Synthesis of Benzyl- or Pentafluorobenzyl-diphenylphosphonio(diphenylphosphino)methanide Complexes of Gold(I) and Gold(III) and Their Use as C-Donor Ligands

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The salts $[AuR_n(Ph_2PCH_2PPh_2CH_2R')]ClO_4$ [R_n = C_6F_5 or $Cl(C_6F_5)_2$, R′ = Ph or C_6F_5] react with an excess of NaH to give neutral methanide complexes $[AuR_n(Ph_2PCHPPh_2CH_2R')]$, which react with gold(I) or silver(I) derivatives to form binuclear complexes of the types $[R_nAu(Ph_2PCHPPh_2CH_2R')AuX]$ (X = C_6F_5 or Cl) or $[(C_6F_5)Au(Ph_2PCHPPh_2CH_2R')M(PPh_3)]ClO_4$ (M = Au or Ag).

We have recently reported a new method for the synthesis of gold(I) and gold(III) ylide complexes[1] which can readily be extended to methanide complexes of the types $[Au(C_6F_5)_2(Ph_2PCHPPh_2)]$[2] or $[AuR_n(Ph_2PCHPPh_2Me)]$[3] (R = C_6F_5, n = 1 or 3) which are C-donor ligands and can be used in the synthesis of polynuclear complexes.[2,3]

In this paper, we describe the preparation of mononuclear complexes $[AuR_n(Ph_2PCHPPh_2CH_2R')]$ [R_n = C_6F_5 or $Cl(C_6F_5)_2$, R′ = Ph or C_6F_5] and their use as C-donor ligands to afford binuclear complexes of the types $[R_nAu(Ph_2PCHPPh_2CH_2R')AuX]$ (X = Cl or C_6F_5) and $[(C_6F_5)Au(Ph_2PCHPPh_2CH_2R')M(PPh_3)]ClO_4$ (M = Au or Ag).

Results and Discussion

Benzyl- or pentafluorobenzyl-diphenyl(diphenylphosphinomethyl)phosphonium perchlorate reacts with $[Au(C_6F_5)(tht)]$ displacing the tetrahydrothiophene (tht) ligand or with $[\{Au(\mu\text{-}Cl)(C_6F_5)_2\}_2]$ cleaving the chloride bridge, to give cationic gold(I) or gold(III) complexes [equation (1)].

$$\left.\begin{array}{c}[Au(C_6F_5)(tht)] \\ \text{or} \\ \tfrac{1}{2}[\{Au(\mu\text{-}Cl)(C_6F_5)_2\}_2]\end{array}\right\} + [Ph_2PCH_2PPh_2CH_2R']ClO_4 \longrightarrow [AuR_n(Ph_2PCH_2PPh_2CH_2R')]ClO_4 \quad (1)$$

$$R_n = C_6F_5,\quad R' = Ph\ \mathbf{(1)}\ \text{or}\ C_6F_5\ \mathbf{(2)}$$
$$R_n = Cl(C_6F_5)_2,\ R' = Ph\ \mathbf{(3)}\ \text{or}\ C_6F_5\ \mathbf{(4)}$$

Complexes **(1)**—**(4)** are air- and moisture-stable white solids at room temperature. In acetone solutions they behave as 1:1 electrolytes (Table 1). Their i.r. spectra show bands at *ca.* 1 100s, br and 620m cm^{-1}, pointing to the presence of the ClO_4 anion;[4] the spectra of **(3)** and **(4)** show two bands at 810m and 785m cm^{-1} due to two mutually *cis* C_6F_5 groups,[5] and the ν(Au–Cl) vibration appears at 315m for **(3)** or 335m cm^{-1} for **(4)**.[6] Proton (phenyl protons not included) and ^{31}P n.m.r. data are collected in Table 2. The phosphinic P atom co-ordinated to the gold centre exhibits multiplets arising from the coupling to the fluorine nuclei of the *trans*-C_6F_5 group, thus confirming the *cis* disposition of the two C_6F_5 groups.

Complexes **(1)**—**(4)** react with a diethyl ether suspension of NaH undergoing deprotonation of the methylene group and simultaneous ClO_4 abstraction (see Scheme) to give the methanide complexes **(5)**, **(6)** (white) and **(7)**, **(8)** (yellow). These are stable in the solid state but sensitive to moisture when in solution. In acetone solution they are non-conducting and monomeric (isopiestic method, in chloroform) (Table 1). Their ^1H n.m.r. spectra confirm that the methylene group of the benzyl substituents is not attacked, the deprotonation taking place at the methylene group bridging the two P atoms.

In the i.r. spectra of complexes **(5)**—**(8)** the two bands due to the ClO_4 group are absent and new bands [not present in the spectra of starting complexes **(1)**—**(4)**] at 1 180m and 1 170m cm^{-1} for **(5)**, 1 210m and 1 185m cm^{-1} for **(6)**, 1 230m cm^{-1} for **(7)**, and 1 215m and 1 180m cm^{-1} for **(8)** appear. We think they are due to a characteristic vibration of the methanide (P–CH–P) system. They are indeed sensitive to the bonding since they are not present in the C-bonding binuclear complexes **(9)**—**(19)** (see below). Two i.r. absorptions in the 800 cm^{-1} region and multiplets in the ^{31}P n.m.r. spectra, assignable to the phosphorus atom bonded to gold, confirm again the *cis* disposition of the two C_6F_5 groups in complexes **(7)** and **(8)**.

Since the methanide C atom in the moiety P–CH–P has an excess of electron density, complexes **(5)**—**(8)** are potential C-donor ligands. They displace weakly co-ordinating ligands, tht in $[Au(C_6F_5)(tht)]$ or ClO_4 in $[Au(OClO_3)(PPh_3)]$ and $[Ag(OClO_3)(PPh_3)]$, to give the binuclear complexes **(9)**—**(19)** (see Scheme). These are air- and moisture-stable white solids. In acetone solution, complexes **(16)**—**(19)** are 1:1 electrolytes; complexes **(9)**—**(15)** are non-conducting. The molecular weights of complexes **(9)**, **(10)**, and **(14)** confirm their binuclear nature; lack of solubility precluded such measurements in the cases of **(11)**—**(13)** and **(15)**.

The i.r. spectra of complexes **(16)**—**(19)** show two bands at *ca.* 1 100s, br and 620m cm^{-1} due to the ClO_4^- anion; ν(Au–Cl) appears at 315m for **(11)**, 335m for **(12)**, 345m for **(13)**, 330m for **(14)**, and 315m cm^{-1} for **(15)**. A new band (not present in the spectra of the starting complexes) appears at 575m for **(9)**, 582m for **(10)**, 585m for **(11)**, 575m for **(12)**, 600m for **(13)**, 580m for **(14)**, 595m for **(15)**, 590m for **(16)**, and 590m cm^{-1} for **(17)** which we tentatively assign to ν(Au–C).[1,3,7]

As a consequence of the donation of electron density to the gold or silver centres, the shielding of the proton in the M–C–H system is less effective and the ^1H n.m.r. signal is shifted to lower fields. The two protons in the P–CH_2R' moiety are non-equivalent being coupled both mutually as well as with the P atom. In complexes **(17)** and **(19)**, assignment of the resonances due to the CH and CH_2 groups is not possible because of the proximity of their resonances. The *cis* disposition of both C_6F_5 groups in complexes **(11)**, **(12)**, and **(15)** is evident from the two i.r. bands in the 800 cm^{-1} region, as well as from the ^{31}P-$\{^1H\}$ n.m.r. spectra (a multiplet assigned to the phosphorus

Table 1. Analytical and physical data for complexes (**1**)—(**19**)

	Complex[a]	Yield (%)	Analysis[b] (%)			Λ_M[c]/Ω^{-1} cm^2 mol^{-1}	M[b,d]	M.p. (°C)
			C	H	Au			
(**1**)	$[AuR(Ph_2PCH_2PPh_2CH_2Ph)]ClO_4$	87	48.3 (48.6)	3.0 (3.1)	21.1 (21.0)	106	—	220 (decomp.)
(**2**)	$[AuR(Ph_2PCH_2PPh_2CH_2C_6F_5)]ClO_4$	80	44.1 (44.35)	2.4 (2.35)	19.1 (19.15)	106	—	218 (decomp.)
(**3**)	$[AuClR_2(Ph_2PCH_2PPh_2CH_2Ph)]ClO_4$	86	45.4 (46.3)	2.55 (2.55)	18.15 (17.25)	108	—	190
(**4**)	$[AuClR_2(Ph_2PCH_2PPh_2CH_2C_6F_5)]ClO_4$	77	42.45 (42.9)	2.1 (1.95)	16.2 (16.0)	130	—	165 (decomp.)
(**5**)	$[AuR(Ph_2PCHPPh_2CH_2Ph)]$	90	54.2 (54.45)	3.45 (3.35)	24.15 (23.5)	3	844 (839)	152
(**6**)	$[AuR(Ph_2PCHPPh_2CH_2C_6F_5)]$	88	48.4 (49.15)	2.5 (2.5)	22.4 (21.2)	8	976 (928)	157
(**7**)	$[AuClR_2(Ph_2PCHPPh_2CH_2Ph)]$	82	50.25 (50.75)	2.75 (2.7)	20.1 (18.9)	13	1 091 (1 041)	117
(**8**)	$[AuClR_2(Ph_2PCHPPh_2CH_2C_6F_5)]$	79	46.3 (46.7)	2.1 (2.05)	18.3 (17.4)	8	1 083 (1 131)	138
(**9**)	$[RAu(Ph_2P\overline{CHPPh_2CH_2Ph)Au}R]$	86	43.9 (43.95)	2.4 (2.35)	33.2 (32.75)	6	1 258 (1 203)	178 (decomp.)
(**10**)	$[RAu(Ph_2P\overline{CHPPh_2CH_2C_6F_5)Au}R]$	91	41.4 (40.9)	1.85 (1.8)	30.9 (30.5)	5	1 235 (1 292)	162 (decomp.)
(**11**)	$[R_2ClAu(Ph_2P\overline{CHPPh_2CH_2Ph)Au}R]$	67	42.7 (42.75)	2.0 (2.0)	28.75 (28.05)	2	*e*	192 (decomp.)
(**12**)	$[R_2ClAu(Ph_2P\overline{CHPPh_2CH_2C_6F_5)Au}R]$	74	39.65 (40.15)	1.4 (1.55)	27.15 (26.35)	12	*e*	198 (decomp.)
(**13**)	$[RAu(Ph_2P\overline{CHPPh_2CH_2Ph)Au}Cl]$	61	42.7 (42.6)	2.95 (2.65)	37.2 (36.8)	5	*e*	177 (decomp.)
(**14**)	$[RAu(Ph_2P\overline{CHPPh_2CH_2C_6F_5)Au}Cl]$	51	39.65 (39.30)	2.15 (2.0)	34.5 (33.95)	16	1 114 (1 161)	182 (decomp.)
(**15**)	$[R_2ClAu(Ph_2P\overline{CHPPh_2CH_2Ph)Au}Cl]$	83	40.95 (41.5)	2.3 (2.2)	31.25 (30.95)	7	*e*	176 (decomp.)
(**16**)	$[RAu(Ph_2P\overline{CHPPh_2CH_2Ph)Au}(PPh_3)]ClO_4$	65	47.9 (48.15)	3.05 (3.1)	28.35 (28.2)	110	—	126
(**17**)	$[RAu(Ph_2P\overline{CHPPh_2CH_2C_6F_5)Au}(PPh_3)]ClO_4$	45	45.2 (45.2)	2.6 (2.55)	27.1 (26.45)	125	—	148 (decomp.)
(**18**)	$[RAu(Ph_2P\overline{CHPPh_2CH_2Ph)Ag}(PPh_3)]ClO_4$	71	52.0 (51.4)	3.2 (3.3)	22.95 (23.3)	135	—	124 (decomp.)
(**19**)	$[RAu(Ph_2P\overline{CHPPh_2CH_2C_6F_5)Ag}(PPh_3)]ClO_4$	56	48.25 (48.1)	3.0 (2.75)	22.1 (21.8)	152	—	141 (decomp.)

[a] R = C_6F_5. [b] Calculated values are given in parentheses. [c] In acetone. [d] In chloroform. [e] Not sufficiently soluble.

atom bonded to a gold centre, coupled with the ^{19}F atoms of the *trans*-C_6F_5 group).

Experimental

The instrumentation and general experimental techniques were as described earlier.[2,3] The yields, melting points, C, H, and Au analyses, conductivities, and molecular weights of the new complexes are listed in Table 1. ^1H and $^{31}P-\{^1H\}$ N.m.r. data are listed in Table 2. All the reactions were performed at room temperature. The salts $[Ph_2PCH_2PPh_2CH_2R']ClO_4$ (R′ = Ph or C_6F_5) were prepared in a similar way to that described for $[Ph_2PCH_2PPh_2Me]ClO_4$.[8]

Preparation of the Complexes.—$[AuR_n(Ph_2PCH_2PPh_2CH_2R')]ClO_4$ [$R_n = C_6F_5$, R′ = Ph (**1**) *or* C_6F_5 (**2**); $R_n = Cl(C_6F_5)_2$, R′ = Ph (**3**) *or* C_6F_5 (**4**)]. A solution of $[Au(C_6F_5)(tht)]$[9] (0.181 g, 0.4 mmol) and the appropriate $[Ph_2PCH_2PPh_2CH_2R']ClO_4$ (R′ = Ph or C_6F_5) (0.4 mmol) in dichloromethane (30 cm^3) was stirred for 2 h. Concentration to *ca.* 5 cm^3 and addition of diethyl ether (20 cm^3) led to the precipitation of white crystals of complex (**1**) or (**2**). Complexes (**3**) and (**4**) were prepared as white solids in a similar way starting from $[\{Au(\mu-Cl)(C_6F_5)_2\}_2]$[10] (0.227 g, 0.2 mmol) and the corresponding phosphine (0.4 mmol) in dichloromethane (20 cm^3).

$[AuR_n(Ph_2PCHPPh_2CH_2R')]$ [$R_n = C_6F_5$, R′ = Ph (**5**) *or* C_6F_5 (**6**); $R_n = Cl(C_6F_5)_2$, R′ = Ph (**7**) *or* C_6F_5 (**8**)]. A diethyl ether (20 cm^3) suspension of NaH (0.3 g, 12.5 mmol) and complex (**1**) (0.282 g, 0.3 mol), (**2**) (0.309 g, 0.3 mmol), (**3**) (0.343 g, 0.3 mmol), or (**4**) (0.369 g, 0.3 mmol) was stirred for 3 h. The excess of NaH and the precipitated $NaClO_4$ were filtered off under N_2 and the solutions were evaporated to *ca.* 2 cm^3; addition of n-hexane (10 cm^3) gave white [(**5**), (**6**)] or yellow [(**7**), (**8**)] solids.

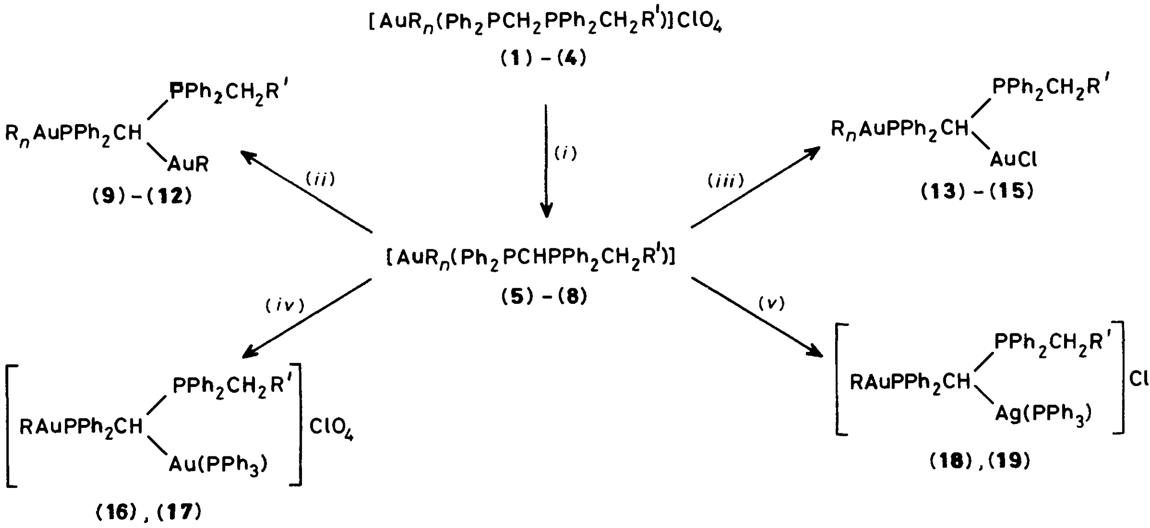
$[R_nAu(Ph_2P\overline{CHPPh_2CH_2R')Au}(C_6F_5)]$ [$R_n = C_6F_5$, R′ = Ph (**9**) *or* C_6F_5 (**10**); $R_n = Cl(C_6F_5)_2$, R′ = Ph (**11**) *or* C_6F_5 (**12**)]. To a solution of $[Au(C_6F_5)(tht)]$ (0.094 g, 0.2 mmol) in diethyl ether (30 cm^3) was added complex (**5**) (0.168 g, 0.2 mmol), (**6**) (0.186 g, 0.2 mmol), (**7**) (0.208 g, 0.2 mmol), or (**8**) (0.226 g, 0.2 mmol) and the mixture was stirred for 3 h, whereupon complexes (**11**) and (**12**) precipitated as white solids and were filtered off. Complexes (**9**) and (**10**) were soluble; evaporation of the solutions to *ca.* 3 cm^3 and subsequent slow addition of hexane (10 cm^3) led to their crystallization.

$[R_nAu(Ph_2P\overline{CHPPh_2CH_2R')Au}Cl]$ [$R_n = C_6F_5$, R′ = Ph (**13**) *or* C_6F_5 (**14**); $R_n = Cl(C_6F_5)_2$, R′ = Ph (**15**)]. To a solution of complexes (**5**)—(**7**) (0.2 mmol) in diethyl ether (20

Table 2. N.m.r. data

	^1H N.m.r.[a]		^{31}P-{^1H} N.m.r.[b]		
Complex	P–CH_2–P or P–CH–P	P–CH_2–R′	Au–P	P–CH_2–R′	M–PPh_3
(1)	4.39 (dd, 23.8)[c]	4.54 (d, 13.8)	25.61 (m)	24.35 (d, 10.5)	
(2)	4.71 (dd, 23.8)[c]	4.76 (d, 14.8)	25.42 (m)	24.41 (m)	
(3)	3.78 (d, 0.6)	4.67 (d, 14.0)	16.61 (m)	23.55 (d, 22.0)	
(4)	5.52 (dd, 11.3; 14.2)	4.98 (d, 14.0)	19.59 (m)	25.20 (d, 34.2)	
(5)	1.35 (dd, 4.5)[c]	4.20 (d, 11.4)	24.81 (m)	23.87 (d, 74.3)	
(6)	1.60 (t, 6.2)[c]	4.16 (d, 11.8)	25.35 (dm)	23.07 (d, 73.0)	
(7)	1.34 (dd, 2.8; 6.4)	3.93 (d, 14.0)	28.06 (m)	25.25 (d, 18.7)	
(8)	1.64 (dd, 8.3)[c]	4.01 (d, 13.3)	23.04 (m)	21.01 (d, 16.0)	
(9)	2.95 (dd, 10.7; 14.6)	4.71 (br t, 13.5), 4.45 (t, 14.0)	38.15 (m)	30.15 (d, 24.4)	
(10)	3.28 (dd, 11.5; 13.1)	4.83 (t, 13.9), 4.43 (t, 13.9)	36.81 (dm)	29.88 (d, 29.9)	
(11)	3.76 (m)	4.65 (br t, 14.4), 4.36 (dd, 9.7; 12.2)	28.98 (m)	25.48 (d, 45.7)	
(12)	4.85 (dd, 9.7; 11.8)	4.74 (dd, 8.8; 13.7)	29.05 (m)	27.09 (d, 39.1)	
(13)	2.97 (dd, 26.1)[c]	4.46 (m)	28.98 (m)	28.75 (d, 15.0)	
(14)	3.29 (t, 12.7)	4.69 (t, 14.4), 4.26 (t, 14.4)	28.61 (dm)	26.43 (d, 16.5)	
(15)	3.86 (br t, 12.4)	4.71 (dd, 10.1; 12.7), 4.59 (br t, 14.4)	29.25 (m)	26.35 (d, 49.7)	
(16)	4.90 (dt, 7.7; 13.2)	4.42 (t, 14.5), 3.90 (br t, 13.4)	32.44 (m)	31.02 (m)	39.65 (t, 10.6)
(17)	4.5 (m)[d]		24.4 (m)	17.31 (d, 7.0)	24.4[e]
(18)	4.20 (dm, 10.6)	4.49 (d, 13.3)[f]	30.85 (m)	29.67 (d, 14.6)	15.70 (dd, 524.4; 605.5)[f,g]
(19)	4.5 (m)[d,f]		30.48 (m)	29.82 (d, 11.2)	16.91 (dd, 534.4; 608.6)[f,g]

[a] Recorded in $CDCl_3$ at 200 MHz with reference to internal $SiMe_4$ unless otherwise specified: s = singlet, d = doublet, t = triplet, m = multiplet, dd = doublet of doublets, and dm = doublet of multiplets. All complexes show a multiplet in the region of 7.8 p.p.m. corresponding to Ph groups. Coupling constants in Hz are shown in parentheses. [b] Referred to external H_3PO_4. [c] Part X or X_2 of an ABX or ABX_2 system, so the values in parentheses are the sum of J_{AX} and J_{BX}. [d] Unambiguous assignment not possible. [e] Superposed with the signal of Au–P. [f] Recorded in $(CD_3)_2CO$. [g] $J(P–^{107}Ag)$ and $J(P–^{109}Ag)$.



Scheme. R_n = C_6F_5 or $Cl(C_6F_5)_2$, R′ = Ph or C_6F_5, and R = C_6F_5. (*i*) NaH; (*ii*) [AuR(tht)]; (*iii*) [AuCl(tht)]; (*iv*) [$Au(OClO_3)(PPh_3)$]; (*v*) [$Ag(OClO_3)(PPh_3)$]

cm^3) was added [AuCl(tht)][10] (0.064 g, 0.2 mmol) and the mixture was stirred for 2 h. Complexes (**13**)—(**15**) precipitated.

[$(C_6F_5)Au(Ph_2PCHPPh_2CH_2R')M(PPh_3)$]$ClO_4$ [M = Au, R′ = Ph (**16**) *or* C_6F_5 (**17**); M = Ag, R′ = Ph (**18**) *or* C_6F_5 (**19**)]. To a solution of [$Au(OClO_3)(PPh_3)$][11] (0.2 mmol) in benzene (20 cm^3) or of [$Ag(OClO_3)(PPh_3)$][12] (0.094 g, 0.2 mmol) in dichloromethane (20 cm^3) was added complex (**5**) or (**6**) (0.2 mmol) and the mixture was stirred for 2 h. A slight turbidity was removed by filtration through a layer of Kieselguhr (1 cm). Partial concentration to *ca.* 3 cm^3 and addition of diethyl ether (15 cm^3) led to precipitation of the white complexes (**16**)—(**19**).

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