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

R. USÓN, A. LAGUNA and P. BRUN

Department of Inorganic Chemistry, University of Zaragoza, Zaragoza (Spain)

(Received April 14th, 1980)

Summary

The reaction of RAuL (R = 2,4,6-$C_6F_3H_2$, 3,6-$C_6F_2H_3$, 4-C_6FH_4 or 3-$CF_3C_6H_4$; L = PPh_3 or $AsPh_3$) or RAudpeAuR * with inorganic acids HA (A = ClO_4, BF_4 or PF_6) leads to binuclear complexes of the types $[R(AuL)_2]A$ or $[R(Au_2dpe)]BF_4$. Similarly, reaction of $NBu_4[Au(2,4,6-C_6F_3H_2)_2]$ with HPF_6 yields the tetranuclear complex $Au_4(2,4,6-C_6F_3H_2)_4$. Addition of RAuL to solutions obtained by treating ClAuL with AgA also gives compounds of the type $[R(AuL)_2]A$.

Introduction

We recently found [1,2] that the C_6F_5, 2,4,6-$C_6F_3H_2$ and 3,6-$C_6F_2H_3$ 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 $[R(AuPR'_3)_2]BF_4$ (R = C_6H_5, *p*-$CH_3C_6H_4$, 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 $[R(AuL)_2]A$ and $[RAu_2(L-L)]A$ (R = 2,4,6-$C_6F_3H_2$, 3,6-$C_6F_2H_3$, 4-C_6FH_4 or 3-$CF_3C_6H_4$; L = PPh_3 or $AsPh_3$; L-L = dpe; A = BF_4, PF_6 or ClO_4) and of $[Au(2,4,6-C_6F_3H_2)]_4$; 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.

---

* dpe = 1,2-bis(diphenylphosphine)ethane.

Results and discussion

Addition of a strong acid HA (A = ClO_4, BF_4 or PF_6) to ether solutions of RAuL at $-10°C$ leads to the formation of a white precipitate of $[R(AuL)_2]A$ (eq. 1)

$$2\,RAuL \quad + \quad HA \quad \longrightarrow \quad \left[\underset{AuL}{\overset{AuL}{\bigcirc}} \right] A \; + \; RH \qquad (1)$$
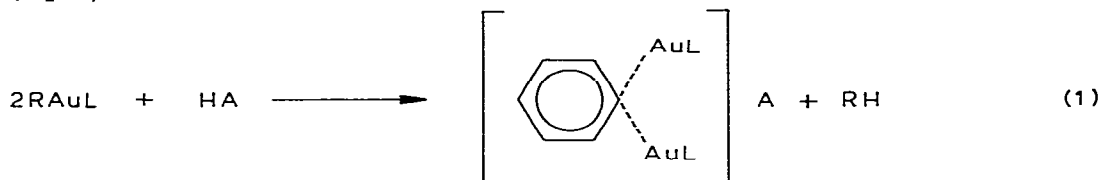
$R = 2,4,6-C_6F_3H_2$, $3,6-C_6F_2H_3$, $4-C_6FH_4$, $3-CF_3C_6H_4$, $\alpha-$naphthyl

$L = PPh_3$, $AsPh_3$

The same compounds can also be obtained by an alternative method. The reaction of the chloro-derivative ClAuL with AgA (A = ClO_4 or BF_4) in dichloromethane or benzene solution leads to solutions which probably contain AAuL [7]. Subsequent addition of RAuL allows isolation of the $[R(AuL)_2]A$ complexes (eq. 2)

$$ClAuL + AgA \xrightarrow[-AgCl]{} [AAuL] \xrightarrow{RAuL} [R(AuL)_2]\,A \qquad (2)$$
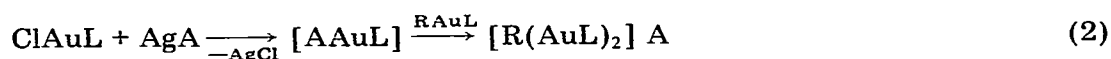
These complexes are of the type described by Nesmeyanov [3], with the arylfluorophenyl groups bridging the gold atoms, as depicted in eq. 1. They are air- and moisture-stable and their conductivities are characteristic of uni-univalent electrolytes (see Table 1).

These compounds can only be obtained, however, if the R group contains less than four substituents in its ring; thus for R = C_6F_5, $2,3,5,6-C_6F_4H$, C_6Cl_5 or C_6Br_5, the reaction with acids takes a different course which leads to $[AuL_2]A$ (L = PPh_3) as shown in eq. 3.

$$RAuPPh_3 + HA \rightarrow [Au(PPh_3)_2]\,A + RH \qquad (3)$$

In these cases, reaction 2 cannot be used either, since $O_3ClOAuPPh_3$ does not react with RAuPPh$_3$ (R = C_6F_5, C_6Cl_5 or C_6Br_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 H_2SO_4 or HCF_3COO leads to sulfato or trifluoroacetato complexes, as represented in equations 4 and 5.

$$2\,C_6F_3H_2AuPPh_3 + H_2SO_4 \rightarrow Ph_3PAuOSO_2OAuPPh_3 + 2\,C_6F_3H_3 \qquad (4)$$

$$C_6F_3H_2AuPPh_3 + HCF_3COO \rightarrow CF_3COOAuPPh_3 + C_6F_3H_3 \qquad (5)$$

The binuclear complexes RAudpeAuR (dpe = 1,2-bis(diphenylphosphine)-ethane) react with HBF_4 in a matter analogous to that represented in eq. 1, to give compounds of the general formula $[RAu_2dpe]BF_4$.

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.) (%))			Λ_M [c] (ohm^{-1} cm^2 mol^{-1})
				C	H	Au	
I	$[C_6F_3H_2(AuPPh_3)_2]BF_4$	44 [a], 55 [b]	145 (d)	43.60 (44.39)	2.60 (2.85)	33.87 (34.67)	116 [d]
II	$[C_6F_3H_2(AuPPh_3)_2]PF_6$	35 [a]	95 (d)	42.38 (42.25)	2.74 (2.70)	33.73 (33.00)	117 [d]
III	$[C_6F_3H_2(AuPPh_3)_2]ClO_4$	25 [a], 50 [b]	160 (d)	44.75 (43.95)	2.74 (2.80)	34.17 (34.29)	145 [d]
IV	$[C_6F_2H_3(AuPPh_3)_2]BF_4$	37 [a]	140 (d)	44.91 (44.39)	2.78 (2.84)	34.53 (34.67)	100 [d]
V	$[C_6F_2H_3(AuPPh_3)_2]PF_6$	27 [a]	125 (d)	42.87 (42.87)	2.84 (2.82)	32.97 (33.49)	116 [d]
VI	$[C_6F_2H_3(AuPPh_3)_2]ClO_4$	24 [a], 58 [b]	140 (d)	44.22 (44.60)	2.97 (2.94)	35.40 (34.83)	140 [d]
VII	$[C_6FH_4(AuPPh_3)_2]BF_4$	41 [a]	119 (d)	45.50 (46.29)	3.03 (3.14)	36.90 (36.16)	111 [d]
VIII	$[CF_3C_6H_4(AuPPh_3)_2]BF_4$	32 [a]	130 (d)	44.44 (44.89)	3.16 (2.97)	33.87 (34.25)	120 [d]
IX	$[CF_3C_6H_4(AuPPh_3)_2]PF_6$	25 [a]	100 (d)	42.87 (42.73)	2.89 (2.83)	31.95 (32.60)	105 [d]
X	$[C_6F_3H_2(AuAsPh_3)_2]BF_4$	32 [a], 62 [b]	50 (d)	41.89 (41.20)	2.20 (2.63)	33.10 (32.18)	150 [d]
XI	$[C_6F_2H_3(AuAsPh_3)_2]ClO_4$	33 [a], 66 [b]	85 (d)	41.04 (41.81)	2.82 (2.75)	31.86 (32.66)	150 [d]
XII	$[\alpha\text{-}C_{10}H_7(AuPPh_3)_2]BF_4$ [f]	30 [a]	127 (d)	47.83 (48.78)	3.33 (3.29)	34.09 (34.79)	145 [d]
XIII	$[\alpha\text{-}C_{10}H_7(AuPPh_3)_2]PF_6$ [f]	30 [a]	139 (d)	45.78 (46.40)	3.27 (3.13)	32.80 (33.09)	149 [d]
XIV	$[C_6F_3H_2(Au_2dpe)]BF_4$	52	130 (d)	37.24 (38.04)	2.45 (2.59)	38.42 (39.00)	94 [e]
XV	$[C_6F_2H_3(Au_2dpe)]BF_4$	50	115 (d)	37.98 (38.70)	3.05 (2.74)	39.08 (39.70)	88 [e]
XVI	$[\alpha\text{-}C_{10}H_7(Au_2dpe)]BF_4$ [f]	45	130 (d)	42.11 (42.96)	3.18 (3.10)	38.70 (39.15)	76 [e]
XVII	$[Au(C_6F_3H_2)]_4$	47	—	20.54 (21.90)	1.00 (0.60)	58.90 (60.05)	9 [d]

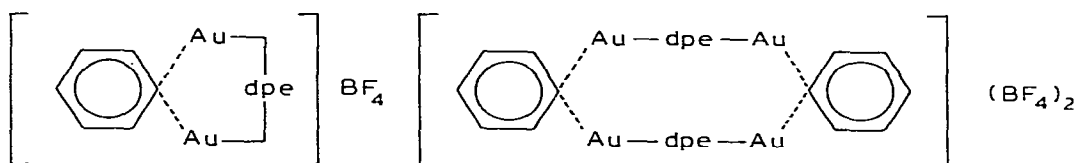[a] Eq. 1; [b] eq. 2; [c] 5×10^{-4} M; [d] in acetone; [e] in nitromethane; [f] $\alpha\text{-}C_{10}H_7 = \alpha$-naphthyl.

Fig. 1. Two possible structures of $[RAu_2dpe]BF_4$.
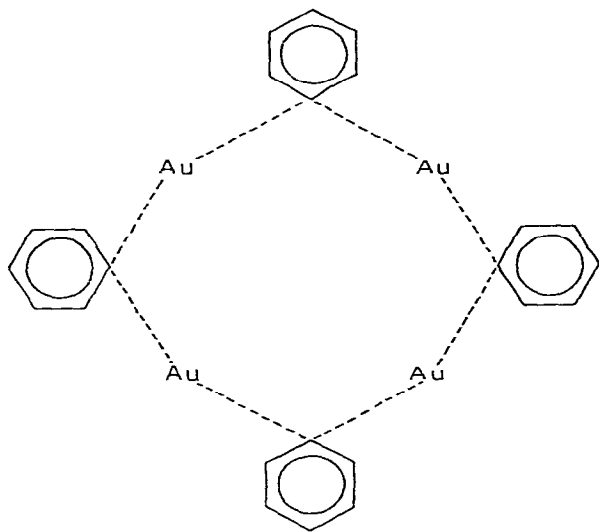
Fig. 2. Tetrameric structure of $[Au(C_6F_3H_2)]_x$.

The plot of the equivalent conductivity versus the square root of the concentration gives straight lines with slope 280 (R = $C_6F_3H_2$), 239 (R = $C_6F_2H_3$) and 207 (R = α-naphthyl), which are characteristic of uni-univalent electrolytes [8]. The complexes must therefore be binuclear species in which the gold atoms are assymetrically double-bridged by an aryl group and a bidentate ligand (eq. 6).

$$RAudpeAuR + HBF_4 \rightarrow [R(Au_2dpe)] \ BF_4 \qquad (6)$$

If $NBu_4[Au(C_6F_3H_2)_2]$ is treated with HPF_6 in ether-dichloromethane (eq. 1) there is a different result. After evaporation of the solvent and addition of ether $[NBu_4][PF_6]$ is precipitated, and after this is removed, evaporation of the filtrate gives $[Au(C_6F_3H_2)]_x$ as a white complex which is not very stable (eq. 7).

$$4 \ NBu_4[Au(C_6F_3H_2)_2] + 4 \ HPF_6 \rightarrow$$

$$4[NBu_4][PF_6] + 4 \ C_6F_3H_3 + [Au(C_6F_3H_2)]_4 \qquad (7)$$
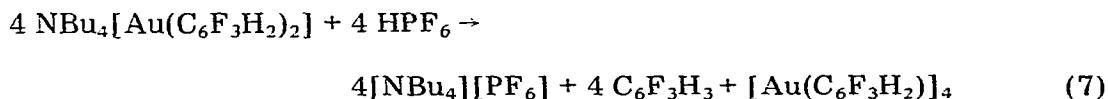
Its molecular weight in benzene solution was found to be 1400 and it must therefore be tetrameric (calcd. 1312).

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

Reaction of $NBu_4[Au(C_6F_2H_3)_2]$ and $NBu_4[Au(CF_3C_6H_4)_2]$ with 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 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 5×10^{-4} M solutions of the novel complexes are collected in Table 1.

Preparation of the complexes

[R(AuL)$_2$]A. These were prepared by two routes: a) To 0.25 mmol of RAuL [1] (R = $C_6F_3H_2$, $C_6F_2H_3$, C_6FH_4, $CF_3C_6H_4$ or α-naphthyl; L = PPh$_3$ or AsPh$_3$) in 30 ml of ether at $-10°$C was added and excess of the acid HA (1.4 mmol) in aqueous (A = ClO$_4$, 60%), ether (A = BF$_4$, 54%), or hexane (A = 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 ClAuL (L = PPh$_3$ or AsPh$_3$) and AgA in dichloromethane at room temperature (A = ClO$_4$) or at $-20°$C (A = BF$_4$) gave a precipitate of AgCl, which was filtered off. RAuL (R = $C_6F_3H_2$ or $C_6F_2H_3$) 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(Au$_2$dpe)]BF$_4$. An excess of HBF$_4$ (1.4 mmol) in ether was added to a solution of RAu—dpe—AuR (R = $C_6F_3H_2$, $C_6F_2H_3$ or α-napthyl) in the same solvent (30 ml). After 30 min stirring at $-10°$C the white precipitate of the complexes XIV—XVI was filtered off and were recrystallized from dichloromethane-ether.

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

References

1 R. Uson, A. Laguna and P. Brun, J. Organometal. Chem., 182 (1979) 449.
2 R. Uson, A. Laguna, J. Garcia and M. Laguna, Inorg. Chim. Acta, 37 (1979) 201.
3 A.N. Nesmeyanov, E.G. Perevalova, F.I. Grandberg, D.A. Lemenovskii, T.V. Baukova and O.B. Afanassova, J. Organometal. Chem., 65 (1974) 131.
4 G. van Koten and J.G. Noltes, J. Organometal. Chem., 84 (1975) 129; G. van Koten, A.J. Leusink and J.G. Noltes, J. Organometal. Chem., 84 (1975) 117.
5 G. van Koten and J.G. Noltes, J. Organometal. Chem., 82 (1974) C53.
6 P.W.J. Graaf, J. Boersma and G.J.M. van der Kerk, J. Organometal. Chem., 127 (1977) 391.
7 R. Uson, A. Laguna and M.V. Castrillo; Synth. React. Inorg. Met-org. Chem., 9 (1979) 317; R. Uson, P. Royo, A. Laguna and J. Garcia, Rev. Acad. Cienc., Zaragoza, 28 (1973) 67.
8 R.D. Feltham and R.G. Hayter, J. Chem. Soc. (A), (1964) 4587; W.J. Geary, Coord. Chem. Rev., 7 (1971) 81.