



Synthesis and structure of $[\text{Tl}(\text{C}_6\text{F}_5)_2\text{Cl}\{\text{Au}(\text{C}_6\text{F}_5)_3(\text{PPh}_2\text{CH}_2\text{PPh}_2(\text{O}))\}_2]$

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Abstract

Two trinuclear gold–thallium–gold complexes, $[\text{Tl}(\text{C}_6\text{F}_5)_2\text{X}\{\text{Au}(\text{C}_6\text{F}_5)_3(\text{PPh}_2\text{CH}_2\text{PPh}_2(\text{O}))\}_2]$ ($\text{X} = \text{C}_6\text{F}_5, \text{Cl}$), have been synthesised by reaction of $[\text{Au}(\text{C}_6\text{F}_5)_3(\text{PPh}_2(\text{O}))]$ with $[\text{Tl}(\text{C}_6\text{F}_5)_2\text{Cl}]$ or $[\text{Tl}(\text{C}_6\text{F}_5)_3(\text{diox})]$, in which the phosphine oxide moiety coordinates to thallium; the crystal structure of the former product has been established by X-ray diffraction.

Keywords: Gold; Thallium; Crystal structure; Pentafluorophenyl

1. Introduction

The structural chemistry of thallium has not been extensively developed, probably because most complexes are only used as intermediates in organic synthesis [1,2]. However, several examples of thallium complexes with various coordination numbers: two (e.g. $[\text{Tl}(\text{Mes})_2]^+$ [3]), four ($[\text{TlCl}_4(\text{Mes})]^-$ [3]), five ($[\text{TlPh}(\text{S}_2\text{P}(\text{C}_6\text{H}_{11})_2)_2]$ [4]) or six ($[\text{Tl}(\text{C}_6\text{F}_5)_2(\text{bipy})\text{(acac)}]$ [5]), have been described.

Moreover, only two structurally characterised gold–thallium(I) compounds are known, the polymeric derivative $[\text{AuTl}(\text{Ph}_2\text{P}(\text{CH}_2)_2\text{S})_2]_n$ [6] and the tetranuclear complex $[\text{AuTl}(\text{C}_5\text{H}_4\text{PPh}_2)_2]_2$ [7], and, to the best of our knowledge, no gold–thallium(III) complex has been described to date.

We have recently reported several bis- and tris-pentafluorophenyl thallium(III) complexes with O-donor ligands, including the polymeric hexacoordinate compound $[\text{Tl}(\text{C}_6\text{F}_5)_2(\text{acac})(\text{O})\text{Ph}_2\text{PCH}_2\text{PPh}_2(\text{O})]$ [8]. We therefore thought that the use of mixed bidentate O-, P-donor ligands could be suitable for the synthesis of gold–thallium complexes.

Here we describe the syntheses of the neutral derivatives $[\text{Tl}(\text{C}_6\text{F}_5)_2\text{X}\{\text{Au}(\text{C}_6\text{F}_5)_3(\text{PPh}_2\text{CH}_2\text{PPh}_2(\text{O}))\}_2]$ (X

$= \text{C}_6\text{F}_5, \text{Cl}$). The structure of the latter has been established by X-ray diffraction.

2. Results and discussion

Treatment of $[\text{Au}(\text{C}_6\text{F}_5)_3(\text{PPh}_2\text{CH}_2\text{PPh}_2)]$ [9] in acetone with an equimolecular amount of H_2O_2 (30%) leads to the oxidation of the free phosphorus atom and the formation of $[\text{Au}(\text{C}_6\text{F}_5)_3(\text{PPh}_2\text{CH}_2\text{PPh}_2(\text{O}))]$ (1) in a good yield. Its IR spectrum shows a band $\nu(\text{P}=\text{O})$ at $1157(\text{m})\text{cm}^{-1}$ [10]. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum shows two different phosphorus environments, which appear as a doublet (23.1 ppm, $J(\text{PP}) = 23.9\text{Hz}$) and a multiplet (11.8 ppm), for the $\text{PPh}_2(\text{O})$ and AuPPh_2 (coupled with the fluorine atoms) respectively.

The oxygen atom of 1 can act as a ligand, and complex 1 thus reacts with the dinuclear $[\text{Tl}(\text{C}_6\text{F}_5)_2\text{Cl}]_2$ [11] in molar ratio 4:1 in dichloromethane to give $[\text{Tl}(\text{C}_6\text{F}_5)_2\text{Cl}\{\text{Au}(\text{C}_6\text{F}_5)_3(\text{PPh}_2\text{CH}_2\text{PPh}_2(\text{O}))\}_2]$ (2) (Eq. (1)). When the same process is carried out in 2:1 molar ratio complex 2 is obtained in a low yield (31%).

In this complex the stretching band $\nu(\text{Tl}-\text{Cl})$ appears at $366(\text{w})\text{cm}^{-1}$ showing its terminal nature [12]. The ^{19}F NMR spectrum, besides the signals from C_6F_5 linked to gold(III) centres, shows a resonance corresponding to C_6F_5 groups coupled with the magnetically

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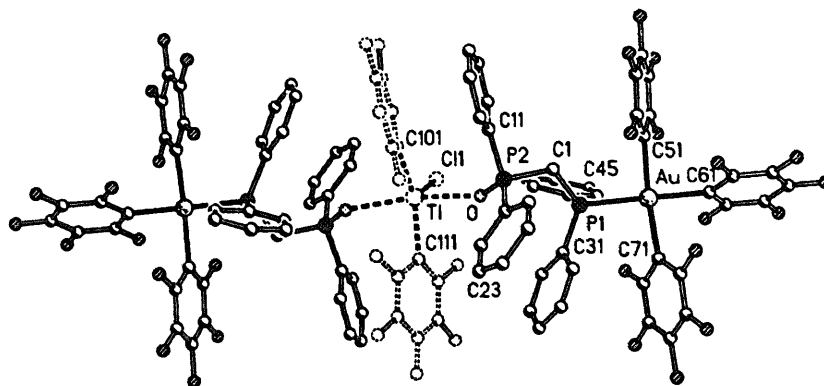


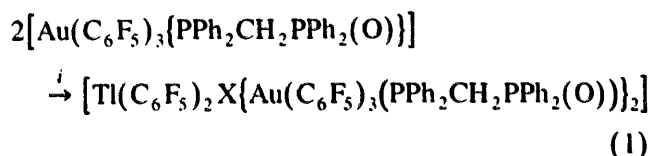
Fig. 1. The molecule of complex **2** in the crystal. Only one position of the disordered thallium (and its ligands) is shown. Radii are arbitrary; hydrogen atoms are omitted.

active 203 , ^{205}Tl nuclei. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum in CDCl_3 solution shows a multiplet at 10.5 ppm (AuPPh_2) and a doublet at 32.04 ppm ($J(\text{PP}) = 28.8 \text{ Hz}$, $\text{PPh}_2(\text{O})$), displaced downfield from that in starting compound (**1**), in agreement with the coordination of the oxygen atom to the thallium centre.

The structure of complex **2** was determined by single crystal X-ray diffraction analysis and the molecule is shown in Fig. 1. Atomic coordinates are found in Table 1 and selected bond lengths and angles in Table 2. Owing to disorder problems, the molecular dimensions should, however, be interpreted with caution (see below).

The thallium atom is coordinated to two oxygen and one chlorine atom in the equatorial plane and to two pentafluorophenyl groups perpendicular to that plane. The coordination polyhedron is that of an irregular trigonal bipyramid. The axial $\text{O}=\text{Tl}=\text{O}^i$ ($i = 1 - x, 1 - y, = z$) angle of $165.89(5)^\circ$ is almost linear; the axial/equatorial angles $\text{Cl}(1)=\text{Tl}=\text{O}$ and $\text{Cl}(1)=\text{Tl}=\text{O}^i$ are $95.1(3)^\circ$ and $97.6(3)^\circ$. The $\text{C}(101)=\text{Tl}=\text{C}(111)$ angle of $142.3(5)^\circ$ is far from its ideal value. This geometry is similar to that found in the five-coordinate complex $[\text{TiPh}(\text{S}_2\text{PPh}_2)_2]$ [4]. The $\text{Tl}-\text{O}$ bond distances are $2.550(7)$ and $2.559(7) \text{ \AA}$, comparable with those in $[\text{Ti}(\text{C}_6\text{F}_5)_2(\text{acac})(\text{OPPh}_2\text{CH}_2\text{PPh}_2\text{O})]$ ($2.531(5) \text{ \AA}$) [8] with a related ligand; however, these distances are longer than those for the acetylacetonate ligand in the latter compound ($2.310(5)$ and $2.338(5) \text{ \AA}$). The $\text{Tl}-\text{C}$ bond lengths are $2.115(13)$ and $2.18(2) \text{ \AA}$, although the difference may not be significant. The shorter is comparable with those in the complex $[\text{Ti}(\text{C}_6\text{F}_5)_2(\text{acac})(\text{OPPh}_2\text{CH}_2\text{PPh}_2\text{O})]$ ($2.129(8)$ and $2.141(7) \text{ \AA}$) [8] and the longer to those in $[\text{Ti}(\text{CH}_2\text{COMe})_2(\mu\text{-CF}_3\text{SO}_3)(\text{bipy})_2]$ [13] ($2.161(8)$ and $2.171(7) \text{ \AA}$). The $\text{Tl}-\text{Cl}(1)$ distance is $2.469(7) \text{ \AA}$, similar to those found for the equatorial chlorine atoms in the complex $\text{NMe}_4[\text{Ti}(\text{C}_6\text{H}_4\text{N}=\text{NPh}-2)\text{Cl}_2]$ ($2.500(4)$ and $2.427(3) \text{ \AA}$) [1]. The gold atoms display regular square-planar geometry with normal $\text{Au}-\text{C}_6\text{F}_5$ and $\text{Au}-\text{P}$ bond distances.

In a similar way, complex **1** reacts with $[\text{Ti}(\text{C}_6\text{F}_5)_3(\text{diox})]$ [14] to give **3** (Eq. (1)).



(i) $1/2[\text{Ti}(\text{C}_6\text{F}_5)_2\text{Cl}]_2$, $\text{X} = \text{Cl}$ (**2**) or $[\text{Ti}(\text{C}_6\text{F}_5)_3(\text{diox})]$, $\text{X} = \text{C}_6\text{F}_5$ (**3**)

We assume that complex **3** has a similar structure to **2**, because it has very similar spectroscopic properties.

3. Experimental

The C,H,N analyses were carried out on a Perkin-Elmer 2400 microanalyser. Conductivities were measured in approximately $5 \times 10^{-4} \text{ mol dm}^{-3}$ acetone solutions, with a Jenway 4010 conductimeter. Melting points were measured on a Gallenkamp apparatus. IR spectra were recorded ($4000\text{--}200 \text{ cm}^{-1}$) on Perkin-Elmer 833 spectrometer, using Nujol mull between polyethylene sheets. The NMR spectra were recorded on Bruker ARX 300 in CDCl_3 . Chemical shifts are cited relative to SiMe_4 (^1H), $85\% \text{ H}_3\text{PO}_4$ (external ^{31}P) and CFCl_3 (external ^{19}F). All the reactions were performed in air and at room temperature.

3.1. Synthesis of $[\text{Au}(\text{C}_6\text{F}_5)_3\{\text{Ph}_2\text{PCH}_2\text{PPh}_2(\text{O})\}]$ (**1**)

To a solution of $[\text{Au}(\text{C}_6\text{F}_5)_3(\text{Ph}_2\text{PCH}_2\text{PPh}_2)]$ [9] (0.27 g , 0.25 mmol) in 20 cm^3 of acetone was added $30\% \text{ H}_2\text{O}_2$ (0.36 cm^3 , 0.25 mmol). The solution was stirred for 5 h and filtered through a 1 cm layer of anhydrous magnesium sulphate. The solution was concentrated to ca. 5 cm^3 . Addition of hexane (20 cm^3) led to precipitation of **1** as a white solid. (Yield 85%). M.p. 185°C (decomp.). A_M $5 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$. IR: $1503(\text{vs})$, $966(\text{vs})$, $750(\text{m}) \text{ cm}^{-1}$ (C_6F_5). ^1H NMR: δ 3.53(t, $J = 11.2 \text{ Hz}$, 2H, CH_2); ^{19}F NMR: δ -120.1 (m, 4F, *o*-F),

Table 1

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$)

	x	y	z	U_{eq}
Au	2449.1(3)	7658.5(3)	4097.4(2)	28.9(1)
Tl	4776.5(9)	4830.3(10)	-23.3(10)	37.4(3)
P(1)	3096(2)	7017(2)	2870.0(14)	30.2(5)
P(2)	5032(2)	5831(2)	2239.2(15)	35.6(6)
O	4602(6)	5736(6)	1401(4)	42(2)
C(1)	3980(8)	6047(7)	2923(6)	33(2)
C(11)	5367(8)	4612(6)	2407(6)	49(3)
C(12)	6388(7)	4534(8)	2763(7)	111(6)
C(13)	6535(8)	3579(10)	2902(8)	127(8)
C(14)	5660(11)	2702(8)	2684(8)	99(6)
C(15)	4639(9)	2780(6)	2328(7)	94(5)
C(16)	4492(7)	3735(7)	2189(6)	74(4)
C(21)	6233(5)	6864(5)	2586(4)	40(2)
C(22)	6733(7)	7374(7)	2047(3)	62(3)
C(23)	7712(7)	8141(7)	2285(5)	76(4)
C(24)	8191(6)	8397(6)	3062(5)	68(4)
C(25)	7690(7)	7887(7)	3600(4)	66(4)
C(26)	6712(6)	7120(6)	3363(4)	49(3)
C(31)	3900(5)	8039(4)	2500(4)	32(2)
C(32)	3625(5)	8176(5)	1756(4)	44(2)
C(33)	4250(7)	8998(6)	1502(4)	69(4)
C(34)	5151(7)	9683(6)	1992(5)	70(4)
C(35)	5425(5)	9545(5)	2736(4)	54(3)
C(36)	4800(6)	8723(5)	2990(3)	39(2)
C(41)	1867(5)	6328(5)	2185(4)	37(2)
C(42)	1960(5)	5615(6)	1487(4)	50(3)
C(43)	1003(7)	5092(6)	978(4)	70(4)
C(44)	-48(5)	5284(7)	1167(4)	68(4)
C(45)	-141(5)	5997(7)	1865(5)	61(3)
C(46)	816(6)	6520(6)	2374(4)	48(3)
C(51)	2156(7)	6165(8)	4306(6)	39(2)
C(52)	1103(9)	5505(8)	4172(6)	46(3)
C(53)	908(10)	4532(9)	4354(7)	56(3)
C(54)	1796(8)	4209(10)	4683(7)	57(3)
C(55)	2856(9)	4820(9)	4830(7)	53(3)
C(56)	3010(8)	5795(8)	4646(6)	40(2)
F(1)	220(5)	5819(6)	3881(4)	62(2)
F(2)	-116(7)	3922(6)	4216(5)	82(3)
F(3)	1618(8)	3250(6)	4855(6)	93(3)
F(4)	3684(7)	4508(6)	5156(5)	72(2)
F(5)	4044(5)	6376(4)	4797(4)	43.8(14)
C(61)	1701(7)	8184(7)	5098(5)	34(2)
C(62)	2125(8)	8236(7)	5847(6)	39(2)
C(63)	1598(8)	8586(8)	6491(6)	46(3)
C(64)	575(9)	8899(9)	6389(7)	52(3)
C(65)	121(9)	8837(9)	5641(6)	48(3)
C(66)	688(8)	8493(8)	5019(6)	41(2)
F(6)	3109(5)	7947(5)	5972(4)	50(2)
F(7)	2036(7)	8653(7)	7221(4)	75(2)
F(8)	40(7)	9241(6)	7011(5)	76(2)
F(9)	-855(6)	9149(6)	5535(5)	71(2)
F(10)	216(5)	8453(5)	4296(4)	54(2)
C(71)	2777(7)	9212(7)	4017(5)	32(2)
C(72)	2395(7)	9552(7)	3389(5)	35(2)
C(73)	2690(9)	10581(8)	3330(6)	46(3)
C(74)	3383(9)	11307(9)	3922(5)	47(3)
C(75)	3773(9)	11015(7)	4567(6)	41(2)
C(76)	3473(8)	9976(7)	4597(5)	34(2)
F(11)	1693(5)	8867(5)	2789(4)	50(2)
F(12)	2297(6)	10860(6)	2694(4)	64(2)
F(13)	3665(7)	12323(5)	3887(5)	69(2)

Table 1 (continued)

F(14)	4458(6)	11718(5)	5153(4)	60(2)
F(15)	3906(5)	9726(4)	5247(3)	42.7(14)
Cl(1)	2733(6)	4172(8)	-380(5)	90(3)
C(101)	5473(11)	3637(10)	317(9)	42(5)
C(102)	6540(11)	3935(9)	729(10)	61(7)
C(103)	7025(11)	3195(11)	995(11)	79(8)
C(104)	6443(12)	2158(10)	849(12)	76(8)
C(105)	5376(12)	1860(9)	438(13)	125(23)
C(106)	4891(10)	2600(10)	172(11)	56(6)
F(16)	7077(14)	4883(12)	911(10)	81(5)
F(17)	8012(17)	3486(17)	1448(13)	112(7)
F(18)	6928(18)	1433(17)	1130(14)	113(7)
F(19)	4822(20)	866(16)	362(14)	117(7)
F(20)	3918(16)	2282(16)	-221(12)	103(6)
C(111)	5228(12)	6422(13)	-187(12)	61(7)
C(112)	6365(11)	6802(14)	-218(12)	70(8)
C(113)	6720(10)	7791(15)	-359(15)	125(15)
C(114)	5936(13)	8398(14)	-468(16)	132(16)
C(115)	4799(12)	8017(14)	-437(14)	85(13)
C(116)	4445(10)	7029(14)	-296(12)	68(7)
F(21)	7110(15)	6230(14)	-153(12)	84(5)
F(22)	7804(26)	8147(27)	-413(23)	195(14)
F(23)	6261(23)	9289(28)	-607(21)	178(13)
F(24)	4045(24)	8595(21)	-553(18)	147(10)
F(25)	3393(16)	6683(16)	-232(13)	108(6)
C(98)	356(36)	2616(37)	1744(21)	277(23)
Cl(2)	1495(28)	2344(24)	1153(19)	523(17)
Cl(3)	1394(12)	3262(12)	2540(9)	276(6)
C(99)	-116(32)	11937(26)	8965(21)	210(15)
Cl(4)	-41(20)	10650(19)	9033(14)	413(12)
Cl(5)	-932(16)	12260(14)	9724(11)	336(8)

U_{eq} is defined as one-third of the trace of the trace of the orthogonalized U_{ij} tensor.

-120.2 (m, 2F, *o*-F), -156.2 (t, $J = 19.2$ Hz, 2F, *p*-F), -157.1 (t, $J = 19.9$ Hz, 1F, *p*-F), -160.5 (m, 4F, *m*-F), -161.0 (m, 2F, *m*-F); $^{31}\text{P}\{^1\text{H}\}$ NMR: δ 101.8 (m, P-Au), 23.1 (d, $J(\text{PP}) = 23.9$ Hz, P-O) Anal. Found: C, 46.8; H, 1.75. $\text{C}_{43}\text{H}_{22}\text{AuF}_{15}\text{OP}_2$. Calc.: C, 47.0; H, 2.0%.

3.2. $[\text{Ti}(\text{C}_6\text{F}_5)_2\text{X}\{\text{Au}(\text{C}_6\text{F}_5)_3(\text{Ph}_2\text{PCH}_2\text{PPh}_2(\text{O}))\}_2] (\text{X} = \text{Cl} (2), \text{C}_6\text{F}_5 (3))$

To a dichloromethane solution (20 cm³) of **1** (0.55 g, 0.5 mmol) was added $[\text{Ti}(\text{C}_6\text{F}_5)_2\text{X}]$ [**11**] (0.143 g, 0.25 mmol) or $[\text{Ti}(\text{C}_6\text{F}_5)_3(\text{diox})]$ [**14**] (0.198 g, 0.25 mmol). After stirring for 24 h the solution was evaporated to ca. 5 cm³ and addition of hexane gave the complexes **2** or **3** as white solids.

2: (yield 77%). M.p. 150°C. M_n 7 $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$. IR: 1636(vs), 1510(vs), 1503(vs), 965(vs,br), 800(vs,br) cm⁻¹ (C_6F_5); 1160 cm⁻¹ ($\nu(\text{P}=\text{O})$). ^1H NMR: δ 3.46 (t, $J = 6.28$ Hz, 2H, CH_2); ^{19}F NMR: δ -120.3 (m, 4F, *o*-F), -121.6 (m, 2F, *o*-F), -155.6 (t, $J = 19.9$ Hz, 2F, *p*-F), -156.7 (t, $J = 19.8$ Hz, 1F, *p*-F), -160.0 (m, 4F, *m*-F), -160.8 (m, 2F, *m*-F) $[\text{Au}(\text{C}_6\text{F}_5)_3]$; -119.9 (dm, $J(^{203,205}\text{Tl}-\text{F}) = 933.7$ Hz,

Table 2
Selected bond lengths (Å) and angles (deg)

Au–C(61)	2.059(10)	Au–C(71)	2.074(9)
Au–C(51)	2.075(10)	Au–P(1)	2.359(3)
Tl–C(101)	2.115(13)	Tl–C(111)	2.18(2)
Tl–C(1)	2.469(7)	Tl–O	2.550(7)
Tl–O#1	2.559(7)	P(1)–C(31)	1.792(5)
P(1)–C(41)	1.817(6)	P(1)–C(1)	1.840(10)
P(2)–O	1.500(7)	P(2)–C(21)	1.779(6)
P(2)–C(1)	1.816(10)	P(2)–C(11)	1.827(8)
C(61)–Au–C(71)	86.3(3)	C(61)–Au–C(51)	88.9(4)
C(71)–Au–C(51)	174.0(3)	C(61)–Au–P(1)	173.3(2)
C(71)–Au–P(1)	94.0(2)	C(51)–Au–P(1)	91.2(3)
C(101)–Tl–C(111)	142.3(5)	C(101)–Tl–C(1)	108.6(4)
C(111)–Tl–C(1)	109.0(5)	C(101)–Tl–O	92.3(5)
C(111)–Tl–O	85.2(5)	Cl(1)–Tl–O	95.1(3)
C(101)–Tl–O#1	89.5(5)	C(111)–Tl–O#1	84.8(5)
Cl(1)–Tl–O#1	97.6(3)	O–Tl–O#1	165.89(5)
C(31)–P(1)–C(41)	110.4(3)	C(31)–P(1)–C(1)	107.6(4)
C(41)–P(1)–C(1)	106.7(4)	C(31)–P(1)–Au	112.9(2)
C(41)–P(1)–Au	107.3(2)	C(1)–P(1)–Au	111.7(3)
O–P(2)–C(21)	113.0(4)	O–P(2)–C(1)	113.1(4)
C(21)–P(2)–C(1)	107.4(4)	O–P(2)–C(11)	113.3(4)
C(21)–P(2)–C(11)	108.5(4)	C(1)–P(2)–C(11)	100.7(4)
P(2)–O–Tl	143.2(4)	P(2)–C(1)–P(1)	120.7(5)

Symmetry transformation used to generate equivalent atoms: #1 $-x + 1, -y + 1, -z$.

4F, *o*-F), -149.5 (dm, $J(^{203,205}\text{Tl}-\text{F}_p) = 72.3$ Hz, 2F, *p*-F), -158.6 (dm, $J(^{203,205}\text{Tl}-\text{F}_m) = 359.4$ Hz, 4F, *m*-F) [$\text{Tl}(\text{C}_6\text{F}_5)_2$]; $^{31}\text{P}\{^1\text{H}\}$ NMR: δ 10.5 (m, P–Au), 32.04 (d, $J(\text{PP}) = 28.8$ Hz, P–O). Anal. Found: C, 40.6; H, 1.6. $\text{C}_{98}\text{H}_{44}\text{Au}_3\text{ClF}_{40}\text{O}_2\text{P}_4\text{Tl} \cdot 4\text{CH}_2\text{Cl}_2$. Calc.: C, 39.4; H, 1.7%.

3: (yield 45%). M.p. 128 °C. IR: 1636(s), 1508(vs), 969(vs), 793(s), 767(s) cm^{-1} (C_6F_5); 1175(vs) cm^{-1} ($\nu(\text{P}=\text{O})$). ^1H NMR: δ 3.5 (t, $J = 10.9$ Hz, 2H, CH_2); ^{19}F NMR: $\delta = 120.3$ (m, 4F, *o*-F), -121.3 (m, 2F, *o*-F), -155.9 (t, $J = 19.14$ Hz, 2F, *p*-F), -156.9 (t, $J = 20.0$ Hz, 1F, *p*-F), -160.2 (m, 4F, *m*-F), -160.6 (m, 2F, *m*-F) [$\text{Au}(\text{C}_6\text{F}_5)_3$]; -118.2 (dm, $J(^{203,205}\text{Tl}-\text{F}_p) = 522.35$ Hz, 4F, *o*-F), -156.8 (dm, $J(^{203,205}\text{Tl}-\text{F}_m) = 84.7$ Hz, 2F, *p*-F), -159.2 (dm, $J(^{203,205}\text{Tl}-\text{F}_m) = 204.7$ Hz, 4F, *m*-F), [$\text{Tl}(\text{C}_6\text{F}_5)_2$]; $^{31}\text{P}\{^1\text{H}\}$ NMR: δ 11.1 (m, P–Au), 29.0 (m, P–O). Anal. Found: C, 43.6; H, 1.75. $\text{C}_{104}\text{H}_{44}\text{Au}_3\text{F}_{45}\text{O}_2\text{P}_4\text{Tl}$. Calc.: C, 43.05; H, 1.55%.

3.3. Crystal structure determination of $2 \cdot 2\text{CH}_2\text{Cl}_2$

3.3.1. Crystal data

$\text{C}_{102}\text{H}_{48}\text{Au}_3\text{Cl}_9\text{F}_{40}\text{O}_2\text{P}_4\text{Tl}$, $M_r = 3106.64$, triclinic, space group $P\bar{1}$, $a = 12.148(4)$, $b = 13.325(4)$, $c = 17.529(6)$ Å, $\alpha = 103.34(2)$, $\beta = 93.18(3)$, $\gamma = 100.62(3)^\circ$, $V = 2699(2)$ Å³, $Z = 1$, $D_c = 1.911$ Mg m⁻³, $\mu = 4.6$ mm⁻¹, $F(000) = 1488$, $T = -130^\circ\text{C}$. Colourless prism $0.70 \times 0.50 \times 0.40$ mm³.

3.3.2. Data collection and reduction

The crystal was mounted in inert oil on a glass fibre. Data were collected using monochromated Mo K α radi-

ation ($\lambda = 0.71073$ Å) on a Stoe STADI-4 diffractometer with an LT-2 low temperature attachment to $2\theta_{\text{max}} 50^\circ$. 9528 intensities were collected of which 9527 were unique. Absorption correction based on Ψ -scans with transmission factors 0.696–0.916. Cell constants were refined from $\pm\omega$ values of 54 reflections in the 2θ range 20 – 22° .

Structure solution: heavy-atom method. Refinement on F^2 for all reflections except 16 with very negative F^2 (program SHELXL-93) [15], hydrogen atoms with riding model. Although the structure crystallises in $P\bar{1}$ with one molecule per cell, the thallium atom does not lie on an inversion centre; it (and its ligands) are disordered over two inversion-related sites. We believe that the disorder model is credible, but the associated dimensions should obviously be interpreted with caution. The half-occupied C_6F_5 groups were refined as regular C_6 hexagons, which is a poor approximation to their normal geometry (narrow angle at the *ipso*-carbon). The solvent molecules are not well defined. The final $wR(F^2)$ was 0.177, conventional $R(F)$ 0.063 for 402 parameters and 106 restraints; $S = 1.019$, max Δ/σ 0.298, max Δ/ρ $2.3\text{e}\text{\AA}^{-3}$.

4. Supplementary material available

Full details of the structure determination have been deposited at the Fachinformationszentrum Karlsruhe, Gesellschaft für Wissenschaftlich-technische Information mbH, 76344 Eggenstein-Leopoldshafen, Germany.

Any request for this material should quote the full literature citation and the reference number CSD 404462.

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References

- [1] J. Vicente, J.A. Abad, J.F. Gutiérrez-Jugo and P.G. Jones, *J. Chem. Soc. Dalton Trans.*, (1989) 2241.
- [2] M.A. Paver, C.A. Russell and D.S. Wright, in G. Wilkinson, F.G. Stone and E.W. Abel (eds.), *Comprehensive Organometallic Chemistry II*, Vol. 1, Pergamon, Oxford, 1995, p. 503. C.J. Carmalt, N.C. Norman and L.M. Clakson, in G. Wilkinson, F.G. Stone and E.W. Abel (eds.), *Comprehensive Organometallic Chemistry II*, Vol. 1, Pergamon, Oxford, 1995, p. 545.
- [3] A. Laguna, E.J. Fernández, A. Mendiá, M.E. Ruiz-Romero and P.G. Jones, *J. Organomet. Chem.*, 365 (1989) 201
- [4] J.S. Casas, E. Castellano, A. Castiñeiras, A. Sánchez, J. Sordo, E.M. Vázquez-López and J. Zukerman-Schpector, *J. Chem. Soc. Dalton Trans.*, (1995) 1403.
- [5] G.B. Deacon and V.N. Garg, *Inorg. Nucl. Chem. Lett.*, 5 (1969) 359.
- [6] S. Wang, J.P. Fackler, Jr., C. King and J.C. Wang, *J. Am. Chem. Soc.*, 110 (1988) 3308. S. Wang, G. Garzón, C. King, J.C. Wang and J.P. Fackler, Jr., *Inorg. Chem.*, 28 (1989) 4623.
- [7] G.K. Anderson and N.P. Rath, *J. Organomet. Chem.*, 414 (1991) 129.
- [8] E.J. Fernández, P.G. Jones, A. Laguna and A. Mendiá, *Inorg. Chim. Acta*, 215 (1994) 229.
- [9] R. Usón, A. Laguna, M. Laguna, E.J. Fernández, P.G. Jones and G.M. Sheldrick, *J. Chem. Soc. Dalton Trans.*, (1982) 1971.
- [10] H. Teichmann and G. Hilgetag, *Angew. Chem. Int. Ed. Engl.*, 6 (1967) 1013.
- [11] R. Usón and A. Laguna, *Inorg. Synth.*, 21 (1982) 71.
- [12] G.B. Deacon and R.J. Phillips, *J. Organomet. Chem.*, 171 (1979) C1.
- [13] J. Vicente, J.A. Abad, G. Cosa and P.G. Jones, *Angew. Chem. Int. Ed. Engl.*, 29 (1990) 1125.
- [14] R. Usón, A. Laguna, J.A. Abad and E. de Jesús, *J. Chem. Soc. Dalton Trans.*, (1983) 1127.
- [15] G.M. Sheldrick, SHELX-93, *A Program for Crystal Structure Refinement*, University of Göttingen, 1993.