Istituto Chimica Generale Università
Via Saldini 50, Milano (Italy)

Ethyldiphenylphosphine-Gold Derivatives with Intermetallic Bonds

F. Cariati, L. Naldini, G. Simonetta and L. Malatesta

Received March 2, 1967

By reaction of $NaBH_4$ on $[LAuCl]$ ($L=PPh_2Et$) in ethanol solution $[L_2Au_3Cl . H_2O]_4$ was obtained and from this by exchange $[L_2Au_3X]_4$ ($X=Br, I, SCN$) and $[L_4Au_6Cl]$ Y ($Y=ClO_4$, PF_6, BPh_4). On the basis of the IR spectra, molecular weights and conductivities structures are proposed for the above compounds having clusters with three gold atoms.

Introduction

Previously we reported the reaction of the triphenylphospine (P) derivatives of I B group metal halides with sodium tetrahydridoborate,[1] which in the case of gold give the cluster compounds $[P_4Au_5]X$ and $[P_2Au_3X]$.[2] We have extended now these researches to gold compounds with different phosphines, in order to study the correlation between the phosphine and the type of reduction compounds obtained.

We report in this paper the results obtained with the monodentate ligand ethyldiphenylphosphine (L) which is more basic than triphenylphosphine and gives generally more soluble compounds.

As usually, we first prepared as starting material the mononuclear gold(I) compounds, which in this case were: $[LAuCl]$ (I) and $[L_2Au(SCN)]$ (II). The reduction of the cholorocompund I by sodium tetrahydridoborate gave a brick-red substance, diamagnetic and non electrolyte, having a composition corresponding to $[L_2Au_3Cl . H_2O]$. The molecular weight determination was carried out on anhydrous compound and corresponded to the tetrameric unit $L_8Au_{12}Cl_4$. We consider that also the hydrated substance was tetramic, that is $[L_2Au_3Cl . H_2O]_4$ (III).

The chloride III, by exchange with nucleophilic anions as bromide, iodide and thiocyanate gives resp.:

$[L_2Au_3Br(H_2O)]_4$ (IV)
$[L_2Au_3I]_4$ (V)
$[L_2Au_3(SCN)]_4$ (VI)

The same chloride III by exchange with anions of very low nucleophilicity as perchlorate, fluorophosphate and tetraphenylborate gives, on the contrary, compounds which behave, in nitrobenzene, as uni-univalent electrolyte and correspond to VII, VIII and IX resp. Analogously, the thiocyanate VI by exchange with lithium perchlorate gave the uni-univalent electrolyte X:

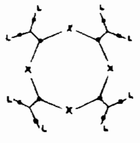
$[L_4Au_6Cl]ClO_4$ (VII)
$[L_4Au_6Cl]PF_6$ (VIII)
$[L_4Au_6Cl]BPh_4$ (IX)
$[L_4Au_6SCN]ClO_4$ (X)

Discussion

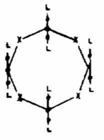
An insight on the structure of compounds III and VI was obtained from their IR spectrum. Compound III in fact has an absorption band at 262 cm^{-1}, which may be compared with the absorption at 315 cm^{-1} showed by compound I. We assign these bands to the stretching of the bridging and terminal chloride resp.[3] Also compound VI shows in its IR spectrum a strong band at 2102 cm^{-1} which may be compared with the band at 2067 cm^{-1} of compound II. These two bands are assigned to the CN stretching of a bridging and a covalently bound SCN resp.[4] This seems to indicate for compounds III, IV, V and VI a structure in which the nucleophilic anions are bridging the L_2Au_3 units to give a tetramerisation confirmed by the data of molecular weight in chloroform. However, these tetramers must be at least partially dissociated in ethanol solution, as proved by the fact that they are transformed in salt-like dimers by the action of bulky non co-ordinating anions and give VII, VIII, IX and X.

The structure of the tetramers may be hypothesized as A or B according whether the triangular or linear disposition of the gold atoms is assumed:

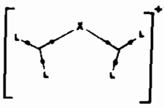
A



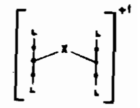
B



C



D



where four clusters of three gold atoms (indicated as ●) are connected by one bridging nucleophilic anion. The intermetallic bond involves in this case three gold atoms instead of five, as in corresponding triphenylphosphine compound $[P_4Au_5]Cl$.

---

(1) (a) F. Cariati e L. Naldini, *Gazzetta, 95*, 3 (1965). (b) F. Cariati e L. Naldini, *ibid.*, 201.
(2) (a) L. Malatesta, L. Naldini, G. Simonetta and F. Cariati, *Chem. Comm.*, 212 (1965). (b) L. Malatesta, L. Naldini, G. Simonetta and F. Cariati: «Coordination Chemistry Reviews», Elsevier, Amsterdam, 255 (1966).
(3) D. M. Adams, J. Chatt, J. M. Davidson and J. Garrett, *J. Chem. Soc.*, 2189 (1963).
(4) R. J. H. Clark and C. S. Williams, *Spect. Acta. 22*, 1801 (1966).

In all known cases where there are clusters formed by three metal atoms, the triangular structure has been proved or considered the most probable; if we hypothesize that this is true in this case too, then the three neutral gold atoms, less one *s* electron, could be bound by a three center molecular orbital containing the two valence electrons. However, in all the cases so far reported, the bonds were between atoms or ions of transitional elements having *d* valence electrons, while, in this case, we have only *s* electrons. On the other hand, it has been affirmed that in $[HCr_2(CO)_{10}]^-$ the Cr-H-Cr atoms have a collinear arrangement with a two electrons tricenter molecular orbital.[5] The structure of the salt-like dimers may correspondently be hypothesized as C or D.

The fact that in this case the average formal oxidation number of gold is higher (1/3) than in the triphenylphosphine compound (1/5) can be considered as a consequence of the stronger basicity of the ethyldiphenylphosphine ligand.

Experimental Section

The IR spectra have been recorded with Perkin-Elmer Spectrometer Model 237 and 621. The magnetic susceptibility has been determined at room temperature by the Gouy balance and all the prepared compounds were found diamagnetic. The molecular weights were determined by differential tensiometry by the Mechrolab Mod. 301 A apparatus.

Table I. IR Frequencies (cm $^{-1}$) in nujol

Compound	ν (CN)	ν_{as} (ClO_4)	ν_{as} (PF_6)	ν (Au—Cl) ν (Au—NCS)	ν (Au—Cl—Au)
[LAuCl]	—	—	—	315 vs	—
$[L_2Au(SCN)]$	2067 vs*	—	—		—
$[L_2Au_3Cl(H_2O)]_4$	—	—	—		262 m
$[L_2Au_3(SCN)]_4$	2102 vs*	—	—	265 m*	—
$[L_4Au_6Cl]ClO_4$	—	1080 s	—		262 m
$[L_4Au_6Cl]PF_6$	—	—	848 vs		272 m
$[L_4Au_5Cl]BPh_4$	—	—	—		265 w
$[L_4Au_5(SCN)]ClO_4$	2103 s	1080 s	—		—

* In CH_2Cl_2

Table II. Molecular weight in $CHCl_3$

Compound	M. calc.	M. found	Concn. %
[LAuCl]	447	476	1,70
$[L_2Au(SCN)]$	683	692	2,38
$[L_2Au_3Cl]_4$*	4216	3980	1,38
$[L_2Au_3Br]_4$*	4396	4425	1,15
$[L_2Au_3I]_4$	4580	4100	1,30
$[L_2Au_3(SCN)]_4$	4304	4050	0,88

* On compounds dried at 60°C in vacuo.

Chloro(ethyldiphenylphosphine)gold. From 50 ml of an ethanol solution of tetrachloroauric acid prepared from 1.03 g of gold (5.27 mmoles) and 2.24 g (10.54 mmoles) of ethyldiphenylphosphine. The white crystalline precipitate was recrystallized from dichloromethane-hexane.

Thiocyanatobis(ethyldiphenylphosphine)gold. From 1.64 g of I (3.7 mmoles) suspended in 30 ml ethanol, 0.79 g of ethyldiphenylphosphine (3.7 mmoles) and 0.39 g of KSCN (4 mmoles) for about 1 h at 50°C. The white product was recrystallized from dichloromethane-hexane.

Tetrakis [μ-chlorobis(ethyldiphenylphosphine)trigold aquo]. From 1.64 g of I (3.7 mmoles) and 0.14 g of $NaBH_4$ (3.7 mmoles). The red brown solution was evaporated to dryness, dissolved in dichloromethane and precipitated by addition of hexane.

*Tetrakis [μ-bromobis(ethyldiphenylphosphine)trigold aquo]**. From 1.1 g of III (0.25 mmoles) suspended in 20 ml of ethanol and 0.87 g of LiBr (1 mmole). The red brown product was recrystallized from dichloromethane-hexane.

Tetrakis [μ-iodobis(ethyldiphenylphosphine)trigold]. From 1.1 g of III (0.25 mmoles) in 20 ml of ethanol and 0.134 g of LiI. The red brown product was recrystallized from dichloromethane-hexane.

Tetrakis [μ-thiocyanatobis(ethyldiphenylphosphine) trigold]. From 1.1 g of III (0.25 mmoles) in 20 ml of ethanol and 0.97 g of KSCN (1 mmole). The red brown product was recrystallized from dichloromethane-hexane.

μ-Chlorobis [bis(ethyldiphenylphosphine)trigold] perchlorate. From 1.1 g of III in 20 ml of ethanol and 0.1 g of $LiClO_4$. The red brown product was recrystallized from dichloromethane-hexane.

μ-Chlorobis[bis(ethyldiphenylphosphine)trigold]hexafluorophosphate. From 1.1 g of III in 20 ml of ethanol and 0.16 g of NH_4PF_6 (1 mmole). The red brown product was recrystallized from dichloromethane-hexane.

μ-Chlorobis[bis(ethyldiphenylphosphine)trigold]tetraphenylborate. From 1.1 g of III in 20 ml of ethanol and 0.34 of $NaBPh_4$ (1 mmole). The red brown product was recrystallized from dichloromethane-hexane.

---

(5) L. B. Handy, P. M. Treichel, L. F. Dahl and R. G. Hayter, *J. Am. Chem. Soc.*, *88*, 366 (1966).

Table III

Compound	C	H	Au	N, O	P	m.p.	(10^{-3} mol) Λ*
$[Au(PPh_2Et)Cl]$	37.6 (37.6)	3.40 (3.36)	44.0 (44.2)	—	—	117	—
$[Au(PPh_2Et)_2(SCN)]$	50.2 (50.9)	4.20 (4.39)	28.0 (28.8)	2.10 (2.05)	—	98	—
$[Au_3(PPh_2Et)_2Cl(H_2O)]_4$	32.0 (31.15)	3.20 (2.98)	53.0 (55.1)	1.52 (1.48)	5.70 (5.64)	138	—
$[Au_3(PPh_2Et)_2Br(H_2O)]_4$	28.9 (30.1)	2.76 (2.86)	52.3 (52.9)	1.50 (1.43)	—	137	—
$[Au_3(PPh_2Et)_2I]_4$	29.1 (29.4)	2.70 (2.62)	51.5 (51.5)	—	5.50 (5.43)	142	—
$[Au_3(PPh_2Et)_2(SCN)]_4$	30.6 (32.4)	2.74 (2.78)	54.1 (54.8)	1.31 (1.29)	—	143	—
$[Au_6(PPh_2Et)_4Cl]ClO_4$	31.5 (30.9)	2.74 (2.78)	54.8 (54.4)	—	6.40 (5.70)	150	22.8
$[Au_6(PPh_2Et)_4Cl]PF_6$	30.1 (30.3)	2.72 (2.70)	53.8 (53.3)	—	7.15 (6.99)	152	23.5
$[Au_6(PPh_2Et)_4Cl]BPh_4$	41.2 (40.1)	3.55 (3.34)	50.3 (49.4)	—	—	143	24.1
$[Au_6(PPh_2Et)_4(SCN)]ClO_4$	31.4 (31.2)	2.54 (2.74)	53.6 (54.0)	0.80 (0.64)	—	139	21

* In $C_6H_5NO_2$. The numbers in parentheses refer to theoretical values.

μ-Thiocyanatobis[bis(ethyldiphenylphosphine)trigold] perchlorate. From 1.1 g of III (0.25 mmoles) in 20 ml of ethanol, 0.1 g of KSCN (1 mmole) and 0.1 g of $LiClO_4$ (1 mmole). The red brown product was recrystallized from dichloromethane-hexane.

Acknowledgment. This work was supported with a Grant of C.N.R. (Italian Research Council).