Reactions of [Au(acac)PPh₃] with Diphosphine Derivatives: Different Coordination Modes of Gold to the Ligand Systems. X-ray Structure of [SPPh₂C(AuPPh₃)₂PPh₂CH(AuPPh₃)COOMe]ClO₄ and [Au₅(C₆F₅){(SPPh₂)₂C}₂(PPh₃)]

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Reactions of various diphosphine ligands with [Au(acac)PPh₃] (acac = acetylacetonate) are reported. In all cases the ligand is deprotonated by displacement of acac as acetylacetone and subsequently coordinates the gold or the AuPPh₃⁺ fragment. The reaction of the diphosphines Ph₂PNHPPh₂ (dppa) or Ph₂PCH₂PPh₂ (dppm) with [Au(acac)PPh₃] leads to the dinuclear complexes [Au(PPh₂)₂N]₂ (1) or [Au(PPh₂)₂CH]₂ (2), with the diphosphines acting as bridging ligands. With the diphosphine disulfides SPh₂PNHPPh₂S or SPh₂PCH₂PPh₂S the reaction takes place in a different manner; with SdppaS the dinuclear complex [Au(SPPh₂)₂N]₂ (3) is formed, while with SdppmS a mixture of [(SPPh₂)₂CH(AuPPh₃)] (4) and [(SPPh₂)₂C(AuPPh₃)₂] (5) is obtained. If the reaction is carried out with 2 equiv of [Au(acac)PPh₃], only the disubstituted product 5 is isolated. The mixed phosphine sulfide–phosphonium derivatives [SPPh₂CH₂-PPh₂R]ClO₄ (R = Me, CH₂Ph, CH₂COOMe) react with [Au(acac)PPh₃] in different stoichiometries to give the deprotonated mononuclear [SPPh₂CH(AuPPh₃)PPh₂R]ClO₄ (R = Me (6)), dinuclear [SPPh₂C(AuPPh₃)₂PPh₂R]ClO₄ (R = Me (7), CH₂Ph (8), CH₂COOMe (9)), or the trinuclear [SPPh₂C(AuPPh₃)₂PPh₂CH(AuPPh₃)COOMe]ClO₄ (10) (R = CH₂COOMe). The reactivity of these methanide complexes toward gold or silver complexes which possess a labile ligand such as tht in [Au(C₆F₅)tht] (tht = tetrahydrothiophene) or ClO₄ in AgClO₄ is different. Complex [SPPh₂CH(AuPPh₃)PPh₂Me]ClO₄ reacts with [Au(C₆F₅)tht] or AgClO₄ leading to the dinuclear derivatives [Au₂(SPPh₂CHPPh₂Me)₂](ClO₄)₂ (11) or [AuAg(SPPh₂CHPPh₂Me)₂]-(ClO₄)₂ (12), and the compounds [Au(C₆F₅)PPh₃] or [Au(PPh₃)₂]ClO₄ are formed as byproducts. Treatment of the complex [(SPPh₂)₂C(AuPPh₃)₂] with 2 equiv of [Au(C₆F₅)tht] gives the pentanuclear complex [Au₅(C₆F₅){(SPPh₂)₂C}₂PPh₃] (13). Single-crystal X-ray structure determinations were performed for compounds 10 and 13. [SPPh₂C(AuPPh₃)₂PPh₂CH(AuPPh₃)-COOMe]ClO₄ (10) crystallizes in space group P1̄, triclinic, with a = 14.448(4) Å, b = 16.645(4) Å, c = 17.780(5) Å, α = 97.26(2)°, β = 93.76(2)°, γ = 89.71(2)°, Z = 2. [Au₅(C₆F₅){(SPPh₂)₂C}₂-PPh₃] (13) crystallizes in space group P1̄, triclinic, a = 11.900(11) Å, b = 18.425(27) Å, c = 18.877(17) Å, α = 87.85(10)°, β = 86.34(8)°, γ = 79.38(10)°, Z = 2.

Introduction

We have recently reported methanide or methanediide complexes of gold synthesized from [Au(C₆F₅)₂{(PPh₂)₂-CH₂)}]ClO₄ by reaction with acetylacetonate gold derivatives.[1] In these reactions deprotonation of the bis-(diphenylphosphino)methane occurs, acac is displaced as acetylacetone, and the coordination of the gold fragment takes place through the methanide carbon atom.

Taking into account that the diphosphine ligand chelates the gold(III) center, the only possibility for further gold coordination is at the carbon atom. We thought it would be interesting to react the acetylacetonate gold derivative, [Au(acac)PPh₃], with various diphosphine derivatives: (i)

XH= NH, CH₂

R= Me, CH₂Ph, CH₂COOMe
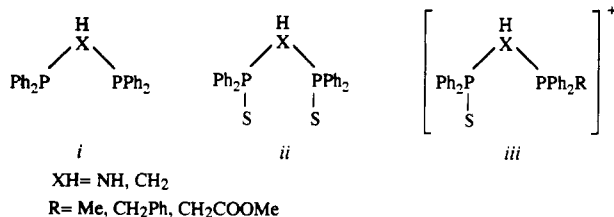
diphosphines such as Ph₂PNHPPh₂ (dppa) or Ph₂PCH₂-PPh₂ (dppm) which offer P–N–P or P–C–P donor centers, after deprotonation, (ii) diphosphine disulfides such as SPh₂PNHPPh₂S or SPh₂PCH₂PPh₂S with S–N–S or S–C–S donor systems, and (iii) mixed phosphine sulfide–phosphonium cations such as [SPPh₂CH₂PPh₂R]ClO₄ with S and C donor centers.

We selected these diphosphine derivatives with the intent of increasing the acidity of the methylene or amine

(1) Fernández, E. J.; Gimeno, M. C.; Jones, P. G.; Laguna, A.; Laguna, M.; López de Luzuriaga, J. M. *J. Chem. Soc., Dalton Trans.* 1992, 3365.

Table I. Analytical Data and Conductivity for the Complexes

complex	yield (%)	analysis (%)[a]		Λ_M[b] (Ω^{-1} cm² mol⁻¹)
		C	H	
[(SPPh₂)₂C(AuPPh₃)₂] (5)	88	53.60 (53.67)	3.91 (3.69)	2
[SPPh₂CH(AuPPh₃)PPh₂Me]ClO₄ (6)	87	53.16 (53.42)	3.99 (3.97)	145
[SPPh₂C(AuPPh₃)₂PPh₂Me]ClO₄ (7)	79	51.85 (51.49)	4.02 (3.69)	133
[SPPh₂C(AuPPh₃)₂PPh₂CH₂Ph]ClO₄ (8)	85	52.53 (52.81)	3.82 (3.77)	151
[SPPh₂C(AuPPh₃)₂PPh₂CH₂COOMe]ClO₄ (9)	80	50.70 (51.05)	3.58 (3.68)	150
[SPPh₂C(AuPPh₃)₂PPh₂CH(AuPPh₃)COOMe]ClO₄ (10)	74	49.88 (50.15)	3.84 (3.54)	159
[AuAg(SPPh₂CHPPh₂Me)₂](ClO₄)₂ (12)	80	45.38 (45.76)	3.45 (3.54)	200
[Au₅(C₆F₅){(SPPh₂)₂C}₂(PPh₃)] (13)	67	38.90 (38.52)	2.48 (2.40)	6

[a] Calculated values in parentheses. [b] In acetone.

Table II.   ³¹P{¹H} NMR Data (δ, ppm) for the Complexes[a]

| complex	SPPh₂	PPh₂R	PPh₃
[(SPPh₂)₂CH(AuPPh₃)] (4)	39.6 (d) (12.2)		43.1 (t) (12.2)
[(SPPh₂)₂C(AuPPh₃)₂] (5)	36.1 (t) (8.6)		46.5 (t) (8.6)
[SPPh₂CH(AuPPh₃)PPh₂Me]ClO₄ (6)	38.9 (dd) (6.2, 12.3)[b]	22.8 (dd) (6.2, 12.3)	39.8 ("t") (12.3)
[SPPh₂C(AuPPh₃)₂PPh₂Me]ClO₄ (7)	49.5 (m)	24.5 (m)	37.1 ("t") (7.8)
[SPPh₂C(AuPPh₃)₂PPh₂CH₂Ph]ClO₄ (8)	50.8 (m)	30.7 (m)	36.7 ("t") (7.0)
[SPPh₂C(AuPPh₃)₂PPh₂CH₂COOMe]ClO₄ (9)	49.7 (m)	27.1 (m)	37.2 ("t") (7.5)
[SPPh₂C(AuPPh₃)₂PPh₂CH(AuPPh₃)COOMe]ClO₄ (10)	50.1 (m, br)	32.5 (m, br)	38.7 (m, br), 36.2 (m, br)
[AuAg(SPPh₂CHPPh₂Me)₂](ClO₄)₂ (12)	43.2 (d) (5.2)	22.4 (d) (5.2)	

[a] Coupling constants in hertz are shown in parentheses; d = doublet, t = triplet, "t" = apparent triplet, m = multiplet. [b] ²J(PP) and ³J(PP).

protons and varying the potential donor ligand to the gold center. Alkylation of one phosphine group forms a phosphonium center, and with very electron-withdrawing groups such as CH₂COOMe, we not only increased the acidity of the protons but also provided the potential for further reaction of other methylene groups with deprotonating reagents. Oxidation of the phosphorus atoms obviously makes the methylene groups more acidic.

Here we report the reactions of these diphosphine derivatives with [Au(acac)PPh₃] in various stoichiometries. The results show that the acac ligand in [Au(acac)-PPh₃] is an excellent base and allows the synthesis of different types of methanide complexes where the ligand has been deprotonated one, two, or three times. The generality of the method is illustrated with the use of several diphosphine derivatives, and although some of them had previously been prepared by us by other procedures, the new complexes present a variety of structural types and some of them, such as the structure of [Au₅(C₆F₅){(SPPh₂)₂C}₂PPh₃], are unprecedented in the chemistry of methanide or diphosphinegold derivatives.

Results and Discussion

1. Reactions of Diphosphines with [Au(acac)-PPh₃]. The reaction of bis(diphenylphosphino)methane or bis(diphenylphosphino)amine with 1 equiv of [Au(acac)-PPh₃] in diethyl ether leads to the precipitation of complexes 1 or 2.

2 [Au(acac)PPh₃] + 2 Ph₂PXHPPh₂ ⟶
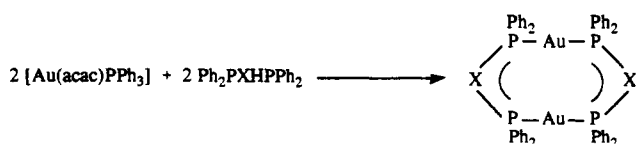

XH= NH(1), CH₂(2)

The basic acac ligand present in [Au(acac)PPh₃] is able to deprotonate the diphosphines, and taking into account the preference of gold for coordination to a P- rather than a C- or N-donor and the great tendency of these diphosphines to act as bridging ligands, the dinuclear deprotonated species are obtained as expected. Complexes 1 and

2 have been previously described by us,[2] synthesized using [AuCl(CH₂PPh₃)] where the ylide ligand is responsible for the deprotonation.

2. Reactions of Diphosphine Disulfides with [Au-(acac)PPh₃]. Different results are observed in the reaction of [Au(acac)PPh₃] with SPh₂PNHPPh₂S or SPh₂-PCH₂PPh₂S. In the first case treatment of the ligand with [Au(acac)PPh₃] in diethyl ether leads to the precipitation of a pale yellow solid, which has been identified as compound 3, previously synthesized by our group,[3] and has the proposed structure

3
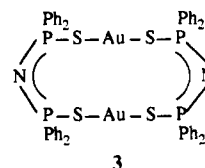
The preference of gold(I) for S- over N-donor ligands is well-known and has been found in other related systems such as mercaptopyridine derivatives.[4]

In the second case the reaction of SdppmS with equimolecular amounts of [Au(acac)PPh₃] leads to a mixture of the mono- (4) and the disubstituted complexes (5), where the coordination of gold takes place through the carbon atom. When the reaction is carried out with 2 equiv of [Au(acac)PPh₃] only complex 5 is obtained

4   5
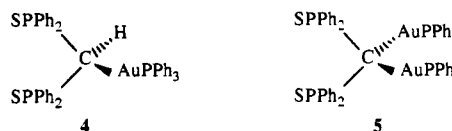
(Table I). The coordination of the AuPPh₃⁺ fragment to the carbon atom is not surprising because it is known that the Au–C bonds in ylide[5,6] and methanide[7] complexes are

(2) Usón, R.; Laguna, A.; Laguna, M.; Gimeno, M. C.; Jones, P. G.; Fittschen, C.; Sheldrick, G. M. *J. Chem. Soc., Chem. Commun.* **1986,** 509.

(3) Laguna, A.; Laguna, M.; Rojo, A.; Fraile, M. N. *J. Organomet. Chem.* **1986,** *315,* 269.

(4) Usón, R.; Laguna, A.; Laguna, M.; Jiménez, J.; Gómez, M. P.; Sainz, A.; Jones, P. G. *J. Chem. Soc., Dalton Trans.* **1990,** 3457.

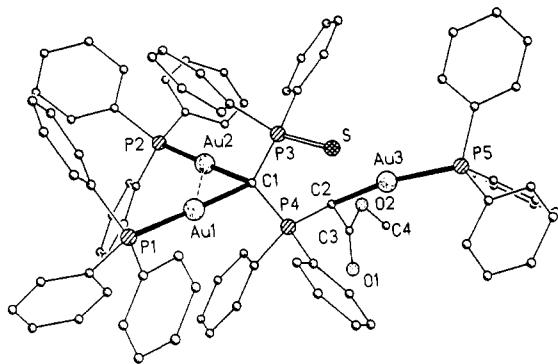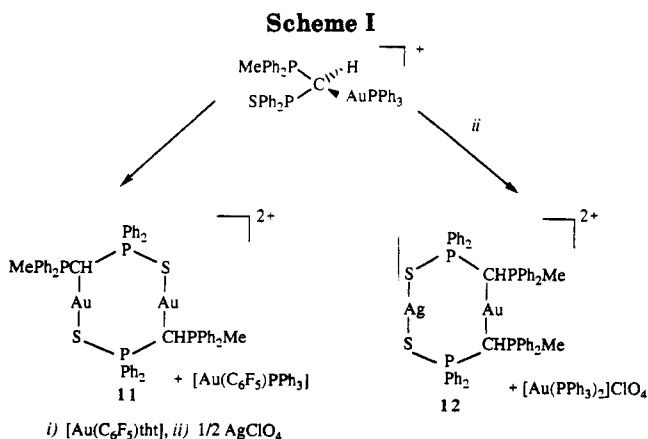(5) Schmidbaur, H. *Angew. Chem., Int. Ed. Engl.* **1983,** *22,* 907.

Figure 1. Structure of the cation of complex **10**, with the atom numbering scheme. Hydrogen atoms are omitted for clarity; atomic radii are arbitrary.

Scheme I

i) [Au(C$_6$F$_5$)tht], *ii)* 1/2 AgClO$_4$

particularly stable and that many S-donor ligands can be easily displaced in gold compounds for other types of ligands.[7]

Complex **4** has only been characterized by ^{31}P{^{1}H} NMR spectroscopy, and the spectrum is a typical AX$_2$ system with a doublet and a triplet for the two different phosphorus environments. Compound **5** is an air- and moisture-stable white solid. It is nonconducting in acetone solution. Its ^{31}P{^{1}H} NMR spectrum shows two triplets characteristic of an A$_2$X$_2$ system.

3. Reactions of Alkyl Sulfide Diphosphines with [Au(acac)PPh$_3$]. The ligands [SPPh$_2$CH$_2$PPh$_2$R]ClO$_4$ (R = Me, CH$_2$Ph, CH$_2$COOMe) react with 1 equiv of [Au-(acac)PPh$_3$] affording the monodeprotonated compound (R = Me) or a mixture of the mono- and dideprotonated complexes (R = CH$_2$Ph or CH$_2$COOMe). This difference in reactivity may be attributed to the higher acidity of the methylene protons in the latter.

[Au(acac)PPh$_3$] + [SPPh$_2$CH$_2$PPh$_2$Me]ClO$_4$ ⟶
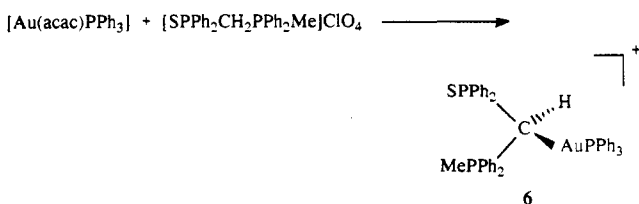
The ^{1}H NMR spectrum of **6** appears as a doublet of doublets of doublets (ddd) for the methine proton as a consequence of the coupling with three different phosphorus atoms and a doublet for the methyl group. The ^{31}P{^{1}H} NMR spectrum shows three different phosphorus environments, and two doublet of doublets for the

diphosphine atoms and a pseudotriplet (PPh$_3$), because of similar coupling constants with the other two phosphorus, are observed. The ^2J(PP) values are small (see Table II) but similar values are found in the alkyl sulfide diphosphines. Oxidation of the alkyl diphosphines [PPh$_2$-CH$_2$PPh$_2$R]ClO$_4$ to give [SPPh$_2$CH$_2$PPh$_2$R]ClO$_4$ produces a change in the ^2J(PP) from 51.8 (R = CH$_2$Ph) to 7.8 Hz.[8]

When the reaction is carried out using 2 equiv of [Au(acac)PPh$_3$], only the disubstituted complexes are obtained in all cases.

2 [Au(acac)PPh$_3$] + [SPPh$_2$CH$_2$PPh$_2$R]ClO$_4$ ⟶

R= Me (7), CH$_2$Ph (8), CH$_2$COOMe (9)
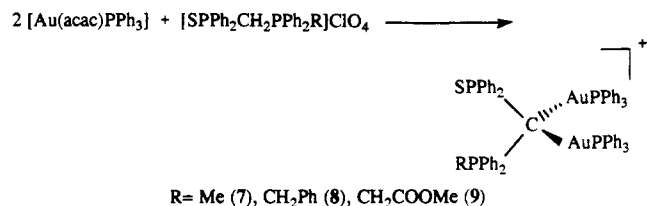
The ^{31}P{^{1}H} NMR are similar, and three different signals appear: a pseudotriplet for [(AuPPh$_3$)$_2$] appears, because these phosphorus atoms, although they are not strictly equivalent, must have very similar chemical shifts; for the other two phosphorus atoms (PPh$_2$S and PPh$_2$R) a doublet of triplets should appear, but because the coupling constants are similar and small these signals appear as multiplets. It is noticeable how the coupling constants have changed relative to the monosubstituted complexes (see Table II). We have observed this effect before in the complexes [R$_2$Au{(PPh$_2$)$_2$CH(AuPPh$_3$)}]$^+$ (^3J(PP) = 13.3 Hz) and [R$_2$Au{(PPh$_2$)$_2$C(AuPPh$_3$)$_2$}]$^+$ (^3J(PP) = 7.0 Hz)[1] and in complexes **4** and **5**. Probably, the special three-center two-electron bond which has been proposed in complexes with the unit C(AuPPh$_3$)$_2$[1,9,10] has a strong influence in decreasing these ^3J(PP) values.

We have carried out the reaction with an excess of [Au-(acac)PPh$_3$] with the ligands [SPPh$_2$CH$_2$PPh$_2$CH$_2$Ph]-ClO$_4$ and [SPPh$_2$CH$_2$PPh$_2$CH$_2$COOMe]ClO$_4$; both possess

(7) Laguna, A.; Laguna, M. *J. Organomet. Chem.* **1990**, *394*, 743.

(8) Usón, R.; Laguna, A.; Laguna, M.; Lázaro, I.; Jones, P. G.; Fittschen, C. *J. Chem. Soc., Dalton Trans.* **1988**, 2323.

(9) Vicente, J.; Chicote, M. T.; Cayuelas, J. A.; Fernández-Baeza, J.; Jones, P. G.; Sheldrick, G. M.; Espinet, P. *J. Chem. Soc., Dalton Trans.* **1985**, 1163.

(10) Vicente, J.; Chicote, M. T.; Lagunas, M. C.; Jones, P. G. *J. Chem. Soc., Dalton Trans.* **1991**, 2579.

(11) Usón, R.; Laguna, A.; Laguna, M.; Lázaro, I.; Jones, P. G. *Organometallics* **1987**, *6*, 2326.

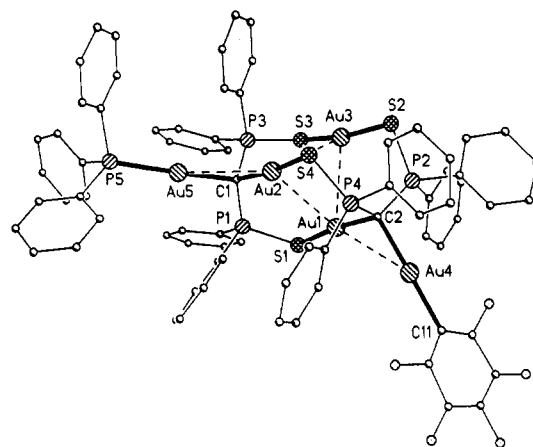(12) Usón, R.; Laguna, A.; Laguna, M.; Usón, A.; Gimeno, M. C. *Organometallics* **1987**, *6*, 682.

Figure 2. Molecular structure of complex **13** showing the labeling scheme. Hydrogen atoms are omitted for clarity; atomic radii are arbitrary.

Scheme II

i) Ph₂PXHPPh₂, ii) SPPh₂NHPPh₂, iii) SPPh₂CH₂PPh₂S, iv) 2 [Au(C₆F₅)tht], v) [SPPh₂CH₂PPh₂Me]⁺,
vi) 1/2 AgClO₄, vii) 1/2 [SPPh₂CH₂PPh₂R]⁺, viii) 1/3 [SPPh₂CH₂PPh₂CH₂COOMe]⁺
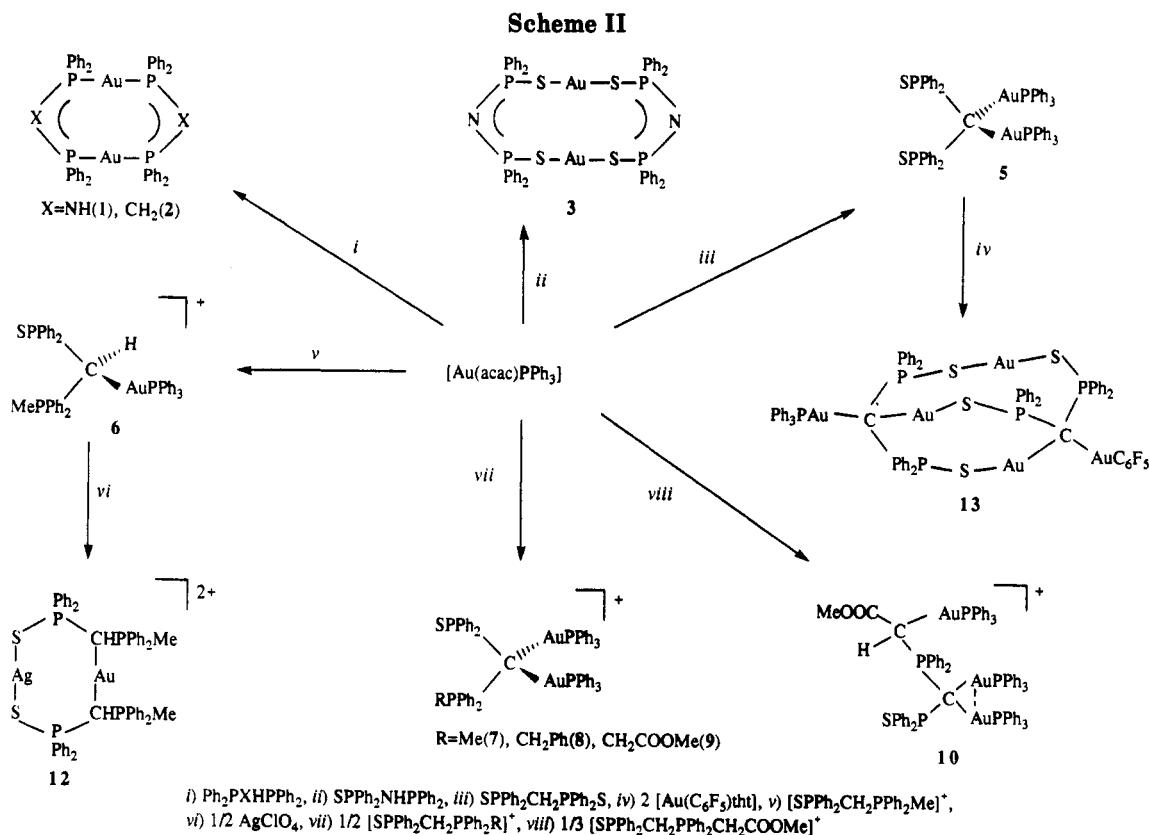
another methylene group that can be deprotonated. The reaction only takes place with R = CH₂COOMe, leading to a complex where the ligand has been deprotonated three times.

[SPPh₂CH₂PPh₂CH₂COOMe]⁺ + 4 [Au(acac)PPh₃] ⟶

10
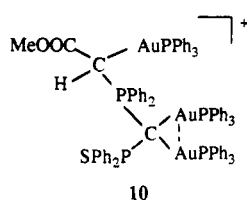
The ¹H NMR spectrum shows resonances for the Me group (singlet) and a multiplet for the methine proton. The ³¹P{¹H} NMR spectrum shows four different phosphorus environments, all appearing as broad signals even at low temperature (–60 °C).

Complexes 6–10 are air- and moisture-stable solids; molar conductivities in acetone correspond to 1:1 electrolytes. The IR spectra show bands due to the ClO₄⁻ anion (T_d), diphosphine ligand, and particularly the band P=S which appears in the area of 600–610 cm⁻¹. In the complexes with R = CH₂COOMe a change in the ν(C=O) stretching frequency is observed; for complex 9, where the substitution of the hydrogen atoms takes place at the methylene groups between both phosphorus atoms, the ν(C=O) is very similar to the free ligand (1738 vs 1736). However in complex 10 the ν(C=O) frequency is lower (1700 cm⁻¹) as a consequence of the substitution of hydrogen by a less electronegative group. The AuPPh₃⁺ group causes appreciable donation of electron density into the CO antibonding orbitals.

The structure of complex 10 was confirmed by X-ray diffraction analysis (Figure 1). It contains a triangular unit Au₂C of the type that we have already observed and

interpreted in terms of a closed three-center, two-electron bond[1,9,10] on the basis of the following features: (i) the Au(1)–Au(2) bond length is 2.908(1) Å with a very narrow Au(1)–C(1)–Au(2) angle of 86.6(4)°, (ii) the P–C bonds are 1.802(10) [P(3)–C(1)] and 1.742(10) [P(4)–C(1)] Å, which are shorter than normal P–C bonds (ca. 1.845 Å), and (iii) the wide angle opposite the Au₂C unit, P(3)–C(1)–P(4), is 117.1(6)°. The geometry around the gold atoms is linear for Au(1) and Au(2) with angles P(2)–Au(2)–C(1) of 178.3(3) and P(1)–Au(1)–C(1) of 178.1(3)°, while the geometry around Au(3) is distorted from linearity, C(5)–Au(3)–P(2) 159.4(3)°, possibly arising from a short contact with the sulfur atom Au(3)···S of 3.057 Å. The Au–C bonds Au(2)–C(1) (2.117(11) Å) and Au(1)–C(1) (2.121(9) Å), are similar to those found in other methanide complexes, whereas Au(3)–C(2) (2.138(11) Å) is longer than previously observed values,[11] although the difference may not be significant.

We have studied the reactivity of some of these derivatives toward gold or silver complexes that possess an easily replaceable ligand. The reaction of [SPPh₂CH-(AuPPh₃)PPh₂Me]ClO₄ with equimolecular amounts of [Au(C₆F₅)tht] or with AgClO₄ (molar ratio 2:1) takes place with formation of [Au(C₆F₅)PPh₃] or [Au(PPh₃)₂]ClO₄, and the resulting fragment dimerizes to give the dinuclear complexes with two gold (11) or one gold and one silver atom (12) bridged by the deprotonated ligand (see Scheme I). These type of reactions, in which ligands are transferred, have been observed and studied previously by our group.[12]

Complex 11 has been described by us before by another procedure.[13] However compound 12 could not be prepared previously. It is a white air- and moisture-stable solid and it behaves in acetone solution as a 1:2 electrolyte.

(13) Usón, R.; Laguna, A.; Laguna, M.; Fraile, M. N.; Lázaro, I.; Gimeno, M. C.; Jones, P. G.; Reihs, C.; Sheldrick, G. M. *J. Chem. Soc., Dalton Trans.* 1990, 333.

Table III. Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Coefficients (Å² × 10⁴) for Complex 10

	x	y	z	U(eq)		x	y	z	U(eq)
Au(1)	2622.4(3)	5589.8(2)	3605.6(3)	278(1)	C(72)	2427(5)	1121(4)	4432(4)	468(32)
Au(2)	2610.5(3)	5192.7(3)	1964.8(3)	306(2)	C(73)	2279	996	5176	586(38)
Au(3)	2704.8(3)	2069.3(3)	2776.6(3)	375(2)	C(74)	2790	411	5518	527(35)
P(1)	2552(2)	6775(2)	4384(2)	305(10)	C(75)	3448	-49	5116	517(35)
P(2)	2508(2)	5924(2)	973(2)	373(11)	C(76)	3596	76	4372	412(30)
P(3)	3876(2)	4058(2)	2986(2)	258(9)	C(71)	3086	661	4030	321(26)
P(4)	1793(2)	3850(2)	2921(2)	276(9)	C(82)	2282(6)	-648(5)	2752(4)	489(33)
P(5)	3223(2)	849(2)	3055(2)	342(10)	C(83)	1717	-1215	2295	552(36)
S	4010(2)	3286(2)	3743(2)	323(9)	C(84)	1420	-1076	1560	598(39)
C(1)	2735(7)	4487(6)	2877(6)	223(22)	C(85)	1688	-371	1283	678(43)
C(2)	1869(7)	2942(6)	2265(6)	301(25)	C(86)	2253	196	1741	564(37)
C(3)	1051(9)	2528(7)	1942(7)	427(30)	C(81)	2550	57	2476	376(28)
C(4)	482(11)	1551(10)	906(9)	719(45)	C(92)	4721(5)	-161(4)	2666(5)	416(30)
O(1)	333(6)	2504(5)	2215(5)	558(24)	C(93)	5662	-316	2587	477(33)
O(2)	1208(6)	2129(5)	1243(5)	592(25)	C(94)	6303	317	2726	529(35)
C(12)	3054(5)	6087(5)	5684(4)	509(34)	C(95)	6004	1106	2944	535(35)
C(13)	2965	5914	6424	501(34)	C(96)	5063	1261	3022	468(32)
C(14)	2270	6285	6852	558(37)	C(91)	4422	627	2883	349(27)
C(15)	1663	6828	6541	698(44)	C(102)	509(5)	4478(5)	1927(4)	440(31)
C(16)	1752	7001	5802	579(38)	C(103)	-258	4941	1734	570(37)
C(11)	2448	6630	5373	317(26)	C(104)	-776	5339	2302	584(38)
C(22)	1641(4)	8262(4)	4425(4)	444(31)	C(105)	-528	5275	3063	598(39)
C(23)	909	8767	4243	467(32)	C(106)	238	4812	3257	451(32)
C(24)	152	8454	3772	556(37)	C(101)	756	4413	2688	321(26)
C(25)	127	7634	3482	437(31)	C(112)	2099(5)	4006(4)	4508(4)	405(30)
C(26)	860	7129	3664	360(28)	C(113)	1958	3793	5227	475(33)
C(21)	1617	7443	4136	343(27)	C(114)	1344	3169	5302	549(36)
C(32)	3798(5)	7507(4)	3597(3)	343(27)	C(115)	870	2757	4660	499(34)
C(33)	4595	7942	3498	498(34)	C(116)	1011	2970	3942	453(32)
C(34)	5185	8229	4125	548(36)	C(111)	1626	3594	3866	320(26)
C(35)	4980	8081	4851	591(38)	C(122)	4986(5)	5340(4)	2676(3)	356(27)
C(36)	4183	7647	4950	417(30)	C(123)	5572	6006	2883	429(31)
C(31)	3592	7359	4323	305(25)	C(124)	5822	6253	3648	369(28)
C(42)	2364(6)	4538(5)	-61(4)	527(35)	C(125)	5486	5834	4206	377(28)
C(43)	2480	4061	-752	554(36)	C(126)	4900	5168	3999	299(25)
C(44)	2949	4372	-1313	634(41)	C(121)	4651	4921	3233	253(23)
C(45)	3302	5159	-1184	664(42)	C(132)	5150(5)	3134(5)	2189(4)	508(34)
C(46)	3187	5636	-493	581(38)	C(133)	5565	2757	1551	575(37)
C(41)	2718	5325	69	439(31)	C(134)	5158	2812	826	515(35)
C(52)	4287(6)	6553(4)	1167(5)	596(38)	C(135)	4336	3243	739	623(40)
C(53)	4954	7167	1259	674(42)	C(136)	3921	3620	1377	457(32)
C(54)	4685	7970	1237	643(41)	C(131)	4328	3566	2102	312(26)
C(55)	3748	8159	1123	659(42)	Cl	7573(2)	7814(2)	2499(2)	496(12)
C(56)	3081	7546	1031	549(36)	O(3)	7616(16)	7784(15)	1731(15)	2296(102)
C(51)	3351	6743	1053	415(30)	O(4)	7961(10)	7094(9)	2702(9)	1242(49)
C(62)	1004(6)	6443(5)	100(4)	535(36)	O(5)	7965(9)	8521(8)	2871(8)	1007(40)
C(63)	138	6805	2	666(42)	O(6)	6656(12)	7786(10)	2558(10)	1453(58)
C(64)	-345	7095	634	602(39)	C(5)	-96(20)	700(17)	3289(18)	1678(109)
C(65)	37	7023	1364	602(39)	C(6)	-646(18)	250(16)	2464(16)	1468(93)
C(66)	903	6661	1461	494(34)	C(7)	-1367(19)	868(16)	2043(16)	1520(97)
C(61)	1386	6370	829	369(28)	C(8)	-2233(32)	1173(28)	1086(29)	2898(216)

The reaction pathway could be first the coordination of the silver to two ligand complexes through the sulfur atoms; then elimination of the fragment AuPPh₃⁺ and PPh₃ forms [Au(PPh₃)₂]⁺ and the unsaturated gold atom is coordinated to the methanide carbon. Two different structures are possible for this complex, namely silver coordinated to the two sulfur atoms (head-to-head) or to one sulfur and one carbon atom (head-to-tail). NMR spectroscopy of ¹H and ³¹P{¹H} does not distinguish the structures, since both should possess the same NMR pattern. The ¹H NMR spectrum of 12 shows, besides the resonances for the phenyl groups, a doublet for the methyl group and a doublet of doublets for the methine proton. The ³¹P{¹H} NMR spectrum appears as a typical AX system with two doublets. The ¹³C{¹H} NMR spectrum shows a pseudo-triplet for the central carbon and a doublet for the methyl group. The facts that silver prefers coordination to S-over C-donor ligands and that in the ¹³C{¹H} NMR spectrum the methine carbons appear as equivalent lead us to propose the structure shown in Scheme I as the most probable.

We have also studied the reaction of [(SPPh₂)₂C-(AuPPh₃)₂] with 2 equiv of [Au(C₆F₅)tht]. One would expect that the disulfide complex replaces the tht ligand, affording the tetranuclear complex. However the result is very different and the pentanuclear complex [Au₅-(C₆F₅){(SPPh₂)₂C}₂PPh₃] is obtained (Scheme II). The yield based on gold is high; therefore the side products are formed in very low quantity and the only one that has been identified is [Au(C₆F₅)PPh₃].

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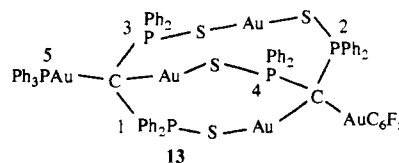
Its IR spectrum shows, besides bands due to the diphosphine ligand, three absorptions at 1495 (vs), 998 (m), and 795 (m) cm⁻¹, characteristic of pentafluorophenyl

Table IV. Selected Bond Lengths (Å) and Angles (deg) for Complex 10

Au(1)–Au(2)	2.908(1)	Au(1)–P(1)	2.268(3)
Au(1)–C(1)	2.121(9)	Au(2)–P(2)	2.263(3)
Au(2)–C(1)	2.117(11)	Au(3)–P(5)	2.263(3)
Au(3)–C(2)	2.138(11)	P(1)–C(11)	1.821(9)
P(1)–C(21)	1.814(7)	P(1)–C(31)	1.811(8)
P(2)–C(41)	1.824(8)	P(2)–C(51)	1.818(8)
P(2)–C(61)	1.797(9)	P(3)–S	1.974(4)
P(3)–C(1)	1.802(10)	P(3)–C(121)	1.817(7)
P(3)–C(131)	1.836(7)	P(4)–C(1)	1.742(10)
P(4)–C(2)	1.797(10)	P(4)–C(101)	1.816(8)
P(4)–C(111)	1.816(8)	P(5)–C(71)	1.823(9)
P(5)–C(81)	1.811(9)	P(5)–C(91)	1.807(7)
C(2)–C(3)	1.421(16)	C(3)–O(1)	1.177(16)
C(3)–O(2)	1.365(16)	C(4)–O(2)	1.472(18)
Au(2)–Au(1)–P(1)	133.2(1)	Au(2)–Au(1)–C(1)	46.6(3)
P(1)–Au(1)–C(1)	178.1(3)	Au(1)–Au(2)–P(2)	134.5(1)
Au(1)–Au(2)–C(1)	46.7(2)	P(2)–Au(2)–C(1)	178.3(3)
P(5)–Au(3)–C(2)	159.4(3)	Au(1)–P(1)–C(11)	112.9(3)
Au(1)–P(1)–C(21)	115.0(3)	C(11)–P(1)–C(21)	106.7(4)
Au(1)–P(1)–C(31)	109.2(2)	C(11)–P(1)–C(31)	108.5(3)
C(21)–P(1)–C(31)	104.0(3)	Au(2)–P(2)–C(41)	113.2(3)
Au(2)–P(2)–C(51)	113.8(3)	C(41)–P(2)–C(51)	104.0(4)
Au(2)–P(2)–C(61)	113.2(3)	C(41)–P(2)–C(61)	105.2(4)
C(51)–P(2)–C(61)	106.7(4)	S–P(3)–C(1)	114.8(4)
S–P(3)–C(121)	111.6(2)	C(1)–P(3)–C(121)	105.1(4)
S–P(3)–C(131)	107.6(3)	C(1)–P(3)–C(131)	114.8(4)
C(121)–P(3)–C(131)	102.3(3)	C(1)–P(4)–C(2)	111.0(5)
C(1)–P(4)–C(101)	106.9(4)	C(2)–P(4)–C(101)	110.4(4)
C(1)–P(4)–C(111)	114.3(4)	C(2)–P(4)–C(111)	110.0(4)
C(101)–P(4)–C(111)	103.9(3)	Au(3)–P(5)–C(71)	114.9(3)
Au(3)–P(5)–C(81)	109.2(3)	C(71)–P(5)–C(81)	104.6(4)
Au(3)–P(5)–C(91)	115.8(3)	C(71)–P(5)–C(91)	105.7(4)
C(81)–P(5)–C(91)	105.8(4)	Au(1)–C(1)–Au(2)	86.6(4)
Au(1)–C(1)–P(3)	111.2(5)	Au(2)–C(1)–P(3)	112.2(5)
Au(1)–C(1)–P(4)	111.6(5)	Au(2)–C(1)–P(4)	114.1(5)
P(3)–C(1)–P(4)	117.1(6)	Au(3)–C(2)–P(4)	109.8(5)
Au(3)–C(2)–C(3)	106.3(8)	P(4)–C(2)–C(3)	120.4(8)
C(2)–C(3)–O(1)	127.5(12)	C(2)–C(3)–O(2)	110.0(10)
O(1)–C(3)–O(2)	122.6(11)	C(3)–O(2)–C(4)	115.7(11)

groups linked to gold(I).[14] In the ¹⁹F NMR spectrum appear the three typical signals for a pentafluorophenyl ring. The ³¹P{¹H} NMR spectrum shows five different phosphorus environments. The assignment is as follows: two doublets of doublets at δ 43.7 and 45.1 correspond to P(1) and P(3) (phosphorus numbering, see Figure 2) with ²J(P(1)P(3)) 13.8 and ³J(P(1)P(5)) = ³J(P(3)P(5)) 4.4 Hz, a pseudotriplet at δ 44.5 for P(5), two doublets at δ 43.0 and 35.9 for P(2) and P(4), ²J(P(2)P(4)) 4.5 Hz. It is difficult to distinguish between P(1)–P(3) and P(2)–P(4) because both pairs have a similar chemical environment.

The structure of complex 13 was confirmed by X-ray diffraction analysis (Figure 2), although the poor precision (due to extreme instability of the crystals because of solvent loss) precludes detailed discussion of molecular dimensions. The molecule can be regarded as a cluster core of three gold atoms with bond lengths Au(1)–Au(2) 2.989(6), Au(1)–Au(3) 3.226(7), and Au(2)–Au(3) 3.182(7) Å bridged by two (Ph₂PS)₂C²⁻ ligands, although these distances are longer than those found in gold clusters of mean oxidation state <1 that possess a central gold atom.[15,16] There also are some interactions with the other gold atoms, namely Au(5)–Au(2) 3.361(8) and Au(1)–Au(4) 3.335(7) Å. The coordination around all the gold(I) atoms is slightly distorted from linearity, with angles lying in the range

167.2(5)–174.2(15)°. The Au–C and Au–S bond lengths are similar to those found in other related complexes.

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 and Λ_M is given in Ω⁻¹ cm² mol⁻¹. C and H analyses were carried out with a Perkin-Elmer 240C microanalyzer. NMR spectra were recorded on Varian XL200 and Varian XL300 Unity spectrometers in CDCl₃. Chemical shifts are cited relative to SiMe₄ (¹H), 85% H₃PO₄ (external, ³¹P), and CFCl₃ (external, ¹⁹F). The yields, analysis, and conductivities for the new complexes are listed in Table I. All reactions were carried out at room temperature.

[Au(PPh₂)₂X]₂ [X = N (1), CH (2)]. To a solution of dppa[17] (0.078 g, 0.2 mmol) or dppm (0.077 g, 0.2 mmol) in diethyl ether (20 mL) was added [Au(acac)PPh₃][18] (0.111 g, 0.2 mmol) under N₂. Although a pale yellow (1) or yellow (2) precipitate appeared immediately, the reaction was left to complete for 1 h. The solid was filtered off and washed with 2 × 5 mL of diethyl ether, giving complexes 1 or 2.

[Au(SPPh₂)₂N]₂ (3). The same procedure as above was used, starting from SdppaS[19] (0.090 g, 0.2 mmol) and [Au(acac)PPh₃] (0.111 g, 0.2 mmol).

[(SPPh₂)₂C(AuPPh₃)₂] (5). To a solution of SdppmS[20] (0.089 g, 0.2 mmol) in dichloromethane (30 mL) was added [Au(acac)-PPh₃] (0.222 g, 0.4 mmol). After 1 h the solvent was evaporated to ca. 5 mL and addition of 15 mL of n-hexane gave complex 5 as a white solid.

[SPPh₂CH(AuPPh₃)PPh₂Me]ClO₄ (6). To a solution of [SPPh₂CH₂PPh₂Me]ClO₄[8] (0.053 g, 0.1 mmol) in dichloromethane (30 mL) was added [Au(acac)PPh₃] (0.056 g, 0.1 mmol). The solution was stirred for 2 h and then concentrated to ca. 5 mL. Addition of diethyl ether completed the precipitation of complex 6 as a white solid. ¹H NMR: δ 2.77 [d, Me, ²J(PH) 13.24 Hz], 4.69 [ddd, CH, J(PH) 14.46, 10.69, and 7.68 Hz], 7–8 (m, Ph).

[SPPh₂C(AuPPh₃)₂PPh₂R]ClO₄ [R = Me (7), CH₂Ph (8), CH₂COOMe (9)]. To a dichloromethane (30 mL) solution of [SPPh₂CH₂PPh₂Me]ClO₄ (0.053 g, 0.1 mmol), [SPPh₂CH₂PPh₂-CH₂Ph]ClO₄[8] (0.061 g, 0.1 mmol), or [SPPh₂CH₂PPh₂CH₂-COOMe]ClO₄[11] (0.059 g, 0.1 mmol) was added [Au(acac)PPh₃] (0.111 g, 0.2 mmol). The mixture was stirred for 3 h (7) or 2 h (8, 9), and then the solution was concentrated to ca. 10 mL. Addition of diethyl ether (15 mL) gave complexes 7, 8, or 9 as white solids. ¹H NMR: (7) δ 2.53 [d, Me, ²J(PH) 12.40 Hz], 7–8 (m, Ph); (8) δ 4.76 [d, CH₂Ph, ²J(PH) 14.11 Hz], 7–8 (m, Ph); (9) δ 3.13 (s, Me), 4.70 [d, CH₂, ²J(PH) 15.14 Hz], 7–8 (m, Ph).

[SPPh₂C(AuPPh₃)₂PPh₂CH(AuPPh₃)COOMe]ClO₄ (10). To a solution of [SPPh₂CH₂PPh₂CH₂COOMe]ClO₄ (0.059 g, 0.1 mmol) in dichloromethane (30 mL) was added [Au(acac)PPh₃] (0.279 g, 0.5 mmol) and stirred for 1 h. The solvent was evaporated to ca. 5 mL and addition of 15 mL of diethyl ether led to complex 10 as a white solid. ¹H NMR: δ 3.38 (s, Me), 3.85 (m, CH), 7–8 (m, Ph).

Crystal Structure Determination of Compound 10. Crystal data: C₈₂H₆₉Au₃ClO₆P₅S; M_r 1963.6, triclinic, space group P1̄; a = 14.448(4), b = 16.645(4), c = 17.780(5) Å; α = 97.26(2), β = 93.76(2), γ = 89.71(2)°; V = 4232.6 Å³; Z = 2; D_{calcd} = 1.54 Mg m⁻³; F(000) 1908; λ(Mo Kα) = 0.710 73 Å; μ = 5.4 mm⁻¹; T = –95 °C.

Data Collection and Reduction. A colorless prism 0.4 × 0.3 × 0.2 mm, obtained from liquid diffusion of petroleum ether into a CH₂Cl₂ solution, was mounted on a glass fiber in inert oil. A total of 19 262 intensities were measured on a Siemens R3 diffractometer with an LT-2 low temperature attachment using

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Table V. Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å² × 10³) for Complex 13

	x	y	z	U(eq)		x	y	z	U(eq)
Au(1)	2280(2)	6701.9(11)	3010.0(9)	59.0(12)	C(225)	5556(20)	8419(18)	3173(17)	85(12)
Au(2)	2526(2)	5425.8(11)	2044.2(10)	62.4(12)	C(226)	4979(25)	8204(18)	2621(13)	74(11)
Au(3)	4710(2)	6175.9(12)	2152.8(11)	70.6(12)	C(311)	5282(31)	3601(19)	3158(19)	93(13)
Au(4)	764(2)	8395.7(13)	2771.2(12)	83.3(14)	C(312)	5887(33)	3685(18)	3747(21)	103(13)
Au(5)	2505(2)	3658(2)	2544.9(15)	112(2)	C(313)	6321(30)	3073(24)	4164(17)	111(14)
P(1)	2520(10)	4888(7)	3639(6)	52(7)	C(314)	6150(32)	2375(20)	3993(20)	110(14)
P(2)	3155(9)	7860(7)	1968(6)	56(7)	C(315)	5545(34)	2290(18)	3405(22)	114(14)
P(3)	4653(10)	4411(7)	2654(6)	54(8)	C(316)	5111(31)	2903(24)	2988(17)	106(13)
P(4)	1130(11)	7168(8)	1589(7)	70(8)	C(321)	5015(49)	4172(26)	1731(20)	132(16)
P(5)	2064(18)	2513(12)	2333(11)	126(16)	C(322)	4213(33)	4104(26)	1245(29)	137(16)
S(1)	2721(11)	5909(7)	3969(6)	65(10)	C(323)	4561(43)	3970(26)	538(26)	151(17)
S(2)	4323(12)	7164(8)	1368(7)	83(9)	C(324)	5711(49)	3904(26)	316(21)	149(17)
S(3)	5504(11)	5227(8)	2873(8)	84(9)	C(325)	6513(33)	3973(27)	802(31)	163(18)
S(4)	1907(12)	6220(8)	1107(7)	76(10)	C(326)	6165(43)	4107(27)	1510(27)	160(17)
C(1)	3129(32)	4610(21)	2807(19)	42(10)	C(411)	-275(24)	7061(20)	1946(20)	87(12)
C(2)	1833(38)	7531(26)	2225(23)	63(13)	C(412)	-1030(32)	6958(21)	1443(14)	101(13)
C(11)	-185(44)	9229(34)	3397(29)	148(17)	C(413)	-2129(29)	6853(21)	1657(18)	103(13)
C(12)	-1261(52)	9234(27)	3541(25)	161(16)	C(414)	-2473(24)	6851(21)	2375(20)	98(13)
C(13)	-2007(35)	9775(26)	4006(23)	168(16)	C(415)	-1718(31)	6954(21)	2878(14)	98(13)
C(14)	-1435(35)	10259(28)	4242(26)	170(16)	C(416)	-619(28)	7059(20)	2664(17)	96(13)
C(15)	-340(36)	10306(26)	4143(23)	167(16)	C(421)	858(31)	7855(19)	819(17)	86(12)
C(16)	286(44)	9716(31)	3679(26)	150(16)	C(422)	156(30)	8537(21)	933(15)	94(13)
F(1)	-1864(41)	8744(23)	3304(21)	191(18)	C(423)	-75(29)	9038(17)	369(21)	96(13)
F(2)	-3122(36)	9714(26)	4125(23)	225(21)	C(424)	396(33)	8859(20)	-308(17)	107(13)
F(3)	-2065(35)	10774(27)	4675(25)	198(18)	C(425)	1098(32)	8177(23)	-422(15)	111(14)
F(4)	259(39)	10784(22)	4406(21)	198(18)	C(426)	1329(29)	7675(17)	142(21)	106(13)
F(5)	1394(38)	9795(25)	3562(22)	192(18)	C(511)	2570(48)	2258(27)	1380(19)	134(16)
C(111)	3106(29)	4279(20)	4368(16)	79(12)	C(512)	1790(31)	2209(26)	874(29)	133(16)
C(112)	3709(29)	4538(16)	4882(19)	82(12)	C(513)	2163(40)	2118(26)	165(24)	127(15)
C(113)	4164(29)	4065(23)	5425(17)	102(13)	C(514)	3317(46)	2076(27)	-39(19)	127(15)
C(114)	4015(33)	3334(21)	5454(18)	116(14)	C(515)	4096(30)	2125(27)	467(30)	146(16)
C(115)	3412(35)	3075(16)	4941(23)	126(15)	C(516)	3723(42)	2216(28)	1177(26)	141(16)
C(116)	2958(31)	3548(22)	4398(19)	118(14)	C(521)	2750(43)	1726(27)	2931(28)	135(16)
C(121)	1008(26)	4823(23)	3696(23)	95(13)	C(522)	3367(45)	1057(34)	2689(20)	148(17)
C(122)	511(38)	4509(23)	4290(19)	130(15)	C(523)	3733(40)	486(24)	3171(33)	141(17)
C(123)	-649(40)	4475(23)	4320(20)	143(16)	C(524)	3483(44)	584(28)	3894(29)	149(17)
C(124)	-1311(27)	4755(25)	3757(26)	129(15)	C(525)	2866(46)	1253(35)	4136(20)	149(17)
C(125)	-813(35)	5069(23)	3164(21)	123(15)	C(526)	2499(40)	1824(24)	3654(32)	141(17)
C(126)	346(37)	5104(22)	3134(19)	112(14)	C(531)	623(39)	2412(43)	2447(28)	149(18)
C(211)	2879(33)	8722(19)	1442(21)	97(13)	C(532)	300(55)	1729(31)	2576(28)	159(18)
C(212)	2439(32)	9391(24)	1762(16)	102(13)	C(533)	-852(66)	1676(30)	2622(29)	171(19)
C(213)	2272(33)	10042(19)	1354(23)	113(14)	C(534)	-1683(38)	2306(46)	2540(30)	177(19)
C(214)	2545(36)	10024(21)	627(22)	124(15)	C(535)	-1361(57)	2990(33)	2412(30)	188(20)
C(215)	2984(35)	9355(27)	308(16)	130(15)	C(536)	-208(69)	3042(28)	2365(29)	176(19)
C(216)	3151(33)	8704(20)	716(22)	117(14)	Cl(1)	764(34)	2591(22)	5365(21)	285(16)
C(221)	3850(25)	8108(17)	2739(14)	63(10)	Cl(2)	-889(49)	2508(31)	4536(30)	400(23)
C(222)	3298(20)	8227(18)	3406(17)	75(11)	C(100)	-509	2368	5292	344(3)
C(223)	3874(27)	8443(19)	3958(13)	91(12)	Cl(3)	3365	650	8584	419(3)
C(224)	5003(27)	8539(19)	3840(15)	89(12)	Cl(4)	3337	9348	8099	568(3)

monochromated Mo Kα radiation ($2\theta_{max}$ 50°), scan type ω. An absorption correction based on ψ-scans was applied, with transmission factors 0.69–0.97. Merging equivalents gave 14 894 unique reflections (R_{int} 0.025), of which 9564 with $F > 4\sigma(F)$ were used for all calculations (program system Siemens SHELXTL-PLUS).[21] Cell constants were refined from setting angles of 50 reflections in the range $2\theta = 20$–23°.

Structure Solution and Refinement. The structure was solved by the heavy atom method and subjected to full-matrix least-squares refinement on F; Au, P, S, and Cl atoms were refined anisotropically, phenyl rings as idealized hexagons with C–C 1.395 Å and all angles 120°, and H atoms were included using a riding model C–H 0.96 Å. An ill defined region of residual electron density was interpreted as disordered pentane (for this reason M_r and D_x—see above—were calculated without solvent). Refinement proceeded to R 0.049 and R_w 0.055 for 303 parameters. The weighting scheme was $w^{-1} = \sigma^2(F) + 0.0005F^2$; $S = 1.3$; maximum Δ/σ 0.74; maximum $\Delta\rho$ 1.66 e Å⁻³.

Atomic positional parameters for **10** are listed in Table III, and Table IV contains selected bond lengths and angles.

[**Au₂(SPPh₂CHPPh₂Me)₂](ClO₄)₂ (11).** To a solution of complex **5** (0.099 g, 0.1 mmol) in dichloromethane (30 mL) was

added [Au(C₆F₅)tht][22] (0.042 g, 0.1 mmol) and the reaction stirred for 1 h. Concentration of the solvent (10 mL) and addition of 20 mL of diethyl ether gave complex **11** as a white solid.

[**AuAg(SPPh₂CHPPh₂Me)₂](ClO₄)₂ (12).** To a solution of complex **5** (0.197 g, 0.2 mmol) in dichloromethane (30 mL) was added AgClO₄ (0.020 g, 0.1 mmol). After 2 h the solvent was evaporated to ca. 15 mL and addition of diethyl ether (25 mL) afforded complex **12** as a white solid. ¹H NMR: δ 1.71 [d, Me, ^2J(PH) 13.19 Hz], 4.38 [dd, CH, ^2J(PH) 16.78 and 11.4 Hz], 7–7.6 (m, Ph). ¹³C{¹H} NMR: δ 12.1 [d, Me, ^1J(PC) 60.9 Hz], 27.0 ["t", CH, ^1J(PC) 41.2 Hz], 128–136 (Ph).

[**Au₅(C₆F₅){(SPPh₂)₂C}₂PPh₃] (13).** To a solution in dichloromethane (30 mL) of complex **4** (0.136, 0.1 mmol) was added [Au(C₆F₅)tht] (0.084 g, 0.2 mmol) and the mixture stirred for 1 h. The solution was filtered through Celite to remove metallic gold. The Celite was washed with 2 × 5 mL of dichloromethane, and the pale yellow filtrates were combined. The solvent was then removed in vacuo, yielding a white solid. Recrystallization of the solid from dichloromethane/petroleum ether gave complex **13**. ¹⁹F NMR: δ –115.5 (m, ortho-F), –164.2 (m, meta-F), and –162.8 [t, para-F, ^3J(FF) 19.5 Hz].

(21) Sheldrick, G. M. SHELXTL-PLUS. University of Göttingen, 1990.

(22) Usón, R.; Laguna, A.; Vicente, J. *J. Chem. Soc., Chem. Commun.* **1976**, 353.

Table VI. Selected Bond Lengths (Å) and Angles (deg) for Complex 13

Au(1)–C(2)	2.108(46)	Au(1)–S(1)	2.308(13)
Au(1)–Au(2)	2.989(6)	Au(1)–Au(3)	3.226(7)
Au(1)–Au(4)	3.335(7)	Au(2)–C(1)	2.101(38)
Au(2)–S(4)	2.321(14)	Au(2)–Au(3)	3.182(7)
Au(2)–Au(5)	3.361(8)	Au(3)–S(3)	2.274(16)
Au(3)–S(2)	2.301(17)	Au(4)–C(11)	2.086(82)
Au(4)–C(2)	2.104(45)	Au(5)–C(1)	2.113(38)
Au(5)–P(5)	2.319(21)		

C(2)–Au(1)–S(1)	172.9(12)	C(2)–Au(1)–Au(2)	96.1(12)
S(1)–Au(1)–Au(2)	90.9(3)	C(2)–Au(1)–Au(3)	89.8(12)
S(1)–Au(1)–Au(3)	94.4(4)	Au(2)–Au(1)–Au(3)	61.44(11)
C(2)–Au(1)–Au(4)	37.6(12)	S(1)–Au(1)–Au(4)	135.8(3)
Au(2)–Au(1)–Au(4)	127.47(12)	Au(3)–Au(1)–Au(4)	121.36(13)
C(1)–Au(2)–S(4)	173.4(11)	C(1)–Au(2)–Au(1)	95.9(10)
S(4)–Au(2)–Au(1)	90.6(4)	C(1)–Au(2)–Au(3)	91.2(10)
S(4)–Au(2)–Au(3)	91.0(3)	Au(1)–Au(2)–Au(3)	62.95(12)
C(1)–Au(2)–Au(5)	37.2(10)	S(4)–Au(2)–Au(5)	137.6(3)
Au(1)–Au(2)–Au(5)	126.12(12)	Au(3)–Au(2)–Au(5)	122.58(13)
S(3)–Au(3)–S(2)	167.2(5)	S(3)–Au(3)–Au(2)	90.1(4)
S(2)–Au(3)–Au(2)	101.5(4)	S(3)–Au(3)–Au(1)	100.5(4)
S(2)–Au(3)–Au(1)	90.5(3)	Au(2)–Au(3)–Au(1)	55.62(11)
C(11)–Au(4)–C(2)	174.2(15)	C(11)–Au(4)–Au(1)	137.7(9)
C(2)–Au(4)–Au(1)	37.7(12)	C(1)–Au(5)–P(5)	171.4(12)
C(1)–Au(5)–Au(2)	37.0(10)	P(5)–Au(5)–Au(2)	150.3(5)

Crystal Structure Determination of Compound 13. Crystal data: $C_{76}H_{59}Au_5Cl_4F_5P_5S_4$; M_r = 2476.95, triclinic, space group $P\bar{1}$; a = 11.900(11), b = 18.425(27), c = 18.877(17) Å; α = 87.85-(10), β = 86.34(8), γ = 79.38(10)°; V = 4058.3 Å³; Z = 2; D_{calcd} = 2.03 Mg m⁻³; $F(000)$ 2324; λ(Mo Kα) = 0.710 73 Å; μ = 9.4 mm⁻¹; T = –95 °C.

Data Collection and Reduction. Single crystals of compound 13 in the form of colorless tablets were obtained by liquid diffusion of hexane into a dichloromethane solution. Once formed, the crystals lose crystallinity very quickly even in the mother liquor. However, samples could be mounted in inert oil and transferred to the cold gas stream of the diffractometer, although the reflection shape was always poor (irregular profiles with asymmetric background). A tablet 0.50 × 0.20 × 0.10 mm was used to collect 8308 intensities to $2\theta_{max}$ 40° (Siemens R3 diffractometer, monochromated Mo Kα radiation), scan type ω. An absorption correction based on ψ-scans was applied, with transmission factors 0.48–1.0. Merging equivalents gave 7448 unique reflections (R_{int} 0.080), of which 7414 were used for all calculations (program system SHELXL-92). Cell constants were refined from setting angles of 50 reflections in the range 2θ = 20–23°.

Structure Solution and Refinement. The structure was solved by the heavy atom method and subjected to full-matrix least-squares refinement on F^2; Au, P, S, F, and Cl atoms were refined anisotropically, phenyl rings as idealized hexagons and the C_6F_5 group constrained to be planar with 2-fold symmetry. H atoms were included using a riding model. Two dichloromethane solvent molecules were identified; one of them could be refined, albeit with high thermal motion (or static disorder) of the chlorine atoms, and the other one was disorded. Refinement proceeded to $R_w(F^2)$ 0.301, conventional $R(F)$ 0.094 for 320 parameters. S = 1.09; maximum $\Delta\rho$ 4.75 e Å⁻³. High displacement parameters for Au(5) and its phosphine ligand may indicate some disorder of this group.

Final atom coordinates for 13 are given in Table V, and selected bond lengths and angles are given in Table VI.

Supplementary Material Available: A description of the crystal structure determinations, including tables of crystal data, data collection, and solution and refinement parameters, atomic coordinates, bond distances and angles, and thermal parameters (16 pages). Ordering information is given on any current masthead page.

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