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Synthesis and structure of the tetrametallic complex $[TlAu(C_5H_4PPh_2)_2]_2$

Gordon K. Anderson * and Nigam P. Rath

Department of Chemistry, University of Missouri — St. Louis, St. Louis, MO 63121 (USA)

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Abstract

The tetrametallic complex $[TlAu(C_5H_4PPh_2)_2]_2$, **1**, is obtained by reaction of $[AuCl(SMe_2)]$ with $TlC_5H_4PPh_2$ in benzene solution. The structure of **1**, as its benzene solvate, has been determined using X-ray diffraction methods, and reveals that each gold is coordinated by two phosphino groups and each thallium is symmetrically bound in η^5 fashion to two cyclopentadienyls. **1** is triclinic, space group $P\bar{1}$, with a 10.572(4), b 11.343(6), c 16.056(6) Å, α 105.09(4), β 98.96(3), γ 107.15(4)°, $Z = 2$, $R = 0.0423$ and $R_w = 0.0438$ for refinement of 398 parameters using 6106 unique reflections.

Introduction

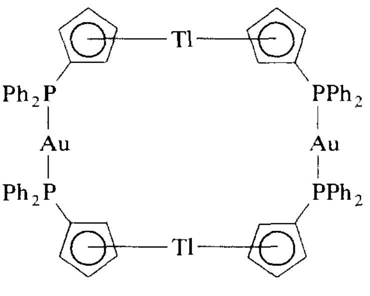
There is interest in the structures of substituted cyclopentadienyl derivatives of thallium, and the crystal structures of $\{TlC_5Me_5\}_n$ [1], $\{TlC_5H_4SiMe_3\}_n$ and $[TlC_5H_3(SiMe_3)_2\text{-}1,3\}_6$ [2], and $TlC_5(CH_2Ph)_5$ [3] have been reported recently. In connection with our work on platinum complexes bridged by the diphenylphosphinocyclopentadienyl (dppc) ligand [4], we attempted to prepare $[Au(C_5H_4PPh_2)]_2$ which we anticipated would contain two linear gold(I) centers bridged by dppc ligands. The reaction of $[AuCl(SMe_2)]$ with $TlC_5H_4PPh_2$, however, produced the tetrametallic complex $[TlAu(C_5H_4PPh_2)_2]_2$, **1**, whose solid state structure is reported here.

Results and discussion

Cyclopentadienylthallium is a convenient reagent for the introduction of a cyclopentadienyl group to a transition metal complex. Metathesis reactions occur between species containing metal-halide bonds and TlC_5H_5, thallium chloride being formed as a byproduct. When a benzene solution of $[AuCl(SMe_2)]$ is treated with $TlC_5H_4PPh_2$, the tetrametallic species $[TlAu(C_5H_4PPh_2)_2]_2$, **1**, is formed as well as a precipitate of TlCl (eq. 1).

$$2\,[AuCl(SMe_2)] + 4\,TlC_5H_4PPh_2 \rightarrow [TlAu(C_5H_4PPh_2)_2]_2 + 2\,TlCl + 2\,SMe_2 \quad (1)$$

Complex **1** has been characterized by elemental analysis, NMR spectroscopy, mass spectrometry, and X-ray crystallography. Its $^{31}P\{^1H\}$ NMR spectrum exhibits a single resonance due to the two phosphorus atoms coordinated to each gold(I) center. The ^1H and $^{13}C\{^1H\}$ NMR spectra are consistent with η^5-bonding of the cyclopentadienyl rings to thallium. Two signals are observed for the cyclopentadienyl protons in the ^1H spectrum, and three signals for the cyclopentadienyl carbons and four signals for the eight phenyl groups are found in the $^{13}C\{^1H\}$ spectrum. Coupling to thallium is not resolved in any of the NMR spectra. Mass spectra of **1** do not yield a molecular ion, but clearly indicate the presence of both thallium and gold.



(**1**)

Complex **1** is soluble in dichloromethane or chloroform, and is somewhat soluble in aromatic hydrocarbons. Attempts to remove the thallium by reaction with metal halide compounds, such as $[AuCl(SMe_2)]$, $[AuCl(PPh_3)]$, $[PtCl_2(cod)]$ or $[Pd_2Cl_4(PMePh_2)_2]$, result only in decomposition.

The crystal structure of $\mathbf{1} \cdot 2C_6H_6$ reveals that it contains two gold and two thallium atoms in the unit cell bridged by four dppc ligands, the phosphorus atoms being coordinated to gold and the thallium atoms bound in η^5 fashion to the cyclopentadienyl rings (Fig. 1). The P–Au–P angle is 176° and the Au–P distances are typical for linear bis(tertiary phosphine)gold(I) species [5]. The bond distances and angles involving phosphorus are as expected, and the bond distances and angles within the cyclopentadienyl pentadienyl rings lie within the ranges 1.375(9)–1.414(12) Å and 106.7(6)–109.7(7)°. Such variations are normal for η^5-cyclopentadienyl compounds [6]. The Tl–C distances lie within the range 2.876(2)–3.048(2) Å for one ring and 2.882(2)–3.103(2) Å for the second. The Tl–Cp(centroid) distances are 2.713 and 2.747 Å, respectively, and the Cp–Tl–Cp angle is 135.3°.

Most compounds containing cyclopentadienyl–thallium linkages have polymeric structures in the solid state, including TlC_5H_5 [7], TlC_5Me_5 [1], $TlC_5H_4SiMe_3$ [2] and $TlC_5H_4C(CN){=}C(CN)_2$ [8]. The only exceptions reported to date are $[TlC_5H_3(SiMe_3)_2\text{-}1,3]$, which forms a cyclic hexamer [2], and $TlC_5(CH_2Ph)_5$, which is monomeric [3]. The Tl–Cp distance in $TlC_5(CH_2Ph)_5$ is 2.494 Å, but the distances are longer when two Tl–Cp interactions are involved, ranging from 2.71 Å in $TlC_5H_4SiMe_3$ to over 3 Å. The Tl–Cp distances and the Cp–Tl–Cp angle found for **1** most closely resemble those found in $TlC_5H_4SiMe_3$ and $[TlC_5H_3(SiMe_3)_2\text{-}1,3]$. Since the two $Au(C_5H_4PPh_2)_2$ units are held together only by the thallium atoms, the Tl–Cp interactions in **1** should be close to optimal. Thus, silicon- or phosphorus-substituted cyclopentadienyl-thallium compounds appear to exhibit shorter Tl–Cp distances than the unsubstituted or organo-substituted species.

Experimental

$[AuCl(SMe_2)]$ was obtained in 95% yield from $NaAuCl_4 \cdot 2H_2O$ and SMe_2 in methanol [9], and $TlC_5H_4PPh_2$ was prepared by a reported method [10]. NMR spectra were recorded for $CDCl_3$ solutions on a Varian XL-300 spectrometer. Chemical shifts are relative to residual $CHCl_3$ at 7.25 ppm (^1H), $CDCl_3$ at 77.0 ppm (^{13}C) or H_3PO_4 (^{31}P). Mass spectra were recorded on a Hewlett-Packard HP 5988A GC-MS system. Analyses were performed by Atlantic Microlab, Inc., Norcross, Georgia.

Preparation of $[TlAu(C_5H_4PPh_2)_2]_2$

$[AuCl(SMe_2)]$ (0.27 g, 0.90 mmol) was dissolved in benzene (10 ml), under argon, and $TlC_5H_4PPh_2$ (0.64 g, 1.42 mmol) was added as a solid. The mixture was stirred at ambient temperature for 3 d, then filtered through alumina (to remove TlCl) to yield a pale yellow solution. Pentane addition gave the product as a pale yellow solid (0.19 g, 30% based on $TlC_5H_4PPh_2$). Found: C, 46.01; H, 3.16. $C_{68}H_{56}Au_2P_4Tl_2$ calcd.: C, 45.38; H, 3.14%. ^1H NMR: $\delta(C_5H_4)$ 5.97, 6.13 (br s); $\delta(C_6H_5)$ 7.4, 7.6 (br s). $^{13}C\{^1H\}$ NMR: $\delta(C_5H_4)$ 99.6 (t, J(P,C) 37 Hz, C_α), 113.4 (s, C_γ), 117.1 (t, J(P,C) 6.5 Hz, C_β); $\delta(C_6H_5)$ 128.8 (t, J(P,C) 5.2 Hz, C_3), 130.6 (s, C_4), 133.5 (t, J(P,C) 6.8 Hz, C_2), 134.3 (t, J(P,C) 30 Hz, C_1). $^{31}P\{^1H\}$ NMR δ(P) 32.0 (s).

X-Ray diffraction study of $1 \cdot 2C_6H_6$

Yellow, irregularly shaped crystals of appropriate dimensions for X-ray diffraction analysis were obtained by slow evaporation of a benzene solution of the complex at ambient temperature. A crystal was mounted on a glass fiber in random orientation. Preliminary examinations and data collection were performed using a Siemens *R3m/V* automated diffractometer equipped with a graphite monochroma-

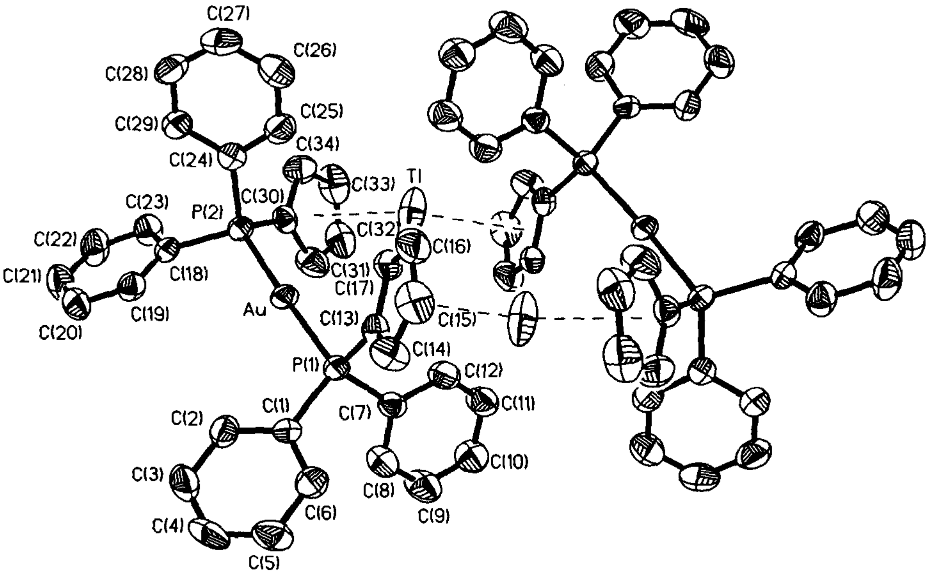


Fig. 1. Projection drawing of $[TlAu(C_5H_4PPh_2)_2]_2 \cdot 2C_6H_6$, $1 \cdot 2C_6H_6$.

Table 1

Crystallographic data for 1 · $2C_6H_6$

Empirical formula	$C_{40}H_{34}AuP_2Tl$
Formula weight	977.9
Color, habit	yellow, irregular
Space group	$P\bar{1}$
a, Å	10.572(4)
b, Å	11.343(6)
c, Å	16.056(6)
α, deg	105.09(4)
β, deg	98.96(3)
γ, deg	107.15(4)
Cell volume, Å^3	1719.0(13)
Z	2
D(calcd), Mg/m^3	1.889
Temperature, K	298
Radiation	graphite monochromated Mo-K_α (λ = 0.71073 Å)
Crystal dimensions, mm	0.5×0.4×0.3
Absorption coefficient, mm^{-1}	9.103
2θ range, deg	3.5–55.0
Scan speed, deg/min	variable, 4.0–15.0
Scan range (ω), deg	0.70 plus K_α separation
Independent reflections	7917
Observed reflections ($F > 4.0\sigma(F)$)	6106
Absorption correction	semi-empirical
Transmission min/max	0.5472/1.0000
No. parameters refined	398
R	0.0423
R_w	0.0438
Goodness of fit	1.43

tor. Mo-K_α radiation (λ = 0.71073 Å) was used for data collection at 25 °C. Indexing 15 automatically centered reflections from the photograph resulted in a triclinic cell. Axial photographs were taken to confirm the Laue symmetry and cell lengths. A set of higher angle data (2θ) was obtained using the initial orientation matrix. Final cell constants and orientation matrix for data collection were calculated by least-squares refinement of 25 reflections ($20° < 2\theta < 25°$). The data were collected using the θ–2θ scan technique with a variable scan rate. As a check on the crystal stability three representative reflections were measured every 50 reflections. As the intensities of these standards remained constant within experimental error, no decay correction was applied. Final cell parameters and crystal data, and intensity collection parameters are listed in Table 1.

Data reduction, structure solution and refinement were carried out using the SHELXTL PLUS (VMS) program [11]. An empirical absorption correction was applied to the data using nine ψ-scan curves with $\chi > 83°$. The structure was solved by the Patterson method and refined successfully in the space group $P\bar{1}$. Full matrix least-squares refinement was carried out by minimizing $\Sigma w(F_o - F_c)^2$. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were added in

Table 2

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^3$)

	x	y	z	U_{eq} [a]
Au	1668(1)	2567(1)	3778(1)	37(1)
Tl	−1891(1)	−755(1)	3098(1)	84(1)
P(1)	2274(2)	3398(2)	5322(1)	35(1)
P(2)	921(2)	1638(2)	2242(1)	36(1)
C(1)	3423(6)	5097(6)	5760(4)	37(2)
C(2)	3788(7)	5747(7)	5166(5)	46(3)
C(3)	4562(8)	7077(7)	5479(6)	62(4)
C(4)	4995(8)	7700(7)	6391(6)	62(4)
C(5)	4636(8)	7080(7)	6984(5)	61(3)
C(6)	3836(8)	5766(7)	6663(5)	53(3)
C(7)	769(6)	3439(6)	5740(4)	37(2)
C(8)	492(7)	4571(7)	6038(5)	54(3)
C(9)	−651(8)	4567(7)	6335(6)	64(4)
C(10)	−1580(7)	3432(8)	6319(6)	58(4)
C(11)	−1366(7)	2286(7)	6010(6)	56(3)
C(12)	−186(7)	2280(7)	5725(5)	51(3)
C(13)	3067(6)	2428(6)	5762(4)	38(3)
C(14)	4096(8)	2810(7)	6544(5)	57(3)
C(15)	4511(7)	1759(9)	6539(6)	63(4)
C(16)	3759(8)	718(8)	5756(6)	61(4)
C(17)	2876(7)	1144(6)	5271(4)	45(3)
C(18)	1314(6)	2827(6)	1653(4)	35(2)
C(19)	2407(7)	3985(7)	2042(4)	45(3)
C(20)	2677(8)	4908(7)	1597(5)	58(3)
C(21)	1873(8)	4631(8)	763(5)	60(4)
C(22)	805(8)	3503(8)	379(5)	62(4)
C(23)	519(7)	2568(7)	811(5)	50(3)
C(24)	1699(6)	451(6)	1811(4)	36(2)
C(25)	1657(8)	−532(7)	2173(5)	54(3)
C(26)	2238(8)	−1450(8)	1881(6)	60(4)
C(27)	2867(8)	−1397(8)	1207(6)	63(4)
C(28)	2926(8)	−422(8)	833(6)	63(4)
C(29)	2367(7)	466(7)	1136(5)	49(3)
C(30)	−869(6)	798(6)	1929(4)	40(3)
C(31)	−1827(8)	1247(7)	2297(6)	60(4)
C(32)	−3121(8)	346(9)	1895(7)	65(4)
C(33)	−3000(8)	−710(9)	1290(6)	70(4)
C(34)	−1604(8)	−443(7)	1300(5)	58(3)
C(35)	6446(27)	5382(22)	1165(12)	141(14)
C(36)	5624(15)	4097(21)	865(8)	122(9)
C(37)	6168(15)	3219(12)	897(7)	96(6)
C(38)	7494(18)	3531(15)	1207(8)	99(8)
C(39)	8316(13)	4779(23)	1500(8)	122(9)
C(40)	7783(24)	5728(14)	1476(10)	132(1)

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

idealized calculated positions and were held fixed. The final residual values were $R = 4.2$ and $R_w = 4.4\%$. Relevant parameters are listed in Table 1. The atomic coordinates of the non-hydrogen atoms are given in Table 2. Selected bond distances and bond angles are presented in Tables 3 and 4.

Table 3

Selected bond distances for **1**·$2C_6H_6$

Au–P(1)	2.319(1)	Au–P(2)	2.315(1)
P(1)–C(1)	1.825(1)	P(1)–C(7)	1.829(1)
P(1)–C(13)	1.783(1)	P(2)–C(18)	1.828(1)
P(2)–C(24)	1.820(1)	P(2)–C(30)	1.770(1)
C(13)–C(14)	1.400(1)	C(13)–C(17)	1.401(1)
C(14)–C(15)	1.385(1)	C(15)–C(16)	1.403(1)
C(16)–C(17)	1.395(1)	C(30)–C(31)	1.402(1)
C(30)–C(34)	1.406(1)	C(31)–C(32)	1.375(1)
C(32)–C(33)	1.385(1)	C(33)–C(34)	1.413(1)
Tl–C(30)	3.004(2)	Tl–C(31)	2.876(2)
Tl–C(32)	2.900(2)	Tl–C(33)	2.976(2)
Tl–C(34)	3.048(2)	Tl–C(13A)	3.103(2)
Tl–C(14A)	3.019(2)	Tl–C(15A)	2.882(2)
Tl–C(16A)	2.904(2)	Tl–C(17A)	3.053(2)
Tl–Cp(centroid)	2.713	Tl–Cp(A)(centroid)	2.747

Table 4

Selected bond angles for **1**·$2C_6H_6$

P(1)–Au–P(2)	176.0(1)	Au–P(1)–C(1)	113.4(1)
Au–P(1)–C(7)	110.3(1)	Au–P(1)–C(13)	109.3(1)
Au–P(2)–C(18)	113.3(1)	Au–P(2)–C(24)	112.2(1)
Au–P(2)–C(30)	109.8(1)	C(1)–P(1)–C(7)	103.6(1)
C(1)–P(1)–C(13)	109.1(1)	C(7)–P(1)–C(13)	111.0(1)
C(18)–P(2)–C(24)	105.7(1)	C(18)–P(2)–C(30)	108.6(1)
C(24)–P(2)–C(30)	106.8(1)	C(14)–C(13)–C(17)	108.1(1)
C(13)–C(14)–C(15)	107.5(1)	C(14)–C(15)–C(16)	109.1(1)
C(15)–C(16)–C(17)	107.2(1)	C(13)–C(17)–C(16)	108.1(1)
C(31)–C(30)–C(34)	106.7(1)	C(30)–C(31)–C(32)	109.7(1)
C(31)–C(32)–C(33)	107.6(1)	C(32)–C(33)–C(34)	108.6(1)
C(30)–C(34)–C(33)	107.2(1)		
Cp–Tl–Cp(A)	135.3		

Complete lists of bond distances and angles, positional and isotropic temperature factors for the hydrogen atoms, and calculated and observed structure factors are available from the authors.

Acknowledgement

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