

## Tris(pentafluorophenyl)gold(III) Complexes †

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The preparation of  $[\text{Au}(\text{C}_6\text{F}_5)_3(\text{tht})]$  (tht = tetrahydrothiophen) by oxidation of  $[\text{Au}(\text{C}_6\text{F}_5)(\text{tht})]$  with  $[\text{Ti}(\text{C}_6\text{F}_5)_2\text{Cl}]$  is described. Displacement of tht by other neutral or anionic unidentate ligands leads to the synthesis of  $[\text{Au}(\text{C}_6\text{F}_5)_3\text{L}]$  [ $\text{L} = \text{NH}_3, \text{py}, \text{PMePh}_2, \text{P}(\text{OPh})_3, \text{AsPh}_3, \text{SbPh}_3$  or  $\text{CNC}_6\text{H}_4\text{Me-}p$ ] or  $[\text{Q}[\text{Au}(\text{C}_6\text{F}_5)_3\text{X}]$  [ $\text{Q} = \text{NEt}_4, \text{NBu}_4, \text{PPh}_3(\text{CH}_2\text{Ph}),$  or  $\text{N}(\text{PPh}_3)_2$ ;  $\text{X} = \text{Cl}, \text{I}, \text{SCN},$  or  $\text{N}_3$ ]. The compound  $[\text{Au}(\text{C}_6\text{F}_5)_3(\text{CNC}_6\text{H}_4\text{Me-}p)]$  adds amines to give the gold(III)-carbene complexes  $[\text{Au}(\text{C}_6\text{F}_5)_3\{\text{C}(\text{NHC}_6\text{H}_4\text{Me-}p)(\text{NR}_2)\}]$  ( $\text{NR}_2 = \text{NHC}_6\text{H}_4\text{Me-}p, \text{NEt}_2,$  or  $\text{NHCH}_2\text{CH}_2\text{NH}_2$ ). The reaction of the compound  $[\text{Au}(\text{C}_6\text{F}_5)_3(\text{tht})]$  with potentially bidentate ligands takes two different courses. (a) *o*-Phenylenebis(dimethylarsine) (pdma) and 1,2-bis(diphenylphosphino)methane (dppm) give four-co-ordinated complexes, in which the ligands are unidentate; the pdma complex has inequivalent methyl hydrogens at low temperature ( $^1\text{H}$  n.m.r.) and the dppm complex inequivalent P atoms ( $^{31}\text{P}$  n.m.r.). An X-ray structure of the pdma complex confirms four-co-ordination in the solid state; space group  $P2_1/n, a = 10.796(3), b = 17.347(6), c = 16.275(5) \text{ \AA}, \beta = 94.47(3)^\circ, Z = 4, R = 0.058$  for 3 357 reflections. (b) 1,2-Bis(diphenylphosphino)ethane (dppe) acts as a bridging ligand leading to the formation of  $[(\text{C}_6\text{F}_5)_3\text{Au}(\mu\text{-dppe})\text{Au}(\text{C}_6\text{F}_5)_3]$ . Similar reactions starting from  $[\text{Au}(\text{C}_6\text{F}_5)(2,4,6\text{-C}_6\text{F}_3\text{H}_2)_2(\text{tht})]$  lead to the compounds  $[\text{Au}(\text{C}_6\text{F}_5)(2,4,6\text{-C}_6\text{F}_3\text{H}_2)_2(\text{PPh}_3)]$  or  $[\text{NBu}_4][\text{Au}(\text{C}_6\text{F}_5)(2,4,6\text{-C}_6\text{F}_3\text{H}_2)_2\text{Br}]$ . The arylation of  $[\text{Au}(\text{C}_6\text{F}_5)_3\text{Cl}]^-$  or  $[\text{Au}(\text{C}_6\text{F}_5)(2,4,6\text{-C}_6\text{F}_3\text{H}_2)_2\text{Br}]^-$  with  $\text{Ag}(\text{C}_6\text{F}_5)$  leads to  $[\text{Au}(\text{C}_6\text{F}_5)_4]^-$  and  $[\text{Au}(\text{C}_6\text{F}_5)_2(2,4,6\text{-C}_6\text{F}_3\text{H}_2)_2]^-$  respectively.

Since the preparation of the first trialkylgold(III) derivatives in 1943<sup>1</sup> these complexes have been the subject of numerous studies and are now widely represented.<sup>2</sup> Nonetheless, this has not been the case for the triaryl derivatives, of which only  $[\text{Au}(\text{C}_6\text{F}_5)_3(\text{PPh}_3)]$ ,<sup>3</sup>  $[\text{Au}(\text{C}_6\text{F}_5)_2(\text{C}_6\text{Br}_3)(\text{PPh}_3)]$ ,<sup>4</sup>  $[\text{Au}(\text{C}_6\text{F}_5)_2\text{R}(\text{tht})]$  ( $\text{R} = \text{C}_6\text{F}_5\text{H}$  or  $\text{C}_6\text{F}_3\text{H}_2$ ),<sup>5</sup> and  $[\text{NBu}_4][\text{Au}(\text{C}_6\text{F}_5)_3\text{Br}]$ <sup>6</sup> are known. In the present paper we describe the synthesis of  $[\text{Au}(\text{C}_6\text{F}_5)_3(\text{tht})]$  (tht = tetrahydrothiophen) and the results obtained upon replacement of tht by other neutral or anionic, uni- or bi-dentate ligands, leading to the preparation of new neutral, anionic, or cationic uni- and bi-nuclear tris(pentafluorophenyl)gold(III) derivatives. Some of these results have been the subject of a preliminary communication.<sup>7</sup>

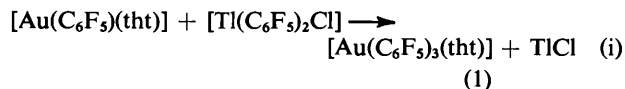
### Results and Discussion

The methods<sup>8-10</sup> generally used for alkylating gold(III) halogeno-complexes, *i.e.* their reaction with alkyl-lithium compounds, lead to decomposition with separation of metallic gold if aryl-lithium derivatives are employed; thus very few triaryl gold complexes are so far known.

Some success has been achieved by using Grignard compounds; thus we have prepared<sup>4</sup> the mixed complex *cis*- $[\text{Au}(\text{C}_6\text{F}_5)_2(\text{C}_6\text{Br}_3)(\text{PPh}_3)]$  by treating *cis*- $[\text{Au}(\text{C}_6\text{Br}_3)(\text{PPh}_3)\text{Cl}_2]$  with  $\text{Mg}(\text{C}_6\text{F}_5)\text{Br}$ . Vaughan and Sheppard<sup>3</sup> obtained  $[\text{Au}(\text{C}_6\text{F}_5)_3(\text{PPh}_3)]$  by adding  $\text{PPh}_3$  to solutions resulting from the addition of solid anhydrous gold trichloride to an ether solution of  $\text{Mg}(\text{C}_6\text{F}_5)\text{Br}$ . A suggestion by Puddephat<sup>11</sup> that these solutions are likely to contain  $[\text{Au}(\text{C}_6\text{F}_5)_3\text{Br}]^-$  has been verified by us, in that the addition of  $[\text{NBu}_4]\text{ClO}_4$  (instead of  $\text{PPh}_3$ ) allows the isolation of  $[\text{NBu}_4][\text{Au}(\text{C}_6\text{F}_5)_3\text{Br}]$ . This method can therefore only be used for the synthesis of complexes of type  $[\text{Au}(\text{C}_6\text{F}_5)_3\text{L}]$  whose neutral ligand L is capable of displacing the Br of the anionic complex  $[\text{Au}(\text{C}_6\text{F}_5)_3\text{Br}]^-$ .

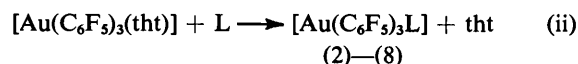
The arylation of gold(I) monoaryl complexes with  $[\text{Ti}(\text{C}_6\text{F}_5)_2\text{Br}]$  is also not feasible, since its reaction with  $[\text{Au}(\text{C}_6\text{F}_5)(\text{tht})]$  leads again to decomposition and precipitation of metallic gold.

We have recently described a method for the synthesis of  $[\text{Ti}(\text{C}_6\text{F}_5)_2\text{Cl}]$ ,<sup>5</sup> which generally behaves similarly to the bromo-derivative. Nevertheless, it reacts with  $[\text{Au}(\text{C}_6\text{F}_5)(\text{tht})]$  according to equation (i). At room temperature the white



complex  $[\text{Au}(\text{C}_6\text{F}_5)_3(\text{tht})]$  (1) is an air- and moisture-stable solid (whilst  $[\text{Au}(\text{C}_6\text{F}_5)(\text{tht})]$  must be stored in a refrigerator<sup>6</sup>), which is non-conducting in acetone. Both in the solid state and, especially, in chloroform solution the characteristic smell of the free ligand can be noticed. The low molecular weight determined in  $\text{CHCl}_3$  solution is due to partial dissociation of tht. The readiness of this dissociation makes complex (1) an excellent precursor for the synthesis of tris(pentafluorophenyl)gold(III) complexes, as may be seen from the following.

(a) *Reaction of (1) with Neutral, Unidentate Ligands.*—As in  $[\text{Au}(\text{C}_6\text{F}_5)(\text{tht})]$ <sup>6,12,13</sup> the tht group can readily be displaced by other N-, P-, As-, Sb-, or C-donor ligands [equation (ii)], where



$\text{L} = \text{NH}_3$  (2), py (pyridine) (3),  $\text{PPh}_3$ ,  $\text{PMePh}_2$  (4),  $\text{P}(\text{OPh})_3$  (5),  $\text{AsPh}_3$  (6),  $\text{SbPh}_3$  (7), or  $\text{CNC}_6\text{H}_4\text{Me-}p$  (8). In some of these derivatives ( $\text{L} = \text{NH}_3$  or  $\text{AsPh}_3$ ) the L can also be substituted by other groups with a higher donor capacity (such as  $\text{PPh}_3$ ). Other potential ligands, such as  $\text{NCCH}_3$ ,  $\text{BiPh}_3$ ,  $\text{OPPh}_3$ ,  $\text{S}_2\text{C}$ , or  $\text{Cl}_2\text{C}=\text{CCl}_2$  are not capable of displacing the tht group, and process (ii) does not take place.

The isocyanide complex (8) reacts with amines to give car-

† Supplementary data available (No. SUP 23349, 27 pp.): observed and calculated structure factors, thermal parameters, hydrogen atom co-ordinates, bond lengths and angles of  $\text{C}_6\text{H}_5$ . See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

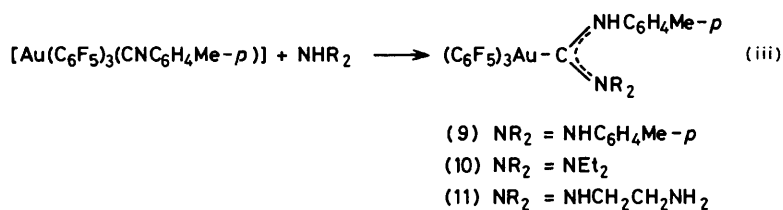


Table 1. Analytical data for complexes (1)–(24)

Complex	Yield (%)	M.p. (°C)	Analysis <sup>a</sup> (%)				$\Lambda_M$ (S cm <sup>2</sup> mol <sup>-1</sup> )	$M^a$
			C	H	N	Au		
(1) $[\text{Au}(\text{C}_6\text{F}_5)_3(\text{tht})]$	82	190	33.65 (33.6)	0.8 (1.05)		24.8 (25.05)	11	658 (786)
(2) $[\text{Au}(\text{C}_6\text{F}_5)_3(\text{NH}_3)]$	93	203 <sup>b</sup>	31.0 (30.25)	0.45 (0.4)	2.0 (1.95)	27.35 (27.55)	4	722 (715)
(3) $[\text{Au}(\text{C}_6\text{F}_5)_3(\text{py})]$	53	254 <sup>b</sup>	35.55 (35.55)	0.8 (0.65)	1.95 (1.8)	25.25 (25.35)	5	761 (777)
(4) $[\text{Au}(\text{C}_6\text{F}_5)_3(\text{PMePh}_2)]$	83	180	41.75 (41.45)	1.5 (1.45)		21.55 (21.9)	7	938 (898)
(5) $[\text{Au}(\text{C}_6\text{H}_5)_3\{\text{P}(\text{OPh})_3\}]$	68	174 <sup>b</sup>	41.9 (42.9)	1.7 (1.5)		18.95 (19.55)	4	1 012 (1 008)
(6) $[\text{Au}(\text{C}_6\text{F}_5)_3(\text{AsPh}_3)]$	58	98 <sup>b</sup>	42.95 (43.05)	1.35 (1.5)		19.85 (19.6)	10	1 039 (1 004)
(7) $[\text{Au}(\text{C}_6\text{F}_5)_3(\text{SbPh}_3)]$	69	168 <sup>b</sup>	41.15 (41.15)	1.55 (1.45)		19.35 (18.75)	8	1 073 (1 051)
(8) $[\text{Au}(\text{C}_6\text{H}_5)_3(\text{CNC}_6\text{H}_4\text{Me}-p)]$	70	197 <sup>b</sup>	38.65 (38.3)	0.9 (0.85)	1.75 (1.7)	24.25 (24.15)	1	843 (815)
(9) $[\text{Au}(\text{C}_6\text{F}_5)_3\{\text{C}(\text{NHC}_6\text{H}_4\text{Me}-p)_2\}]$	39	238 <sup>b</sup>	43.45 (42.95)	1.8 (1.75)	3.0 (3.05)	21.55 (21.35)	12	955 (922)
(10) $[\text{Au}(\text{C}_6\text{F}_5)_3\{\text{C}(\text{NHC}_6\text{H}_4\text{Me}-p)(\text{NEt}_2)\}]$	43	168 <sup>b</sup>	39.7 (40.55)	2.15 (2.05)	3.0 (3.15)	21.85 (22.15)	0.5	936 (888)
(11) $[\text{Au}(\text{C}_6\text{F}_5)_3\{\text{C}(\text{NHC}_6\text{H}_4\text{Me}-p)(\text{NHCH}_2\text{CH}_2\text{NH}_2)\}]$	41	120	39.5 (38.4)	1.85 (1.75)	4.75 (4.8)	21.85 (22.2)	1	895 (875)
(12) $[\text{Au}(\text{C}_6\text{F}_5)_3(\text{pdma})]$	65	157	34.15 (34.15)	1.1 (1.65)		20.5 (20.0)	12	1 014 (984)
(13) $[\text{Au}(\text{C}_6\text{F}_5)_3(\text{dppm})]$	60	185	47.7 (47.7)	1.8 (2.05)		17.95 (18.8)	2	1 110 (1 082)
(14) $[\text{Au}(\text{C}_6\text{F}_5)_3(\text{PPh}_2\text{CH}_2\text{PMePh}_2)]\text{BF}_4$	54	238	45.35 (44.6)	2.1 (2.15)		17.0 (16.65)	163	
(15) $[(\text{C}_6\text{F}_5)_3\text{Au}(\mu\text{-dppm})\text{Au}(\text{PPh}_3)]\text{ClO}_4$	50	186 <sup>b</sup>	44.85 (44.65)	2.45 (2.25)		23.75 (24.0)	156	
(16) $[(\text{C}_6\text{F}_5)_3\text{Au}(\mu\text{-dpppe})\text{Au}(\text{C}_6\text{F}_5)_3]$	64	255 <sup>b</sup>	41.85 (41.5)	1.55 (1.35)		20.3 (20.95)	1	1 855 (1 794)
(17a) $[\text{NEt}_4][\text{Au}(\text{C}_6\text{F}_5)_3\text{Cl}]$	55	192 <sup>b</sup>	36.25 (36.15)	2.45 (2.35)	1.8 (1.6)	23.3 (22.8)	117	
(17b) $[\text{PPh}_3(\text{CH}_2\text{Ph})][\text{Au}(\text{C}_6\text{F}_5)_3\text{Cl}]$	85	185 <sup>b</sup>	47.9 (47.5)	2.25 (2.05)		18.3 (18.1)	108	
(17c) $[\text{N}(\text{PPh}_3)_2][\text{Au}(\text{C}_6\text{F}_5)_3\text{Cl}]$	82	164	50.95 (51.0)	2.55 (2.4)	1.4 (1.1)	15.1 (15.5)	112	
(18) $[\text{NBu}_4][\text{Au}(\text{C}_6\text{F}_5)_3\text{I}]$	50	126	37.5 (38.25)	3.1 (3.4)	1.45 (1.3)	17.6 (18.45)	101	
(19a) $[\text{PPh}_3(\text{CH}_2\text{Ph})][\text{Au}(\text{C}_6\text{F}_5)_3(\text{SCN})]$	80	116 <sup>b</sup>	47.25 (47.6)	2.1 (2.0)	1.25 (1.25)	18.05 (17.75)	102	
(19b) $[\text{N}(\text{PPh}_3)_2][\text{Au}(\text{C}_6\text{F}_5)_3(\text{SCN})]$	75	109 <sup>b</sup>	51.8 (51.0)	2.15 (2.35)	2.25 (2.15)	15.35 (15.2)	85	
(20) $[\text{PPh}_3(\text{CH}_2\text{Ph})][\text{Au}(\text{C}_6\text{F}_5)_3(\text{N}_3)]$	55	107	46.5 (47.25)	2.15 (2.05)	3.65 (3.85)	17.8 (18.0)	93	
(21) $[\text{N}(\text{PPh}_3)_2][\text{Au}(\text{C}_6\text{F}_5)_4]$	95	215 <sup>b</sup>	51.3 (51.35)	2.45 (2.15)	1.15 (1.0)	14.4 (14.05)	90	
(22) $[\text{Au}(\text{C}_6\text{F}_5)(\text{C}_6\text{F}_3\text{H}_2)_2(\text{PPh}_3)]$	87	207	48.0 (48.65)	2.15 (2.15)		21.95 (22.15)	1	875 (888)
(23) $[\text{NBu}_4][\text{Au}(\text{C}_6\text{F}_5)(\text{C}_6\text{F}_3\text{H}_2)_2\text{Br}]$	83	105	43.45 (43.05)	4.5 (4.25)	1.5 (1.45)	21.6 (20.75)	131	
(24) $[\text{NBu}_4][\text{Au}(\text{C}_6\text{F}_5)_2(\text{C}_6\text{F}_3\text{H}_2)_2]$	65	210	46.25 (46.4)	3.75 (3.9)	1.41 (1.35)	19.2 (19.0)	102	

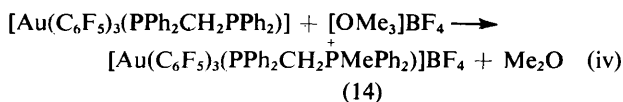
<sup>a</sup> Calculated values in parentheses. <sup>b</sup> With decomposition.

benzene complexes [equation (iii)]. The behaviour is similar to that found<sup>14</sup> for  $[\text{Au}(\text{C}_6\text{F}_5)(\text{CNC}_6\text{H}_4\text{Me-}p)]$ , although in the present case the reactions come to completion after shorter treatment [2, 4, or  $\frac{1}{2}$  h when  $\text{NHR}_2 = \text{NH}_2\text{C}_6\text{H}_4\text{Me-}p$ ,  $\text{NHEt}_2$ , or  $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$  respectively] than for the gold(I) complexes<sup>14</sup> (8, 15, or  $\frac{1}{2}$  h respectively). The value of  $\nu(\text{C}\equiv\text{N})$  decreases from  $2\,262\text{ cm}^{-1}$  in the isocyanide to  $1\,575\text{--}1\,555\text{ cm}^{-1}$  in the carbene. The neutral tris(pentafluorophenyl)-gold(III) complexes are white, air- and moisture-stable solids, which are monomeric and non-conducting in solution (Table 1).

(b) *Reactions with Neutral Bidentate Ligands.*—Neutral bidentate ligands such as *o*-phenylenebis(dimethylarsine) (pdma) or bis(diphenylphosphino)methane (dppm) lead, by reactions analogous to equation (ii), to  $[\text{Au}(\text{C}_6\text{F}_5)_3(\text{pdma})]$  (12) and  $[\text{Au}(\text{C}_6\text{F}_5)_3(\text{dppm})]$  (13) respectively. In every case the substitution takes place at room temperature. For  $\text{L} = \text{pdma}$  the treatment should not last longer than five minutes since a progressive reduction to give  $[\text{Au}(\text{pdma})_2][\text{Au}(\text{C}_6\text{F}_5)_2]$ <sup>13</sup> then occurs [after 1 h stirring at room temperature the gold(I) complex is obtained in 24% yield]. No reduction is observed with any of the other uni- or bi-dentate ligands.

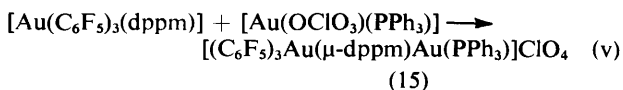
The <sup>1</sup>H n.m.r. spectrum of (12) in  $\text{CDCl}_3$  at room temperature shows only two peaks at  $\tau\,2.57$  (m, 4 H,  $\text{C}_6\text{H}_4$ ) and  $\tau\,8.41$  (s, 12 H, AsMe) indicating the complete equivalence of both As atoms. On cooling the sample the spectrum broadens (at  $-30^\circ\text{C}$ ) and, finally (below  $-50^\circ\text{C}$ ), the single sharp signal due to the methyl groups splits into two peaks at  $\tau\,8.13$  and  $8.65$ , showing that the ligand pdma is unidentate although an exchange between the two As-donor atoms takes place at room temperature. Despite the strong chelating properties of the ligand it is also unidentate in the solid state as may be seen from the X-ray determination of the structure of (12) (see below).

The <sup>31</sup>P n.m.r. spectrum ( $\text{CDCl}_3$ ) of (13), on the other hand, shows at room temperature two resonances at  $-14.3$  (d of multiplets) and  $+30.8$  p.p.m. [d,  $J(\text{P-P}) = 65\text{ Hz}$ ], thus indicating that only one of the two phosphorus atoms of the diphosphine is co-ordinated to the central metal ion.<sup>15,16</sup> The free end can readily be methylated with  $[\text{OMe}_3]\text{BF}_4$  to give the cationic complex (14), [equation (iv)]. The conductivity of

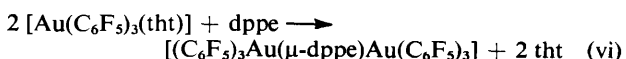


(14) in acetone is characteristic for a uni-univalent electrolyte.

Owing to the existence of an unco-ordinated atom in (13), this complex can be used as a ligand to displace the perchlorato-group of  $[\text{Au}(\text{OClO}_3)(\text{PPh}_3)]$ , as may be seen from equation

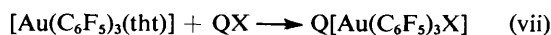


(v). Nonetheless, (13) is not capable of displacing tht in complex (1), and after stirring for 2 h at room temperature the unchanged starting compounds are recovered. Nor is it possible to prepare the binuclear derivative  $[(\text{C}_6\text{F}_5)_3\text{Au}(\mu\text{-dppm})\text{Au}(\text{C}_6\text{F}_5)_3]$  by adding a stoichiometric amount of the diphosphine to solutions of (1); whatever the reagent ratio, complex (13) is obtained. However, addition of 1,2-bis(diphenylphosphino)ethane (dppe) to a dichloromethane solution of (1) leads to the formation of (16) [equation (vi)], whilst the



corresponding mononuclear derivative could not be isolated [even by using a molar ratio dppe : (1) = 1.5 : 1].

(c) *Reactions with Anionic Ligands.*—Anionic ligands such as halogen or pseudohalogen can also displace tht in complex (1) [equation (vii)] where  $\text{X} = \text{Cl}$  (17), Br, I (18), SCN (19), or  $\text{N}_3$

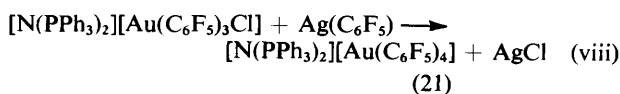


(20) and where  $\text{Q} = \text{NEt}_4$ ,  $\text{NBu}_4$ ,  $\text{PPh}_3(\text{CH}_2\text{Ph})$ , or  $\text{N}(\text{PPh}_3)_2$ . The i.r. spectrum and melting point of the bromo-derivative agree with those previously reported.<sup>6</sup>

The tris(pentafluorophenyl)aurate(III) complexes (17)–(20) are white air- and moisture-stable solids, which in acetone behave as 1 : 1 electrolytes. In the spectra of the chloro-complexes (17a), (17b), and (17c) the vibration  $\nu(\text{Au-Cl})$  is at  $325\text{m}$ ,  $320\text{m}$ , or  $322\text{m cm}^{-1}$  respectively which is characteristic of a terminal gold–chloride bond.<sup>17</sup> For the  $\text{X} = \text{SCN}$  derivatives the absorption band arising from  $\nu(\text{C}\equiv\text{N})$  is observed at  $2\,125\text{m}$  (19a) and  $2\,135\text{m}$  (19b)  $\text{cm}^{-1}$ ; determination of the internal standard ratio<sup>18</sup> gives 0.30 and 0.12 respectively, which confirms the S-bonded structure of these complexes. In dichloromethane solution, however, we observe, along with the strong band at  $2\,120\text{ cm}^{-1}$ , a weaker band at  $2\,070\text{ cm}^{-1}$  [in (19a) and (19b)], which indicates that some of the  $\text{Au-NCS}$  isomer<sup>19</sup> should also be present in the solution (ratio of absorption band areas  $\text{Au-NCS} : \text{Au-SCN} = 0.6 : 1$ ). The presence of the  $\text{N}_3$  group in (20) is supported by bands located at  $2\,050\text{vs}$ ,  $1\,290\text{m}$ ,  $580\text{m}$ , and  $395\text{m cm}^{-1}$ , characteristic for an end-on azide ligand.<sup>20,21</sup>

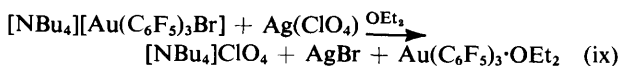
All neutral, anionic, or cationic tris(pentafluorophenyl)gold complexes described in this paper show three strong bands at ca.  $810$ ,  $798$ , and  $790\text{ cm}^{-1}$ , although in several cases the latter two overlap to form a broad and asymmetric band. These X-sensitive vibrations of the  $\text{C}_6\text{F}_5$  group are assignable<sup>22,23</sup> to a mode involving predominantly C–X stretching, which can be related to the symmetry of the compound, as has been done for  $\text{Ti}$ ,<sup>24</sup>  $\text{Au}$ ,<sup>25</sup> and  $\text{Pd}$  and  $\text{Pt}$ .<sup>26</sup>

The ligand tht can also be displaced by a  $\text{C}_6\text{F}_5$  group. Nevertheless, the reaction of complex (1) with  $\text{Li}(\text{C}_6\text{F}_5)$  followed by addition of  $[\text{NBu}_4]\text{Br}$  gives rise to a partial reduction to gold(I) leading to a mixture of  $[\text{NBu}_4][\text{Au}(\text{C}_6\text{F}_5)_2]$  and  $[\text{NBu}_4][\text{Au}(\text{C}_6\text{F}_5)_4]$ , which can be separated because of the higher solubility of the former in dichloromethane. Since the organoaurate(III) is obtained in only 22% yield, there is no advantage compared with previously used methods.<sup>6</sup> The arylation of (17c) with  $\text{Ag}(\text{C}_6\text{F}_5)$  [equation (viii)] leads to

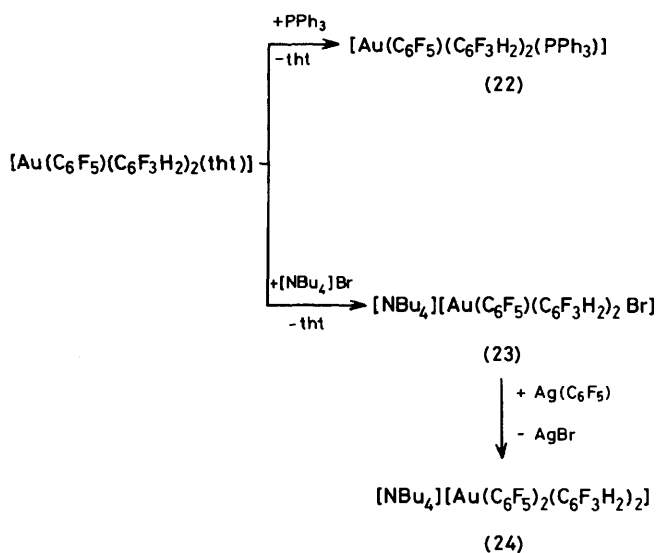


much better results. Since no reduction takes place in this case, 95% yields are obtained.

Ether solutions of  $\text{Au}(\text{C}_6\text{F}_5)_3$  are prepared by reacting equimolecular amounts of  $[\text{NBu}_4][\text{Au}(\text{C}_6\text{F}_5)_3\text{Br}]$  with  $\text{Ag}(\text{ClO}_4)$  [equation (ix)] at  $-10^\circ\text{C}$ . After removing the quantitatively



precipitated  $\text{AgBr}$  and  $[\text{NBu}_4]\text{ClO}_4$  the solutions are stable up to  $10^\circ\text{C}$ . Warming or evaporation of the solvent leads to decomposition and precipitation of metallic gold. In these solutions the  $\text{Au}(\text{C}_6\text{F}_5)_3$  is stabilized in the form of its etherate, whereas the reaction in dichloromethane leads to the complete precipitation of metallic gold, even at  $-75^\circ\text{C}$ . No reaction could be observed between (17b) or (17c) and  $\text{Ag}(\text{ClO}_4)$ .



Reactions (ii), (vii), and (viii) can also be extended to other complexes. Thus, the reaction of  $[\text{Au}(\text{C}_6\text{F}_5)(2,4,6\text{-C}_6\text{F}_3\text{H}_2)_2(\text{tht})]^{5-}$  with  $\text{PPh}_3$  leads to  $[\text{Au}(\text{C}_6\text{F}_5)(\text{C}_6\text{F}_3\text{H}_2)_2(\text{PPh}_3)]$  (22); that with  $[\text{NBu}_4]\text{Br}$  gives  $[\text{NBu}_4][\text{Au}(\text{C}_6\text{F}_5)(\text{C}_6\text{F}_3\text{H}_2)_2\text{Br}]$  (23), whilst the latter reacts with  $\text{Ag}(\text{C}_6\text{F}_5)$  giving  $[\text{NBu}_4][\text{Au}(\text{C}_6\text{F}_5)_2(\text{C}_6\text{F}_3\text{H}_2)_2]$  (24) (Scheme).

### Experimental

Infrared spectra were recorded on a Perkin-Elmer 577 spectrophotometer using Nujol mulls between polyethylene sheets. Conductivities were measured in  $ca. 5 \times 10^{-4} \text{ mol dm}^{-3}$  acetone solutions with a Philips PW 9501/01 conductometer. Molecular weights were determined in chloroform solution with a Hitachi-Perkin-Elmer 115 osmometer. Proton n.m.r. spectra were recorded on a Varian Associates HA 100 spectrometer at 100 MHz,  $^{31}\text{P}$  spectra were measured on a JEOL PFT-100 spectrometer at 40.48 MHz; chemical shifts are relative to  $\text{H}_3\text{PO}_4$  as external reference. Analyses (C, H, and N) were carried out with a Perkin-Elmer 240 microanalyser. Gold was determined by ashing the samples with an aqueous solution of hydrazine. The yields, melting points, C, H, N, and Au analyses, conductivities, and molecular weights of the novel complexes are collected in Table 1.

**Preparation of the Complexes.**—If not otherwise indicated the reactions were carried out at room temperature.

$[\text{Au}(\text{C}_6\text{F}_5)_3(\text{tht})]$ . Addition of  $[\text{Ti}(\text{C}_6\text{F}_5)_2\text{Cl}]^{5-}$  (1.148 g, 2 mmol) to a solution of  $[\text{Au}(\text{C}_6\text{F}_5)(\text{tht})]^{6-}$  (0.904 g, 2 mmol) in benzene (20  $\text{cm}^3$ ) at 6 °C led after a few seconds to a yellow colour and to precipitation of  $\text{TiCl}$ . After stirring for 45 min, followed by refluxing for 2 h, the  $\text{TiCl}$  was filtered off and the filtrate evaporated to dryness to give the white complex (1), which was recrystallized from diethyl ether–hexane.

$[\text{Au}(\text{C}_6\text{F}_5)_3\text{L}]$  [L =  $\text{NH}_3$ , py,  $\text{PMePh}_2$ ,  $\text{P(OPh)}_3$ ,  $\text{AsPh}_3$ ,  $\text{SbPh}_3$ ,  $\text{CNC}_6\text{H}_4\text{Me-}p$ , pdma, or dppm]. The respective ligand (0.4 mmol) was added to a solution of complex (1) (0.31 g, 0.4 mmol) in diethyl ether or dichloromethane (20  $\text{cm}^3$ ). After stirring for 2 h (only 5 min when L = pdma in order to prevent reduction to  $[\text{Au}(\text{pdma})_2][\text{Au}(\text{C}_6\text{F}_5)_2]$ ) the solution was evaporated to dryness to isolate complexes (2)–(8) and (12) and (13), which were recrystallized from diethyl ether–hexane.

$[\text{Au}(\text{C}_6\text{F}_5)_3(\text{C}(\text{NHC}_6\text{H}_4\text{Me-}p)(\text{NR}_2))]^{7-}$  ( $\text{NR}_2 = \text{NHC}_6\text{H}_4\text{-Me-}p$ ,  $\text{NET}_2$ , or  $\text{NHCH}_2\text{CH}_2\text{NH}_2$ ). The amine  $\text{NHR}_2$  (0.2 mmol) was added to a solution of complex (7) (0.011 g, 0.1 mmol) in chloroform (15  $\text{cm}^3$ ) and stirred for 2, 4, or  $\frac{1}{2}$  h respectively. (The course of the reaction was monitored by i.r. spectroscopy until disappearance of the absorption at 2262  $\text{cm}^{-1}$ , characteristic for the isocyanide group.) Evaporation to dryness rendered the white complexes (9)–(11), which were recrystallized from dichloromethane–hexane.

$[\text{Au}(\text{C}_6\text{F}_5)_3(\text{PPh}_2\text{CH}_2\text{PMePh}_2)]\text{BF}_4$ . The compound  $[\text{OMe}_3]\text{BF}_4$  (0.052 g, 0.35 mmol) in acetonitrile (7  $\text{cm}^3$ ) was added to a solution of complex (8) (0.334 g, 0.31 mmol) in the same solvent (7  $\text{cm}^3$ ). After stirring for 45 min the solution was vacuum evaporated to dryness. The white residue was treated with dichloromethane (to remove excess  $[\text{OMe}_3]\text{BF}_4$ ), filtered, evaporated to dryness, and recrystallized from dichloromethane–hexane to isolate complex (14).

$[(\text{C}_6\text{F}_5)_3\text{Au}(\mu\text{-dppm})\text{Au}(\text{PPh}_3)]\text{ClO}_4$ . Complex (8) (0.359 g, 0.33 mmol) was added to a solution of  $[\text{Au}(\text{OCIO}_3)(\text{PPh}_3)]^{27}$  (0.36 mmol) in dichloromethane (20  $\text{cm}^3$ ) and stirred for 1 h. Concentration to  $ca. 5 \text{ cm}^3$  and addition of hexane (20  $\text{cm}^3$ ) rendered a colourless oil. The hexane was decanted off and the oil was vigorously stirred with diethyl ether to separate the white complex (15), which was recrystallized from dichloromethane–hexane.

$[(\text{C}_6\text{F}_5)_3\text{Au}(\mu\text{-dppe})\text{Au}(\text{C}_6\text{F}_5)_3]$ . 1,2-Bis(diphenylphosphino)ethane (dppe) (0.099 g, 0.25 mmol) was added to a solution of complex (1) (0.314 g, 0.4 mmol) in diethyl ether (20  $\text{cm}^3$ ). Stirring for 1 h and evaporation to dryness afforded the white complex (16), which was recrystallized from dichloromethane–hexane.

$[\text{Q}[\text{Au}(\text{C}_6\text{F}_5)_3\text{X}]]$  [Q =  $\text{NET}_4$ ,  $\text{NBu}_4$ ,  $\text{PPh}_3(\text{CH}_2\text{Ph})$ , or  $\text{N}(\text{PPh}_3)_2$ ; X = Cl, I, SCN, or  $\text{N}_3$ ]. The compound QX (0.4 mmol) was added to a solution of complex (1) (0.314 g, 0.4 mmol) in dichloromethane (20  $\text{cm}^3$ ). After stirring for 2 h, partial evaporation to  $ca. 5 \text{ cm}^3$ , and addition of hexane (15  $\text{cm}^3$ ) the complexes (17)–(20) were obtained. They were recrystallized from dichloromethane–hexane.

$[\text{N}(\text{PPh}_3)_2][\text{Au}(\text{C}_6\text{F}_5)_4]$ . A solution of complex (17c) (0.509 g, 0.4 mmol) and  $\text{Ag}(\text{C}_6\text{F}_5)^{28}$  (0.13 g, 0.4 mmol) in diethyl ether (30  $\text{cm}^3$ ) was stirred for 1 h and evaporated to dryness. The residue was treated with dichloromethane (40  $\text{cm}^3$ ) and the precipitated  $\text{AgCl}$  was filtered off. Evaporation of the filtrate yielded complex (21) which was recrystallized from dichloromethane–hexane.

$[\text{Au}(\text{C}_6\text{F}_5)_3(\text{OEt}_2)]$  (Solution). The compound  $\text{Ag}(\text{ClO}_4)$  (0.083 g, 0.4 mmol) was added to a solution of  $[\text{NBu}_4][\text{Au}(\text{C}_6\text{F}_5)_3\text{Br}]^{6-}$  (0.408 g, 0.4 mmol) in diethyl ether (20  $\text{cm}^3$ ) at  $-10^\circ\text{C}$ . After stirring for 1 h at the same temperature the precipitated  $\text{AgBr}$  and  $[\text{NBu}_4]\text{ClO}_4$  were filtered off. The resulting colourless filtrate decomposes with formation of metallic gold when warmed to  $>10^\circ\text{C}$  or upon evaporation of the solvent.

$[\text{Au}(\text{C}_6\text{F}_5)(\text{C}_6\text{F}_3\text{H}_2)_2(\text{PPh}_3)]$ . Addition of triphenylphosphine (0.131 g, 0.5 mmol) to a solution of  $[\text{Au}(\text{C}_6\text{F}_5)(2,4,6\text{-C}_6\text{F}_3\text{H}_2)_2(\text{tht})]^{5-}$  (0.357 g, 0.5 mmol) in diethyl ether (30  $\text{cm}^3$ ) led after stirring for 1 h, concentration to  $ca. 5 \text{ cm}^3$ , and addition of hexane (20  $\text{cm}^3$ ) to the precipitation of complex (22), which was recrystallized from dichloromethane–hexane.

$[\text{NBu}_4][\text{Au}(\text{C}_6\text{F}_5)(\text{C}_6\text{F}_3\text{H}_2)_2\text{Br}]$ . A mixture of  $[\text{NBu}_4]\text{Br}$  (0.161 g, 0.5 mmol) and  $[\text{Au}(\text{C}_6\text{F}_5)(2,4,6\text{-C}_6\text{F}_3\text{H}_2)_2(\text{tht})]^{5-}$  (0.357 g, 0.5 mmol) in dichloromethane (20  $\text{cm}^3$ ) was stirred for 1 h. Partial evaporation to  $ca. 5 \text{ cm}^3$  and addition of hexane (20  $\text{cm}^3$ ) precipitated the white complex (23), which was recrystallized from dichloromethane–hexane.

$[\text{NBu}_4][\text{Au}(\text{C}_6\text{F}_5)_2(\text{C}_6\text{F}_3\text{H}_2)_2]$ . Complex (23) (0.095 g, 0.1 mmol) was added to a solution of  $\text{Ag}(\text{C}_6\text{F}_5)$  (0.034 g, 0.1 mmol) in diethyl ether (20  $\text{cm}^3$ ), stirred for 30 min, and evaporated.

**Table 2.** Atomic co-ordinates ( $\times 10^4$ ) with estimated standard deviations in parentheses

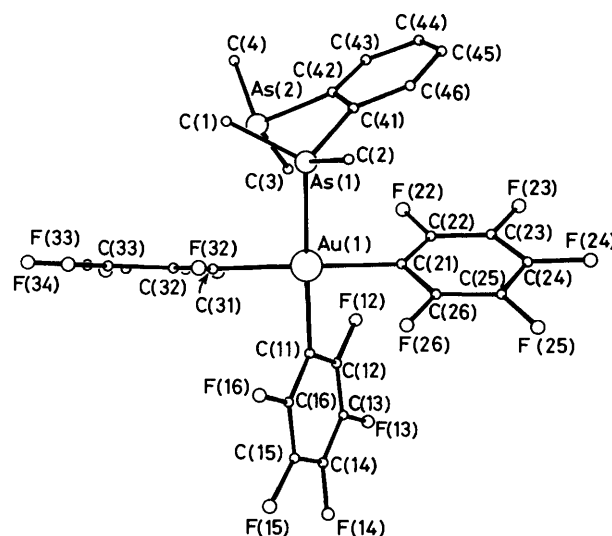
Atom	x	y	z
Au(1)	4 200(1)	1 807(1)	7 425(1)
As(1)	3 148(1)	601(1)	7 002(1)
As(2)	708(1)	1 702(1)	6 298(1)
C(11)	5 195(11)	2 796(7)	7 831(7)
C(12)	4 666(11)	3 349(7)	8 311(7)
C(13)	5 329(11)	3 951(7)	8 633(7)
C(14)	6 554(11)	4 042(7)	8 481(7)
C(15)	7 093(12)	3 511(7)	8 004(8)
C(16)	6 420(12)	2 890(7)	7 691(7)
F(12)	3 456(6)	3 302(4)	8 466(4)
F(13)	4 810(7)	4 488(4)	9 108(4)
F(14)	7 227(7)	4 642(4)	8 780(5)
F(15)	8 274(7)	3 593(5)	7 811(5)
F(16)	6 969(6)	2 361(4)	7 237(5)
C(21)	4 032(10)	1 501(6)	8 651(7)
C(22)	2 983(12)	1 595(7)	9 030(7)
C(23)	2 872(11)	1 387(8)	9 826(8)
C(24)	3 857(15)	1 068(8)	10 276(8)
C(25)	4 958(13)	976(7)	9 925(8)
C(26)	5 026(10)	1 192(7)	9 100(7)
F(22)	1 959(6)	1 910(4)	8 633(4)
F(23)	1 800(7)	1 443(5)	10 199(4)
F(24)	3 798(8)	823(5)	11 053(5)
F(25)	5 978(7)	669(4)	10 346(4)
F(26)	6 097(6)	1 057(4)	8 755(4)
C(31)	4 387(10)	2 115(7)	6 216(6)
C(32)	3 776(10)	2 739(7)	5 875(7)
C(33)	3 797(11)	2 948(7)	5 058(8)
C(34)	4 467(11)	2 497(8)	4 563(7)
C(35)	5 122(12)	1 887(7)	4 877(7)
C(36)	5 077(12)	1 713(7)	5 692(8)
F(32)	3 074(7)	3 189(4)	6 331(4)
F(33)	3 199(7)	3 568(5)	4 755(5)
F(34)	4 490(8)	2 678(6)	3 764(4)
F(35)	5 833(8)	1 454(5)	4 413(5)
F(36)	5 741(7)	1 086(4)	6 005(5)
C(41)	1 548(11)	473(6)	7 465(6)
C(42)	519(12)	932(7)	7 180(7)
C(43)	-565(12)	842(7)	7 551(8)
C(44)	-648(12)	338(7)	8 177(8)
C(45)	315(14)	-99(8)	8 437(9)
C(46)	1 427(13)	-34(7)	8 095(8)
C(1)	2 952(11)	329(8)	5 851(7)
C(2)	4 147(12)	-256(7)	7 443(9)
C(3)	434(13)	2 625(7)	6 942(7)
C(4)	-946(13)	1 623(9)	5 728(9)

**Table 3.** Selected bond lengths (Å)

Au(1)-As(1)	2.453(1)	Au(1)-C(11)	2.104(12)
Au(1)-C(21)	2.085(11)	Au(1)-C(31)	2.065(11)
As(1)-C(41)	1.950(12)	As(1)-C(1)	1.927(12)
As(1)-C(2)	1.941(12)	As(2)-C(42)	1.983(12)
As(2)-C(3)	1.949(13)	As(2)-C(4)	1.952(14)
C(41)-C(46)	1.364(16)	C(41)-C(42)	1.416(16)
C(43)-C(44)	1.350(18)	C(42)-C(43)	1.366(19)
C(45)-C(46)	1.367(21)	C(44)-C(45)	1.329(19)

**Table 4.** Selected bond angles ( $^\circ$ )

As(1)-Au(1)-C(11)	176.2(3)	As(1)-Au(1)-C(21)	88.8(3)
C(11)-Au(1)-C(21)	89.3(4)	As(1)-Au(1)-C(31)	91.8(3)
C(11)-Au(1)-C(31)	90.1(4)	C(21)-Au(1)-C(31)	179.3(4)
Au(1)-As(1)-C(41)	113.1(3)	Au(1)-As(1)-C(1)	119.7(4)
C(41)-As(1)-C(1)	108.3(5)	Au(1)-As(1)-C(2)	108.5(4)
C(41)-As(1)-C(2)	104.6(5)	C(1)-As(1)-C(2)	100.9(6)
C(42)-As(2)-C(3)	97.8(5)	C(42)-As(2)-C(4)	98.9(6)
C(3)-As(2)-C(4)	98.2(6)	Au(1)-C(11)-C(12)	121.2(9)
Au(1)-C(11)-C(16)	121.4(9)	Au(1)-C(21)-C(22)	123.3(9)
Au(1)-C(21)-C(26)	119.4(8)	Au(1)-C(31)-C(32)	121.0(8)
Au(1)-C(31)-C(36)	124.1(9)	As(1)-C(41)-C(42)	120.3(8)
As(1)-C(41)-C(46)	120.2(9)	C(42)-C(41)-C(46)	119.3(11)
As(2)-C(42)-C(41)	119.6(9)	As(2)-C(42)-C(43)	122.5(9)
C(41)-C(42)-C(43)	117.9(11)	C(42)-C(43)-C(44)	121.1(12)
C(43)-C(44)-C(45)	120.9(13)	C(44)-C(45)-C(46)	120.8(13)
C(41)-C(46)-C(45)	119.9(12)		

**Figure.** The molecule of  $[\text{Au}(\text{C}_6\text{F}_5)_3(\text{pdma})]$ , showing atom numbering

ated to dryness. The residue was extracted with acetone, the insoluble AgBr was filtered off, and the filtrate was reduced to ca. 5 cm<sup>3</sup>. Addition of diethyl ether precipitated the white complex (24), which was recrystallized from dichloromethane-hexane.

**Crystal Data.**—C<sub>28</sub>H<sub>16</sub>As<sub>2</sub>AuF<sub>15</sub>,  $M = 984.22$ , Monoclinic, space group  $P2_1/n$ ,  $a = 10.796(3)$ ,  $b = 17.347(6)$ ,  $c = 16.275(5)$  Å,  $\beta = 94.47(3)^\circ$ ,  $U = 3 039 \text{ \AA}^3$ ,  $Z = 4$ ,  $D_c = 2.15 \text{ g cm}^{-3}$ ,  $F(000) = 1 856$ ,  $\lambda(\text{Mo-K}\alpha) = 0.710 69 \text{ \AA}$ ,  $\mu(\text{Mo-K}\alpha) = 7.1 \text{ mm}^{-1}$ .

A crystal  $0.25 \times 0.12 \times 0.08 \text{ mm}$  was used to collect 5 660 reflexions in the range  $7 < 2\theta < 50^\circ$  on a Stoe four-circle diffractometer. After application of Lorentz, polarisation, and absorption corrections, averaging equivalent reflexions gave 5 340 unique reflexions, 3 357 of which with  $F > 4\sigma(F)$  were used for all calculations. The structure was solved by the heavy-atom method and refined to  $R$  0.058,  $R'$  0.047. The weighting scheme was  $w^{-1} = \sigma^2(F) + 0.000 25F^2$ . All non-

hydrogen atoms were refined anisotropically; hydrogen atoms (riding on C atoms with C-H 0.96 Å) were assigned isotropic temperature factors equal to 1.2 times the equivalent isotropic temperature factor of their respective C atoms. A final difference map showed no peaks greater than  $1 \text{ e \AA}^{-3}$ . Calculations were performed with the SHELXTL program system (written by G. M. S.).

Final atomic co-ordinates are given in Table 2, with derived bond lengths and angles in Tables 3 and 4. The co-ordination at gold is square planar, only one As atom of the pdma ligand being bonded to gold; As(2) is bonded neither to Au(1) nor to any symmetry generated equivalent  $[\text{As}(2) \cdots \text{Au}(1) = 4.07$

Å]. This is reflected in average C-As-C bond angles of 105 and 98° for As(1) and As(2) respectively.

The adoption of five-co-ordination by gold(III) seems to be restricted to those cases where the bidentate ligand is rigid enough to force the second donor atom to lie within the co-ordination sphere of the metal; thus the bidentate N-donor ligands 2,2'-biquinoline, 2,9-dimethyl-1,10-phenanthroline, and 2-(2'-pyridyl)quinoline form distorted five-co-ordinate complexes of formula AuLX<sub>3</sub> (X = Cl or Br),<sup>29-31</sup> whereas in the analogous thianthrene complex<sup>32</sup> and in the current structure four-co-ordinate gold(III) is observed.

A barely significant *trans* effect is observed, in that Au-C(11) (*trans* to As) is the longest Au-C bond. The average Au-C bond length is 2.084 Å {cf. 2.051 Å in [Au(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>]<sup>-13</sup>}. The Au-As bond is somewhat shorter than in [Au(pdma)<sub>2</sub>]<sup>+</sup> (average 2.471 Å<sup>13</sup>); no other Au<sup>III</sup>-As bond lengths are available for comparison.

## References

- 1 L. A. Woods and H. Gilman, *Proc. Iowa Acad. Sci.*, 1943, **49**, 286.
- 2 H. Schmidbauer, 'Organogold Compounds,' Gmelin Handbuch der Anorganischen Chemie, Springer Verlag, Berlin 1980, p. 78.
- 3 L. G. Vaughan and W. A. Sheppard, *J. Organomet. Chem.*, 1970, **22**, 739.
- 4 R. Usón and A. Laguna, *Synth. React. Inorg. Met. Org. Chem.*, 1975, **5**, 17.
- 5 R. Usón, A. Laguna, and T. Cuenca, *J. Organomet. Chem.*, 1980, **194**, 271; R. Usón and A. Laguna, *Inorg. Synth.*, in the press.
- 6 R. Usón, A. Laguna, and J. Vicente, *J. Chem. Soc., Chem. Commun.*, 1976, 353; *J. Organomet. Chem.*, 1977, **131**, 471.
- 7 R. Usón, A. Laguna, and E. Fernandez, *Inorg. Chim. Acta*, 1980, **45**, L177.
- 8 H. Gilman and L. A. Woods, *J. Am. Chem. Soc.*, 1948, **70**, 550.
- 9 A. Shiotani and H. Schmidbauer, *Chem. Ber.*, 1971, **104**, 2838.
- 10 C. F. Shaw and R. S. Tobias, *Inorg. Chem.*, 1973, **12**, 965.
- 11 R. J. Puddephat, 'The Chemistry of Gold,' Elsevier, Amsterdam, 1978, p. 123.
- 12 R. Usón, A. Laguna, J. Vicente, and J. García, *Rev. Acad. Cienc. Exactas Fis. Quim. Nat. Zaragoza*, 1976, **31**, 77.
- 13 R. Usón, A. Laguna, J. Vicente, J. García, P. G. Jones, and G. M. Sheldrick, *J. Chem. Soc., Dalton Trans.*, 1981, 655.
- 14 R. Usón, A. Laguna, J. Vicente, J. García, and B. Bergareche, *J. Organomet. Chem.*, 1979, **173**, 349, and unpublished results.
- 15 E. E. Isaacs and W. A. G. Graham, *Inorg. Chem.*, 1975, **14**, 2560.
- 16 S. O. Grim, W. L. Brigs, R. C. Barth, C. A. Tolman, and J. P. Jesson, *Inorg. Chem.*, 1974, **13**, 1095.
- 17 R. Usón, A. Laguna, and J. Vicente, *Rev. Acad. Cienc. Exactas Fis. Quim. Nat. Zaragoza*, 1976, **31**, 211.
- 18 R. A. Bailey, T. W. Michelson, and W. N. Mills, *J. Inorg. Nucl. Chem.*, 1971, **33**, 3206.
- 19 J. L. Burmeister and J. B. Melpolder, *J. Chem. Soc., Chem. Commun.*, 1973, 613.
- 20 K. Nakamoto, 'Infrared and Raman Spectra of Inorganic and Coordination Compounds,' 3rd edn., Wiley, New York, 1978, p. 278.
- 21 R. Usón, A. Laguna, and M. V. Castrillo, *Synth. React. Inorg. Met. Org. Chem.*, 1975, **9**, 317.
- 22 G. B. Deacon and H. H. S. Green, *Spectrochim. Acta, Part A*, 1968, **24**, 1125.
- 23 G. B. Deacon, J. H. S. Green, and W. Kynaston, *J. Chem. Soc. A*, 1967, 158.
- 24 R. Usón, A. Laguna, and J. A. Abad, *J. Organomet. Chem.*, 1980, **194**, 265.
- 25 R. Usón, A. Laguna, J. García, and M. Laguna, *Inorg. Chim. Acta*, 1979, **37**, 201.
- 26 R. Usón, J. Forniés, P. Espinet, F. Martínez, and M. Tomás, *J. Chem. Soc., Dalton Trans.*, 1981, 463.
- 27 R. Usón, P. Royo, A. Laguna, and J. García, *Rev. Acad. Cienc. Zaragoza*, 1973, **28**, 67.
- 28 K. K. Sun and W. T. Miller, *J. Am. Chem. Soc.*, 1970, **92**, 6985.
- 29 R. J. Charlton, C. M. Harris, H. Patil, and N. C. Stephenson, *Inorg. Nucl. Chem. Lett.*, 1966, **2**, 409.
- 30 W. T. Robinson and E. Sinn, *J. Chem. Soc., Dalton Trans.*, 1975, 726.
- 31 C. J. O'Connor and E. Sinn, *Inorg. Chem.*, 1978, **17**, 2067.
- 32 N. W. Alcock, K. P. Ang, K. F. Mok, and S. F. Tan, *Acta Crystallogr., Sect. B*, 1978, **34**, 3364.

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