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TRIPHENYLPHOSPHINE–GOLD(0)/GOLD(I) COMPOUNDS

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It has previously been reported by two of us that the triphenylphosphine-copper and -silver halides reacted with sodium hydridoborate in ethanol giving $[L_2CuBH_4]$ and $[L_2AgBH_4]$ (L = triphenylphosphine)[1,2] in which a BH_4^- group acted as a chelating ligand forming hydrogen bridges between the metal and boron atoms.

In order to undertake an analogous research on gold, we prepared the gold(I) triphenylphosphine derivatives, reported in Table I together with the few previously known[3–8] compounds of this class.

TABLE I

SOME TRIPHENYLPHOSPHINE GOLD(I) COMPLEXES

Compounds		*Covalency*	*m.w. calc.*	*m.w. found*	*Λ (10⁻³ mol)*	*m.p.*
I	[AuClL]	2	495	520 a	—	242°
II	$[AuNO_3L]$	2	521	544 b 576 a	—	157°
III	$[AuL_2]NO_3$	2	783	718 a 388 c	30.8 d	244°
IV	$[AuL_2]ClO_4$	2	820	1166 b	32.2 d	203°
V	$[AuL_2]BPh_4$	2	1040	528 b	14.5 d	179°
VI	$[AuClL_2]$	3	756	701 b	—	203°
VII	$[AuIL_2]$	3	848	585 b	—	235°
VIII	$[AuL_3]NO_3$	3	1045	444 b 1135 a	30.4 d	202°
IX	$[AuL_4]ClO_4$	4	1344	751 b	23.7 d	203°
X	$[AuL_4]BPh_4$	4	1564	488 b	16.7 d	163°

a = in benzene; b = in chloroform; c = in ethanol; d = in nitrobenzene.

RESULTS AND DISCUSSION

From Table I it appears that the triphenylphosphinegold(I) compounds can display the covalency three and four besides the more usual dicovalency. The most stable compound derived from AuCl is in fact AuClL, but with an excess of

phosphine $AuClL_2$ could also be obtained. In these conditions the species $[AuL_3]^+$ and $[AuL_4]^+$ should also be present in solution because on addition of $LiClO_4$ and $NaBPh_4$ the compounds $[AuL_4]ClO_4$ and $[AuL_4]BPh_4$ have been separated.

We then studied the reaction of some of these compounds with sodium tetrahydridoborate, but as the preliminary results indicated that in the reaction products the L/Au ratio never was higher than unity, we carried out our research only on [AuClL].

This compound[13] when suspended in ethanol reacted with $NaBH_4$ giving a red crystalline substance not containing boron, soluble in chloroform and dichloromethane, which appeared not to be an hydride, at least in that it did not release hydrogen either with acids or with halogens and it did not show any I.R. band in the Au–H stretching region. This compound corresponded analytically to $Au_5L_4Cl \cdot 4H_2O$ (XI) and it could be also obtained from [AuClL] both by means of lithium tetrahydridoaluminate in tetrahydrofuran and by potassium hydroxyde in methanol.

The hydrated compound (XI), which at room temperature was only slightly soluble in methanol, by digestion in this solvent went little by little into solution and could be recovered as the solvate $Au_5L_4Cl \cdot 4CH_3OH$ (XII). This compound by exchange reaction with lithium nitrate and perchlorate and with sodium tetraphenylborate gave the corresponding non-solvated salts $Au_5L_4NO_3$ (XIII), $Au_2L_4ClO_4$ (XIV), and $Au_2L_4BPh_4$ (XV) respectively, which behaved in nitrobenzene solution as uni–univalent electrolytes (Table II).

The perchlorate (XIV) could also be obtained directly from $[AuL_4]ClO_4$ and sodium tetrahydridoborate.

With anhydrous tin(II) chloride the analogous trichlorostannate(II) has been isolated (XVI).

The solvate (XII) reacted with potassium cyanide giving a red diamagnetic compound, which did not show any conductance in solution and corresponded to

TABLE II

POLYNUCLEAR TRIPHENYLPHOSPHINE GOLD COMPLEXES

Compound		*m.w. calc.*	*m.w. found*	*Λ (10^{-3} mol)*	*m.p.*[d]
XI	$[Au_5L_4]Cl \cdot 4H_2O$	2140.5	—	11	156°
XII	$[Au_5L_4]Cl \cdot 4CH_3OH$	2196	—	12.7	136°
XIII	$[Au_5L_4]NO_3$	2095	1005 b	35.5	153°
XIV	$[Au_5L_4]ClO_4$	2132	—	—	160°
XV	$[Au_5L_4]BPh_4$	2352	702 b	19	158°
XVI	$[Au_5L_4]SnCl_3$	2258	2480 b	11	161°
XVII	$[Au_3(CN)L_3]$	1141	—	—	182°
XVIII	$[Au_3IL_2]$	1242	—	4	146°
XIX	$[Au_3(SnI_3)L_2]$	1624	1690 b	—	135°

b = in chloroform, d = with decomposition.

$[Au_3CNL_2]$ (XVII). With potassium iodide, the compound (XII) yielded $[Au_3IL_2]$ (XVIII), a compound very similar to the cyanocompound (XVII), which reacted with tin(II) iodide giving the non-electrolyte $[Au_3(SnI_3)L_2]$.

The water present in the hydrated chlorotetra(triphenylphosphine)pentagold derives from humidity in the solvents. In absolute absence of water, the solvent itself acts as solvating agent giving the much more soluble compound (XII). The behaviour of the chloride was found in accordance with the formula reported above, in which we may consider one atom of gold as having oxidation number one, and the other four atoms as having oxidation number zero: in fact, when the methanol solution of $Au_5L_4Cl \cdot 4CH_3OH$ was refluxed in an inert atmosphere for 24 h, $\frac{4}{5}$ of the gold were separated as metal while $\frac{1}{5}$ was recovered from the solution as $[AuClL_2]$. For the cation $[Au_5L_4]^+$ we suggest a structure in which a central monovalent gold ion is surrounded by four gold atoms having zero oxidation number, each of them coordinated to a triphenylphosphine. The diamagnetism displayed by all these compounds, shows that the electrons of the gold(0) atoms must be paired to give place to two distinct pairs or to a kind of metallic bond.

The stability of metal-to-metal bonds for I B group metals, and particularly for gold, has been emphasized by Nyholm, who prepared[9] a series of compounds of type $(LAu)_n$–ML_m', none of which however had gold-to-gold bonds. In our case in addition to these bonds among the four gold(0) atoms, there must be other interactions between these four paired electrons and the vacant orbitals of the central Au^I atom, which neutralizes at least a part of its charge. The Au^0 atoms carry in fact some excess of negative charge due to phosphine-to-gold bonds. The behaviour of the $[Au_5L_4]^+$ cation with the nucleophilic anions I^- and CN^-, which have a strong affinity for Au^I, does not contradict this structure. Such anions apparently displace one Au_2L_2 group (which however we were not able to isolate) giving resp. the diamagnetic, non-electrolyte $[Au_3IL_2]$ and $[Au_3CNL_2]$. These compounds can be considered hypothetically formed by two groups Au^0L and by one group Au^IX, bond through the gold atoms in a triangle. In this case too, we have two electrons and at least three orbitals forming a bond which could be tricentric or highly delocalized.

The iodobis(triphenylphosphine)trigold reacts with tin(II) iodide giving the triodostannato(II)bis(triphenylphosphine)trigold $[Au_3(SnI_3)L_2]$, in which there appears to be a cluster of three gold atoms and a tin atom forming intermetallic bonds. From the I.R. frequencies reported in Table III some other information about the structure of these compounds can be deduced.

The NO stretching bands seem to indicate[10] that the NO_3 group does act as ligand in compound (II), while it is not covalently bound to the metal in compounds (III), (VIII), and (XIII).

The I.R. spectra of the chloroderivatives (XI) and (XII) are very similar except for the bands at 2930 and 2860 cm^{-1}, assignable to stretching vibrations characteristic of the CH_3 group of methanol.

TABLE III

INFRARED SPECTRA OF SOME TRIPHENYLPHOSPHINE GOLD COMPLEXES

Compound		*Frequencies (cm^{-1})*	*Anion symmetry*
II	$[AuNO_3L]$	1502 vs, $\nu_{as}(NO_2)$ 1272 vs, $\nu_s(NO_2)$ 977 vs, $\nu(NO)$ 780 m δ	C_{2v}
III	$[AuL_2]NO_3$	1362 vs, $\nu_{as}(NO_3)$ 822 w δ	D_{3h}
VIII	$[AuL_3]NO_3$	1360 vs, $\nu_{as}(NO_3)$ 825 w δ	D_{3h}
IV	$[AuL_2]ClO_4$	1080 vs, $\nu_{as}(ClO_4)$	*Td*
IX	$[AuL_4]ClO_4$	1085 vs, $\nu_{as}(ClO_4)$	*Td*
XI	$[Au_5L_4]Cl \cdot 4H_2O$	+3400 w, (very broad) $\nu(OH)$	—
XII	$[Au_5L_4]Cl \cdot 4CH_3OH$	+3400 w, (very broad) $\nu(OH)$ 2930 w, $\nu_{as}(CH_3)$ 2860 w, $\nu_s(CH_3)$	—
XIII	$[Au_5L_4]NO_3$	1360 vs, $\nu_{as}(NO_3)$ 825 w, δ	D_{3h}
XIV	$[Au_5L_4]ClO_4$	1090 vs, $\nu_{as}(ClO_4)$	*Td*
XVII	$[Au_3CNL_2]$	2120 vs, $\nu(CN)$	—

+ in hexachlorobutadiene; ν_{as} asym. stretch.; ν_s sym. stretch; δ, NO_3 group deformation.

The cyano compound (XVII) shows the stretching band assigned to the CN group at 2120 cm^{-1}, that is at a frequency intermediate between that of the free CN^- ion[11] and that of the CN^- group bonded such as in[12] $Au(CN_2)^-$.

EXPERIMENTAL PART

The I.R. spectra were recorded with a Perkin-Elmer Model 237 spectrophotometer.

The magnetic susceptibilities at room temperature were determined by the Gouy method.

The molecular weights were measured with a Mechrolab Osmometer Model 301 A.

Chlorotriphenylphosphinegold(I), (I). This compound was obtained as described by Levi Malvano[4].

Nitratotriphenylphosphinegold(I), (II). To 10 g of (I) dissolved in 150 ml dichloromethane 8.5 g of $AgNO_3$ in ethanol were added; the silver chloride was filtered off and the solution evaporated to dryness. The residue crystallized from dichloromethane–ethanol gave white cristalline needles of (II), soluble in chloroform and dichloromethane, insoluble in alcohols and hydrocarbons.

Bis(triphenylphosphine)gold(I)nitrate, (III). 1 g (1.9 mmole) of (II) and 0.56 g (1.9 mmoles) of triphenylphosphine were dissolved in 15 ml dichloromethane; by slow addition of 30 ml hexane the compound (III) separated as white needles, soluble in ethanol, insoluble in benzene.

Bis(triphenylphosphine)gold(I)perchlorate, (IV). When an ethanol solution of compound (VI) was mixed with an excess $NaClO_4$ in ethanol compound (IV) separated as white crystals which were recrystallized in chloroform–ethanol.

Bis(triphenylphosphine)gold(I) tetraphenylborate, (V). White needles as above, but with $NaBPh_4$ instead of $NaClO_4$.

Chlorobis(triphenylphosphine)gold(I) (VI). 5.0 g (10 mmoles) of (I) and 2.6 g triphenylphosphine (10 mmoles) were mixed in 30 ml dichloromethane; by adding slowly 30 ml hexane white crystals of (VI) separated which were recrystallized with dichloromethane–hexane. Recrystallization in tetrahydrofuran or in warm methanol and hexane yielded instead compound (I).

Iodobis(triphenylphosphine)gold(I), (VII). 2 g (4 mmoles) of potassium iodide and 4 g (4 mmoles) of tetrachloroauric acid in ethanol mixed with 2.1 g (8 mmoles) of triphenylphosphine: the white needles which separated were recrystallized from chloroform–ethanol.

Tris(triphenylphosphine)gold(I) nitrate, (VIII). 0.5 g (1 mmole) of compound (II) and 0.52 g (2 mmoles) triphenylphosphine were dissolved in dichloromethane (5 ml). The compound (VIII) (0.6 g) separated on adding 20 ml of benzene as white needles, soluble in ethanol and chloroform.

Tetrakis(triphenylphosphine)gold(I) perchlorate, (IX). 5 g (0.01 mole) of compound (I) and 13 g (0.05 mole) of triphenylphosphine dissolved in 50 ml ethanol by addition of an excess of sodium perchlorate immediately precipitated compound (IX) as white crystals, soluble in chloroform, insoluble in ethanol.

Tetrakis(triphenylphosphine)gold(I) tetraphenylborate, (X). As above, but by addition of 3.4 g (0.01 mole) sodium tetraphenylborate.

Tetrakis(triphenylphosphine)pentagold chloride:
(a) *Hydrated form* – (XI). To 20 g (40 mmoles) of compound (I) suspended in 200 ml ethanol, 1.6 g (40 mmoles) sodium hydridoborate in ethanol was slowly added; compound (XI) as red crystals separated, which after washing with ethanol was recrystallized in chloroform–ethanol (yield 15%).
(b) *Methanol solvate* – (XII). 2 g of the compound (XI) was suspended in 200 ml

TABLE IV

COMPOSITION OF SOME TRIPHENYLPHOSPHINE GOLD(I) COMPLEXES

	Compound	*C*	*H*	*Au*	*Cl, I, N*	*P*	*Sn*
I	[AuClL]	44.41 (43.7)	3.45 (3.06)	39.8 (39.8)	7.1 (7.1)	6.2 (6.3)	
II	$[Au(NO_3)L]$	41.8 (41.5)	2.80 (2.88)	37.6 (37.8)	2.70 (2.68)	5.75 (5.95)	
III	$[AuL_2]NO_3$	55.6 (55.2)	4.01 (3.83)	25.0 (25.1)	1.80 (1.79)	7.52 (7.91)	
IV	$[AuL_2]ClO_4$	52.6 (52.7)	3.51 (3.67)	24.0 (24.0)		7.42 (7.56)	
V	$[AuL_2]BPh_4$	70.3 (69.2)	4.85 (4.81)	19.0 (18.9)			
VI	$[AuClL_2]$	58.1 (57.2)	3.82 (3.97)	25.8 (26.1)	4.67 (4.70)		
VII	$[AuIL_2]$	50.5 (50.9)	3.45 (3.53)	23.3 (23.2)	15.0 (14.9)		
VIII	$[AuL_3]NO_3$	62.5 (62.1)	4.55 (4.31)	18.9 (18.9)	1.35 (1.34)	8.90 (8.89)	
IX	$[AuL_4]ClO_4$	64.2 (64.2)	4.08 (4.46)	14.7 (14.6)			
X	$[AuL_4]BPh_4$	72.9 (73.0)	5.14 (5.11)	12.8 (12.6)			
XI	$[Au_2L_4]Cl \cdot 4H_2O$	40.7 (40.3)	2.99 (3.25)	45.7 (45.8)	1.55 (1.66)		
XII	$[Au_2L_4]Cl \cdot 4CH_3OH$	41.8 (41.4)	3.40 (3.46)	44.6 (44.8)			
XIII	$[Au_2L_4]NO_3$	41.3 (41.2)	2.82 (2.86)	45.9 (47.0)	0.65 (0.67)		
XIV	$[Au_2L_4]ClO_4$	40.2 (40.6)	2.82 (2.82)	45.9 (46.2)			
XV	$[Au_2L_4]BPh_4$	48.8 (49.0)	3.51 (3.40)	41.5 (41.9)			
XVI	$[Au_2L_4]SnCl_3$	38.0 (38.3)	2.67 (2.66)	42.8 (43.5)	4.55 (4.65)		4.96 (5.30)
XVII	$[Au_3CNL_2]$	38.6 (38.9)	2.72 (2.62)	52.0 (51.8)	1.21 (1.22)		
XVIII	$[Au_2I_2]$	34.3 (34.7)	2.47 (2.42)	46.5 (47.5)	9.8 (10.2)		
XIX	$[Au_3(SnI_3)L_2]$	28.0 (27.0)	2.01 (1.87)	36.9 (36.6)	23.3 (23.6)		7.09 (7.32)

The numbers in parentheses refer to the theoretical values.

cold methanol and stirred under nitrogen for 20 h until they completely dissolved. The solution, by evaporating *in vacuo*, gave compound (XII), which was recrystallized in chloroform–hexane (yield 85%).

Tetrakis(triphenylphosphine)pentagold nitrate, (XIII). A saturated solution of 2 g of compound (XII) in methanol by addition of 0.1 g of lithium nitrate in 10 ml methanol yielded compound (XIII), which was recrystallized from chloroform–hexane (yield 70%).

Tetrakis(triphenylphosphine)pentagold perchlorate, (XIV). The compound was prepared and purified as above, but using 0.15 g of lithium perchlorate (yield 70%), instead of lithium nitrate.

Tetrakis(triphenylphosphine)pentagold tetraphenylborate, (XV). The compound was prepared and purified as above, but using 0.5 g of sodium tetraphenylborate (yield 74%).

Tetrakis(triphenylphosphine)pentagold trichlorostannate, (XVI). The compound was prepared and purified as above, but using 0.38 g anhydrous $SnCl_2$ (2 mmoles) (yield 50%).

Cyanobis(triphenylphosphine)trigold, (XVII). A solution of 2 g of (XI) in 150 ml methanol gave by addition of a methanol solution of 0.065 g potassium cyanide, compound (XVII) as red needles (yield 54%), almost insoluble in all solvents.

Iodobis(triphenylphosphine)trigold, (XVIII). When 2 g of (XI) in 150 ml methanol was treated with an excess potassium iodide and stirred for three h the compound (XVIII) separated (yield 90%). It is soluble in chloroform from which it could be recrystallized by addition of hexane.

Triodostannatebis(triphenylphosphine)trigold, (XIX). To a solution of 1.25 g of the iodocompound (XVIII) in 150 ml methanol, 0.37 g anhydrous SnI_2 were added. A brown compound (yield 20%) immediately separated, which was purified by dissolving in chloroform and precipitating with hexane.

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