Inorganica Chimica Acta, *215* (1994) 229–233

Note

Synthesis of bis- or tris(pentafluorophenyl) thallium(III) complexes with bidentate ligands. X-ray crystal structure of $[Tl(C_6F_5)_2(acac)\{(O)Ph_2PCH_2PPh_2(O)\}]$

Eduardo J. Fernández[a], Peter G. Jones[b], Antonio Laguna[c,]* and Aránzazu Mendía[a]

[a]*Departamento de Química, Universidad de La Rioja, 26001 Logroño (Spain)*
[b]*Institut fur Anorganische und Analytische Chemie der Technischen Universitat, Postfach 3329, 38023 Braunschweig (Germany)*
[c]*Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza, C S I C, 50009 Zaragoza (Spain)*

(Received July 9, 1993; revised September 8, 1993)

Abstract

The reaction of $Tl(C_6F_5)_2Cl$ or $Tl(C_6F_5)_3(diox)$ (diox = 1,4 dioxane) with bidentate ligands ($L = PPh_2CH_2PPh_2$, $(O)PPh_2CH_2PPh_2(O)$ or $(S)PPh_2CH_2PPh_2(S)$) gives $Tl(C_6F_5)_2ClL$ or $Tl(C_6F_5)_3L$, respectively. Displacement of chloride gives new cationic or neutral complexes, $[Tl(C_6F_5)_2\{(O)PPh_2CH_2PPh_2(O)\}]^+BF_4^-$ or $[Tl(C_6F_5)_2(acac)\{(O)PPh_2CH_2PPh_2(O)\}]$ (acac = acetylacetonate), respectively. The structure of the latter was determined by single-crystal X-ray diffraction at 143 K. Crystals are monoclinic, space group $P2_1/n$, $a = 12\ 733(3)$, $b = 23.717(8)$, $c = 14.981(4)$ Å, $\beta = 110.37(3)°$, $Z = 4$ and $R(F) = 0.046$. The structure forms a chain polymer.

Key words. Crystal structures, Thallium complexes, Perfluoroaryl complexes; Bidentate ligand complexes

Introduction

A number of interesting di- or triaryl thallium(III) complexes of the types $[TlR_2ClL]$ or $[TlR_3L]$ (R = aryl group) have been described [1–5], but no derivatives containing a neutral bidentate ligand, such as $PPh_2CH_2PPh_2$, $(O)PPh_2CH_2PPh_2(O)$ or $(S)PPh_2CH_2PPh_2(S)$, have been reported.

We describe here the preparation of the neutral $[Tl(C_6F_5)_2XL]$ (X = Cl or acac), or $[Tl(C_6F_5)_3L]$ with $L = PPh_2CH_2PPh_2$, $(O)PPh_2CH_2PPh_2(O)$ or $(S)PPh_2CH_2PPh_2(S)$ or the cationic complex $[Tl(C_6F_5)_2\{(O)PPh_2CH_2PPh_2(O)\}]BF_4$. The structure of $[Tl(C_6F_5)_2(acac)\{(O)PPh_2CH_2PPh_2(O)\}]$ has been established by X-ray diffraction.

Experimental

Instrumentation and general experimental techniques were as described earlier [5]. Nuclear magnetic resonance spectra were recorded on a Varian UNITY 300 spectrometer in $CDCl_3$. Chemical shifts are quoted relative to $SiMe_4$ (^1H), 85% H_3PO_4 (external, ^{31}P) and $CFCl_3$ (external, ^{19}F). Conductivities, $^{31}P\{^1H\}$, ^1H and ^{19}F NMR data are listed in Table 1. All the reactions were performed at room temperature and carried out under nitrogen atmosphere. Anhydrous and deoxygenated solvents were used.

Preparation of the complexes

$[Tl(C_6F_5)_2ClL]$ ($L = PPh_2CH_2PPh_2$ (1), $(O)PPh_2CH_2PPh_2(O)$ (2) or $(S)PPh_2CH_2PPh_2(S)$ (3))

To a solution of $Tl(C_6F_5)_2Cl$ [6] (0.143 g, 0.25 mmol) in diethyl ether (30 ml) or dichloromethane (20 ml, $L = (S)PPh_2CH_2PPh_2(S)$) was added the neutral ligand, $L = PPh_2CH_2PPh_2$ (0.096 g, 0.25 mmol), $(O)PPh_2CH_2PPh_2(O)$ (0.104 g, 0.25 mmol) or $L = (S)PPh_2CH_2PPh_2(S)$ (0.112 g, 0.25 mmol). The solution was stirred for 1 h and the white precipitate of **2** was filtered off and washed with 2×3 ml of hexane (0.223 g, 90% yield). *Anal.* Found: C, 45.05; H, 2.3. Calc. for $C_{37}H_{22}F_{10}ClO_2P_2Tl$: C, 44.85; H, 2.25%. The evaporation of the solutions to *c.* 2 ml and addition of hexane led to the separation of **1** (0.156 g, 65% yield; *Anal.* Found: C, 45.5; H, 2.35. Calc. for $C_{37}H_{22}ClF_{10}P_2Tl$: C, 46.35; H, 2.3%) or **3** (0.146 g, 57% yield; *Anal.* Found: C, 44.7; H, 2.4. Calc. for $C_{37}H_{22}ClF_{10}S_2P_2Tl$: C, 43.45; H, 2.15%).

$[Tl(C_6F_5)_3L]$ ($L = PPh_2CH_2PPh_2$ (4) or $(O)PPh_2CH_2PPh_2(O)$ (5))

The same procedure as above was used, starting from $Tl(C_6F_5)_3(diox)$ (diox = dioxane) [5] (0.159 g, 0.2 mmol) and $L = PPh_2CH_2PPh_2$ (0.077 g, 0.2 mmol), or $(O)PPh_2CH_2PPh_2(O)$ (0.083 g, 0.2 mmol). **4**: 0.157 g, 72% yield. *Anal.* Found: C, 47.45; H, 1.9. Calc. for

---

*Author to whom correspondence should be addressed

SSDI 0020-1693(93)03690-C

TABLE 1 Conductivities and NMR data of the complexes

Compound	Λ_M[a]	^1H NMR[b] (δ)	$^{31}P\{^1H\}$ NMR[c] (δ)	^{19}F NMR[d] (δ)		
		CH_2		*o*-F	*m*-F	*p*-F
$Tl(C_6F_5)_2Cl(PPh_2CH_2PPh_2)$ (**1**)	27	3 50(t) (13 5)	-12 8(s)	−118.6(dm) (759 2)	−159 6(dm) (321 1)	−152 0(dm) (78.5)
$Tl(C_6F_5)_2Cl\{(O)PPh_2CH_2PPh_2(O)\}$ (**2**)	32	3 59(t) (13 4)	30 3(s)	−119 1(dm) (877 7)	−159 8(dm) (373 4)	−152 2(dm) (68 9)
$Tl(C_6F_5)_2Cl\{(S)PPh_2CH_2PPh_2(S)\}$ (**3**)	3	4 56(t) (13 5)	38 1(s)	−118 8(dm) (719 9)	−158 7(dm) (310 3)	−151 4(dt) (18 0, 79 2)[e]
$Tl(C_6F_5)_3(PPh_2CH_2PPh_2)$ (**4**)	58	3.17(m)	−11 5(s, br)	−116 6(dm) (456 5)	−160 0(dm) (181 2)	−153 4(dt) (19 7, 56 9)[e]
$Tl(C_6F_5)_3\{(O)PPh_2CH_2PPh_2(O)\}$ (**5**)	14	3 36(m)	29 5(s)	−116.9(dm) (571 8)	−158.3(dm) (206 6)	−151 4(dm) (57 8)
$[Tl(C_6F_5)_2\{(O)PPh_2CH_2PPh_2(O)\}]BF_4$ (**6**)	124	3 72(t) (12 8)	34 8(s)	−120 3(dm) (987 9)	−158 3(dm) (398 2)	−149 6(dm) (56 5)
$Tl(C_6F_5)_2(acac)\{(O)PPh_2CH_2PPh_2(O)\}$ (**7**)	2	3 56(t) (14 8)	26 2(s)	−119.7(dm) (883 2)	−158.3(dm) (383 0)	−149 6(dm) (84 0)

[a] In acetone, Ω^{-1} cm^2 mol^{-1} [b] Recorded in $CDCl_3$ at 300 MHz referred to internal TMS Coupling constants (P–H) in Hz are show in parentheses, t = triplet, m = multiplet, dt = doublet of triplets, dm = doublet of multiplets, br = broad [c] Referred to external H_3PO_4, at room temperature [d] Referred to external $CFCl_3$ Coupling constants ($^{203, 205}Tl$–F) in Hz are shown in parentheses. [e] J(F–F), $J(^{203, 205}Tl$–F)

$C_{43}H_{22}F_{15}P_2Tl$: C, 47.4; H, 2 05%. **5** 0 195 g, 87% yield. *Anal.* Found: C, 44.4; H, 1.9. Calc. for $C_{43}H_{22}F_{15}O_2P_2Tl$ CH_2Cl_2 C, 43.8; H, 2.0%.

[Tl(C$_6$F$_5$)$_2${(O)PPh$_2$CH$_2$PPh$_2$(O)}]BF$_4$ (6)

To a solution of complex **2** (0.182 g, 0.18 mmol) in dichloromethane (20 ml) was added $Ag(BF_4)$ (0.036 g, 0.18 mmol) and the mixture was stirred for 1 h. The white precipitate of AgCl was filtered off and the solution was concentrated to 3 ml. Addition of hexane (20 ml) gave complex **6** as a white solid (0.145 g, 75% yield). *Anal.* Found. C, 42.25; H, 2.0. Calc. for $C_{37}H_{22}BF_{14}O_2P_2Tl$: C, 42.65; H, 2 15%.

[Tl(C$_6$F$_5$)$_2$(acac){(O)PPh$_2$CH$_2$PPh$_2$(O)}] (7)

The following procedures were used.

(a) To a suspension of complex **2** (0.198 g, 0.2 mmol) in diethyl ether (30 ml) was added $Au(acac)(PPh_3)$ [7] (0 112 g, 0 2 mmol), and the mixture was stirred for 3 h at room temperature. A white solid was filtered off and identified as a mixture of $AuCl(PPh_3)$ and **7** The clear solution was evaporated to *c* 2 ml and addition of hexane (20 ml) led to a pure crop of complex **7** (0 069 g, 33% yield). *Anal.* Found: C, 47.5; H, 2.8. Calc for $C_{42}H_{29}F_{10}O_4P_2Tl$: C, 47.85; H, 2.75%.

(b) To a solution of complex **2** (0 149 g, 0.15 mmol) in dichloromethane (20 ml) was added Tl(acac) (0.045 g, 0.15 mmol) and the mixture was stirred for 3 days The TlCl precipitated was filtered off and the filtrate was evaporated to *c*. 5 ml. Addition of hexane (20 ml) precipitated complex **7** as a white solid (0 087 g, 55% yield)

(c) To a solution of $Tl(C_6F_5)_2(acac)$ [8] (0.064 g, 0.1 mmol) in diethyl ether (30 ml) was added the ligand $(O)PPh_2CH_2PPh_2(O)$ (0.042 g, 0.1 mmol), and the mixture was stirred for 1.5 h. Complex **7** was filtered off and washed with 2×3 ml of hexane (0 085 g, 65% yield) A second crop was obtained from the filtrate by concentrating to 5 ml and cooling it to −20 °C (0.020 g, 15% yield)

Crystal structure determination of compound 7 (dichloromethane solvate)

Crystal data

Crystals of **7** suitable for X-ray studies were obtained from dichloromethane/hexane $C_{43}H_{31}Cl_2F_{10}O_4P_2Tl$, $M_r = 1138.89$, monoclinic, $P2_1/n$, $a = 12\ 733(3)$, $b = 23.717(8)$, $c = 14.981(4)$ Å, $\beta = 110.37(3)°$, $V = 4241(2)$ Å^3, $Z = 4$, $D_x = 1.784$ Mg m^{-3}, λ(Mo Kα) = 0.71073 Å, $\mu = 4.1$ mm^{-1}, $F(000) = 2224$, $T = -130$ °C.

Data collection and reduction

A colourless prism 0.65×0 15×0.1 mm was mounted in inert oil on a glass fibre and transferred to the cold gas stream of the diffractometer (Stoe STADI-4 with

Siemens LT-2 low temperature attachment). A total of 11 238 reflections was registered to $2\theta_{max}$ 50°; crystal decay of 10% was allowed for. An absorption correction based on Ψ-scans was applied, with transmission factors ranging between 0.78 and 0.96. Cell constants were refined from $\pm\omega$ values of 60 reflections in the 2θ range 20–22°. 7399 unique reflections (R_{int} 0.043) were used for all calculations (program system SHELXL-92) [9].

Structure solution and refinement

The structure was solved by the heavy-atom method and refined anisotropically on F^2. The carbon atom of the dichloromethane molecule is disordered over two sites. Hydrogen atoms were included using a riding model (rigid methyl groups). The final $R_w(F^2)$ was 0.108 for all reflections; the corresponding $R(F)$ was 0.046. The weighting scheme was $w^{-1} = \sigma^2(F^2) + (aP)^2 + bP$, with $3P = (F_o^2 + 2F_c^2)$. 560 parameters; 486 restraints; S 1.07; max.Δ/σ 0.508 for the methyl group at C(2), which may be disordered; max. Δ/ρ 1.1 e Å^{-3}. Final atomic coordinates are given in Table 2, with selected bond lengths and angles in Table 3.

Results and discussion

The syntheses of $Tl(C_6F_5)_2Cl$ and $Tl(C_6F_5)_3(diox)$ (diox = 1,4 dioxane) have been described elsewhere [5, 6]. The reaction of $Tl(C_6F_5)_2Cl$ with neutral ligands gives $Tl(C_6F_5)_2ClL$ (L = $PPh_2CH_2PPh_2$ (**1**), $(O)PPh_2CH_2PPh_2(O)$ (**2**) or $(S)PPh_2CH_2PPh_2(S)$ (**3**)).

The dioxane in $Tl(C_6F_5)_3(diox)$ can be readily replaced [5] by other ligands to give neutral complexes, $Tl(C_6F_5)_3L$ (L = $PPh_2CH_2PPh_2$ (**4**) or $(O)PPh_2CH_2PPh_2(O)$ (**5**)).

Precipitation of the chloride of complex **2** with $Ag(BF_4)$ leads to the cationic complex $[Tl(C_6F_5)_2\{(O)PPh_2CH_2PPh_2(O)\}]^+BF_4^-$ (**6**).

Similar behaviour is observed in the reaction of complex **2** with Tl(acac) (acac = acetylacetonate) which leads to the precipitation of TlCl and formation of $[Tl(C_6F_5)_2(acac)\{(O)PPh_2CH_2PPh_2(O)\}]$ (**7**). Complex **7** can also be obtained by reaction of $Tl(C_6F_5)_2(acac)$ with the diphosphine dioxide or of complex **2** with $Au(acac)PPh_3$, according to eqn. (1).

$$\begin{aligned} &Tl(C_6F_5)_2Cl\{(O)PPh_2CH_2PPh_2(O)\} \\ &\quad + Au(acac)PPh_3 \longrightarrow \\ &Tl(C_6F_5)_2(acac)\{(O)PPh_2CH_2PPh_2(O)\} \\ &\quad + AuCl(PPh_3) \qquad (1) \end{aligned}$$

Complexes **2**–**7** are air and moisture stable white solids. The white complex **1** slowly oxidizes in solution or in solid state to give complex **2**. The cationic derivative

TABLE 2 Atomic coordinates (×10^4) and equivalent isotropic displacement parameters (Å^2×10^3) for complex 7

	x	y	z	U_{eq}
Tl	6749.1(2)	3494.61(11)	7869 4(2)	26.0(2)
P(1)	4666(2)	3383 2(7)	5356 0(12)	24.1(10)
P(2)	4727(2)	2387 0(7)	3902 5(12)	24.2(11)
O(1)	5556(4)	3674(2)	6149(3)	28(3)
O(2)	3510(4)	2250(2)	3589(3)	29(3)
O(3)	5545(5)	4216(2)	7904(4)	41(4)
O(4)	7384(5)	3681(2)	9504(4)	39(4)
C(1)	5245(6)	2747(3)	5042(5)	26(4)
C(2)	4517(8)	4908(3)	8358(6)	47(4)
C(3)	5485(7)	4497(3)	8600(6)	40(4)
C(4)	6196(7)	4454(3)	9541(6)	40(4)
C(5)	7081(8)	4070(3)	9937(5)	39(4)
C(6)	7755(8)	4109(4)	11000(5)	52(5)
C(11)	4183(5)	3835(3)	4326(5)	28(4)
C(12)	3285(6)	3691(3)	3535(5)	36(3)
C(13)	2959(7)	4044(3)	2742(5)	42(4)
C(14)	3522(6)	4540(3)	2767(5)	41(5)
C(15)	4407(7)	4689(3)	3563(5)	38(4)
C(16)	4743(6)	4335(3)	4358(5)	35(4)
C(21)	3511(7)	3180(2)	5696(5)	34(3)
C(22)	3275(6)	3526(3)	6354(5)	34(3)
C(23)	2414(6)	3391(3)	6683(5)	38(3)
C(24)	1778(7)	2916(3)	6365(5)	40(3)
C(25)	2019(6)	2565(3)	5735(6)	39(3)
C(26)	2869(6)	2697(3)	5388(5)	36(3)
C(31)	5610(6)	1766(3)	4172(5)	34(3)
C(32)	5343(6)	1350(3)	4717(5)	36(3)
C(33)	6028(7)	888(3)	5003(5)	41(3)
C(34)	6966(6)	830(3)	4764(6)	48(3)
C(35)	7218(7)	1234(3)	4215(6)	45(3)
C(36)	6561(6)	1705(3)	3925(5)	39(3)
C(41)	5068(5)	2809(3)	3043(5)	31(3)
C(42)	4293(6)	2807(3)	2122(5)	36(3)
C(43)	4493(7)	3133(3)	1429(5)	38(3)
C(44)	5434(5)	3452(3)	1638(5)	39(3)
C(45)	6192(6)	3459(3)	2543(5)	37(3)
C(46)	6024(6)	3142(3)	3259(5)	37(3)
C(51)	8002(7)	3930(2)	7501(4)	32(3)
C(52)	8372(6)	3732(3)	6800(5)	34(3)
C(53)	9263(6)	3955(3)	6610(5)	43(3)
C(54)	9818(7)	4403(3)	7136(5)	49(4)
C(55)	9474(6)	4628(3)	7821(6)	46(3)
C(56)	8588(6)	4387(3)	7999(5)	38(3)
F(1)	7832(4)	3284(2)	6252(3)	45(3)
F(2)	9586(5)	3734(2)	5922(4)	75(4)
F(3)	10707(5)	4622(2)	6969(5)	85(4)
F(4)	10005(4)	5072(2)	8340(4)	60(4)
F(5)	8305(4)	4617(2)	8722(3)	42(3)
C(61)	5768(6)	2785(3)	7992(4)	32(3)
C(62)	5052(6)	2797(3)	8505(5)	34(4)
C(63)	4458(6)	2331(3)	8611(5)	37(3)
C(64)	4599(6)	1832(3)	8209(5)	40(4)
C(65)	5277(6)	1800(3)	7676(5)	37(4)
C(66)	5847(6)	2276(2)	7573(5)	33(3)
F(6)	4903(4)	3275(2)	8928(3)	43(3)
F(7)	3774(4)	2361(2)	9116(4)	58(3)
F(8)	4027(5)	1372(2)	8314(4)	63(4)
F(9)	5373(4)	1314(2)	7250(4)	52(3)
F(10)	6523(3)	2224(2)	7062(3)	32(3)
Cl(1)	2732(4)	317(2)	9339(3)	138(4)
Cl(2)	3691(5)	−559(2)	10670(3)	157(5)
C(7)	3709(16)	−198(7)	9722(12)	77(5)
C(7′)	2571(14)	−148(7)	10126(13)	77(5)

TABLE 3. Selected bond lengths (Å) and angles (°) for complex **7**

Tl–C(51)	2.129(8)	Tl–C(61)	2.141(7)
Tl–O(3)	2.310(5)	Tl–O(4)	2.338(5)
Tl–O(1)	2.531(5)	Tl–O(2i)	2.761(5)
P(1)–O(1)	1.494(5)	P(1)–C(21)	1.783(8)
P(1)–C(11)	1.802(7)	P(1)–C(1)	1.812(7)
P(2)–O(2)	1.491(5)	P(2)–C(41)	1.799(7)
P(2)–C(31)	1.811(8)	P(2)–C(1)	1.815(7)
O(3)–C(3)	1.262(9)	O(4)–C(5)	1.263(9)
C(2)–C(3)	1.513(11)	C(3)–C(4)	1.388(11)
C(4)–C(5)	1.409(11)	C(5)–C(6)	1.526(11)
C(51)–Tl–C(61)	156.4(2)	C(51)–Tl–O(3)	102.1(2)
C(61)–Tl–O(3)	99.7(2)	C(51)–Tl–O(4)	99.4(2)
C(61)–Tl–O(4)	93.3(2)	O(3)–Tl–O(4)	80.0(2)
C(51)–Tl–O(1)	83.9(2)	C(61)–Tl–O(1)	93.3(2)
O(3)–Tl–O(1)	74.4(2)	O(4)–Tl–O(1)	154.3(2)
C(51)–Tl–O(2i)	80.3(2)	C(61)–Tl–O(2i)	83.2(2)
O(3)–Tl–O(2i)	156.9(2)	O(4)–Tl–O(2i)	77.0(2)
O(1)–Tl–O(2i)	128.52(14)	O(1)–P(1)–C(21)	111.7(3)
O(1)–P(1)–C(11)	110.2(3)	C(21)–P(1)–C(11)	109.6(3)
O(1)–P(1)–C(1)	109.1(3)	C(21)–P(1)–C(1)	107.4(3)
C(11)–P(1)–C(1)	108.8(3)	O(2)–P(2)–C(41)	112.3(3)
O(2)–P(2)–C(31)	113.0(3)	C(41)–P(2)–C(31)	109.1(3)
O(2)–P(2)–C(1)	113.4(3)	C(41)–P(2)–C(1)	108.2(3)
C(31)–P(2)–C(1)	100.3(3)	P(1)–O(1)–Tl	138.8(3)
P(2)–O(2)–Tl(ii)	151.2(3)	C(3)–O(3)–Tl	129.9(5)
C(5)–O(4)–Tl	128.3(5)	P(1)–C(1)–P(2)	126.1(4)
O(3)–C(3)–C(4)	126.4(8)	O(3)–C(3)–C(2)	114.9(7)
C(4)–C(3)–C(2)	118.7(7)	C(3)–C(4)–C(5)	128.2(7)
O(4)–C(5)–C(4)	126.7(7)	O(4)–C(5)–C(6)	114.7(8)
C(4)–C(5)–C(6)	118.5(7)	C(56)–C(51)–C(52)	114.7(7)
C(66)–C(61)–C(62)	115.9(7)		

Symmetry operators: (i) $0.5+x, 0.5-y, 0.5+z$, (ii) $-0.5+x, 0.5-y, -0.5+z$.

6 behaves as a 1:1 electrolyte in acetone solutions (see Table 1) and the IR spectrum shows a band at 1085(s) which is characteristic of the BF_4^- anion [10]. Complexes **1**, **2**, **4** and **5** are slightly conducting in acetone solutions, though their conductivities are lower than the expected for 1:1 electrolytes. Complexes **2**, **5**, **6** and **7** show strong absorptions at 1185, 1180, 1160 and 1180 cm^{-1} respectively, assignable to $\nu(P=O)$ [11]. The $\nu(P=S)$ vibration [11, 12] of complex **3** appears at 594 cm^{-1}. The IR spectrum of the acetylacetonate derivative **7** exhibits a strong band at 1598 cm^{-1}, assignable to the acac acting as O-donor bidentate ligand [13].

The ^1H NMR spectra show a multiplet at δ *c*. 7.8 corresponding to the phenyl groups and a triplet or multiplet from the CH_2 group (see Table 1). In complex **7** there are two other resonances at δ 5.10(s) and 1.85(s) for the CH and CH_3 groups of the acetylacetonate The ^{19}F NMR spectra at room temperature show three groups of signals, as expected for equivalent pentafluorophenyl rings. The resonance of the fluorine atoms of BF_4 in complex **6** appears as a singlet at δ -149.2

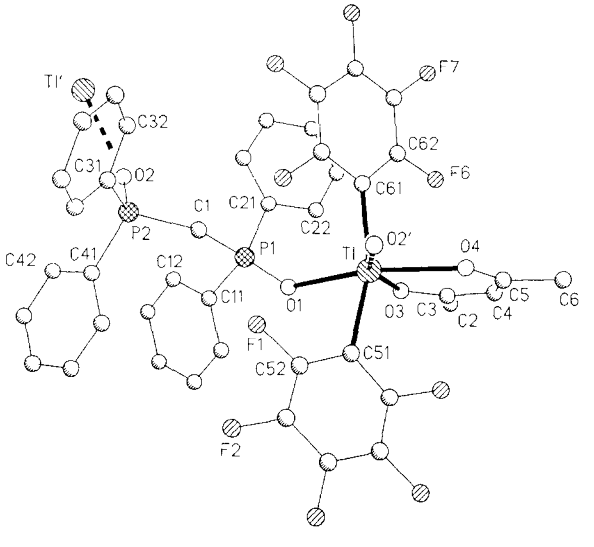

Fig. 1 The molecule of complex **7** in the crystal, showing the atom numbering scheme Hydrogen atoms are omitted for clarity, atom radii are arbitrary

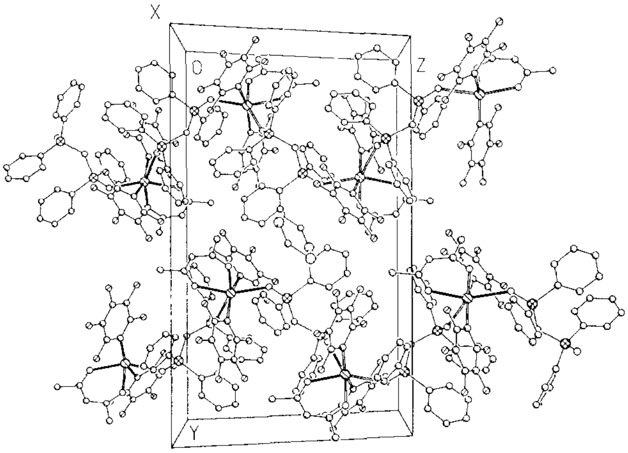

Fig. 2 The polymeric chains of complex **7** in the unit cell. Atom radii are arbitrary

The $^{31}P\{^1H\}$ NMR spectra at room temperature show a singlet. On cooling to -50 °C this signal still remains sharp for complexes **3** and **7** or broadens slightly for complexes **1** and **2**. It splits into two broad doublets at δ 4.1 (J(Tl–P) 98 Hz) and -28.5 (J(Tl–P) 88 Hz) for compound **4** and into a doublet at δ 28.9 (J(Tl–P) 179 Hz) and a broad singlet at δ 22.5 for compound **5**.

The structure of **7** was determined by X-ray diffraction. The coordination at thallium is irregular (Fig. 1), but the geometry is similar to that found in $[Tl\{CH_2C(O)Me\}_2(CF_3SO_3)(bipy)]_2$ [14]. The shortest bonds (Tl–C 2.129, 2.141 Å) involve the C_6F_5 ligands, the C–Tl–C angle being 156.4°. The acac ligand chelates the thallium atom, with Tl–O 2.310, 2.338 Å and a bite angle of 80.0°. These distances are slightly shorter than those found in $TlMe_2(acac)$ (2 45 Å) [15], but the bite angle found in this complex is very similar, 79.1°. The coordination sphere is completed by longer bonds (2.531, 2.761 Å) to the oxygen atoms of two $(O)PPh_2CH_2PPh_2(O)$ molecules, thus forming a chain polymer (Fig. 2) parallel to the z axis with O1–Tl–O2′ 128.5° (O2′ is generated from O2 by the n glide). The conformation of $(O)PPh_2CH_2PPh_2(O)$ is defined by the torsion angle O1–P1...P2–O2 164°, i.e. the oxygen atoms are almost antiperiplanar with respect to the P...P axis.

Supplementary material

Further details of the structure determination (complete bond lengths and angles, H atom coordinates, structure factors, temperature factors) have been deposited at the Fachinformationszentrum Karlsruhe, Gesellschaft fur Wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen 2, Germany. Any request for this material should quote a full literature citation and the reference number CSD 400269.

Acknowledgements

We thank the Dirección General de Investigación Científica y Técnica (No. PB91-0122), the Instituto de Estudios Riojanos and the Fonds der Chemischen Industrie for financial support.

References

1 H Kurosawa and R. Okawara, *Organomet Chem Rev, Sect A, 6* (1970) 65.

2 H Kurosawa, *Comprehensive Organometallic Chemistry,* Vol. 1 Pergamon, Oxford, 1982, p 725.

3 K Henrick, M McPartlin, G B. Deacon and R J Phillips, *J Organomet Chem, 204* (1981) 287

4 K. Henrick, M. McPartlin and R.W Matthews, *J Organomet Chem., 193* (1980) 13.

5 R. Usón, A Laguna, J A Abad and E de Jesús, *J Chem Soc, Dalton Trans,* (1983) 1127.

6 R Usón and A. Laguna, *Inorg Synth, 21* (1982) 71

7 D Gibson, B F G. Johnson and J. Lewis, *J Chem Soc A,* (1970) 367.

8 G.B. Deacon and V.N Garg, *Inorg Nucl Chem Lett, 5* (1969) 359

9 G.M. Sheldrick, *SHELXL-92*, a program for crystal structure refinement (pre-release version), University of Gottingen, Germany, 1992.

10 N N Greenwood, *J Chem Soc,* (1959) 3811

11 H Teichmann and G Hilgetag, *Angew Chem, Int Ed Engl, 6* (1967) 1013

12 D W. Meek and P Nicpon, *J Am Chem Soc, 87* (1965) 4951

13 K Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds,* Wiley, New York, 4th edn, 1986, p 266

14 J. Vicente, J A Abad, G. Cara and P.G Jones, *Angew Chem, Int Ed Engl, 29* (1990) 1125.

15 Y.M. Chow and D Britton, *Acta Crystallogr, Sect B, 31* (1975) 1929