

## (Polyhalophenyl)silver(I) complexes as arylating agents: Crystal structure of $[(\mu\text{-}2,4,6\text{-C}_6\text{F}_3\text{H}_2)(\text{AuPPh}_3)_2]\text{ClO}_4$

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### Abstract

The arylsilver derivatives  $\text{AgR}$  ( $\text{R} = \text{C}_6\text{F}_5$ ,  $2,4,6\text{-C}_6\text{F}_3\text{H}_2$  or  $\text{C}_6\text{Cl}_5$ ) react with chlorogold(I) precursors  $[\text{AuCl}(\text{tht})$ ,  $\text{AuCl}(\text{PPh}_3)$ ,  $\text{ClAu}(\text{dppm})\text{AuCl}$  ( $\text{tht} =$  tetrahydrothiophene,  $\text{dppm} =$  bis(diphenylphosphino)methane)], to give the corresponding arylgold complexes in good yield. With gold precursors in higher oxidation state,  $\text{AgC}_6\text{Cl}_5$  either causes reduction to gold(I) or gives no reaction, whereas  $\text{AgC}_6\text{F}_5$  and  $\text{AgC}_6\text{F}_3\text{H}_2$  lead to gold(II) complexes ( $\text{R}_2\text{Au}(\text{dppm})\text{AuR}_2$ ) or gold(III) complexes  $[\text{Au}(\text{C}_6\text{F}_3\text{H}_2)(\text{C}_6\text{F}_5)_2(\text{PPh}_3)]$ ;  $\text{Au}(\text{C}_6\text{F}_3\text{H}_2)_2(\text{C}_6\text{F}_5)(\text{tht})$ ;  $\text{Au}(\text{C}_6\text{F}_5)_3(\text{tht})$ ;  $\text{Au}(\text{C}_6\text{F}_3\text{H}_2)_3(\text{tht})$ .

### Introduction

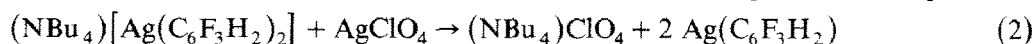
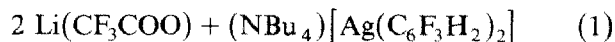
Stable polyhalophenyl gold(I) or gold(III) derivatives have been obtained mainly by use of aryllithium or Grignard compounds as arylating agents [1–3]. With gold in oxidation states higher than +1, partial or total reduction has sometimes been observed. For example, the reactions between  $\text{LiC}_6\text{F}_5$  and  $\text{Au}(\text{C}_6\text{F}_5)_3(\text{tht})$  ( $\text{tht} =$  tetrahydrothiophene) [4], or  $\text{K}[\text{AuCl}_4]$  and  $\text{AuCl}_3(\text{tht})$  [5] give mixtures of  $[\text{Au}(\text{C}_6\text{F}_5)_2]^-$  and  $[\text{Au}(\text{C}_6\text{F}_5)_4]^-$ , and reactions of the gold(II) complex  $(\mu\text{-PPh}_2\text{NHPPH}_2)\text{Au}_2(\text{C}_6\text{F}_5)_2\text{Cl}_2$  with  $\text{LiC}_6\text{F}_5$  give not the totally arylated gold(II) compound but instead the binuclear gold(I) derivative  $(\text{C}_6\text{F}_5)\text{AuPPh}_2\text{NHPPH}_2\text{Au}(\text{C}_6\text{F}_5)$  [6].

Use of  $\text{AgC}_6\text{F}_5$  as arylating agent with  $[\text{N}(\text{PPh}_3)_2][\text{Au}(\text{C}_6\text{F}_5)_3\text{Cl}]$  or  $(\mu\text{-PPh}_2\text{NH-PPh}_2)\text{Au}_2(\text{C}_6\text{F}_5)_2\text{Cl}_2$  as the starting gold complex leads to  $[\text{N}(\text{PPh}_3)_2][\text{Au}(\text{C}_6\text{F}_5)_4]$  [4] or  $(\mu\text{-PPh}_2\text{NHPPH}_2)\text{Au}_2(\text{C}_6\text{F}_5)_4$  [7], respectively, as the only isolated products, i.e. no reduction of the gold centres is observed.

In the present paper we describe the results of a study of polyhalophenylsilver reagents ( $\text{AgR}$ ,  $\text{R} = \text{C}_6\text{F}_5$ ,  $\text{C}_6\text{Cl}_5$ ,  $2,4,6\text{-C}_6\text{F}_3\text{H}_2$ ) and their reactions with halo complexes of gold(I), gold(II) or gold(III).

## Results and discussion

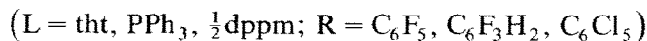
The syntheses of  $\text{AgC}_6\text{F}_5$  and  $\text{AgC}_6\text{Cl}_5$  have been described elsewhere [8]. The same procedure (eq. 1 and 2) gave the new complexes  $(\text{NBu}_4)[\text{Ag}(\text{C}_6\text{F}_3\text{H}_2)_2]$  and  $\text{Ag}(\text{CF}_3\text{COO}) + 2 \text{LiC}_6\text{F}_3\text{H}_2 + (\text{NBu}_4)(\text{CF}_3\text{COO}) \rightarrow$



$\text{Ag}(\text{C}_6\text{F}_3\text{H}_2)$  as white solids. At room temperature the former is air and moisture stable, and its acetone solutions show the expected conductivity for 1/1 electrolytes ( $96 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ , in  $5 \times 10^{-4} \text{ M}$  solution). The neutral  $\text{Ag}(\text{C}_6\text{F}_3\text{H}_2)$  decomposes slowly at room temperature but can be preserved for months at  $-20^\circ\text{C}$ . Both complexes must be protected from light. The IR spectra of both complexes show bands due to the  $\text{C}_6\text{F}_3\text{H}_2$  group at ca. 1605(m), 1585(vs), 985(vs), 970(vs), 830(s) and 600(m)  $\text{cm}^{-1}$ .  $\text{Ag}(\text{C}_6\text{F}_3\text{H}_2)$  and  $\text{AgC}_6\text{F}_5$  are soluble in the common organic solvents except aliphatic hydrocarbons.  $\text{AgC}_6\text{Cl}_5$  is insoluble in organic solvents [8], and therefore reacts appreciably more slowly than the soluble  $\text{Ag}(\text{C}_6\text{F}_5)$  or  $\text{Ag}(\text{C}_6\text{F}_3\text{H}_2)$ .

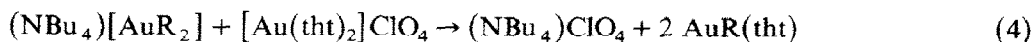
### (a) Arylation of gold(I) precursors

The three  $\text{AgR}$  derivatives react (eq. 3) with gold(I) chloro complexes ( $\text{ClAu}(\text{tht})$ ,  $\text{AuCl}(\text{PPh}_3)$  or  $(\mu\text{-dppm})(\text{AuCl})_2$ ) to give the corresponding aryl compounds, all of which have been described previously [5,9–13]



$\text{AuCl}(\text{tht})$  is unstable at room temperature, and so are the  $\text{AuR}(\text{tht})$  derivatives; the formation of a mirror of metallic gold is often observed during the preparation involving the corresponding  $\text{LiR}^*$ . We obtained  $\text{Au}(\text{C}_6\text{F}_5)(\text{tht})$  (73% yield) and  $\text{Au}(\text{C}_6\text{F}_3\text{H}_2)(\text{tht})$  (22% yield, compared with 0% when arylation was with  $\text{Li}(\text{C}_6\text{F}_3\text{H}_2)$ ). The synthesis of  $\text{Au}(\text{C}_6\text{Cl}_5)(\text{tht})$  was not attempted because of the longer reaction time (see above).

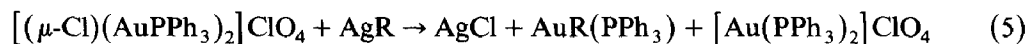
A much better synthetic route is shown in eq. 4:



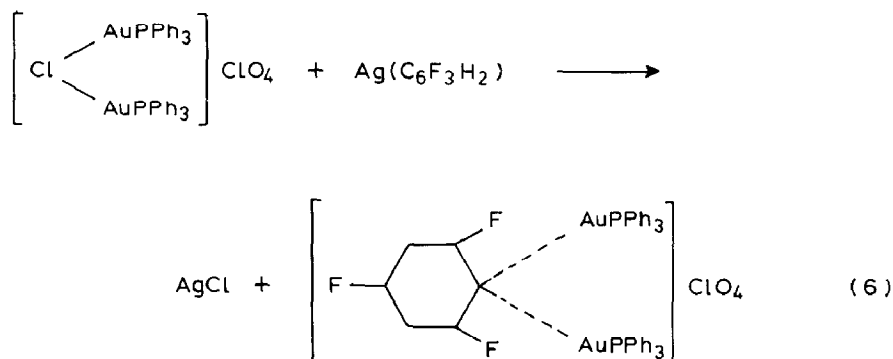
This affords  $\text{AuR}(\text{tht})$  in 85% ( $\text{R} = \text{C}_6\text{F}_5$ ), 75% ( $\text{R} = \text{C}_6\text{F}_3\text{H}_2$ ) or 89% ( $\text{R} = \text{C}_6\text{Cl}_5$ ) yield [13].

$\text{AuCl}(\text{PPh}_3)$ , which contains a more basic neutral ligand, reacts with  $\text{AgR}$  to give  $\text{AuR}(\text{PPh}_3)$  in ca. 80% yield in all three cases, and good results were also obtained in the arylation of  $\text{ClAu}(\text{dppm})\text{AuCl}$ , which gave 92, 78, and 82% yield, respectively.

The single chloro bridge in  $[(\mu\text{-Cl})(\text{AuPPh}_3)_2]\text{ClO}_4$  [14] is cleaved by  $\text{AgC}_6\text{F}_5$  and  $\text{AgC}_6\text{Cl}_5$  (eq. 5) to give a mixture of mononuclear gold(I) complexes. With  $\text{Ag}(\text{C}_6\text{-}$



$\text{F}_3\text{H}_2$ ) the chloro bridge is replaced by the aryl group (eq. 6):



In contrast the reaction of the same precursor with a 2 molar proportion of  $\text{Li}(\text{C}_6\text{F}_3\text{H}_2)$  gives lithium chloride, lithium perchlorate, and  $\text{Au}(\text{C}_6\text{F}_3\text{H}_2)\text{PPh}_3$ .

Since there had been no previous determination of the structure of a binuclear polyhalophenyl-bridged gold compound, we prepared suitable crystals of  $[(\mu\text{-}$

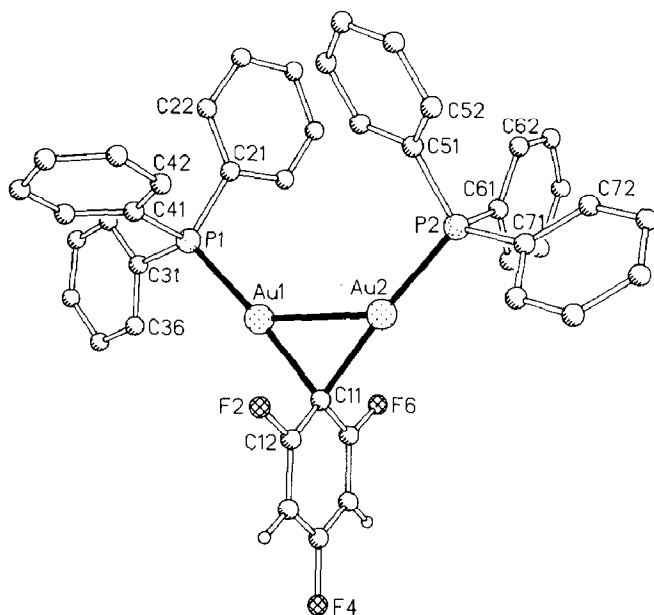


Fig. 1. The cation of  $[(\mu\text{-2,4,6-C}_6\text{F}_3\text{H}_2)(\text{AuPPh}_3)_2]^+$  (from the crystal structure of its perchlorate salt). Radii are arbitrary. Hydrogen atoms of the  $\text{PPh}_3$  ligands have been omitted for clarity. Selected bond lengths ( $\text{\AA}$ ) and angles (deg.):  $\text{Au}(1)\text{-Au}(2)$  2.759(1),  $\text{Au}(1)\text{-P}(1)$  2.260(2),  $\text{Au}(1)\text{-C}(11)$  2.162(8),  $\text{Au}(2)\text{-P}(2)$  2.267(3),  $\text{Au}(2)\text{-C}(11)$  2.160(9),  $\text{P}(1)\text{-Au}(1)\text{-C}(11)$  174.9(3),  $\text{P}(2)\text{-Au}(2)\text{-C}(11)$  174.1(2),  $\text{Au}(1)\text{-C}(11)\text{-Au}(2)$  79.3(3),  $\text{C}(12)\text{-C}(11)\text{-C}(16)$  114.4(8).

$C_6F_3H_2)(AuPPh_3)_2]ClO_4$  by slow diffusion of diethyl ether into a dichloromethane solution of the compound, and used these in an X-ray diffraction study. The structure of the cation is shown in Fig. 1.

The only structurally characterized complex with two gold atoms bridged by an aryl group is the pentamer  $Au_5(\text{mesityl})_5$  [15]. Other aryl-bridged gold(I) complexes of the type  $[(\mu-R)(AuPR_3)_2]^+$  ( $R = C_6H_5$ ,  $p\text{-}CH_3C_6H_4$  [16],  $C_6F_3H_2$  [17]) have been reported, but the only known X-ray structure of such a binuclear species is that of  $R = C_5H_5FeC_5H_4$  [16], which is strictly not an aryl species although closely analogous. A comparison of related structural parameters is instructive:

Compound	Au–C–Au	Au–C	Au–Au	C–C <sub>ipso</sub> –C
$C_5H_5FeC_5H_4(AuPPh_3)_2^+$ [16]	78(1)	2.12, 2.25(4)	2.768(2)	102(4)
$C_6F_3H_2(AuPPh_3)_2^+$	79.3(3)	2.162(8), 2.160(9)	2.759(1)	114.4(8)
$Au_5(\text{mes})_5$ [15]	75.9–78.2 (csd's: ca. 1°)	2.12–2.20 0.02Å	2.692–2.710 0.004Å	116.0–118.7 none given)

The angles at the bridging carbon are acute in each case, as was observed in complexes for which 3c,2e-bonding was postulated ( $Al_2Ph_6$  [18] 77°;  $Al_2Ph_2Me_4$  [19] 77.8°).

The Au–C bond lengths were not determined with high precision, but are all ca. 2.16 Å except for one long bond of 2.25 Å in the ferrocenyl compound. (This bond could be affected by the short Au...Fe contact of 2.82 Å, but other bond lengths and angles do not seem to be affected; a more likely explanation is that the apparent increase in bond length is not significant.) Normal, 2c,2e-bonds between Au and aryl groups are generally shorter; 2.06, 2.04(2) Å in  $[Au(C_6F_5)_2]^-$  [20], 2.07(2) Å in  $Ph_3PAu(C_6F_5)$  [21], 2.048(8) Å in  $(C_6F_5)Au\{CH(PPh_2)_2Au(C_6F_5)_2\}$  [22].

The Au–Au distances are shorter in all three complexes than in metallic gold (2.88 Å); this has often been considered as evidence for appreciable gold–gold bonding. However, it is often difficult to decide whether two bridged gold(I) atoms are subject to mutual bonding interactions or whether the short gold–gold distance is merely imposed by the ligand. If the linear geometry at the gold(I) centres is significantly distorted, the existence of a gold–gold bond can be postulated with more confidence. This could be the case for the ferrocenyl complex (one angle 168°, the other “normal” at 175°) and especially for the mesityl pentamer (angles 148–153°). For the present trifluorophenyl compound, however, the ambiguity remains because the angles are 174.9 and 174.1°. Moreover, formally non-bonded gold(I)–gold(I) interactions of ca. 2.8 Å are well documented [23]; theoretical considerations [24] show that the mixing in of higher orbitals on gold (6s, 6p) can lead to bonding interactions even though the electron configuration of gold(I) is formally closed-shell.

There is some evidence for three-centre bonding interactions in the  $Au_2C$  units of gold(I) complexes of carbonyl-stabilized phosphorus ylides [25]; the gold–gold distances are ca. 2.9 Å, the Au–C–Au angles 85–90° and the P–Au–C angles average 170°. Here again, however, the picture is not entirely clear because the deviations from linearity are not always such as to bend the gold atoms towards each other, and because there are additional interactions between formally separate  $Au_2C$  units.

The aromatic ring of the present compounds displays an angle of  $114.4(8)^\circ$  at the *ipso* carbon; such distortions are a common feature of pentafluorophenyl complexes of transition metals [26].

(b) Arylation of gold(II) precursors

The complex  $\text{Cl}_2\text{Au}(\text{dppm})\text{AuCl}_2$  can be used to give both the  $\text{C}_6\text{F}_5$  and the  $\text{C}_6\text{F}_3\text{H}_2$  derivatives (eq. 7).



(  $\text{R} = \text{C}_6\text{F}_5$  (60% yield) ;  $\text{R} = \text{C}_6\text{F}_3\text{H}_2$  (74% yield) )

With  $\text{AgC}_6\text{F}_5$  partial reduction was observed, and  $\text{C}_6\text{F}_5\text{Au}(\text{dppm})\text{AuC}_6\text{F}_5$  (20% yield) was also isolated. With  $\text{AgC}_6\text{Cl}_5$ ,  $\text{C}_6\text{Cl}_5\text{Au}(\text{dppm})\text{AuC}_6\text{Cl}_5$  was obtained along with a mixture of non-identified products. With  $\text{Ag}(\text{C}_6\text{F}_3\text{H}_2)$  no reduction was observed.

The new binuclear gold(II) complexes are air- and moisture-stable yellow solids at room temperature. Acetone solution of the  $\text{C}_6\text{F}_5$  derivative are non-conducting, whereas solutions of the  $\text{C}_6\text{F}_3\text{H}_2$  compound show a low conductivity ( $19 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ ). In chloroform solution both compounds are monomeric.

The IR spectra show bands at  $1620(\text{m})$ ,  $1490(\text{s})$ ,  $1060(\text{s})$ ,  $962(\text{vs})$  and  $788(\text{s}) \text{ cm}^{-1}$  ( $\text{C}_6\text{F}_5$ ) and, respectively, bands at  $1620(\text{s})$ ,  $1590(\text{vs})$ ,  $1161(\text{s})$ ,  $1018(\text{s})$ ,  $992(\text{vs})$ ,  $843(\text{s})$  and  $608(\text{m}) \text{ cm}^{-1}$  ( $\text{C}_6\text{F}_3\text{H}_2$ ). The two bands at  $788(\text{s})$  and  $962(\text{vs}) \text{ cm}^{-1}$  in the  $\text{C}_6\text{F}_5$  derivative are indicative of  $\text{C}_6\text{F}_5$  groups bonded to a gold(II) centre, in agreement with previous observations [7].

(c) Arylation of gold(III) precursors

The reactions between  $\text{AgR}$  and the gold(III) complexes *cis*- $\text{AuCl}(\text{C}_6\text{F}_5)_2(\text{PPh}_3)$ , *trans*- $\text{AuCl}_2(\text{C}_6\text{F}_5)(\text{tht})$ ,  $\text{AuCl}_3(\text{tht})$  and  $[\text{N}(\text{PPh}_3)_2][\text{AuCl}_4]$  have been studied. With  $\text{AgC}_6\text{Cl}_5$  no reaction was observed. It seems that  $\text{AgC}_6\text{Cl}_5$  is not a suitable arylating agent for gold complexes in oxidation state higher than I.

The use of  $\text{AgC}_6\text{F}_5$  leads to the corresponding complexes  $\text{Au}(\text{C}_6\text{F}_5)_3(\text{PPh}_3)$  (86%),  $\text{Au}(\text{C}_6\text{F}_5)_3(\text{tht})$  (32 or 52%, respectively). The latter has previously been obtained by transfer of two  $\text{C}_6\text{F}_5$  groups from  $\text{Tl}(\text{C}_6\text{F}_5)_2\text{Cl}$  to the appropriate gold(I) precursor [4,27]. With  $[\text{N}(\text{PPh}_3)_2][\text{AuCl}_4]$  reduction takes place and  $[\text{N}(\text{PPh}_3)_2][\text{Au}(\text{C}_6\text{F}_5)_2]$  (53%) is obtained.

Similar results are obtained when  $\text{R} = \text{C}_6\text{F}_3\text{H}_2$ . The complexes  $\text{Au}(\text{C}_6\text{F}_3\text{H}_2)(\text{C}_6\text{F}_5)_2(\text{PPh}_3)$  (73%) and  $\text{Au}(\text{C}_6\text{F}_3\text{H}_2)_3(\text{tht})$  (48%) are described here for the first time, but  $\text{Au}(\text{C}_6\text{F}_3\text{H}_2)_2(\text{C}_6\text{F}_5)(\text{tht})$  (49%) has previously been reported [28]. At room temperature the two new complexes are air- and moisture-stable white solids. In acetone solution they are non-conducting, and they are monomeric in chloroform. The IR spectrum of  $\text{Au}(\text{C}_6\text{F}_3\text{H}_2)(\text{C}_6\text{F}_5)_2(\text{PPh}_3)$  shows two bands at  $810(\text{s})$  and

795(s)  $\text{cm}^{-1}$  indicative of two mutually *cis*- $\text{C}_6\text{F}_5$  groups [29]; therefore the arylation of the precursor occurs with stereoretention. Finally, arylation of  $[\text{N}(\text{PPh}_3)_2][\text{AuCl}_4]$  gives  $[\text{N}(\text{PPh}_3)_2][\text{Au}(\text{C}_6\text{F}_3\text{H}_2)_2]$  (40% yield) and a mixture of products containing the unchanged starting gold(III) complex.

## Experimental

The instrumentation employed and general experimental techniques were as described earlier [4,8]. All the reactions were carried out under  $\text{N}_2$  at room temperature unless otherwise stated.

$[\text{NBu}_4][\text{Ag}(\text{C}_6\text{F}_3\text{H}_2)_2]$ . To a diethyl ether solution of  $\text{Li}(2,4,6\text{-C}_6\text{F}_3\text{H}_2)$  (30 mmol) [29] at  $-78^\circ\text{C}$  was added  $\text{Ag}(\text{CF}_3\text{COO})$  (2.21 g, 10 mmol). The mixture was stirred for 5 min,  $(\text{NBu}_4)_2\text{O}_2\text{CCF}_3$  (5.28 g, 15 mmol) was added, and the mixture was allowed to warm to room temperature (2 h). The precipitate was filtered off and washed with water ( $2 \times 5$  ml) then extracted with 30 ml of dichloromethane. The extract was filtered and concentrated to ca. 5 ml and diethyl ether was added to give crystals of the white complex (83% yield). (Found: C, 54.5; H, 6.6; N, 2.55.  $\text{C}_{28}\text{H}_{40}\text{AgF}_6\text{N}$  calcd.: C, 54.9; H, 6.6; N, 2.3%. M.p.  $80^\circ\text{C}$  (decomp.).  $\Lambda_{\text{M}}$  in acetone  $96 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ ).

$\text{Ag}(\text{C}_6\text{F}_3\text{H}_2)$ .  $(\text{NBu}_4)[\text{Ag}(\text{C}_6\text{F}_3\text{H}_2)_2]$  (0.306 g, 0.5 mmol) was added to a solution of  $\text{AgClO}_4$  (0.104 g, 0.5 mmol) in 25 ml of diethyl ether and the mixture was stirred for 3 h. The precipitated  $(\text{NBu}_4)\text{ClO}_4$  was filtered off and the filtrate was evaporated to dryness. The resulting white solid,  $\text{Ag}(\text{C}_6\text{F}_3\text{H}_2)$ , was washed with hexane and stored under nitrogen (80% yield) (Found: C, 30.30; H, 1.20.  $\text{C}_6\text{H}_2\text{AgF}_3$  calcd.: C, 30.15; H, 0.85%. M.p.  $200^\circ\text{C}$  (decomp.).  $\Lambda_{\text{M}}$  in acetone  $2 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ ).

### Reactions of $\text{AgR}$ ( $R = \text{C}_6\text{F}_5$ , $\text{C}_6\text{F}_3\text{H}_2$ or $\text{C}_6\text{Cl}_5$ )

*With  $\text{AuCl}(\text{tht})$ ,  $\text{AuCl}(\text{PPh}_3)$  or  $\text{ClAu}(\text{dppm})\text{AuCl}$ .* To a freshly prepared diethyl ether solution (25 ml) of  $\text{AgC}_6\text{F}_5$  [8] (0.5 mmol) or  $\text{AgC}_6\text{F}_3\text{H}_2$  (0.5 mmol) or to a dichloromethane suspension (25 ml) of  $\text{AgC}_6\text{Cl}_5$  [8] (0.179 g, 0.5 mmol) was added  $\text{AuCl}(\text{tht})$  [5] (0.161 g, 0.5 mmol),  $\text{AuCl}(\text{PPh}_3)$  [30] (0.256 g, 0.5 mmol), or  $\text{ClAu}(\text{dppm})\text{AuCl}$  [31] (0.212 g, 0.25 mmol). After 1 h ( $R = \text{C}_6\text{F}_5$ ,  $\text{C}_6\text{F}_3\text{H}_2$ ) or 5 h ( $R = \text{C}_6\text{Cl}_5$ ) stirring the  $\text{AgCl}$  (and the metallic gold in the reaction of  $\text{AuCl}(\text{tht})$  with  $\text{AgC}_6\text{F}_3\text{H}_2$ ) was filtered off and the filtrate concentrated to ca. 5 ml. Addition of n-hexane (20 ml) gave a white precipitate of  $\text{AuR}(\text{tht})$ ,  $\text{AuR}(\text{PPh}_3)$ , or  $\text{RAu}(\text{dppm})\text{AuR}$ .

*With  $[(\mu\text{-Cl})(\text{AuPPh}_3)_2]\text{ClO}_4$ .* (a) To a freshly prepared diethyl ether solution (40 ml) of  $\text{AgC}_6\text{F}_5$  [8] (0.8 mmol) was added  $[(\mu\text{-Cl})(\text{AuPPh}_3)_2]\text{ClO}_4$  [14] (0.843 g, 0.8 mmol). After 2 h stirring the precipitate was filtered off and extracted with dichloromethane (30 ml). The insoluble  $\text{AgCl}$  was filtered off, and the filtrate was concentrated to 5 ml. Addition of n-hexane (10 ml) precipitated  $[\text{Au}(\text{PPh}_3)_2]\text{ClO}_4$ . The ether solution was evaporated to 5 ml and addition of n-hexane gave  $\text{Au}(\text{C}_6\text{F}_5)(\text{PPh}_3)$  as a white solid.

(b) To a tetrahydrofuran solution (30 ml) of  $[(\mu\text{-Cl})(\text{AuPPh}_3)_2]\text{ClO}_4$  [14] (0.727 g, 0.69 mmol) was added  $\text{AgC}_6\text{Cl}_5$  [8] (0.247 g, 0.69 mmol). The mixture was stirred for 4 h. The precipitated  $\text{AgCl}$  and metallic gold were filtered off and the solution was evaporated to ca. 5 ml. Addition of diethyl ether (15 ml) precipitated

$[\text{Au}(\text{PPh}_3)_2]\text{ClO}_4$  as a white solid. The  $[\text{Au}(\text{PPh}_3)_2]\text{ClO}_4$  was filtered off and the solution was concentrated to 5 ml. Addition of n-hexane (15 ml) precipitated  $\text{Au}(\text{C}_6\text{Cl}_5)(\text{PPh}_3)$ .

(c) To a freshly prepared diethyl ether solution (25 ml) of  $\text{Ag}(\text{C}_6\text{F}_3\text{H}_2)$  (0.5 mmol) was added  $[(\mu\text{-Cl})(\text{AuPPh}_3)_2]\text{ClO}_4$  [14] (0.421 g, 0.4 mmol). The mixture was stirred for 3 h then the precipitate was filtered off and extracted with dichloromethane (25 ml) to leave the insoluble  $\text{AgCl}$ . The  $\text{AgCl}$  was filtered off and the solution was concentrated to ca. 5 ml. Addition of diethyl ether (20 ml) precipitated  $[(\mu\text{-C}_6\text{F}_3\text{H}_2)(\text{AuPPh}_3)_2]\text{ClO}_4$  as a white solid.

*With  $\text{Cl}_2\text{Au}(\text{dppm})\text{AuCl}_2$ .* To a freshly prepared diethyl ether solution (40 ml) of  $\text{AgC}_6\text{F}_5$  [8] (0.8 mmol) or  $\text{Ag}(\text{C}_6\text{F}_3\text{H}_2)$  (0.8 mmol) was added  $\text{Cl}_2\text{Au}(\text{dppm})\text{AuCl}_2$  [32] (0.158 g, 0.17 mmol). The mixture was stirred for 2 h, the  $\text{AgCl}$  was filtered off, and the yellow solution was concentrated to 5 ml. Addition of n-hexane (25 ml) gave a yellow solid, which was recrystallised by liquid diffusion of n-hexane into dichloromethane solutions at  $-20^\circ\text{C}$ . For  $\text{R} = \text{C}_6\text{F}_5$  we obtained a mixture of white and yellow crystals, which were separated by hand and identified as  $\text{C}_6\text{F}_5\text{Au}(\text{dppm})\text{AuC}_6\text{F}_5$  [33] (20% yield) and  $(\text{C}_6\text{F}_5)_2\text{Au}(\text{dppm})\text{Au}(\text{C}_6\text{F}_5)_2$ , respectively (60% yield). (Found: C, 41.0; H, 1.6; Au, 26.2%;  $M$ , 1484.  $\text{C}_{49}\text{H}_{22}\text{Au}_2\text{F}_{20}\text{P}_2$  calcd.: C, 41.65; H, 1.55; Au, 27.2%,  $M$ , 1446. M.p.  $123^\circ\text{C}$ ). For  $\text{R} = \text{C}_6\text{F}_3\text{H}_2$  only yellow crystals of  $(\text{C}_6\text{F}_3\text{H}_2)_2\text{Au}(\text{dppm})\text{Au}(\text{C}_6\text{F}_3\text{H}_2)_2$  were obtained (74% yield) (Found: C, 44.9; H, 2.6; Au, 31.25%;  $M$ , 1280.  $\text{C}_{49}\text{H}_{30}\text{Au}_2\text{F}_{12}\text{P}_2$  requires: C, 45.15; H, 2.3; Au, 30.25%;  $M$ , 1302. M.p.  $93^\circ\text{C}$  (decomp.).  $\Lambda_M$  in acetone:  $19\text{ ohm}^{-1}\text{ cm}^2\text{ mol}^{-1}$ ).

*With  $\text{cis-AuCl}(\text{C}_6\text{F}_5)_2\text{PPh}_3$ ,  $\text{trans-AuCl}_2(\text{C}_6\text{F}_5)(\text{tht})$  or  $\text{AuCl}_3(\text{tht})$ .* To a freshly prepared diethyl ether solution (50 ml) of  $\text{AgC}_6\text{F}_5$  [8] (1.0 mmol) or  $\text{Ag}(\text{C}_6\text{F}_3\text{H}_2)$  (1.0 mmol) was added  $\text{cis-AuCl}(\text{C}_6\text{F}_5)_2(\text{PPh}_3)$  [9] (0.829 g, 1.0 mmol),  $\text{trans-AuCl}_2(\text{C}_6\text{F}_5)(\text{tht})$  [34] (0.261 g, 0.5 mmol), or  $\text{AuCl}_3(\text{tht})$  [35] (0.130 g, 0.33 mmol). The mixture was stirred for 4 h, the  $\text{AgCl}$  was filtered off, and the filtrate concentrated to ca. 5 ml. Addition of n-hexane (25 ml) precipitated the new complexes  $\text{AuR}(\text{C}_6\text{F}_5)_2(\text{PPh}_3)$ ,  $\text{AuR}_2(\text{C}_6\text{F}_5)(\text{tht})$  or  $\text{AuR}_3(\text{tht})$ , respectively, as white solids:  $\text{cis-Au}(\text{C}_6\text{F}_3\text{H}_2)(\text{C}_6\text{F}_5)_2\text{PPh}_3$  (73% yield) (Found: C, 45.5; H, 2.2.; Au, 22.4%.  $\text{C}_{36}\text{H}_{17}\text{F}_{13}\text{AuP}$  calcd.: C, 46.75; H, 1.85; Au, 21.3%. M.p.  $121^\circ\text{C}$  (decomp.).  $\Lambda_M$  in acetone,  $12\text{ ohm}^{-1}\text{ cm}^2\text{ mol}^{-1}$ ) and  $\text{Au}(\text{C}_6\text{F}_3\text{H}_2)_3(\text{tht})$  (48% yield) (Found: C, 38.2; H, 2.15; Au, 29.1%;  $M$ , 637.  $\text{C}_{22}\text{H}_{14}\text{AuF}_9\text{S}$  calcd.: C, 38.95; H, 2.1; Au, 29.05%;  $M$ , 678. M.p.  $99^\circ\text{C}$  (decomp.).  $\Lambda_M$  in acetone,  $1\text{ ohm}^{-1}\text{ cm}^2\text{ mol}^{-1}$ ). No reaction was observed when  $\text{AgC}_6\text{Cl}_5$  was added to a dichloromethane solution of the gold(III) complexes.

*With  $[\text{N}(\text{PPh}_3)_2][\text{AuCl}_4]$ .* To a freshly prepared diethyl ether solution (50 ml) of  $\text{AgC}_6\text{F}_5$  [8] (1.1 mmol) or  $\text{Ag}(\text{C}_6\text{F}_3\text{H}_2)$  (1.1 mmol) was added  $[\text{N}(\text{PPh}_3)_2][\text{AuCl}_4]$  (0.219 g, 0.25 mmol). The suspension was stirred for 6 h then evaporated to dryness. The solid was extracted with dichloromethane (30 ml) and the insoluble  $\text{AgCl}$  was filtered off. The solution was concentrated to 5 ml and addition of n-hexane (25 ml) gave  $[\text{N}(\text{PPh}_3)_2][\text{Au}(\text{C}_6\text{F}_5)_2]$  or a mixture of  $[\text{N}(\text{PPh}_3)_2][\text{Au}(\text{C}_6\text{F}_3\text{H}_2)_2]$  and starting product, respectively.

#### *X-Ray structure determination of $[(\mu\text{-}2,4,6\text{-C}_6\text{F}_3\text{H}_2)(\text{AuPPh}_3)_2]\text{ClO}_4$*

*Crystal data.*  $\text{C}_{42}\text{H}_{32}\text{Au}_2\text{ClF}_3\text{O}_4\text{P}_2 \cdot \text{CH}_2\text{Cl}_2$ ,  $M = 1234$ , monoclinic, space group  $\text{P}2_1/n$ ,  $a$  24.763(7),  $b$  17.825(5),  $c$  9.981(3) Å,  $\beta$   $99.02(3)^\circ$ ,  $U$  4351 Å<sup>3</sup>,  $Z = 4$ ,  $D_x$

Table 1

Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for  $[(\mu\text{-}2,4,6\text{-C}_6\text{F}_3\text{H}_2)(\text{AuPPh}_3)_2]\text{ClO}_4 \cdot \text{CH}_2\text{Cl}_2$

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}^a$
Au(1)	1744.0(1)	6205.4(2)	3166.3(4)	46(1)
Au(2)	1245.7(1)	5660.6(2)	5254.1(4)	48(1)
P(1)	2497(1)	5847(1)	2314(2)	44(1)
P(2)	1355(1)	4590(2)	6493(2)	48(1)
C(11)	1056(3)	6646(6)	4009(8)	45(3)
C(12)	1165(3)	7333(6)	4655(9)	49(3)
C(13)	827(4)	7944(6)	4458(11)	67(4)
C(14)	346(5)	7846(7)	3604(13)	73(5)
C(15)	203(4)	7192(7)	2956(10)	62(4)
C(16)	559(4)	6606(6)	3188(9)	52(4)
F(2)	1643(2)	7414(3)	5497(6)	78(2)
F(4)	2(3)	8426(4)	3390(9)	126(4)
F(6)	410(2)	5971(4)	2573(6)	75(2)
C(21)	2578(3)	4851(6)	2313(8)	48(3)
C(22)	3087(4)	4497(7)	2594(11)	71(5)
C(23)	3118(6)	3711(9)	2541(13)	93(6)
C(24)	2659(8)	3302(8)	2167(14)	112(8)
C(25)	2162(6)	3643(7)	1887(14)	92(6)
C(26)	2128(4)	4398(6)	1971(10)	63(4)
C(31)	2528(3)	6139(5)	574(9)	45(3)
C(32)	2894(4)	5823(7)	-149(10)	71(4)
C(33)	2893(5)	6025(7)	-1464(11)	83(5)
C(34)	2553(5)	6565(8)	-2053(12)	83(5)
C(35)	2180(4)	6887(7)	-1352(11)	80(5)
C(36)	2168(4)	6663(6)	-17(10)	66(4)
C(41)	3105(3)	6205(6)	3366(9)	51(3)
C(42)	3201(5)	6019(9)	4710(11)	106(6)
C(43)	3673(5)	6271(10)	5546(12)	129(8)
C(44)	4033(5)	6715(8)	5031(13)	94(6)
C(45)	3939(4)	6908(8)	3714(12)	88(5)
C(46)	3484(4)	6654(6)	2888(11)	71(4)
C(51)	2067(3)	4311(5)	6908(9)	48(3)
C(52)	2309(4)	4187(6)	8217(10)	67(4)
C(53)	2857(4)	3983(7)	8481(11)	79(5)
C(54)	3148(4)	3900(7)	7453(12)	77(5)
C(55)	2909(5)	4025(8)	6150(12)	89(6)
C(56)	2370(4)	4231(7)	5868(11)	80(5)
C(61)	1002(4)	3832(6)	5522(9)	51(3)
C(62)	1183(4)	3103(7)	5682(11)	72(5)
C(63)	890(5)	2536(8)	4976(14)	94(6)
C(64)	421(6)	2672(9)	4082(13)	91(6)
C(65)	244(5)	3410(9)	3914(12)	89(6)
C(66)	532(4)	3986(7)	4637(10)	66(4)
C(71)	1093(3)	4638(6)	8082(9)	55(4)
C(72)	960(4)	3994(6)	8747(10)	58(4)
C(73)	753(4)	4040(7)	9933(10)	61(4)
C(74)	671(4)	4728(8)	10476(11)	69(4)
C(75)	800(4)	5370(7)	9854(10)	68(4)
C(76)	1007(3)	5322(6)	8646(10)	56(4)
Cl	662(1)	7682(2)	9455(4)	94(2)
O(1)	843(5)	7493(11)	8273(10)	253(12)
O(2)	1052(3)	7460(7)	10518(10)	161(6)
O(3)	176(3)	7308(6)	9494(9)	140(6)



Table 1 (continued)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{eq}$
O(4)	574(7)	8421(6)	9575(24)	398(21)
Cl(1)	536(6)	352(8)	3645(15)	413(7)
Cl(2A)	372(7)	-258(11)	1354(18)	273(7)
Cl(2B)	-553(7)	109(11)	3478(19)	265(7)
C(1A)	13(16)	436(23)	2398(43)	158(14)
C(1B)	-516(20)	31(30)	2041(55)	214(20)

<sup>a</sup> Equivalent isotropic  $U$  defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

1.88 g cm<sup>-3</sup>,  $\lambda(\text{Mo-}K_{\alpha})$  0.71069 Å,  $\mu$  7.0 mm<sup>-1</sup>,  $F(000) = 2360$ . Data collection, processing and reduction: A crystal 0.65 × 0.2 × 0.1 mm was sealed in a glass capillary and used to collect 8451 profile-fitted intensities on a Stoe-Siemens four-circle diffractometer [36] (monochromated Mo- $K_{\alpha}$  radiation,  $2\theta_{\text{max}}$  50°). An absorption correction based on  $\psi$ -scans was applied; transmission factors ranged from 0.46–0.89. Averaging equivalents gave 7632 unique reflections ( $R_{\text{int}}$  0.021), of which 5482 with  $F > 4\sigma(F)$  were used for all calculations (program system SHELX-76, locally modified by its author). Cell constants were refined from  $2\theta$  values of 40 reflections in the range 20–23°. Structure solution and refinement: The structure was solved by the heavy-atom method and refined to  $R = 0.047$ ,  $R_w = 0.043$ ; all non-H atoms, except those of a disordered dichloromethane molecule, were refined anisotropically, H atoms using a riding model. 508 parameters, weighting scheme  $w^{-1} = \sigma^2(F) + 0.00025F^2$ ,  $S$  1.5, max. residual electron density 0.7 e Å<sup>-3</sup> associated with the perchlorate anion.

Final atomic coordinates are presented in Table 1, with selected bond lengths and angles in the caption of Fig. 1. Further details of the structure determination (complete bond lengths and angles, temperature factors, structure factors, H atom coordinates) have been deposited with the Fachinformationszentrum Energie Physik Mathematik, 7514 Eggenstein-Leopoldshafen 2, W. Germany. Any request for this material should quote the reference number CSD-52977 and a full literature citation.

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## References

- 1 R. Usón and A. Laguna, *Syn. React. Inorg. Metal-org. Chem.*, 7 (1977) 463.
- 2 H. Schmidbaur, *Organogold Compounds*, Gmelin Handbuch der Anorganischen Chemie, Springer Verlag, 1980.
- 3 R. Usón and A. Laguna, *Coord. Chem. Rev.*, 70 (1986) 1.
- 4 R. Usón, A. Laguna, M. Laguna, E. Fernández, P.G. Jones and G.M. Sheldrick, *J. Chem. Soc., Dalton Trans.*, (1982) 1971.
- 5 R. Usón, A. Laguna and J. Vicente, *J. Organomet. Chem.*, 131 (1977) 471.
- 6 R. Usón, A. Laguna and M. Laguna, unpublished results.
- 7 R. Usón, A. Laguna, M. Laguna, M.N. Fraile, P.G. Jones and G.M. Sheldrick, *J. Chem. Soc., Dalton Trans.*, (1986) 291.

- 8 R. Usón, A. Laguna and J.A. Abad, *J. Organomet. Chem.*, 246 (1983) 341.
- 9 R.S. Nyholm and P. Royo, *J. Chem. Soc., Chem. Commun.*, (1969) 421.
- 10 R. Usón, A. Laguna and J. Pardo, *Syn. React. Inorg. Metal-org. Chem.*, 4 (1974) 499.
- 11 R. Usón, A. Laguna, M.U. de la Orden and M.L. Arrese, *Syn. React. Inorg. Metal-org. Chem.*, 14 (1984) 369.
- 12 R. Usón, A. Laguna and P. Brun, *J. Organomet. Chem.*, 182 (1979) 449.
- 13 R. Usón, A. Laguna, A. Navarro, R.V. Parish and L.S. Moore, *Inorg. Chim. Acta*, 112 (1986) 205.
- 14 R. Usón, A. Laguna and M.V. Castillo, *Syn. React. Inorg. Metal-org. Chem.*, 9 (1979) 317.
- 15 S. Gambarotta, C. Floriani, A. Chiesi-Villa and C. Guastini, *J. Chem. Soc., Chem. Commun.*, (1983) 1304.
- 16 A.N. Nesmeyanov, E.G. Perevalova, K.I. Grandberg, D.A. Lemenovskii, T.V. Baukova and O.B. Afanassova, *Organomet. Chem.*, 65 (1974) 131; V.G. Andrianov, Y.T. Struchkov and E.R. Rosinskaya, *J. Struct. Chem.*, 15 (1974) 65.
- 17 R. Usón, A. Laguna and P. Brun, *J. Organomet. Chem.*, 197 (1980) 369.
- 18 J.F. Malone and V.S. McDonald, *J. Chem. Soc., Chem. Commun.*, (1967) 444.
- 19 J.F. Malone and V.S. McDonald, *J. Chem. Soc., Chem. Commun.*, (1970) 280.
- 20 R. Usón, A. Laguna, J. Vicente, J. García, P.G. Jones and G.M. Sheldrick, *J. Chem. Soc., Dalton Trans.*, (1981) 655.
- 21 R.W. Baker and P. Pauling, *J. Chem. Soc., Dalton Trans.*, (1972) 2264.
- 22 R. Usón, A. Laguna, M. Laguna, B.R. Manzano, P.G. Jones and G.M. Sheldrick, *J. Chem. Soc., Dalton Trans.*, (1984) 839.
- 23 P.G. Jones, *Gold Bull.*, 14 (1981) 102; 16 (1983) 114.
- 24 Y. Jiang, S. Alvarez and R. Hoffmann, *Inorg. Chem.*, 24 (1985) 749.
- 25 J. Vicente, M.T. Chicote, J.A. Cayuelas, J. Fernandez-Baeza, P.G. Jones, G.M. Sheldrick and P. Espinet, *J. Chem. Soc., Dalton Trans.*, (1985) 1163; J. Vicente, M.T. Chicote, I. Saura-Llamas, P.G. Jones, K. Meyer-Bäse and C. Freire Erdrügger, *Organometallics*, 7 (1988) 997.
- 26 P.G. Jones, *J. Organomet. Chem.*, 345 (1988) 405.
- 27 L.G. Vaughan and W.A. Sheppard, *J. Organomet. Chem.*, 22 (1970) 739.
- 28 R. Usón, A. Laguna and T. Cuenca, *J. Organomet. Chem.*, 194 (1980) 271.
- 29 R. Usón, A. Laguna, J. García and M. Laguna, *Inorg. Chim. Acta*, 37 (1979) 201.
- 30 L. Malvano, *Atti. Acad. Naz. Lincei*, 17 (1908) 857.
- 31 H. Schmidbauer, J.R. Mandl, A. Frank and G. Huttner, *Chem. Ber.*, 109 (1976) 466.
- 32 H. Schmidbauer, A. Wolleben, F.E. Wagner, D.F. van der Vondel and G.P. van der Kelen, *Chem. Ber.*, 110 (1977) 2758.
- 33 R. Usón, A. Laguna, J. Vicente and J. García, *Rev. Acad. Cienc. Exactas Fis. Quim. Nat. Zaragoza*, 31 (1976) 77.
- 34 R. Usón, A. Laguna and B. Bergareche, *J. Organomet. Chem.*, 184 (1980) 411.
- 35 E.A. Allen and W. Wilkinson, *Spectrochim. Acta A*, 28 (1972) 2257.
- 36 W. Clegg, *Acta Crystallogr., A*, 37 (1981) 22.