Mixed Four-Coordinate Gold(I) Complexes with Diphosphines or Diphosphine Disulfides as Ligands. Crystal Structure of $[Au\{(PPh_2)_2C_2B_{10}H_{10}\}\{(SPPh_2)_2CH_2\}]ClO_4 \cdot CH_2Cl_2$

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The reaction of the three-coordinate complex $[Au\{o\text{-}(PPh_2)_2C_2B_{10}H_{10}\}tht]ClO_4$ (tht = tetrahydrothiophene) with diphosphines such as $Ph_2PCH_2CH_2PPh_2$ (dppe), $o\text{-}Ph_2PC_6H_4PPh_2$ (dppph), or $cis\text{-}Ph_2PCH{=}CHPPh_2$ (dppey) afforded the mixed four-coordinate gold(I) complexes $[Au(P\text{-}P)(P'\text{-}P')]ClO_4$. The same reaction was also investigated with the diphosphine disulfides $SPPh_2NHPPh_2S$ (SdppaS) and $SPPh_2CH_2PPh_2S$ (SdppmS) and led to the mixed compounds $[Au(P\text{-}P)(S\text{-}S)]ClO_4$. All the complexes exhibit exceptionally high thermodynamic and kinetic stabilities in solution. The structure of the complex $[Au\{o\text{-}(PPh_2)_2C_2B_{10}H_{10}\}\{(SPPh_2)_2CH_2\}]ClO_4$ has been determined by X-ray diffraction. It crystallizes in the monoclinic space group $P2_1/n$ with cell constants a = 13.271(3) Å, b = 20.766(5) Å, c = 20.517(4) Å, β = 95.50(2)°, and Z = 4. The gold atom exhibits tetrahedral coordination involving two phosphorus and two sulfur atoms, with Au−P = 2.380, 2.389(2) Å and Au−S = 2.485, 2.661(2) Å; the bite angles are P−Au−P = 89.72(6)° and S−Au−S = 95.32(5)°.

Introduction

The chemistry of gold(I) complexes is dominated by linear two-coordinate species;[1,2] three- and four-coordination are less well established. In particular only a few four-coordinated complexes are known and, although some studies in solution have been carried out, not many examples have been characterized in the solid state. Complexes with stoichiometries $[AuL_4]^+$ or $[AuXL_3]$, where L is a monodentate ligand, are known with varying degrees of distortion; with L = PPh_3, different modifications revealed either trigonal geometry with one very distant ligand or a disorder between trigonal and tetrahedral sites.[3-5] Tetrahedral coordination was first established for $[Au(PMePh_2)_4]^+$,[6] with crystallographic $\bar{4}$ symmetry, and more recently for $[Au(SbPh_3)_4]^+$,[7,8] with three independent cations of symmetry 3.

Polydentate phosphine or arsine ligands also form complexes of the type $[Au(L\text{-}L)_2]^+$ and have been structurally characterized for L-L = o-phenylenebis(dimethylarsine) (diars),[9] bis(diphenylphosphino)ethane (dppe),[10,11] and bis((diphenylphosphino)methyl)phenylarsine;[12] furthermore, a dinuclear four- coordinate complex has been reported with the tetradentate tetraphosphine ligand tris(2-(diphenylphosphino)ethyl)phosphine, $[Au_2(\mu\text{-}PP_3)_2]Cl_2$.[13]

In contrast, no complexes containing mixed diphosphine ligands or mixed diphosphine and diphosphine disulfide ligands have been described. We have previously studied the chemistry of the bis(diphenylphosphino)-o-carborane ligand with gold(I), reporting the structure of the three-coordinate complex $[Au\{o\text{-}(PPh_2)_2C_2B_{10}H_{10}\}PPh_3]ClO_4$;[14] we have also described a tetranuclear complex, with bis(diphenylphosphino)-o-carborane and the related 1,2-dimercapto-o-carborane as ligands, where two of the gold atoms are tetra-coordinate.[15] Here we report the use of the three-coordinate complex $[Au\{o\text{-}(PPh_2)_2C_2B_{10}H_{10}\}tht]ClO_4$ (tht = tetrahydrothiophene) as a precursor in the synthesis of mixed four-coordinate species and the structural characterization by X-ray diffraction of one such species.

Results and Discussion

The complexes were synthesized by reaction of $[Au\{o\text{-}(PPh_2)_2C_2B_{10}H_{10}\}tht]ClO_4$ with the bidentate phosphine or phosphine disulfide ligand in dichloromethane in a 1:1 ratio (see Scheme 1). They are colorless or pale-yellow solids that exhibit a high stability both in solid and solution. All of them behave as 1:1 electrolytes in acetone solution.

The IR spectra of complexes **1**−**5** show absorptions in the region 2627−2580 (vs, br) cm^{-1} [ν(B−H)] and also bands arising from the ClO_4^- anion (1100 vs, br and 620 m cm^{-1}) and the phosphine ligands. The ν(P−S) bands appear at 593 (m) and 595 (m) cm^{-1} in complexes **4** and **5**, respectively.

The $^{31}P\{^1H\}$ NMR spectra for complexes **1**−**3** are consistent with A_2X_2 systems and therefore appear as two triplets for the two different phosphorus environments. The ^2J(PP) values becomes considerably smaller on changing from two- to three- and four-coordinate species. A coupling constant of 302 Hz is observed for the *trans* phosphorus atoms in the linear complex

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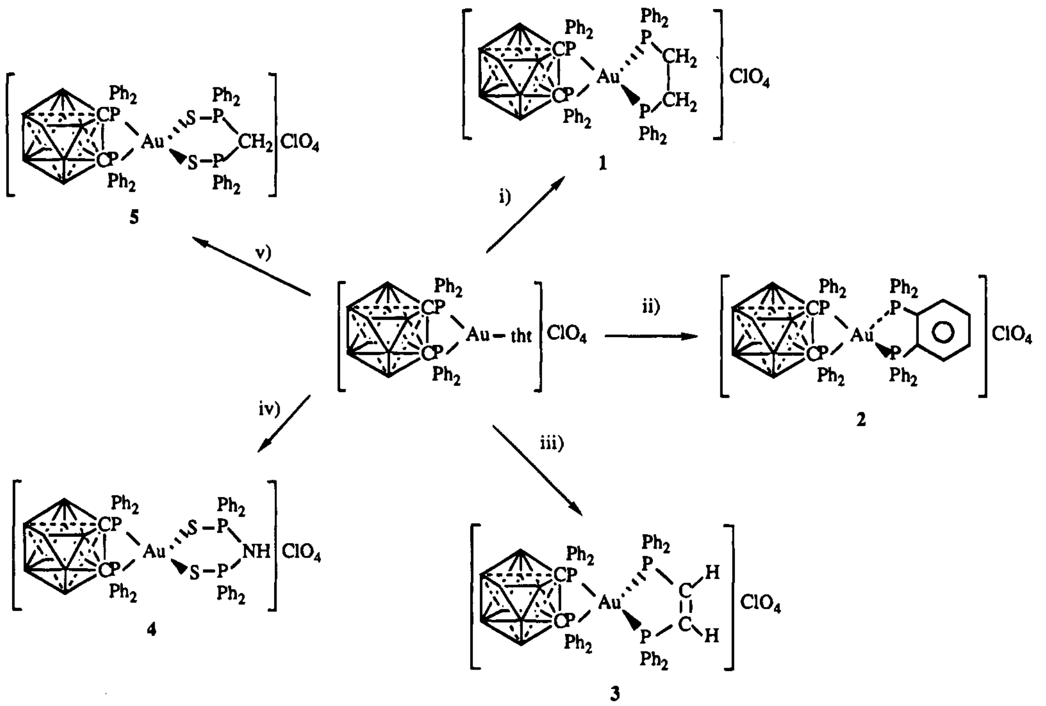
Scheme 1[a]



[a] Key: (i) dppe; (ii) dppph; (iii) dppey; (iv) SdppaS; (v) SdppmS.

Table 1. Analytical, Conductivity, and $^{31}P\{^1H\}$ NMR Data for Complexes **1**–**5**

			anal. (%)[a]			$^{31}P\{^1H\}$ NMR (δ)[c]		
no.	complex	yield (%)	C	H	Λ_M[b]	P-P	L-L	J(PP)
1	$[Au\{(PPh_2)_2C_2B_{10}H_{10}\}\{(PPh_2)_2(CH_2)_2\}]ClO_4$	75	52.04 (51.72)	4.84 (4.5)	132	46.6 (t)	18.3 (t)	50.3
2	$[Au\{(PPh_2)_2C_2B_{10}H_{10}\}\{(PPh_2)_2(C_6H_4)\}]ClO_4$	83	53.28 (53.57)	4.24 (4.33)	125	45.3 (t)	20.2 (t)	53.6
3	$[Au\{(PPh_2)_2C_2B_{10}H_{10}\}\{(PPh_2)_2(CH{=}CH)\}]ClO_4$	82	52.05 (51.81)	4.38 (4.34)	140	45.7 (t)	20.4 (t)	53.5
4	$[Au\{(PPh_2)_2C_2B_{10}H_{10}\}\{(SPPh_2)_2NH\}]ClO_4$	88	47.41 (47.71)	4.22 (4.08)	130	43.1 (s)	57.8 (s)	
5	$[Au\{(PPh_2)_2C_2B_{10}H_{10}\}\{(SPPh_2)_2CH_2\}]ClO_4$	65	48.96 (48.53)	4.00 (4.15)	111	47.1 (s)	37.7 (s)	

[a] Calculated values are given in parentheses. [b] In acetone, values in Ω^{-1} cm^2 mol^{-1}. [c] In $CDCl_3$, values in ppm, coupling constant in Hz, t = triplet, s = singlet.

$[Ph_3PAuPPh_2C(PPh_2AuPPh_2)_2CPPh_2AuPPh_3]_2^+$ (an AB system),[16] while 136–138 Hz are observed in the three-coordinate derivatives $[Au\{(PPh_2)_2C_2B_{10}H_{10}\}PR_3]ClO_4$ (as AB_2 systems)[14] and *ca.* 50 Hz in the four-coordinate compounds **1**–**3** (Table 1). The spectra of **4** and **5** appear as two singlets because there is no coupling between the phosphorus of the diphosphine and those of the diphosphine disulfide. The ^1H NMR spectra show broad resonances for the B–H protons, and other signals include multiplets for the methylene protons of complexes **1** and **5** and phenyl groups; the ethylene protons for the dppey ligand are overlapped with the B–H broad signal.

In the positive fast atom bombardment spectra the molecular cation peaks appear among the most intense at *m/z* = 1108 (**1**, 100%), 1156 (**2**, 62%), 1106 (**3**, 93%), 1159 (**4**, 100%), and 1158 (**5**, 100%). The fragments $Au(P\text{-}P)^+$ and $Au(P'\text{-}P')^+$ are also present with high intensity. The expected isotopic distribution is found for all the peaks.

We have also attempted to prepare this type of complex with other bidentate phosphines such as $Ph_2PCH_2PPh_2$ (dppm) or $Ph_2PNHPPh_2$ (dppa) without success; the homoleptic $[Au\{(PPh_2)_2C_2B_{10}H_{10}\}_2]ClO_4$ previously described by us[14] and other gold(I) complexes are obtained.

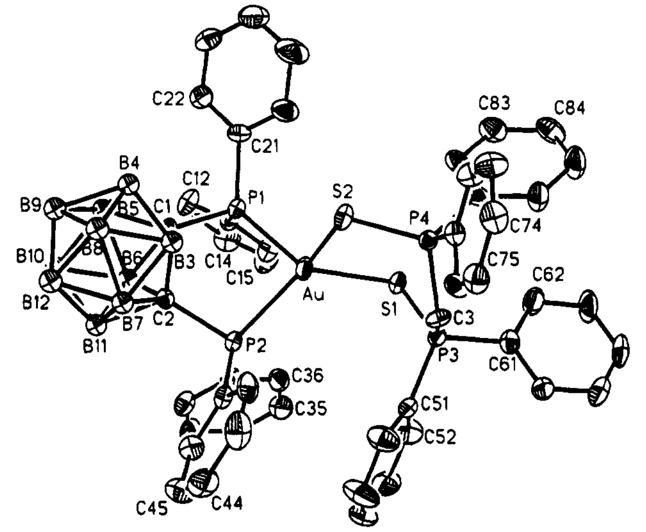


Figure 1. Structure of the cation of complex **5** in the crystal. Hydrogen atoms are omitted for clarity. Atomic radii are arbitrary.

The crystal structure of complex **5** has been established by X-ray diffraction. The molecular structure of the cation of **5** is shown in Figure 1. Atomic coordinates are found in Table 2, and selected bond lengths and angles, in Table 3. The gold atom is chelated by one diphosphine and one diphosphine disulfide ligand, thus presenting a somewhat distorted tetrahedral geometry. The distortions arise in part from the restricted bite of the diphosphine, P(1)–Au–P(2) = 89.72(6)°, and the diphosphine disulfide, S(1)–Au–S(2) = 95.32(5)°. These are

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Table 2. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for compound **5** with U(eq) Defined as One-Third of the Trace of the Orthogonalized $\mathbf{U}_{ij}$ Tensor

	x	y	z	U(eq)		x	y	z	U(eq)
Au	3670.4(2)	6118.2(1)	6959.8(1)	26.2(1)	C(41)	4708(5)	7148(3)	8395(3)	24.1(14)
S(1)	4828.4(12)	5695.9(7)	6178.4(8)	22.5(3)	C(42)	4552(5)	7695(3)	8014(3)	34(2)
S(2)	2901.0(12)	7052.7(8)	6175.8(8)	26.6(4)	C(43)	4890(6)	8290(3)	8251(4)	45(2)
P(1)	2292.5(12)	5512.1(8)	7301.5(8)	19.8(3)	C(44)	5391(6)	8343(4)	8866(4)	42(2)
P(2)	4167.7(12)	6395.3(8)	8074.2(8)	19.7(3)	C(45)	5567(6)	7799(4)	9245(4)	41(2)
P(3)	5765.0(12)	6430.9(8)	6084.7(8)	20.1(3)	C(46)	5234(5)	7203(3)	9008(3)	30(2)
P(4)	3868.5(12)	7237.9(8)	5526.2(8)	18.6(3)	C(51)	6638(5)	6561(3)	6805(3)	24.8(14)
C(1)	1954(5)	5957(3)	8046(3)	21.8(14)	C(52)	7273(5)	6058(4)	7008(3)	40(2)
C(2)	2919(5)	6404(3)	8445(3)	20.6(13)	C(53)	7932(5)	6115(4)	7564(4)	47(2)
C(3)	5167(4)	7211(3)	5900(3)	23.5(14)	C(54)	7978(6)	6679(4)	7918(4)	49(2)
B(3)	1987(6)	6785(4)	7951(4)	25(2)	C(55)	7357(7)	7170(4)	7716(4)	57(2)
B(4)	838(6)	6364(4)	8058(4)	24(2)	C(56)	6675(6)	7125(4)	7168(4)	44(2)
B(5)	1139(5)	5707(4)	8588(4)	23(2)	C(61)	6530(5)	6268(3)	5422(3)	27.0(15)
B(6)	2474(5)	5718(3)	8807(3)	21(2)	C(62)	6245(6)	5817(4)	4948(3)	41(2)
B(7)	2451(5)	7106(4)	8729(4)	24(2)	C(63)	6845(6)	5713(4)	4438(4)	51(2)
B(8)	1135(6)	7086(4)	8497(4)	26(2)	C(64)	7709(6)	6055(4)	4399(3)	43(2)
B(9)	615(6)	6417(4)	8896(4)	26(2)	C(65)	7991(5)	6505(4)	4860(4)	39(2)
B(10)	1627(5)	6014(4)	9367(4)	25(2)	C(66)	7419(5)	6611(3)	5384(3)	31(2)
B(11)	2764(6)	6449(3)	9261(4)	24(2)	C(71)	3701(5)	8045(3)	5212(3)	22.1(13)
B(12)	1611(6)	6866(4)	9306(4)	27(2)	C(72)	2922(5)	8167(3)	4733(3)	30(2)
C(11)	2627(4)	4697(3)	7566(3)	22.0(13)	C(73)	2742(5)	8786(3)	4511(3)	35(2)
C(12)	2036(5)	4299(3)	7915(3)	33(2)	C(74)	3331(5)	9289(3)	4759(3)	31(2)
C(13)	2341(6)	3680(3)	8071(4)	40(2)	C(75)	4102(5)	9171(3)	5238(3)	31(2)
C(14)	3234(6)	3444(4)	7885(4)	41(2)	C(76)	4296(5)	8551(3)	5469(3)	26.7(14)
C(15)	3820(6)	3831(4)	7538(4)	49(2)	C(81)	3739(4)	6717(3)	4822(3)	22.5(13)
C(16)	3522(5)	4458(3)	7385(4)	35(2)	C(82)	3202(5)	6150(3)	4817(3)	30.1(15)
C(21)	1101(5)	5445(3)	6789(3)	25.3(14)	C(83)	3099(6)	5764(3)	4269(3)	38(2)
C(22)	253(5)	5117(3)	6960(3)	31(2)	C(84)	3538(6)	5948(3)	3720(4)	42(2)
C(23)	−598(5)	5059(3)	6523(4)	36(2)	C(85)	4068(6)	6515(4)	3704(4)	43(2)
C(24)	−613(6)	5335(4)	5914(4)	48(2)	C(86)	4176(5)	6900(3)	4260(3)	35(2)
C(25)	206(6)	5666(5)	5739(4)	61(2)	Cl(1)	6390.9(13)	8985.9(10)	6800.9(9)	39.6(4)
C(26)	1070(6)	5719(4)	6174(3)	42(2)	O(1)	6974(7)	9045(6)	7388(4)	145(5)
C(31)	4956(4)	5754(3)	8465(3)	21.8(13)	O(2)	5485(4)	8630(3)	6894(3)	67(2)
C(32)	5064(5)	5599(3)	9123(3)	30.0(15)	O(3)	6889(6)	8651(4)	6346(5)	111(3)
C(33)	5750(5)	5132(3)	9362(3)	34(2)	O(4)	6177(6)	9592(4)	6537(5)	116(3)
C(34)	6324(5)	4811(3)	8939(3)	34(2)	C(4)	5770(9)	3111(6)	8803(6)	96(4)
C(35)	6219(5)	4964(3)	8291(4)	37(2)	Cl(2)	5553(3)	2416(2)	8367(3)	179(3)
C(36)	5544(5)	5431(3)	8048(3)	34(2)	Cl(3)	4853(3)	3282(3)	9319(2)	162(2)

Table 3. Selected Bond Lengths (Å) and Angles (deg) for Complex **5**

Au−P(1)	2.380(2)	Au−P(2)	2.389(2)
Au−S(1)	2.485(2)	Au−S(2)	2.661(2)
S(1)−P(3)	1.989(2)	S(2)−P(4)	1.975(2)
P(1)−C(21)	1.818(6)	P(1)−C(11)	1.819(6)
P(1)−C(1)	1.876(6)	P(2)−C(41)	1.817(7)
P(2)−C(31)	1.831(6)	P(2)−C(2)	1.889(6)
P(3)−C(61)	1.804(6)	P(3)−C(51)	1.809(7)
P(3)−C(3)	1.827(6)	P(4)−C(81)	1.800(6)
P(4)−C(71)	1.803(6)	P(4)−C(3)	1.820(6)
P(1)−Au−P(2)	89.72(6)	P(1)−Au−S(1)	122.93(6)
P(2)−Au−S(1)	124.85(6)	P(1)−Au−S(2)	107.61(6)
P(2)−Au−S(2)	117.24(6)	S(1)−Au−S(2)	95.32(5)
P(3)−S(1)−Au	102.85(8)	P(4)−S(2)−Au	108.26(8)
C(21)−P(1)−C(11)	106.0(3)	C(21)−P(1)−C(1)	104.2(3)
C(11)−P(1)−C(1)	106.6(3)	C(21)−P(1)−Au	121.3(2)
C(11)−P(1)−Au	114.1(2)	C(1)−P(1)−Au	103.3(2)
C(41)−P(2)−C(31)	106.2(3)	C(41)−P(2)−C(2)	100.2(3)
C(31)−P(2)−C(2)	108.5(3)	C(41)−P(2)−Au	128.1(2)
C(31)−P(2)−Au	109.7(2)	C(2)−P(2)−Au	102.4(2)
C(61)−P(3)−C(51)	106.3(3)	C(61)−P(3)−C(3)	105.9(3)
C(51)−P(3)−C(3)	105.6(3)	C(61)−P(3)−S(1)	109.3(2)
C(51)−P(3)−S(1)	113.1(2)	C(3)−P(3)−S(1)	115.9(2)
C(81)−P(4)−C(71)	105.8(3)	C(81)−P(4)−C(3)	109.5(3)
C(71)−P(4)−C(3)	105.0(3)	C(81)−P(4)−S(2)	114.0(2)
C(71)−P(4)−S(2)	110.9(2)	C(3)−P(4)−S(2)	111.1(2)

compensated for by the exterior angles, which range from 107.61(6) to 124.85(6)°. The bite angles compare well with those found in other tetrahedral gold(I) complexes: [Au(dppe)$_2$]X (X = Cl or SbF$_6$), 85.4(1)−87.1(1)°;[10,11] [Au(diars)$_2$]$^+$, 86.7(2) and 87.5(2)°.[9] They are very similar to those in the isostructural silver complex [Ag{(PPh$_2$)$_2$C$_2$B$_{10}$H$_{10}$}{(SPPh$_2$)$_2$CH$_2$}]ClO$_4$ [P−Ag−P = 84.56(5)°, S−Ag−S = 90.20(5)°].[17] The dihedral angle between the two planes defined by Au, P(1), P(2) and Au, S(1), S(2) is 85.6°, close to the ideal 90°. The five-membered chelate ring displays an envelope conformation, with Au 0.94 Å out of the plane of the other four atoms; the six-membered chelate ring approximates to a twist conformation, with large positive torsion angles about Au−S1 and C3−P4.

The Au−P distances are 2.380(2) and 2.389(2) Å and are of the same order as those found in [Au(dppe)$_2$]$^+$ [2.389(3)-2.416(3) Å][10,11] and shorter than in the regular tetrahedral compound [Au(PMePh$_2$)$_4$]PF$_6$ [2.449(1) Å].[6] Surprisingly, the Au−S distances are very dissimilar, 2.485(2) and 2.661(2) Å. Not many Au−S distances in tetrahedral complexes are available for comparison. In the tetranuclear complex [Au$_4$(S$_2$C$_2$B$_{10}$H$_{10}$)$_2${(PPh$_2$)$_2$C$_2$B$_{10}$H$_{10}$}$_2$],[15] where the gold atom is also four-coordinate, the Au−S bond lengths are 2.584(2) and 2.614(2) Å, midway between those found in the mononuclear compound **5**.

Experimental Section

Infrared spectra were recorded in the range 4000−200 cm^{-1} on a Perkin-Elmer 883 spectrophotometer using Nujol mulls between polyethylene sheets. Conductivities were measured in ca. 5 × 10^{-4} mol dm^{-3} solutions with a Philips 9509 conductimeter. C and H analyses were carried out with a Perkin-Elmer 240C microanalyzer.

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Table 4. Details of Data Collection and Structure Refinement for Complex **5**·CH_2Cl_2

chem formula	$C_{52}H_{54}AuB_{10}Cl_3O_4P_4S_2$	$2\theta_{max}$/deg	50
cryst habit	pale-yellow prism	μ(Mo Kα)/mm^{-1}	3.0
cryst size/mm	0.80 × 0.20 × 0.15	transm	0.84−1.0
space group	$P2_1/n$	no. of reflcns measd	10 439
a/Å	13.271(3)	no. of unique reflcns	9942
b/Å	20.766(5)	no. of reflcns used	9902
c/Å	20.517(4)	R_{int}	0.036
β/deg	95.50(2)	R^a $(I, I > 2\sigma(I))$	0.048
V/Å	5628(2)	wR^b (F^2, all reflcns)	0.110
Z	4	no. of params	630
D_c/Mg m^{-3}	1.584	no. of restraints	473
M	1342.37	S^c	1.084
$F(000)$	2680	max $\Delta\varrho$/e Å^{-3}	1.34
T/°C	−100		

[a] $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR(F^2) = [\Sigma\{w(F_o^2 - F_c^2)^2/\Sigma\{w(F_o^2)^2\}]^{0.5}$; $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, where $P = [F_o^2 + 2F_c^2]/3$ and a and b are constants adjusted by the program. [c] $S = [\Sigma\{w(F_o^2 - F_c^2)^2\}/(n - p)]^{0.5}$, where n is the number of data and p the number of parameters.

NMR spectra were recorded on a Varian 300 Unity spectrometer in $CDCl_3$. Chemical shifts are cited relative to $SiMe_4$ (^1H) and 85% H_3PO_4 (external, ^{31}P). Mass spectra were recorded on a VG autospec, with the FAB technique, using nitrobenzyl alcohol as matrix. All reactions were carried out at room temperature.

Materials. The complex $[Au\{(PPh_2)_2C_2B_{10}H_{10}\}tht]ClO_4$ was prepared as previously described by us.[14] The ligands $Ph_2PCH_2CH_2PPh_2$, $Ph_2PC_6H_4PPh_2$, and *cis*-$Ph_2PCH{=}CHPPh_2$ were purchased from Strem chemicals. The diphosphine disulfide ligands $SPh_2PCH_2PPh_2S$[18] and $SPPh_2NHPPh_2S$[19] were prepared according to the literature.

Safety Note! Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of material should be prepared, and these should be handled with great caution.

Synthesis of $[Au\{(PPh_2)_2C_2B_{10}H_{10}\}(L\text{-}L)]ClO_4$. To a stirred solution of $[Au\{(PPh_2)_2C_2B_{10}H_{10}\}tht]ClO_4$ (0.089 g, 0.1 mmol) in dichloromethane (20 mL) was added dppe (0.039 g, 0.1 mmol), dppph (0.044 g, 0.1 mmol), dppey (0.039, 0.1 mmol), SdppaS (0.044 g, 0.1 mmol), or SdppmS (0.044 g, 0.1 mmol). The mixture was stirred for 30 min, and the solvent was concentrated to ca. 5 mL. Addition of diethyl ether (15 mL) gave complexes **1**−**5** as colorless or pale-yellow solids.

Crystal Structure Determination of Compound 5. The crystal was mounted in inert oil (type RS 3000, donated by Riedel de Haën) on a glass fiber. Data were collected using monochromated Mo Kα radiation (λ = 0.710 73 Å) on a Stoe STADI-4 diffractometer with a Siemens LT-2 low-temperature attachment. The scan type was $\omega-\theta$. Cell constants were refined from ± angles of 60 reflections in the range 2θ = 20−22°. Absorption corrections were applied on the basis of Ψ-scans.

The structure was solved by the heavy-atom method and refined anisotropically on F^2 using the program SHELXL-93.[20] Hydrogen atoms were included using a riding model. The complex crystallizes with one molecule of dichloromethane. Other data are collected in Table 4.

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Supplementary Material Available: Tables of crystal data, data collection, and solution and refinement parameters, hydrogen atomic coordinates and thermal parameters, bond distances and angles, and anisotropic thermal parameters (7 pages). Ordering information is given on any current masthead page.

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