Preparation of Three- and Four-co-ordinate Gold(I) Complexes; Crystal Structure of Bis[*o*-phenylenebis(dimethylarsine)]gold(I) Bis(pentafluorophenyl)aurate(I)

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The addition of 1,10-phenanthroline, *o*-phenylenebis(dimethylarsine), or triphenylstibine to pentafluorophenyl-(tetrahydrothiophen)gold(I) leads respectively to $[Au(C_6F_5)(phen)]$, $[Au(pdma)_2][Au(C_6F_5)_2]$, and $[Au(SbPh_3)_4][Au(C_6F_5)_2]$, the pdma derivative being the first four-co-ordinate gold(I) complex whose structure has been fully determined by *X*-ray diffraction; space group $P\bar{1}$, a = 10.340(3), b = 10.982(3), c = 17.612(5) Å, α = 75.45(2), β = 82.35(2), γ = 87.23(2)°, Z = 2, R = 0.043 for 5 558 unique observed reflections. The Au–As bond lengths range from 2.462 to 2.478 Å. The two independent anions are exactly linear at Au.

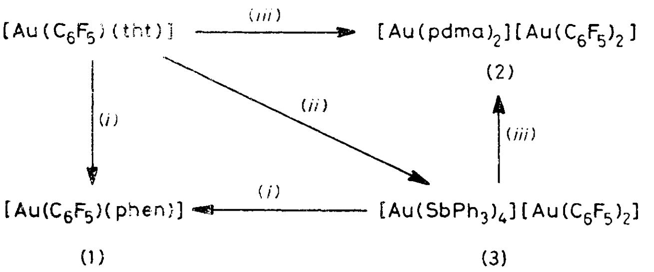
GOLD(I) usually displays linear two-co-ordination; few complexes with higher co-ordination numbers are known. Three-co-ordination (both regular [1] and distorted [2]) has been established in a few cases by *X*-ray diffraction, and also indicated by Mössbauer spectroscopy.[3] Complexes of the form $[AuL_4]^+$ [4] and $[AuXL_3]$ [5] have been reported but the sole indications of four-co-ordinate gold(I) are a partial *X*-ray analysis [6] and a Mössbauer spectrum of $[Au(PPh_3)_4][BPh_4]$.[7]

The complex $[Au(C_6F_5)(tht)]$ [8] (tht = tetrahydrothiophen, a readily displaceable neutral ligand) might be a suitable precursor to gold(I) complexes with co-ordination numbers greater than two, by its reaction (1) with chelating ligands, L–L.

$$[Au(C_6F_5)(tht)] + L\text{–}L \xrightarrow{OEt_2} [Au(C_6F_5)(L\text{–}L)] \quad (1)$$

RESULTS AND DISCUSSION

Attempts at process (1) with 2,2′-bipyridyl and various diphosphine ligands $Ph_2P(CH_2)_nPPh_2$ (n = 1, 2, or 4) lead respectively to metallic gold and the binuclear complexes $[(C_6F_5)AuL\text{–}LAu(C_6F_5)]$.[9] Only 1,10-phenanthroline (phen) and *o*-phenylenebis(dimethylarsine) (pdma) give compounds of the correct stoicheiometry (see Scheme).



SCHEME Reagents: (*i*), phen; (*ii*), $SbPh_3$; (*iii*), pdma

The compound $[Au(C_6F_5)(phen)]$ (1) forms as an orange precipitate in 84% yield, is non-conducting (4 ohm^{-1} cm^2 mol^{-1} in acetone), and its molecular weight [505 (osmometric in benzene), 544 (mass spectrometric)] agrees with the calculated value (544). Its low solubility precludes n.m.r. studies.

The white $Au(C_6F_5)(pdma)$ precipitates partially; further amounts (total yield 80%) are obtained by evaporation of the solvent. Its properties are quite different from those of (1) and we formulate it as $[Au(pdma)_2][Au(C_6F_5)_2]$ (2). Thus its conductivity is that of a 1 : 1 electrolyte (110 ohm^{-1} cm^2 mol^{-1} in acetone) and its molecular weight [732 (osmometric in benzene)] is approximately half the formula weight (1 300). Its ^1H n.m.r. spectrum (in $CDCl_3$, 100 MHz) shows resonances at τ 2.36 (m, 8 H, C_6H_4) and 8.38 (s, 24 H, $AsMe_2$); its ^{13}C n.m.r. spectrum ($CDCl_3$, ^1H decoupled, 25.15 MHz) exhibited only four resonances (141.7, 131.1, 130.4, and 16.6 p.p.m.; C–As, *o*- and *m*-C, and As–CH_3 respectively), indicating that the pdma molecules are equivalent.

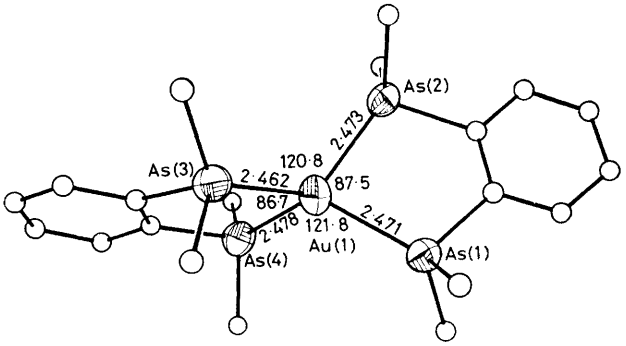


FIGURE 1 The $[Au(pdma)_2]^+$ cation showing bond lengths (Å, ±0.002) and angles (°, ±0.2) at the gold atom. The C atoms are plotted as circles, rather than thermal ellipsoids, for clarity; H atoms are omitted. Other angles: As(1)–Au(1)–As(3) 123.0, As(2)–Au(1)–As(4) 121.1°

Treatment of $[Au(C_6F_5)(tht)]$ with unidentate Group 5B ligands leads to $[Au(C_6F_5)L]$ for L = NEt_3, PEt_3, PPh_3, $P(C_6H_{11})_3$, and $AsPh_3$; $BiPh_3$ causes decomposition to metallic gold. The reaction with $SbPh_3$ gave a white precipitate whose yield is maximised by a 1 : 2 Au : Sb ratio. Its properties in solution are similar to those of (2) and it is thus formulated as $[Au(SbPh_3)_4]$-

TABLE 1

Atom co-ordinates (× 10^4) with standard deviations in parentheses

Atom	*x/a*	*y/b*	*z/c*
Au(1)	2 700(1)	1 354(1)	2 664(1)
Au(2)	0	0	0
Au(3)	5 000	5 000	5 000
As(1)	4 296(1)	1 674(1)	1 458(1)
As(2)	3 932(1)	2 903(1)	3 076(1)
As(3)	2 210(1)	−732(1)	3 554(1)
As(4)	320(1)	1 616(1)	2 600(1)
C(11)	5 411(7)	3 006(6)	1 535(4)
C(12)	5 253(7)	3 527(6)	2 176(4)
C(13)	6 035(8)	4 522(7)	2 191(5)
C(14)	6 957(8)	4 969(7)	1 563(5)
C(15)	7 134(9)	4 482(8)	925(5)
C(16)	6 381(8)	3 490(8)	909(5)
C(21)	324(9)	−732(6)	3 830(5)
C(22)	−453(8)	175(7)	3 406(5)
C(23)	−1 795(9)	76(9)	3 569(7)
C(24)	−2 363(11)	−866(10)	4 161(8)
C(25)	−1 572(13)	−1 735(10)	4 587(8)
C(26)	−247(11)	−1 692(7)	4 433(6)
C(1)	5 563(10)	394(9)	1 279(7)
C(2)	3 741(11)	2 318(10)	421(5)
C(3)	5 019(9)	2 338(9)	3 917(5)
C(4)	3 212(8)	4 447(7)	3 312(5)
C(5)	2 392(9)	−2 208(8)	3 124(6)
C(6)	2 903(13)	−1 349(9)	4 557(6)
C(7)	−483(12)	1 548(11)	1 690(6)
C(8)	−650(10)	2 996(7)	2 901(6)
C(31)	−854(8)	1 689(7)	−514(4)
C(32)	−2 026(9)	1 768(8)	−801(4)
C(33)	−2 634(9)	2 884(9)	−1 123(5)
C(34)	−2 069(9)	3 976(8)	−1 158(5)
C(35)	−896(9)	3 958(7)	−872(5)
C(36)	−314(9)	2 819(8)	−566(5)
C(41)	3 394(8)	4 347(7)	5 779(5)
C(42)	2 170(8)	4 808(8)	5 704(5)
C(43)	1 100(10)	4 415(10)	6 230(7)
C(44)	1 225(11)	3 549(12)	6 892(7)
C(45)	2 421(12)	3 039(12)	7 021(6)
C(46)	3 476(10)	3 402(10)	6 474(7)
F(32)	−2 663(7)	695(5)	−791(4)
F(33)	−3 810(6)	2 895(6)	−1 394(4)
F(34)	−2 655(7)	5 082(5)	−1 441(3)
F(35)	−335(6)	5 044(5)	−916(4)
F(36)	836(5)	2 869(5)	−296(3)
F(42)	1 963(6)	5 687(5)	5 036(4)
F(43)	−108(6)	4 892(7)	6 104(5)
F(44)	194(7)	3 133(9)	7 438(4)
F(45)	2 550(9)	2 085(9)	7 692(5)
F(46)	4 619(7)	2 845(8)	6 621(5)

$[Au(C_6F_5)_2]$ (3). Its conductivity is 95 ohm^{-1} cm^2 mol^{-1} in acetone, whilst its molecular weight (osmometric in benzene) is very low (found 552, formula weight 2 140) probably because of an equilibrium such as $[AuL_4]^+ \rightleftharpoons [AuL_2]^+ + 2L$. Compound (3) can also be obtained by metathesis in CH_2Cl_2 of $[NBu_4][Au(C_6F_5)_2]$ [8] and $[Au(SbPh_3)_4][ClO_4]$, the latter made by addition (4 : 1) of $SbPh_3$ to a benzene solution of $[Au(OClO_3)(tht)]$.

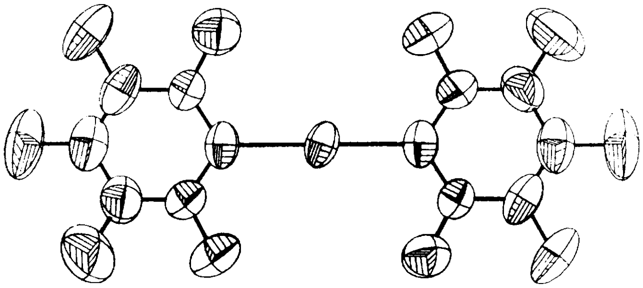


FIGURE 2 One of the two $[Au(C_6F_5)_2]^-$ anions. Au–C bond lengths: are 2.04 (here), 2.06 Å (±0.02 Å)

The preparation of (1) and (2) in good yields can also be achieved by treating (3) with phen or pdma (see Scheme).

TABLE 2

Bond lengths (Å) and angles (°)

Au(2)–C(31)	2.062(8)	Au(3)–C(41)	2.041(9)
As(1)–Au(1)	2.471(2)	As(1)–C(11)	1.947(9)
As(1)–C(1)	1.931(11)	As(1)–C(2)	1.939(11)
As(2)–Au(1)	2.473(2)	As(2)–C(12)	1.954(7)
As(2)–C(3)	1.938(10)	As(2)–C(4)	1.937(9)
As(3)–Au(1)	2.462(2)	As(3)–C(21)	1.947(10)
As(3)–C(5)	1.946(11)	As(3)–C(6)	1.944(12)
As(4)–Au(1)	2.478(2)	As(4)–C(22)	1.962(8)
As(4)–C(7)	1.919(14)	As(4)–C(8)	1.923(10)
C(11)–C(12)	1.377(12)	C(11)–C(16)	1.402(11)
C(12)–C(13)	1.398(13)	C(13)–C(14)	1.366(12)
C(14)–C(15)	1.349(15)	C(15)–C(16)	1.377(14)
C(21)–C(22)	1.381(12)	C(21)–C(26)	1.384(12)
C(22)–C(23)	1.383(14)	C(23)–C(24)	1.363(15)
C(24)–C(25)	1.367(18)	C(25)–C(26)	1.362(19)
C(31)–C(32)	1.364(14)	C(31)–C(36)	1.363(13)
C(32)–C(33)	1.375(13)	C(32)–F(32)	1.372(12)
C(33)–C(34)	1.343(15)	C(33)–F(33)	1.364(13)
C(34)–C(35)	1.371(15)	C(34)–F(34)	1.340(11)
C(35)–C(36)	1.376(12)	C(35)–F(35)	1.331(11)
C(36)–F(36)	1.346(13)	C(41)–C(42)	1.351(13)
C(41)–C(46)	1.401(14)	C(42)–C(43)	1.358(14)
C(42)–F(42)	1.356(11)	C(43)–C(44)	1.323(17)
C(43)–F(43)	1.355(13)	C(44)–C(45)	1.357(18)
C(44)–F(44)	1.349(14)	C(45)–C(46)	1.359(16)
C(45)–F(45)	1.384(14)	C(46)–F(46)	1.330(14)
As(1)–Au(1)–As(2)	87.5(2)	As(1)–Au(1)–As(3)	123.0(2)
As(2)–Au(1)–As(3)	120.8(2)	As(1)–Au(1)–As(4)	121.8(2)
As(2)–Au(1)–As(4)	121.1(2)	As(3)–Au(1)–As(4)	86.7(2)
Au(1)–As(1)–C(11)	104.5(3)	Au(1)–As(1)–C(1)	122.0(4)
C(11)–As(1)–C(1)	101.7(5)	Au(1)–As(1)–C(2)	120.8(4)
C(11)–As(1)–C(2)	102.4(5)	C(1)–As(1)–C(2)	102.2(6)
Au(1)–As(2)–C(12)	104.6(3)	Au(1)–As(2)–C(3)	119.8(4)
C(12)–As(2)–C(3)	100.8(4)	Au(1)–As(2)–C(4)	125.2(4)
C(12)–As(2)–C(4)	102.2(4)	C(3)–As(2)–C(4)	100.4(5)
Au(1)–As(3)–C(21)	105.1(3)	Au(1)–As(3)–C(5)	119.2(4)
C(21)–As(3)–C(5)	98.7(5)	Au(1)–As(3)–C(6)	123.5(4)
C(21)–As(3)–C(6)	104.8(5)	C(5)–As(3)–C(6)	102.0(5)
Au(1)–As(4)–C(22)	104.6(4)	Au(1)–As(4)–C(7)	123.5(5)
C(22)–As(4)–C(7)	102.3(5)	Au(1)–As(4)–C(8)	121.5(4)
C(22)–As(4)–C(8)	101.3(5)	C(7)–As(4)–C(8)	100.2(6)
As(1)–C(11)–C(12)	122.1(6)	As(1)–C(11)–C(16)	119.6(7)
C(12)–C(11)–C(16)	118.3(8)	As(2)–C(12)–C(11)	121.0(6)
As(2)–C(12)–C(13)	118.7(7)	C(11)–C(12)–C(13)	120.3(7)
C(12)–C(13)–C(14)	119.2(9)	C(13)–C(14)–C(15)	121.9(10)
C(14)–C(15)–C(16)	119.3(9)	C(11)–C(16)–C(15)	120.9(9)
As(3)–C(21)–C(22)	120.7(6)	As(3)–C(21)–C(26)	119.4(8)
C(22)–C(21)–C(26)	119.8(9)	As(4)–C(22)–C(21)	120.9(7)
As(4)–C(22)–C(23)	120.0(7)	C(21)–C(22)–C(23)	119.1(8)
C(22)–C(23)–C(24)	121.3(10)	C(23)–C(24)–C(25)	118.4(12)
C(24)–C(25)–C(26)	122.2(11)	C(21)–C(26)–C(25)	119.1(10)
Au(2)–C(31)–C(32)	122.8(7)	Au(2)–C(31)–C(36)	122.4(8)
C(32)–C(31)–C(36)	114.7(8)	C(31)–C(32)–C(33)	123.9(10)
C(31)–C(32)–F(32)	120.3(8)	C(33)–C(32)–F(32)	115.8(10)
C(32)–C(33)–C(34)	119.4(10)	C(32)–C(33)–F(33)	120.9(10)
C(34)–C(33)–F(33)	119.7(9)	C(33)–C(34)–C(35)	119.4(9)
C(33)–C(34)–F(34)	121.1(10)	C(35)–C(34)–F(34)	119.4(9)
C(34)–C(35)–C(36)	119.1(9)	C(34)–C(35)–F(35)	119.2(8)
C(36)–C(35)–F(35)	121.7(10)	C(31)–C(36)–C(35)	123.5(10)
C(31)–C(36)–F(36)	120.4(8)	C(35)–C(36)–F(36)	116.1(9)
Au(3)–C(41)–C(42)	124.4(7)	Au(3)–C(41)–C(46)	122.3(8)
C(42)–C(41)–C(46)	113.2(9)	C(41)–C(42)–C(43)	125.1(9)
C(41)–C(42)–F(42)	118.4(8)	C(43)–C(42)–F(42)	116.3(9)
C(42)–C(43)–C(44)	119.8(11)	C(42)–C(43)–F(43)	122.0(10)
C(44)–C(43)–F(43)	118.2(10)	C(43)–C(44)–C(45)	119.1(11)
C(43)–C(44)–F(44)	122.2(11)	C(45)–C(44)–F(44)	118.6(11)
C(44)–C(45)–C(46)	120.4(11)	C(44)–C(45)–F(45)	119.5(11)
C(46)–C(45)–F(45)	119.9(12)	C(41)–C(46)–C(45)	122.2(11)
C(41)–C(46)–F(46)	119.9(9)	C(45)–C(46)–F(46)	117.9(10)

The structure of (2) was confirmed by *X*-ray crystallography. Suitable single crystals were grown from dichloromethane–n-hexane. The cation is shown in Figure 1. The gold atom is co-ordinated by four arsenic atoms in a close approximation to D_{2d} symmetry, the bite of pdma being too small to allow exact tetrahedral co-ordination. There are two independent $[Au(C_6F_5)_2]^-$ anions, each with the Au atom on a crystallographic centre of symmetry (Figure 2). The co-ordination at gold is thus exactly linear. The Au–C bond lengths are similar to the 2.07(2) Å in $[Au(C_6F_5)(PPh_3)]$.[10]

This is the first full *X*-ray analysis of a four-co-ordinate gold(I) complex and also the first of an $[AuR_2]^-$ anion, where R is an organic group.

EXPERIMENTAL

Infrared spectra were recorded on a Perkin-Elmer 577 spectrophotometer using Nujol mulls between polyethylene sheets. Conductivities were measured in *ca.* 5×10^{-4} mol dm^{-3} solutions with a Philips PW 9501/01 conductimeter. Molecular weights were determined either mass spectrometrically on an A.E.I. MS 902 spectrometer operating at 70 eV,* or in solution with a Hitachi–Perkin-Elmer 115 osmometer. Proton n.m.r. spectra were recorded on a Varian Associates HA 100 spectrometer at 100 MHz. Carbon-13 n.m.r. spectra were obtained on a JEOL PFT-100 spectrometer at 25.15 MHz; chemical shifts are relative to $SiMe_4$ as external reference. Carbon, H, and N analyses were carried out on a Perkin-Elmer 240 microanalyser, Au analyses by ashing in a crucible with aqueous hydrazine.

Preparation of the Complexes.—All reactions were carried out at room temperature.

$[Au(C_6F_5)(phen)]$ (1). To a solution of $[Au(C_6F_5)(tht)]$ (0.45 g, 1 mmol) in diethyl ether (30 cm^3) was added phen (0.18 g, 1 mmol). After 5 min an orange precipitate of (1) was formed, yield 84%, m.p. 172 °C (decomp.) (Found: C, 39.9; H, 1.5; Au 36.3; N, 5.3%; *M* 544. $C_{18}H_8AuF_5N_2$ requires C 39.7; H, 1.5; Au, 36.2; N, 5.2%; *M* 544). Complex (1) could also be obtained in 75% yield by adding phen (0.1 g, 0.46 mmol) to a solution of (3) (0.5 g, 0.23 mmol) in dichloromethane (20 cm^3).

$[Au(pdma)_2][Au(C_6F_5)_2]$ (2). *o*-Phenylenebis(dimethylarsine) (0.19 cm^3, 1 mmol) was added to $[Au(C_6F_5)(tht)]$ (0.45 g, 1 mmol) in diethyl ether (50 cm^3). After 5 min a white precipitate of (2) was formed. The volume of solvent was reduced to 10 cm^3, affording further quantities of (2), total yield 80%, m.p. 178 °C (Found: C, 29.6; H, 2.3; Au, 29.9. $C_{32}H_{32}As_4Au_2F_{10}$ requires C, 29.7; H, 2.5; Au, 30.3%). Complex (2) could also be obtained in 95% yield by adding pdma (0.11 cm^3, 0.6 mmol) to a solution of (3) (0.5 g, 0.23 mmol) in dichloromethane (20 cm^3).

$[Au(SbPh_3)_4][Au(C_6F_5)_2]$ (3). Triphenylstibine (0.7 g, 2 mmol) was added to a solution of $[Au(C_6F_5)(tht)]$ (0.45 g, 1 mmol) in diethyl ether (30 cm^3). After 5 min a white precipitate of (3) was formed, 89% yield, m.p. 188 °C (decomp.) (Found: C, 47.1; H, 2.8; Au, 18.2. $C_{84}H_{60}Au_2F_{10}Sb_4$ requires C, 47.1; H, 2.8; Au, 18.4%).

Complex (3) could also be obtained by treating $[NBu^n_4][Au(C_6F_5)_2]$[8] (0.5 g, 0.64 mmol) with $[Au(SbPh_3)_4][ClO_4]$ {1.1 g, 0.64 mmol; obtained by addition (4 : 1) of $SbPh_3$ to a benzene or dichloromethane solution of $[Au(OClO_3)(tht)]$} in dichloromethane (30 cm^3). After stirring for 6 h the solution was evaporated to dryness to give a mixture of $[NBu^n_4][ClO_4]$ and (3), which could be separated by treatment with dichloromethane–hexane, in which (3) is more soluble. Yield 53%.

Crystal Data.—$C_{32}H_{32}As_4Au_2F_{10}$, $M = 1\,300.21$, Triclinic, space group $P\bar{1}$, $a = 10.340(3)$, $b = 10.982(3)$, $c = 17.612(5)$ Å, $\alpha = 75.45(2)$, $\beta = 82.35(2)$, $\gamma = 87.23(2)°$, $U = 1\,918$ Å^3, $Z = 2$, $D_c = 2.251$ g cm^{-3}, $F(000) = 1\,207.6$, $\lambda(\text{Mo-}K_\alpha) = 0.710\,69$ Å, $\mu(\text{Mo-}K_\alpha) = 111$ cm^{-1}, crystal dimensions $0.4 \times 0.25 \times 0.15$ mm.

Data collection on a Stoe four-circle diffractometer in the range $7 < 2\theta < 50°$ afforded 6 731 unique reflections, 5 558 with $F > 4\sigma(F)$ after Lorentz, polarisation, and absorption corrections. Calculations were performed using the SHELXTL system of programs (written by G. M. S.).

The structure was solved by direct methods (to locate Au) and successive difference syntheses, and refined to $R' = 0.046$, $R = 0.043$ (with all non-hydrogen atoms anisotropic, riding model for ring H atoms, and methyls as rigid groups). A final difference map showed no peaks >1 e Å^{-3}.

Final co-ordinates are given in Table 1, bond lengths and angles in Table 2. The hydrogen-atom co-ordinates, thermal parameters, and structure-factor tables are available as Supplementary Publication No. SUP 22958 (39 pp.).†

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* Throughout this paper: 1 eV ≈ 1.60×10^{-19} J.

† For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

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