ν(Tl—Cl)$_{bridge}$ are located at lower frequencies (205—201 cm^{-1}) which is in good agreement with literature data [15,21].

The absorption assignable to ν(CN) [22] is located at 2090 cm^{-1} in [Tl-(C$_6$Cl$_5$)$_3$NCS]$^-$ and the standard ratio of 1.0 points to an N-bonded complex [22].

Experimental

IR spectra were recorded on a Perkin Elmer 599 spectrophotometer (over the range 4000—200 cm^{-1}) using Nujol mulls between polyethylene sheets.

Conductivities were measured in approx. 5×10^{-4} M acetone or nitromethane solutions with a Philips PW 9501/01 conductimeter. C, H and N analyses were carried out with a Perkin Elmer 240 microanalyzer. Thallium was determined according to ref. 24.

The analytical data, melting points and conductivities of the novel complexes are listed in Table 1.

Preparation of the complexes $Q[TlR_4]$ ($R = C_6F_5$, C_6Cl_5) and $Q[Tl(C_6F_5)_2R_2]$ ($R = C_6H_5$, C_6Cl_5)

These were synthesized by three different methods A). To 50 ml of an ether or toluene solution of 6 mmol of LiR at −78°C (R = C_6F_5 [25]), at −10°C (R = C_6Cl_5 [26]) or room temperature (R = C_6H_5 [27]) was added Tl-$(C_6F_5)_2$Br [1] (0.93 g, 1.5 mmol). After a few minutes, QX (1.5 mmol) was added. The mixture was allowed to warm to room temperature and stirred for 4 h under nitrogen. After 10 minutes exposure to air to hydrolyze the excess of the lithium derivative, the solution was filtered and the filtrate evaporated to dryness. The white residue was recrystallized from dichloromethane-hexane. The initially formed oils gave crystals after vigorous stirring. Yields: Complex I (97%), II (54%), VI (71%) and VII (41%)

(B) $TlCl_3$ (2.17 g, 7 mmol) was added to a solution of 42 mmol of LiC_6F_5 in 80 ml of ether at −78°C and stirred for 15 min. Addition of Bu_4NBr (2.24 g, 7 mmol) and work up as before led to complex II (89% yield). For complex III: after 3 h stirring at room temperature and removal of the excess of the lithium derivative with a few drops of water (to avoid its reaction with the phosphonium chloride) [Ph_3BzP]Cl (7 mmol) was added. Yield 96%.

(C) 2 mmol of $Q[TlCl_3Br]$ (obtained by reacting equimolecular amounts of $TlCl_3$ with QBr) were added to an ether solution of RLi. Work-up as in method A gave the complexes I (Yield 30%). II (60%), IV (50%) and V (78%).

Preparation of $[Bu_4N]_3$ $[Tl(C_6F_5)_6]$

To an ether solution of C_6F_5Li (6 mmol) at −78°C were added $Tl(C_6F_5)_2$Br (0.62 g, 1 mmol) and Bu_4NBr (0.96 g, 3 mmol). The mixture was stirred for 1 h, and slowly allowed to warm to 0°C (2 h). The white precipitate was filtered off and recrystallized from dichloromethane-hexane to give complex VIII (44% yield).

Reaction of $Bu_4N[Tl(C_6F_5)_4]$ and $TlCl_3$

A mixture of $Bu_4N[Tl(C_6F_5)_4]$ (2.24 g, 2 mmol) and $TlCl_3$ (0.62 g, 2 mmol) was dissolved in ether (60 ml) and stirred for 48 h at room temperature. The slowly formed white precipitate was recrystallized from ethanol and identified as XIV (16% yield). The ether filtrate was evaporated to dryness to give an oil which crystallized upon stirring with dibutyl ether. The white solid was recrystallized from dichloromethane-hexane and identified as IX (88% yield).

Reaction of $Bu_4N[Tl(C_6Cl_5)_4]$ and $TlCl_3$

Reaction of a mixture of $Bu_4N[Tl(C_6Cl_5)_4]$ (0.90 g, 0.62 mmol) and $TlCl_3$ (0.19 g, 0.62 mmol) in 40 ml of CH_2Cl_2 immediately gave a white solid. Further amounts of this solid were obtained by concentrating the solution to ca. 20 ml.

The solid was filtered off and identified as $Tl(C_6Cl_5)_3$ (46.5% yield referred to total Tl). The filtrate was evaporated to ca. 5 ml, and XIII crystallized out upon addition of hexane (XIII, 37% yield).

$Ph_3BzP[Tl(C_6F_5)Cl_3]$

To a solution of $Ph_3BzP[TlCl_4]$ (0.70 g, 1 mmol) in dichloromethane (30 ml) was added $Tl(C_6F_5)_2Cl$ (0.57 g, 1 mmol). After 2 h stirring at room temperature the solution was evaporated to dryness and the residue was treated with ether. The insoluble white solid was recrystallized from dichloromethane-hexane and identified as XII (56% yield), ca. 50% of the used $Tl(C_6F_5)_2Cl$ can be recovered from the ether solution.

$Bu_4N[(\mu\text{-}Cl)\{Tl(C_6F_5)_3\}_2]$

An ether solution (50 ml) of $Bu_4N[Tl(C_6F_5)_4]$ (0.56 g, 0.5 mmol) and $Tl(C_6F_5)_2Cl$ (0.29 g, 0.5 mmol) was stirred for 6 h at room temperature. Evaporation to ca. 10 ml and addition of hexane gave a white solid, which was recrystallized from dichloromethane-hexane. (Complex XV, 73% yield).

$Q[Tl(C_6Cl_5)_3X]$ $(X = Br \text{ or } SCN)$

To a suspension of $Tl(C_6Cl_5)_3$ (0.48 g, 0.5 mmol) in 30 ml of dichloromethane was added an equimolecular amount of Bu_4NBr or $Ph_3BzP(SCN)$. The solution immediately became colourless. It was stirred for 1 h at room temperature then evaporated, and the residue was recrystallized from dichloromethane-hexane to give complex X (83%) or XI (77%) as white crystals.

References

1 G.B. Deacon, J.H.S. Green and R.S. Nyholm, J. Chem. Soc., (1965) 3411.
2 J.L.W. Polhman and F.E. Brinckmann, Z. Naturforsch., 20b (1965) 5.
3 G.B. Deacon and J.C. Parrot, J. Organometal. Chem., 15 (1968) 11.
4 R.S. Nyholm and P. Royo, J. Chem. Soc., Chem. Commun., (1969) 421.
5 R. Usón, P. Royo and A. Laguna, J. Organometal. Chem., 69 (1974) 361.
6 P. Royo and R. Serrano, J. Organometal. Chem., 136 (1977) 309.
7 S. Numata, H. Kurosawa and R. Okawara, J. Organometal. Chem., 102 (1975) 259.
8 G. Faraglia, L.R. Fiorani, B.L. Pepe and R. Barbieri, Inorg. Nucl. Chem. Lett., 2 (1966) 277; J. Organometal. Chem., 10 (1967) 363.
9 T. Ehemann and K. Dehnicke, J. Organometal. Chem., 71 (1974) 191.
10 A.T. Weibel and J.P. Oliver, J. Organometal. Chem., 74 (1974) 155.
11 R. Usón, A. Laguna, J. Vicente and J.A. Abad. J. Organometal. Chem., 131 (1977) C5.
12 R.D. Feltham and R.G. Hayter, J. Chem. Soc. A, (1964) 4587
13 D.A. Long and D. Steele, Spectrochim. Acta, 19 (1963) 1955.
14 G.B. Deacon and J.H.S. Green, Spectrochim. Acta A, 24 (1968) 1125.
15 G.B. Deacon, J.H.S. Green and W. Kynaston, J. Chem. Soc., (1967) 158.
16 R. Usón, J. Forniés, F. Martínez and M. Tomás, J. Chem. Soc., Dalton, in press.
17 R. Usón, J. Forniés, J. Gimeno, P. Espinet and R. Navarro J. Organometal. Chem., 81 (1974) 115.
18 J. Casabó, J.M. Coronas and J. Sales, Inorg. Chim. Acta, 11 (1974) 5.
19 F.E. Paulik. S.I.E. Green and R.E. Dessy J. Organometal. Chem., 3 (1965) 229.
20 R. Usón, A. Laguna and J. Pardo, Synth. React. Inorg. Metal-Org. Chem., 4 (1974) 499.
21 A.G. Lee, J. Organometal. Chem., 22 (1970) 537.
22 K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds 3rd Ed., Wiley-Interscience, New York, 1978, p. 270.
23 R.A. Bailey, T.W. Michelsen and W.N. Mills, J. Inorg. Nucl. Chem., 33 (1971) 3206.
24 A.I. Vogel, Quantitative Inorganic Analysis, Longmans-Green, London, 1951, p. 447.
25 P.L. Coe, R. Stephens and J.G. Tatlow, J. Chem. Soc. A, (1962) 3227.
26 M.D. Rausch, F.E. Tibbetts and H.B. Gordon, J. Organometal. Chem., 5 (1966) 493.
27 W.J. Trepka and R.J. Sonnenfeld, J. Organometal. Chem., 16 (1969) 317.