Bi-, Tetra-, and Poly-nuclear Complexes of Gold(I) and Silver(I) with Bis(diphenylphosphino)-methanide or -amide acting as Six-electron Donors

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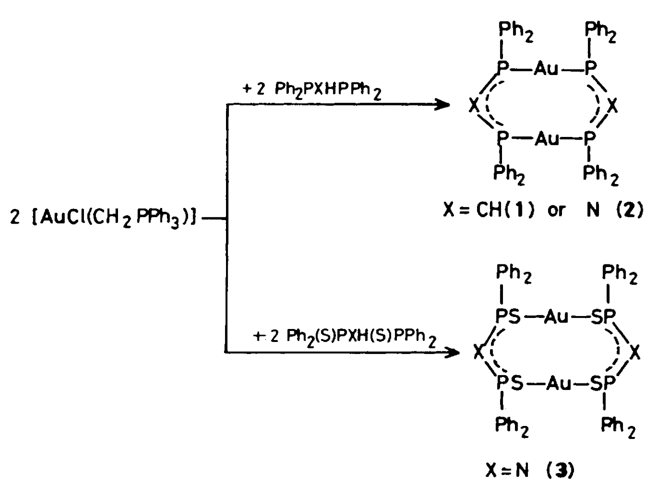
The reaction of $[AuCl(CH_2PPh_3)]$ or $[Ag(CH_2PPh_3)_2]ClO_4$ with bis(diphenylphosphino)amine, bis(diphenylphosphino)methane, or bis(diphenylthiophosphoryl)amine leads to neutral complexes $[X(Ph_2PAuPPh_2)_2X]$ [X = CH (**1**) or N (**2**)], $[N\{Ph_2P(S)Au(S)PPh_2\}_2N]$ (**3**), $[N(Ph_2PAgPPh_2)_2N]$ (**4**), or $[N\{Ph_2P(S)Ag(S)PPh_2\}_2N]$ (**5**). Complexes (**1**), (**2**), and (**4**) react further with gold or silver complexes giving tetranuclear ring-system derivatives in which the amido or methanido ligand is acting as a six-electron donor ligand.

Ligands of the type R_2PXPR_2 [X = CH, *e.g.* bis-(diphenylphosphino)methanide;[1-10] X = N, *e.g.* bis(diphenylphosphino)amide][11-14] are the subject of much current attention because of their co-ordinative versatility. They contain three donor atoms but their potential as tridentate ligands has been little studied, so far: a few complexes containing tridentate $Ph_2PCHPPh_2$ have been reported.[15-21]

In the present paper, we describe the synthesis of gold and silver derivatives of the type $[M_2(\mu\text{-}Ph_2PXPPh_2)_2]$ (M = Au, X = CH or N; M = Ag, X = N) *via* a novel reaction. These complexes can be used further as ligands, because of the excess of electron density on the C(methanide) or N(amide) atoms, to obtain homo- or hetero-nuclear derivatives in which the Ph_2PXPPh_2 ligands are acting as six-electron donors. Part of this work has been the subject of a brief communication.[22]

Results and Discussion

The chloro-ylide-gold(I) complex $[AuCl(CH_2PPh_3)]$ reacts (1:1) in acetone solution with $Ph_2PCH_2PPh_2$, $Ph_2PNHPPh_2$, or $Ph_2P(S)NH(S)PPh_2$ to give cyclic binuclear gold(I) complexes containing the deprotonated methanido or amido ligands [equation (1)]. These reactions are the first examples of the novel reaction of a co-ordinated ylide acting as a base to deprotonate a diphosphine. They are reminiscent of transylidation reactions, although the result here is the synthesis of methanido or amido derivatives. Since complexes (**1**)—(**3**) are insoluble or very slightly soluble in acetone, whilst the phosphonium salt $[PPh_3Me]Cl$ is soluble, their isolation is very easy. The reaction rate is fairly rapid (*ca.* 2 h) for the diphosphines [complexes (**1**) and (**2**)] but slower (*ca.* 7 d) for the disulphide [complex (**3**)].



(1)

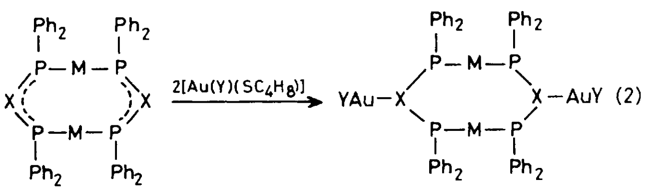
The first rate-determining step may be the interaction of one end of the phosphine ligands with the gold atom in the ylide complex to give a three-co-ordinated intermediate, followed by transfer of a proton from the (acidic) CH_2 or NH groups to the (basic) CH_2 group in the ylide, thereby forming the phosphonium cation. The co-ordinatively unsaturated Au–P–X–P fragment rapidly dimerizes to give the binuclear compound. Some indirect support for this view comes from the fact that $Ph_2AsCH_2AsPh_2$ (weaker co-ordinating ligand, less acidic CH_2 protons) does not react [equation (1)].

On the other hand, it is interesting that addition of free $Ph_2PNHPPh_2$ to complex (**1**) gives (**2**), whilst addition of the disulphide to either (**1**) or (**2**) does not lead to complex (**3**).

If we try to extend the synthetic method of equation (1) to the preparation of similar silver methanide complexes, by the reaction of $[Ag(CH_2PPh_3)_2]ClO_4$ with the same bidentate ligands used above, only the binuclear complex $[N(Ph_2PAgPPh_2)_2N]$ (**4**), which is also insoluble in acetone, can readily be isolated. No immediate precipitation takes place either with $Ph_2PCH_2PPh_2$ or $Ph_2P(S)CH_2(S)PPh_2$, and upon evaporation of the solutions and washing with ethanol somewhat less-soluble $[N\{Ph_2P(S)Ag(S)PPh_2\}_2N]$ (**5**) can be isolated, albeit in low yield (*ca.* 20%). With $Ph_2PCH_2PPh_2$ the differences in solubility are so small that the binuclear silver complex cannot be separated from the reaction mixture. Complex (**5**) is soluble enough to measure its conductivity (non-conducting in acetone solution) and its molecular weight [isopiestic, in chloroform (Found: 1 196. Calc. 1 115)]. The $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum shows a singlet at 36.3 p.p.m.

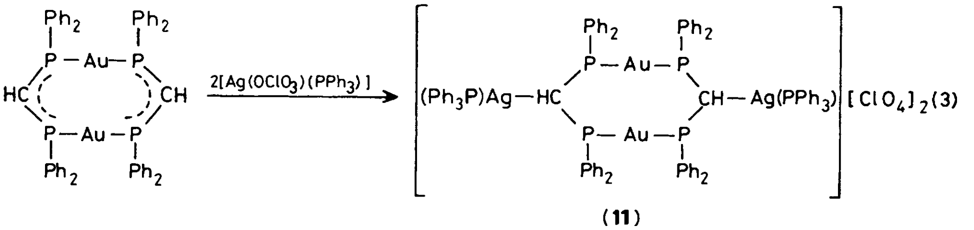
Although the synthetic procedure is a novel one, complexes (**1**)—(**3**)[5,8,14,23] have previously been prepared by other methods. The binuclear silver complexes (**4**) and (**5**) are described for the first time.

By treating dichloromethane suspensions of the insoluble complexes (**1**) and (**2**), or (**4**), with soluble gold(I) or silver(I) derivatives containing one weakly co-ordinating ligand, such



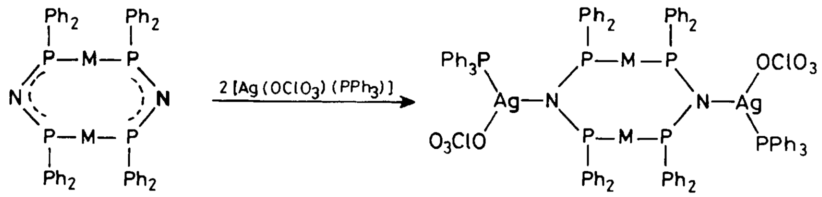
(2)

	M	X	Y
(6)	Au	CH	C_6F_5
(7)	Au	CH	Cl
(8)	Au	N	C_6F_5
(9)	Au	N	Cl
(10)	Ag	N	C_6F_5



(3)

(11)



(4)

M = Au (**12**) or Ag (**13**)

as tetrahydrothiophene (tht) in $[Au(C_6F_5)(SC_4H_8)]$ or $[AuCl(SC_4H_8)]$ or perchlorate in $[Ag(OClO_3)(PPh_3)]$, tetranuclear complexes can be obtained [equations (2)—(4)]. Complexes (**3**) and (**5**) do not react.

Complexes (**6**)—(**13**) are air- and moisture-stable white solids, non-conducting in acetone solutions [(**6**)—(**10**)] or showing conductivities characteristic of 1:2 electrolytes [(**11**)—(**13**)].[24] Complex (**8**) has a molecular weight (isopiestic method in chloroform) of 1 880 (calc. 1 891).

The i.r. spectrum of complex (**1**) shows an absorption of 1 167 cm^{-1}, assignable to the P–CH–P system,[25] which is not present in the spectra of complexes (**6**), (**7**), and (**11**). Similarly, the absorptions at 1 128 (**2**) or 1 130 cm^{-1} (**4**) due to the P–N–P system are not present in the spectra of complexes (**8**)—(**10**), (**12**) and (**13**). Complex (**11**) shows absorptions at 1 100s(br) and 620s cm^{-1} due to the presence of the $[ClO_4]^-$ anion, whilst the spectra of (**12**) and (**13**) show absorptions at 1 105s(br), 1 055s, 930m, and 620m (**12**) or, respectively, 1 100s(br), 1 060s, 930w, and 620m cm^{-1} (**13**) which are characteristic of the $-OClO_3$ group, bonded to a metal centre as a unidentate ligand.[26]

The $^{31}P-\{^1H\}$ n.m.r. spectra of the soluble complexes are in agreement with their formulation (δ in p.p.m. and J in Hz): (**6**), 35.88s, Au–P; (**8**), 81.24s, Au–P; (**10**), 87.73 [dd, $J(^{109}Ag-P) = 288.1$, $J(^{107}Ag-P) = 252.6$, Ag–P]; (**11**), 40.27s, Au–P; 16.46 [dd, $J(^{109}Ag-P) = 574.2$, $J(^{107}Ag-P) = 495.3$, Ag–P]; (**12**), 77.33s, Au–P, 18.26 [dd, $J(^{109}Ag-P) = 727.8$, $J(^{107}Ag-P) = 629.6$, Ag–P]; and (**13**), 68.08 [dm, J(Ag–P)(average) 523.6], 17.74 [dm, J(Ag–P)(average) = 643.4, Ag–PPh_3].

The structures of (**6**) and (**12**) have been established by single-crystal X-ray studies.[22]

By treating the binuclear complexes (**1**) or (**2**) with metal centres which are ligand free $[Ag(ClO_4)]$ or contain weak, readily displaceable ligands $\{[Au(SC_4H_8)_2]ClO_4\}$, insoluble precipitates of stoicheiometry $[M\{X(Ph_2PAuPPh_2)_2X\}]_n$-$[ClO_4]_n$ [X = CH, M = Au (**14**) or Ag (**15**), X = N, M = Au (**16**) or Ag (**17**)] are formed. Complexes (**14**)—(**17**) are air- and moisture-stable white solids that are insoluble in all common organic solvents. Therefore, the only data we were able to collect were the C, H, N, and metal analyses (Table) and the i.r. spectra (Nujol mulls), where the absorptions due to the P–CH–P or P–N–P systems have disappeared and the absorptions at 1 100s(br) and 620s or m cm^{-1} due to ionic $[ClO_4]^-$ are present.

Experimental

Instrumentation and general experimental techniques were as described earlier.[19,25] The yields, melting points, conductivities, and analyses are listed in the Table. The complexes $[Au(C_6F_5)(tht)]$,[27] $[Au(tht)_2]ClO_4$,[28] $[AuCl(CH_2PPh_3)]$,[29]

Table. Physical data for the new complexes

Complex	Yield (%)	Analyses (%)[a] C	H	N	Au or Au + Ag	$\Lambda_M{}^b/\Omega^{-1}$ cm^2 mol^{-1}	M.p.[c] (°C)
(**4**) $[N(Ph_2PAgPPh_2)_2N]$	77	58.4 (58.55)	4.0 (4.1)	2.7 (2.85)			240
(**5**) $[N\{Ph_2P(S)Ag(S)PPh_2\}_2N]^d$	20	51.4 (51.7)	3.25 (3.0)	2.5 (2.5)		2	148
(**6**) $[(F_5C_6)AuHC(Ph_2PAuPPh_2)_2CHAu(C_6F_5)]$	87	39.15 (39.4)	2.25 (2.25)		42.15 (41.7)	2	280
(**7**) $[ClAuHC(Ph_2PAuPPh_2)_2CHAuCl]$	78	36.5 (36.95)	2.55 (2.6)		48.8 (48.45)		293
(**8**) $[(F_5C_6)AuN(Ph_2PAuPPh_2)_2NAu(C_6F_5)]^e$	73	38.1 (38.1)	2.45 (2.15)	1.6 (1.5)	42.1 (41.65)	4	210
(**9**) $[ClAuN(Ph_2PAuPPh_2)_2NAuCl]$	94	35.05 (35.4)	2.55 (2.45)	1.9 (1.7)	48.45 (48.4)	7	221
(**10**) $[(F_5C_6)AuN(Ph_2PAgPPh_2)_2NAu(C_6F_5)]$	90	42.3 (42.1)	2.45 (2.35)	1.6 (1.65)	36.05 (35.6)		170
(**11**) $[(Ph_3P)AgHC(Ph_2PAuPPh_2)_2CHAg(PPh_3)][ClO_4]_2$	81	48.85 (49.2)	3.45 (3.45)		28.55 (29.05)	194	212
(**12**) $[(Ph_3P)(O_3ClO)AgN(Ph_2PAuPPh_2)_2NAg(OClO_3)(PPh_3)]$	86	47.9 (48.0)	3.4 (3.1)	1.15 (1.35)	29.0 (28.55)	206	230
(**13**) $[(Ph_3P)(O_3ClO)AgN(Ph_2PAgPPh_2)_2NAg(OClO_3)(PPh_3)]$	85	52.35 (52.45)	3.7 (3.65)	1.5 (1.45)		247	161
(**14**) $[Au\{HC(Ph_2PAuPPh_2)_2CH\}]_n[ClO_4]_n$	70	40.85 (41.15)	3.1 (2.9)		40.0 (40.5)		288
(**15**) $[Ag\{HC(Ph_2PAuPPh_2)_2CH\}]_n[ClO_4]_n$	78	43.55 (43.9)	3.3 (3.1)		36.35 (36.7)		237
(**16**) $[Au\{N(Ph_2PAuPPh_2)_2N\}]_n[ClO_4]_n$	86	39.1 (39.5)	2.75 (2.75)	1.8 (1.9)	40.85 (40.5)		230
(**17**) $[Ag\{N(Ph_2PAuPPh_2)_2N\}]_n[ClO_4]_n$	76	41.95 (42.1)	2.95 (2.95)	1.85 (2.05)	37.0 (36.6)		242

[a] Calculated values in parentheses. [b] In acetone (5×10^{-4} mol dm^{-3}). [c] Decomposition. [d] *M* 1 196 (calc. 1 115). [e] *M* 1 880 (calc. 1 891).

$[Ag(OClO_3)(PPh_3)]$,[30] and $[Ag(CH_2PPh_3)_2]ClO_4$,[31] and the ligands $Ph_2PNHPPh_2$ and $Ph_2P(S)NH(S)PPh_2$ were prepared as described elsewhere.[32]

Preparation of $[HC(Ph_2PAuPPh_2)_2CH]$ (**1**), $[N(Ph_2PAuPPh_2)_2N]$ (**2**), *or* $[N\{Ph_2P(S)\text{-}Au\text{-}(S)PPh_2\}_2N]$ (**3**).—To a solution of $[AuCl(CH_2PPh_3)]$ (0.203 g, 0.4 mmol) in acetone (30 cm^3) was added $Ph_2PCH_2PPh_2$ (0.154 g, 0.4 mmol). The solution turned yellow and a yellow precipitate was formed. After 2 h the resulting precipitate [(**1**)] was filtered off and washed with acetone (3 × 5 cm^3).

The white complex (**2**) was prepared in a similar way but using $Ph_2PNHPPh_2$ (0.154 g, 0.4 mmol). The white complex (**3**) was obtained analogously, using $Ph_2P(S)NH(S)PPh_2$ (0.180 g, 0. 4 mmol) with a reaction time of 7 d.

Preparation of $[N(Ph_2PAgPPh_2)_2N]$ (**4**) *and* $[N\{Ph_2P(S)Ag(S)PPh_2\}_2N]$ (**5**).—To a solution of $[Ag(CH_2PPh_3)_2]ClO_4$ (0.303 g, 0.4 mmol) in acetone (50 cm^3) was added $Ph_2PNHPPh_2$ (0.154 g, 0.4 mmol). After 3 h the resulting white precipitate [(**4**)] was filtered off and washed with acetone (2 × 5 cm^3).

When using $Ph_2P(S)NH(S)PPh_2$ (0.179 g, 0.4 mmol) a clear solution was obtained. After 3 d at room temperature, evaporation to dryness and washing with ethanol (4 × 5 cm^3) gave complex (**5**), but in low yield (20%).

Preparation of Tetra- and Poly-nuclear Complexes (**6**)—(**17**).—To a suspension (0.1 mmol) of the corresponding binuclear derivative (**1**) (0.116 g), (**2**) (0.116 g), or (**4**) (0.093 g) in dichloromethane (30 cm^3) was added 0.2 mmol of $[Au(C_6F_5)(tht)]$ (0.090 g), $[AuCl(tht)]$ (0.064 g), $[Ag(OClO_3)(PPh_3)]$ (0.094 g), or 0.1 mmol of $[Au(tht)_2]ClO_4$ (0.047 g) or $Ag(ClO_4)$ (0.021 g). After 45 min the initial precipitate dissolved and a clear solution formed, except for the chlorides (**7**) and (**9**) and the polynuclear derivatives (**14**)—(**17**) where a new precipitate was formed and filtered off. The solutions were evaporated to 5 cm^3 and on addition of n-hexane (15 cm^3) complexes (**6**), (**8**), and (**10**)—(**13**) were obtained.

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