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Reactions of thallium(III) chloride with (aryl)silver(I) complexes. Crystal structure of $[Tl(mes)_2][TlCl_3(mes)]$ (mes = mesityl)

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Abstract

The arylsilver derivatives AgR (R = mesityl, $C_6F_3H_2$, C_6F_5) react with $TlCl_3$ to give arylthallium(III) complexes of the types $[TlR_2][TlCl_3R]$, $TlClR_2$ or TlR_3. The structure of $[Tl(mes)_2][TlCl_3(mes)]$ has been established by X-ray crystallography; it consists of linear $[Tl(mes)_2]^+$ cations and tetrahedral $[TlCl_3(mes)]^-$ anions, linked into chains by additional weak Tl...Cl interactions.

Introduction

We recently reported the use of (polyhalophenyl)silver(I) complexes as arylating agents for halogold-(I), -(II) or -(III) derivatives [1]. We have now extended the study to the synthesis of arylthallium(III) complexes of the types $[TlR_2][TlCl_3R]$, $TlClR_2$ or TlR_3 (where R = C_6F_5, 2,4,6-$C_6F_3H_2$ or mesityl) by the reaction of AgR with thallium(III) chloride.

Results and discussion

The syntheses of AgC_6F_5, $Ag(C_6F_3H_2)$, and Ag(mes) (mes = mesityl) have been described elsewhere [1–3]. The reaction of AgR with $TlCl_3$ gives different products, depending on the molar ratio and the R group. For a $TlCl_3$/AgR ratio of 1/1.5,

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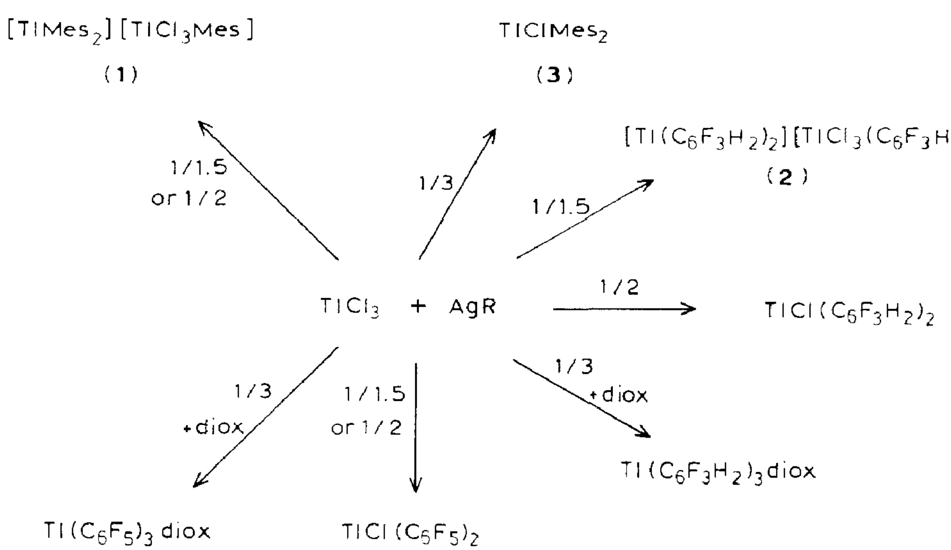

Scheme 1

$[TlR_2][TlCl_3R]$ is obtained for R = mes (**1**, 53% yield) or $R = C_6F_3H_2$ (**2**, 55% yield), but $TlClR_2$ (45% yield) for $R = C_6F_5$ (Scheme 1). (The last compound had already been prepared by other means [4,5].) Complexes **1** and **2** are air- and moisture-stable white solids. They are soluble in acetone, dichloromethane, chloroform, and nitromethane, and slightly soluble or insoluble in diethyl ether and aliphatic hydrocarbons.

The structure of complex **1** was established by X-ray diffraction studies. Single crystals were obtained by slow diffusion of diethyl ether into a concentrated dichloromethane solution of **1** at $-10\,^\circ$C. The complex (Fig. 1) consists to a first approximation of isolated $[Tl(mes)_2]^+$ cations and $[TlCl_3(mes)]^-$ anions. The cations are essentially linear at thallium (C–Tl–C 173.1(4)°), with Tl–C bond lengths of 2.121(11), 2.131(10) Å and a dihedral angle of 9° between the aromatic rings.

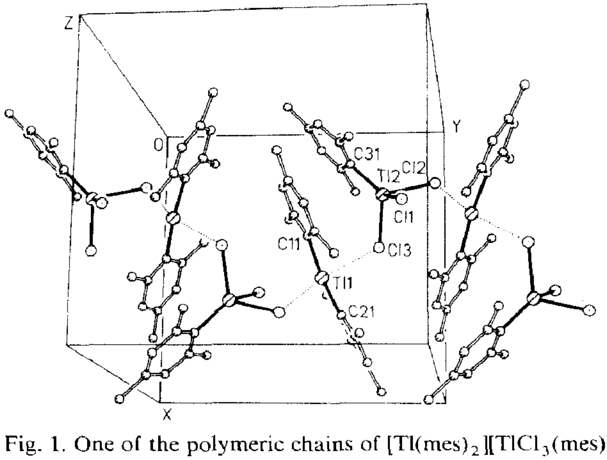

Fig. 1. One of the polymeric chains of $[Tl(mes)_2][TlCl_3(mes)]$ in the unit cell; the other chain (related by a centre of symmetry) is omitted. Radii are arbitrary. The weak Tl...Cl contacts are indicated by dotted lines.

Isolated TlR_2^+ cations are well known for R = Me [6], but we are not aware of any other examples R = aryl; thallium(III) has an appreciable tendency to increase its coordination number by dimer or polymer formation, often involving irregular coordination geometry (see, e.g., refs. 7). The anions adopt a somewhat distorted tetrahedral coordination geometry, with Tl–Cl 2.464, 2.482, 2.536(3), Tl–C 2.149(10) Å and bond angles 90.1–129.3°. This appears to be the first example of a Cl_3C coordination sphere for Tl^{III}; Cl_2C_2 is known in the $(Me_3SiCH_2)_2TlCl$ dimer [8], in which, however, both Tl–Cl bonds are long (2.76,2.99 Å). Clearly there is no clear-cut separation between isolated TlR_2^+ and X^- ions on the one hand and covalently linked TlR_2X on the other. In the title compound, the ions are linked into polymeric chains by even longer weak interactions of 3.046 and 3.119 Å between the anion Cl and cation Tl (cf. Tl... Cl 3.029 Å in $TlMe_2^+Cl^-$ [6b]).

Complexes **1** and **2** behave as non-electrolytes in chloroform or nitromethane solution, but they are moderately conducting in acetone, although the measured molar conductivities are lower (38 and 33 ohm^{-1} cm^2 mol^{-1}, respectively) than expected for 1/1 electrolytes [9]. The ^1H NMR spectrum of **1** shows two multiplets at 2.56 and 2.29 ppm (ratio 2/1), confirming the presence of two inequivalent mesityl groups.

When a molar ratio $TlCl_3/AgR$ of 1/2 is used, complex **1** (73% yield) and the known complexes $TlCl(C_6F_3H_2)_2$ (70%) [10] and $TlCl(C_6F_5)_2$ (78%) [5] are obtained (Scheme 1). A different result is observed for a molar ratio 1/3, which gives $TlCl(mes)_2$ (**3**) (57% yield) or solutions of TlR_3, from which the addition of dioxane (diox) allows the isolation of the known complexes TlR_3(diox), R = $C_6F_3H_2$ (55%) or C_6F_5 (60%) [11]. At room temperature, complex **3** is an air- and moisture-stable white solid. It behaves as a non-electrolyte in acetone and is dimeric (isopiestic method, M = 894, calc. 478 for the monomer) in chloroform, as has been found for other $TlClR_2$ derivatives [4,10,12,13].

Experimental

The instrumentation employed and general experimental techniques were as previously described [11].

Reactions of $TlCl_3$ with AgR

(a) Molar ratio 1/1.5. Thallium(III) chloride (0.311 g, 1.0 mmol) was added to a diethyl ether (25 ml, R = $C_6F_3H_2$ or C_6F_5) or tetrahydrofuran (50 ml, R = mes) solution of AgR (R = mes [3] (0.340 g, 1.5 mmol), R = $C_6F_3H_2$ [1] (0.352 g, 1.5 mmol) or R = C_6F_5 [2] (0.412 g, 1.5 mmol)) and the mixture was stirred for 3 h under nitrogen. The AgCl was filtered off and the solution concentrated to ca. 10 ml. Addition of n-hexane (20 ml) gave a white precipitate of $[Tl(mes)_2][TlCl_3(mes)]$ (**1**) (Found: C, 37.2; H, 4.0. $C_{27}H_{33}Cl_3Tl_2$ calcd.: C, 37.2; H, 3.8%. M.p. 186°C), $[Tl(C_6F_3H_2)_2][TlCl_3(C_6F_3H_2)]$ (**2**) (Found: C, 24.3; H, 0.75. $C_{18}H_6Cl_3F_9Tl_2$ calcd.: C, 23.8; H, 0.65%. M.p. 145°C, dec.) or $TlCl(C_6F_5)_2$.

(b) Molar ratio 1/2. Thallium(III) chloride (0.311 g, 1.0 mmol) was added to a tetrahydrofuran solution (40 ml) of AgR (R = mes, 0.454 g, 2 mmol; R = $C_6F_3H_2$, 0.470 g, 2 mmol; R = C_6F_5, 0.549 g, 2 mmol). After 2 h stirring under nitrogen, the AgCl was filtered off and the filtrate concentrated to ca. 10 ml. Addition of

n-hexane (20 ml) gave a white precipitate of [Tl(mes)$_2$][TlCl$_3$(mes)] (**1**), TlCl($C_6F_3H_2$)$_2$ or TlCl(C_6F_5)$_2$.

(c) Molar ratio 1/3. Thallium(III) chloride (0.311 g, 1.0 mmol) was added to a tetrahydrofuran solution (40 ml) of AgR (R = mes, 0.681 g, 3 mmol; R = $C_6F_3H_2$, 0.705 g, 3 mmol; R = C_6F_5, 0.825 g, 3 mmol) and the mixture was stirred under nitrogen for 3 h. The AgCl was filtered off and the solution concentrated to ca. 10 ml. For R = mes, addition of n-hexane (20 ml) precipitated white TlCl(mes)$_2$ (**3**) (Found: C, 45.0; H, 4.85%. $C_{18}H_{22}$TlCl calcd.: C, 45.2; H, 4.65%. M.p. 200 ° C). For R = $C_6F_3H_2$ or C_6F_5, dioxan (1 ml) was added to the solution, and the products TlR$_3$(diox) were recrystallized from diethyl ether/hexane.

Crystal structure determination of [Tl(mes)$_2$][TlCl$_3$(mes)] (1)

Crystal data: $C_{27}H_{33}Cl_3Tl_2$, $M = 872.7$, monoclinic, space group $P2_1/c$, a 12.956(2), b 13.218(2), c 16.889(3) Å, β 91.31(2)°, V 2891.5 Å^3, $Z = 4$, D_x 2.005 g cm^{-3}, $F(000)$ 1632, λ(Mo-K_α) 0.71069 Å, μ 11.5 mm^{-1}.

Table 1

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å^2 $\times 10^3$) for complex **1**

	x	y	z	U_{eq} [a]
Tl(1)	6014.3(3)	5994.0(4)	2270.1(3)	61(1)
Tl(2)	3074.0(3)	8003.9(4)	2178.8(3)	65(1)
Cl(2)	3666(3)	8747(3)	3448(2)	86(1)
Cl(2)	2521(3)	9740(2)	1691(2)	83(1)
Cl(3)	4795(2)	7837(2)	1576(2)	80(1)
C(11)	4760(7)	5622(8)	3011(6)	56(4)
C(12)	3936(7)	5099(8)	2694(6)	50(3)
C(13)	3135(9)	4829(9)	3215(7)	70(5)
C(14)	3164(8)	5111(9)	4003(7)	65(4)
C(15)	4011(9)	5673(9)	4290(7)	69(4)
C(16)	4822(8)	5952(8)	3811(6)	57(4)
C(17)	3826(9)	4805(10)	1832(6)	74(5)
C(18)	2281(9)	4816(11)	4550(7)	91(5)
C(19)	5657(9)	6630(10)	4122(7)	75(5)
C(21)	7186(8)	6541(9)	1524(6)	63(4)
C(22)	8018(8)	7081(9)	1870(7)	67(4)
C(23)	8780(9)	7416(10)	1353(8)	85(5)
C(24)	8673(11)	7285(11)	538(9)	107(6)
C(25)	7829(11)	6766(11)	229(8)	88(6)
C(26)	7079(10)	6394(10)	694(7)	77(5)
C(27)	8123(10)	7304(11)	2748(7)	84(5)
C(28)	9540(10)	7774(13)	−1(11)	134(7)
C(29)	6158(12)	5889(12)	332(7)	93(6)
C(31)	1902(7)	6883(8)	1953(6)	54(4)
C(32)	1786(9)	6490(9)	1178(8)	75(5)
C(33)	1025(9)	5735(10)	1079(8)	88(5)
C(34)	398(11)	5387(10)	1673(9)	93(6)
C(35)	570(9)	5803(10)	2411(9)	80(5)
C(36)	1302(8)	6577(9)	2573(7)	63(4)
C(37)	2434(10)	6871(12)	484(7)	94(6)
C(38)	−438(11)	4610(11)	1499(11)	115(7)
C(39)	1438(9)	6988(10)	3408(7)	76(5)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 2

Bond lengths (Å) for complex **1**

Tl(1)–Cl(3)	3.119(3)	Tl(1)–C(11)	2.131(10)
Tl(1)–C(21)	2.121(11)	Tl(1)–Cl(2a)	3.046(3)
Tl(2)–Cl(1)	2.464(3)	Tl(2)–Cl(2)	2.536(3)
Tl(2)–Cl(3)	2.482(3)	Tl(2)–C(31)	2.149(10)
C(11)–C(12)	1.371(14)	C(11)–C(16)	1.419(14)
C(12)–C(13)	1.422(15)	C(12)–C(17)	1.510(15)
C(13)–C(14)	1.382(16)	C(14)–C(15)	1.402(16)
C(14)–C(18)	1.538(17)	C(15)–C(16)	1.391(16)
C(16)–C(19)	1.491(16)	C(21)–C(22)	1.409(16)
C(21)–C(26)	1.418(16)	C(22)–C(23)	1.404(17)
C(22)–C(27)	1.514(17)	C(23)–C(24)	1.392(21)
C(24)–C(25)	1.383(20)	C(24)–C(28)	1.598(21)
C(25)–C(26)	1.357(19)	C(26)–C(29)	1.487(19)
C(31)–C(32)	1.412(17)	C(31)–C(36)	1.380(16)
C(32)–C(33)	1.410(18)	C(32)–C(37)	1.543(18)
C(33)–C(34)	1.384(20)	C(34)–C(35)	1.375(21)
C(34)–C(38)	1.516(20)	C(35)–C(36)	1.416(17)
C(36)–C(39)	1.519(17)		

Table 3

Bond angles (°) for complex **1** [a]

Cl(3)–Tl(1)–C(11)	90.8(3)	Cl(3)–Tl(1)–C(21)	82.7(3)
C(11)–Tl(1)–C(21)	173.1(4)	Cl(3)–Tl(1)–Cl(2a)	161.0(1)
C(11)–Tl(1)–Cl(2a)	90.5(3)	C(21)–Tl(1)–Cl(2a)	94.8(3)
Cl(1)–Tl(2)–Cl(2)	90.1(1)	Cl(1)–Tl(2)–Cl(3)	97.3(1)
Cl(2)–Tl(2)–Cl(3)	101.3(1)	Cl(1)–Tl(2)–C(31)	129.3(3)
Cl(2)–Tl(2)–C(31)	111.9(3)	Cl(3)–Tl(2)–C(31)	120.2(3)
Tl(2)–Cl(2)–Tl(1a)	97.9(1)	Tl(1)–Cl(3)–Tl(2)	111.5(1)
Tl(1)–C(11)–C(12)	119.0(7)	Tl(1)–C(11)–C(16)	117.4(7)
C(12)–C(11)–C(16)	123.6(9)	C(11)–C(12)–C(13)	117.2(9)
C(11)–C(12)–C(17)	124.2(9)	C(13)–C(12)–C(17)	118.6(9)
C(12)–C(13)–C(14)	121.6(10)	C(13)–C(14)–C(15)	118.7(10)
C(13)–C(14)–C(18)	120.4(10)	C(15)–C(14)–C(18)	120.9(10)
C(14)–C(15)–C(16)	122.4(10)	C(11)–C(16)–C(15)	116.4(9)
C(11)–C(16)–C(19)	123.0(10)	C(15)–C(16)–C(19)	120.4(10)
Tl(1)–C(21)–C(22)	118.5(8)	Tl(1)–C(21)–C(26)	119.0(8)
C(22)–C(21)–C(26)	122.4(10)	C(21)–C(22)–C(23)	116.4(11)
C(21)–C(22)–C(27)	123.8(10)	C(23)–C(22)–C(27)	119.9(11)
C(22)–C(23)–C(24)	121.4(12)	C(23)–C(24)–C(25)	119.7(13)
C(23)–C(24)–C(28)	117.2(12)	C(25)–C(24)–C(28)	123.1(14)
C(24)–C(25)–C(26)	122.1(13)	C(21)–C(26)–C(25)	117.9(11)
C(21)–C(26)–C(29)	121.8(11)	C(25)–C(26)–C(29)	120.2(12)
Tl(2)–C(31)–C(32)	118.6(8)	Tl(2)–C(31)–C(36)	118.4(8)
C(32)–C(31)–C(36)	123.0(10)	C(31)–C(32)–C(33)	115.5(11)
C(31)–C(32)–C(37)	122.4(11)	C(33)–C(32)–C(37)	122.2(12)
C(32)–C(33)–C(34)	124.7(13)	C(33)–C(34)–C(35)	115.9(12)
C(33)–C(34)–C(38)	120.8(14)	C(35)–C(34)–C(38)	123.2(14)
C(34)–C(35)–C(36)	123.9(13)	C(31)–C(36)–C(35)	116.8(11)
C(31)–C(36)–C(39)	123.0(10)	C(35)–C(36)–C(39)	120.1(11)

[a] Symmetry operator: (a) $1-x$, $0.5+y$, $0.5-z$.

Data collection and reduction. A colourless needle 0.65 × 0.12 × 0.12 mm was mounted in a glass capillary and used to collect 7425 profile-fitted intensities [14] on a Stoe–Siemens four-circle diffractometer using monochromated Mo-K_α radiation ($2\theta_{max}$ 50°). Merging equivalents gave 5065 unique reflections (R_{int} 0.039), of which 3605 with $F > 4\sigma(F)$ were used for all calculations (program system SHELX-76, modified by its author Prof. G.M. Sheldrick). Absorption corrections based on ψ-scans were applied, with transmission factors 0.80–0.88. Cell constants were refined from 2θ values of 50 reflections in the range 20–22°.

Structure solution and refinement: Heavy-atom method, followed by anisotropic least-squares refinement on F (full-matrix). H aoms included using a riding model. Weighting scheme $w^{-1} = \sigma^2(F) + 0.00015\ F^2$. Final R 0.053 for 289 parameters; R_w 0.043; S 1.76; max. Δ/σ 0.08; max. $\Delta\rho$ 1 e Å^{-3}. Final atomic coordinates are given in Table 1, with derived bond lengths and angles in Tables 2 & 3. Further details of the structure determination (H atom coordinates, thermal parameters, structure factors) have been deposited at the Fachinformationszentrum Energie Physik Mathematik, 7514 Eggenstein-Leopoldshafen 2, Fed. Rep. of Germany. Any request for this material should quote a full literature citation and the reference number CSD 53457.

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