Synthesis and Structural Characterization of Polynuclear Complexes containing the Eight-electron Donor Bis(diphenylphosphino)methanediide Ligand†

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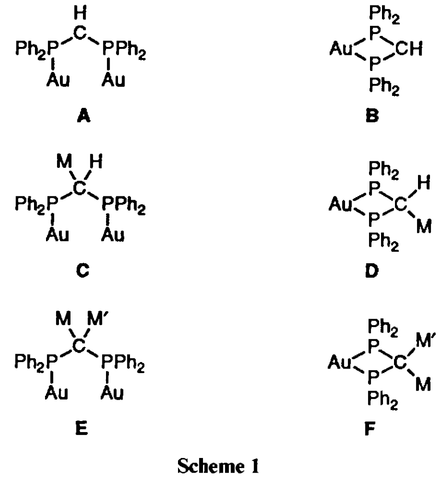
The compound $[AuR_2\{(Ph_2P)_2CH\}]$ ($R = C_6F_5$) reacts with various gold(I) or silver(I) compounds possessing a labile ligand such as tetrahydrothiophene or perchlorate to give $[AuR_2\{(Ph_2P)_2CH(ML)\}]ClO_4$ ($ML = AuPPh_3$, $AuCH_2PPh_3$ or $AgPPh_3$). Treatment of these derivatives with $[Au(acac)(PPh_3)]$ or $[N(PPh_3)_2][Au(acac)Cl]$ (acac = acetylacetonate) leads to $[AuR_2\{(Ph_2P)_2C(AuPPh_3)(ML)\}]ClO_4$ or $[AuR_2\{(Ph_2P)_2C(AuPPh_3)(AuCl)\}]$, in which the doubly deprotonated bis(diphenylphosphino)methanediide ligand is an eight-electron donor. The compound $[AuR_2\{(Ph_2P)_2C(AuPPh_3)_2\}]ClO_4$ can also be obtained by reaction of $[AuR_2\{(Ph_2P)_2CH_2\}]ClO_4$ and $[Au(acac)(PPh_3)]$ in 1:2 molar ratio. The reaction of $[AuR_2\{(Ph_2P)_2CH(AuR)\}]$ with $[Au(acac)(PPh_3)]$ or $[N(PPh_3)_2][Au(acac)Cl]$ gives the trinuclear complexes $[AuR_2\{(Ph_2P)_2C(AuR)(AuPPh_3)\}]$ or $[N(PPh_3)_2][AuR_2\{(Ph_2P)_2C(AuR)(AuCl)\}]$, whereas it reacts with $[N(PPh_3)_2][Au(acac)_2]$ (molar ratio 2:1) affording the pentanuclear complex $[N(PPh_3)_2][\{AuR_2[(Ph_2P)_2C(AuR)]\}_2Au]$. Another pentanuclear derivative $[\{AuR_2[(Ph_2P)_2C(AuPPh_3)]\}_2Au]ClO_4$ is obtained by treatment of $[\{AuR_2[(Ph_2P)_2CH]\}_2Au]ClO_4$ with 2 equivalents of $[Au(acac)(PPh_3)]$. The compounds were characterized by elemental analysis, IR and NMR spectroscopy, and some by fast atom bombardment mass spectrometry. The crystal structure of $[AuR_2\{(Ph_2P)_2C(AuPPh_3)_2\}]ClO_4\cdot CH_2Cl_2$ was confirmed by X-ray diffraction analysis. The complex contains a triangular Au_2C unit with a short Au ··· Au contact of 2.826(2) Å and a narrow Au(1)–C(1)–Au(2) angle of 85.4(7)°.

Bis(diphenylphosphino)methanide (dppm − H) has been studied as a versatile ligand in co-ordination chemistry. Usually, it acts as a bi- or tri-dentate ligand by bonding to one, two or three metal atoms through the phosphorus and the central carbon atom.[1]

We have reported the synthesis of a variety of methanide gold-(I) and -(III) complexes.[2] Our studies have focused on obtaining methanide complexes from diphosphine derivatives using NaH as deprotonating agent; this procedure has allowed us to prepare complexes with co-ordination form **B**[3] (Scheme 1), while form **A** was achieved starting from [AuX(ylide)] derivatives by reaction with dppm.[4,5] Forms **A** and **B** possess an excess of electron density, which has been used to co-ordinate to further gold or silver fragments[3–5] (forms **C** and **D**). However, our efforts to obtain the ligand as eight-electron donor forms **E** or **F** had been unsuccessful.

Very few examples of complexes with the ligand dppm − 2H have been reported; these were the iron(III) complexes $[Fe(CNPh)_3L\{(Ph_2P)_2C(AuPPh_3)_2\}]^{n+}$ (L = I or CNPh),[6] the mercury derivative $[Hg_2(O_2CMe)_2\{(Ph_2P)_2C(HgO_2CMe)_2]$[7] and the mixed palladium and platinum complex $[\{Pd(\mu\text{-}Cl)_2Pt[(Ph_2P)_2C]\}_n]$.[8] A possible alternative route to such complexes was suggested by the use of acetylacetonate (acac) complexes, mainly by Vicente and co-workers, as excellent precursors for abstracting one proton and leaving one or two free co-ordination sites.[9,10]



Scheme 1

Here we have studied the reactivity of bis(diphenylphosphino)methane or bis(diphenylphosphino)methanide complexes of gold(III) towards $[Au(acac)(PPh_3)]$, $[N(PPh_3)_2][Au(acac)Cl]$ or $[N(PPh_3)_2][Au(acac)_2]$, leading to complexes

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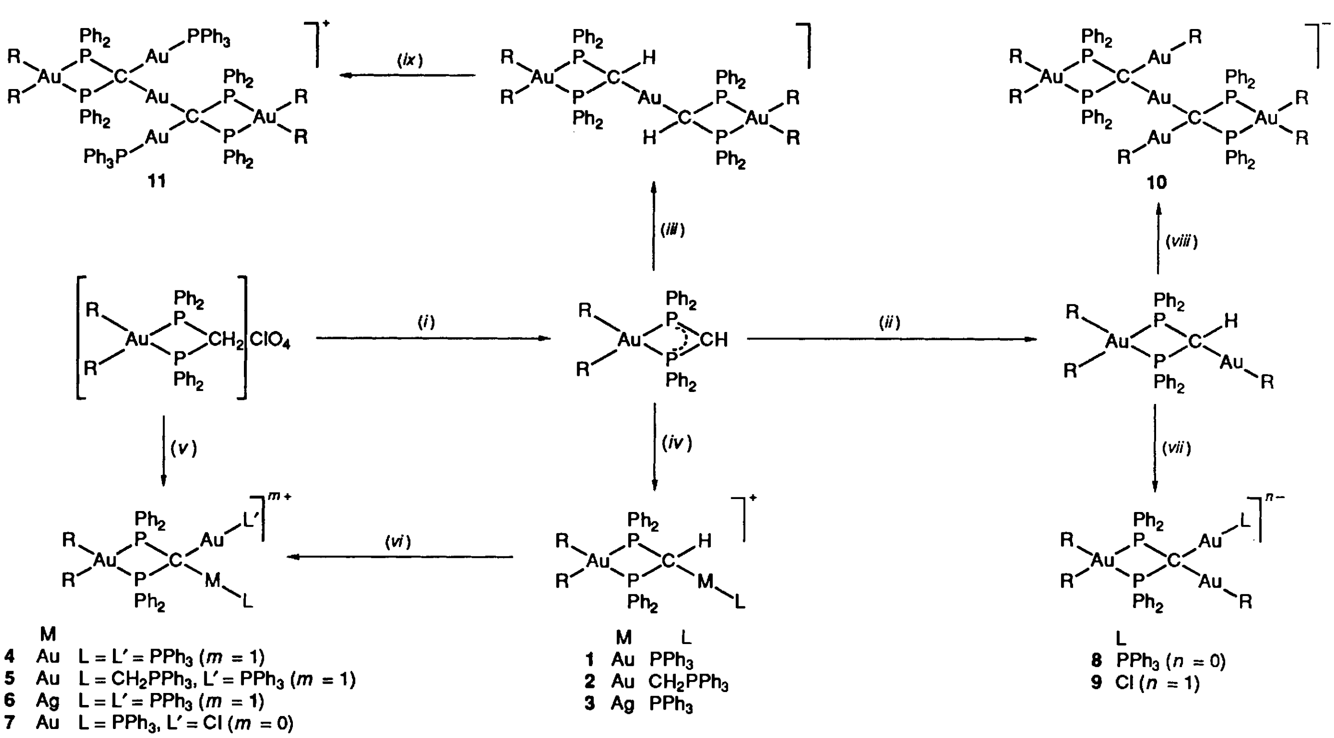
† *Supplementary data available:* further details of the structure determination (complete bond lengths and angles, H-atom coordinates, structure factors, thermal parameters) have been deposited at the Fachinformationszentrum Karlsruhe, Gesellschaft für Wissenschaftlich-technische Information mbH, W-7514 Eggenstein-Leopoldshafen 2, Germany. Any request for this material should quote a full literature citation and the reference number CSD 56550.



Scheme 2 R = C_6F_5. (*i*) NaH; (*ii*) [AuR(tht)]; (*iii*) $[Au(tht)_2]ClO_4$; (*iv*) $[ML]^+$; (*v*) 2[Au(acac)L]; (*vi*) $[Au(acac)L']^{n-}$; (*vii*) $[Au(acac)L]^{n-}$; (*viii*) $[Au(acac)_2]^-$; (*ix*) $2[Au(acac)(PPh_3)]$

of different structural types. We have succeeded in obtaining complexes containing the eight-electron donor ligand dppm − 2H.

Results and Discussion

The bis(diphenylphosphino)methanide complex $[Au(C_6F_5)_2\{(Ph_2P)_2CH\}]$ possesses an excess of electron density on the methanide carbon, causing it to act as a C-donor nucleophile. Therefore it can displace weakly co-ordinated ligands such as tetrahydrothiophene (tht) or perchlorate from $[Au(tht)L]ClO_4$ or $[Ag(OClO_3)(PPh_3)]$, forming the binuclear complexes $[Au(C_6F_5)_2\{(Ph_2P)_2CH(ML)\}]ClO_4$ (ML = $AuPPh_3$ **1**, $AuCH_2PPh_3$ **2** or $AgPPh_3$ **3**) (see Scheme 2).

Complexes **1**–**3** are air- and moisture-stable white solids. In acetone solution they behave as 1:1 electrolytes. Their IR spectra show bands at 1100s (br) and 625m cm^{-1} which arise from the ClO_4^- anion (T_d), and also at 1507m, 965m, 808m and 798m cm^{-1} consistent with the presence of C_6F_5 groups linked to a gold(III) centre, the last two confirming the *cis* disposition.[11] The band at 581w cm^{-1} for compound **2** is assigned to ν(Au–C) of the ylide group.[12,13] The absorption at 1125 cm^{-1}, characteristic of the $Ph_2PCHPPh_2$ system, is no longer observed.

The ^{19}F NMR spectra of complexes **1**–**3** show the presence of equivalent pentafluorophenyl rings. The methanide H of **1** appears in the ^1H NMR spectrum as a triplet of doublets at δ 6.54 by coupling to the phosphorus of the diphosphine and the triphenylphosphine [^2J(PH) = 8.06 and ^3J(PH) = 6.85 Hz]; **2** shows a doublet at δ 1.74, J(PH) = 13.2 Hz (ylide protons), and a triplet at δ 5.79, J(PH) = 8.6 Hz (methine proton), while **3** shows a multiplet at δ 6.11 for the CH group.

Particularly interesting are the ^{31}P-{^1H} NMR spectra, where the diphosphine phosphorus always appears as a multiplet because of the coupling to ^{19}F nuclei of the *trans*-C_6F_5 group. The phosphorus of the ligand L appears as a triplet for complex **1** [^3J(PP) = 13.3 Hz], a singlet for **2** and a doublet of doublets for **3** as a result of the coupling with both ^{107}Ag and ^{109}Ag [$^1J(^{107}AgP)$ = 507.5, $^1J(^{109}AgP)$ = 596.1 Hz].

The chemical shifts of the diphosphine atoms lie in the range δ −21.9 to −33.2; these values are close to those of the free dppm ligand (δ −21.9, $CDCl_3$) or even more shielded. This effect is similar to that found in other transition-metal complexes such as those of platinum,[14] and has been studied by Garrou[15] in compounds containing chelating phosphorus ligands in terms of a specific ring contribution, Δ_R, to the co-ordination shift.

The reaction of complexes **1**–**3** with $[Au(acac)(PPh_3)]$ or $[N(PPh_3)_2][Au(acac)Cl]$ leads to proton substitution by the fragments $Au(PPh_3)^+$ and AuCl and formation of acetylacetone. Following this procedure we have prepared the cationic complexes $[Au(C_6F_5)_2\{(Ph_2P)_2C(ML)(AuPPh_3)\}]ClO_4$ (ML = $AuPPh_3$ **4**, $AuCH_2PPh_3$ **5** or $AgPPh_3$ **6**) and the neutral $[Au(C_6F_5)_2\{(Ph_2P)_2C(AuPPh_3)(AuCl)\}]$ **7**; these are the first gold derivatives in which the dppm − 2H ligand is an eight-electron donor, linked only to gold or gold and silver atoms. Compound **4** can also be prepared by direct reaction of the diphosphine complex $[Au(C_6F_5)_2\{(Ph_2P)_2CH_2\}]ClO_4$ with 2 equivalents of $[Au(acac)(PPh_3)]$.

Complexes **4**–**7** are air- and moisture-stable yellow solids; they behave as 1:1 electrolytes in acetone, except for **7** which is non-conducting. Their IR spectra show similar absorptions to those of the starting materials, but two new bands in the region 800–900 cm^{-1} appear for all the complexes, possibly attributable to the system CM_2.

The ^{19}F NMR spectra show the presence of equivalent C_6F_5 groups. In the ^{31}P-{^1H} NMR spectra the diphosphine atoms appear as multiplets and other signals are assigned as follows: **4**, a triplet (PPh_3 groups) with ^3J(PP) = 7 Hz; **5**, a triplet ^3J(PP) = 10.3 Hz (PPh_3) and a singlet (ylide); **6**, a triplet ^3J(PP) = 7 Hz ($AuPPh_3$) and a doublet of doublets ($AgPPh_3$) with $J(^{107}AgP)$ = 522.6 and $J(^{109}AgP)$ = 603.6 Hz; and **7**, a triplet ^3J(PP) = 10.8 Hz (PPh_3).

For the diphosphine phosphorus there is an upfield shift from the starting materials to these compounds where the dppm ligand is an eight-electron donor.

Compounds **4**–**6** were also characterized by fast atom bombardment (FAB) mass spectroscopy. The highest peaks

Table 1 Analytical data and properties of the complexes **1**–**11** ($R = C_6F_5$)

Complex	Yield (%)	Analysis (%)[a] C	Analysis (%)[a] H	Λ_M[b]/Ω^{-1} cm^2 mol^{-1}	M.p./°C
1 $[AuR_2\{(Ph_2P)_2CH(AuPPh_3)\}]ClO_4\cdot CH_2Cl_2$	80	43.15 (43.15)	2.8 (2.5)	148	122
2 $[AuR_2\{(Ph_2P)_2CH(AuCH_2PPh_3)\}]ClO_4$	70	44.9 (45.25)	2.75 (2.55)	156	118 (decomp.)
3 $[AuR_2\{(Ph_2P)_2CH(AgPPh_3)\}]ClO_4\cdot CH_2Cl_2$	91	45.8 (45.8)	2.6 (2.6)	146	116 (decomp.)
4 $[AuR_2\{(Ph_2P)_2C(AuPPh_3)_2\}]ClO_4$	75	45.7 (45.4)	2.9 (2.6)	166	124
5 $[AuR_2\{(Ph_2P)_2C(AuCH_2PPh_3)(AuPPh_3)\}]ClO_4$	64	45.4 (45.6)	3.3 (2.7)	178	82 (decomp.)
6 $[AuR_2\{(Ph_2P)_2C(AuPPh_3)(AgPPh_3)\}]ClO_4$	66	46.4 (46.1)	2.7 (2.7)	147	120
7 $[AuR_2\{(Ph_2P)_2C(AuPPh_3)(AuCl)\}]$	30	40.7 (41.1)	2.2 (2.2)	30	88 (decomp.)
8 $[AuR_2\{(Ph_2P)_2C(AuR)(AuPPh_3)\}]$	69	41.9 (41.5)	2.3 (2.05)	28	118 (decomp.)
9 $[N(PPh_3)_2][AuR_2\{(Ph_2P)_2C(AuR)(AuCl)\}]$[c]	50	46.85 (46.5)	2.6 (2.45)	132	64
10 $[N(PPh_3)_2][\{AuR_2[(Ph_2P)_2C(AuR)]\}_2Au]$[c]	94	45.1 (44.70)	2.2 (2.15)	146	78 (decomp.)
11 $[\{AuR_2[(Ph_2P)_2C(AuPPh_3)]\}_2Au]ClO_4$	50	44.35 (43.95)	3.0 (2.6)	118	157

[a] Calculated values in parentheses. [b] In acetone. [c] **9**, N 0.55 (0.70); **10**, N 0.30 (0.40)%.

Table 2 $^{31}P-\{^1H\}$ and ^{19}F NMR data for complexes **1**–**11**

	$^{31}P-\{^1H\}$		^{19}F		
Complex	δ(PP)	δ(ML)(*J*/Hz)	δ(*o*-F)	δ(*p*-F)	δ(*m*-F)
1	−24.6 (m)	39.4 [t, *J*(PP) 13.3]	−120.2 (m)	−155.3 [t, *J*(FF) 19.6]	−159.9 (m)
2	−21.9 (m)	32.5 (s)	−119.8 (m)	−155.9 [t, *J*(FF) 20.7]	−160.2 (m)
3	−33.2 (m)	14.7 [dd, $J(^{109}AgP)$ 596.1, $J(^{107}AgP)$ 507.5]	−120.7 (m)	−155.7 [t, *J*(FF) 19.2]	−160.3 (m)
4	−29.5 (m)	38.1 [t, *J*(PP) 7.0]	−121.5 (m)	−156.3 [t, *J*(FF) 19.6]	−160.5 (m)
5	−32.5 (m)	31.4 (s)	−121.0 (m)	−156.9 [t, *J*(FF) 19.3]	−160.9 (m)
		34.9 [t, *J*(PP) 10.3]			
6	−35.3 (m)	44.6 [t, *J*(PP) 7.0]	−121.6 (m)	−156.6 [t, *J*(FF) 19.3]	−160.8 (m)
		12.9 [dd, $J(^{109}AgP)$ 603.6, $J(^{107}AgP)$ 522.6]			
7	−28.0 (m)	34.1 [t, *J*(PP) 10.8]	−120.2 (m)	−156.9 [t, *J*(FF) 19.5]	−160.8 (m)
8	−32.5 (m)	35.0 [t, *J*(PP) 10.2]	−116.7 (m)	−157.4 [t, *J*(FF) 19.5]	−161.1 (m)
			−120.5 (m)	−161.7 [t, *J*(FF) 20.6]	−163.7 (m)
9	−26.9 (m)		−115.2 (m)	−158.9 [t, *J*(FF) 19.3]	−162.0 (m)
			−115.7 (m)	−163.5 [t, *J*(FF) 20.6]	−164.7 (m)
10	−34.0 (m)		−114.4 (m)	−158.9 [t, *J*(FF) 20.1]	−161.9 (m)
			−115.5 (m)	−163.1 [t, *J*(FF) 20.1]	−165.2 (m)
11	−31.0 (m)	35.0 [t, *J*(PP) 12.5]	−121.5 (m)	−156.2 [t, *J*(FF) 20.1]	−160.5 (m)

at *m*/*z* = 1831 (**4**), 1845 (**5**) and 1743 (**6**), correspond to the cations $[Au(C_6F_5)_2\{(Ph_2P)_2C(AuPPh_3)_2\}]^+$, $[Au(C_6F_5)_2\{(Ph_2P)_2C(AuCH_2PPh_3)(AuPPh_3)\}]^+$ and $[Au(C_6F_5)_2\{(Ph_2P)_2C(AgPPh_3)(AuPPh_3)\}]^+$, respectively. A common feature among them is the presence of high-intensity peaks at *m*/*z* 841 assigned to the fragment $Au(dppm - 2H)(PPh_3)^+$ and at 459 assigned to $Au(PPh_3)^+$. Complex **5** also shows a peak at *m*/*z* = 1831 with relative intensity 95%, which corresponds to loss of methylene from the ylide group.

Crystal Structure of Compound **4**.—The structure of complex **4** was confirmed by X-ray diffraction analysis (Fig. 1), although the moderate precision precludes detailed discussion of molecular dimensions. The co-ordination of the gold(III) atom is slightly distorted from square planar, whereby the restricted 'bite' of the diphosphine ligand [P(3)–Au(3)–P(4) 70.5(3)°] represents the major deviation from ideal geometry. The Au(3) atom lies 0.047 Å out of the plane formed by P(3), P(4) C(111) and C(121). The Au(3)–P [2.343(8) and 2.351(8) Å] and P–C [1.764(25) and 1.838(25) Å] distances in the four-membered ring, which is planar to within ±0.02 Å, are similar to those found in the methanide complex $[Au(C_6F_5)_2\{(Ph_2P)_2CH(AuC_6F_5)\}]$ [Au(1)–P 2.354(2), P–C(1) 1.815(6) Å][3] and slightly shorter than in the precursor $[Au(C_6F_5)_2\{(Ph_2P)_2CH_2\}]ClO_4$ [Au–P 2.361(3), P–C(1) 1.845(9) Å].[16]

The Au(1) ··· Au(2) contact is 2.826(2) Å [*cf.* 2.6–3.2 Å in gold clusters but formally non-bonded contacts as short as *ca.* 2.8 Å in some gold(I) complexes].[17–19] A three-centre two-electron bond has previously been suggested for complexes containing the $(Ph_3P)AuAu(PPh_3)$ moiety,[20,21] as well as for Au_2(ylide) centres[22,23] on the basis of the narrow Au–C–Au angle [Au(1)–C(1)–Au(2) 85.4(7)° in our complex], the slightly shortened P–C bond [P(3)–C(1) 1.764(25) Å, *cf.* P–CH_2 1.845(9) Å in the starting material], and the wide angle opposite to the (CAu_2) unit [however P(3)–C(1)–P(4) 97.6(10)° is in fact narrower than ideal sp^3 in **1**, presumably constrained by the four-membered ring]. For these reasons the geometry at C(1) is distorted from tetrahedral [Au(2)–C(1)–P(3) 117.9(12) and

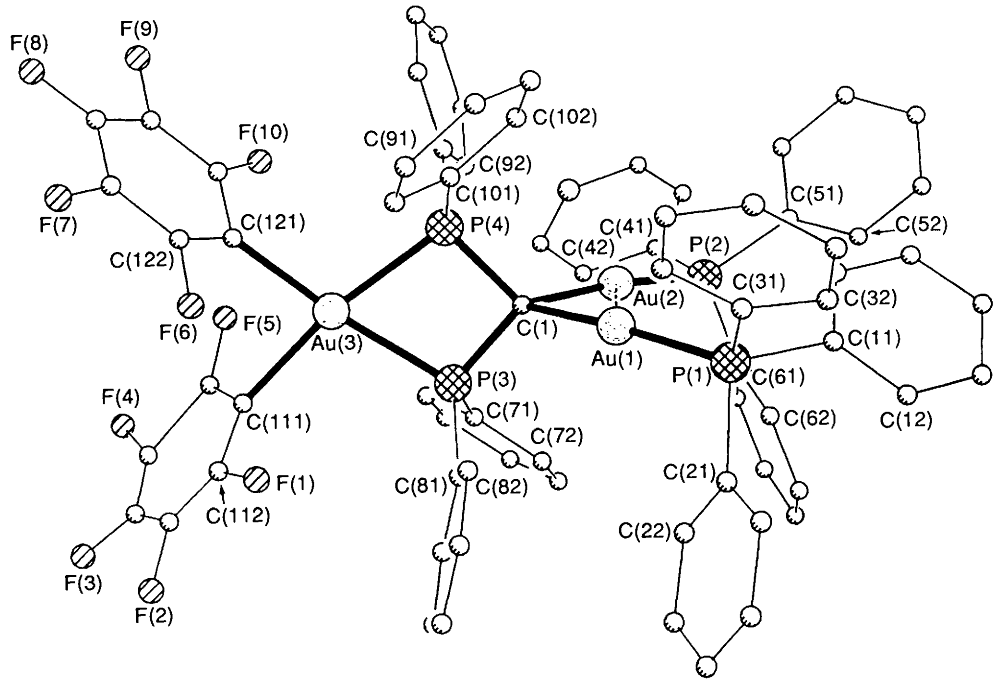


Fig. 1 Structure of the cation of complex **4**, with the atom numbering scheme. Hydrogen atoms are omitted for clarity; atomic radii are arbitrary

Table 3 Selected bond lengths (Å) and angles (°) for compound **4**

Au(1)–Au(2)	2.826(2)	Au(1)–P(1)	2.257(10)
Au(1)–C(1)	2.087(25)	Au(2)–P(2)	2.278(9)
Au(2)–C(1)	2.079(25)	Au(3)–P(3)	2.343(8)
Au(3)–P(4)	2.351(8)	Au(3)–C(111)	2.154(33)
Au(3)–C(121)	2.053(28)	P(1)–C(11)	1.827(25)
P(1)–C(21)	1.840(29)	P(1)–C(31)	1.844(29)
P(2)–C(41)	1.802(26)	P(2)–C(51)	1.802(26)
P(2)–C(61)	1.793(21)	P(3)–C(1)	1.764(25)
P(3)–C(71)	1.794(21)	P(3)–C(81)	1.823(27)
P(4)–C(1)	1.838(25)	P(4)–C(91)	1.766(25)
P(4)–C(101)	1.810(23)		
Au(2)–Au(1)–P(1)	129.2(3)	Au(2)–Au(1)–C(1)	47.2(7)
P(1)–Au(1)–C(1)	173.5(7)	Au(1)–Au(2)–P(2)	136.6(2)
Au(1)–Au(2)–C(1)	47.4(7)	P(2)–Au(2)–C(1)	170.9(7)
P(3)–Au(3)–P(4)	70.5(3)	P(3)–Au(3)–C(111)	100.5(9)
P(4)–Au(3)–C(111)	171.0(9)	P(3)–Au(3)–C(121)	169.8(8)
P(4)–Au(3)–C(121)	101.0(8)	C(111)–Au(3)–C(121)	87.9(12)
Au(1)–P(1)–C(11)	112.8(9)	Au(1)–P(1)–C(21)	110.3(8)
C(11)–P(1)–C(21)	108.3(11)	Au(1)–P(1)–C(31)	117.1(9)
C(11)–P(1)–C(31)	105.7(11)	C(21)–P(1)–C(31)	101.8(14)
Au(2)–P(2)–C(41)	108.9(9)	Au(2)–P(2)–C(51)	115.9(8)
C(41)–P(2)–C(51)	109.8(13)	Au(2)–P(2)–C(61)	107.5(9)
C(41)–P(2)–C(61)	107.6(11)	C(51)–P(2)–C(61)	106.7(11)
Au(3)–P(3)–C(1)	97.1(8)	Au(3)–P(3)–C(71)	118.2(8)
C(1)–P(3)–C(71)	110.8(12)	Au(3)–P(3)–C(81)	111.3(7)
C(1)–P(3)–C(81)	113.6(12)	C(71)–P(3)–C(81)	106.0(9)
Au(3)–P(4)–C(1)	94.7(8)	Au(3)–P(4)–C(91)	109.2(7)
C(1)–P(4)–C(91)	117.0(12)	Au(3)–P(4)–C(101)	116.4(8)
C(1)–P(4)–C(101)	113.9(11)	C(91)–P(4)–C(101)	105.7(10)
Au(1)–C(1)–Au(2)	85.4(7)	Au(1)–C(1)–P(3)	119.5(17)
Au(2)–C(1)–P(3)	117.9(12)	Au(1)–C(1)–P(4)	118.5(12)
Au(2)–C(1)–P(4)	119.9(17)	P(3)–C(1)–P(4)	97.6(10)

Au(1)–C(1)–P(4) 118.5(12)°]. The Au ··· Au contact could be responsible for the moderate deviation from linearity at the gold(I) centres (9.1°).

We have also studied the reactivity of the bis(diphenylphosphino)methanide complex $[Au(C_6F_5)_2\{(Ph_2P)_2CH(AuC_6F_5)\}]$ with the gold(I) acetylacetonate complexes; the reaction with $[Au(acac)(PPh_3)]$ or $[N(PPh_3)_2][Au(acac)Cl]$ affords neutral $[Au(C_6F_5)_2\{(Ph_2P)_2C(AuC_6F_5)(AuPPh_3)\}]$ **8** or the anionic complex $[N(PPh_3)_2][Au(C_6F_5)_2\{(Ph_2P)_2C(AuC_6F_5)(AuCl)\}]$ **9**. Compounds **8** and **9** are air- and moisture-stable yellow solids; **8** is non-conducting in acetone solution, **9** is a 1:1 electrolyte. Their IR spectra show, in addition to the absorptions of the pentafluorophenyl rings bonded to gold(III) (965 cm^{-1}), the presence of a new band at 953m cm^{-1}, diagnostic for a C_6F_5 group linked to a gold(I) centre; for **9** ν(Au–Cl) appears at 326m cm^{-1}.

The ^{19}F NMR spectra of compounds **8** and **9** show two different types of C_6F_5 groups with chemical shifts characteristic of gold-(I) or -(III) complexes. The ^{31}P-$\{^1H\}$ NMR spectrum of **8** shows a multiplet at δ −32.5 for the diphosphine phosphorus and a triplet ($AuPPh_3$) at δ 35.0 with a coupling constant $^2J(PP)$ = 10.2 Hz; for **9** only a multiplet at δ −26.9 and the $N(PPh_3)_2$ signal at δ 21.7 are observed.

A FAB mass spectrum was also recorded for compound **8**, showing that the complex readily loses C_6F_5 under these conditions. The molecular ion peak is not present but peaks at m/z = 1569 $[M - C_6F_5]^+$ (10%) and 1402 $[M - 3C_6F_5]^+$ (53%) appear. The highest-intensity peaks correspond to the fragments $Au(dppm - 2H)(PPh_3)^+$ and $Au(PPh_3)^+$.

A structurally different type of complex, $[N(PPh_3)_2][\{Au(C_6F_5)_2[(Ph_2P)_2C(AuC_6F_5)]\}_2Au]$ **10**, is obtained when $[Au(C_6F_5)_2\{(Ph_2P)_2CH(AuC_6F_5)\}]$ is treated with a half-equivalent of $[N(PPh_3)_2][Au(acac)_2]$, which has the ability to abstract two protons and thus to afford higher-nuclearity derivatives. Compound **10** is an orange solid, moderately stable at room temperature and behaving in acetone solution as a 1:1 electrolyte. Its IR spectrum shows absorptions of the C_6F_5 groups linked to gold(I) (951 cm^{-1}) and gold(III) (963 cm^{-1}) centres. There is also a band at 853 cm^{-1}, possibly arising from the CM_2 group.

The ^{19}F NMR spectrum of compound **10**, as expected, shows two types of pentafluorophenyl groups. The ^{31}P-$\{^1H\}$ NMR spectrum shows only two signals: a multiplet at δ −34.0 for the diphosphine phosphorus and a singlet at δ 21.7 for the $N(PPh_3)_2$ cation. The FAB mass spectrum shows a peak at m/z = 2751 corresponding to the anion $[\{Au(C_6F_5)_2[(Ph_2P)_2C(AuC_6F_5)]\}_2Au]^-$.

We have prepared a further pentanuclear complex by a different route. The reaction of the trinuclear complex $[\{Au(C_6F_5)_2[(Ph_2P)_2CH]\}_2Au]ClO_4$ with 2 equivalents of $[Au(acac)(PPh_3)]$ leads to the substitution of the methine protons by the fragment $Au(PPh_3)^+$, whereupon the com-

Table 4 Atomic coordinates (× 10^4) for compound **4**

Atom	*x*	*y*	*z*
Au(1)	2119.2(6)	765.1(4)	503.7(5)
Au(2)	3006.9(6)	1424.5(5)	507.4(5)
Au(3)	2560.9(6)	1073.7(5)	−1426.8(4)
P(1)	1770(4)	397(3)	1226(4)
P(2)	3672(4)	1760(3)	1150(4)
P(3)	3201(4)	896(3)	−614(3)
P(4)	1919(4)	1308(3)	−643(3)
C(1)	2567(13)	1097(9)	−133(8)
C(11)	1997	603	1903
C(12)	2208(12)	384(6)	2360(10)
C(13)	2362	555	2872
C(14)	2305	944	2927
C(15)	2094	1163	2470
C(16)	1940	992	1958
C(21)	2233	−65	1178
C(22)	2935(12)	−70(8)	919(9)
C(23)	3312	−410	841
C(24)	2986	−745	1023
C(25)	2284	−740	1283
C(26)	1907	−400	1361
C(31)	769	263	1265
C(32)	421(16)	154(9)	1762(9)
C(33)	−353	90	1774
C(34)	−779	135	1290
C(35)	−432	244	793
C(36)	343	308	781
C(41)	4094	2160	809
C(42)	4348(14)	2104(7)	265(11)
C(43)	4544	2412	−66
C(44)	4486	2776	149
C(45)	4232	2831	693
C(46)	4037	2523	1024
C(51)	3153	1914	1755
C(52)	3507(11)	1947(9)	2272(10)
C(53)	3121	2104	2722
C(54)	2381	2227	2655
C(55)	2028	2194	2138
C(56)	2414	2037	1687
C(61)	4418	1465	1399
C(62)	4248(9)	1105(7)	1592(9)
C(63)	4820	872	1790
C(64)	5562	1000	1796
C(65)	5732	1360	1603
C(66)	5160	1593	1404
C(71)	4135	1074	−508
C(72)	4540(11)	963(6)	−37(8)
C(73)	5251	1115	65
C(74)	5557	1376	−305
C(75)	5152	1487	−776
C(76)	4441	1336	−877
C(81)	3274	386	−559
C(82)	2633(9)	169(7)	−467(8)
C(83)	2671	−222	−509
C(84)	3351	−396	−643
C(85)	3993	−178	−736
C(86)	3954	213	−694
C(91)	1893	1804	−677
C(92)	2539(9)	2012(7)	−558(8)
C(93)	2523	2403	−595
C(94)	1862	2587	−751
C(95)	1216	2378	−870
C(96)	1232	1987	−833
C(101)	951	1159	−561
C(102)	527(12)	1310(7)	−125(9)
C(103)	−191	1169	−14
C(104)	−484	878	−339
C(105)	−60	728	−776
C(106)	658	869	−887
C(111)	3266(17)	818(12)	−2052(13)
C(112)	3392(21)	477(14)	−2189(16)
C(113)	3788(22)	338(14)	−2542(17)
C(114)	4166(21)	530(14)	−2843(16)
C(115)	4191(19)	887(14)	−2810(15)
C(116)	3694(23)	1109(15)	−2358(18)
C(121)	1829(15)	1217(10)	−2055(12)
C(122)	1363(16)	996(12)	−2333(13)
C(123)	871(15)	1097(11)	−2744(12)
C(124)	776(20)	1465(14)	−2894(15)
C(125)	1233(20)	1690(13)	−2615(15)
C(126)	1718(19)	1592(13)	−2196(15)
F(1)	2972(14)	262(8)	−1874(9)
F(2)	3919(14)	−3(11)	−2627(12)
F(3)	4709(12)	483(11)	−3264(10)
F(4)	4552(13)	1211(11)	−3080(9)
F(5)	3609(12)	1499(9)	−2294(8)
F(6)	1440(11)	621(8)	−2210(8)
F(7)	444(11)	819(9)	−2979(9)
F(8)	300(13)	1536(9)	−3275(10)
F(9)	1133(17)	2061(9)	−2754(10)
F(10)	2161(13)	1875(7)	−1980(8)
Cl(1)	2234(4)	1393(3)	4498(4)
O(1)	1851(14)	1064(9)	4369(10)
O(2)	2942(21)	1407(13)	4346(15)
O(3)	1728(26)	1683(15)	4480(18)
O(4)	2284(30)	1428(18)	5094(23)
C(2)	2778(30)	2082(18)	5813(21)
Cl(2)	2867(9)	1826(6)	6443(7)
Cl(3)	3614(7)	2355(6)	5736(6)

pound $[\{Au(C_6F_5)_2[(Ph_2P)_2C(AuPPh_3)]\}_2Au]ClO_4$ **11** can be isolated.

Complex **11** is an air- and moisture-stable orange solid and behaves as a 1:1 electrolyte in acetone solution. All the pentafluorophenyl rings are equivalent in the ^{19}F NMR spectrum, and in the ^{31}P-$\{^1H\}$ NMR spectrum a multiplet at δ −31.0 corresponding to the diphosphine phosphorus is observed. Coupling between them and the triphenylphosphine gives a triplet at δ 35.0 with $^2J(PP)$ = 12.5 Hz. The FAB mass spectrum shows a peak at *m*/*z* = 2942 which is assigned to $[\{Au(C_6F_5)_2[(Ph_2P)_2C(AuPPh_3)]\}_2Au]^+$. Apart from the peaks at *m*/*z* = 841 and 459 observed in all these types of compounds, another peak at *m*/*z* = 1831 (relative intensity 45%) is present, corresponding to the cation $[Au(C_6F_5)_2\{(Ph_2P)_2C(AuPPh_3)_2\}]^+$.

Experimental

The instrumentation and general experimental techniques were as described earlier.[3] The NMR spectra were recorded on Varian XL200 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, the ^{31}P-$\{^1H\}$ and ^{19}F NMR data in Table 2. All reactions were carried out at room temperature and under a nitrogen atmosphere. Solvents were distilled prior to use.

Syntheses.—$[N(PPh_3)_2][Au(acac)Cl]$. To a solution of [AuCl(tht)] (0.064 g, 0.2 mmol) in dichloromethane (20 cm^3) was added $[N(PPh_3)_2][acac]$ [prepared from Tl(acac) and $N(PPh_3)_2Cl$] (0.127 g, 0.2 mmol). After 30 min the solution was filtered over Celite and the solvent was concentrated to *ca.* 5 cm^3. Addition of diethyl ether (15 cm^3) gave $[N(PPh_3)_2][Au(acac)Cl]$ as a white solid. Yield 80%.

$[N(PPh_3)_2][Au(acac)_2]$. To a solution of $[N(PPh_3)_2][Au(acac)Cl]$ (0.232 g, 0.27 mmol) in dichloromethane (20 cm^3) was added Tl(acac) (0.097 g, 0.32 mmol). After stirring for 4 h the precipitated TlCl was filtered off. The solution was evaporated to *ca.* 5 cm^3 and addition of diethyl ether led to $[N(PPh_3)_2][Au(acac)_2]$ as a white solid. Yield 88%.

$[Au(C_6F_5)_2\{(Ph_2P)_2CH(ML)\}]ClO_4$ (ML = $AuPPh_3$ **1**, $AuCH_2PPh_3$ **2** *or* $AgPPh_3$ **3**). To a dichloromethane solution (20 cm^3) of $[Au(C_6F_5)_2\{(Ph_2P)_2CH\}]$[3] (0.091 g, 0.1 mmol) was added $[Au(tht)(PPh_3)]ClO_4$[24] (0.064 g, 0.1 mmol), $[Au(tht)(CH_2PPh_3)]ClO_4$[25] (0.066 g, 0.1 mmol) or $[Ag(OClO_3)(PPh_3)]$[26] (0.047 g, 0.1 mmol). After stirring the mixture for 30 min the solvent was concentrated to *ca.* 5 cm^3. Addition of diethyl ether (15 cm^3) gave complexes **1**–**3** as white solids.

$[Au(C_6F_5)_2\{(Ph_2P)_2C(AuPPh_3)(ML)\}]ClO_4$ (ML = $AuPPh_3$ **4**, $AuCH_2PPh_3$ **5** *or* $AgPPh_3$ **6**). To a solution of complex **1** (0.147 g, 0.1 mmol), **2** (0.148 g, 0.1 mmol) or **3** (0.138 g, 0.1 mmol) in dichloromethane (20 cm^3) was added $[Au(acac)(PPh_3)]$[27] (0.056 g, 0.1 mmol). After stirring for 1 h the solution was evaporated to *ca.* 5 cm^3 and addition of diethyl ether (15 cm^3) gave yellow solids **4**–**6**. Complex **4** was also prepared by treatment of a dichloromethane solution (20 cm^3) of $[Au(C_6F_5)_2\{(Ph_2P)_2CH_2\}]ClO_4$[16] (0.101 g, 0.1 mmol) with 2 equivalents of $[Au(acac)(PPh_3)]$ (0.112 g, 0.2 mmol), stirring the mixture for 30 min. The solvent was evaporated to *ca.* 5 cm^3 and addition of diethyl ether (15 cm^3) led to complex **4**.

$[Au(C_6F_5)_2\{(Ph_2P)_2C(AuPPh_3)(AuCl)\}]$ **7**. A dichloromethane solution (20 cm^3) of compound **1** (0.147 g, 0.1 mmol) was treated with $[N(PPh_3)_2][Au(acac)Cl]$ (0.087 g, 0.1 mmol). After stirring the mixture for 30 min the solvent was evaporated to dryness. The precipitated $[N(PPh_3)_2]ClO_4$ was filtered off, and the solution evaporated to *ca.* 5 cm^3. Addition of hexane (15 cm^3) afforded complex **7** as a yellow solid.

$[Au(C_6F_5)_2\{(Ph_2P)_2C(AuC_6F_5)(AuPPh_3)\}]$ **8**. To a solution of $[Au(C_6F_5)_2\{(Ph_2P)_2CH(AuC_6F_5)\}]$[3] (0.128 g, 0.1 mmol) in dichloromethane (20 cm^3) was added $[Au(acac)(PPh_3)]$ (0.056 g, 0.1 mmol). After stirring for 2 h the solvent was evaporated to *ca.* 5 cm^3. Addition of hexane (15 cm^3) gave complex **8** as a yellow solid.

$[N(PPh_3)_2][Au(C_6F_5)_2\{(Ph_2P)_2C(AuC_6F_5)(AuCl)\}]$ **9**. To a solution of $[Au(C_6F_5)_2\{(Ph_2P)_2CH(AuC_6F_5)\}]$ (0.128 g, 0.1 mmol) in dichloromethane (20 cm^3) was added $[N(PPh_3)_2][Au(acac)Cl]$ (0.087 g, 0.1 mmol). After 1 h the solution was concentrated to *ca.* 5 cm^3 and addition of hexane (15 cm^3) gave complex **9** as a yellow solid.

$[N(PPh_3)_2][\{Au(C_6F_5)_2[(Ph_2P)_2C(AuC_6F_5)]\}_2Au]$ **10**. To a solution of $[Au(C_6F_5)_2\{(Ph_2P)_2CH(AuC_6F_5)\}]$ (0.128 g, 0.1 mmol) in dichloromethane (20 cm^3) was added $[N(PPh_3)_2][Au(acac)_2]$ (0.049 g, 0.05 mmol) and the mixture stirred for 2 h. Concentration of the solvent to *ca.* 5 cm^3 and addition of hexane (15 cm^3) led to complex **10** as an orange solid.

$[\{Au(C_6F_5)_2[(Ph_2P)_2C(AuPPh_3)]\}_2Au]ClO_4$ **11**. A solution of $[\{Au(C_6F_5)_2[(Ph_2P)_2CH]\}_2Au]ClO_4$[3] (0.210 g, 0.1 mmol) in dichloromethane (20 cm^3) was treated with $[Au(acac)(PPh_3)]$ (0.112 g, 0.2 mmol). After stirring for 2 h the solvent was evaporated to *ca.* 5 cm^3. Addition of diethyl ether (15 cm^3) gave an orange solid of complex **11**.

X-Ray Structure Determination of Compound **4**.—*Crystal data.* $C_{73}H_{50}Au_3ClF_{10}O_4P_4 \cdot CH_2Cl_2$, $M_r = 2016.3$, orthorhombic, space group *Pbcn*, $a = 17.775(3)$, $b = 35.555(7)$, $c = 23.962(3)$ Å, $U = 15\,143(4)$ Å^3, $Z = 8$, $D_c = 1.769$ Mg m^{-3}, $F(000) = 7728$, λ(Mo-Kα) = 0.710 69 Å, $\mu = 6.06$ mm^{-1}, $T = -95$ °C.

Data collection and reduction. Single crystals of compound **4** in the form of colourless plates were obtained by liquid diffusion of hexane into a dichloromethane solution. Despite ready solvent loss in air, samples could be mounted in an inert oil and transferred to the cold gas stream of the diffractometer without appreciable loss of crystallinity. A tablet 0.8 × 0.4 × 0.05 mm was used to collect 14 471 intensities to $2\theta_{max}$ 50° (Siemens R3 diffractometer, monochromated Mo-Kα radiation). An absorption correction based on ψ scans was applied, with transmission factors 0.41–1.00. Merging equivalents gave 13 407 unique reflections (R_{int} 0.039), of which 5340 with $F > 4\sigma(F)$ were used for all calculations (program system Siemens SHELXTL-PLUS).[28] Cell constants were refined from the setting angles of 50 reflections in the range 2θ 20–23°.

Structure solution and refinement. The structure was solved by the heavy-atom method. The weak data precluded a full anisotropic refinement; only Au, P, F and Cl atoms were refined anisotropically, phenyl groups with idealized geometry and other H atoms using a riding model. The final *R* value was 0.083, with *R′* 0.101 for 373 parameters. The weighting scheme was $w^{-1} = \sigma^2(F) + 0.0015F^2$; *S* 1.6; maximum Δ/σ 0.02; maximum $\Delta\rho$ 3.6 e Å^{-3}. Selected bond lengths and angles are given in Table 3, final atomic coordinates in Table 4.

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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