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Synthesis and Characterization of Gold(I) Complexes with the Ligand 1,2-Dithiolate-*o*-carborane. Crystal Structures of $[Au_2(\mu\text{-}S_2C_2B_{10}H_{10})(PPh_3)_2]$, $[Au_2(\mu\text{-}S_2C_2B_{10}H_{10})(\mu\text{-}\{(PPh_2)_2(CH{=}CH)\})]$, and $[Au_2(\mu\text{-}S_2C_2B_{10}H_{10})(\mu\text{-}\{(PPh_2)_2(C_6H_4)\})]$

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Treatment of 1,2-dimercapto-*o*-carborane with 2 equiv of [AuClL] in the presence of Na_2CO_3 gave the dinuclear complexes $[Au_2(\mu\text{-}S_2C_2B_{10}H_{10})L_2]$ [L = PPh_3 (**1**), PPh_2Me (**2**), $PPh_2(C_6H_4Me\text{-}4)$ (**3**), $SPPh_3$ (**4**)] where the dithiolate ligand bridges both gold atoms. Further reaction of **1** with $[Au(OTf)(PPh_3)]$ (OTf = trifluoromethanesulfonate) leads to the trinuclear species $[Au_3(S_2C_2B_{10}H_{10})(PPh_3)_3](OTf)$ (**5**). The anionic derivative $(PPh_3Me)_2[Au_2(C_6F_5)_2(\mu\text{-}S_2C_2B_{10}H_{10})]$ (**6**) was prepared by reaction of $1,2\text{-}(SH)_2C_2B_{10}H_{10}$ with $(PPh_3Me)[AuBr(C_6F_5)]$. Dinuclear complexes with two bridging ligands were synthesized: the neutral heterobridged species $[Au_2(\mu\text{-}S_2C_2B_{10}H_{10})(\mu\text{-}P{-}P)]$ [P−P = dppm (**7**), dppey (**8**), dppp (**9**), dppph (**10**), dppe (**11**)] obtained from $1,2\text{-}(SH)_2C_2B_{10}H_{10}$ and $[Au_2Cl_2(\mu\text{-}P{-}P)]$ and the homobridged anionic derivative $NBu_4[Au_2(\mu\text{-}S_2C_2B_{10}H_{10})_2]$ (**12**) prepared by treatment of the 1,2-dimercapto-*o*-carborane with [AuCl(tht)] (tht = tetrahydrothiophene) (molar ratio 1:1) and NBu_4Br. The crystal structures of complexes **1**, **8**, and **10** were determined by X-ray diffraction studies.

Introduction

There is a continuing interest in transition metal complexes, and those of gold in particular, with thiolate ligands for several reasons. Among these are the revelance to biological systems,[1−4] the potential of chemistry relating to S−C bond cleavage reactions and desulfurization,[5,6] the novel structure of such complexes,[7−9] and the possible applications in organosulfur chemistry. Interest in the coordination chemistry of thiolate gold(I) complexes arises in part from the potential use of these derivatives in medicine. Water-soluble, polymeric gold(I) thiolates such as gold sodium thiomalate (Myochrysine) and gold sodium thiosulfate (Sanachrysin) are used in the treatment of rheumatoid arthritis.[10−12] Other compounds employed in this context are the monomeric lipid-soluble triethylphosphino−gold(I)−thioglucose derivative, Auranofin,[13,14] which also shows cytotoxic activity,[15,16] and Solganol (gold(I) thioglucosate), which also has in vitro inhibitory effects on human inmunodeficiency virus 1, the etiologic agent of AIDS.[17]

The synthesis of dinuclear gold(I) complexes has received

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much attention in recent years[18−21] because they provide an excellent framework for the study of the weak bonding interactions between the closed shell d^{10} gold(I) atoms, brought about by relativistic effects.[22,23] Homobridged systems, in particular those containing diphosphines or dithiolates as ligands, have been widely studied,[18−21] but recently more interest has focused on the study of heterobridged and "open-ring" systems.[24−29] Here we report on the synthesis of 1,2-dithiolate-*o*-carborane gold(I) complexes; this ligand has been scarcely studied and only a few complexes of Co^{II} and Ni^{II} have been previously described.[30,31] Furthermore, complexes incorporating an *o*-carborane backbone are receiving much attention for the potential use in tumor-seeking drugs for boron neutron capture therapy.[32,33]

Results and Discussion

The reaction of 1,2-dimercapto-*o*-carborane with 2 equiv of [AuClL] in dichloromethane and in the presence of Na_2CO_3 leads to the dinuclear species $[Au_2(\mu\text{-}S_2C_2B_{10}H_{10})L_2]$ [L = PPh_3 (**1**), PPh_2Me (**2**), $PPh_2(C_6H_4Me\text{-}4)$ (**3**), $SPPh_3$ (**4**)]. Complexes **1**−**4** are white solids, air- and moisture-stable, and they behave as nonconductors in acetone solutions. Their IR spectra show bands arising at the B−H stretching modes of the *o*-carborane nucleus between 2579 and 2608 cm^{-1} (s, br) and also the vibrations v(Au−S) appearing around 330 cm^{-1} (s). The IR spectrum of **4** also presents the v(P=S) band at 590 cm^{-1} (s).

The $^{31}P\{^1H\}$ NMR spectra show only one singlet because of the equivalence of the phosphorus atoms. A downfield displacement from the starting materials is observed, which is typical for the coordination of the gold atom to a sulfur ligand. The ^1H NMR spectra for **2** and **3** present a doublet and a singlet, respectively, for the methyl protons of the phosphine. In the positive-ion fast-atom bombardment (FAB) mass spectra, the molecular peaks appear at m/z = 1125 (**1**, 6%), 1001 (**2**, 8%), and 1153 (**3**, 8%), although the most abundant peaks are assigned to the fragments $[M + AuPR_3]^+$, $[Au(PR_3)_2]^+$, or $[AuPR_3]^+$. All these data seem to confirm that the structure of complexes **1**−**4** corresponds to dinuclear species with the 1,2-dithiolate-*o*-carborane ligand bridging both gold atoms. We have confirmed this structure with an X-ray diffraction study for complex **1**. The molecule is shown in Figure 1, with selected bond lengths and angles in Table 1. The molecule has crystallographic twofold symmetry. The coordination of the gold atoms is linear with an angle P−Au−S of 175.75(6)°. This represents a difference from related compounds with dithiolate ligands, e.g., $[Au_2(\mu\text{-}1,2\text{-}S_2C_6H_4)(PPh_3)_2]$,[27] $[Au_2(\mu\text{-}3,4\text{-}S_2C_6H_3Me)(PPh_3)_2]$,[26] or $[Au_2(\mu\text{-MNT})(PPh_3)_2]$ (MNT = 1,2-dicyanoethene-1,2-dithiolate)[24] where one of the gold atoms has a very distorted trigonal-planar geometry because of a weak interaction (<3 Å) with the second sulfur atom. In complex **1** the intramolecular Au···S′ contact is longer at 3.226 Å, and an intramolecular Au···Au contact is 3.0746(9) Å, typical of this type of dinuclear derivative and attributed to relativistic effects in the valence orbitals of gold. The Au−P and Au−S bond distances, 2.260(2) and 2.329(2) Å, respectively, are similar to those found in the dithiolate complexes mentioned above.

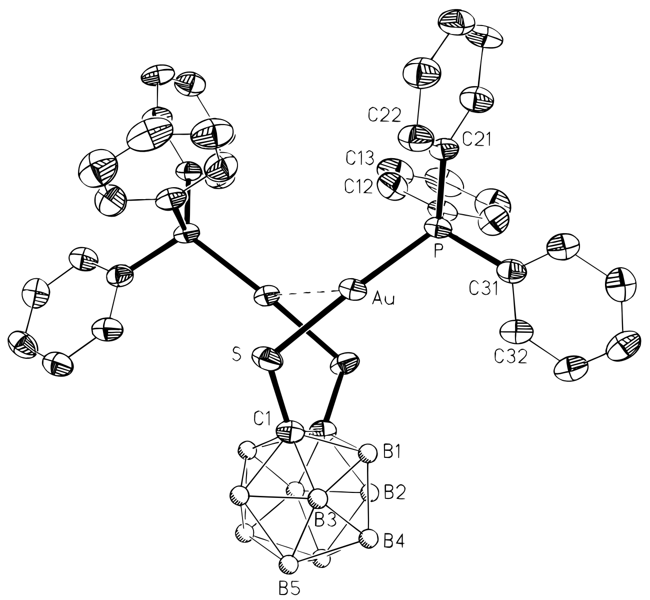

Figure 1. Molecule of complex **1** in the crystal with the atom numbering scheme. H atoms are omitted for clarity; radii are arbitrary.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for **1**

Au−P	2.260(2)	Au−S	2.329(2)
Au−Au[a]	3.0746(9)	S−C(1)	1.774(6)
C(1)−B(2)[a]	1.697(10)	C(1)−B(3)	1.702(10)
C(1)−B(1)	1.712(10)	C(1)−B(1)[a]	1.739(10)
C(1)−C(1)[a]	1.782(12)	P−C(21)	1.810(6)
P−C(31)	1.811(7)	P−C(11)	1.822(7)
P−Au−S	175.75(6)	P−Au−Au[a]	111.97(4)
S−Au−Au[a]	71.83(5)	C(1)−S−Au	104.5(2)
B(2)[a]−C(1)−B(3)	63.3(4)	B(2)[a]−C(1)−B(1)	113.6(5)
B(3)−C(1)−B(1)	62.8(4)	B(2)[a]−C(1)−B(1)[a]	62.6(4)
B(3)−C(1)−B(1)[a]	113.5(5)	B(1)−C(1)−B(1)[a]	109.9(5)
B(2)[a]−C(1)−S	117.2(5)	B(3)−C(1)−S	121.7(5)
B(1)−C(1)−S	122.7(4)	B(1)[a]−C(1)−S	115.7(4)
B(2)[a]−C(1)−C(1)[a]	108.6(4)	B(3)−C(1)−C(1)[a]	109.5(4)
B(1)−C(1)−C(1)[a]	59.6(4)	B(1)[a]−C(1)−C(1)[a]	58.2(4)
S−C(1)−C(1)[a]	122.0(2)	C(1)−B(1)−C(1)[a]	62.2(5)
C(1)−B(1)−B(3)	58.3(4)	C(1)[a]−B(1)−B(3)	108.1(5)
C(1)−B(1)−B(4)	105.8(5)	C(1)[a]−B(1)−B(4)	105.2(5)
C(1)−B(1)−B(2)	107.7(5)	C(1)[a]−B(1)−B(2)	57.6(4)
C(1)[a]−B(2)−B(5)[a]	105.3(6)	C(1)[a]−B(2)−B(4)	107.0(6)
C(1)[a]−B(2)−B(3)[a]	58.5(4)	C(1)[a]−B(2)−B(1)	59.8(4)
C(1)−B(3)−B(5)	105.6(5)	C(1)−B(3)−B(1)	58.9(4)
C(1)−B(3)−B(4)	106.3(5)	C(1)−B(3)−B(2)[a]	58.2(4)
C(21)−P−C(31)	106.7(3)	C(21)−P−C(11)	104.9(3)
C(31)−P−C(11)	105.7(3)	C(21)−P−Au	116.5(2)
C(31)−P−Au	108.8(2)	C(11)−P−Au	113.6(2)

[a] Symmetry transformations used to generate equivalent atoms: $-x + 1$, y, $-z + {}^1/_2$.

We previously observed that ligands with an *o*-carborane backbone are extremely rigid and consequently have a marked tendency to act as chelate ligands.[34,35] Therefore we investigated

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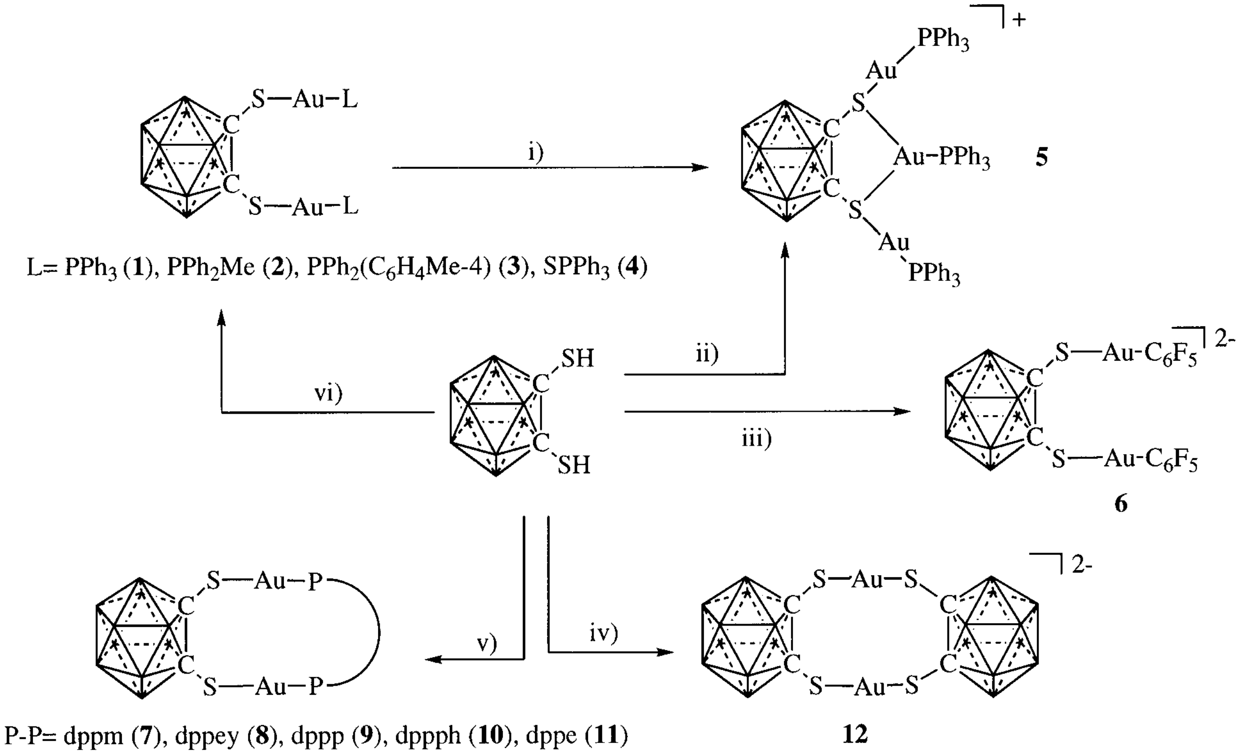
Scheme 1[a]



[a] Conditions: (i) [Au(OTf)(PPh$_3$)], (ii) 3[Au(OTf)(PPh$_3$)], (iii) 2(PPh$_3$Me)[AuBr(C$_6$F$_5$)], (iv) [AuCl(tht)], 2NBu$_4$Br, (v) [Au$_2$Cl$_2$(μ-P−P)], and (vi) 2[AuClL].

the reaction of 1,2-(SH)$_2$C$_2$B$_{10}$H$_{10}$ with 1 equiv of [AuCl(PR$_3$)] in the presence of [(PPh$_3$)$_2$N]Cl in the hope of obtaining the three-coordinate derivatives. The result is, however, a mixture of the linear and the trigonal species, the latter being formed in smaller quantities.

As mentioned above, the mass spectra of complexes **1**−**3** indicate that the fragment [M + AuPPh$_3$]$^+$ is stable, and thus we have carried out further reaction of complex **1** with [Au(OTf)(PPh$_3$)] to give the trinuclear derivative [Au$_3$(S$_2$C$_2$B$_{10}$H$_{10}$)(PPh$_3$)$_3$](OTf) (**5**). Compound **5** behaves as a 1:1 electrolyte in acetone solutions. Its IR spectrum shows, apart from the v(B−H) bands, others arising from ionic triflate (C_{3v}): v_{as}(SO$_3$) 1265 (vs, br), v_s(CF$_3$) 1223 (s), and v_{asi}(CF$_3$) 1150 (s) cm^{-1}. The ^{31}P{^{1}H} NMR spectrum at room temperature shows a broad singlet that splits into two singlets of ~2:1 ratio at low temperature.

In its FAB+ mass spectrum the cation peak appears at *m*/*z* = 1584 (27%) and no other fragment is observed at higher *m*/*z* ratio. We propose a structure with two gold atoms with a linear geometry and the third one three-coordinate (Scheme 1); this structure has been found in the related complex [Au$_3$(3,4-S$_2$C$_6$H$_3$Me)(PPh$_3$)$_3$]ClO$_4$.[26] Complex **5** does not react further with [Au(OTf)(PPh$_3$)].

The reaction of 1,2-(SH)$_2$C$_2$B$_{10}$H$_{10}$ with 2 equiv of (PPh$_3$Me)[AuBr(C$_6$F$_5$)] in dichloromethane in the presence of sodium carbonate gives the anionic derivative (PPh$_3$Me)$_2$[Au$_2$(C$_6$F$_5$)$_2$(μ-S$_2$C$_2$B$_{10}$H$_{10}$)] (**6**). Complex **6** behaves as a 2:1 electrolyte in acetone solutions. Its IR spectrum shows, apart from the v(B−H) bands at 2563 (vs) cm^{-1}, others at 1504 (vs), 954 (vs), and 792 (m) cm^{-1} characteristic of a pentafluorophenyl group bonded to gold(I). The ^{19}F NMR spectrum shows the typical pattern of equivalent C$_6$F$_5$ groups with two multiplets and a triplet for the various fluorine atoms.

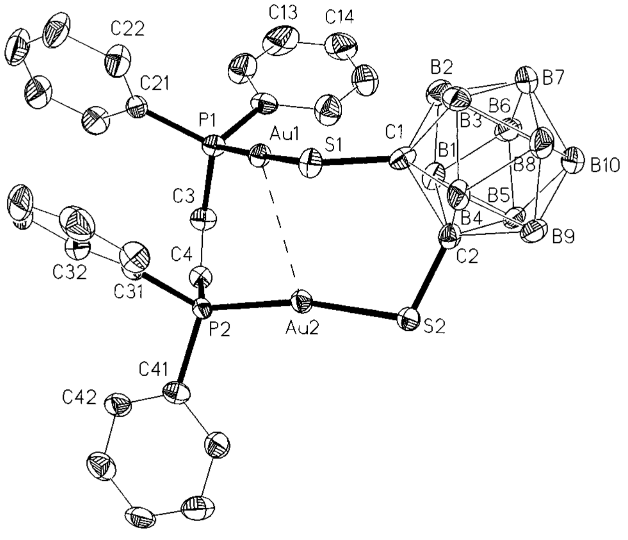


Figure 2. Molecule of complex **8** in the crystal showing the atom labeling scheme. Hydrogen atoms are omitted for clarity; radii are arbitrary.

Treatment of 1,2-dimercapto-*o*-carborane with the dinuclear derivatives [Au$_2$Cl$_2$(μ-P−P)] in the presence of Na$_2$CO$_3$ leads to the heterobridged species [Au$_2$(μ-S$_2$C$_2$B$_{10}$H$_{10}$)(μ-P−P)] (P−P = dppm (**7**), dppey (**8**), dppp (**9**), dppph (**10**), dppe (**11**)].

We have carried out this reaction with various diphosphines of differing steric requirements, with the aim of obtaining products of differing structures. We previously reported in a communication that the treatment of 1,2-dimercapto-*o*-carborane with the gold(I) compound [Au$_2$Cl$_2${μ-(PPh$_2$)$_2$C$_2$B$_{10}$H$_{10}$}] results in the formation of the tetranuclear derivative [Au$_4$(S$_2$C$_2$B$_{10}$H$_{10}$)$_2${(PPh$_2$)$_2$C$_2$B$_{10}$H$_{10}$}$_2$], where two of the gold atoms are four-coordinate, chelated by one diphosphine and one dithiolate

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Table 2. Selected Bond Lengths (Å) and Angles (deg) for **8**

Au(1)−P(1)	2.249(2)	Au(1)−S(1)	2.301(2)
Au(1)−Au(2)	3.0195(5)	Au(2)−P(2)	2.265(2)
Au(2)−S(2)	2.309(2)	S(1)−C(1)	1.768(7)
S(2)−C(2)	1.778(6)	P(1)−C(21)	1.809(6)
P(1)−C(3)	1.818(7)	P(1)−C(11)	1.821(7)
P(2)−C(31)	1.814(7)	P(2)−C(4)	1.820(7)
P(2)−C(41)	1.826(7)	C(1)−C(2)	1.762(8)
C(3)−C(4)	1.328(9)		
P(1)−Au(1)−S(1)	177.96(6)	P(1)−Au(1)−Au(2)	108.70(5)
S(1)−Au(1)−Au(2)	73.21(4)	P(2)−Au(2)−S(2)	168.11(6)
P(2)−Au(2)−Au(1)	78.08(4)	S(2)−Au(2)−Au(1)	113.74(4)
C(1)−S(1)−Au(1)	105.7(2)	C(2)−S(2)−Au(2)	108.3(2)
C(21)−P(1)−C(3)	105.5(3)	C(21)−P(1)−C(11)	107.8(3)
C(3)−P(1)−C(11)	102.2(3)	C(21)−P(1)−Au(1)	114.6(2)
C(3)−P(1)−Au(1)	114.5(2)	C(11)−P(1)−Au(1)	111.3(2)
C(31)−P(2)−C(4)	105.7(3)	C(31)−P(2)−C(41)	105.7(3)
C(4)−P(2)−C(41)	100.5(3)	C(31)−P(2)−Au(2)	114.1(2)
C(4)−P(2)−Au(2)	116.6(2)	C(41)−P(2)−Au(2)	113.0(2)
B(2)−C(1)−S(1)	124.2(4)	B(3)−C(1)−S(1)	119.0(4)
B(1)−C(1)−S(1)	123.0(5)	B(4)−C(1)−S(1)	113.3(5)
C(2)−C(1)−S(1)	119.6(4)	B(5)−C(2)−S(2)	119.0(4)
B(1)−C(2)−S(2)	119.9(5)	B(9)−C(2)−S(2)	118.6(4)
B(4)−C(2)−S(2)	118.5(5)	C(1)−C(2)−S(2)	122.4(4)
C(4)−C(3)−P(1)	127.8(5)	C(3)−C(4)−P(2)	129.2(5)
C(12)−C(11)−P(1)	123.6(6)	C(16)−C(11)−P(1)	117.5(5)
C(22)−C(21)−P(1)	120.0(5)	C(26)−C(21)−P(1)	121.1(5)
C(32)−C(31)−P(2)	122.0(5)	C(36)−C(31)−P(2)	118.5(5)
C(46)−C(41)−P(2)	119.9(5)	C(42)−C(41)−P(2)	120.9(5)

Table 3. Selected Bond Lengths (Å) and Angles (deg) for **10**

Au(1)−P(1)	2.257(2)	Au(1)−S(1)	2.313(2)
Au(1)−Au(2)	2.9771(10)	Au(2)−P(2)	2.267(2)
Au(2)−S(2)	2.321(2)	P(1)−C(21)	1.813(8)
P(1)−C(11)	1.815(7)	P(1)−C(51)	1.835(7)
P(2)−C(31)	1.804(7)	P(2)−C(41)	1.820(6)
P(2)−C(52)	1.830(7)	S(1)−C(1)	1.765(7)
S(2)−C(2)	1.756(7)	C(1)−C(2)	1.824(10)
P(1)−Au(1)−S(1)	167.50(7)	P(1)−Au(1)−Au(2)	104.88(5)
S(1)−Au(1)−Au(2)	83.86(6)	P(2)−Au(2)−S(2)	169.18(7)
P(2)−Au(2)−Au(1)	83.41(5)	S(2)−Au(2)−Au(1)	107.27(5)
C(21)−P(1)−C(11)	107.6(3)	C(21)−P(1)−C(51)	105.0(3)
C(11)−P(1)−C(51)	104.3(3)	C(21)−P(1)−Au(1)	115.8(3)
C(11)−P(1)−Au(1)	103.4(2)	C(51)−P(1)−Au(1)	119.6(2)
C(31)−P(2)−C(41)	106.4(3)	C(31)−P(2)−C(52)	103.6(3)
C(41)−P(2)−C(52)	103.7(3)	C(31)−P(2)−Au(2)	117.1(2)
C(41)−P(2)−Au(2)	105.6(2)	C(52)−P(2)−Au(2)	119.1(2)
C(1)−S(1)−Au(1)	102.4(2)	C(2)−S(2)−Au(2)	105.1(2)
B(2)−C(1)−S(1)	125.2(5)	B(3)−C(1)−S(1)	122.0(5)
B(4)−C(1)−S(1)	115.3(5)	B(1)−C(1)−S(1)	120.7(5)
B(8)−C(2)−S(2)	121.0(5)	B(9)−C(2)−S(2)	123.7(5)
B(1)−C(2)−S(2)	121.1(5)	B(4)−C(2)−S(2)	116.4(5)
S(2)−C(2)−C(1)	119.6(5)		

ligand.[36] In the FAB+ mass spectrum of this complex, the molecular peak appeared with coincident experimental and isotopic distribution. In the FAB+ mass spectra of complexes **7**−**11**, the peaks assigned to the fragments $[M]^+$ and $[2M]^+$ also appear. Thus, we carried out the crystal structure determination by X-ray diffraction for two of these derivatives, **8** and **10**. In both cases, we have confirmed a dimeric structure, as expected, similar to that found in other gold complexes with dithiolate ligands.

The typical characterization features of complexes **7**−**11** include a strong band in the IR spectra around 2500 cm^{-1} corresponding to the B−H strech mode of the carborane ligand. Also, a singlet is observed in all cases in the $^{31}P\{^1H\}$ NMR spectra, which indicates the presence of two equivalent phosphorus atoms at room temperature. Again, there is a downfield shift of the singlet relative to that of the starting material, indicating coordination to the sulfur ligand.

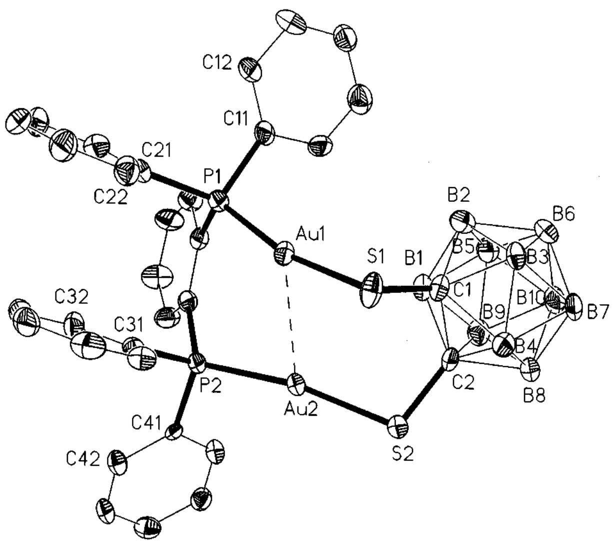

Figure 3. Molecular structure of complex **10** in the crystal with the atom labeling scheme. H atoms are omitted for clarity; radii are arbitrary.

The molecule of complex **8** is shown in Figure 2, with selected distances and angles in Table 2. The gold atoms are in a distorted linear geometry with P−Au−S angles of 168.11(6) and 177.96(6)°. These distortions may be a consequence of the Au−Au interaction of 3.0195(5) Å. The gold centers are bridged by one diphosphine and one dithiolate ligand with Au−P distances of 2.249(2) and 2.265(2) Å and Au−S bond lengths of 2.309(2) and 2.301(2). These distances are of the same order as those found in complex **1** and also those in the compounds $[Au_2\{\mu\text{-}S_2(CH_2)_3\}(\mu\text{-dppm})]$[24] and $[Au_2(\mu\text{-}^{i}MNT)(\mu\text{-dppey})]$[25] which possess related bridging ligands.

The molecule of complex **10** is shown in Figure 3 with selected bond lengths and angles in Table 3. The structural dimensions are very similar to those in complex **8**. The change to a more rigid diphosphine causes greater deviations from linearity at the gold atoms, the P−Au−S angles being 167.50(7) and 169.18(7)°. Consequently the gold−gold contact is shorter than in complex **8**, 2.9771(10) Å. The Au−P, 2.257(2) and 2.267(2) Å, and the Au−S distances, 2.313(2) and 2.321(2) Å, are, however, slightly longer than those in **8**, although still of the same order as those in $[Au_2\{\mu\text{-}S_2(CH_2)_3\}(\mu\text{-dppm})]$.[24]

Finally, we have synthesized a dinuclear homoleptic complex, $(NBu_4)_2[Au_2(\mu\text{-}S_2C_2B_{10}H_{10})_2]$ (**12**), by reaction of equimolar amounts of 1,2-dimercapto-*o*-carborane and [AuCl(tht)] with 2 equiv of NBu_4Br in the presence of sodium carbonate. Complex **12** behaves as a 2:1 electrolyte in acetone solutions. In the negative-ion mass spectrum (FAB−) of this derivative, the molecular peak does not appear, but the peaks assigned to the fragments $[M - NBu_4]^-$ at $m/z = 1049$ (42%), $[M - 2NBu_4]^-$ at $m/z = 807$ (75%), and $[M - 2NBu_4 - Au]^-$ at $m/z = 609$ (52%) are present.

Experimental Section

Instrumentation. 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 $\sim 5 \times 10^{-4}$ mol dm^{-3} solutions with a Philips 9509 conductimeter. C and H analyses were carried out with a Perkin-Elmer 2400 microanalyzer. Mass spectra were recorded on a VG Autospec, with the FAB technique, using nitrobenzyl alcohol as matrix. NMR spectra were recorded on a Varian Unity 300 spectrometer and a Bruker ARX 300 spectrometer in $CDCl_3$. Chemical shifts are cited relative to $SiMe_4$

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(36) Crespo, O.; Gimeno, M. C.; Jones, P. G.; Laguna, A. J. *Chem. Soc., Chem Commun.* **1993**, 1696.

Table 4. Analytical, Conductivity, and NMR Data and υ(B−H) Frequencies for Complexes **1**−**12**

		analysis^a (%)			NMR^b		
	yield (%)	C	H	$\Lambda_M{}^c$	$^{31}P\{^1H\}$	^1H	υ(B−H)(cm^{-1})
$[Au_2(\mu\text{-}S_2C_2B_{10}H_{10})(PPh_3)_2]$ (**1**)	71	40.9 (40.6)	3.62 (3.58)	2	36.5 (s)		2579
$[Au_2(\mu\text{-}S_2C_2B_{10}H_{10})(PPh_2Me)_2]$ (**2**)	85	33.75 (33.6)	3.95 (3.6)	5	19.9 (s)	2.14 (d, 8.97)	2608
$[Au_2(\mu\text{-}S_2C_2B_{10}H_{10})\{PPh_2(C_6H_4Me\text{-}4)\}_2]$ (**3**)	71	41.5 (41.75)	3.8 (3.85)	4	35.7 (s)	2.3 (s)	2590
$[Au_2(\mu\text{-}S_2C_2B_{10}H_{10})(SPPh_3)_2]$ (**4**)	77	39.45 (39.4)	3.3 (3.4)	10	44.0 (s)		2592
$[Au_3(S_2C_2B_{10}H_{10})(PPh_3)_3]OTf^d$ (**5**)	71	39.65 (39.40)	3.35 (3.2)	100	35.6 (s, br) 34.2 (s, br)		2598
$(PPh_3Me)_2[Au_2(C_6F_5)_2(\mu\text{-}S_2C_2B_{10}H_{10})]$ (**6**)	76	42.05 (41.95)	3.2 (3.1)	230			2563
$[Au_2(\mu\text{-}S_2C_2B_{10}H_{10})(\mu\text{-dppm})]$ (**7**)	61	33.05 (32.95)	3.25 (3.25)	4	29.2 (s)	3.64 (t, br)	2586
$[Au_2(\mu\text{-}S_2C_2B_{10}H_{10})(\mu\text{-dppey})]$ (**8**)	65	34.4 (33.75)	3.2 (3.25)	1	30.07(s)		2606
$[Au_2(\mu\text{-}S_2C_2B_{10}H_{10})(\mu\text{-dppp})]$ (**9**)	99	34.35 (34.4)	3.55 (3.6)	2	30.9 (s)	1.92 (m) 2.67 (m)	2594
$[Au_2(\mu\text{-}S_2C_2B_{10}H_{10})(\mu\text{-dppph})]$ (**10**)	89	36.3 (36.7)	3.55 (3.3)	3	31.2 (s)		2589
$[Au_2(\mu\text{-}S_2C_2B_{10}H_{10})(\mu\text{-dppe})]$ (**11**)	86	33.55 (33.65)	3.25 (3.45)	3	33.2 (s)	2.64 (d, br)	2599
$(NBu_4)_2[Au_2(\mu\text{-}S_2C_2B_{10}H_{10})_2]$ (**12**)	68	33.65 (33.45)	7.35 (7.2)	243			2633

[a] Calculated values in parentheses. [b] Recorded in $CDCl_3$, values in ppm. Coupling constants J(PH) in Hz. [c] In acetone, Ω^{-1} cm^2 mol^{-1}. [d] $^{31}P\{^1H\}$ RMN at −55 °C.

Table 5. Details of Data Collection and Structure Refinement for the Complexes **1**, **8**, and **10**

compound	$1{\cdot}CH_2Cl_2$	8	10
chem formula	$C_{39}H_{42}Au_2B_{10}Cl_2P_2S_2$	$C_{28}H_{32}Au_2B_{10}P_2S_2$	$C_{32}H_{34}Au_2B_{10}P_2S_2$
cryst habit	colorless prism	colorless hexagonal tablet	colorless prism
cryst size (mm)	0.55 × 0.20 × 0.15	0.45 × 0.45 × 0.20	0.60 × 0.30 × 0.20
space group	C2/c	$P2_1/c$	$P\bar{1}$
a (Å)	13.991(3)	13.304(2)	11.921(3)
b (Å)	22.228(5)	13.416(3)	12.894(4)
c (Å)	15.067(4)	20.351(4)	14.342(4)
α (deg)	−	−	114.11(2)
β (deg)	97.16(2)	109.12(2)	91.63(2)
γ (deg)	−	−	115.010(12)
U (Å^3)	4649(2)	3432.1(11)	1768.7(9)
Z	4	4	2
D_c (Mg m^{-3})	1.728	1.929	1.965
M	1209.72	996.63	1046.69
F(000)	2320	1880	992
T (°C)	−100	−130	−130
$2\theta_{max}$ (deg)	55	50	50
μ(Mo Kα) (mm^{-1})	6.606	8.775	8.519
transmission	0.79−0.94	0.347−1.0	0.642−0.843
no. of reflctns measd	11041	9312	8775
no. of unique reflctns	5182	6032	6230
R_{int}	0.029	0.045	0.037
R^a (F, $F > 4\sigma(F)$)	0.033	0.033	0.035
wR^b(F^2, all refl)	0.096	0.084	0.088
no. of parameters	228	397	433
no. of restraints	171	337	400
S^c	1.133	1.066	1.046
max $\Delta\rho$ (eÅ^{-3})	1.83	1.336	2.669

[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.

(^1H, external), 85% H_3PO_4 (^{31}P, external) and $CFCl_3$ (^{19}F, external). The yields, analyses, conductivities, NMR data, and υ(B−H) frequencies are listed in Table 4.

Materials. The starting materials $[AuCl(PR_3)]$,[37] $(MePPh_3)[AuBr(C_6F_5)]$,[38] and [AuCl(tht)][39] were prepared by published procedures. $[Au(OTf)(PPh_3)]$ was obtained from $[AuCl(PPh_3)]$ by reaction with AgOTf and $[Au_2Cl_2(\mu\text{-}P{-}P)]$ from 2 equiv of [AuCl(tht)] and 1 equiv of the diphosphine.

Synthesis of $[Au_2(\mu\text{-}S_2C_2B_{10}H_{10})L_2]$. To a solution of $(SH)_2C_2B_{10}H_{10}$ (0.020 g, 0.1 mmol) in dichloromethane (30 mL) were added $[AuCl(PPh_3)]$ (0.098 g, 0.2 mmol), $[AuCl(PPh_2Me)]$ (0.086 g, 0.2 mmol), $[AuCl\{PPh_2(C_6H_4Me\text{-}4)\}]$ (0.101 g, 0.2 mmol), or $[AuCl(SPPh_3)]$

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(0.105 g, 0.2 mmol) and excess of Na_2CO_3. The mixture was stirred for 30 min, the excess of Na_2CO_3 filtered off, and the solution concentrated to ∼5 mL. Addition of diethyl ether gave complexes **1**−**4** as white solids.

Synthesis of [$Au_3(S_2C_2B_{10}H_{10})(PPh_3)_3$](OTf). To a freshly prepared dichloromethane solution (20 mL) of [Au(OTf)PPh_3] (0.1 mmol) was added [$Au_2(\mu$-$S_2C_2B_{10}H_{10})(PPh_3)_2$] (0.110 g, 0.1 mmol), and the solution was stirred for 30 min. The solvent was removed in vacuo, and addition of diethyl ether gave complex **5** as a white solid.

Synthesis of ($PPh_3Me)_2[Au_2(C_6F_5)_2(\mu$-$S_2C_2B_{10}H_{10})$]. To a solution of $(SH)_2C_2B_{10}H_{10}$ (0.020 g, 0.1 mmol) in dichloromethane (30 mL) were added (PPh_3Me)[AuBr(C_6F_5)] (0.144 g, 0.2 mmol) and excess of Na_2CO_3. The mixture was stirred for 30 min and then filtered to remove the sodium carbonate. Concentration of solvent to ∼5 mL and addition of diethyl ether afforded complex **6** as a white solid. ^{19}F NMR: δ, −115.7 (m, 2F, *o*-F), −163.9 (m, 2F, *m*-F), −162.3 (t, 1F, *p*-F, J(FF) 19.9 Hz).

Synthesis of [$Au_2(\mu$-$S_2C_2B_{10}H_{10})(\mu$-P−P)]. To a solution of $(SH)_2C_2B_{10}H_{10}$ (0.020 g, 0.1 mmol) in dichloromethane (30 mL) were added [$Au_2Cl_2(\mu$-dppm)] (0.085 g, 0.1 mmol), [$Au_2Cl_2(\mu$-dppey)] (0.085 g, 0.1 mmol), [$Au_2Cl_2(\mu$-dppp)] (0.087 g, 0.1 mmol), [$Au_2Cl_2(\mu$-dppph)] (0.091 g, 0.1 mmol), or [$Au_2Cl_2(\mu$-dppe)] (0.086 g, 0.1 mmol) and excess of Na_2CO_3. The suspension was stirred for 30 min and then the excess of sodium carbonate filtered off. Upon evaporation of the solvent and addition of diethyl ether, complexes **7**−**11** were isolated as white solids.

Synthesis of ($NBu_4)_2[Au_2(\mu$-$S_2C_2B_{10}H_{10})_2$]. To a solution of $(SH)_2C_2B_{10}H_{10}$ (0.020 g, 0.1 mmol) in dichloromethane (30 mL) were added [AuCl(tht)] (0.032 g, 0.1 mmol), NBu_4Br (0.064 g, 0.2 mmol), and excess of Na_2CO_3. The mixture was stirred for 30 min and then filtered off to remove the sodium carbonate. Concentration of solvent to ∼5 mL and addition of diethyl ether afforded complex **12** as a white solid.

Crystal Structure Determinations. The crystals were mounted in inert oil on glass fibers and transferred to the cold gas stream of a Siemens R3 (**1**) or a Stoe STADI-4 (**8**, **10**) diffractometer, both with a Siemens LT-2 low-temperature attachment. Data were collected using monochromated Mo Kα radiation ($\lambda = 0.710\ 73$ Å) scan type ω (**1**), ω/θ (**8**,**10**). Cell constants were refined from setting angles (**1**) or $\pm\omega$ angles (**8**, **10**) of ∼50 reflections in the range 2θ 20−23°. Absorption corrections were applied on the basis of Ψ-scans. Structures were solved by the heavy-atom method and refined on F^2 using the program SHELXL-93.[41] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included using a riding model. A system of restraints was used for local ring geometry and light atom *U* components. Special refinement details for complex **1**: a poorly defined solvent region was interpreted as disordered dichloromethane. A 1:1 solvate was assumed in calculating the formula weight and associated parameters. Further details are given in Table 5.

Acknowledgment. We thank the Dirección General de Investigación Científica y Técnica (PB94-0079) and the Fonds der Chemischen Industrie for financial support.

Supporting Information Available: Tables of crystal data, data collection and solution and refinement parameters, atomic parameters, bond distances and angles, anisotropic thermal parameters, and hydrogen atom parameters, (20 pages). Ordering information is given on any current masthead page.

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(41) Sheldrick, G. M.; SHELXL-93, *Program for Crystal Structure Refinement.* University of Göttingen, Göttingen, Germany, 1993.