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# NEUTRAL BIS(PENTAFLUOROPHENYL)TRIPHENYLARSINEGOLD(III) COMPLEXES

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## Summary

The complexes $XAu(C_6F_5)_2AsPh_3$ have been prepared by substitution of chloro- or perchlorato-bis(pentafluorophenyl)triphenylarsinegold(III) with alkali or with silver salts MX (X = $NO_3$, $CH_3COO$, $NO_2$, $CF_3COO$, CN, SCN, $N_3$ and $C_6H_5COO$). Decomposition of the nitrato or acetato complex leads to $C_6F_5AuAsPh_3$.

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## Introduction

Recently we reported [1-3] the reactions of $ClAu(C_6F_5)_2PPh_3$ or $O_3ClOAu(C_6F_5)_2PPh_3$ with different sodium or silver salts MX (X = Br, I, CN, SCN, $NO_3$, $NO_2$, $CH_3COO$, $CF_3COO$, $CO_3H$, $N_3$, $ClO_4$, $SO_4$), which lead to the precipitation of metal chloride or perchlorate and to solutions of $XAu(C_6F_5)_2PPh_3$, from which the complex can be isolated by evaporating off the solvent.

Herein we describe the results, which were obtained by extending our studies to the preparation of similar gold(III) complexes with triphenylarsine instead of triphenylphosphine as a ligand.

## Results and discussion

We studied two different types of reactions: (a) those of $ClAu(C_6F_5)_2AsPh_3$ with silver salts and (b) those of $O_3ClOAu(C_6F_5)_2AsPh_3$ with sodium and silver salts.

As a rule, the alkaline salts were used in all the cases where the silver salt of the studied anion is less soluble than silver chloride, which is formed in the reactions of type (a).

### *(a) Reactions of $ClAu(C_6F_5)_2AsPh_3$*

When acetone or benzene solutions of the chlorine complex react with solutions of AgX (X = $NO_3$, $CH_3COO$, $NO_2$, $CF_3COO$, $ClO_4$) in the same solvent

TABLE 1

CONDUCTIVITY AND MOLECULAR WEIGHT DATA FOR THE TRIPHENYLARSINEGOLD COMPLEXES AND MELTING POINTS COMPARED TO THOSE OF THE ANALOGOUS TRIPHENYLPHOSPHINE COMPLEXES

| Complex | $\Lambda_M$ (ohm$^{-1}$cm$^2$mol$^{-1}$) | Mol. wt. found (benzene) (calcd.) | M.p. (°C) [M.p. of analogous $PPh_3$ complex] |
|---|---|---|---|
| $C_6F_5AuAsPh_3$ | 2.1$^a$ | 670<br>(670.3) | 182 dec.<br>[170] |
| $NO_3Au(C_6F_5)_2AsPh_3$ | 15.8$^b$ | 754<br>(899.1) | room temp.<br>[141 dec.] |
| $CH_3COOAu(C_6F_5)_2AsPh_3$ | 13.5$^a$ | 845<br>(896.1) | room temp.<br>[152 dec.] |
| $O_2NAu(C_6F_5)_2AsPh_3$ | 11.0$^a$ | 812<br>(883.1) | 146 dec.<br>[128 dec.] |
| $CF_3COOAu(C_6F_5)_2AsPh_3$ | 13.3 | 871<br>(950.0) | 147<br>[151 dec.] |
| $CNAu(C_6F_5)_2AsPh_3$ | 3.2$^a$ | 817<br>(863.1) | 182 dec.<br>[184] |
| $NCSAu(C_6F_5)_2AsPh_3$ | 3.6$^a$ | 880<br>(895.4) | 136<br>[130 dec.] |
| $N_3Au(C_6F_5)_2AsPh_3$ | 8.2$^b$ | 903<br>(879.4) | 140<br>[142] |
| $C_6H_5COOAu(C_6F_5)_2AsPh_3$ | 0$^b$ | 891$^c$<br>(958.3) | 164 dec.<br>[–] |

$^a$ = Nitromethane. $^b$ = Acetone. $^c$ Chloroform.

and are magnetically stirred at room temperature for several hours, eqn. 1 takes place quantitatively.

$$ClAu(C_6F_5)_2AsPh_3 + AgX \rightarrow AgCl + XAu(C_6F_5)_2AsPh_3 \qquad (1)$$

Silver chloride precipitates, and the complex $XAu(C_6F_5)_2AsPh_3$ can be recrystallized from the resulting solutions.

Whilst the nitrato and acetato complexes of bis(pentafluorophenyl)triphenylphosphinegold(III) are stable at room temperature [1], the analogous triphenylarsine complexes are unstable, and clearly show signs of decomposition after several hours (the nitrato complex), or after several days (the acetato complex). Because of the low stability of these complexes, $C_6F_5AuAsPh_3$ crystallizes from the solution as the final product, after removing the silver chloride by filtration, whenever the reaction 1 is continued for more than two hours or is carried out in the refluxing solvent.

When X = $ClO_4$, the solid complex is so unstable that it cannot be characterized, either by analysis or by the IR spectra. Its benzene solutions, however, are stable enough for a few hours to permit use for preparative purposes, as described below.

### (b) Reactions of $O_3ClOAu(C_6F_5)_2AsPh_3$

When solid MX (MX = KCN, KSCN, $NaN_3$, $NaOOCC_6H_5$) is added to a benzene solution of the perchlorato complex, and the mixture is magnetically stirred at room temperature, $MClO_4$ precipitates and the neutral complexes can be crystallized from solution:

$$O_3ClOAu(C_6F_5)_2AsPh_3 + MX \rightarrow MClO_4 + XAu(C_6F_5)_2AsPh_3 \qquad (2)$$

### (c) Stability

All complexes, with the exception of the aforementioned nitrato, acetato and perchlorato complexes are stable at room temperature, and, as may be seen from their decomposition points, their stability does not seem to be different from that of the analogous triphenylphosphine complexes (see Table 1).

### (d) Conductivity and molecular weight

As may be seen from the data collected in Table 1 the neutral complexes are non-conductors in nitromethane or acetone and are monomeric in benzene solution.

### (e) IR spectra

The spectra of all the complexes show, in addition to the vibrations due to the pentafluorophenyl [4] and triphenylarsine [5] ligands, the following characteristics:

The acetato complex shows bands at 1650 s and 1300 s $cm^{-1}$, assigned to the $\nu_{as}$ and $\nu_s$ vibrations of the carboxyl group. The difference between the two absorptions ($\Delta\nu = 350\ cm^{-1}$) confirms that the acetate group acts as a monodentate ligand [6].

The benzoato complex exhibits two bands at 1640 s and 1325 s $cm^{-1}$, assigned similarly. Since $\Delta\nu = 315\ cm^{-1}$, it follows that this group is also monodentate [6].

In the spectrum of the trifluoroacetato complex the $\nu_{as}$ vibration is observed at 1700 $cm^{-1}$, whereas the symmetric vibration, which is masked by the intense absorption of the pentafluorophenyl and triphenylarsine groups at 1480-1420 $cm^{-1}$, cannot be assigned. Further bands [7] due to the trifluoroacetate group are found at 1210 s, 1190 vs, 1160 s, and 860 m $cm^{-1}$.

The nitrato complex exhibits two bands at 1265 s and 810 m $cm^{-1}$, assignable to the $\nu_s(NO_2)$ and $\delta$ $(NO_3)$ vibrations, respectively. These two bands alone do not provide a reliable criterion for elucidating how the nitrate group is bonded to the gold atom [8]. The bands due to the pentafluorophenyl group at 1520 s and 950 s $cm^{-1}$ are, however, much broader than those found normally. This broadening can be accounted for by the superposition of the expected nitrate absorptions in this range, provided that the nitrate group is coordinated to the gold atom through one of its oxygen atoms.

In the spectrum of the nitrito complex the band due to $\nu_{as}$, which could be expected at ca. 1380 $cm^{-1}$, is masked by the absorptions of the triphenylarsine group and those of Nujol. The bands at 1315 s, 530 w, 410 w and 369 w $cm^{-1}$ are characteristic for a nitro complex [9] with a *N*-bonded $NO_2$ group.

The cyano complex shows absorptions at 420 m and 280 m $cm^{-1}$, which have been assigned to the CN group which is covalently bonded to the central atom [2,10].

While it was possible to assign six bands in the spectrum of the $NCSAu(C_6F_5)_2PPh_3$ [2], only the band at 2135 m $cm^{-1}$ could be unambiguosly assigned in the triphenylarsine—thiocyanato complex, because of the superposition of numerous bands due to the other ligands. Nevertheless, the high value of $\bar{\nu}$ of the mentioned band makes it possible [11] to propose that the thiocyanato group is *S*-bonded to the central atom.

The azido complex shows absorptions at 2040 vs, 1250 s, 390 w, and 380 w $cm^{-1}$, which account for an azide group which is covalently bonded to the gold atom [12].

## Experimental

IR Spectra were recorded on a Beckman IR 20A spectrophotometer (over the range 4000 - 250 $cm^{-1}$) using Nujol mulls between polyethylene sheets. Molecular weights were measured in benzene or chloroform with a Hitachi—Perkin—Elmer model 115 osmometer, and conductivities in $5 \times 10^{-4}$ acetone or nitromethane solution with a Philips PW 9501/01 conductimeter. C, H and N analyses were made with a Perkin—Elmer 240 microanalyzer. The measured analytical data are in reasonable agreement with the proposed formulae, provided that difficulties which arise from the presence of F in our samples are taken into account.

### *(I).* $C_6F_5AuAsPh_3$

$AgNO_3$ or $AgCO_2CH_3$ (2mmol) was added to an acetone solution of $ClAu(C_6F_5)_2AsPh_3$ (0.79 g, 1 mmol) and the mixture was refluxed for eight hours. Precipitated AgCl was filtered off and the solution evaporated to dryness. After extracting the residue with diethyl ether and filtering off the insoluble silver nitrate, ethanol was added to the solution. On evaporating the solvent, complex I was obtained in both cases as colourless crystals, m.p. 182°(dec.); $\Lambda_M$ = 4.31 $ohm^{-1}$ $cm^2$ $mol^{-1}$ (nitromethane). Complex I is soluble in acetone, benzene, chloroform and carbon tetrachloride, slightly soluble in methanol and ethanol, and insoluble in petroleum ether and hexane. Found: C, 43.18; H, 1.80; Au, 28.80 (for the reaction with silver nitrate); C, 42.90 ; H, 1.63; Au, 28.93 (for the reaction with silver acetate); mol. wt. 667 (in 0.48% benzene solution). $C_{24}H_{15}AuAsF_5$ calcd.: C, 43.00; H, 2.25; Au, 29.39%; mol. wt. 670.2.

*(II). $NO_3Au(C_6F_5)_2AsPh_3$*

$AgNO_3$ (0.34 g, 2 mmol) was added to a solution of $ClAu(C_6F_5)_2AsPh_3$ (0.87 g, 1 mmol) in 30 ml of ether. After 2 h stirring at room temperature the precipitated AgCl was filtered off and the solution was evaporated to dryness. The residue was extracted with diethyl ether, filtered, and hexane was added. The solution was evaporated to yield the colourless crystals of complex II which showed signs of decomposition after several hours. $\Lambda_M$ = 15.8 $ohm^{-1}$ $cm^2$ $mol^{-1}$ (in acetone). Found: C, 40.34; H, 2.06; Au, 20.65; N, 1.29; mol. wt. 754 (in 0.37% benzene solution). $C_{30}H_{15}AsAuF_{10}NO_3$ calcd.: C, 40.07; H, 1.67; Au, 21.91; N, 1.56%; mol. wt. 899.1.

*(III). $CH_3COOAu(C_6F_5)_2AsPh_3$*

A mixture of $AgCO_2CH_3$ (0.34 g, 2 mmol) and $ClAu(C_6F_5)_2AsPh_3$ (0.87 g, 1 mmol) in 40 ml of acetone was stirred at room temperature for two hours. The procedure was continued as for II to yield yellowish-white crystals of complex III which decomposed after several days storage at room temperature. $\Lambda_M$ = 13.5 $ohm^{-1}$ $cm^2$ $mol^{-1}$ (in nitromethane). Found: C, 42.92; H, 2.60; Au, 22.22; mol. wt. 845 (in 1.39% benzene solution). $C_{32}H_{18}AsAuF_{10}O_2$ calcd.: C, 42.82; H, 2.01; Au, 21.98%; mol. wt. 896.1.

*(IV). $O_2NAu(C_6F_5)_2AsPh_3$*

$AgNO_2$ (0.31 g, 2 mmol) was added to $ClAu(C_6F_5)_2AsPh_3$ in 40 ml of acetone. After stirring the mixture at room temperature for two hours the procedure was followed as for II. Complex IV was obtained in the form of yellowish-white crystals, m.p. 146° (dec.); $\Lambda_M$ = 11.0 $ohm^{-1}$ $cm^2$ $mol^{-1}$ (in nitromethane) Found: C, 40.53; H, 2.10; Au, 22.22; N, 1.32; mol. wt. 812 (in 0.86% benzene solution). $C_{30}H_{15}AsAuF_{10}O_2N$ calcd.: C, 40.80; H, 1.70; Au, 21.98; N, 1.58%; mol. wt. 883.1.

*(V). $CF_3COOAu(C_6F_5)_2AsPh_3$*

A mixture of $AgCO_2CF_3$ (0.44 g, 2 mmol) and $ClAu(C_6F_5)_2AsPh_3$ in 50 ml of benzene was stirred at room temperature for two hours. Upon continuing as for II, colourless crystals of complex V were obtained, m.p. 147°; $\Lambda_M$ = 13.3 $ohm^{-1}$ $cm^2$ $mol^{-1}$ (in nitromethane). Found: C, 40.58; H, 2.29; Au, 20.47; mol. wt. 871 (in 0.73% benzene solution). $C_{32}H_{15}AsAuF_{13}O_2$ calcd.: C, 40.45; H, 1.58; Au, 20.73%; mol. wt. 950.0.

*(VI). $CNAu(C_6F_5)_2AsPh_3$*

KCN (0.13 g, 2 mmol) was added to a solution of $O_3ClOAu(C_6F_5)_2AsPh_3$

(1 mmol) in 30 ml of benzene. After 5 h stirring at room temperature the precipitated $KClO_4$ and the excess of KCN were filtered off, and the solution was evaporated to dryness. The resulting residue was recrystallized from ether/hexane to yield the colourless crystals of complex VI, m.p. 182° (dec.). $\Lambda_M = 3.2$ ohm$^{-1}$ cm$^2$ mol$^{-1}$ (in nitromethane). Found: C, 41.82; H, 1.67; Au, 21.26; N, 1.54; mol. wt. 817(in 0.89% benzene solution). $C_{31}H_{15}AsAuF_{10}N$ calcd.: C, 43.13; H, 1.74; Au, 22.82; N, 1.74%; mol. wt. 863.1.

*(VII).* $NCSAu(C_6F_5)_2AsPh_3$

A mixture of KSCN (0.19 g, 2 mmol) and $O_3ClOAu(C_6F_5)_2AsPh_3$ (1 mmol) in 50 ml of benzene was stirred at room temperature for five hours. Upon working-up as for VI, complex VII was obtained in the form of yellowish-white crystals, m.p. 136°; $\Lambda_M = 3.61$ ohm$^{-1}$ cm$^2$ mol$^{-1}$ (in nitromethane). Found: C, 41.41; H, 2.15; Au, 22.50; N, 1.31; mol. wt. 880 (in 1.16% benzene solution). $C_{31}H_{15}AsAuF_{10}NS$ calcd.: C, 41.59; H, 1.68 Au, 22.01; N, 1.67%; mol. wt. 895.2.

*(VIII).* $N_3Au(C_6F_5)_2AsPh_3$

$NaN_3$ (0.13 g, 2 mmol) was added to a solution of $O_3ClOAu(C_6F_5)_2AsPh_3$ (1 mmol) in 50 ml of benzene. After 10 h stirring at room temperature the procedure was continued as for VI to give the yellowish-white crystals of complex VIII, m.p. 140°; $\Lambda_M = 8.2$ ohm$^{-1}$ cm$^2$ mol$^{-1}$ (in acetone). Found: C, 40.33; H, 2.35; Au, 21.16; N, 3.76; mol. wt. 903 (in 0.52% benzene solution). $C_{30}H_{15}AsAuF_{10}N_3$ calcd.: C, 40.97; H, 2.04; Au, 22.41; N, 4.77; mol. wt. 879.4.

*(IX).* $C_6H_5COOAu(C_6F_5)_2AsPh_3$

A solution of $C_6H_5COONa$ (0.24 g, 2 mmol) and $O_3ClOAu(C_6F_5)_2AsPh_3$ (1 mmol) in 50 ml of benzene was stirred at room temperature for 8 h. On proceeding as in VI the colourless crystals of complex IX were obtained, m.p. 164°(dec.); $\Lambda_M$ = nil (in acetone). Found: C, 45.66; H, 2.65; Au, 20.81; mol. wt. 891 (in 0.17% chloroform solution). $C_{37}H_{20}AsAuF_{10}O_2$ calcd.: C, 46.36; H, 2.10; Au, 20.56; mol. wt. 958.3.

## References

1 A. Laguna, P. Royo and R. Usón, Rev. Acad. Cienc. Zaragoza, 27 (1972) 19.
2 A. Laguna, P. Royo and R. Usón, Rev. Acad. Cienc. Zaragoza, 28 (1973) 71.
3 R. Usón, P. Royo and A. Laguna, Syn. Inorg. Metalorg. Chem., 3 (1973) 237.
4 D.A. Long and K. Steele, Spectrochim. Acta, 19 (1961) 1955.
5 Own observations.
6 N.N. Greenwood, Spectroscopic Properties of Inorganic and Organometallic Compounds, The Chemical Society (London), Vol. 2, 1968, p. 333.
7 M.J. Baillie, D.H. Brown, K.C. Moss and D.W.A. Sharp, J. Chem. Soc., (1968) 3110; G.B. Deacon, J.H.S. Green and R.S. Nyholm, J. Chem. Soc., (1965) 3411; J.N. Gerlach and G.L. Gard, Inorg. Chem., 9 (1970) 1565.
8 B.O. Field and C.J. Hardy, Quart. Rev. (London), (1964) 361.
9 M.J. Cleare and W.P. Griffith, J. Chem. Soc. A, (1967) 1144.
10 L.H. Jones, Inorg. Chem., 3 (1964) 1581; ibid. 4 (1965) 1472.
11 A. Sabatini and J. Bertini, Inorg. Chem., 4 (1965) 959.
12 Z. Dori and R.F. Ziolo, Chem. Rev., 73 (1973) 247.