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Five-membered Methanediide Auracycles. Crystal Structure of $[Au(C_6F_5)_2\{Ph_2PC(AuPPh_3)(AuC_6F_5)PPh_2(CHCO_2Me)\}]$†

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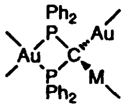
Reaction of NaH with $[Au(C_6F_5)_2\{Ph_2PCH(MPPh_3)PPh_2(CHCO_2Me)\}]ClO_4$ (M = Au or Ag) results in both deprotonation of the PCHP group and elimination of the anion and leads to the auracycles $[Au(C_6F_5)_2\{Ph_2PC(MPPh_3)PPh_2(CHCO_2Me)\}]$. The methanediide C atom in these neutral complexes is a nucleophile and can function as a donor atom [by reaction with gold(I) or silver(I) complexes] to form neutral or cationic trinuclear complexes: $[Au(C_6F_5)_2\{Ph_2PC(MPPh_3)(AuC_6F_5)PPh_2(CHCO_2Me)\}]$ or $[Au(C_6F_5)_2\{Ph_2PC(MPPh_3)(M'PPh_3)PPh_2(CHCO_2Me)\}]ClO_4$. The structure of $[Au(C_6F_5)_2\{Ph_2PC(AuPPh_3)(AuC_6F_5)PPh_2(CHCO_2Me)\}]$ was solved by X-ray crystallography. It crystallizes in space group $P\bar{1}$, with $a = 14.257(5)$, $b = 14.404(5)$, $c = 17.756(6)$ Å, $\alpha = 80.15(3)$, $\beta = 66.37(3)$, $\gamma = 73.84(3)°$, $Z = 2$ and $R(F) = 0.052$ (at −100 °C). The configuration at the methanediide carbon is *R* and at the ester-bearing carbon is *S* (both enantiomers are present). The $Au^I \cdots Au^I$ distance is 2.957(2) Å.

The synthesis of gold-(I) and -(III) methanide complexes from diphosphinomethane derivatives using NaH as deprotonating agent is well documented,[1] but only single deprotonation of the PCH_2P group of the diphosphine and formation of complexes with the $[PCHP]^-$ ligand was observed. Only very few examples of methanediide gold(III) complexes of the type shown have been recently reported[2] by reaction of [bis(disphenylphosphino)methanide]gold(III) complexes with $[Au(acac)(PPh_3)]$ or $[Au(acac)_2]^-$ (acac = acetylacetonate).

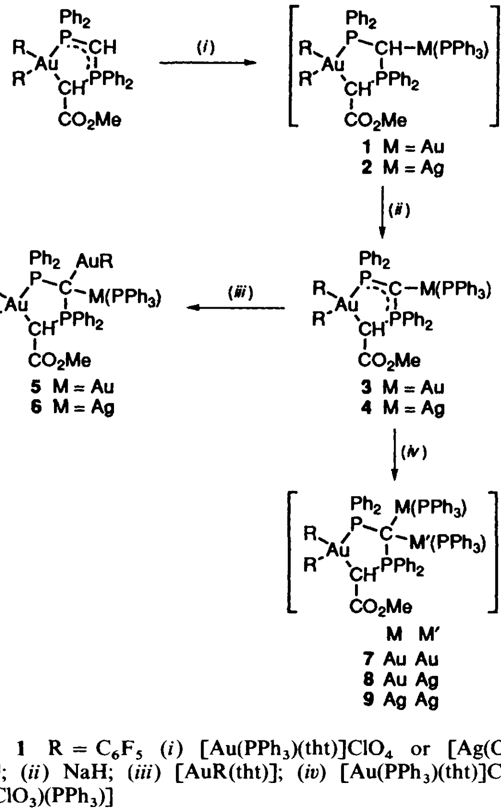


M = Au or Ag

Here we describe the preparation of $[Au(C_6F_5)_2\{Ph_2PC(MPPh_3)PPh_2(CHCO_2Me)\}]$ (M = Au or Ag) by reaction of $[Au(C_6F_5)_2\{Ph_2PCH(MPPh_3)PPh_2(CHCO_2Me)\}]ClO_4$ and NaH, and their reactions with several gold(I) and silver(I) complexes. The structure of the trinuclear complex $[Au(C_6F_5)_2\{Ph_2PC(AuPPh_3)(AuC_6F_5)PPh_2(CHCO_2Me)\}]$ has been established by single-crystal X-ray analysis.

Results and Discussion

The previously described[3] five-membered methanide auracycle $[Au(C_6F_5)_2\{Ph_2PCHPPh_2(CHCO_2Me)\}]$ possesses an excess of electron density at the PCHP group, causing it to act as a C-donor ligand. Thus, it reacts with $[Au(PPh_3)(tht)]ClO_4$ (tht = tetrahydrothiophene) or $[Ag(OClO_3)(PPh_3)]$ to give the binuclear complexes **1** or the previously reported[3] **2** (see Scheme 1). Complex **1** or **2** reacts with NaH to give the neutral methanediide complex **3** or **4** (see Scheme 1) as the result of the precipitation of the perchlorate anion (as the sodium salt) and the simultaneous deprotonation of the $CHMPPh_3$ group. The basic nature of the methanediide $CMPPh_3$ group in complex **3**



Scheme 1 R = C_6F_5 (*i*) $[Au(PPh_3)(tht)]ClO_4$ or $[Ag(OClO_3)(PPh_3)]$; (*ii*) NaH; (*iii*) [AuR(tht)]; (*iv*) $[Au(PPh_3)(tht)]ClO_4$ or $[Ag(OClO_3)(PPh_3)]$

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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 400121.

Table 1 Analytical data for complexes (R = C_6F_5)

Complex	Yield (%)	Analysis (%)[a] C	Analysis (%)[a] H	Λ_M[b]
1 $[AuR_2\{Ph_2PCH(AuPPh_3)PPh_2(CHCO_2Me)\}]ClO_4$	91	45.2 (45.1)	2.65 (2.6)	128
3 $[AuR_2\{Ph_2PC(AuPPh_3)PPh_2(CHCO_2Me)\}]$	80	47.8 (48.2)	2.65 (2.7)	8
4 $[AuR_2\{Ph_2PC(AgPPh_3)PPh_2(CHCO_2Me)\}]$	72	51.25 (51.4)	2.85 (2.9)	7
5 $[AuR_2\{Ph_2PC(AuPPh_3)(AuR)PPh_2(CHCO_2Me)\}]$	85	42.8 (42.5)	2.35 (2.15)	5
6 $[AuR_2\{Ph_2PC(AgPPh_3)(AuR)PPh_2(CHCO_2Me)\}]$	80	44.5 (44.7)	2.4 (2.3)	3
7 $[AuR_2\{Ph_2PC(AuPPh_3)_2PPh_2(CHCO_2Me)\}]ClO_4$	86	45.5 (45.55)	2.7 (2.7)	120
8 $[AuR_2\{Ph_2PC(AuPPh_3)(AgPPh_3)PPh_2(CHCO_2Me)\}]ClO_4$	82	47.45 (47.7)	2.75 (2.85)	116
9 $[AuR_2\{Ph_2PC(AgPPh_3)_2PPh_2(CHCO_2Me)\}]ClO_4$	87	49.6 (50.0)	3.35 (3.0)	109

[a] Calculated values in parentheses. [b] In acetone, ohm^{-1} cm^2 mol^{-1}.

Table 2 NMR data

	^1H[a] (δ)		$^{31}P-\{^1H\}$[b] (δ)			
Compound	Me	CHCO	AuP	CPC	$MPPh_3$	$M'PPh_3$
1a	3.55 (s)	4.21 (m)	35.7 (dm)	51.0 (dd) (47.3, 4.7)	40.6 (dd) (9.5, 4.7)	
1b	3.17 (s)	4.11 (m)	35.0 (dm)	49.9 (dd) (52.5, 10.3)	38.0 (m)	
3	3.12 (s)	4.03 (m)	40.7 (dm)	45.3 (dd) (96.0, 11.4)	44.02 (dd) (11.4, 4.4)	
4	3.19 (s)	3.69 (m)	31.7 (dm)	42.6 (d) (96.1)	8.6 (br s)	
5a	3.17 (s)	4.23 (m)	48.8 (dm)	53.9 (dd) (73.5, 8.2)	33.3 ('t') (8.2)	
5b	3.12 (s)	4.45 (m)	41.6 (dm)	54.3 (dd) (62.6, 10.5)	34.7 ('t') (10.5)	
6	3.52 (s)	4.58 (m)	46.5 (dm)	51.6 (dd) (73.2, 14.1)	12.0 (dd) (632.1, 544.4)[c]	
7	3.37 (s)	4.18 (m)	45.5 (dm)	57.1 (dd) (67.4, 4.5)	38.2 (d) (7.3)	35.3 ('t') (4.5)
8	3.49 (s)	4.13 (m)	43.4 (dm)	53.1 (ddd) (67.6, 8.2, 7.6)	42.5 ('t') (8.2)	11.8 (br dd) (629.0, 544.2)[c]
9	3.60 (s)	4.60 (m)	44.3 (dm)	53.5 (dm) (62.1)	15.9 (dd) (523.8, 451.9)[c]	13.8 (br dd) (604.9, 524.9)[c]

[a] Recorded in $CDCl_3$ at 200 MHz and referenced to internal $SiMe_4$. Coupling constants in Hz are shown in parentheses; s = singlet, d = doublet, 't' = apparent triplet, m = multiplet, dd = doublet of doublets, dm = doublet of multiplets, ddd = doublet of doublet of doublets. [b] Referred to external H_3PO_4. [c] $J(P-^{107}Ag)$ and $J(P-^{109}Ag)$.

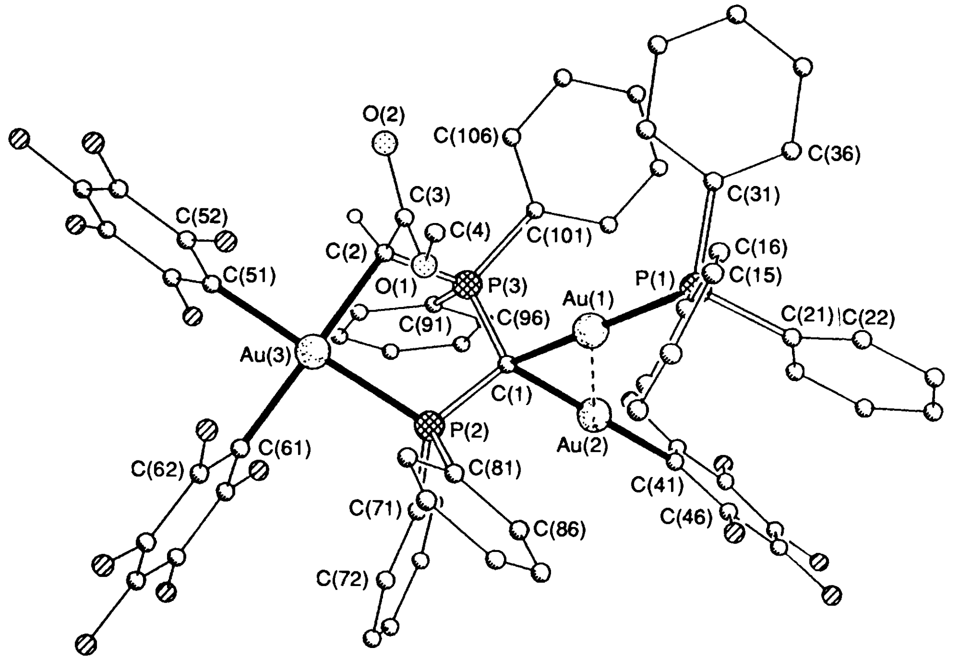

Fig. 1 Structure of complex **5**, with the atom numbering scheme. Hydrogen atoms are omitted for clarity; atomic radii are arbitrary

or **4** can be demonstrated through reactions with other neutral centres containing one weakly co-ordinated ligand such as tetrahydrothiophene {*e.g.* $[Au(C_6F_5)(tht)]$, $[Au(PPh_3)(tht)]ClO_4$} or perchlorate {*e.g.* $[Ag(OClO_3)(PPh_3)]$} which afford neutral (**5** or **6**) or cationic (**7**–**9**) trinuclear complexes.

Complexes **1** and **5**–**9** are air and moisture-stable white solids; **3** and **4** are yellow solids, which slowly decompose at room temperature, but remain unchanged for weeks when stored at −20 °C under nitrogen. The cationic derivatives **1** and **7**–**9** behave as 1 : 1 electrolytes in acetone solutions (see Table 1), and their IR spectra show bands at 1100s(br) and 620m cm^{-1}, which are characteristic of the ClO_4^- anion.[4] In contrast, acetone solutions of complexes **5** and **6** are non-conducting. Two strong bands in the 800 cm^{-1} region confirm that the C_6F_5 groups in complexes **1**–**9** are mutually *cis*.[5] The ^{19}F NMR spectra also confirm the presence of two (**1**–**4**, **7**–**9**) or three (**5**, **6**) different C_6F_5 groups (see Experimental section). The ν(CO) vibration appears at *ca.* 1690s cm^{-1} and it is not very sensitive to

Table 3 Atomic coordinates (× 10^4) for complex **5**

Atom	*x*	*y*	*z*
Au(1)	5 619.4(5)	3 491.4(5)	2 613.4(4)
Au(2)	6 223.8(5)	5 325.2(5)	2 517.0(4)
Au(3)	8 927.8(5)	2 118.5(4)	2 943.8(4)
P(1)	4 143(3)	3 242(3)	2 570(3)
P(2)	7 406(3)	3 389(3)	3 392(3)
P(3)	8 035(3)	3 446(3)	1 642(3)
C(1)	6 999(11)	3 854(10)	2 550(9)
C(2)	8 635(14)	2 184(12)	1 843(11)
C(3)	7 971(25)	1 496(22)	1 960(20)
C(4)	6 507(30)	588(27)	2 948(24)
O(1)	7 173(18)	1 442(16)	2 685(15)
O(2)	8 325(26)	814(24)	1 439(22)
C(11)	3 545(9)	2 361(7)	3 366(6)
C(12)	3 579(9)	2 357(8)	4 138(7)
C(13)	3 108(10)	1 733(9)	4 780(6)
C(14)	2 603(9)	1 112(8)	4 650(6)
C(15)	2 569(9)	1 116(8)	3 879(7)
C(16)	3 040(10)	1 740(9)	3 236(6)
C(21)	3 092(7)	4 343(6)	2 719(7)
C(22)	2 051(8)	4 291(6)	2 963(7)
C(23)	1 259(6)	5 136(8)	3 072(8)
C(24)	1 509(7)	6 032(6)	2 936(8)
C(25)	2 550(8)	6 084(5)	2 693(7)
C(26)	3 342(6)	5 239(7)	2 584(7)
C(31)	4 375(10)	2 821(9)	1 586(7)
C(32)	5 219(9)	2 043(9)	1 281(8)
C(33)	5 411(10)	1 685(9)	541(9)
C(34)	4 757(12)	2 105(10)	107(7)
C(35)	3 912(11)	2 882(10)	412(8)
C(36)	3 721(9)	3 240(8)	1 152(8)
C(41)	5 498(9)	6 768(12)	2 458(7)
C(42)	5 982(12)	7 420(10)	1 908(10)
C(43)	5 548(15)	8 424(13)	1 888(13)
C(44)	4 577(12)	8 768(17)	2 441(10)
C(45)	4 047(15)	8 147(13)	3 001(13)
C(46)	4 524(12)	7 153(10)	2 986(10)
F(1)	6 962(9)	7 125(8)	1 332(8)
F(2)	6 073(13)	9 027(8)	1 318(10)
F(3)	4 147(10)	9 720(9)	2 452(8)
F(4)	3 076(9)	8 480(9)	3 540(8)
F(5)	3 948(8)	6 571(7)	3 569(7)
C(51)	10 280(10)	988(9)	2 513(9)
C(52)	10 175(11)	76(10)	2 542(9)
C(53)	11 048(12)	−708(12)	2 226(11)
C(54)	12 006(14)	−497(13)	1 894(13)
C(55)	12 173(13)	395(11)	1 828(13)
C(56)	11 264(11)	1 144(10)	2 160(11)
F(6)	9 218(7)	−138(7)	2 876(7)
F(7)	10 914(10)	−1 584(7)	2 254(7)
F(8)	12 866(8)	−1 242(8)	1 557(8)
F(9)	13 110(7)	592(10)	1 457(8)
F(10)	11 437(7)	2 033(7)	2 105(7)
C(61)	9 271(10)	2 046(7)	3 983(9)
C(62)	9 067(10)	1 338(9)	4 619(7)
C(63)	9 338(11)	1 279(10)	5 305(8)
C(64)	9 840(12)	1 944(8)	5 339(10)
C(65)	10 051(12)	2 669(10)	4 732(8)
C(66)	9 781(11)	2 698(10)	4 051(8)
F(11)	8 618(7)	638(6)	4 586(6)
F(12)	9 141(7)	565(7)	5 892(5)
F(13)	10 104(8)	1 901(7)	5 996(6)
F(14)	10 545(8)	3 314(7)	4 766(6)
F(15)	10 034(7)	3 401(6)	3 445(5)
C(71)	7 680(8)	4 318(7)	3 818(6)
C(72)	7 564(9)	4 212(7)	4 642(6)
C(73)	7 836(9)	4 872(8)	4 958(5)
C(74)	8 224(9)	5 637(7)	4 451(7)
C(75)	8 340(9)	5 743(7)	3 628(6)
C(76)	8 068(9)	5 083(7)	3 312(5)
C(81)	6 323(7)	3 007(7)	4 253(6)
C(82)	6 396(7)	2 040(6)	4 542(7)
C(83)	5 573(9)	1 771(6)	5 217(7)
C(84)	4 677(8)	2 469(8)	5 604(6)
C(85)	4 604(7)	3 436(7)	5 315(7)
C(86)	5 427(8)	3 705(5)	4 639(6)
C(91)	9 049(8)	4 145(7)	1 302(7)
C(92)	9 993(9)	3 763(7)	1 421(8)
C(93)	10 680(8)	4 351(9)	1 277(9)
C(94)	10 424(9)	5 321(9)	1 015(9)
C(95)	9 481(10)	5 703(6)	896(8)
C(96)	8 794(7)	5 115(7)	1 039(8)
C(101)	7 604(9)	3 558(8)	790(6)
C(102)	6 824(9)	4 342(7)	691(7)
C(103)	6 487(9)	4 395(8)	48(8)
C(104)	6 930(11)	3 665(10)	−498(7)
C(105)	7 710(11)	2 881(9)	−399(7)
C(106)	8 047(9)	2 827(7)	244(8)
Cl(1)	1 298(12)	1 559(11)	56(10)
Cl(1′)	2 274(26)	1 850(24)	−2 507(21)
Cl(2′)	640(34)	1 702(30)	−1 310(28)
Cl(2″)	2 005(23)	−381(20)	−88(18)

the different environments in complexes **1**–**9**, which is in agreement[6] with the fact that deprotonation and subsequent addition of $Au(C_6F_5)$ or $M(PPh_3)^+$ (M = Au or Ag) fragments occurs at the carbon of the PCP group.

Compounds **5**, **7** and **8** were also characterized by fast atom bombardment (FAB) mass spectrometry. The highest peaks at *m*/*z* = 1808 (**5**), 1903 (**7**) and 1815 (**8**) correspond to the cations $[Au(C_6F_5)_2\{Ph_2PC(AuPPh_3)(AuC_6F_5)PPh_2(CHCO_2Me)\}]^+$, $[Au(C_6F_5)_2\{Ph_2PC(AuPPh_3)_2PPh_2(CHCO_2Me)\}]^+$ and $[Au(C_6F_5)_2\{Ph_2PC(AuPPh_3)(AgPPh_3)PPh_2(CHCO_2Me)\}]^+$, respectively. A common feature is the presence of peaks at *m*/*z* = 913 assigned to the fragment $[Au(C_6F_5)_2(Ph_2PCPPh_2)]^+$ and at 459 assigned to $[Au(PPh_3)]^+$.

Complexes **1**, **5**, **6** and **8** have two chiral carbon centres and the ^1H and ^{31}P NMR spectra show the presence of the two diastereomers for **1** (**a**, 77; **b**, 23%) and **5** (**a**, 56; **b**, 44%), but only one is observed for **6** and **8**. The methanide PCHP of complex **1** appears in the ^1H NMR spectrum as a multiplet at δ 4.85 (**1a**) or 4.82 (**1b**). Table 2 presents ^1H NMR data for the complexes (the phenyl protons, which appear as multiplets between δ 7 and 8, are omitted. The resonances due to the Me or CHCO groups appear as singlets or multiplets, respectively. The $^{31}P-\{^1H\}$ NMR spectra show two coupled P atoms of the diphosphine in all cases. The P atom bonded to gold gives rise to a doublet of multiplets as a result of coupling with the fluorine nuclei of the *trans* C_6F_5 and the P atoms of PPh_3, and the CPC group appears as a doublet of doublets (complexes **1**, **3**–**6**), a doublet of doublet of doublets (**8**, coupled to two different PPh_3), or a doublet of multiplets (**7** and **9**, probably a poorly resolved doublet of doublets of doublets). Other resonances corresponding to $AuPPh_3$ or $AgPPh_3$ are presented in Table 2. The P atom of $AgPPh_3$ appears coupled to both ^{107}Ag and ^{109}Ag nuclei, but the coupling constants with the other P atoms are not well resolved.

The structure of complex **5** was determined by X-ray diffraction and is shown in Fig. 1. The Au(3) atom displays *cis*-square-planar co-ordination. The 'bite' of the ligand, 87.5(5)°, is much less narrow than that [71.5(2)°] in $[Au(C_6F_5)_2(dppm)]ClO_4$[7] (dppm = $Ph_2PCH_2PPh_2$), and the geometry around the gold(III) centre is therefore close to ideal (mean deviation 2.6°). The Au(3)–$C(C_6F_5)$ distances 2.110(15) and 2.069(16) Å are similar to those found in other $[Au(C_6F_5)_2(L-L)]^+$ complexes.[2,7–10] The bond from the gold(III) centre to the methanide carbon, Au(3)–C(2) 2.139(17) Å, is insignificantly

Table 4 Selected bond lengths (Å) and angles (°) for complex **5**

Au(1)–C(1)	2.127(14)	Au(1)–P(1)	2.265(4)
Au(1) ⋯ Au(2)	2.957(2)	Au(2)–C(41)	2.053(17)
Au(2)–C(1)	2.103(14)	Au(3)–C(61)	2.069(16)
Au(3)–C(51)	2.110(15)	Au(3)–C(2)	2.139(17)
Au(3)–P(2)	2.365(4)	P(1)–C(31)	1.820(10)
P(1)–C(21)	1.825(8)	P(1)–C(11)	1.832(9)
P(2)–C(1)	1.777(15)	P(2)–C(81)	1.821(9)
P(2)–C(71)	1.841(8)	P(3)–C(1)	1.749(15)
P(3)–C(101)	1.817(10)	P(3)–C(2)	1.823(17)
P(3)–C(91)	1.836(9)	C(2)–C(3)	1.488(33)

C(1)–Au(1)–P(1)	173.5(4)	C(1)–Au(1)–Au(2)	45.3(4)
P(1)–Au(1)–Au(2)	129.84(11)	C(41)–Au(2)–C(1)	178.6(4)
C(41)–Au(2)–Au(1)	134.8(4)	C(1)–Au(2)–Au(1)	46.0(4)
C(61)–Au(3)–C(51)	87.4(5)	C(61)–Au(3)–C(2)	177.9(6)
C(51)–Au(3)–C(2)	90.9(6)	C(61)–Au(3)–P(2)	94.2(4)
C(51)–Au(3)–P(2)	178.4(4)	C(2)–Au(3)–P(2)	87.5(5)
C(31)–P(1)–C(21)	106.4(6)	C(31)–P(1)–C(11)	106.3(6)
C(21)–P(1)–C(11)	104.2(5)	C(31)–P(1)–Au(1)	112.2(4)
C(21)–P(1)–Au(1)	112.3(4)	C(11)–P(1)–Au(1)	114.7(4)
C(1)–P(2)–C(81)	109.3(6)	C(1)–P(2)–C(71)	112.9(6)
C(81)–P(2)–C(71)	103.2(5)	C(1)–P(2)–Au(3)	108.5(5)
C(81)–P(2)–Au(3)	113.0(4)	C(71)–P(2)–Au(3)	109.9(4)
C(1)–P(3)–C(101)	112.4(6)	C(1)–P(3)–C(2)	108.2(8)
C(101)–P(3)–C(2)	110.0(7)	C(1)–P(3)–C(91)	111.7(6)
C(101)–P(3)–C(91)	106.1(6)	C(2)–P(3)–C(91)	108.3(7)
P(3)–C(1)–P(2)	108.5(8)	P(3)–C(1)–Au(2)	116.3(8)
P(2)–C(1)–Au(2)	117.5(7)	P(3)–C(1)–Au(1)	108.9(7)
P(2)–C(1)–Au(1)	115.7(8)	Au(2)–C(1)–Au(1)	88.7(5)
C(3)–C(2)–P(3)	114.4(16)	C(3)–C(2)–Au(3)	108.8(16)
P(3)–C(2)–Au(3)	106.5(8)	C(46)–C(41)–C(42)	114.3(17)
C(52)–C(51)–C(56)	117.7(16)	C(62)–C(61)–C(66)	116.1(15)

longer than the corresponding Au^I-C(methanediide) distances [Au(1)–C(1) 2.127(14), Au(2)–C(1) 2.103(14) Å]. Similarly, the bond length Au(3)–P(2) 2.365(4) Å is longer than Au(1)–P(1) 2.265(4) Å, although these values are in the normal range for Au^{III}–P and Au^I–P distances.[2,7,8] The Au(3) atom lies 0.0133 Å out of the plane formed by P(2), C(2) and C(51) and C(61) of the two pentafluorophenyl groups.

The compound contains a triangular Au_2C unit of the type that has been already observed in other ylide or methanediide complexes, and has been interpreted in terms of a closed three-centre two-electron bond.[2,6,11] The Au ⋯ Au contact is 2.957(2) Å, slightly longer than that found in $[Au(C_6F_5)_2\{(Ph_2P)_2C(AuPPh_3)_2\}]ClO_4$, 2.826(2) Å,[2] where both gold fragments are the same; this fact and the Au(1)–C(1)–Au(2) angle of 88.7(5)° [again greater than in ref. 2, 85.4(7)°] suggest that the three-centre bonding contributes less to the overall bonding scheme in our compound. The geometry at the gold(I) centre Au(1) is distorted from linearity with P–Au–C 173.5(4)°, but is almost linear at Au(2) with C–Au–C 178.6(4)°. The atoms C(1) and C(2) are chiral and the coordinates correspond to the *R*/*S* diastereomer, but both enantiomers are present in the crystal.

Experimental

Instrumentation and general experimental techniques were as described earlier.[3] Mass spectra were recorded on a VG Autospec with the FAB technique, using 3-nitrobenzyl alcohol as matrix. The yields, C and H analyses, and conductivities of the new complexes are listed in Table 1. Proton and $^{31}P-\{^1H\}$ NMR data are listed in Table 2. All the reactions were performed at room temperature, under a nitrogen atmosphere and using freshly distilled solvents. Complex **2** was prepared as reported.[3]

Syntheses.—$[Au(C_6F_5)_2\{Ph_2PCH(AuPPh_3)PPh_2(CHCO_2Me)\}]ClO_4$ **1**. To a solution of $[Au(C_6F_5)_2\{Ph_2PCHPPh_2(CHCO_2Me)\}]$[3] (0.197 g, 0.2 mmol) in dichloromethane (20 cm^3) was added $[Au(PPh_3)(tht)]ClO_4$[12] (0.129 g, 0.2 mmol). The mixture was stirred for 2 h and then concentrated to *ca.* 5 cm^3. Addition of diethyl ether (10 cm^3) afforded complex **1** as a white solid. ^{19}F NMR ($CDCl_3$): δ −120.7 (m), −121.3(m) and −122.9(m) (*o*-F); −155.9 [t, *J*(F–F) 19.3] and −156.0 [t, *J*(F–F) 18.7 Hz] (*p*-F, isomer **1a**); −156.1 (t) and −156.4 (t) (*p*-F, isomer **1b**); and −160.1 (m) and −160.9 (m) (*m*-F).

$[Au(C_6F_5)_2\{Ph_2PC(MPPh_3)PPh_2(CHCO_2Me)\}]$ (M = Au **3** *or* Ag **4**). To a suspension of complex **1** (0.313 g, 0.2 mmol) or **2** (0.292, 0.2 mmol) in diethyl ether (50 cm^3) was added NaH (0.3 g, 12.5 mmol). The mixture was stirred for 2 h, during which time evolution of H_2 was observed. The resulting suspension was filtered under N_2 and the yellow solution evaporated to dryness. Addition of hexane (20 cm^3) gave complex **3** or **4** as a yellow solid. ^{19}F NMR: **3**, δ −120.3 (m) and −122.4 (m) (*o*-F); −159.2 [t, *J*(F–F) 19.8] and −160.2 [t, *J*(F–F) 19.8] (*p*-F); and −161.8 (m, br) (*m*-F); **4**, −120.6 (m) and −122.7 (m) (*o*-F); −158.2 [t, *J*(F–F) 19.3] and −158.7 [t, *J*(F–F) 19.3 Hz] (*p*-F); and −162.0 (br m) (*m*-F).

$[Au(C_6F_5)_2[Ph_2PC(MPPh_3)(AuC_6F_5)PPh_2(CHCO_2Me)\}]$ (M = Au **5** *or* Ag **6**). To a solution of complex **3** (0.147 g, 0.1 mmol) or **4** (0.138 g, 0.1 mmol) in diethyl ether (20 cm^3) was added $[Au(C_6F_5)(tht)]$[13] (0.045, 0.1 mmol). After 1 h the colourless solution was concentrated to *ca.* 5 cm^3 and addition of diethyl ether (20 cm^3) gave complex **5** or **6**, respectively. ^{19}F NMR: **5**, δ −116.5 (m, *o*-F, Au^I–C_6F_5, isomer **5a**), −116.9 (m, *o*-F, Au^I–C_6F_5, isomer **5b**); −120.3 (m), −120.9 (m), −121.8 (m) and −122.7 (m) (*o*-F, Au^{III}–C_6F_5); −162.0 [t, *J*(F–F) 20.6, *p*-F, Au^I–C_6F_5, isomer **5a**], −161.9 [t, *J*(F–F) 19.3, *p*-F, Au^I–C_6F_5, isomer **5b**]; −157.6 [t, *J*(F–F) 20.6], −158.1 [t, *J*(F–F) 19.3] and −158.4 [t, *J*(F–F) 19.3 Hz] (*p*-F, Au^{III}–C_6F_5); −163.8 [m, *m*-F, Au^I–C_6F_5]; and −161.0 (m) and −161.5 (m) (*m*-F, Au^{III}–C_6F_5).

$[Au(C_6F_5)_2\{Ph_2PC(MPPh_3)(M'PPh_3)PPh_2(CHCO_2Me)\}]ClO_4$ (M = M′ = Au **7**; M = Au, M′ = Ag **8**; M = M′ = Ag **9**). To a solution of complex **3** (0.147 g, 0.1 mmol) or **4** (0.138 g, 0.1 mmol) in dichloromethane (20 cm^3) was added $[Au(PPh_3)(tht)]ClO_4$[12] (0.065 g, 0.1 mmol) or $[Ag(OClO_3)(PPh_3)]$[14] (0.047 g, 0.1 mmol) and then stirred for 1 h. The solution was concentrated to *ca.* 5 cm^3 and addition of diethyl ether led to complex **7**, **8** or **9** as a white solid. ^{19}F NMR: **7**, δ −120.6 (m), −121.2 (m), −122.2 (m) and −122.4 (m) (*o*-F); −156.6 [t, *J*(F–F) 19.8] and −156.9 [t, *J*(F–F) 20.1] (*p*-F) and −160.8 (br, m) (*m*-F); **8**, −120.9 (m), −121.4 (m), −122.2 (m) and −123.1 (m) (*o*-F); −156.9 [t, *J*(F–F) 19.6] and 157.2 [t, *J*(F–F) 19.3 Hz] (*p*-F); and −160.8 (m) and −161.1 (m) (*m*-F).

Crystal Structure Determination of Compound **5**.—*Crystal data*. $C_{65}H_{41}Au_3Cl_2F_{15}O_2P_3$, M_r = 1893.7, triclinic, space group $P\bar{1}$, *a* = 14.257(5), *b* = 14.404(5), *c* = 17.756(6) Å, α = 80.15(3), β = 66.37(3), γ = 73.84(3)°, *U* = 3201.3(19) Å^3, *Z* = 2, D_c = 1.96 Mg m^{-3}, *F*(000) = 1796, λ(Mo-Kα) = 0.710 73 Å, μ = 7.1 mm^{-1}, *T* = −100 °C.

Data collection and reduction. Single crystals of compound **5** in the form of colourless needles were obtained by slow evaporation of diethyl ether into a dichloromethane solution. The crystals lose solvent in air and were mounted in inert oil and transferred to the cold gas stream of the diffractometer. A needle 0.6 × 0.15 × 0.05 mm was used to collect 10 739 intensities to $2\theta_{max}$ 45° (Siemens R3 diffractometer, monochromated Mo-Kα radiation). An absorption correction based on ψ scans was applied, with transmission factors 0.62–1.00. Merging equivalents gave 8408 independent reflections (R_{int} 0.041), of which all were used for all calculations (program system SHELXL 92).[15] Cell constants were refined from setting angles of 50 reflections in the range 2θ 20–23°.

Structure solution and refinement. The structure was solved by the heavy-atom method, and subjected to full-matrix least-squares refinement on F^2; Au, P and F atoms were refined anisotropically, other atoms were refined isotropically, phenyl rings as idealized hexagons. Hydrogen atoms were included using a riding model. An ill defined region of residual electron density was interpreted as disordered dichloromethane. The weighting scheme was of the form $w^{-1} = \sigma^2(F^2) + (aP)^2 + bP$, where $P = (F_o^2 + 2F_c)^2/3$, $a = 0.0499$ and $b = 77.3519$. Refinement proceeded to $R'(F^2)$ 0.151, with a conventional $R(F)$ of 0.052, for 386 parameters and 214 restraints; S 1.08, maximum $\Delta\rho$ 2.9 e Å^{-3}.

Final atomic coordinates are given in Table 3, selected bond lengths and angles 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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References

1 A. Laguna and M. Laguna, *J. Organomet. Chem.*, 1990, **394**, 743 and refs. therein.

2 E. J. Fernandez, M. C. Gimeno, P. G. Jones, A. Laguna, M. Laguna and J. M. Lopez de Luzuriaga, *J. Chem. Soc., Dalton Trans.*, 1992, 3365.

3 R. Usón, A. Laguna, M. Laguna and I. Lázaro, *Organometallics*, 1987, **6**, 2326.

4 B. J. Hathaway and A. E. Underhill, *J. Chem. Soc.*, 1961, 3091.

5 R. Usón, A. Laguna, J. García and M. Laguna, *Inorg. Chim. Acta*, 1979, **37**, 201.

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

7 R. Usón, A. Laguna, M. Laguna, E. Fernandez, M. D. Villacampa, P. G. Jones and G. M. Sheldrick, *J. Chem. Soc., Dalton Trans.*, 1983, 1679.

8 R. Usón, A. Laguna, M. Laguna, B. R. Manzano, P. G. Jones and G. M. Sheldrick, *J. Chem. Soc., Dalton Trans.*, 1984, 839.

9 R. Usón, A. Laguna, M. D. Villacampa, P. G. Jones and G. M. Sheldrick, *J. Chem. Soc., Dalton Trans.*, 1984, 2035.

10 R. Usón, A. Laguna, M. Laguna, M. N. Fraile, P. G. Jones and C. F. Erdbrügger, *J. Chem. Soc., Dalton Trans.*, 1989, 73.

11 J. Vicente, M. T. Chicote, M. C. Lagunas and P. G. Jones, *J. Chem. Soc., Dalton Trans.*, 1991, 2579.

12 R. Usón, A. Laguna, M. Laguna, J. Jimenez, M. P. Gómez, A. Sainz and P. G. Jones, *J. Chem. Soc., Dalton Trans.*, 1990, 3457.

13 R. Usón, A. Laguna and J. Vicente, *J. Organomet. Chem.*, 1977, **131**, 471.

14 F. A. Cotton, L. R. Falvello, R. Usón, J. Forniés, M. Tomás, J. M. Casas and I. Ara, *Inorg. Chem.*, 1987, **26**, 1366.

15 G. M. Sheldrick, SHELXL 92, University of Göttingen, 1992.

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