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PERCHLORATOBIS(PENTAFLUOROPHENYL)TRIPHENYLPHOSPHINE-GOLD(III) AS A PRECURSOR OF NEW GOLD COMPLEXES

R. USON, A. LAGUNA and J.L. SANJOAQUIN
Department of Inorganic Chemistry, University of Zaragoza (Spain)

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Summary

The perchlorato ligand of perchloratobis(pentafluorophenyl)triphenylphosphinegold(III) can easily be displaced by different types of ligands. Neutral complexes are obtained by adding anionic ligands (N_3^-, HCO_3^-), while cationic complexes are obtained by adding neutral monodentate ligands ($OPPh_3$, $OAsPh_3$, ONC_5H_5, ONC_9H_7, NC_9H_7, PEt_3, PBu_3, PPh_2Me). Only with very weak σ-donors (SO_2, CO_2, NC_5F_5, NC_5Cl_5) does no reaction take place. The addition of neutral bidentate ligands leads to cationic gold(III) complexes with diphosphines and diarsines, whereas nitrogen- or oxygen-donors give rise to reductive elimination reactions which lead to gold(I) complexes.

No reaction takes place with mono-olefins while cyclopolyolefins give rather unstable gold(I) complexes which readily decompose. Only the gold(I) complex with 1,5-cyclooctadiene can be isolated.

Introduction

We have recently shown that perchlorato complexes provide a convenient way for the synthesis of new complexes, since the very poor coordination capacity of the perchlorato ligand leads to its ready replacement by other ligands, both neutral or anionic. The complexes $[O_3ClOAu(C_6F_5)_2PPh_3]$ [1], $[O_3ClOAuPPh_3]$ [2], $[O_3ClOPd(C_6F_5)(PPh_3)_2]$ [3] and $[O_3ClOPt(C_6F_5)(PEt_3)_2]$ [4] have been used for the syntheses of neutral and cationic Au^{III}, Au^{I}, Pd^{II} and Pt^{II} complexes, respectively.

This paper reports the results of the reactions of $[O_3ClOAu(C_6F_5)_2PPh_3]$ with anionic, neutral monodentate, neutral bidentate and olefin ligands which have led to new gold(III) and gold(I) complexes.

Results and discussion

Benzene or chloroform solutions of perchloratobis(pentafluorophenyl)-triphenylphosphinegold(III) were prepared by mixing solutions of the chlorocomplex with those of silver perchlorate [1]. The precipitated silver chloride was filtered off and the ligand was then added to the perchlorato complex, with the results given below.

(a) Anionic ligands

The ligands N_3^-, HCO_3^-, F^- and $C_2O_4^{2-}$ were used in the form of their sodium salts, and $C_5H_5^-$ as TlC_5H_5. Only the first two ligands gave rise to substitution according to eqn. 1. No reaction took place with NaF and $Na_2C_2O_4$, probably

$$[O_3ClOAu(C_6F_5)_2PPh_3] + NaX \rightarrow [XAu(C_6F_5)_2PPh_3] + NaClO_4 \qquad (1)$$

$(X = N_3^-, HCO_3^-)$

because of the low solubility of these salts.

With TlC_5H_5 a reaction took place and $TlClO_4$ was precipitated. The filtered solution was evaporated and yielded $[C_6F_5AuPPh_3]$ [5] as a result of the reductive elimination of the radicals C_5H_5 and C_6F_5 from the complex $[C_5H_5Au(C_6F_5)_2PPh_3]$ expected from reaction 1.

When $[O_3ClOAuPPh_3]$ [2] was treated with TlC_5H_5, $TlClO_4$ was precipitated and metallic gold separated from the solution, forming a mirror inside the flask. This result was quite unexpected since the complex which should be formed according to eqn. 2 had already been described in the literature [6] and was stated to be stable up to above 100°.

$$[O_3ClOAuPPh_3] + TlC_5H_5 \rightarrow TlClO_4 + [C_5H_5AuPPh_3] \qquad (2)$$

(b) Neutral monodentate ligands

Generally, when neutral monodentate ligands were added to benzene or chloroform solutions of the perchlorato complex, the neutral ligand readily displaced the perchlorato group to give cationic complexes which precipitated from the benzene solution; with chloroform solutions precipitation took place only after adding alcohol (eqn. 3).

$$[O_3ClOAu(C_6F_5)_2PPh_3] + L \rightarrow [LAu(C_6F_5)_2PPh_3]ClO_4 \qquad (3)$$

$(L = OPPh_3, OAsPh_3, ONC_5H_5, ONC_9H_7, NC_9H_7, PEt_3, PBu_3, PPh_2Me)$

Nevertheless, when neutral ligands with very poor donor capacity, such as SO_2, CO_2, NC_5F_5 or NC_5Cl_5 were used, process 3 did not take place and the unchanged starting complex could be recovered.

When the ligand L was a reductor (which is so with all the phosphines), it was necessary to work with the exact stoichiometric amount because the use of an excess of the ligand gave the reduction product $[(phosphine)AuPPh_3]ClO_4$. With $L = SPPh_3$ the cationic perchlorate of gold(I) was obtained even when less than the stoichiometric amount of the ligand was used. The same product was obtained when $SPPh_3$ was added to a benzene solution of perchloratotriphenylphosphinegold(I).

(c) Neutral bidentate ligands

We have found two different types of behavior:

(i) The addition of benzene solutions of bipyridine, *o*-phenanthroline or 1,2-bis(diphenylphosphine)ethane dioxide caused the reductive elimination of the two C_6F_5 groups and the formation of cationic gold(I) complexes of the $[(Ph_3P)Au(A{-}A)]ClO_4$ type. They were also obtained directly by starting from the perchlorato gold(I) complex according to eqn. 4.

$$[Ph_3PAuOClO_3] + (A{-}A) \rightarrow [Ph_3PAu(A{-}A)]ClO_4 \qquad (4)$$

(ii) Cationic gold(III)perchlorates were obtained with diphosphines and diarsines, such as 1,2-bis(diphenylphosphino)ethane and 1,2-bis(diphenylarsino)-ethane (eqn. 5). It would certainly be of interest to establish whether the

$$[O_3ClOAu(C_6F_5)_2PPh_3] + (A{-}A) \rightarrow [(A{-}A)Au(C_6H_5)_2PPh_3]ClO_4 \qquad (5)$$

bidentate ligands behave as such, that is to say, whether the gold(I) complexes are tricoordinated and those of gold(III) are pentacoordinated. Our data do not allow us to determine this except for $[Ph_3PAu(Ph_2P(O)CH_2CH_2P(O)Ph_2)]ClO_4$, whose IR spectrum shows that the ligand is attached through only one of its donor atoms (see below).

(d) Olefins

Again we met with different patterns of behavior depending on the olefin used. The olefin was always added to a benzene solution of perchloratobis(pentafluorophenyl)triphenylphosphinegold(III) at room temperature.

(i) No reaction took place with monoolefins such as n-heptene or cyclohexene and the unchanged starting complex was recovered.

(ii) A white precipitate was formed with cyclopolyolefins such as cyclopentadiene, 1,3-cyclohexadiene, 1,4-cyclohexadiene, cycloheptatriene, 1,5-cyclooctadiene or cyclooctatetraene. The precipitate decomposed readily and left metallic gold. Only with 1,5-cyclooctadiene was the white precipitate sufficiently stable to be isolated, analyzed and identified as $[(C_8H_{12})AuPPh_3]ClO_4$. The same result was obtained by adding 1,5-cyclooctadiene to a benzene solution of perchloratotriphenylphosphinegold(I). This means that a reductive elimination of the two C_6F_5 groups took place and that the gold(I) perchlorate which was formed was usually unstable at room temperature and decomposed. These unstable intermediate complexes could perhaps be isolated by working at lower temperatures, but we have not tried to confirm this supposition.

(e) IR spectra

Of the neutral complexes obtained according to eqn. 1, the spectrum of the azido derivative shows absorption bands at 2030 s and 1258 m cm^{-1}, which are assigned to the N_3^- group [7], whereas among the vibrations which are characteristic of the HCO_3^- group, only those at 1261 m and 320 m cm^{-1} can be identified while the others are masked by other ligands [8].

All the cationic complexes show bands at 1085 vs (br) and 615 m cm^{-1} which are characteristic of the perchlorate anion (T_d) [9]. The presence of these bands proves that the perchlorato ligand has been displaced by ligand L (see reactions 3, 4 and 5) and that cationic complexes are formed.

Tables 1 and 2 contain the vibrations characteristic of each ligand which could be observed in the complex since they were not masked by vibrations of

TABLE 1

FREQUENCIES ASSIGNED TO L IN $[LAu(C_6F_5)_2PPh_3]ClO_4$

Ligand L	Frequencies (cm^{-1})	Assignment	Ref.
$OPPh_3$	1125 vs	ν(P—O)	10
$OAsPPh_3$	855 s	ν(As—O)	11
	460 s, 348 m	Internal vibrations	
ONC_5H_5	1189 m	ν(N—O)	12
	1610 w, 1170 m, 772 m, 570 m	Internal vibrations	12
ONC_9H_7	1210 mw	ν(N—O)	12
	1582 w, 764 m, 579 w, 560 w	Internal vibrations	13
NC_9H_7	1590 w, 785 m, 565 w	Internal vibrations	13
dae [a]	450 s, 310 m	Internal vibrations	14

[a] 1,2-bis(diphenylarsino)ethane.

other ligands. In particular, no new vibrations could be observed when L = PEt_3, PBu_3, PPh_2Me and $Ph_2PCH_2CH_2PPh_2$ because of the simultaneous presence of PPh_3 in the starting complex.

The free 1,2-bis(diphenylphosphino)ethane dioxide shows two absorption bands at 1185 s and 1175 s cm^{-1}, which are assignable to the vibrations ν(P—O) and δ(C—H) and are the only ones that appear in the 1140—1250 cm^{-1} region. The complex $[(Ph_2P(O)CH_2CH_2P(O)Ph_2)AuPPh_3]ClO_4$ shows four intense bands in that region at 1180 s, 1155 s, 1146 s and 1118 s cm^{-1}, which we attribute to the fact that the ligand is attached to the central ion through only one of its oxygen donor atoms.

(f) Conductivities

All the cationic complexes behave as completely dissociated 1/1 electrolytes when dissolved in acetone, their measured molar conductivities ranging between 130 and 160 $ohm^{-1}cm^2mol^{-1}$. The neutral complexes (with L = N_3^- or HCO_3^-) are non-conducting (Λ_M = 2 and 9.5 $ohm^{-1}cm^2mol^{-1}$, respectively) in acetone solution [19] and monomeric in benzene solution.

Experimental

Molecular weights were measured in benzene with a Hitachi—Perkin—Elmer model 115 osmometer and conductivities in $\approx 5\ 10^{-4}$ *M* solution with a Philips PW 9501/01 conductimeter. IR spectra were recorded on a Beckmann IR 20A

TABLE 2

FREQUENCIES ASSIGNED TO L IN $[LAuPPh_3]ClO_4$

Ligand L	Frequencies (cm^{-1})	Assignment	Ref.
$SPPh_3$	595 s	ν(P—S)	15
bipy [a]	1596 s, 1160 m, 752 vs 735 m, 412 m, 352 w	Internal vibrations	16
o phen [b]	1584 w, 1518 m, 1150 m 870 w, 848 s, 770 m, 749 w	Internal vibrations	16
dpeo [c]	1180 s, 1155 s, 1146 s, 1118 s	ν(P—O), δ(C—H)	17
1,5-C_8H_{12} [d]	1237 w, 980 w, 818 m, 765 m, 615 w	Internal vibrations	18

[a] 2,2'-bipyridine. [b] 1,10-phenanthroline. [c] 1,2-bis(diphenylphosphino)ethane dioxide. [d] 1,5-cyclooctadiene.

spectrophotometer (over the range 4000—250 cm^{-1}) using Nujol mulls between polyethylene sheets. C, H and N analyses were made with a Perkin—Elmer 240 microanalyzer. The analytical results are in reasonable agreement with the proposed formulae, if the difficulties which arise from the presence of P and F in our samples are taken into account [20].

I. $[N_3Au(C_6F_5)_2PPh_3]$. A suspension of 0.130 g (2 mmol) of NaN_3 and 1 mmol of $O_3ClOAu(C_6F_5)_2PPh_3$ in 25 ml of benzene [1] was stirred at room temperature for 5 h. The $NaClO_4$ was filtered off and the solution was evaporated to dryness. Complex I was obtained in the form of yellowish-white crystals by recrystallizing the residue from chloroform—ethanol. The complex was very soluble in hexane and ethanol and melted at 142°. Λ_M = 2 ohm^{-1}cm^{2}mol^{-1} in acetone. (Found: C, 43.35; H, 2.06; Au, 24.96; N, 4.10; mol.wt. 807. Calcd.: C, 43.11; H, 1.70; Au, 23.59; N, 5.00%; mol.wt. 835.)

II. $[HCO_3Au(C_6F_5)_2PPh_3]$. 0.16 g (1 mmol) of $NaHCO_3$ was added to a benzene solution of 1 mmol of the perchlorate complex. The mixture was stirred at room temperature for three hours and the subsequent procedure was as for I. The colourless crystals of complex II were obtained by recrystallizing from diethyl ether—hexane. Complex II was soluble in acetone, benzene and chloroform but practically insoluble in hexane and ethanol; it decomposed at 130°; Λ_M = 9.5 ohm^{-1}cm^{2}mol^{-1} in nitromethane. (Found: C, 43.40; H, 1.82; Au, 23.61; mol. wt. 834. Calcd.: C, 43.58; H, 1.89; Au, 23.06%; mol. wt. 854.)

III. $[C_6F_5AuPPh_3]$. 0.27 g (1 mmol) of TlC_5H_5 [21] was added to a benzene solution of 1 mmol of the perchlorato complex. The mixture was stirred at room temperature for 30 min. The drab coloured $TlClO_4$ precipitated a few minutes after the beginning of the reaction. The solution was filtered and evaporated in vacuo to dryness. Complex III was obtained in the form of colourless crystals by recrystallizing the residue from chloroform—hexane. It melted at 170°. (Found: C, 45.95; H, 2.52; Au, 30.42. Calcd.: C, 46.02; H, 2.41; Au, 31.45%.)

IV. $[(OPPh_3)Au(C_6F_5)_2PPh_3]ClO_4$. 0.278 g (1 mmol) of $OPPh_3$ was added to a solution of 1 mmol of the perchlorato complex in 25 ml of benzene. The mixture was stirred for 15 min at room temperature. The white complex IV precipitated, was filtered and washed with small quantities of benzene. It was soluble in chloroform and acetone and decomposed at 130°. Λ_M = 142 ohm^{-1}cm^{2}mol^{-1}. (Found: C, 49.90; H, 3.09; Au, 17.67. Calcd.: C, 49.20; H, 2.56; Au, 16.83%.)

V. $[(OAsPh_3)Au(C_6F_5)_2PPh_3]ClO_4$. 0.322 g (1 mmol) of $OAsPh_3$ was added to a solution of the perchlorato complex in 25 ml of chloroform. The solution was stirred at room temperature for 15 min. The crystalline complex V was obtained after evaporating the solution to 10 ml and adding ethanol. It was soluble in acetone, chloroform and nitromethane but insoluble in hexane, ethanol and benzene. It decomposed at 158°. Λ_M = 124 ohm^{-1}cm^{2}mol^{-1} in acetone. (Found: C, 47.46; H, 3.11; Au, 15.28. Calcd.: C, 47.44; H, 2.47; Au, 16.22%.)

VI. $[(ONC_5H_5)Au(C_6F_5)_2PPh_3]ClO_4$. A small excess of pyridine oxide was added to a chloroform solution of the perchlorato complex and the subsequent procedure was as for V. Complex VI was obtained in the form of colourless crystals, which decomposed at 132°. Λ_M = 135 ohm^{-1}cm^{2}mol^{-1} in acetone. (Found: C, 40.87; H, 2.21; Au, 21.60; N, 1.42. Calcd.: C, 42.50; H, 2.02; Au, 19.96; N, 1.41%.)

VII. $[(ONC_9H_7)Au(C_6F_5)_2PPh_3]ClO_4$. Complex VII was obtained in the form of a microcrystalline precipitate when the stoichiometric amount of quinoline oxide was added to a benzene solution of the perchlorato complex. It decomposed at 130°. Λ_M = 134 ohm^{-1}cm^{2}mol^{-1} in acetone. (Found: C, 45,53; H, 2.46; Au, 19.80; N, 1.24. Calcd.: C, 45.13; H, 2.12; Au, 19.01; N, 1.35%.)

VIII $[(NC_9H_7)Au(C_6F_5)_2PPh_3]ClO_4$. Complex VIII was obtained in the form of a white solid by adding the stoichiometric amount of quinoline to a benzene solution of the perchlorato complex. It decomposed at 160°. Λ_M = 150 ohm cm^2 mol^{-1} in acetone. (Found: C, 45.86; H, 2.75; Au, 18.27; N, 1.98. Calcd.: C, 45.81; H, 2.15; Au, 19.20; N, 1.37%.)

IX. $[(PEt_3)Au(C_6F_5)_2PPh_3]ClO_4$. A little less than the stoichiometric amount of triethylphosphine was added to a benzene solution of the perchlorato complex. The procedure was the same as for IV. Complex IX was a white microcrystalline precipitate, which decomposed at 139°. Λ_M = 137 ohm^{-1}cm^{2}mol^{-1} in acetone. (Found: C, 41.93; H, 3.92; Au, 18.47. Calcd.: C, 42.77; H, 2.97; Au, 19.45%.)

X. $[(PBu_3)Au(C_6F_5)_2PPh_3]ClO_4$. A little less than the stoichiometric amount of tributylphosphine was added to a benzene solution fo the perchlorato complex; the procedure was as in IV. Complex X precipitated in the form of a microcrystalline solid, which decomposed at 150°. Λ_M = 124 ohm^{-1}cm^{2}mol^{-1} in acetone. (Found: C, 46.53; H, 3.40; Au, 18.25. Calcd.: C, 46.04; H, 3.82; Au, 18.00%.)

XI. $[(PPh_2Me)Au(C_6F_5)_2PPh_3]ClO_4$. The addition of diphenylmethylphosphine, carried out as in former reactions, led to the formation of complex XI. It decomposed at 155°. Λ_M = 140 ohm^{-1} cm^2 mol^{-1} in acetone. (Found: C, 45.35; H, 3.02; Au, 19.60. Calcd.: C, 47.23; H, 2.56; Au, 18.05%.)

XII. $[(SPPh_3)AuPPh_3]ClO_4$. The addition of triphenylphosphine sulphide carried out as in former reactions led to the preparation of complex XII. It melted at 307°. Λ_M = 134 ohm^{-1}cm^{2}mol^{-1} in acetone. (Found: C, 49.58; H, 3.77; Au, 24.60. Calcd.: C, 50.70; H, 3.52; Au, 23.12%.)

Complex XII could also be obtained by adding $SPPh_3$ to the stoichiometric amount of perchloratotriphenylphosphinegold(I) [2] in benzene solution. (Found: C, 50.09; H, 4.02; Au, 23.65%.)

XIII. $[(Ph_2PCH_2CH_2PPh_2)Au(C_6F_5)_2PPh_3]ClO_4$. A solution of 0.40 g (1 mmol) of 1,2-bis(diphenylphosphino)ethane in 20 ml of benzene was slowly added to a benzene solution of 1 mmol of the perchlorato complex. The immediate precipitation of the microcrystalline complex XIII took place. Once the addition of the ligand had been finished (15 min) the solution was stirred for a further 20 min at room temperature. The solid was filtered and washed with small quantities of benzene and then dried in vacuo. It decomposed at 170°. Λ_M = 145 ohm^{-1}cm^{2}mol^{-1} in acetone. It was slightly soluble in acetone and chloroform but insoluble in benzene, ethanol and hexane. (Found: C, 51.69; H, 3.77; Au, 16.05. Calcd.: C, 52.08; H, 3.04; Au, 15.25%.)

XIV. $[(Ph_2AsCH_2CH_2AsPh_2)Au(C_6F_5)_2PPh_3]ClO_4$. A solution of 0.47 g (1 mmol) of 1,2-bis(diphenylarsino)ethane in 20 ml of benzene was slowly added to a benzene solution of 1 mmol of the perchlorato complex. Complex XIV was obtained as for XIII. It decomposed at 180°. Λ_M = 140 ohm^{-1}cm^{2}mol^{-1} in acetone. Its solubility in organic solvents is similar to that of complex XIII. (Found: C, 48.64; H, 3.55; Au, 14.82. Calcd.: C, 48.76; H, 2.85; Au, 14.28%.)

XV. $[(bipy)AuPPh_3]ClO_4$. When a benzene solution of the stoichiometric amount of 2,2′-bipyridine was added to a benzene solution of the perchlorato complex immediate precipitation of the white complex XV could be observed. It melted at 215° with decomposition. Λ_M = 158 ohm^{-1}cm^{2}mol^{-1} in acetone. It was slightly soluble in acetone and nitromethane but insoluble in benzene, chloroform and hexane. (Found: C, 47.21; H, 3.74; Au, 27.22; N, 4.26. Calcd.: C, 47.04; H, 3.24; Au, 27.55; N, 3.91%.)

Complex XV was also obtained by adding 2,2′-bipyridine to a benzene solution of perchloratotriphenylphosphinegold(I) [2]. (Found: C, 46.54; H, 3.64; Au, 27.78; N, 4.35%.)

XVI. $[(o\text{-}phen)AuPPh_3]ClO_4$. The addition of 1,10-phenanthroline, carried out as for compound XV led to the preparation fo complex XVI It decomposed at 180°. Λ_M = 141 ohm^{-1}cm^{2}mol^{-1} in acetone. It was slightly soluble in acetone but insoluble in benzene, chloroform, diethyl ether, nitromethane and hexane. (Found: C, 48.45; H, 3.78; Au, 27.86; N, 3.98. Calcd.: C, 48.76; H, 3.14: Au, 26.66; N, 3.79%.)

As with XV, the addition of the ligand to a benzene solution of perchloratotriphenylphosphinegold(I) led to complex XVI. (Found: C, 50.08; H, 3.53; Au, 26.51; N, 4.00%.)

XVII. $[(Ph_2P(O)CH_2CH_2P(O)Ph_2)AuPPh_3]ClO_4$. The addition of 1,2-bis-(diphenylphosphino)ethane dioxide, carried out as in XV led to complex XVII. It melted at 128°. Λ_M = 167 ohm^{-1}cm^{2}mol^{-1} in acetone. It was slightly soluble in acetone and nitromethane. (Found: C, 52.95; H, 4.57; Au, 20.99. Calcd.: C, 53.42; H, 3.97; Au, 19.91%.)

XVIII $[(C_8H_{12})AuPPh_3]ClO_4$. When 0.12 ml (1 mmol) of 1,5-cyclooctadiene was added to a benzene solution of 1 mmol of the perchlorato complex the immediate precipitation of the white complex XVIII could be observed. The solution was filtered after 30 min stirring at room temperature and the solid was washed with small quantities of benzene and kept at –30°. At room temperature it showed signs of decomposition after a few hours. Λ_M = 161 ohm^{-1} cm^2 mol^{-1} in acetone. It was slightly soluble in acetone and nitromethane but insoluble in benzene, chloroform, carbon tetrachloride, diethyl ether and hexane. (Found: C, 47.20; H, 4.32; Au, 30.76. Calcd.: C, 46.82; H, 4.08; Au, 29.53%.)

The same result was obtained by adding the diolefin to a benzene solution of perchloratotriphenylphosphinegold(I) [2]. (Found: C, 48.13; H, 4.64; Au, 28.79%.)

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