Two-, Three- and Four-co-ordinate Gold(I) Complexes of 1,2-Bis(diphenylphosphino)-1,2-dicarba-*closo*-dodecaborane†

Olga Crespo,[a] **M. Concepción Gimeno,**[a] **Antonio Laguna***[,a] **and Peter G. Jones***[,b]
[a] *Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza-C.S.I.C., 50009 Zaragoza, Spain*
[b] *Institut für Anorganische und Analytische Chemie der Technischen Universität, Hagenring 30, 3300 Braunschweig, Republic of Germany*

Treatment of $(PPh_2)_2C_2B_{10}H_{10}$ with gold(I)complexes [AuX(tht)] (tht = tetrahydrothiophene, X = Cl or C_6F_5) gives two-co-ordinate $[(AuX)_2\{(PPh_2)_2C_2B_{10}H_{10}\}]$ or three-co-ordinate $[AuX\{(PPh_2)_2C_2B_{10}H_{10}\}]$ species. Other three-co-ordinate compounds have been prepared starting from $[Au(tht)L]ClO_4$ (L = tht, PR_3, or ylide) by reaction with the diphosphine. Substitution of tht in $[Au(tht)\{(PPh_2)_2C_2B_{10}H_{10}\}]ClO_4$ affords $[AuL\{(PPh_2)_2C_2B_{10}H_{10}\}]ClO_4$ where, depending on the ligand, three-co-ordinate (L = $SPPh_3$, $AsPh_3$, or C_5H_4NSH) or four-co-ordinate complexes [L = 1,10-phenanthroline or $(PPh_2)_2C_2B_{10}H_{10}$] can be synthesised. The bis-chelated gold(I) phosphine complex $[Au\{(PPh_2)_2C_2B_{10}H_{10}\}_2]ClO_4$ has been isolated. The crystal structure of $[Au(PPh_3)\{(PPh_2)_2C_2B_{10}H_{10}\}]ClO_4\cdot CH_2Cl_2$ has been established by X-ray crystallography: monoclinic space group $P2_1/n$, a = 11.760(3), b = 20.290(5), c = 21.375(6) Å, β = 105.10(2)°, Z = 4, R = 0.032. The gold atom exhibits trigonal-planar co-ordination, by three phosphorus atoms with Au–P 2.318(1), 2.405(1) and 2.417(1) Å (the longer bonds are to the diphosphine).

The most commonly observed geometry for gold(I) is linear two-co-ordinate.[1] Three- and four-co-ordinate complexes are appreciably less common. Several examples are known with monodentate phosphines both three-co-ordinate $[Au(PR_3)_3]^+$, $[AuX(PR_3)_2]$ and $[Au(bipy)(PR_3)]^+$ (bipy = 2,2′-bipyridine)[2–5] and four-co-ordinate $[Au(PR_3)_4]^+$ [6,7] and $[AuX(PR_3)_3]$[8,9] species. In contrast only a few studies of gold(I) complexes with bidentate phosphines have been reported. Although compounds of the type $[(AuX)_2(L–L)]$[10,11] are known for a great variety of diphosphines L–L, there are few examples of three-co-ordinate complexes $[AuX(L–L)]$[12] since four-co-ordinate compounds are preferred for L–L ligands that usually contain rigid backbones: $[Au(pdma)_2]^+$ [pdma = *o*-phenylenebis(dimethylarsine)],[13] $[Au(tdpep)_2]^+$ [tdpep = tris(2-diphenylphosphinoethyl)phosphine][14] or bis[*cis*-bis(diphenylphosphino)ethylene]gold(I).[15]

The observation that a number of simple gold(I) complexes of phosphine ligands, including two-, three- and four-co-ordinate forms, have significant antitumour activities has increased interest in these species. Co-ordination of the bidentate phosphine ligand $Ph_2PCH_2CH_2PPh_2$ (dppe) to gold(I) enhances its cytotoxic and antitumour activity and complexes $[(AuX)_2(dppe)]$ or $[Au(dppe)_2]^+$ are, therefore, active against a wide spectrum of tumours *in vivo*.[16,17]

Here, we have studied the co-ordination of 1,2-bis(diphenylphosphino)-1,2-dicarba-*closo*-dodecaborane as a bridging or chelating ligand with gold(I) compounds. We synthesised cationic and neutral three-co-ordinate species and chelated four-co-ordinate ones.

Results and Discussion

The dinuclear complexes $[(AuX)_2\{(PPh_2)_2C_2B_{10}H_{10}\}]$ (X = Cl **1** or C_6F_5 **2**) have been prepared by treating [AuX(tht)] (tht = tetrahydrothiophene) with the diphosphine $(PPh_2)_2C_2B_{10}H_{10}$ in 2:1 molar ratio. When the reaction is carried out with 2 equivalents of phosphine the mononuclear species $[AuX\{(PPh_2)_2C_2B_{10}H_{10}\}]$ (X = Cl **3** or C_6F_5 **4**) are obtained (see Scheme 1).

The $^{31}P-\{^1H\}$ NMR spectra of complexes **1** and **2** in $CDCl_3$ show a single resonance at δ 50.1 and 56.4, respectively. We assume that the structure of these complexes involves two linear gold(I) units bridged by the bidentate ligand, similar to those of other complexes with diphosphines.[10,11] However, the $^{31}P-\{^1H\}$ NMR spectra for complexes **3** and **4** display single peaks at δ 36.2 and 39.8 even at low temperature, suggesting the presence of three-co-ordination. Although $^{31}P-\{^1H\}$ NMR chemical shifts alone do not appear to be a reliable guide to gold(I) co-ordination numbers, some studies of bis(tertiary phosphine) complexes have been carried out.[16–18] These including diphosphines such as dppe or dadpe ($Ph_2PCH_2CH_2AsPh_2$) show an upfield displacement from dinuclear two-co-ordinate to mononuclear four-co-ordinate species. For our complexes there is a displacement to lower frequencies with increasing co-ordination number.

The stoichiometry of the reaction implies the presence of mononuclear $[AuX\{(PPh_2)_2C_2B_{10}H_{10}\}]$ or dinuclear $[Au_2X_2\{(PPh_2)_2C_2B_{10}H_{10}\}_2]$ species. Although complexes of the type $[Au_2X_2(dppm)_2]$ (dppm = $Ph_2PCH_2PPh_2$)[10] have been structurally characterized, we consider that steric interactions in the carborane species would destabilize the dinuclear complexes with respect to the three-co-ordinate chelated complexes. The presence of a rigid 1,2-dicarborane backbone should encourage chelation. The molecular weights of complexes **3** and **4** in $CHCl_3$ solution (isopiestic method) confirms that they are monomeric [714 (744) and 902 (877) for **3** and **4**, respectively].

Compounds **1**–**4** are yellow in solution but in the solid state the colour is less marked. They are air- and moisture-stable solids, and their acetone solutions are non-conducting. Their IR spectra show absorptions at 2500 [ν(BH)] cm^{-1}. The

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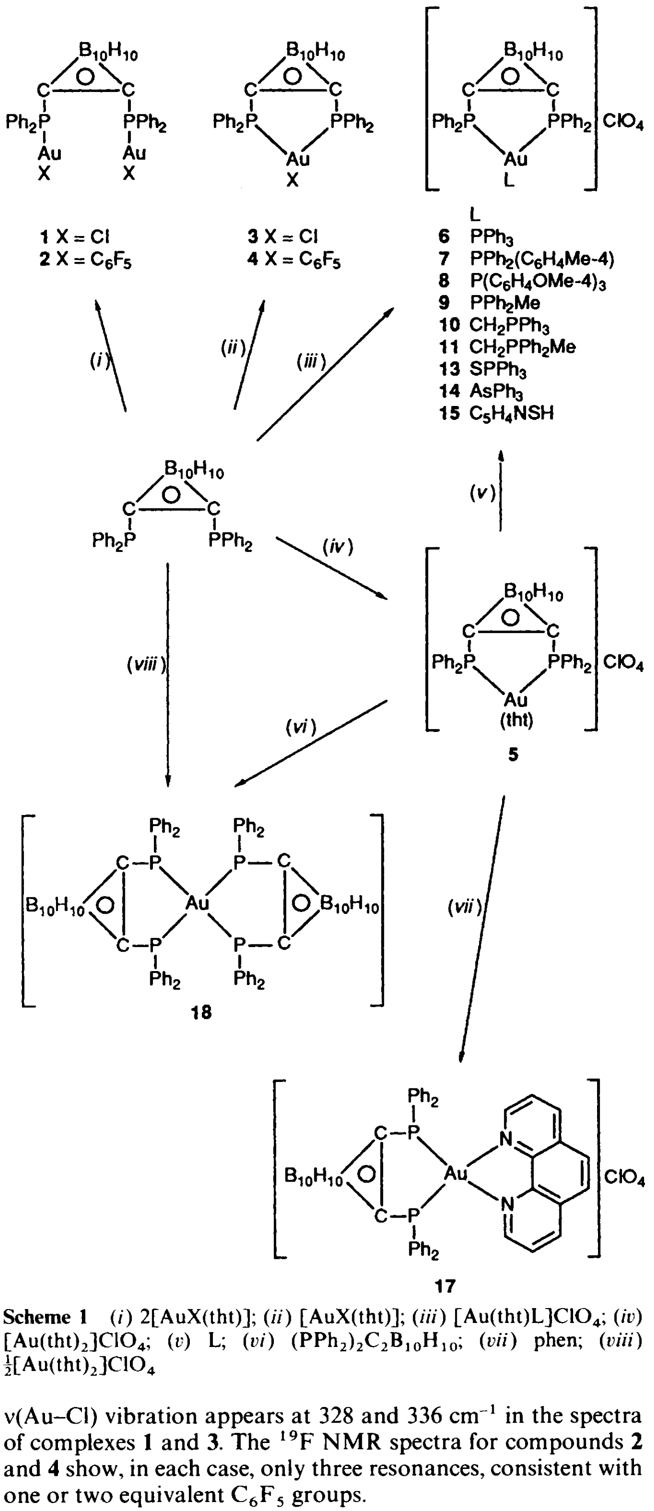
† *Supplementary data available:* Further details of the structure determination (complete bond lengths and angles, H-atom co-ordinates, structure factors, thermal parameters) have been deposited at the Fachinformationszentrum Karlsruhe, Gesellschaft für Wissenschaftlich-techniche Information mbH, D-7514 Eggenstein-Leopoldshafen 2, Germany. Any request for this material should quote a full literature citation and the reference number CSD 56060.



Scheme 1 (*i*) 2[AuX(tht)]; (*ii*) [AuX(tht)]; (*iii*) [Au(tht)L]ClO$_4$; (*iv*) [Au(tht)$_2$]ClO$_4$; (*v*) L; (*vi*) (PPh$_2$)$_2$C$_2$B$_{10}$H$_{10}$; (*vii*) phen; (*viii*) $\frac{1}{2}$[Au(tht)$_2$]ClO$_4$

ν(Au–Cl) vibration appears at 328 and 336 cm^{-1} in the spectra of complexes **1** and **3**. The ^{19}F NMR spectra for compounds **2** and **4** show, in each case, only three resonances, consistent with one or two equivalent C$_6$F$_5$ groups.

Reactions of [Au(tht)L]ClO$_4$ with the diphosphine give [AuL{(PPh$_2$)$_2$C$_2$B$_{10}$H$_{10}$}]ClO$_4$ [L = tht **5**, PPh$_3$ **6**, PPh$_2$(C$_6$H$_4$Me-4) **7**, P(C$_6$H$_4$OMe-4)$_3$ **8**, PPh$_2$Me **9**, CH$_2$PPh$_3$ **10** or CH$_2$PPh$_2$Me **11**] even in 2:1 molar ratio. This confirms the higher chelating tendency of the ligand. Their ^{31}P-{^{1}H} NMR spectra are consistent with three-co-ordination. When L = tht the spectrum shows a single peak; for L = PPh$_2$Me, CH$_2$PPh$_3$ or CH$_2$PPh$_2$Me the spectra are AX$_2$ systems and appear as a doublet (diphosphine phosphorus) and a triplet (phosphine or ylide phosphorus) (Table 1). In contrast, when L = PPh$_3$, PPh$_2$(C$_6$H$_4$Me-4) or P(C$_6$H$_4$OMe-4)$_3$ the spectra correspond to AB$_2$ systems, with eight observed transitions. Spin simulation for an AB$_2$ system is in agreement with the observed spectra.

In contrast, when L = CH$_2$PPhMe$_2$ only the dinuclear complex [Au$_2$(CH$_2$PPhMe$_2$)$_2${(PPh$_2$)$_2$C$_2$B$_{10}$H$_{10}$}][ClO$_4$]$_2$ **12** with the phosphine as bridging ligand is obtained. The ^{31}P-{^{1}H} NMR spectrum shows an A$_2$X$_2$ system with two doublets at δ 28.7 (ylide phosphorus) and 64.5 (diphosphine phosphorus) and coupling constant 9.7 Hz. It is worth mentioning the difference from the three-co-ordinate related species, both in the pattern and the chemical shift (downfield for the two-co-ordinate compound), and the higher coupling constant is probably due to the *trans* disposition of the different phosphorus atoms. The ^{1}H NMR spectrum shows resonances for CH$_2$ (doublet of doublets) and Me (doublet).

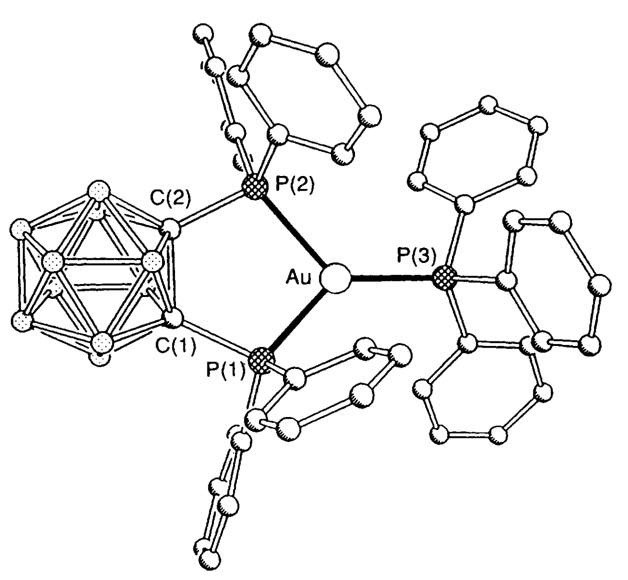


Fig. 1 The cation of complex **6** in the crystal. Radii are arbitrary; H atoms excluded for clarity. Selected bond lengths (Å) and angles (°): Au–P(1) 2.405(1), Au–P(2) 2.417(1), Au–P(3) 2.318(1), P(1)–C(1) 1.883(5), P(2)–C(2) 1.870(5) and C(1)–C(2) 1.743(6); P(1)–Au–P(2) 90.2(1), P(1)–Au–P(3) 135.6(1), P(2)–Au–P(3) 132.2(1), Au–P(1)–C(1) 106.1(1), P(1)–C(1)–C(2) 116.5(3), C(1)–C(2)–P(2) 116.4(3) and C(2)–P(2)–Au 106.2(2)

Compounds **5**–**12** are air- and moisture-stable pale yellow solids. In acetone solution, they are conducting and behave as 1:1 (**5**–**11**) and 1:2 (**12**) electrolytes. The IR spectra show a strong absorption at 2500 cm^{-1} [ν(BH)] and the bands at 1100s(br) and 620m cm^{-1} arise from the ClO$_4^-$ anion.[19]

Complex **5** can also be prepared by an alternative method: the reaction of **3** with [Ag(OClO$_3$)(tht)]. This reagent is very useful since it allows the substitution of a halide ligand by the weakly co-ordinating tht.

The crystal structure of complex **6** has been established by X-ray diffraction. The cation is shown in Fig. 1. The co-ordination at the gold atom is to a reasonable approximation trigonal planar; it lies 0.18 Å out of the plane of the three phosphorus atoms in the direction of a weak contact to a perchlorate oxygen [Au ··· O(4) 3.18(1) Å]. The restricted 'bite' of the diphosphine ligand [90.2(1)°] represents the major deviation from ideal geometry. The bond to the monodentate phosphine is appreciably shorter than to those to the diphosphine [2.318(1), *cf.* 2.405(1) and 2.417(1) Å], consistent with the principle that the shortest bond is opposite the narrowest angle. Bond lengths Au–P in the [Au(PPh$_3$)$_3$]$^+$ cation (three independent investigations[6,20,21]), where the bond angles are more ideal, lie in the range 2.345–2.408 Å. The chelate ring displays an envelope conformation, with the gold atom 0.59 Å out of the plane of the other four atoms.

The complex [Au(tht){(PPh$_2$)$_2$C$_2$B$_{10}$H$_{10}$}]ClO$_4$ reacts with SPPh$_3$, AsPh$_3$ or pyridine-2-thiol (C$_5$H$_4$NSH) leading to [AuL{(PPh$_2$)$_2$C$_2$B$_{10}$H$_{10}$}]ClO$_4$ (L = SPPh$_3$ **13**, AsPh$_3$ **14** or C$_5$H$_4$NSH **15**. The ^{31}P-{^{1}H} NMR spectra of **14** and **15** exhibit single resonances, while for complex **13** two peaks (SPPh$_3$ and

Table 1 Analytical, conductivity and ^{31}P NMR data for complexes **1**–**18**

Complex	Yield (%)	Analysis (%)[a]		Λ_M[b]/Ω^{-1} cm^2 mol^{-1}	$\delta(^{31}P)$ (J/Hz)
		C	H		
1 $[(AuCl)_2\{(PPh_2)_2C_2B_{10}H_{10}\}]$	92	31.95 (31.95)	3.35 (3.65)	6	50.2 (s)
2 $[(AuC_6F_5)_2\{(PPh_2)_2C_2B_{10}H_{10}\}]$	83	37.25 (36.80)	2.50 (2.45)	4	56.4 (s)
3 $[AuCl\{(PPh_2)_2C_2B_{10}H_{10}\}]$	87	41.95 (41.95)	4.25 (4.05)	11	36.2 (s)
4 $[Au(C_6F_5)\{(PPh_2)_2C_2B_{10}H_{10}\}]$	88	44.20 (43.85)	3.65 (3.45)	1	39.8 (s)
5 $[Au(tht)\{(PPh_2)_2C_2B_{10}H_{10}\}]ClO_4$	91	39.95 (40.15)	4.35 (4.25)	139	57.1 (s)
6 $[Au(PPh_3)\{(PPh_2)_2C_2B_{10}H_{10}\}]ClO_4$	84	49.20 (49.35)	4.15 (4.25)	158	44.9, 60.4 (136.3)
7 $[Au\{PPh_2(C_6H_4Me\text{-}4)\}\{(PPh_2)_2C_2B_{10}H_{10}\}]ClO_4$	84	51.15 (49.80)	4.50 (4.35)	130	44.3, 60.5 (136.0)
8 $[Au\{P(C_6H_4OMe\text{-}4)_3\}\{(PPh_2)_2C_2B_{10}H_{10}\}]ClO_4$	76	48.55 (48.60)	4.60 (4.40)	132	41.2, 60.0 (138.0)
9 $[Au(PPh_2Me)\{(PPh_2)_2C_2B_{10}H_{10}\}]ClO_4$	79	46.50 (46.40)	4.25 (4.30)	138	59.6 [d, J(PP) 138.3], 26.9 (t)
10 $[Au(CH_2PPh_3)\{(PPh_2)_2C_2B_{10}H_{10}\}]ClO_4$	87	49.45 (49.80)	4.30 (4.35)	132	38.1 [d, J(PP) 3.5], 31.3 (t)
11 $[Au(CH_2PPh_2Me)\{(PPh_2)_2C_2B_{10}H_{10}\}]ClO_4$	79	46.55 (46.95)	4.70 (4.45)	148	39.0 [d, J(PP) 6], 29.1 (t)
12 $[Au_2(CH_2PPhMe_2)_2\{(PPh_2)_2C_2B_{10}H_{10}\}][ClO_4]_2$	73	34.85 (34.45)	4.05 (3.70)	184	64.5 [d, J(PP) 9.7], 28.7 (d)
13 $[Au(SPPh_3)\{(PPh_2)_2C_2B_{10}H_{10}\}]ClO_4$	62	47.70 (47.90)	4.45 (4.10)	135	55.4 (s), 46.4 (s)
14 $[Au(AsPh_3)\{(PPh_2)_2C_2B_{10}H_{10}\}]ClO_4$	76	46.95 (47.40)	4.10 (4.05)	132	61.4 (s)
15 $[Au(C_5H_4NSH)\{(PPh_2)_2C_2B_{10}H_{10}\}]ClO_4$[c]	75	40.05 (40.45)	3.75 (3.85)	133	54.4 (s)
16 $[Au_2(AsPh_3)_2\{(PPh_2)_2C_2B_{10}H_{10}\}][ClO_4]_2$	69	43.65 (43.35)	3.85 (3.50)	190	65.5 (s)
17 $[Au(phen)\{(PPh_2)_2C_2B_{10}H_{10}\}]ClO_4$[d]	84	46.45 (46.15)	4.40 (4.35)	131	48.8 (s)
18 $[Au\{(PPh_2)_2C_2B_{10}H_{10}\}_2]ClO_4$	96	47.60 (47.25)	4.95 (4.55)	124	42.5 (s)

[a] Calculated values in parentheses. [b] In acetone. [c] N, 1.30 (1.50) %. [d] N, 2.90 (2.85) %.

diphosphine) are present. Complexes **13**–**15** are air- and moisture-stable yellow solids. Their acetone solutions are 1:1 electrolytes. The IR spectrum of **15** shows absorptions at 3300[ν(NH)] and 1620 [δ(NH)] cm^{-1}, which means the ligand must be S-bonded to gold.[22]

Treatment of complex **5** with 2 equivalents of $AsPh_3$ leads to the two-co-ordinate dinuclear complex $[Au_2(AsPh_3)_2\{(PPh_2)_2C_2B_{10}H_{10}\}][ClO_4]_2$ **16**, while treatment with the bidentate ligand phen (1,10-phenanthroline) affords the mixed four-co-ordinate complex $[Au(phen)\{(PPh_2)_2C_2B_{10}H_{10}\}]ClO_4$ **17**. The $^{31}P\text{-}\{^1H\}$ NMR spectra of **16** and **17** show only one peak for the phosphine.

The bis-chelated complex $[Au\{(PPh_2)_2C_2B_{10}H_{10}\}_2]ClO_4$ **18** was prepared starting from $[Au(tht)_2]ClO_4$ and the ligand in 1:2 molar ratio, and also by reaction of **5** with the diphosphine. Attempts to obtain this derivative had been reported before,[23] but were unsuccessful (only a tentative $^{31}P\text{-}\{^1H\}$ NMR signal assignment was made on the basis of the titration of $[NBu_4][AuBr_2]$ with the diphosphine). A sharp peak at δ 42.5 is observed in $^{31}P\text{-}\{^1H\}$ NMR spectrum. Unfortunately no suitable crystals could be grown for X-ray diffraction studies, but the structure may be similar to that of $[Au(dppe)_2]SbF_6$,[18] which contains gold(I) with a flattened (approximately D_{2d}) co-ordination geometry (P–Au–P 85–130°) chelated by two diphosphine ligands.

Compounds **16**–**18** are air- and moisture-stable yellow (**16**, **18**) and orange (**17**) solids. In acetone solutions they behave as 1:1 (**17**, **18**) and 1:2 (**16**) electrolytes.

We have attempted to extend this chemistry to gold(III) compounds with potential five-co-ordination, but unfortunately reduction to gold(I) occurs even with $[Au(C_6F_5)_3(tht)]$, which usually gives stable gold(III) phosphine complexes. Oxidation of gold(I) complexes is an alternative route to gold(III), but the usual reagents such as halogens lead to substitution of protons in the carborane cage.

Experimental

Instrumentation and general experimental techniques were as described earlier.[22] The yields, melting points, analyses, conductivities and NMR data for the new complexes are listed in Table 1. The NMR spectra were recorded on a Varian XL 200 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). All reactions were carried out at room temperature.

Syntheses.—$[(AuX)_2\{(PPh_2)_2C_2B_{10}H_{10}\}]$. (*a*) A dichloromethane solution (20 cm^3) of $[AuCl(tht)]$[24] (0.064 g, 0.2 mmol) was treated with $(PPh_2)_2C_2B_{10}H_{10}$[25] (0.51 g, 0.1 mmol). After stirring the mixture for 30 min the solvent was concentrated to *ca.* 5 cm^3. Addition of diethyl ether (15 cm^3) led to the precipitation of complex **1** as a white solid.

(*b*) In a similar experiment a dichloromethane solution (20 cm^3) of $[Au(C_6F_5)(tht)]$[24] (0.090 g, 0.2 mmol) was treated with $(PPh_2)_2C_2B_{10}H_{10}$ (0.051 g, 0.1 mmol). Complex **2** was obtained upon addition of hexane (15 cm^3). ^{19}F NMR δ −116.05 (m, *o*-F), −162.95 (m, *m*-F) and −158.85 [t, *p*-F, J(FF) 19.8 Hz].

Table 2 Atomic coordinates (× 10^4) for compound **6**

Atom	*x*	*y*	*z*
Au	2108.4(2)	1859.0(1)	1482.1(1)
P(1)	4077(1)	1892.8(6)	2178.4(5)
P(2)	2362(1)	710.0(6)	1252.6(5)
P(3)	455(1)	2526.0(6)	1307.3(6)
C(1)	4864(4)	1158(2)	1952(2)
C(2)	3986(4)	558(2)	1475(2)
B(3)	4689(5)	406(3)	2284(3)
B(4)	6091(5)	801(3)	2441(3)
B(5)	6157(5)	1240(3)	1725(3)
B(6)	4787(5)	1102(3)	1133(3)
B(7)	5964(6)	−49(3)	2250(3)
B(8)	4640(5)	−186(3)	1653(3)
B(9)	4703(5)	239(3)	943(3)
B(10)	6073(5)	657(3)	1099(3)
B(11)	6870(6)	465(3)	1907(3)
B(12)	5979(6)	−150(3)	1424(3)
C(11)	5078(4)	2563(2)	2130(2)
C(12)	4960(4)	2830(3)	1511(2)
C(13)	5732(5)	3309(3)	1420(3)
C(14)	6613(5)	3532(3)	1940(3)
C(15)	6695(4)	3291(3)	2552(3)
C(16)	5946(4)	2805(3)	2654(2)
C(21)	3998(4)	1769(2)	3014(2)
C(22)	4970(5)	1644(2)	3543(2)
C(23)	4776(5)	1528(3)	4151(2)
C(24)	3651(5)	1540(3)	4231(2)
C(25)	2698(5)	1677(3)	3718(2)
C(26)	2875(4)	1795(2)	3111(2)
C(31)	1880(4)	467(2)	404(2)
C(32)	1876(4)	957(3)	−43(2)
C(33)	1516(5)	825(3)	−698(2)
C(34)	1163(4)	195(3)	−908(2)
C(35)	1150(5)	−295(3)	−465(2)
C(36)	1503(4)	−163(2)	192(2)
C(41)	1792(4)	152(2)	1769(2)
C(42)	1851(4)	−537(3)	1759(2)
C(43)	1398(5)	−908(3)	2177(2)
C(44)	884(5)	−611(3)	2610(3)
C(45)	808(5)	68(3)	2625(3)
C(46)	1263(4)	448(3)	2204(2)
C(51)	−67(4)	2479(2)	2040(2)
C(52)	−570(4)	1893(3)	2178(2)
C(53)	−873(5)	1824(3)	2759(3)
C(54)	−682(5)	2332(3)	3200(3)
C(55)	−185(5)	2915(3)	3064(2)
C(56)	135(4)	2996(2)	2486(2)
C(61)	−781(4)	2268(2)	648(2)
C(62)	−1950(5)	2319(3)	676(3)
C(63)	−2853(5)	2143(3)	137(3)
C(64)	−2579(6)	1918(3)	−418(3)
C(65)	−1428(6)	1880(3)	−449(3)
C(66)	−532(5)	2050(2)	83(2)
C(71)	614(5)	3400(2)	1156(2)
C(72)	1693(5)	3638(3)	1108(2)
C(73)	1798(7)	4301(3)	961(3)
C(74)	848(8)	4713(3)	878(3)
C(75)	−217(7)	4484(3)	938(3)
C(76)	−337(6)	3827(3)	1073(3)
Cl(1)	3003(1)	2746.8(8)	−299.7(6)
O(1)	2481(5)	2339(3)	−837(2)
O(2)	4236(3)	2704(3)	−125(2)
O(3)	2671(5)	3399(3)	−497(3)
O(4)	2533(3)	2559(2)	228(2)
C(3)	5231(8)	5743(4)	552(4)
Cl(2)	3696(3)	5608(2)	306(2)
Cl(3)	6031(3)	5219(1)	1162(1)

$[\mathrm{AuX}\{(\mathrm{PPh_2})_2\mathrm{C_2B_{10}H_{10}}\}]$. (*a*) To a solution of [AuCl(tht)] (0.032 g, 0.1 mmol) in dichloromethane (20 $\mathrm{cm^3}$) was added $(\mathrm{PPh_2})_2\mathrm{C_2B_{10}H_{10}}$ (0.051 g, 0.1 mmol) and the mixture stirred for 30 min. Concentration of the solvent to *ca.* 5 $\mathrm{cm^3}$ and addition of diethyl ether (15 $\mathrm{cm^3}$) gave complex **3**.

(*b*) In a similar synthesis $[\mathrm{Au(C_6F_5)(tht)}]$ (0.045 g, 0.1 mmol) and $(\mathrm{PPh_2})_2\mathrm{C_2B_{10}H_{10}}$ (0.051 g, 0.1 mmol) were mixed in dichloromethane (20 $\mathrm{cm^3}$). Upon addition of hexane (15 $\mathrm{cm^3}$) complex **4** was obtained as a pale yellow solid. ^{19}F NMR: δ −114.7 (m, *o*-F), −162.82 (m, *m*-F) and −159.52 [t, *p*-F, *J*(FF) 20.1 Hz].

$[\mathrm{AuL}\{(\mathrm{PPh_2})_2\mathrm{C_2B_{10}H_{10}}\}]\mathrm{ClO_4}$. (*a*) To a dichloromethane solution (20 $\mathrm{cm^3}$) of $[\mathrm{Au(tht)_2}]\mathrm{ClO_4}$[22] (0.047 g, 0.1 mmol) was added $(\mathrm{PPh_2})_2\mathrm{C_2B_{10}H_{10}}$ (0.051 g, 0.1 mmol) and the mixture was stirred for 15 min. Evaporation of solvent to *ca.* 5 $\mathrm{cm^3}$ and addition of diethyl ether (15 $\mathrm{cm^3}$) gave complex **5** as a white solid. This compound was also prepared by treatment of a dichloromethane solution (20 $\mathrm{cm^3}$) of complex **3** (0.074 g, 0.1 mmol) with $[\mathrm{Ag(OClO_3)(tht)}]$[26] (0.029 g, 0.1 mmol) and stirring the suspension for 1 h. The precipitated AgCl was filtered off and the solution evaporated to *ca.* 5 $\mathrm{cm^3}$. Addition of diethyl ether (15 $\mathrm{cm^3}$) led to complex **5**. ^{1}H NMR: δ 2.27 (m, 4 H, $\mathrm{C_4H_8S}$), 3.57 (m, 4 H, $\mathrm{C_4H_8S}$), 7.59 and 7.96 (m, 20 H, Ph).

(*b*) To a solution of $[\mathrm{Au(tht)(PPh_3)}]\mathrm{ClO_4}$[22] (0.066 g, 0.1 mmol), $[\mathrm{Au(tht)(PPh_2Me)}]\mathrm{ClO_4}$[27] (0.055 g, 0.1 mmol), $[\mathrm{Au(tht)\{PPh_2(C_6H_4Me\text{-}4)\}}]\mathrm{ClO_4}$[27] (0.066 g, 0.1 mmol) or $[\mathrm{Au(tht)\{P(C_6H_4OMe\text{-}4)_3\}}]\mathrm{ClO_4}$[27] (0.073 g, 0.1 mmol) in dichloromethane (20 $\mathrm{cm^3}$) was added $(\mathrm{PPh_2})_2\mathrm{C_2B_{10}H_{10}}$ (0.051 g, 0.1 mmol). After stirring for 30 min the solution was concentrated to *ca.* 5 $\mathrm{cm^3}$. Addition of diethyl ether (15 $\mathrm{cm^3}$) gave complexes **6** ($\mathrm{L = PPh_3}$), **7** $[\mathrm{PPh_2(C_6H_4Me\text{-}4)}]$, **8** $[\mathrm{P(C_6H_4OMe\text{-}4)_3}]$, or **9** ($\mathrm{PPh_2Me}$) as pale yellow solids. ^{1}H NMR δ **7**, 2.42 (s, 3 H, $\mathrm{C_6H_4}$*Me*); **8**, 3.85 (s, 9 H, OMe); **9**, 2.54 [d, 3 H, PMe, *J*(PH) 9.9 Hz].

(*c*) Using the same procedure complex **10** was obtained starting from $[\mathrm{Au(tht)(CH_2PPh_3)}]\mathrm{ClO_4}$[27] (0.066 g, 0.1 mmol) and $(\mathrm{PPh_2})_2\mathrm{C_2B_{10}H_{10}}$ (0.051 g, 0.1 mmol).

(*d*) Similarly, complex **11** was prepared from $[\mathrm{Au(tht)(CH_2PPh_2Me)}]\mathrm{ClO_4}$[27] (0.060 g, 0.1 mmol) and $(\mathrm{PPh_2})_2\mathrm{C_2B_{10}H_{10}}$ (0.051 g, 0.1 mmol). ^{1}H NMR: δ 2.14 [d, 2 H, $\mathrm{CH_2}$, *J*(PH) 13.9], 2.42 [d, 3 H, PMe, *J*(PH) 13.0 Hz] and 7.2–7.7 (m, 30 H, Ph).

(*e*) Compound **12** was obtained from $[\mathrm{Au(tht)(CH_2PPhMe_2)}]\mathrm{ClO_4}$[27] (0.106 g, 0.2 mmol) and $(\mathrm{PPh_2})_2\mathrm{C_2B_{10}H_{10}}$ (0.051 g, 0.1 mmol) in a similar way. ^{1}H NMR: δ 2.0 [dd, 2 H, *J*(PH) 13.4, 8.8], 2.16 [d, 6 H, *J*(PH) 13.2 Hz] and 7.2–7.9 (m, 30 H, Ph).

Reactions of $[\mathrm{Au(tht)}\{(\mathrm{PPh_2})_2\mathrm{C_2B_{10}H_{10}}\}]\mathrm{ClO_4}$. (*a*) To a solution of complex **5** (0.089 g, 0.1 mmol) in dichloromethane (20 $\mathrm{cm^3}$) was added $\mathrm{SPPh_3}$ (0.029 g, 0.1 mmol) and the mixture stirred for 30 min. Concentration to *ca.* 5 $\mathrm{cm^3}$ and addition of diethyl ether (15 $\mathrm{cm^3}$) afforded complex **13**.

(*b*) Similarly, complex **14** was obtained from **5** (0.089 g, 0.1 mmol) and $\mathrm{AsPh_3}$ (0.031 g, 0.1 mmol).

(*c*) Starting from complex **5** (0.089 g, 0.1 mmol) and pyridine-2-thiol (0.012 g, 0.1 mmol), compound **15** was prepared.

(*d*) In a similar synthesis, $\mathrm{AsPh_3}$ (0.062 g, 0.2 mmol) and complex **5** (0.089 g, 0.1 mmol) led to complex **16**.

(*e*) Treatment of complex **5** (0.089 g, 0.1 mmol) with phen (0.019 g, 0.1 mmol) gave **17** as a yellow solid.

$[\mathrm{Au}\{(\mathrm{PPh_2})_2\mathrm{C_2B_{10}H_{10}}\}_2]\mathrm{ClO_4}$. To a solution of $[\mathrm{Au(tht)_2}]\mathrm{ClO_4}$ (0.047 g, 0.1 mmol) in dichloromethane (20 $\mathrm{cm^3}$) was added $(\mathrm{PPh_2})_2\mathrm{C_2B_{10}H_{10}}$ (0.102 g, 0.2 mmol). After stirring for 30 min the solvent was reduced to *ca.* 1 $\mathrm{cm^3}$. Addition of diethyl ether (10 $\mathrm{cm^3}$) gave the yellow complex **18**. This compound was also obtained by adding a dichloromethane solution (20 $\mathrm{cm^3}$) of complex **5** (0.089 g, 0.1 mmol) to $(\mathrm{PPh_2})_2\mathrm{C_2B_{10}H_{10}}$ (0.051 g, 0.1 mmol) and stirring the mixture for 30 min.

Concentration of solvent to *ca.* 1 cm^3 and addition of diethyl ether (10 cm^3) led to complex **18**.

X-Ray Structure Determination of Compound **6**.—*Crystal data.* $C_{44}H_{45}AuB_{10}ClO_4P_3 \cdot CH_2Cl_2$, $M_r = 1156.2$, monoclinic, space group $P2_1/n$, $a = 11.760(3)$, $b = 20.290(5)$, $c = 21.375(6)$ Å, $\beta = 105.10(2)°$, $U = 4924$ Å^3, $Z = 4$, $D_c = 1.559$ Mg m^{-3}, $F(000) = 2296$, λ(Mo-Kα) = 0.710 69 Å, $\mu = 3.3$ mm^{-1}, $T = -95$ °C.

Data collection and reduction. A pale yellow tablet 0.4 × 0.4 × 0.2 mm was mounted in inert oil on a glass fibre and transferred to the cold gas stream of the diffractometer (Siemens R3 diffractometer, LT-2 low-temperature attachment, monochromated Mo-Kα radiation). 11 541 Intensities were measured to $2\theta_{max}$ 50°. An absorption correction based on ψ scans was applied, with transmission factors 0.56–1.00. Merging equivalents gave 8634 unique reflections (R_{int} 0.017), of which 6764 with $F > 4\sigma(F)$ were used for all calculations (program system Siemens SHELXTL PLUS).[28] Cell constants were refined from setting angles of 50 reflections in the range 2θ 20–24°.

Structure solution and refinement: The Au atom was located from the Patterson function and other atoms (including all borane H atoms) in subsequent difference syntheses. Borane H atoms were shifted along the B–H vector to an idealized B–H bond length of 1 Å and then fixed; the other H atoms were included in the refinement using a riding model. A dichloromethane solvent molecule could be refined, albeit with high thermal motion (or static disorder) of the chlorine atoms. Anisotropic full-matrix refinement on F proceeded to R 0.032, R' 0.034 for 545 parameters. The weighting scheme was $w^{-1} = \sigma^2(F) + 0.0002F^2$; S 1.4; maximum Δ/σ 0.001; maximum $\Delta\rho$ 1.0 e Å^{-3}.

Final atomic coordinates are given in Table 2.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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