Organometallics 1988, *7*, 997–1006 997

Synthesis of Gold(I), Gold(III), and Silver(I) Complexes with Ylide Ligands Derived from Carbonylbis(methylenetriphenylphosphonium) Diperchlorate. Crystal and Molecular Structures of $[Au_2\{\mu\text{-}\{\{CH(PPh_3)\}_2CO\}\}_2](ClO_4)_2$, $[(Ph_3PCCl_2)_2CO][AuCl_4](ClO_4)$, $[(AuL)_2\{\mu\text{-}\{C(PPh_3)C(O)CH(PPh_3)(AuL)\}\}](ClO_4)_2$ ($L = PPh_3$), and $[\{Au(PMe_2Ph)\}_4\{\mu\text{-}\{\{C(PPh_3)\}_2CO\}\}](ClO_4)_2$

Jose Vicente,* Maria-Teresa Chicote, and Isabel Saura-Llamas

Departamento de Quimica Inorganica, Universidad de Murcia, 30.071-Murcia, Spain

Peter G. Jones,* Karen Meyer-Bäse, and Cristina Freire Erdbrügger

Institut für Anorganische Chemie der Universität, Tammannstrasse 4, 3400 Göttingen, West Germany

Received July 7, 1987

Transylidation reactions between the diphosphonium salt $[(Ph_3PCH_2)_2CO](ClO_4)_2$ and $[M\{CH(PPh_3)C(O)CH_3\}_2]ClO_4$ (1:1) (M = Ag, Au) give $[M_2\{\mu\text{-}\{\{CH(PPh_3)\}_2CO\}\}_2](ClO_4)_2$ [M = Ag (**1**), Au (**2**)]. Complex **1** reacts with [AuCl(tht)] (1:1; tht = tetrahydrothiophene) to give **2**. This complex reacts with an excess of chlorine to give *trans*-$[(AuCl_2)_2\{\mu\text{-}\{\{CH(PPh_3)\}_2CO\}\}_2](ClO_4)_2$ (**3**), but slow diffusion of the reacting solutions into each other gives instead the new diphosphonium salt $[(Ph_3PCCl_2)_2CO][AuCl_4](ClO_4)$ (**3a**). The diphosphonium salt $[(Ph_3PCH_2)_2CO](ClO_4)_2$ reacts with $[AuCl\{CH(PPh_3)C(O)CH_3\}]$ leading to an equilibrium between the starting compounds and the products of successive transylidation reactions, $[AuCl\{CH(PPh_3)C(O)CH_2PPh_3\}]ClO_4$ (**4**) and $[(AuCl)_2\{\mu\text{-}\{\{CH(PPh_3)\}_2CO\}\}]$ (**5**). From the reaction mixture only **5** can be isolated as a pure compound. However, when the new ylide–phosphonium salt $[Ph_3PCHC(O)CH_2PPh_3]ClO_4$ is reacted with [AuCl(tht)], complex **4** can be isolated. It reacts with $[AuCl\{CH(PPh_3)C(O)CH_3\}]$ (1:1) to give **5**, which, in turn, reacts with chlorine to give the gold(III) complex $[(AuCl_3)_2\{\mu\text{-}\{\{CH(PPh_3)\}_2CO\}\}]$ (**6**). [Au(acac)L] (acac = acetylacetonate) reacts with the diphosphonium salt $[(Ph_3PCH_2)_2CO](ClO_4)_2$ (molar ratio ≥ 4:1) to give complexes of the type $[(AuL)_2\{\mu\text{-}\{C(PPh_3)C(O)CH(PPh_3)(AuL)\}\}](ClO_4)_2$ [$L = PPh_3$ (**7**)] or $[(AuL)_4\{\mu\text{-}\{\{C(PPh_3)\}_2CO\}\}](ClO_4)_2$ [$L = PhMe_2P$ (**8**)]. Single-crystal X-ray structure determinations were performed for compounds **2**, **3a**, **7**, and **8**. Compound **2** possesses a central eight-membered ring with a short transannular Au···Au contact of 2.876 Å. Compound **3a**, the nature of which was only revealed by the X-ray study, contains centrosymmetric $[AuCl_4]^-$ anions, ClO_4^- anions, and the novel, highly chlorinated phosphonium ion $[(Ph_3PCCl_2)_2CO]^{2+}$. Compounds **7** and **8** contain triangular Au_2C units (Au–Au = 2.86–3.01 Å) to which three-center bonding probably makes a significant contribution; further short Au···Au contacts are observed between the Au_2 groups and gold atoms farther away (3.15–3.34 Å). The Au–C–CO–C–Au backbone of compound **7** is disordered over two positions (occupation factors of ca. 89 and 11%); only the gold atoms of the minor disorder component could be identified.

Introduction

The acidic character of the methylene protons in the carbonyl–phosphonium salts $[Ph_3PCH_2C(O)R]^+$ has allowed us to prepare dinuclear gold(I) complexes, $[(AuL)_2\{\mu\text{-}C(PPh_3)C(O)R\}]^+$ ($L = PPh_3$, R = OMe, OEt,[1] Me, Ph,[2] $L = AsPPh_3$, R = Me[2]), by reacting such onium salts with the corresponding [Au(acac)L] complexes (1:2 molar ratio); the products display an unusual type of ylide coordination.[3] In this paper we report the extension of this acid–base reaction starting from the diphosphonium salt $[(Ph_3PCH_2)_2CO](ClO_4)_2$ from which we have succeeded in preparing tri- and tetranuclear gold(I) complexes containing the conjugate bases $[Ph_3PCC(O)CH(PPh_3)]^-$ and $[(Ph_3PC)_2CO]^{2-}$.

In addition, we have synthesized complexes with the two other conjugate bases, the new ylide–phosphonium salt $[Ph_3PCHC(O)CH_2PPh_3]^+$ and the still unisolated[4,5] diylide $(Ph_3PCH)_2CO$. The Au(I) complexes of this diylide ligand, and also one Ag(I) complex, have been obtained by transylidation reactions. This term is used to describe the acid–base reactions between an ylide and an onium salt[6] [e.g., $R_3PCHR' + [R''_3PCH_2R''']^+ \rightarrow R''_3PCHR''' + [R_3PCH_2R']^+$], but we expect that it could be extended to those reactions between a coordinated ylide and an onium salt (a phosphonium salt in our case) to give complexes with its conjugate base. We have not found any precedent for such a synthesis of ylide complexes.

The diylide $(Ph_3PCH)_2CO$ belongs to the group of triatomic bridging ligands (A–C) that are usually designed to promote metal–metal bonds, unusual oxidation states [e.g. Au(II),[7] Pd(I),[8] Pt(I)[9]], and the synthesis of hetero-

---

[1] Vicente, J.; Chicote, M. T.; Cayuelas, J. A.; Fernandez-Baeza, J.; Jones, P. G.; Sheldrick, G. M.; Espinet, P. *J. Chem. Soc., Dalton Trans.* **1985**, 1163.

[2] Vicente, J.; Chicote, M. T.; Saura-Llamas, I.; Turpin, J.; Fernandez-Baeza, J. *J. Organomet. Chem.* **1987**, *333*, 129.

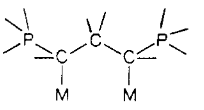
[3] Schmidbaur, H. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 907. Kaska, W. C. *Coord. Chem. Rev.* **1983**, *48*, 1.

[4] Ford, J. A.; Wilson, C. V. *J. Org. Chem.* **1961**, *26*, 1433.

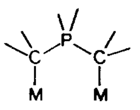
[5] Denney, D. B.; Song, J. *J. Org. Chem.* **1964**, *29*, 495.

[6] Schmidbaur, H. *Acc. Chem. Res.* **1975**, *8*, 62.

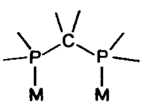
0276-7333/88/2307-0997$01.50/0



A



B



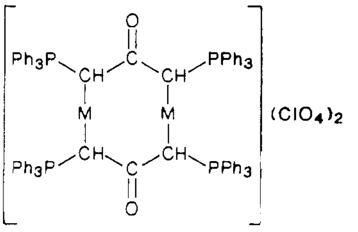
C

bimetallic complexes;[10] some examples are ligands of type B having a CPC skeleton (e.g., anionic ylides)[6] and type C having a PCP bridge [e.g., complexes with bis(diphenylphosphino)methane]. However, CCC-bridging ligands (type A), such as $(Ph_3PCH)_2CO$, are very rare.[9b]

Diylide ligands having a carbon chain between both carbon donor atoms are also very unusual. As far as we know there are only a few complexes with such ligands, coordinated to Ni(II)[11] [e.g., $[Ni\{CH(PPh_3)(CH_2)_nCHPPh_3\}(\eta^5\text{-}C_5H_5)]PF_6$; $n = 1\text{–}3$] and Sn(IV)[12] [e.g., $[SnR_xCl_{4-x}\{CR'(PPh_3)C(O)(CH_2)_nC(O)CR'PPh_3\}]$ (R = Me, Ph; $x = 1\text{–}3$; R′ = H, Me, CO_2Me; $n = 0, 2$)], but in these complexes the diylides are probably chelating ligands, whereas in the complexes reported here they are bridging ligands.

Results and Discussion

The reactions of $[M\{CH(PPh_3)C(O)CH_3\}_2]ClO_4$ (M = Ag,[13] Au[2]) with $[(Ph_3PCH_2)_2CO](ClO_4)_2$ (1:1) in acetone lead to the precipitation of complexes **1** and **2** as acetone



1, M = Ag
2, M = Au

solvates. The solvent of crystallization can easily be removed.[14] From the mother liquors the phosphonium salt $[Ph_3PCH_2C(O)CH_3]ClO_4$ can be isolated by adding diethyl ether. This transylidation reaction (see Introduction) is probably successful because of the insolubility of complexes **1** and **2**. An alternative synthesis of complex **2** (eq 1) makes use of a recently reported[3,13,15] synthesis of ylide complexes by "ylide transfer reactions",[15] which involve the transfer of an ylide ligand from one metal center to another. In our case there is a double "ylide transfer" from silver to gold. This procedure gives **2** in a better yield.

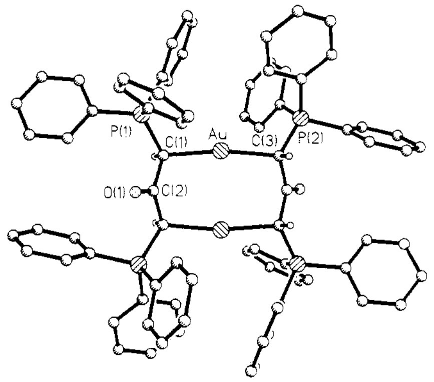
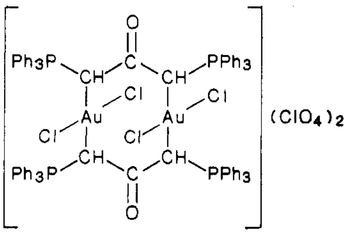


Figure 1. Crystal structure of the cation of compound **2**. Radii are arbitrary, and phenyl H are omitted for clarity.

$$\underset{\mathbf{1}}{[Ag_2\{\mu\text{-}\{\{CH(PPh_3)\}_2CO\}\}_2](ClO_4)_2} + 2[AuCl(tht)] \rightarrow$$
$$\underset{\mathbf{2}}{[Au_2\{\mu\text{-}\{\{CH(PPh_3)\}_2CO\}\}_2](ClO_4)_2} + 2AgCl + 2tht \quad (1)$$

The structure of this complex has been determined by single-crystal X-ray methods (Figure 1). The presence of disordered solvent of crystallization was responsible for the low precision of this structure, but the basic features are clear. The cations contain the eight-membered rings that are a common feature of gold(I) chemistry;[17] crystallographic inversion symmetry is imposed. The transannular gold–gold distance, formally nonbonded, is 2.876 Å; such contacts are also well-known for gold(I).[18] There is considerable deviation from linearity at gold (170°), presumably to avoid yet shorter contacts between the gold atoms. The four carbon atoms bonded to the gold atoms are chiral. However, because of the existence of the center of inversion, the molecule is one of the meso forms.

When a suspension of **2** in dichloromethane is treated with a saturated solution of chlorine in carbon tetrachloride,[16] complex **3** is formed as a yellow precipitate.



3

Complex **3** is not very stable and slowly decomposes at room temperature to give the starting complex **2** among other products. When the chlorination was carried out by slow diffusion of the reacting solutions (in an attempt to obtain single crystals of **3**), the diphosphonium salt $[(Ph_3PCCl_2)_2CO][AuCl_4](ClO_4)$ (**3a**) was obtained instead.

The nature of compound **3a** was revealed by an X-ray diffraction study (Figures 2 and 3). The cations occupy general positions, and there are two independent $[AuCl_4]^-$ anions (both lying on centers of symmetry) and one general ClO_4^- anion. The $[AuCl_4]^-$ ions show no unusual features; the average Au–Cl bond length is 2.276 Å.[19] Of more interest is the cation; we are not aware of any other phosphonium cations bearing the $Cl_2C\text{–}CO\text{–}CCl_2$ moiety.

---

(7) See, for example: Schmidbaur, H.; Hartmann, C.; Riede, J.; Huber, B.; Müller, G. *Organometallics* **1986**, *5*, 1652. Murray III, H. H.; Fackler, J. P., Jr.; Porter, L. C.; Mazany, A. M. *J. Chem. Soc., Chem. Commun.* **1986**, 321.

(8) See, for example: Espinet, P.; Fornies, J.; Fortuño, C.; Hidalgo, G.; Martinez, F.; Tomas, M. *J. Organomet. Chem.* **1986**, *317*, 105.

(9) See, for example: Fisher, J. R.; Mills, A. J.; Sumner, S.; Brown, M. P.; Thompson, M. A.; Puddephatt, R. J.; Frew, A. A.; Manojlovic-Muir, L.; Muir, K. N. *Organometallics* **1982**, *1*, 1421.

(10) (a) See, for example: Carr, S. W.; Shaw, B. L.; Thornton-Pett, M. *J. Chem. Soc., Dalton Trans.* **1985**, 213. (b) Fontaine, X. L. R.; Jacobsen, G. B.; Shaw, B. L.; Thornton-Pett, M. *J. Chem. Soc., Chem. Commun.* **1987**, 662.

(11) Booth, B. L.; Smith, K. G. *J. Organomet. Chem.* **1981**, *220*, 229.

(12) Sanchi, R. R.; Bonsal, K.; Mehrotra, R. C. *J. Organomet. Chem.* **1986**, *303*, 351.

(13) Vicente, J.; Chicote, M. T.; Fernandez-Baeza, J.; Martin, J.; Saura-Llamas, I.; Turpin, J.; Jones, P. G. *J. Organomet. Chem.* **1987**, *331*, 409.

(14) By heating in the solid state at 60 °C for 3 h. In the case of **2** recrystallization from dichloromethane/diethyl ether gives crystals that readily lose solvent to give the unsolvated complex.

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

(16) Either stoichiometric or excess chlorine or $PhICl_2$ ($2{:}PhICl_2 = 1{:}2$) can be used as chlorinating agents.

(17) Jones, P. G. *Gold Bull.* **1981**, *14*, 102; **1983**, *16*, 114; **1986**, *19*, 46.

(18) Jiang, Y.; Alvarez, S.; Hoffmann, R. *Inorg. Chem.* **1985**, *24*, 749.

(19) Jones, P. G. *Gold Bull.* **1981**, *14*, 159.

Table I. Details of Data Collection and Structure Refinement

	2	3a	7	8
formula	$C_{78}H_{64}Au_2O_2P_4^{2+}$ $2ClO_4^-$	$C_{39}H_{30}Cl_4OP_2^{2+}$ $AuCl_4^-ClO_4^-$	$C_{93}H_{76}Au_3OP_5^{2+}$ $2ClO_4^-$	$C_{71}H_{74}Au_4OP_6^{2+}$ $2ClO_4^-$
fw	*a*	1157	*a*	2116
space group	$P\bar{1}$	$P2_1/n$	$P\bar{1}$	$P2_1/n$
cell consts				
a (Å)	13.104 (5)	8.476 (2)	13.352 (4)	14.746 (3)
b (Å)	13.737 (7)	36.244 (5)	18.127 (7)	17.914 (4)
c (Å)	14.105 (5)	14.156 (2)	19.109 (7)	28.009 (6)
α (deg)	62.42 (3)	90	95.67 (4)	90
β (deg)	88.55 (5)	95.66 (2)	99.14 (4)	92.80 (2)
γ (deg)	71.38 (4)	90	92.04 (4)	90
V (Å^3)	2110	4327	4538	7390
Z	1	4	2	4
D_{calcd} (g cm^{-3})	*a*	1.78	*a*	1.90
$F(000)$	*a*	2264	*a*	4048
μ (mm^{-1})	3.8	4.0	5.0	8.2
cryst size (mm); habit	0.25 × 0.1 × 0.1; colorless prism	0.4 × 0.25 × 0.15; yellow prism	0.45 × 0.25 × 0.1; colorless plate	0.45 × 0.4 × 0.3 colorless prism
transmissn	0.61–0.75	0.55–0.66	0.61–0.97	0.46–0.83
$2\theta_{max}$ (deg)	45	50	44	45
reflectns				
measd	9605	11906	11715	11058
unique	5483	7573	11077	9614
R_{int}	0.063	0.031	0.036	0.037
obsd	3882	4913	7508	9614
R	0.098	0.069	0.078	0.065
R_w	0.090	0.060	0.069	0.053
g	0.001	0.0002	0.00035	0.0002
parameters	163	241	336	342

[a] Uncertain because of solvent of crystallization

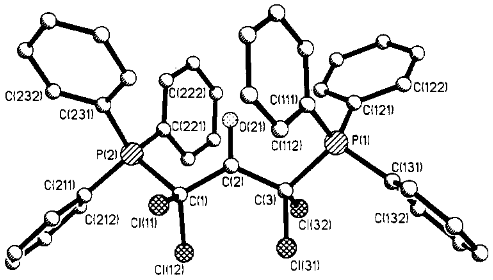
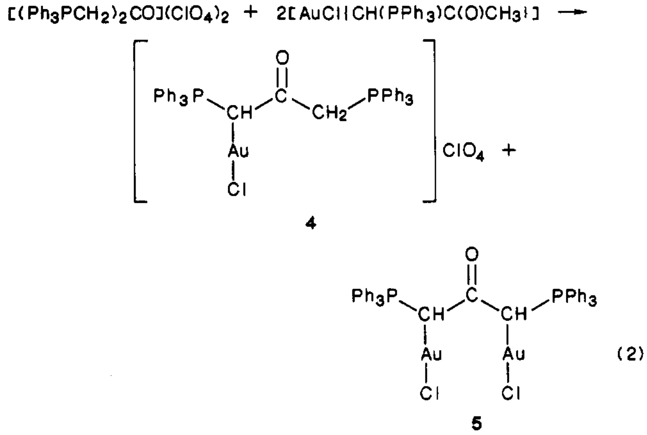


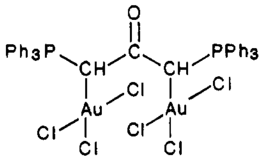
Figure 2. Crystal structure of the cation of compound **3a**. Radii are arbitrary, and H atoms are omitted.

The bond angle at the sp^2 carbon, C(1)–C(2)–C(3), is wide (125.2°). The P–C(sp^3) bond lengths are, as expected, significantly shorter than P–C(sp^2) bond lengths (average 1.887 and 1.776 Å, respectively). The conformation of the cations is somewhat unexpected; looking along the direction of C(1)–C(3), the substituents are staggered but the bulky phosphine groups are "synclinal". It is not yet clear how compound **3a** was formed, although a radical mechanism cannot be ruled out (the reaction mixture was not protected from light).

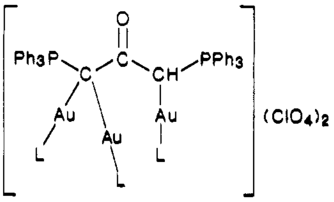
The reaction of **2** with $PhICl_2$ in 1:1 molar ratio did not give the desired gold(II) complex $[(AuCl)_2\{\mu\text{-}\{\{CH(PPh_3)\}_2CO\}\}_2](ClO_4)_2$. Instead, a mixture of **2** and **3** was obtained. It is likely that the coordination sites for the chlorine ligands[7] were too crowded (see Figure 1).



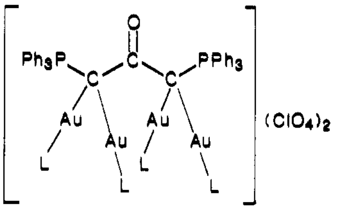
The transylidation reaction shown in eq 2 gives a mixture of products from which, by suitable treatment, **5** and unreacted phosphonium salt can be isolated as the only pure compounds. The result can be understood if two stepwise transylidation reactions in equilibrium are assumed. The presence of the intermediate **4** in the mixture was postulated from IR evidence (see below). This compound was later synthesized by treating the ylide–phosphonium salt $[Ph_3PCHC(O)CH_2PPh_3]ClO_4$ with [AuCl(tht)], but it always was contaminated with trace amounts of $[(Ph_3PCH_2)_2CO](ClO_4)_2$ and **5** (by IR and ^{31}P NMR spectroscopy). These are the products of the intermolecular transylidation reaction of **4**. Complex **5** can also be obtained by the transylidation reaction between **4** and $[AuCl\{CH(PPh_3)C(O)CH_3\}]$. The reaction of **5** with chlorine gives the gold(III) complex **6**. The reactions between $[(Ph_3PCH_2)_2CO](ClO_4)_2$ and [Au(acac)L] (molar ratio of 1:4) give the trinuclear complex $[(AuL)_2\{\mu\text{-}\{C(PPh_3)C(O)CH(PPh_3)(AuL)\}\}](ClO_4)_2$ [L = PPh_3 (**7**)] or the tetranuclear $[(AuL)_4\{\mu\text{-}\{\{C(PPh_3)\}_2CO\}\}](ClO_4)_2$ [L = $PhMe_2P$ (**8**)] (see Figures 4–7). It is probable that steric hindrance prevents the tetrasubstitution when L = PPh_3 (even if molar ratios less than 1:4 were used) because it is attained with the less bulky phosphine Me_2PhP (complex **8**, see Figures 6 and 7). These reactions are of the



6



7, L = PPh$_3$



8, L = PMe$_2$Ph

same type as those previously reported by us[1,2] between [Au(acac)L] (L = PPh$_3$, AsPh$_3$) and the monophosphonium salts [Ph$_3$PCH$_2$COR]ClO$_4$ (R = MeO, EtO, Me, Ph) which give dinuclear [(AuL)$_2${μ-C(PPh$_3$)C(O)-R}]ClO$_4$ complexes and acetylacetone.

All the complexes show molar conductivities in acetone or acetonitrile consistent with their formulations. The molecular weight of **5**, determined osmometrically in chloroform, is also consistent with its dinuclear formulation.

The crystal structures of compounds **7** and **8** were determined. Crystals of **7** diffracted weakly and contained a solvent of crystallization that was easily lost to the atmosphere; these solvent molecules could not be refined adequately (two regions of ill-defined electron density correspond to disordered solvent), and the corresponding precision is low, as was the case for complex **2**. Initial attempts to solve the structure of **7** proved puzzling; three gold atoms and five triphenylphosphine moieties were located without difficulty, but the remaining electron density showed impossibly short contacts between "atoms". This was interpreted as a twofold disorder; the phosphines form a "cage" within which the backbone of the molecule can adopt two different orientations (see Figures 4 and 5, parts a and b). The sites Au(1′) and Au(3′) are occupied to the extent of 11.4%. In view of these problems, the molecular dimensions should be discussed with caution.

The structure determination of complex **8** produced no such disorder problems. Because **7** and **8** are chemically so similar, their structures will be discussed together. However, the minor disorder component of **7** will not be discussed further. Both compounds contain triangular Au$_2$C units (see Figures 4–7) of the type that we had already observed in a binuclear complex[1] and that we had interpreted in terms of a closed three-center, two-electron bond. The Au–Au bond lengths are 2.892 Å,[1] 2.862 Å (compound **7**) and 2.950 and 3.008 Å (compound **8**), with corresponding Au–C–Au angles of 86.3, 85.9, 88.9, and 91.1°. The larger angles and longer bonds in **8** suggest that the three-center bonding contributes less to the overall bonding scheme in this compound. The precision of the P–C bond lengths does not allow a comparison of the bond orders.

Table II. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for Compound 2

	x	y	z	U(eq), Å^2
Au	4435 (1)	4676 (1)	923 (1)	39 (1)[a]
P(1)	4993 (6)	1924 (5)	2368 (5)	47 (3)[a]
P(2)	2975 (5)	6942 (5)	1163 (5)	46 (3)[a]
O(1)	6812 (13)	2151 (12)	1086 (11)	53 (9)[a]
C(1)	4880 (17)	3022 (16)	988 (16)	35 (5)
C(2)	5898 (18)	2890 (18)	505 (17)	34 (5)
C(3)	4129 (18)	6415 (18)	633 (18)	46 (6)
C(12)	3704 (12)	2259 (13)	3875 (12)	66 (7)
C(13)	2707	2611	4212	95 (10)
C(14)	1740	3091	3510	82 (9)
C(15)	1771	3218	2471	88 (9)
C(16)	2768	2865	2133	84 (9)
C(11)	3735	2385	2836	51 (7)
C(22)	6578 (14)	623 (12)	4167 (14)	73 (8)
C(23)	7407	443	4895	75 (8)
C(24)	7769	1357	4715	78 (8)
C(25)	7300	2453	3807	79 (8)
C(26)	6471	2633	3079	69 (8)
C(21)	6109	1718	3259	61 (7)
C(32)	4445 (12)	−54 (14)	3062 (13)	73 (8)
C(33)	4586	−1174	3226	91 (9)
C(34)	5461	−1746	2869	64 (7)
C(35)	6195	−1197	2348	82 (9)
C(36)	6053	−77	2184	79 (8)
C(31)	5178	494	2541	50 (6)
C(42)	3849 (14)	5109 (14)	3190 (15)	81 (9)
C(43)	4008	4566	4317	102 (10)
C(44)	3561	5214	4844	98 (10)
C(45)	2955	6405	4244	101 (10)
C(46)	2796	6948	3117	86 (9)
C(41)	3243	6300	2590	53 (6)
C(52)	3498 (11)	8860 (14)	806 (13)	72 (8)
C(53)	3300	10048	433	77 (8)
C(54)	2274	10870	−101	103 (11)
C(55)	1445	10506	−262	129 (13)
C(56)	1643	9319	111	92 (9)
C(51)	2669	8496	645	50 (6)
C(62)	1739 (12)	6413 (14)	22 (12)	63 (7)
C(63)	836	6178	−191	83 (9)
C(64)	6	6179	447	69 (8)
C(65)	78	6416	1299	71 (8)
C(66)	980	6652	1513	71 (8)
C(61)	1811	6650	874	49 (6)
Cl	2790 (7)	4152 (7)	8195 (7)	95 (6)[a]
O(2)	1971 (29)	5280 (23)	7826 (36)	204 (28)
O(3)	2820 (35)	3495 (32)	9328 (16)	139 (18)
O(4)	2435 (28)	3613 (28)	7681 (24)	81 (11)
O(5)	3802 (25)	4261 (45)	7924 (38)	383 (84)
O(6)	2588 (35)	4875 (36)	8695 (36)	160 (21)
O(7)	3176 (32)	2961 (21)	9009 (30)	185 (26)
O(8)	3632 (22)	4369 (25)	7559 (24)	68 (11)
O(9)	1844 (25)	4427 (45)	7533 (30)	253 (37)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table III. Bond Lengths (Å) and Angles (deg) for Compound 2

	Bond Lengths		
Au–C(1)	2.115 (18)	Au–C(3)	2.128 (21)
P(1)–C(1)	1.799 (20)	P(1)–C(11)	1.794 (18)
P(1)–C(21)	1.818 (18)	P(1)–C(31)	1.797 (17)
P(2)–C(3)	1.764 (22)	P(2)–C(41)	1.774 (19)
P(2)–C(51)	1.810 (17)	P(2)–C(61)	1.797 (17)
O(1)–C(2)	1.280 (23)	C(1)–C(2)	1.480 (26)
Au···Au[a]	2.876		
	Bond Angles		
C(3)–Au–C(1)	170.5 (8)	P(1)–C(1)–Au	108.7 (9)
C(2)–C(1)–Au	105.4 (13)	C(2)–C(1)–P(1)	115.1 (15)
O(1)–C(2)–C(3)[a]	118.6 (19)	C(1)–C(2)–C(3)[a]	119.9 (19)
C(1)–C(2)–O(1)	121.1 (18)	Au–C(3)–C(2)[a]	106.4 (13)
P(2)–C(3)–Au	113.2 (11)	P(2)–C(3)–C(2)[a]	115.7 (14)

[a] Symmetry operator: 1 − x, 1 − y, −z.

Short Au···Au contacts are observed between the Au$_2$ units of **8** and from Au$_2$ to the single Au atom in **7**. These contacts, as mentioned above, are a common feature of the structural chemistry of gold(I)[17,18] (see Figures 5, parts a and b, and 7). They are significantly longer (3.227 Å in **7** and 3.149, 3.307, and 3.343 Å in **8**) than the assumed three-center bonding interactions. It is, therefore, more suitable to regard the Au$_2$ units as separate groups with

Table IV. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for Compound 3a

	x	y	z	U(eq)
Au(1)	0	0	0	48 (1)[a]
Au(2)	5000	0	5000	81 (1)[a]
Cl(1)	1205 (4)	−11 (1)	1512 (2)	73 (1)[a]
Cl(2)	−2046 (4)	328 (1)	500 (2)	79 (1)[a]
Cl(3)	4818 (6)	504 (1)	4034 (3)	128 (2)[a]
Cl(4)	7491 (5)	184 (1)	5540 (4)	130 (2)[a]
Cl(5)	2670 (3)	2151 (1)	2524 (2)	49 (1)[a]
O(1)	2537 (10)	2340 (3)	3382 (8)	118 (5)[a]
O(2)	3633 (8)	1836 (2)	2700 (5)	66 (3)[a]
O(3)	1136 (8)	2043 (2)	2115 (6)	81 (3)[a]
O(4)	3440 (12)	2387 (3)	1910 (7)	103 (4)[a]
P(1)	1986 (3)	1204 (1)	5781 (2)	33 (1)[a]
P(2)	659 (3)	1543 (1)	9444 (2)	28 (1)[a]
Cl(11)	−860 (3)	892 (1)	8436 (2)	47 (1)[a]
Cl(12)	−2115 (3)	1623 (1)	7981 (2)	48 (1)[a]
Cl(31)	−1400 (3)	1114 (1)	6109 (2)	49 (1)[a]
Cl(32)	−47 (3)	1856 (1)	6150 (2)	50 (1)[a]
C(1)	−374 (10)	1363 (2)	8290 (6)	34 (2)
C(2)	801 (10)	1377 (2)	7533 (6)	31 (2)
O(21)	2192 (7)	1369 (2)	7787 (4)	39 (2)[a]
C(3)	338 (10)	1388 (2)	6445 (6)	34 (2)
C(212)	−1256 (7)	2017 (1)	10357 (4)	44 (3)
C(213)	−2523	2094	10884	51 (3)
C(214)	−3435	1807	11197	57 (3)
C(215)	−3080	1442	10982	56 (3)
C(216)	−1814	1365	10455	45 (3)
C(211)	−902	1653	10142	29 (2)
C(222)	3386 (6)	1946 (1)	9385 (4)	44 (2)
C(223)	4288	2236	9077	57 (3)
C(224)	3551	2522	8537	52 (3)
C(225)	1913	2516	8306	44 (2)
C(226)	1011	2226	8614	38 (2)
C(221)	1747	1941	9154	30 (2)
C(232)	2057 (7)	1239 (1)	11050 (4)	42 (2)
C(233)	3034	995	11600	50 (3)
C(234)	3847	718	11163	59 (3)
C(235)	3684	686	10176	58 (3)
C(236)	2707	930	9626	49 (3)
C(231)	1893	1206	10064	31 (2)
C(112)	1804 (6)	533 (2)	6718 (4)	46 (3)
C(113)	2455	252	7308	65 (3)
C(114)	4073	252	7607	73 (4)
C(115)	5041	533	7316	68 (3)
C(116)	4391	814	6725	53 (3)
C(111)	2772	813	6426	34 (2)
C(122)	4324 (8)	1524 (2)	4885 (4)	50 (3)
C(123)	5559	1771	4781	55 (3)
C(124)	5953	2038	5473	54 (3)
C(125)	5111	2059	6270	52 (3)
C(126)	3876	1812	6375	48 (3)
C(121)	3482	1545	5682	36 (2)
C(132)	521 (8)	1379 (1)	4030 (5)	52 (3)
C(133)	−300	1295	3154	63 (3)
C(134)	−543	928	2883	81 (4)
C(135)	36	645	3489	83 (4)
C(136)	857	729	4365	62 (3)
C(131)	1100	1096	4636	41 (2)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table V. Bond Lengths (Å) and Angles (deg) for Compound 3a

	Bond Lengths		
Au(1)–Cl(1)	2.280 (3)	Au(1)–Cl(2)	2.272 (3)
Au(2)–Cl(3)	2.279 (4)	Au(2)–Cl(4)	2.273 (4)
Cl(5)–O(1)	1.409 (9)	Cl(5)–O(2)	1.410 (7)
Cl(5)–O(3)	1.425 (7)	Cl(5)–O(4)	1.424 (9)
P(1)–C(3)	1.882 (9)	P(1)–C(111)	1.777 (7)
P(1)–C(121)	1.787 (6)	P(1)–C(131)	1.761 (7)
P(2)–C(1)	1.893 (8)	P(2)–C(211)	1.771 (6)
P(2)–C(221)	1.782 (6)	P(2)–C(231)	1.782 (6)
Cl(11)–C(1)	1.773 (9)	Cl(12)–C(1)	1.770 (9)
Cl(31)–C(3)	1.802 (9)	Cl(32)–C(3)	1.768 (9)
C(1)–C(2)	1.534 (12)	C(2)–O(21)	1.199 (10)
C(2)–C(3)	1.552 (11)		
	Bond Angles		
Cl(2)–Au(1)–Cl(1)	90.1 (1)	Cl(4)–Au(2)–Cl(3)	88.4 (2)
O(2)–Cl(5)–O(1)	109.6 (6)	O(3)–Cl(5)–O(1)	109.7 (5)
O(3)–Cl(5)–O(2)	109.8 (5)	O(4)–Cl(5)–O(1)	108.3 (7)
O(4)–Cl(5)–O(2)	107.6 (5)	O(4)–Cl(5)–O(3)	111.8 (6)
C(111)–P(1)–C(3)	106.6 (3)	C(121)–P(1)–C(3)	111.1 (3)
C(121)–P(1)–C(111)	111.0 (3)	C(131)–P(1)–C(3)	105.5 (4)
C(131)–P(1)–C(111)	113.7 (3)	C(131)–P(1)–C(121)	108.8 (3)
C(211)–P(2)–C(1)	104.5 (3)	C(221)–P(2)–C(1)	106.6 (3)
C(221)–P(2)–C(211)	112.4 (3)	C(231)–P(2)–C(1)	112.7 (3)
C(231)–P(2)–C(211)	108.3 (3)	C(231)–P(2)–C(221)	112.1 (3)
Cl(11)–C(1)–P(2)	109.0 (4)	Cl(12)–C(1)–P(2)	109.4 (4)
Cl(12)–C(1)–Cl(11)	110.2 (5)	C(2)–C(1)–P(2)	108.4 (6)
C(2)–C(1)–Cl(11)	106.7 (6)	C(2)–C(1)–Cl(12)	113.1 (6)
O(21)–C(2)–C(1)	118.5 (8)	C(3)–C(2)–C(1)	125.2 (7)
C(3)–C(2)–O(21)	116.3 (8)	Cl(31)–C(3)–P(1)	107.5 (4)
Cl(32)–C(3)–P(1)	110.6 (5)	Cl(32)–C(3)–Cl(31)	109.9 (5)
C(2)–C(3)–P(1)	111.0 (6)	C(2)–C(3)–Cl(31)	111.5 (6)
C(2)–C(3)–Cl(32)	106.4 (6)	Cl(3)–Au(2)–Cl(4)[b]	91.6 (1)
Cl(1)–Au(1)–Cl(2)[a]	89.9 (1)		

[a] Symmetry operator: $-x, -y, -z$. [b] Symmetry operator: $1 - x, -y, 1 - z$.

additional slight bonding interactions rather than as parts of tri- or tetranuclear clusters. The bond angles P–Au–C all deviate somewhat from the linear geometry of simple gold(I) complexes: the range is 166–174° and the average of seven bonds 170.6°.

The Au_2 units of **8** are not eclipsed; a Newman-type projection along C(1)···C(3) shows a mutual rotation of ca. 40° similar to that of the cation in compound **3a**. In complex **7** the single gold atom Au(3) is rotated away from the Au_2 unit by ca. 37° in a similar Newman projection (see Figures 2, 5a, and 7). The C(3) atom is chiral (see Figures 4 and 5a), but both enantiomers are present in the crystal.

The ν(CO) frequency for all the complexes is lower by 25–210 cm^{-1} than that of the diphosphonium salt (1715 cm^{-1}). This is a well-established effect in silver and gold complexes containing other carbonyl-stabilized phosphorus ylides.[1,2] In general, the value of the ν(CO) frequency is lower as a consequence of the substitution of hydrogen by less electronegative groups, and, correspondingly, when similar complexes are compared, the ν(CO) frequencies follow the order Ag(I) > Au(I) and Au(I) > Au(III). The number of substituted hydrogen atoms has a notable influence on ν(CO). Thus in **4** it appears at 1650 cm^{-1} while in **5** it is observed at 1600 cm^{-1}. Trisubstitution, as in **7**, decreases this value to 1560 cm^{-1}, and, finally, tetrasubstitution leads to the lowest value (1505 cm^{-1} in **8**).

The values of the Au–Cl stretching frequency trans to the ylide ligand (ν_t) in **4** and **5** (320 cm^{-1}) are very similar to those found[1,2] in complexes of formula [AuCl(ylide)]. The three bands observed in complex **6** at 310 (s), 330 (w), and 350 (s) cm^{-1} can be assigned to ν_t, $\nu_{sym}(AuCl_2)$, and $\nu_{asym}(AuCl_2)$ according to the above and other[1,2] assignments in complexes of the same stoichiometry. Accordingly, the band at 370 (br, m) cm^{-1} in **3** allows us to assign to it a trans geometry as in several $[AuCl_2(ylide)_2]^+$ complexes.[2,3,20] A cis geometry should give rise to two bands around 320 cm^{-1}.

The limited solubility of all the complexes, except **4**, **7**, and **8**, in organic solvents has prevented us from recording their NMR spectra. These could have informed us about the relative proportions of diastereoisomers present in solution of such complexes because they have two (complexes **5** and **6**) or four (complexes **1**–**3**) chiral centers.

---

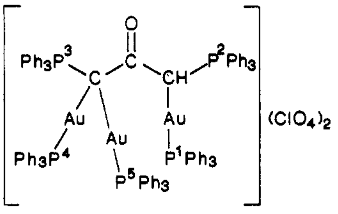
[20] Schmidbaur, H. *Gmelin Handbuch der Anorganischen Chemie, Organogold Compounds*; Springer-Verlag, Berlin, 1980.

Table VI. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for Compound 7

	x	y	z	U(eq)
Au(1)	1777 (1)	1922 (1)	2537 (1)	38 (1)[a]
Au(2)	3627 (1)	1622 (1)	3418 (1)	39 (1)[a]
Au(3)	2364 (1)	3442 (1)	1916 (1)	42 (1)[a]
P(1)	4739 (4)	745 (3)	3171 (3)	41 (2)[a]
P(2)	4506 (4)	4011 (3)	2874 (3)	42 (2)[a]
P(3)	918 (4)	1193 (3)	1543 (3)	49 (2)[a]
P(4)	1929 (4)	2495 (3)	4187 (3)	42 (2)[a]
P(5)	1245 (5)	3914 (3)	1053 (3)	57 (2)[a]
C(212)	6820 (12)	870 (8)	3189 (6)	81 (8)
C(213)	7820	1057	3513	124 (11)
C(214)	8029	1348	4227	88 (8)
C(215)	7238	1453	4618	68 (7)
C(216)	6237	1266	4294	65 (7)
C(211)	6028	974	3580	48 (6)
C(222)	3472 (9)	−383 (8)	3454 (8)	65 (7)
C(223)	3235	−1108	3584	94 (9)
C(224)	3999	−1611	3679	95 (9)
C(225)	5000	−1390	3645	115 (10)
C(226)	5237	−666	3515	105 (10)
C(221)	4474	−162	3420	46 (5)
C(232)	4603 (10)	−13 (6)	1797 (8)	75 (7)
C(233)	4571	−41	1062	94 (9)
C(234)	4658	614	744	74 (7)
C(235)	4779	1297	1162	65 (7)
C(236)	4811	1325	1898	53 (6)
C(231)	4724	670	2215	41 (5)
C(312)	3476 (9)	5293 (7)	3201 (6)	66 (7)
C(313)	3162	6003	3085	69 (7)
C(314)	3431	6345	2514	70 (7)
C(315)	4013	5977	2058	84 (8)
C(316)	4327	5266	2173	66 (7)
C(311)	4058	4925	2744	39 (5)
C(322)	5674 (10)	4743 (6)	4106 (7)	65 (7)
C(323)	6388	4752	4725	68 (7)
C(324)	6738	4087	4955	64 (7)
C(325)	6375	3413	4565	66 (7)
C(326)	5661	3404	3946	63 (7)
C(321)	5311	4069	3716	41 (5)
C(332)	4890 (10)	3414 (9)	1551 (9)	92 (9)
C(333)	5510	3272	1036	105 (9)
C(334)	6545	3477	1194	138 (12)
C(335)	6960	3823	1867	126 (11)
C(336)	6340	3966	2382	104 (9)
C(331)	5305	3761	2225	57 (6)
C(412)	1873 (10)	−136 (8)	1245 (7)	74 (7)
C(413)	2135	−856	1366	84 (8)
C(414)	1722	−1216	1875	79 (8)
C(415)	1047	−855	2263	93 (9)
C(416)	785	−135	2141	97 (9)
C(411)	1198	224	1632	56 (6)
C(422)	−883 (12)	1718 (8)	1878 (8)	77 (7)
C(423)	−1938	1734	1800	105 (10)
C(424)	−2547	1185	1348	119 (11)
C(425)	−2101	621	974	119 (10)
C(426)	−1045	605	1052	88 (8)
C(421)	−436	1154	1505	71 (7)
C(432)	2256 (9)	1633 (8)	718 (7)	82 (8)
C(433)	2575	1774	82	86 (8)
C(434)	1888	1679	−556	112 (10)
C(435)	882	1444	−556	80 (8)
C(436)	563	1302	81	56 (6)
C(431)	1250	1397	718	45 (5)
C(512)	762 (9)	1200 (8)	3921 (7)	68 (7)
C(513)	546	456	3995	91 (8)
C(514)	1192	87	4476	84 (8)
C(515)	2054	462	4883	117 (10)
C(516)	2270	1206	4808	89 (8)
C(511)	1624	1575	4328	39 (5)
C(522)	−26 (13)	2834 (7)	4437 (7)	77 (7)
C(523)	−964	3144	4269	103 (9)
C(524)	−1141	3569	3696	119 (11)
C(525)	−379	3684	3290	116 (10)
C(526)	560	3375	3458	74 (7)
C(521)	736	2950	4031	59 (6)
C(532)	3699 (10)	2937 (8)	5108 (7)	60 (6)
C(533)	4261	3188	5773	79 (8)
C(534)	3764	3416	6341	85 (8)
C(535)	2705	3393	6242	124 (11)
C(536)	2143	3141	5577	100 (9)
C(531)	2640	2913	5009	47 (6)
C(612)	−451 (11)	2969 (8)	686 (6)	76 (7)
C(613)	−1295	2637	222	78 (8)
C(614)	−1405	2717	−504	69 (7)
C(615)	−672	3129	−767	89 (8)
C(616)	171	3461	−303	74 (7)
C(611)	282	3381	424	50 (6)
C(622)	995 (9)	4974 (9)	2140 (8)	80 (8)
C(623)	486	5521	2487	93 (9)
C(624)	−489	5691	2187	76 (7)
C(625)	−956	5313	1539	83 (8)
C(626)	−447	4766	1192	64 (7)
C(621)	528	4597	1492	58 (6)
C(632)	2708 (11)	3898 (6)	208 (8)	75 (7)
C(633)	3450	4211	−127	101 (9)
C(634)	3557	4980	−121	95 (9)
C(635)	2922	5436	221	77 (7)
C(636)	2181	5123	556	57 (6)
C(631)	2073	4354	550	51 (6)
O(1)	2985 (10)	3801 (7)	3787 (7)	46 (4)
C(1)	2611 (13)	2479 (10)	3475 (10)	28 (5)
C(2)	3054 (16)	3223 (13)	3422 (13)	46 (6)
C(3)	3551 (14)	3277 (11)	2755 (10)	33 (5)
Cl(1)	889 (5)	7434 (3)	3678 (3)	77 (3)[a]
Cl(2)	4611 (6)	7741 (4)	864 (4)	113 (3)[a]
O(11)	94 (15)	6942 (11)	3707 (11)	122 (7)
O(12)	1829 (18)	7167 (13)	4074 (13)	155 (9)
O(13)	730 (13)	8146 (10)	4023 (10)	106 (6)
O(14)	989 (16)	7463 (12)	2978 (12)	133 (8)
O(21)	4505 (22)	6973 (18)	720 (16)	221 (13)
O(22)	3874 (26)	8070 (20)	279 (20)	260 (17)
O(23)	4319 (22)	8010 (17)	1492 (17)	212 (13)
O(24)	5283 (34)	7938 (23)	552 (22)	302 (21)
Au(1′)	1357 (6)	2858 (4)	1569 (4)	51 (3)
Au(3′)	3188 (6)	3103 (5)	3091 (5)	38 (3)
Cl(01)	8230 (23)	9198 (19)	2491 (18)	564 (20)
Cl(02)	7996 (32)	8510 (25)	3118 (23)	687 (29)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Such study was possible with the related complexes obtained from the phosphonium salts $[Ph_3PCH_2COR]^+$.[1] The $^{31}P\{^1H\}$ NMR spectrum (δ in ppm, H_3PO_4 as reference) of 4 shows two doublets centered at δ 24.4 and 20.8 ($^4J_{PP}$ = 9 Hz). Other signals at δ 19.8 (s) and 25.6 (s) correspond to the presence of the phosphonium salt and, probably, to the presence of 5. Both impurities could be present in solution as a consequence of a disproportionation reaction (see above), although small amounts could also be present in the solid state because very weak bands at 1600 and 1715 cm^{-1} could correspond to such impurities. The methylene and methine proton resonances in the ^1H NMR spectrum of 4 appear as signals too weak to be assigned. The assignment of signals for complex 7 are $\delta(P^1)$ 39.2 [doublet (d), $^3J_{P^1P^2}$ = 12.6 Hz], $\delta(P^2)$ 22.9 (dd, $^4J_{P^2P^3}$ = 16.2 Hz), $\delta(P^3)$ 30.3 [apparent d of triplets, $^3J_{P^3P^4}$ = $^3J_{P^3P^5}$ = 3.2 Hz], $\delta(P^4)$ or $\delta(P^5)$ 37.9 or 37.5 (apparently two triplets, $^4J_{P^4P^5}$ = $^3J_{P^4P^3}$ = $^3J_{P^5P^3}$ = 3.2 Hz). The $^{31}P\{^1H\}$ NMR



7

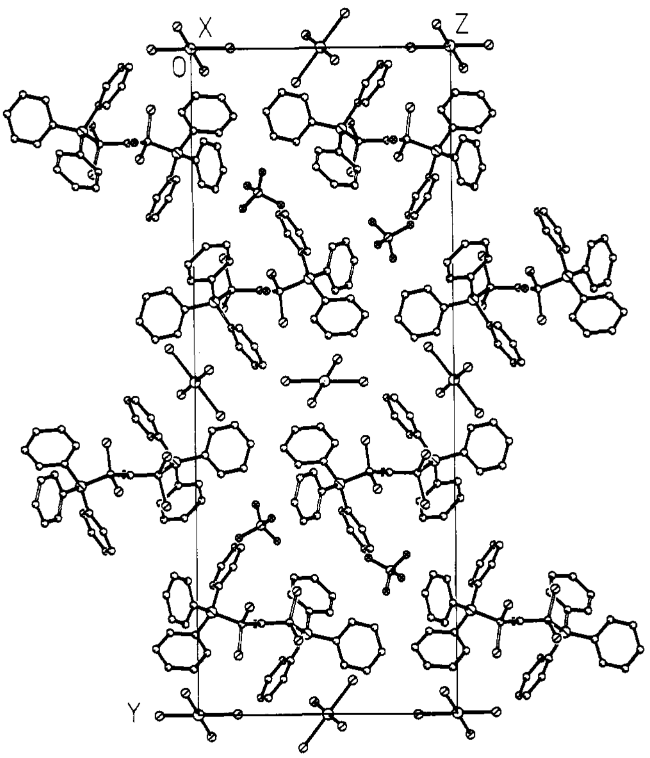


Figure 3. Packing diagram of compound 3a projected down the x axis. H atoms are omitted. The $AuCl_4^-$ ions lie on centers of symmetry.

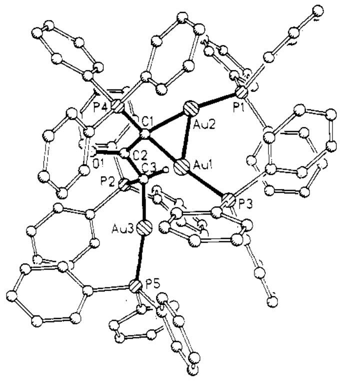


Figure 4. Crystal structure of the cation of compound 7. Radii are arbitrary, and phenyl H atoms are omitted. Only the major disorder component is shown.

spectrum of 8 is deceptively simple because instead of an $A_2XX'A'_2$ spin system it shows two triplets at δ 9.25 (AA′) and 25.8 (XX′) with an apparent coupling constant of 70 Hz.

The ^{1}H NMR spectrum of complex 7 shows a multiplet centered at 5.2 ppm, corresponding to the methine proton. Complex 8 shows a doublet centered at 1.43 ppm ($\delta(CH_3)$; $^2J_{PH}$ = 9.4 Hz).

Experimental Section

Infrared spectra were recorded in the range 4000–200 cm^{-1} on a Perkin-Elmer 1430 spectrophotometer using Nujol mulls between polyethylene sheets. Conductivities were measured in ca. 10^{-4} mol dm^{-3} solutions with a Philips 9501 conductimeter and Λ_M is given in Ω^{-1} cm^2 mol^{-1}. Melting points were determined on a Reichert apparatus and are uncorrected. C and H analyses were carried out with a Perkin-Elmer 240C microanalyzer; Au was determined by ashing the samples with an aqueous solution of hydrazine. NMR spectra were recorded on a Varian FT-80 spectrometer. The molecular weight of 5 was determined with a Knauer vapor-pressure osmometer.

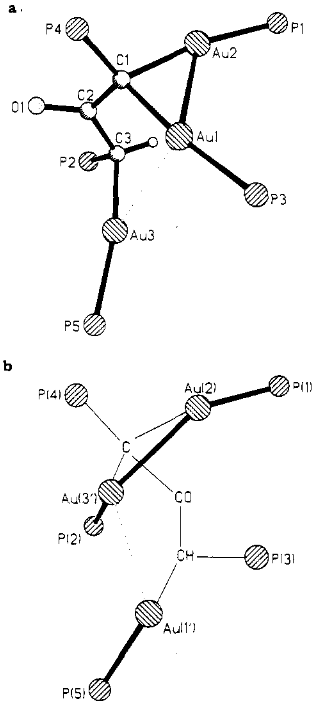


Figure 5. a. The central moiety of the cation of compound 7, showing the short Au···Au contact. This is the major disorder component. b. The minor disorder component of compound 7. The view direction is the same as in a. Au(2) and the phosphorus atoms are common to both components; Au(1′) and Au(3′) are the minor disorder components of the gold atoms. The light atoms indicated only by chemical symbols represent assumed positions; these atoms were not located crystallographically.

Table VII. Selected Bond Lengths (Å) and Angles (deg) for Compound 7

	Bond Lengths		
Au(1)–Au(2)	2.862 (1)	Au(1)–Au(3)	3.227 (1)
Au(1)–P(3)	2.317 (5)	Au(1)–C(1)	2.098 (17)
Au(2)–P(1)	2.279 (5)	Au(2)–C(1)	2.105 (19)
Au(3)–P(5)	2.295 (6)	Au(3)–C(3)	2.120 (18)
P(1)–C(211)	1.790 (15)	P(1)–C(221)	1.796 (15)
P(1)–C(231)	1.815 (16)	P(2)–C(311)	1.806 (14)
P(2)–C(321)	1.780 (13)	P(2)–C(331)	1.796 (17)
P(2)–C(3)	1.782 (19)	P(3)–C(411)	1.827 (16)
P(3)–C(421)	1.796 (17)	P(3)–C(431)	1.774 (16)
P(4)–C(511)	1.758 (15)	P(4)–C(521)	1.815 (17)
P(4)–C(531)	1.786 (13)	P(4)–C(1)	1.752 (21)
P(5)–C(611)	1.795 (13)	P(5)–C(621)	1.813 (16)
P(5)–C(631)	1.792 (17)	O(1)–C(2)	1.215 (26)
C(1)–C(2)	1.472 (29)	C(2)–C(3)	1.537 (32)
Au(1′)–P(5)	2.236 (10)	Au(3′)–P(2)	2.478 (10)
Au(1′)–Au(3′)	3.470 (12)	Au(2)–Au(3′)	2.877 (9)
	Bond Angles		
Au(3)–Au(1)–Au(2)	102.8 (1)	P(3)–Au(1)–Au(2)	127.6 (1)
P(3)–Au(1)–Au(3)	103.6 (2)	C(1)–Au(1)–Au(2)	47.2 (5)
C(1)–Au(1)–Au(3)	81.4 (5)	C(1)–Au(1)–P(3)	174.0 (5)
P(1)–Au(2)–Au(1)	127.0 (1)	C(1)–Au(2)–Au(1)	47.0 (5)
C(1)–Au(2)–P(1)	170.4 (6)	P(5)–Au(3)–Au(1)	120.3 (2)
C(3)–Au(3)–Au(1)	72.9 (5)	C(3)–Au(3)–P(5)	166.0 (5)
Au(2)–C(1)–Au(1)	85.9 (7)	P(4)–C(1)–Au(1)	111.8 (9)
P(4)–C(1)–Au(2)	115.3 (10)	C(2)–C(1)–Au(1)	116.7 (14)
C(2)–C(1)–Au(2)	114.5 (13)	C(2)–C(1)–P(4)	110.8 (14)
C(1)–C(2)–O(1)	128.9 (22)	C(3)–C(2)–O(1)	116.6 (20)
C(3)–C(2)–C(1)	114.0 (18)	P(2)–C(3)–Au(3)	110.7 (10)
C(2)–C(3)–Au(3)	106.5 (12)	C(2)–C(3)–P(2)	112.6 (13)

The diphosphonium salt[4,5] and the starting gold(I) and silver(I) complexes[1,2] were obtained as reported.

All the reactions were carried out at room temperature with magnetic stirring and without any special precautions against air,

Table VIII. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for Compound 8

	x	y	z	U(eq)		x	y	z	U(eq)
Au(1)	3422.7 (5)	1843.2 (4)	494.7 (2)	35 (1)[a]	C(516)	3447	−41	47	53 (5)
Au(2)	1498.9 (5)	1861.3 (4)	805.5 (2)	37 (1)[a]	C(511)	2643	150	259	40 (5)
Au(3)	2749.1 (5)	3108.5 (4)	1280.1 (2)	39 (1)[a]	C(522)	1050 (8)	157 (5)	1361 (4)	47 (5)
Au(4)	4518.6 (5)	2383.1 (4)	1494.1 (2)	36 (1)[a]	C(523)	263	−209	1489	63 (6)
P(1)	4217 (3)	2338 (3)	−107 (2)	42 (2)[a]	C(524)	70	−924	1315	66 (6)
P(2)	109 (3)	2372 (3)	640 (2)	52 (2)[a]	C(525)	665	−1273	1013	68 (6)
P(3)	2466 (4)	4251 (3)	945 (2)	57 (2)[a]	C(526)	1451	−907	885	52 (5)
P(4)	6018 (4)	2652 (3)	1448 (2)	49 (2)[a]	C(521)	1644	−192	1059	44 (5)
P(5)	2649 (3)	296 (2)	895 (1)	30 (2)[a]	C(532)	4428 (8)	233 (5)	1252 (3)	39 (5)
P(6)	3111 (3)	2258 (2)	2300 (1)	32 (2)[a]	C(533)	5184	−117	1470	57 (6)
O(1)	2828 (7)	892 (6)	1811 (3)	34 (3)	C(534)	5139	−868	1600	67 (6)
C(1)	2678 (10)	1263 (8)	1005 (5)	29 (4)	C(535)	4338	−1269	1511	68 (6)
C(2)	2892 (10)	1406 (8)	1518 (5)	27 (4)	C(536)	3581	−918	1292	41 (5)
C(3)	3161 (11)	2168 (8)	1675 (5)	31 (4)	C(531)	3626	−168	1163	33 (4)
C(17)	4630 (13)	3285 (10)	−12 (6)	65 (6)	C(612)	2016 (7)	1759 (7)	3019 (4)	65 (6)
C(18)	5193 (13)	1787 (11)	−228 (7)	74 (6)	C(613)	1195	1518	3194	58 (6)
C(27)	−698 (15)	1647 (12)	599 (8)	96 (8)	C(614)	431	1441	2884	71 (6)
C(28)	−38 (14)	2855 (11)	73 (6)	75 (7)	C(615)	488	1604	2400	61 (6)
C(37)	1761 (15)	4856 (12)	1280 (7)	90 (8)	C(616)	1308	1845	2225	51 (5)
C(38)	3515 (16)	4775 (13)	911 (8)	106 (9)	C(611)	2072	1922	2535	37 (4)
C(47)	6661 (14)	2021 (11)	1112 (7)	80 (7)	C(622)	4378 (9)	2167 (6)	3079 (4)	69 (6)
C(48)	6594 (14)	2625 (12)	2034 (6)	82 (7)	C(623)	5159	1892	3319	80 (7)
C(12)	2915 (9)	1860 (7)	−754 (4)	68 (6)	C(624)	5623	1290	3132	79 (7)
C(13)	2446	1830	−1198	103 (8)	C(625)	5307	961	2704	65 (6)
C(14)	2693	2300	−1567	93 (8)	C(626)	4526	1236	2463	44 (5)
C(15)	3410	2801	−1491	85 (7)	C(621)	4062	1839	2650	34 (4)
C(16)	3879	2832	−1047	65 (6)	C(632)	2374 (6)	3628 (6)	2551 (3)	41 (5)
C(11)	3631	2362	−678	38 (4)	C(633)	2387	4403	2598	47 (5)
C(22)	269 (8)	3163 (8)	1487 (5)	89 (7)	C(634)	3180	4799	2521	57 (6)
C(23)	−38	3628	1844	114 (9)	C(635)	3961	4421	2396	55 (5)
C(24)	−886	3971	1786	90 (8)	C(636)	3948	3646	2349	48 (5)
C(25)	−1426	3849	1371	85 (7)	C(631)	3155	3249	2426	34 (4)
C(26)	−1119	3383	1013	79 (7)	Cl(1)	2578 (3)	7049 (2)	527 (2)	60 (2)[a]
C(21)	−272	3040	1072	54 (5)	O(11)	2372 (14)	7326 (12)	62 (4)	83 (10)[b]
C(32)	2144 (8)	3698 (6)	30 (4)	47 (5)	O(12)	3323 (12)	6544 (11)	503 (8)	71 (8)[b]
C(33)	1785	3727	−439	52 (5)	O(13)	2831 (17)	7621 (10)	855 (7)	101 (10)[b]
C(34)	1256	4335	−592	72 (6)	O(14)	1821 (11)	6650 (11)	694 (7)	81 (9)[b]
C(35)	1086	4914	−276	72 (7)	Cl(2)	7938 (3)	364 (3)	2241 (2)	130 (4)[a]
C(36)	1445	4885	194	56 (6)	O(21)	8579 (24)	942 (20)	2197 (19)	560 (82)[b]
C(31)	1975	4277	347	44 (5)	O(22)	8306 (27)	−338 (14)	2122 (14)	202 (22)[b]
C(42)	6474 (9)	3682 (7)	754 (4)	66 (6)	O(23)	7150 (14)	510 (17)	1946 (9)	119 (12)[b]
C(43)	6574	4402	576	84 (7)	O(24)	7675 (28)	327 (30)	2722 (6)	353 (42)[b]
C(44)	6412	5018	864	90 (8)	O(11A)	3474 (9)	6933 (15)	719 (8)	127 (13)[b]
C(45)	6149	4913	1331	92 (8)	O(12A)	2590 (15)	7667 (9)	206 (7)	97 (11)[b]
C(46)	6048	4192	1510	70 (6)	O(13A)	1976 (13)	7222 (14)	889 (7)	135 (14)[b]
C(41)	6211	3576	1221	48 (5)	O(14A)	2281 (20)	6410 (10)	267 (8)	200 (20)[b]
C(512)	1839 (7)	223 (6)	−21 (4)	40 (5)	O(21A)	8728 (11)	−45 (13)	2385 (9)	125 (13)[b]
C(513)	1840	104	−513	67 (6)	O(22A)	8080 (18)	715 (13)	1796 (5)	155 (16)[b]
C(514)	2644	−88	−725	76 (7)	O(23A)	7158 (12)	−86 (13)	2228 (11)	255 (28)[b]
C(515)	3448	−160	−445	81 (7)	O(24A)	7870 (18)	947 (11)	2586 (7)	143 (15)[b]

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor. [b] Disorder component with occupation factor 0.5.

moisture, or light, except that reactions with silver complexes were protected against light by using aluminum foil.

Preparation of [Ag_2{μ-{{CH(PPh$_3$)}$_2$CO}}$_2$](ClO$_4$)$_2$ (1). To a solution of [$(Ph_3PCH_2)_2CO$]$(ClO_4)_2$ (500 mg, 0.64 mmol) in acetone (25 cm^3) was added solid [Ag{CH(PPh$_3$)C(O)CH$_3$}$_2$]ClO$_4$ (541 mg, 0.64 mmol). After 3 h, the suspension was filtered and the resulting white solid washed with acetone (5 cm^3) and diethyl ether (5 cm^3) to give 1 (427 mg, 85% yield): mp 238 °C dec; Λ_M = 216 (3.6 × 10^{-4} mol dm^{-3} acetonitrile); IR ν(CO) 1690 (vs) cm^{-1}. Anal. Calcd for $C_{78}H_{64}Ag_2Cl_2O_{10}P_4$: C, 59.60; H, 4.10. Found: C, 59.70; H, 4.41.

Preparation of [Au_2{μ-{{CH(PPh$_3$)}$_2$CO}}$_2$](ClO$_4$)$_2$ (2). To a suspension of 1 (200 mg, 0.13 mmol) in dichloromethane (30 cm^3) was added solid [AuCl(tht)] (82 mg, 0.26 mmol). After 3 h, the suspension was filtered, the resulting solution concentrated (to 3 cm^3), and diethyl ether added to precipitate 2 as a white solid (193 mg, 85% yield): mp 180 °C dec; Λ_M = 260 (2.3 × 10^{-4} mol dm^{-3} acetonitrile); IR ν(CO) 1610 (vs) cm^{-1}. Anal. Calcd for $C_{78}H_{64}Au_2Cl_2O_{10}P_4$: C, 53.53; H, 3.69; Au, 22.51. Found: C, 53.27; H, 3.92; Au, 22.81.

Preparation of *trans*-[(AuCl$_2$)$_2${μ-{{CH(PPh$_3$)}$_2$CO}}$_2$](ClO$_4$)$_2$ (3). To a suspension of 2 (100 mg, 0.057 mmol) in dichloromethane (5 cm^3) was added a saturated solution (1 cm^3) of chlorine in carbon tetrachloride. After 15 min the suspension was filtered and the resulting yellow solid washed with diethyl ether to give 3 (85 mg, 79% yield): mp 161 °C dec.; Λ_M = 205 (5 × 10^{-4} mol dm^{-3} acetone); IR ν(CO) 1645 (vs), ν(AuCl$_2$) 370 (m) cm^{-1}. Anal. Calcd. for $C_{78}H_{64}Au_2Cl_6O_{10}P_4$: C, 49.52; H, 3.41; Au, 20.82. Found: C, 49.50; H, 3.80; Au, 20.29.

In an attempt to prepare single crystals of compound 3, a saturated solution of 2 was carefully layered onto a saturated solution of chlorine in CCl$_4$. After 4 days, well-formed yellow prisms of 3a had appeared; these were removed from the mother liquor and mounted in glass capillaries for crystallographic investigation.

Preparation of [AuCl{CH(PPh$_3$)C(O)CH$_2$PPh$_3$}]ClO$_4$ (4). The ylide–phosphonium salt used as a ligand in complex 4 was prepared as follows. To a solution of [$(Ph_3PCH_2)_2CO$]$(ClO_4)_2$ (500 mg, 0.64 mmol) in acetone (20 cm^3) was added solid [Tl(acac)] (195 mg, 0.64 mmol). After 2 h the solvent was evaporated, the resulting solid extracted with dichloromethane (10 cm^3), the suspension filtered, the resulting solution concentrated (to 3 cm^3), and diethyl ether added to precipitate the ligand as a white solid (300 mg, 70% yield): mp 228 °C dec; Λ_M = 108 (5.9 × 10^{-4} mol

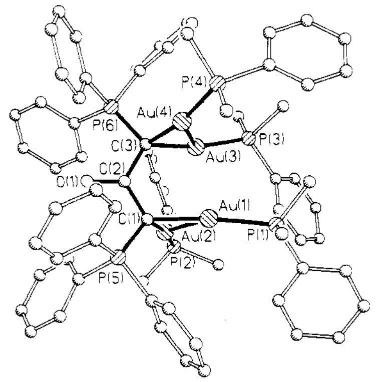


Figure 6. Crystal structure of the cation of compound 8. Radii are arbitrary, and H atoms are omitted.

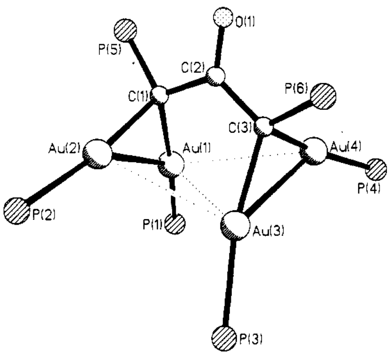


Figure 7. The central moiety of compound 8, showing the short Au···Au contacts.

dm^{-3} acetone); IR ν(CO) 1550 (vs) cm^{-1}; ^{31}P{^{1}H} NMR 22.1, 14.2 ppm; ^{1}H NMR 4.3 ppm (m). Anal. Calcd for $C_{39}H_{33}ClO_5P_2$: C, 68.98; H, 4.90. Found: C, 68.32; H, 4.99. To prepare 4, solid [AuCl(tht)] (47 mg, 0.15 mmol) was added to a solution of the ylide–phosphonium salt (100 mg, 0.15 mmol) in dichloromethane (6 cm^3). After 1 h the suspension was filtered, the resulting solution concentrated (2 cm^3), and diethyl ether added to precipitate crude 4 (126 mg, 92% yield). Several recrystallizations from acetone/diethyl ether gave 4 as a white solid (50% yield): mp 169 °C dec; Λ_M = 124 (4.4 × 10^{-4} mol dm^{-3} acetone); IR ν(CO) 1650 (vs), ν(AuCl) 320 (w) cm^{-1}. Anal. Calcd for $C_{39}H_{33}AuCl_2O_5P_2$: C, 51.39; H, 3.65; Au, 21.61. Found: C, 50.87; H, 3.73; Au, 19.28.

Preparation of [(AuCl)$_2${μ-{{CH(PPh$_3$)}$_2$CO}}] (5). To a solution of [(Ph$_3$PCH$_2$)$_2$CO](ClO$_4$)$_2$ (198 mg, 0.25 mmol) in acetone (7 cm^3) was added solid [AuCl{CH(PPh$_3$)C(O)CH$_3$}] (285 mg, 0.52 mmol). After 2.5 h the resulting suspension was filtered and the solid washed with acetone (3 cm^3) and diethyl ether (6 cm^3) to give a mixture of 4 and 5. Two recrystallizations from dichloromethane/acetone gave 5 as a white solid (40 mg, 15% yield): mp 161 °C dec; 5 is not soluble enough for its conductivity to be measured; IR ν(CO) 1600 (vs), ν(AuCl) 320 (m) cm^{-1}. Anal. Calcd for $C_{39}H_{32}Au_2Cl_2OP_2$: C, 44.89; H, 3.09; Au, 37.75 mol wt, 1043. Found: C, 44.37; H, 3.44; Au, 37.25; mol wt (in chloroform), 998.

Preparation of [(AuCl$_3$)$_2${μ-{{CH(PPh$_3$)}$_2$CO}}] (6). To a solution of 5 (30 mg, 0.028 mmol) in dichloromethane (3 cm^3) was added a saturated solution (1 cm^3) of chlorine in carbon tetrachloride. After 15 min diethyl ether was added (15 cm^3) to precipitate 6 as a yellow solid (26 mg, 81% yield): mp 165 °C dec; Λ_M = 19 (3 × 10^{-4} mol dm^{-3} acetone); IR ν(CO) 1650 (vs), ν(AuCl) 310 (s), 320 (w), 350 (s) cm^{-1}. Anal. Calcd for $C_{39}H_{32}Au_2Cl_6OP_2$: C, 39.52; H, 2.72; Au, 33.23. Found: C, 39.17; H, 2.82; Au, 33.70.

Preparation of [(AuL)$_2${μ-{C(PPh$_3$)C(O)CH(PPh$_3$)(AuL)}}](ClO$_4$)$_2$ [L = PPh$_3$ (7)]. To a solution of [Au(acac)PPh$_3$] (172 mg, 0.31 mmol) in acetone (15 cm^3) was added solid [(Ph$_3$PCH$_2$)$_2$CO](ClO$_4$)$_2$ (60 mg, 0.077 mmol). After 12 h the suspension was filtered, the resulting solution concentrated (2 cm^3) and diethyl ether added to precipitate 7 as a white solid (152 mg, 83% yield): mp 169 °C; Λ_M = 210 (1.8 × 10^{-4} mol dm^{-3} acetone); IR ν(CO) 1560 cm^{-1}. Anal. Calcd for $C_{93}H_{76}Au_3Cl_2O_9P_5$: C, 51.85; H, 3.56; Au, 27.43. Found: C, 51.87; H, 4.03; Au, 27.80.

Preparation of [{Au(PMe$_2$Ph)}$_4${μ-{{C(PPh$_3$)}$_2$CO}}](ClO$_4$)$_2$ (8). The same procedure as for 7 but with a molar ratio of 1:4.6 gave 8 as a white solid [81 mg, 85% yield, from 35 mg (0.045 mmol) of the diphosphonium salt]: mp 200 °C dec; Λ_M = 214 (1.9 × 10^{-4} mol dm^{-3} acetone); IR ν(CO) 1505 cm^{-1}. Anal. Calcd for $C_{71}H_{74}Au_4Cl_2O_9P_6$: C, 40.30; H, 3.52; Au, 37.23. Found: C, 40.10; H, 3.72; Au, 36.96.

Crystal Structure Determinations. Profile-fitted data[21] were collected on a Stoe-Siemens four-circle diffractometer using monochromated Mo Kα radiation. Absorption corrections were based on Ψ scans. Cell constants were refined from 2θ values of strong reflections in the range 20–23°.

The structures were solved by the heavy-atom method and refined on *F*. Phenyl rings were refined as rigid groups with C–C

Table IX. Selected Bond Lengths (Å) and Angles (deg) for Compound 8

	Bond Lengths		
Au(1)–Au(2)	3.008 (1)	Au(1)–Au(3)	3.343 (1)
Au(1)–Au(4)	3.307 (1)	Au(1)–P(1)	2.280 (5)
Au(1)–C(1)	2.118 (15)	Au(2)–Au(3)	3.149 (1)
Au(2)–P(2)	2.272 (5)	Au(2)–C(1)	2.095 (15)
Au(3)–Au(4)	2.950 (1)	Au(3)–P(3)	2.282 (5)
Au(3)–C(3)	2.089 (15)	Au(4)–P(4)	2.273 (5)
Au(4)–C(3)	2.124 (16)	P(1)–C(17)	1.817 (19)
P(1)–C(18)	1.791 (20)	P(1)–C(11)	1.779 (13)
P(2)–C(27)	1.762 (23)	P(2)–C(28)	1.812 (19)
P(2)–C(21)	1.809 (15)	P(3)–C(37)	1.799 (22)
P(3)–C(38)	1.815 (24)	P(3)–C(31)	1.792 (12)
P(4)–C(47)	1.775 (21)	P(4)–C(48)	1.812 (19)
P(4)–C(41)	1.802 (13)	P(5)–C(1)	1.760 (16)
P(5)–C(511)	1.798 (12)	P(5)–C(521)	1.798 (12)
P(5)–C(531)	1.796 (11)	P(6)–C(3)	1.763 (15)
P(6)–C(611)	1.801 (12)	P(6)–C(621)	1.832 (12)
P(6)–C(631)	1.811 (12)	O(1)–C(2)	1.241 (17)
C(1)–C(2)	1.477 (19)	C(2)–C(3)	1.483 (21)
	Bond Angles		
Au(2)–Au(1)–Au(3)	59.2 (1)	Au(2)–Au(1)–Au(4)	100.4 (1)
Au(3)–Au(1)–Au(4)	52.7 (1)	Au(2)–Au(1)–P(1)	137.4 (1)
Au(3)–Au(1)–P(1)	113.8 (1)	Au(4)–Au(1)–P(1)	105.4 (1)
Au(2)–Au(1)–C(1)	44.1 (4)	Au(3)–Au(1)–C(1)	73.0 (4)
Au(4)–Au(1)–C(1)	79.6 (4)	P(1)–Au(1)–C(1)	173.1 (4)
Au(1)–Au(2)–Au(3)	65.7 (1)	Au(1)–Au(2)–P(2)	143.1 (1)
Au(3)–Au(2)–P(2)	107.7 (1)	Au(1)–Au(2)–C(1)	44.8 (4)
Au(3)–Au(2)–C(1)	77.8 (4)	P(2)–Au(2)–C(1)	171.6 (4)
Au(1)–Au(3)–Au(2)	55.1 (1)	Au(1)–Au(3)–Au(4)	63.0 (1)
Au(2)–Au(3)–Au(4)	105.5 (1)	Au(1)–Au(3)–P(3)	113.0 (1)
Au(2)–Au(3)–P(3)	111.8 (1)	Au(4)–Au(3)–P(3)	128.4 (2)
Au(1)–Au(3)–C(3)	73.4 (4)	Au(2)–Au(3)–C(3)	78.5 (4)
Au(4)–Au(3)–C(3)	46.0 (4)	P(3)–Au(3)–C(3)	169.7 (4)
Au(1)–Au(4)–Au(3)	64.3 (1)	Au(1)–Au(4)–P(4)	116.8 (1)
Au(3)–Au(4)–P(4)	138.5 (1)	Au(1)–Au(4)–C(3)	73.8 (4)
Au(3)–Au(4)–C(3)	45.1 (4)	P(4)–Au(4)–C(3)	169.3 (4)
Au(1)–P(1)–C(17)	115.8 (6)	Au(1)–P(1)–C(18)	111.9 (7)
C(17)–P(1)–C(18)	106.0 (9)	Au(1)–P(1)–C(11)	115.4 (5)
C(17)–P(1)–C(11)	104.7 (7)	C(18)–P(1)–C(11)	101.7 (7)
Au(2)–P(2)–C(27)	108.4 (8)	Au(2)–P(2)–C(28)	116.0 (7)
C(27)–P(2)–C(28)	104.1 (10)	Au(2)–P(2)–C(21)	115.9 (4)
C(27)–P(2)–C(21)	107.5 (9)	C(28)–P(2)–C(21)	104.0 (8)
Au(3)–P(3)–C(37)	115.1 (7)	Au(3)–P(3)–C(38)	110.3 (8)
C(37)–P(3)–C(38)	103.4 (10)	Au(3)–P(3)–C(31)	117.7 (4)
C(37)–P(3)–C(31)	104.7 (8)	C(38)–P(3)–C(31)	104.2 (8)
Au(4)–P(4)–C(47)	116.2 (7)	Au(4)–P(4)–C(48)	111.0 (7)
C(47)–P(4)–C(48)	103.0 (9)	Au(4)–P(4)–C(41)	112.7 (5)
C(47)–P(4)–C(41)	107.5 (8)	C(48)–P(4)–C(41)	105.6 (8)
C(1)–P(5)–C(511)	108.4 (6)	C(1)–P(5)–C(521)	116.5 (6)
C(1)–P(5)–C(531)	111.7 (6)	C(3)–P(6)–C(611)	114.2 (6)
C(3)–P(6)–C(621)	115.3 (7)	C(3)–P(6)–C(631)	106.2 (6)
Au(1)–C(1)–Au(2)	91.1 (6)	Au(1)–C(1)–P(5)	112.0 (7)
Au(2)–C(1)–P(5)	116.4 (8)	Au(1)–C(1)–C(2)	118.5 (10)
Au(2)–C(1)–C(2)	107.8 (10)	P(5)–C(1)–C(2)	110.1 (10)
O(1)–C(2)–C(1)	119.7 (13)	O(1)–C(2)–C(3)	121.0 (12)
C(1)–C(2)–C(3)	119.3 (12)	Au(3)–C(3)–Au(4)	88.9 (6)
Au(3)–C(3)–P(6)	115.3 (8)	Au(4)–C(3)–P(6)	107.8 (7)
Au(3)–C(3)–C(2)	121.2 (10)	Au(4)–C(3)–C(2)	109.7 (10)
P(6)–C(3)–C(2)	110.8 (10)		

= 1.395 Å, C–H = 0.96 Å, and all angles = 120°. Other H atoms were included by using a riding model. The disordered perchlorate ions of compounds 2 and 8 were restrained to an approximately tetrahedral geometry.

Compounds 2 and 7 contained ill-defined regions of residual electron density that probably correspond to solvent, but no suitable model could be refined. Compound 7 displayed disorder of the central (gold-containing) moiety; this is described in more detail in the Discussion. Weighting schemes of the form $w^{-1} = \sigma^2(F) + gF^2$ were employed. Full details of the individual data collections and refinements are given in Table I; atom coordinates and derived bond lengths and angles are given in Tables II–IX.

Acknowledgment. We thank the Fonds der Chemischen Industrie and the Comision Asesora de Investigacion Cientifica y Tecnica (Spain) (PB85-0295) for financial support; I.S. is grateful for a grant from Ministerio de Educacion y Ciencia (Spain).

Registry No. 1, 112596-62-0; 2, 112596-64-2; 3, 112596-66-4; 3a, 112596-76-6; 4, 112596-68-6; 5, 112596-69-7; 6, 112596-70-0; 7, 112596-72-2; 8, 112596-74-4; $\{CH(PPh_3)ClO)CH_2PPh_3\}ClO_4$, 112576-37-1; $[(Ph_3P(CH_2)_2CO](ClO_4)_2$, 107526-65-8; $[Ag\{CH(PPh_3)C(O)CH_3\}_2]ClO_4$, 112620-95-8; $[AuCl\{CH(PPh_3)C(O)CH_3\}]$, 112596-77-7; [AuCl(tht)], 39929-21-0; $[Au(acac)PPh_3]$, 98255-79-9.

Supplementary Material Available: Tables of anisotropic displacement parameters and H-atom coordinates for 2, 3a, 7, and 8 and tables of bond lengths and angles for 7 and 8 (15 pages); listings of structure factor amplitudes for 2, 3a, 7, and 8 (151 pages). Ordering information is given on any current masthead page.

Communications

Synthesis and Structures of Hypervalent Species of Silicon and Germanium: Toward Heptacoordination?

C. Brelière, F. Carré, R. J. P. Corriu,* and G. Royo

Université des Sciences et Techniques du Languedoc
et Unité associée au CNRS, U.A. No. 1097
Place E. Bataillon, F-34060 Montpellier, France

Received October 28, 1987

Summary: The compounds $(2\text{-}Me_2NCH_2C_6H_4)_3MH$ (M = Si, Ge) have been prepared. The crystal structure of the germanium compound shows symmetrical intramolecular chelation of three NMe_2 groups to the germanium atom at the centers of the three tetrahedral faces containing the hydrogen atom, giving a pseudoheptacoordinate environment. The silicon compound appears to have the same structure.

In the course of our studies concerning hypervalent species of silicon, we have observed that penta- and hexacoordinated species display unusual reactivity toward nucleophiles.[1] The overall results of these reactions are substitution by a nucleophile at a hypervalent silicon.[2] The detailed mechanisms (and the driving force) of these reactions have not yet been elucidated. We have sought evidence for the possibility of a process involving extension of coordination; in the case of pentacoordinate silicon, the possibility of conversion to hexacoordinate species is well-documented.[3] For hexacoordinate species the question is open; dubious examples of heptacoordination have been claimed[4] whereas kinetic studies of the hydrolyses have been interpreted as involving rate-determining steps that are dissociative in nature.[5]

Dunitz[6] has demonstrated that molecular interactions in the solid state, even if relatively weak, may well be

Scheme I

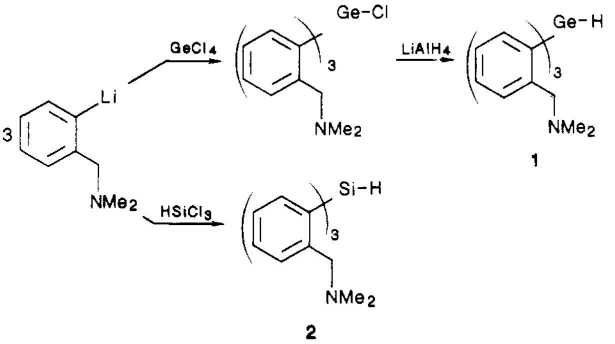


Table I. X-ray Powder Diagrams for Products 1 and 2

germane 1		silane 2	
d_{hkl}	intensity	d_{hkl}	intensity
8.8876	h	8.7677	h
7.7282	h	7.7417	h
7.6351	vh	7.6351	vh
7.2249	m	7.2366	m
6.8673	m	6.8673	m
6.5629	m	6.5532	m
6.1541	w	6.1287	w
5.9011	w	5.9168	w
4.4095	h	4.3836	h
3.9206	m	3.9621	m
3.5984	w	3.5841	w
3.5503	w	3.5309	w

---

(1) Corriu, R. J. P.; Kpoton, K.; Poirier, M.; Royo, G. *J. Organomet. Chem.* **1984**, *277*, C25. Boyer, J.; Corriu, R. J. P.; Kpoton, A.; Mazhar, M.; Royo, G. *J. Organomet. Chem.* **1986**, *301*, 131. Boyer, J.; Brelière, C.; Corriu, R. J. P.; Kpoton, A.; Poirier, M.; Royo, G. *J. Organomet. Chem.* **1986**, *331*, C29. Corriu, R. J. P.; Lanneau, G.; Perrot, M. *Tetrahedron Lett.* **1987**, 3943.

(2) Boudin, A.; Cerveau, G.; Chuit, C.; Corriu, R. J. P.; Reye, C. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 473. Boudin, A.; Cerveau, G.; Chuit, C.; Corriu, R. J. P.; Reye, C. *Angew. Chem., Int. Ed. Engl.* **1986**, 474. Boudin, A.; Cerveau, G.; Chuit, C.; Corriu, R. J. P.; Reye, C. *Angew. Chem., Int. Ed. Engl.* **1986**, 479. Corriu, R. J. P.; Guérin, C.; Henner, B. J. L.; Wong Chi Man, W. W. C. *Organometallics*, in press.

(3) Marat, R. K.; Janzen, A. F. *Can J. Chem.* **1977**, *55*, 3845. Marat, R. K.; Janzen, A. F. *J. Chem. Soc., Chem. Commun.* **1977**, 671.

(4) Biradar, N. S.; Roddabasanagoudar, V. L.; Aminabhavi, T. M. *Indian J. Chem. Sect. A* **1985**, *24A*, 873.

(5) Farnham, W. B.; Whitney, J. F. *J. Am. Chem. Soc.* **1984**, *106*, 3992. Inoue, T, *Inorg. Chem.* **1983**, *22*, 2435.

(6) Bürgi, H. B.; Dunitz, J. D. *Acc. Chem. Res.* **1983**, *16*, 153 and references therein. Britton, D.; Dunitz, J. D. *J. Am. Chem. Soc.* **1981**, *103*, 2971. Bürgi, H. B.; Dunitz, J. D.; Schaffer, E. *J. Am. Chem. Soc.* **1973**, *95*, 5065.

0276-7333/88/2307-1006$01.50/0