

## BI- AND TETRANUCLEAR POLYFLUOROPHENYL-BRIDGED GOLD(I) COMPLEXES

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### Summary

The reaction of  $\text{RAuL}$  ( $\text{R} = 2,4,6\text{-C}_6\text{F}_3\text{H}_2$ ,  $3,6\text{-C}_6\text{F}_2\text{H}_3$ ,  $4\text{-C}_6\text{FH}_4$  or  $3\text{-CF}_3\text{C}_6\text{H}_4$ ;  $\text{L} = \text{PPh}_3$  or  $\text{AsPh}_3$ ) or  $\text{RAudpeAuR}$  \* with inorganic acids  $\text{HA}$  ( $\text{A} = \text{ClO}_4$ ,  $\text{BF}_4$  or  $\text{PF}_6$ ) leads to binuclear complexes of the types  $[\text{R}(\text{AuL})_2]\text{A}$  or  $[\text{R}(\text{Au}_2\text{dpe})]\text{BF}_4$ . Similarly, reaction of  $\text{NBu}_4[\text{Au}(2,4,6\text{-C}_6\text{F}_3\text{H}_2)_2]$  with  $\text{HPF}_6$  yields the tetranuclear complex  $\text{Au}_4(2,4,6\text{-C}_6\text{F}_3\text{H}_2)_4$ . Addition of  $\text{RAuL}$  to solutions obtained by treating  $\text{ClAuL}$  with  $\text{AgA}$  also gives compounds of the type  $[\text{R}(\text{AuL})_2]\text{A}$ .

### Introduction

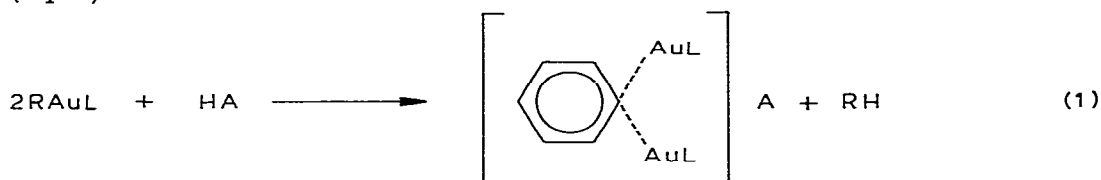
We recently found [1,2] that the  $\text{C}_6\text{F}_5$ ,  $2,4,6\text{-C}_6\text{F}_3\text{H}_2$  and  $3,6\text{-C}_6\text{F}_2\text{H}_3$  groups can in some cases be transferred from one gold atom to another. We think that these processes probably take place via binuclear intermediates in which the polyfluorophenyl-group are linked to both gold atoms, the aryl-bridge being similar to that described by Nesmeyanov et al. [3] for complexes of the type  $[\text{R}(\text{AuPR}'_3)_2]\text{BF}_4$  ( $\text{R} = \text{C}_6\text{H}_5$ ,  $p\text{-CH}_3\text{C}_6\text{H}_4$ , or ferrocenyl).

This suggested the possible existence of polyfluoroaryl-bridged complexes, and in this paper we report the preparation of binuclear complexes of the general formulae  $[\text{R}(\text{AuL})_2]\text{A}$  and  $[\text{RAu}_2(\text{L-L})]\text{A}$  ( $\text{R} = 2,4,6\text{-C}_6\text{F}_3\text{H}_2$ ,  $3,6\text{-C}_6\text{F}_2\text{H}_3$ ,  $4\text{-C}_6\text{FH}_4$  or  $3\text{-CF}_3\text{C}_6\text{H}_4$ ;  $\text{L} = \text{PPh}_3$  or  $\text{AsPh}_3$ ;  $\text{L-L} = \text{dpe}$ ;  $\text{A} = \text{BF}_4$ ,  $\text{PF}_6$  or  $\text{ClO}_4$ ) and of  $[\text{Au}(2,4,6\text{-C}_6\text{F}_3\text{H}_2)]_4$ ; the latter is the only hitherto described tetranuclear aryl-bridged gold complex, though similar compounds containing four copper atoms [4], two gold and two copper atoms [5] or two gold and two zinc atoms [6] have previously been reported.

\*  $\text{dpe} = 1,2\text{-bis}(\text{diphenylphosphine})\text{ethane}$ .

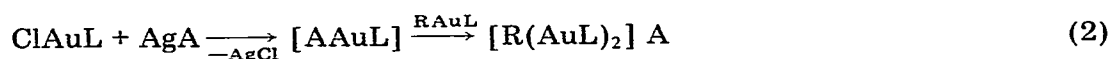
## Results and discussion

Addition of a strong acid HA ( $A = \text{ClO}_4$ ,  $\text{BF}_4$  or  $\text{PF}_6$ ) to ether solutions of  $\text{RAuL}$  at  $-10^\circ\text{C}$  leads to the formation of a white precipitate of  $[\text{R}(\text{AuL})_2]\text{A}$  (eq. 1)



$\text{R} = 2,4,6\text{-C}_6\text{F}_3\text{H}_2$ ,  $3,6\text{-C}_6\text{F}_2\text{H}_3$ ,  $4\text{-C}_6\text{FH}_4$ ,  $3\text{-CF}_3\text{C}_6\text{H}_4$ ,  $\alpha\text{-naphthyl}$   
 $\text{L} = \text{PPh}_3$ ,  $\text{AsPh}_3$

The same compounds can also be obtained by an alternative method. The reaction of the chloro-derivative  $\text{ClAuL}$  with  $\text{AgA}$  ( $A = \text{ClO}_4$  or  $\text{BF}_4$ ) in dichloromethane or benzene solution leads to solutions which probably contain  $\text{AAuL}$  [7]. Subsequent addition of  $\text{RAuL}$  allows isolation of the  $[\text{R}(\text{AuL})_2]\text{A}$  complexes (eq. 2)



These complexes are of the type described by Nesmeyanov [3], with the arylfluorophenyl groups bridging the gold atoms, as depicted in eq. 1. They are air- and moisture-stable and their conductivities are characteristic of uni-univalent electrolytes (see Table 1).

These compounds can only be obtained, however, if the R group contains less than four substituents in its ring; thus for  $\text{R} = \text{C}_6\text{F}_5$ ,  $2,3,5,6\text{-C}_6\text{F}_4\text{H}$ ,  $\text{C}_6\text{Cl}_5$  or  $\text{C}_6\text{Br}_5$ , the reaction with acids takes a different course which leads to  $[\text{AuL}_2]\text{A}$  ( $\text{L} = \text{PPh}_3$ ) as shown in eq. 3.



In these cases, reaction 2 cannot be used either, since  $\text{O}_3\text{ClOAuPPh}_3$  does not react with  $\text{RAuPPh}_3$  ( $\text{R} = \text{C}_6\text{F}_5$ ,  $\text{C}_6\text{Cl}_5$  or  $\text{C}_6\text{Br}_5$ ).

The anion of the acid used is also of great importance, since the formation of binuclear polyfluorophenyl-bridged complexes is only possible if the anions of the acids have poor coordinating ability. For example, the reaction with  $\text{H}_2\text{SO}_4$  or  $\text{HCF}_3\text{COO}$  leads to sulfato or trifluoroacetato complexes, as represented in equations 4 and 5.



The binuclear complexes  $\text{RAudpeAuR}$  (dpe = 1,2-bis(diphenylphosphine)-ethane) react with  $\text{HBF}_4$  in a manner analogous to that represented in eq. 1, to give compounds of the general formula  $[\text{RAu}_2\text{dpe}]\text{BF}_4$ .

Conductance studies in nitromethane solutions allow the two possible structures shown in Figure 1 to be distinguished.

TABLE 1  
ANALYTICAL DATA FOR COMPLEXES I—XVII

		Yield (%)	M.p. (°C)	Anal. (found (calcd.) (%))			$\Lambda_M^c$ (ohm <sup>-1</sup> cm <sup>2</sup> mol <sup>-1</sup> )
				C	H	Au	
I	[C <sub>6</sub> F <sub>3</sub> H <sub>2</sub> (AuPPh <sub>3</sub> ) <sub>2</sub> ] BF <sub>4</sub>	44 <sup>a</sup> , 55 <sup>b</sup>	145 (d)	43.60 (44.39)	2.60 (2.85)	33.87 (34.67)	116 <sup>d</sup>
II	[C <sub>6</sub> F <sub>3</sub> H <sub>2</sub> (AuPPh <sub>3</sub> ) <sub>2</sub> ] PF <sub>6</sub>	35 <sup>a</sup>	95 (d)	42.38 (42.25)	2.74 (2.70)	33.73 (33.00)	117 <sup>d</sup>
III	[C <sub>6</sub> F <sub>3</sub> H <sub>2</sub> (AuPPh <sub>3</sub> ) <sub>2</sub> ] ClO <sub>4</sub>	25 <sup>a</sup> , 50 <sup>b</sup>	160 (d)	44.75 (43.95)	2.74 (2.80)	34.17 (34.29)	145 <sup>d</sup>
IV	[C <sub>6</sub> F <sub>2</sub> H <sub>3</sub> (AuPPh <sub>3</sub> ) <sub>2</sub> ] BF <sub>4</sub>	37 <sup>a</sup>	140 (d)	44.91 (44.39)	2.78 (2.84)	34.53 (34.67)	100 <sup>d</sup>
V	[C <sub>6</sub> F <sub>2</sub> H <sub>3</sub> (AuPPh <sub>3</sub> ) <sub>2</sub> ] PF <sub>6</sub>	27 <sup>a</sup>	125 (d)	42.87 (42.87)	2.84 (2.82)	32.97 (33.49)	116 <sup>d</sup>
VI	[C <sub>6</sub> F <sub>2</sub> H <sub>3</sub> (AuPPh <sub>3</sub> ) <sub>2</sub> ] ClO <sub>4</sub>	24 <sup>a</sup> , 58 <sup>b</sup>	140 (d)	44.22 (44.60)	2.97 (2.94)	35.40 (34.83)	140 <sup>d</sup>
VII	[C <sub>6</sub> FH <sub>4</sub> (AuPPh <sub>3</sub> ) <sub>2</sub> ] BF <sub>4</sub>	41 <sup>a</sup>	119 (d)	45.50 (46.29)	3.03 (3.14)	36.90 (36.16)	111 <sup>d</sup>
VIII	[CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub> (AuPPh <sub>3</sub> ) <sub>2</sub> ] BF <sub>4</sub>	32 <sup>a</sup>	130 (d)	44.44 (44.89)	3.16 (2.97)	33.87 (34.25)	120 <sup>d</sup>
IX	[CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub> (AuPPh <sub>3</sub> ) <sub>2</sub> ] PF <sub>6</sub>	25 <sup>a</sup>	100 (d)	42.87 (42.73)	2.89 (2.83)	31.95 (32.60)	105 <sup>d</sup>
X	[C <sub>6</sub> F <sub>3</sub> H <sub>2</sub> (AuAsPh <sub>3</sub> ) <sub>2</sub> ] BF <sub>4</sub>	32 <sup>a</sup> , 62 <sup>b</sup>	50 (d)	41.89 (41.20)	2.20 (2.63)	33.10 (32.18)	150 <sup>d</sup>
XI	[C <sub>6</sub> F <sub>2</sub> H <sub>3</sub> (AuAsPh <sub>3</sub> ) <sub>2</sub> ] ClO <sub>4</sub>	33 <sup>a</sup> , 66 <sup>b</sup>	85 (d)	41.04 (41.81)	2.82 (2.75)	31.86 (32.66)	150 <sup>d</sup>
XII	[ $\alpha$ -C <sub>10</sub> H <sub>7</sub> (AuPPh <sub>3</sub> ) <sub>2</sub> ] BF <sub>4</sub> <sup>f</sup>	30 <sup>a</sup>	127 (d)	47.83 (48.78)	3.33 (3.29)	34.09 (34.79)	145 <sup>d</sup>
XIII	[ $\alpha$ -C <sub>10</sub> H <sub>7</sub> (AuPPh <sub>3</sub> ) <sub>2</sub> ] PF <sub>6</sub> <sup>f</sup>	30 <sup>a</sup>	139 (d)	45.78 (46.40)	3.27 (3.13)	32.80 (33.09)	149 <sup>d</sup>
XIV	[C <sub>6</sub> F <sub>3</sub> H <sub>2</sub> (Au <sub>2</sub> dpe)] BF <sub>4</sub>	52	130 (d)	37.24 (38.04)	2.45 (2.59)	38.42 (39.00)	94 <sup>e</sup>
XV	[C <sub>6</sub> F <sub>2</sub> H <sub>3</sub> (Au <sub>2</sub> dpe)] BF <sub>4</sub>	50	115 (d)	37.98 (38.70)	3.05 (2.74)	39.08 (39.70)	88 <sup>e</sup>
XVI	[ $\alpha$ -C <sub>10</sub> H <sub>7</sub> (Au <sub>2</sub> dpe)] BF <sub>4</sub> <sup>f</sup>	45	130 (d)	42.11 (42.96)	3.18 (3.10)	38.70 (39.15)	76 <sup>e</sup>
XVII	[Au(C <sub>6</sub> F <sub>3</sub> H <sub>2</sub> ) <sub>4</sub> ]	47	—	20.54 (21.90)	1.00 (0.60)	58.90 (60.05)	9 <sup>d</sup>

<sup>a</sup> Eq. 1; <sup>b</sup> eq. 2; <sup>c</sup>  $5 \times 10^{-4}$  M; <sup>d</sup> in acetone; <sup>e</sup> in nitromethane; <sup>f</sup>  $\alpha$ -C<sub>10</sub>H<sub>7</sub> =  $\alpha$ -naphthyl.

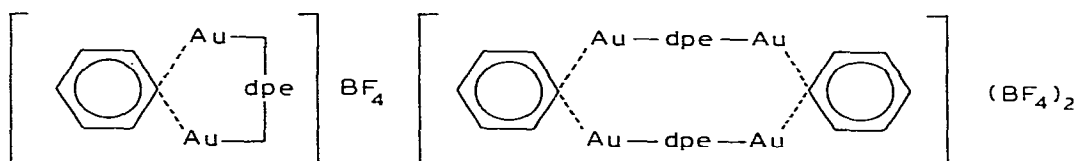


Fig. 1. Two possible structures of [RAu<sub>2</sub>dpe]BF<sub>4</sub>.

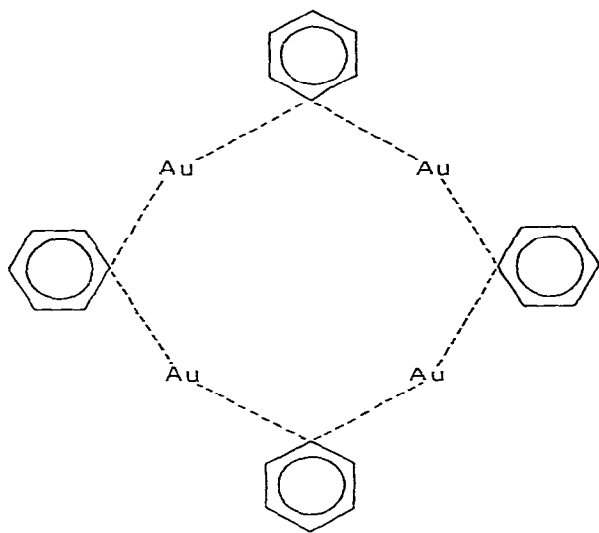
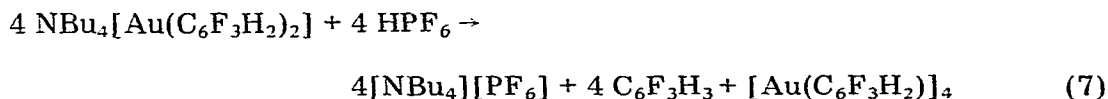


Fig. 2. Tetrameric structure of  $[\text{Au}(\text{C}_6\text{F}_3\text{H}_2)]_x$ .

The plot of the equivalent conductivity versus the square root of the concentration gives straight lines with slope 280 ( $\text{R} = \text{C}_6\text{F}_3\text{H}_2$ ), 239 ( $\text{R} = \text{C}_6\text{F}_2\text{H}_3$ ) and 207 ( $\text{R} = \alpha\text{-naphthyl}$ ), which are characteristic of uni-univalent electrolytes [8]. The complexes must therefore be binuclear species in which the gold atoms are assymmetrically double-bridged by an aryl group and a bidentate ligand (eq. 6).



If  $\text{NBu}_4[\text{Au}(\text{C}_6\text{F}_3\text{H}_2)_2]$  is treated with  $\text{HPF}_6$  in ether-dichloromethane (eq. 1) there is a different result. After evaporation of the solvent and addition of ether  $[\text{NBu}_4][\text{PF}_6]$  is precipitated, and after this is removed, evaporation of the filtrate gives  $[\text{Au}(\text{C}_6\text{F}_3\text{H}_2)]_x$  as a white complex which is not very stable (eq. 7).



Its molecular weight in benzene solution was found to be 1400 and it must therefore be tetrameric (calcd. 1312).

The analytical data (see Table 1) are in reasonable agreement with theoretical if we take into account that the complex is unstable above  $-20^\circ\text{C}$  and that it picks up traces of moisture when weighed.

Reaction of  $\text{NBu}_4[\text{Au}(\text{C}_6\text{F}_2\text{H}_3)_2]$  and  $\text{NBu}_4[\text{Au}(\text{CF}_3\text{C}_6\text{H}_4)_2]$  with  $\text{HBF}_4$  led to mixtures of products which could not be resolved.

In the light of the analogy with the results obtained for neutral complexes (reactions 1 and 6) and also with those obtained by Van Koten and Noltes for copper complexes [4,5] we assume that the four gold atoms are linked via polyfluorophenyl bridges (see Fig. 2). The results seem to provide the hitherto missing link between the binuclear complexes described by Nesmeyanov and the tetranuclear ones prepared by Van Koten and Noltes by an analogous route.

## Experimental

IR spectra were recorded (over the range 4000–200  $\text{cm}^{-1}$ ) on a Perkin-Elmer 597 spectrophotometer using Nujol mulls between polyethylene sheets. Conductivities were measured in acetone or nitromethane solutions with a Philips PW 9501/01 conductimeter. Molecular weights were measured in benzene solution with a Hitachi Perkin-Elmer 115 osmometer. C and H analyses were carried out with a Perkin-Elmer 240 microanalyzer. Au was determined by ashing the samples in a crucible together with an aqueous solution of hydrazine.

The yields, melting points, C, H and Au analyses, as well as, the conductivities of  $5 \times 10^{-4}$  M solutions of the novel complexes are collected in Table 1.

### Preparation of the complexes

$[R(\text{AuL})_2]A$ . These were prepared by two routes: a) To 0.25 mmol of  $\text{RAuL}$  [1] ( $R = \text{C}_6\text{F}_3\text{H}_2$ ,  $\text{C}_6\text{F}_2\text{H}_3$ ,  $\text{C}_6\text{FH}_4$ ,  $\text{CF}_3\text{C}_6\text{H}_4$  or  $\alpha$ -naphthyl;  $L = \text{PPh}_3$  or  $\text{AsPh}_3$ ) in 30 ml of ether at  $-10^\circ\text{C}$  was added excess of the acid HA (1.4 mmol) in aqueous ( $A = \text{ClO}_4$ , 60%), ether ( $A = \text{BF}_4$ , 54%), or hexane ( $A = \text{PF}_6$ , 56%). After 20 min stirring the white precipitate was filtered off and recrystallized from dichloromethane-hexane (complexes I–XIII). b) Reaction of equimolar amounts (0.25 mmol) of  $\text{ClAuL}$  ( $L = \text{PPh}_3$  or  $\text{AsPh}_3$ ) and  $\text{AgA}$  in dichloromethane at room temperature ( $A = \text{ClO}_4$ ) or at  $-20^\circ\text{C}$  ( $A = \text{BF}_4$ ) gave a precipitate of  $\text{AgCl}$ , which was filtered off.  $\text{RAuL}$  ( $R = \text{C}_6\text{F}_3\text{H}_2$  or  $\text{C}_6\text{F}_2\text{H}_3$ ) was added to the filtrate and the mixture was stirred for 1 h. Evaporation to dryness gave white solids which were recrystallized from dichloromethane-hexane (complexes I, III, VI, X and XI).

$[R(\text{Au}_2\text{dpe})]\text{BF}_4$ . An excess of  $\text{HBF}_4$  (1.4 mmol) in ether was added to a solution of  $\text{RAu-dpe-AuR}$  ( $R = \text{C}_6\text{F}_3\text{H}_2$ ,  $\text{C}_6\text{F}_2\text{H}_3$  or  $\alpha$ -naphthyl) in the same solvent (30 ml). After 30 min stirring at  $-10^\circ\text{C}$  the white precipitate of the complexes XIV–XVI was filtered off and were recrystallized from dichloromethane-ether.

$\text{Au}_3(\text{C}_6\text{F}_3\text{H}_2)_4$ . To a solution of 0.2 g (0.28 mmol) of  $\text{NBu}_4[\text{Au}(\text{C}_6\text{F}_3\text{H}_2)_2]$  [2] in ether-dichloromethane (1 : 1) at  $-78^\circ\text{C}$  was added 1.4 mmol of  $\text{H}_2\text{PF}_6$  (in 56% hexane solution). After 20 min stirring the solution was slowly allowed to reach  $0^\circ\text{C}$  ( $\sim 30$  min). Evaporation of the solvent left an oil which was treated with ether to leave a white residue which was identified as  $[\text{NBu}_4][\text{PF}_6]$ . Evaporation of the ether extract followed by recrystallization gave complex XVII.

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