Di-, Tri- and Tetra-nuclear Gold(I) Complexes with Tris(diphenylphosphino)-methane or -methanide as Ligand. Crystal Structures of Two Modifications of $[(O)Ph_2PC(PPh_2AuPPh_2)_2CPPh_2(O)]\cdot 4CH_2Cl_2$†

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The reaction of $[Au(tht)_2]ClO_4$ or $[Au(acac)(PPh_3)]$ (tht = tetrahydrothiophene, acac = acetylacetonate) with $CH(PPh_2)_3$ led to dinuclear complexes, $[Ph_2PCH(PPh_2AuPPh_2)_2CHPPh_2][ClO_4]_2$ or $[Ph_2PC(PPh_2AuPPh_2)_2CPPh_2]$, with react further with $[AuX(tht)]$ (X = C_6F_5 or Cl) or $[Au(PPh_3)(tht)]ClO_4$ to give tetranuclear cationic, $[XAuPPh_2CH(PPh_2AuPPh_2)_2CHPPh_2AuX][ClO_4]_2$ or $[(Ph_3P)AuPPh_2C(PPh_2AuPPh_2)_2CPPh_2Au(PPh_3)][ClO_4]_2$, or neutral complexes, $[XAuPPh_2C(PPh_2AuPPh_2)_2CPPh_2AuX]$. Trinuclear complexes, such as $[CH(PPh_2AuPPh_2)_3CH][ClO_4]_3$ or $[CH\{PPh_2Au(C_6F_5)\}_3]$, were obtained by reaction of $[Au(tht)_2]ClO_4$ or $[Au(C_6F_5)(tht)]$ with $CH(PPh_2)_3$. Oxidation of $[Ph_2PC(PPh_2AuPPh_2)_2CPPh_2]$ with H_2O_2 gives $[(O)Ph_2PC(PPh_2AuPPh_2)_2CPPh_2(O)]$. The structures of two forms of the latter compound have been established by X-ray crystallography. Both involve an eight-membered ring with a very short transannular gold–gold contact.

Although in recent years the chemistry of the bis(diphenylphosphino)-methane or -methanide ligand has received a great deal of attention,[1-3] and some examples of gold derivatives have been prepared,[3-5] no systematic study of the tris(diphenylphosphino)methane ligand has been carried out until now. A few transition-metal complexes with $CH(PPh_2)_3$ have been prepared,[6-8] but only very few examples such as $[CH(PPh_2AuCl)_3]$[9] and $[Au_3Cl\{CH(PPh_2)_3\}_2][ClO_4]_2$[10] are known with gold.

Here we describe the preparation of the dinuclear $[Ph_2PC(PPh_2AuPPh_2)_2CPPh_2]$ or $[Ph_2PCH(PPh_2AuPPh_2)_2CHPPh_2][ClO_4]_2$, or trinuclear complexes $[CH(PPh_2AuPPh_2)_3CH][ClO_4]_3$, by reaction of $[Au(acac)(PPh_3)]$ (acac = acetylacetonate) or $[Au(tht)_2]ClO_4$ (tht = tetrahydrothiophene) with the triphosphine and their reactions with other gold(I) complexes. The structures of two forms of $[(O)Ph_2PC(PPh_2AuPPh_2)_2CPPh_2(O)]$ have been established by single-crystal X-ray analysis.

Results and Discussion

The tetrahydrothiophene ligand in $[Au(tht)_2]ClO_4$ can easily be displaced by the triphosphine $CH(PPh_2)_3$ to give dinuclear, $[Ph_2PCH(PPh_2AuPPh_2)_2CHPPh_2][ClO_4]_2$ **1** (molar ratio 1:1), or trinuclear complexes, $[CH(PPh_2AuPPh_2)_3CH][ClO_4]_3$ **2** (molar ratio 3:2) (see Scheme 1). Complex **2** can also be obtained by equimolecular reaction of **1** and $[Au(tht)_2]ClO_4$. It has been reported[10] that complex **2** could not be obtained either by prolonged heating of $[AuCl_4]^-$ and $CH(PPh_2)_3$ in the presence of 2,2′-thiodiethanol, or by reaction of $[Au_3Cl\{CH(PPh_2)_3\}_2][ClO_4]_2$ with silver(I).

Complex **1** reacts with NaH or $NBu_4(acac)$ in diethyl ether to give the neutral methanide complex **3** (see Scheme 1) as the result of the precipitation of the perchlorate anion (as the sodium or NBu_4 salt) and the simultaneous deprotonation of the CH group. The protonation of complex **3** with $HClO_4$ gives the cationic complex **1**. The same methanide complex **3** can also be obtained by reaction of $[Au(acac)(PPh_3)]$ and the triphosphine.

The presence of a free PPh_2 group in complexes **1** or **3** can be confirmed through reactions with gold(I) derivatives containing one weakly co-ordinated ligand such as tetrahydrothiophene $\{$*e.g.* $[AuX(tht)]$ (X = C_6F_5 or Cl) or $[Au(PPh_3)(tht)]ClO_4\}$, which afford neutral (**4** or **5**) or cationic (**6** or **7**) tetranuclear complexes. No co-ordination to the C-methanide of complex **3**, such as occurs for other methanide complexes of gold,[3] has been observed. The reaction of complex **1** with $[Au(acac)(PPh_3)]$ leads to the deprotonation of the CH group and formation of acetylacetone, but the fragment $[Au(PPh_3)]^+$ is co-ordinated to the free phosphorus instead of the C-methanide as observed for other derivatives,[5,11] and the tetranuclear complex **6** is formed.

The free terminal PPh_2 of the triphosphine of complex **3** can be oxidized; thus the reaction with H_2O_2 leads to complex **8**.

The reaction of $[Au(C_6F_5)(tht)]$ with the triphosphine leads to the displacement of the tetrahydrothiophene ligand and formation of a trinuclear complex **9**, Scheme 2.

Complexes **1**, **2** and **4**–**9** are air- and moisture-stable white (**1**, **2**, **7**–**9**) or pale yellow (**4**–**6**) solids. The yellow complex **3** slowly oxidizes in solution or in solid state to give complex **8**. The cationic derivatives **1**, **6** or **7** behave as 1:2 electrolytes in acetone solutions (complex **2** is insoluble in acetone), and their IR spectra show bands at 1100s (br) and 620m cm^{-1}, which are characteristic of the ClO_4^- anion. In contrast, acetone solutions of complexes **3**–**5**, **8** and **9** are non-conducting.

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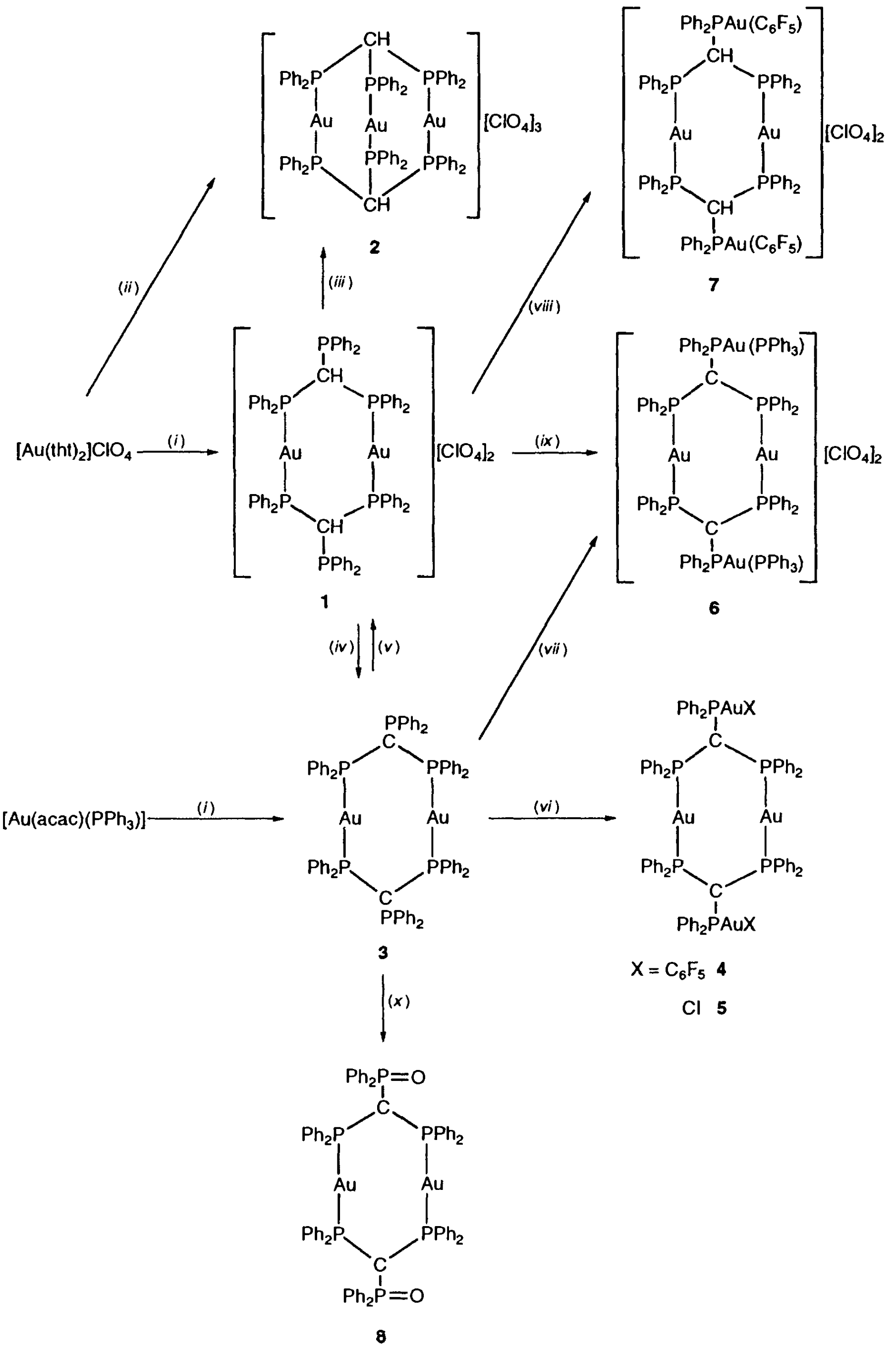
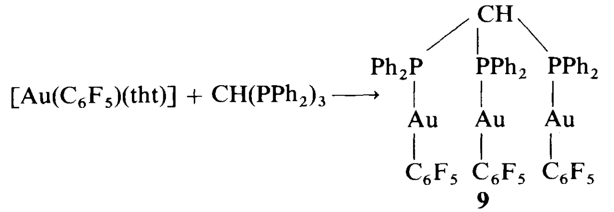
† *Supplementary data available:* Further details of the structure determination (complete bond lengths and angles, H-atom coordinates, structure factors, thermal parameters) have been deposited at the Fachinformationszentrum Karlsruhe, Gesellschaft für Wissenschaftlich-technische Information mbH, 76344 Eggenstein-Leopoldshafen, Germany. Any request for this material should quote a full literature citation and the reference numbers CSD 400362 and 400363.



Scheme 1 (*i*) $CH(PPh_2)_3$ (1:1), (*ii*) $CH(PPh_2)_3$ (3:2), (*iii*) $[Au(tht)_2]ClO_4$, (*iv*) NaH or $NBu_4(acac)$, (*v*) $HClO_4$, (*vi*) [AuX(tht)], (*vii*) $[Au(PPh_3)(tht)]ClO_4$, (*viii*) $[Au(C_6F_5)(tht)]$, (*ix*) $[Au(acac)(PPh_3)]$, (*x*) H_2O_2



Scheme 2

The methanide group in complexes **3**–**6** and **8** gives rise to a strong absorption in the IR spectra (at 896 **3**, 903 **4**, 902 **5**, 909 **6** or 910 **8** cm^{-1}), probably assignable to the CP_3 system,[12,13] which is absent in the protonated complexes **1**, **2**, **7** and **9**. The IR spectra of the pentafluorophenyl complexes **4**, **7** and **9** show bands at approximately 1500vs, 955vs and 790m cm^{-1} arising from the C_6F_5 group. Complex **5** has a medium ν(Au–Cl) band at 325 cm^{-1} and complex **8** has a strong ν(P=O) band at 1153 cm^{-1}.

Compound **3** was also characterized by fast atom bombardment (FAB) mass spectrometry. The highest peak at *m*/*z* = 1529 (12%) corresponds to the parent ion; other peaks appear at *m*/*z* = 961 ($[Au_2C(PPh_2)_3]^+$) or 841 ($[AuC(PPh_2)_3]^+$).

The $^{31}P-\{^1H\}$ NMR spectra of complexes **3**, **5** and **8** show a triplet and a quintuplet for the phosphorus of the ring $C(PPh_2AuPPh_2)_2C$ and the other PPh_2 respectively (see Table 2), probably due to a virtual coupling between the two different phosphorus environments; the coupling constant for the methanide complex **3** (26.5 Hz) is higher than for complexes **5** and **8** (6.4 and 6.0, respectively). Complex **7** shows a similar pattern with a triplet and a multiplet due to the coupling with the fluorine atoms of the C_6F_5 groups. The spectrum of complex **1** at room temperature shows only a broad singlet at δ 26.5, but on cooling to −55 °C the signal splits into two broad singlets. The coupling constants for complexes **1** (at −55 °C) and **4** are probably so small that only broad singlets are observed. The

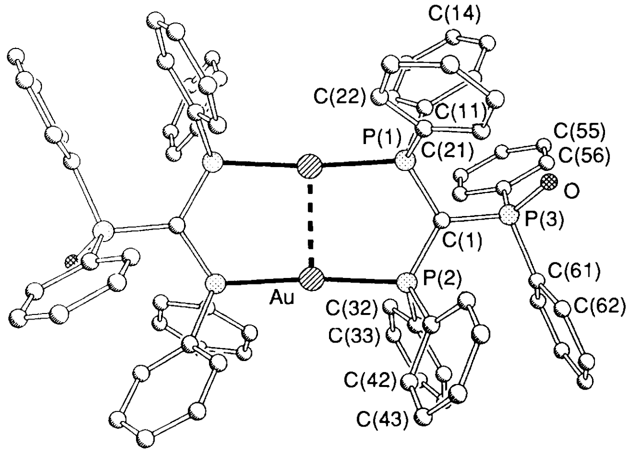


Fig. 1 The molecule of complex **8a** in the crystal, showing the numbering scheme of the asymmetric unit. Radii are arbitrary

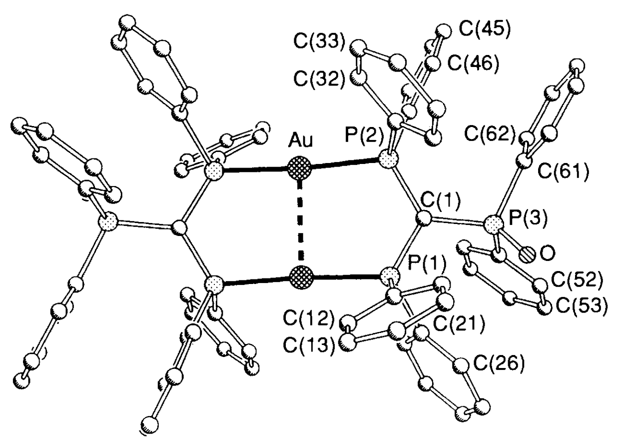


Fig. 2 The molecule of complex **8b** in the crystal, showing the numbering scheme of the asymmetric unit. Radii are arbitrary

Table 1 Analytical and physical data of the complexes

Complex	Yield (%)	M.p.[b]/°C	Analysis[a] (%) C	H	Λ_M[c]
$[Ph_2PCH(PPh_2AuPPh_2)_2CHPPh_2][ClO_4]_2$ **1**	95	208	50.75 (51.35)	3.4 (3.6)	189
$[CH(PPh_2AuPPh_2)_3CH][ClO_4]_3$ **2**	93	240	43.45 (43.8)	2.95 (3.1)	*d*
$[Ph_2PC(PPh_2AuPPh_2)_2CPPh_2]$ **3**	87	134	57.6 (58.1)	4.0 (3.95)	10
$[\{(C_6F_5)Au\}Ph_2PC(PPh_2AuPPh_2)_2CPPh_2\{Au(C_6F_5)\}]$ **4**	60	170	45.35 (45.7)	2.6 (2.65)	12
$[(ClAu)Ph_2PC(PPh_2AuPPh_2)_2CPPh_2(AuCl)]$ **5**	74	188	44.75 (44.55)	3.5 (3.55)	8
$[(Ph_3PAu)Ph_2PC(PPh_2AuPPh_2)_2CPPh_2(AuPPh_3)][ClO_4]_2$ **6**	80	168	50.35 (49.95)	3.65 (3.4)	255
$[\{(C_6F_5)Au\}Ph_2PCH(PPh_2AuPPh_2)_2CHPPh_2\{Au(C_6F_5)\}][ClO_4]_2$ **7**	85	228	41.6 (42.0)	2.55 (2.55)	198
$[(O)Ph_2PC(PPh_2AuPPh_2)_2CPPh_2(O)]$ **8**	60	130	57.35 (56.95)	3.0 (3.85)	19
$[CH\{PPh_2Au(C_6F_5)\}_3]$ **9**	83	220	39.4 (39.75)	1.85 (1.9)	1

[a] Calculated values in parentheses. [b] With decomposition. [c] In acetone, Ω^{-1} cm^2 mol^{-1}. [d] Insoluble in acetone.

Table 2 NMR data of the complexes

Compound	δ_H[a](CH)	δ_P[b] Au–P	PPh$_2$	δ_F[c] *o*-F	*p*-F	*m*-F
1	6.73 (m)	4.44 (br s)[d]	−14.5 (br s)[d]			
2	6.34 (m)	45.8 (s)				
3		50.3 (t) (26.5)	5.1 (q)			
4		48.3 (br s)	43.1 (br s)	−115.2 (m)	−159.6 (t) (20.6)	−162.8 (m)
5		47.5 (t) (6.4)	30.3 (q)			
6		47.7 (s)	*e*			
7	6.88 (m)	50.8 (t) (16.2)	39.8 (q)	−114.5 (m)	−156.5 (t) (20.7)	−160.7 (m)
8		44.2 (t) (6.0)	34.2 (q)			
9	6.04 (q) (10.2)	40.3 (m)		−115.9 (m)	−158.9(t) (19.5)	−163.6 (m)

[a] Recorded in $CDCl_3$ at 300 MHz referenced to internal $SiMe_4$. Coupling constants in Hz are given in parentheses; s = singlet, t = triplet, q = quintet, m = multiplet. [b] Referenced to external H_3PO_4. [c] Referenced to external $CFCl_3$. [d] At −55 °C. [e] AB system δ_A 45.7, δ_B 45.3, $J(AB)$ 302 Hz.

spectrum of complex **6** corresponds to an ABX_2 system with J(AX) and J(BX) ≈ 0. In complexes **2** and **9** only one resonance is observed and appears as a singlet (**2**) or as multiplet (**9**), due to the coupling with the fluorine atoms of the C_6F_5 groups.

The ^1H NMR spectra of complexes **1**, **2**, **7** and **9** show a multiplet at *ca.* δ 6.8 corresponding to a CH proton. The ^{19}F NMR spectra show three groups of signals in all the pentafluorophenyl complexes (**4**, **7** and **9**), as expected for one C_6F_5 group.

The structures of two forms of complex **8** (**8a** and **8b**) have been established by X-ray diffraction (Figs. 1 and 2). Both are monoclinic, possess a symmetry centre and crystallize as 1:4 dichloromethane solvates. The two modifications display very similar molecular structures; the major difference lies in the conformations of the eight membered rings, which are chair forms in both modifications but much flatter for **8a** than **8b** (mean absolute torsion angle excluding Au atoms being 23 and 37°, respectively).

The co-ordination at the gold atoms is slightly distorted from linear with P(2)–Au–P(1′) 172.17(7)° (modification **8a**), 174.64(8)° (modification **8b**) probably because of the very short Au • • • Au contacts 2.7639(11) (**8a**) and 2.7988(12) (**8b**) Å. The Au • • • Au interaction in modification **8a** is similar to that found in the complex $[Pr_2NC(SAuS)_2CNPr_2]$, 2.76(1) Å;[14] these are among the shortest in gold(I) dimers bridged by difunctional ligands.[15–17]

Table 3 Details of data collection and structure refinement for **8a**·$4CH_2Cl_2$ and **8b**·$4CH_2Cl_2$

	8a	**8b**
Space group	$P2_1/c$	$P2_1/n$
a/Å	11.245(4)	12.866(5)
b/Å	13.795(4)	19.842(7)
c/Å	23.806(6)	14.519(6)
β/°	93.27(2)	95.09(3)
U/Å^3	3687(2)	3692(3)
D_c/Mg m^{-3}	1.712	1.710
μ(Mo-Kα)/mm^{-1}	4.44	4.4
Crystal size/mm	0.40 × 0.20 × 0.15	0.84 × 0.44 × 0.28
Transmission	0.77–0.82	0.49–0.91
Reflections measured	7880	7064
Unique reflections	6519	6490
R_{int}	0.038	0.031
Weighting scheme, a,b	0.0501, 22.0572	0.1084, 42.6653
$R[F > 4\sigma(F)]$	0.041	0.060
$R'(F^2$, all reflections)	0.123	0.180
Restraints	342	354
Parameters	433	423
$S(F^2)$	1.025	1.021

Details in common: molecular formula $C_{78}H_{68}Au_2Cl_8O_2P_6$, M = 1900.7, monoclinic, Z = 2, F(000) = 1872, $2\theta_{max}$ = 50°.

The Au–P distances are slightly longer in the modification **8b** 2.335(2) and 2.335(2) Å [compared with 2.324(2) and 2.326(2) Å], although the differences are not highly significant, and are similar to those found in gold phosphine complexes. The P–C(1) bond lengths lie in the range 1.746(9)–1.794(9) Å and are shorter than the P–C distances in free $CH(PPh_2)_3$[18] [1.867(1)–1.877(1) Å] or in other phosphine derivatives. This difference arises from a certain degree of multiple P–C bonding in the methanide ligand. The angles around the central methanide carbon fall in the range 116.1(5)–127.0(6) Å, close to the ideal value of 120° for sp^2 hybridisation. The smallest angles are observed for the P–C(1)–P units that bridge both gold atoms. C(1) lies 0.02 (**8a**), 0.09 (**8b**) Å out of the plane formed by the three phosphorus atoms. The distances P–O 1.491(6) (**8a**) and 1.495(7) (**8b**) Å compare well with the values reported for other phosphine oxides and correspond to normal double bonds.[19]

Experimental

The instrumentation and general experimental techniques were as described earlier.[5] The NMR spectra were recorded on Varian XL 200 and 300 spectrometers in $CDCl_3$. Chemical shifts are cited relative to $SiMe_4$ (^1H), 85% H_3PO_4 (external ^{31}P) and $CFCl_3$ (external, ^{19}F). Mass spectra were recorded on a VG Autospec. The yields, melting points, elemental analyses and conductivities for the new complexes are listed in Table 1 and the NMR data in Table 2. All reactions were carried out at room temperature and, except for complex **8**, under a nitrogen atmosphere.

Syntheses.—$[Ph_2PCH(PPh_2AuPPh_2)_2CHPPh_2][ClO_4]_2$ **1**. To a dichloromethane solution (30 cm^3) of $[Au(tht)_2]ClO_4$[20] (0.236 g, 0.5 mmol) was added $CH(PPh_2)_3$ (0.284 g, 0.5 mmol). After stirring for 1 h a white precipitate of complex **1** was filtered off. Evaporation of the filtrate to *ca.* 5 cm^3 and addition of diethyl ether (15 cm^3) rendered a second crop.

$[CH(PPh_2AuPPh_2)_3CH][ClO_4]_3$ **2**. (*a*) To a dichloro-

Table 4 Atomic coordinates (× 10^4) for complex **8a**

Atom	x	y	z
Au	6 149.9(3)	5 356.9(2)	5 043.0(1)
P(1)	4 097(2)	3 988(2)	4 071.0(8)
P(2)	6 651(2)	4 633(2)	4 207.0(8)
P(3)	5 898(2)	2 992(2)	3 352.7(9)
O	5 135(5)	3 063(5)	2 821(2)
C(1)	5 579(6)	3 850(6)	3 876(3)
C(11)	3 357(7)	2 809(6)	4 045(3)
C(12)	3 260(8)	2 292(6)	4 540(4)
C(13)	2 766(9)	1 372(7)	4 536(5)
C(14)	2 376(9)	964(7)	4 030(5)
C(15)	2 438(8)	1 457(7)	3 535(5)
C(16)	2 919(8)	2 390(7)	3 545(4)
C(21)	3 129(7)	4 697(6)	3 578(3)
C(22)	2 205(7)	5 223(6)	3 802(4)
C(23)	1 396(8)	5 731(7)	3 451(4)
C(24)	1 500(8)	5 733(8)	2 876(4)
C(25)	2 418(8)	5 238(8)	2 652(4)
C(26)	3 244(8)	4 718(7)	2 994(3)
C(31)	8 030(7)	3 988(6)	4 436(3)
C(32)	7 944(8)	3 356(6)	4 886(3)
C(33)	8 942(8)	2 854(7)	5 097(4)
C(34)	10 021(8)	3 008(7)	4 864(4)
C(35)	10 123(8)	3 645(7)	4 427(4)
C(36)	9 129(7)	4 142(7)	4 205(4)
C(41)	7 081(7)	5 620(6)	3 756(3)
C(42)	7 994(8)	6 258(6)	3 947(4)
C(43)	8 237(9)	7 071(7)	3 630(4)
C(44)	7 557(9)	7 293(8)	3 153(4)
C(45)	6 662(9)	6 680(7)	2 962(4)
C(46)	6 422(8)	5 852(7)	3 256(3)
C(51)	5 803(8)	1 783(7)	3 654(4)
C(52)	5 985(8)	1 591(7)	4 227(4)
C(53)	4 929(10)	639(8)	4 425(5)
C(54)	5 681(10)	− 107(8)	4 053(5)
C(55)	5 503(10)	64(7)	3 491(5)
C(56)	5 550(8)	1 013(7)	3 280(4)
C(61)	7 463(8)	3 095(7)	3 190(4)
C(62)	7 757(9)	3 797(8)	2 813(4)
C(63)	8 923(9)	3 874(10)	2 653(4)
C(64)	9 790(10)	3 250(9)	2 867(5)
C(65)	9 484(9)	2 533(9)	3 226(6)
C(66)	8 313(8)	2 443(8)	3 391(5)
C(2)	3 814(10)	7 484(8)	3 522(4)
Cl(1)	2 709(3)	8 320(3)	3 670.1(15)
Cl(2)	4 657(3)	7 162(2)	4 135.5(13)
C(3)	385(19)	4 378(13)	712(7)
Cl(3)	345(23)	5 130(22)	282(9)
Cl(4)	793(13)	4 786(10)	1 287(6)

methane solution (30 cm^3) of $CH(PPh_2)_3$ (0.284 g, 0.50 mmol) was added $[Au(tht)_2]ClO_4$ (0.354 g, 0.75 mmol). After stirring for 30 min the solvent was evaporated, the white precipitate of complex **2** was filtered off and washed with dichloromethane (2 × 2 cm^3).

(*b*) This complex can also be prepared by treatment of a dichloromethane suspension (20 cm^3) of complex **1** (0.432 g, 0.25 mmol) with $[Au(tht)_2]ClO_4$ (0.118 g, 0.25 mmol). The resulting clear solution was stirred for 30 min and a white precipitate of **2** was formed when the solvent was evaporated.

$[Ph_2PC(PPh_2AuPPh_2)_2CPPh_2]$ **3**. To a solution of $CH(PPh_2)_3$ (0.284 g, 0.5 mmol) in diethyl ether (30 cm^3) was added $[Au(acac)(PPh_3)]$[21] (0.279 g, 0.5 mmol). After stirring the mixture for 2 h the solvent was concentrated to *ca.* 5 cm^3. Addition of *n*-hexane (20 cm^3) gave complex **3** as a yellow solid.

$[(XAu)Ph_2PC(PPh_2AuPPh_2)_2CPPh_2(AuX)]$ ($X = C_6F_5$ **4** or Cl **5**). To a solution of complex **3** (0.39 g, 0.25 mmol) in dichloromethane (20 cm^3) was added $[Au(C_6F_5)(tht)]$[22,23] (0.226 g, 0.5 mmol) or $[AuCl(tht)]$[23] (0.16 g, 0.5 mmol). After stirring for 1 h the solution was evaporated to *ca.* 5 cm^3 and addition of *n*-hexane (20 cm^3) led to precipitation of complexes **4** or **5** as pale yellow solids.

Table 5 Selected bond lengths (Å) and angles (°) for complex **8a**

Au–P(2)	2.324(2)	Au–P(1′)	2.326(2)
Au ··· Au′	2.7639(11)	P(1)–C(1)	1.766(7)
P(1)–C(11)	1.826(9)	P(1)–C(21)	1.838(8)
P(2)–C(1)	1.770(8)	P(2)–C(41)	1.817(8)
P(2)–C(31)	1.844(8)	P(3)–O	1.491(6)
P(3)–C(1)	1.770(8)	P(3)–C(51)	1.820(10)
P(3)–C(61)	1.830(9)		
P(2)–Au–P(1′)	172.17(7)	P(2)–Au–Au′	93.14(5)
P(1′)–Au–Au′	92.65(6)	C(1)–P(1)–C(11)	109.3(4)
C(1)–P(1)–C(21)	115.0(4)	C(11)–P(1)–C(21)	101.6(4)
C(1)–P(1)–Au′	116.3(3)	C(11)–P(1)–Au′	107.4(3)
C(21)–P(1)–Au′	106.0(2)	C(1)–P(2)–C(41)	113.1(4)
C(1)–P(2)–C(31)	112.2(4)	C(41)–P(2)–C(31)	106.8(4)
C(1)–P(2)–Au	116.8(2)	C(41)–P(2)–Au	105.6(3)
C(31)–P(2)–Au	101.2(2)	O–P(3)–C(1)	115.0(4)
O–P(3)–C(51)	110.6(4)	C(1)–P(3)–C(51)	108.5(4)
O–P(3)–C(61)	109.2(4)	C(1)–P(3)–C(61)	109.5(4)
C(51)–P(3)–C(61)	103.5(4)	P(1)–C(1)–P(3)	119.3(4)
P(1)–C(1)–P(2)	116.5(4)	P(3)–C(1)–P(2)	124.2(4)

Primed atoms related to equivalent unprimed atoms by symmetry operation $-x + 1, -y + 1, -z + 1$.

$[(Ph_3PAu)Ph_2PC(PPh_2AuPPh_2)_2CPPh_2(AuPPh_3)][ClO_4]_2$ **6**. (*a*) To a dichloromethane solution (20 cm^3) of complex **3** (0.39 g, 0.25 mmol) was added $[Au(PPh_3)(tht)]ClO_4$[20] (0.323 g, 0.5 mmol) and the mixture stirred for 1 h. Concentration of the solution to *ca.* 5 cm^3 and addition of diethyl ether (15 cm^3) gave a pale yellow solid of complex **6**.

(*b*) A dichloromethane suspension (20 cm^3) of complex **1** (0.432 g, 0.25 mmol) and $[Au(acac)(PPh_3)]$ (0.279 g, 0.5 mmol) was stirred for 2 h. The solution was evaporated to *ca.* 5 cm^3 and addition of diethyl ether (20 cm^3) led to complex **6**.

$[\{(C_6F_5)Au\}Ph_2PCH(PPh_2AuPPh_2)_2CHPPh_2\{Au(C_6F_5)\}][ClO_4]_2$ **7**. To a suspension of complex **1** (0.432 g, 0.25 mmol) in dichloromethane (30 cm^3) was added $[Au(C_6F_5)(tht)]$ (0.226 g, 0.5 mmol). The resulting clear solution was stirred for 1 h and the solution was concentrated to *ca.* 5 cm^3. Addition of 20 cm^3 of diethyl ether gave **7** as a white solid.

$[(O)Ph_2PC(PPh_2AuPPh_2)_2CPPh_2(O)]$ **8**. To a dichloromethane solution of complex **3** (0.39 g, 0.25 mmol) was added two drops of H_2O_2 (30% in H_2O). The solution was stirred for 30 min and filtered through a 1 cm layer of anhydrous magnesium sulfate. The solution was concentrated to *ca.* 5 cm^3. Addition of diethyl ether (20 cm^3) led to precipitation of **8** as a white solid.

$[CH\{PPh_2Au(C_6F_5)\}_3]$ **9**. To a diethyl ether solution of $[Au(C_6F_5)(tht)]$ (0.407 g, 0.9 mmol) was added $CH(PPh_2)_3$ (0.17 g, 0.3 mmol). After stirring the mixture for 1 h the resulting white solid **9** was filtered off and washed with diethyl ether (2 × 5 cm^3).

X-Ray Structure Determination of Complex **8**.—The following conditions were common to the structure determinations of both modifications: Simens R3 diffractometer with an LT-2 low-temperature attachment, monochromated Mo-Kα radiation, absorption correction based on ψ scans, and cell constants refined from 2θ values of 50 reflections in the range 2θ 20–23°. Solutions by heavy-atom method, full-matrix least-squares refinement on F^2 (program system SHELXL 92;[24] non-hydrogen atoms were refined anisotropically, phenyl rings were constrained to be planar and to have two-fold symmetry, H atoms were included using a riding model. Weighting schemes were of the form $w^{-1} = \sigma^2(F^2) + (aP)^2 + bP$, where

Table 6 Atomic coordinates (× 10^4) for complex **8b**

Atom	*x*	*y*	*z*
Au	5981.2(3)	5110.0(2)	4681.6(2)
P(1)	3708(2)	3983.9(12)	4305(2)
P(2)	5761(2)	4258.4(12)	3572(2)
P(3)	3902(2)	3587.8(12)	2317(2)
O	3447(6)	2905(3)	2450(5)
C(1)	4473(7)	3984(4)	3352(6)
C(11)	3816(7)	3195(5)	4998(7)
C(12)	3754(8)	3239(5)	5945(7)
C(13)	3827(10)	2661(6)	6484(8)
C(14)	3978(9)	2045(6)	6081(7)
C(15)	4038(8)	1998(5)	5143(8)
C(16)	3963(8)	2577(5)	4591(7)
C(21)	2324(7)	4004(4)	3899(6)
C(22)	1869(8)	4628(6)	3743(8)
C(23)	818(9)	4664(7)	3442(10)
C(24)	244(9)	4105(6)	3307(10)
C(25)	682(8)	3482(6)	3456(8)
C(26)	1728(7)	3427(5)	3762(7)
C(31)	6685(7)	3578(5)	3890(7)
C(32)	7695(7)	3747(5)	4275(7)
C(33)	8376(8)	3248(6)	4595(8)
C(34)	8090(9)	2574(6)	4548(9)
C(35)	7090(9)	2402(5)	4164(9)
C(36)	6399(8)	2909(5)	3850(7)
C(41)	6272(7)	4652(5)	2570(7)
C(42)	5868(8)	5288(5)	2291(7)
C(43)	6257(9)	5630(5)	1562(7)
C(44)	7048(9)	5344(6)	1095(8)
C(45)	7475(9)	4728(6)	1382(8)
C(46)	7088(8)	4382(5)	2114(7)
C(51)	2900(7)	4148(5)	1767(6)
C(52)	2039(7)	3858(5)	1290(7)
C(53)	1255(8)	4256(6)	855(8)
C(54)	1338(9)	4950(5)	897(8)
C(55)	2199(8)	5244(5)	1371(8)
C(56)	2971(8)	4843(5)	1811(7)
C(61)	4837(8)	3535(4)	1452(6)
C(62)	4964(8)	4013(5)	781(7)
C(63)	5661(9)	3908(6)	127(7)
C(64)	6230(10)	3326(6)	122(8)
C(65)	6110(10)	2844(6)	792(8)
C(66)	5441(9)	2943(6)	1456(8)
C(2)	6524(14)	3081(9)	6887(11)
Cl(1)	6080(5)	3231(2)	7929(3)
Cl(2)	6445(5)	3820(3)	6212(3)
C(3)	1378(16)	3860(12)	7152(14)
Cl(3)	1153(4)	4080(3)	6027(4)
Cl(4)	236(5)	3746(3)	7752(4)

Table 7 Selected bond lengths (Å) and angles (°) for complex **8b**

Au–P(2)	2.335(2)	Au–P(1′)	2.335(2)
Au ··· Au′	2.7988(12)	P(1)–C(1)	1.768(10)
P(1)–C(21)	1.827(10)	P(1)–C(11)	1.859(10)
P(2)–C(1)	1.746(9)	P(2)–C(41)	1.824(10)
P(2)–C(31)	1.831(10)	P(3)–O	1.495(7)
P(3)–C(1)	1.794(9)	P(3)–C(61)	1.817(11)
P(3)–C(51)	1.831(10)		
P(2)–Au–P(1′)	174.64(8)	P(2)–Au–Au′	93.27(6)
P(1′)–Au–Au′	91.21(6)	C(1)–P(1)–C(21)	110.0(4)
C(1)–P(1)–C(11)	113.8(4)	C(21)–P(1)–C(11)	102.5(4)
C(1)–P(1)–Au′	114.7(3)	C(21)–P(1)–Au′	107.1(3)
C(11)–P(1)–Au′	107.9(3)	C(1)–P(2)–C(41)	113.0(4)
C(1)–P(2)–C(31)	113.6(4)	C(41)–P(2)–C(31)	104.1(4)
C(1)–P(2)–Au	114.0(3)	C(41)–P(2)–Au	102.1(3)
C(31)–P(2)–Au	108.8(3)	O–P(3)–C(1)	115.2(4)
O–P(3)–C(61)	109.1(4)	C(1)–P(3)–C(61)	111.0(4)
O–P(3)–C(51)	109.7(4)	C(1)–P(3)–C(51)	108.6(4)
C(61)–P(3)–C(51)	102.5(4)	P(2)–C(1)–P(1)	116.2(5)
P(2)–C(1)–P(3)	127.0(6)	P(1)–C(1)–P(3)	116.1(5)

Primed atoms related to equivalent unprimed atoms by symmetry operation $-x + 1, -y + 1, -z + 1$.

$P = [F_o^2 + 2F_c^2]/3$. Further details are given in Table 3, atom coordinates for **8a** in Table 4 and selected bond lengths and angles in Table 5 and for **8b** atom coordinates in Table 6 and selected bond lengths and angles in Table 7.

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

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