Synthesis and Reactivity of Bimetallic Au–Ag Polyfluorophenyl Complexes; Crystal and Molecular Structures of $[\{AuAg(C_6F_5)_2(SC_4H_8)\}_n]$ and $[\{AuAg(C_6F_5)_2(C_6H_6)\}_n]$ †

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The reaction of $[NBu^n_4][AuR_2]$ (R = C_6F_5 or $C_6F_3H_2$-2,4,6) with $Ag[ClO_4]$ leads to complexes $[\{AuAgR_2\}_n]$, which react with neutral ligands to give complexes $[\{AuAgR_2L\}_n]$ (L = neutral O-, N-, S- or P-donor ligand, alkene, or alkyne). For R = C_6F_5 and L = diphenylacetylene, the product is $[\{AuAgR_2{\cdot}0.5L\}_n]$; the 0.5L can be displaced by other ligands, such as acetone, arenes, or alkenes, to reform $[\{AuAgR_2L\}_n]$. An *X*-ray diffraction study of $[\{AuAgR_2L\}_n]$ (R = C_6F_5, L = tetrahydrothiophene) reveals $(AuAg)_2$ rings with Au–Ag 2.726 and 2.718 Å (the first reported Au–Ag bond lengths), linked by Au ··· Au short contacts (2.889 Å) to form infinite metal-atom chains. This complex crystallizes in space group *Pccn*, with *a* = 11.185(3), *b* = 22.475(6), *c* = 14.802(4) Å, *Z* = 8, *R* = 0.041 for 2 005 reflections. The complex $[\{AuAgR_2L\}_n]$ (R = C_6F_5, L = benzene) crystallizes in space group *C2/c*, with *a* = 24.231(5), *b* = 7.570(1), *c* = 22.613(5) Å, β = 117.49(2)°, *Z* = 8, and *R* = 0.035 for 3 008 reflections; it shows the same type of metal-atom chain (Au ··· Au 3.013; Au–Ag 2.702 and 2.792 Å). The benzene ring is co-ordinated by one edge to silver. In both structures the gold atoms lie on a crystallographic two-fold axis.

There is much evidence that metal centres M can act as Lewis bases towards other metal centres M′, thus forming M→M′ donor bonds. The stability of such compounds is dependent upon the respective M and M′; the most important stabilizing factor is a large electron density on the metal atom M (*i.e.* low oxidation state, or electron-donating ligands attached to M), whilst the presence of bridging groups between M and M′ seems of minor importance, because compounds with very different bridges are known. Moreover, transition-metal basicity generally increases going down a group.[1]

We have therefore chosen the anion $[AuR_2]^-$ (R = C_6F_5 or $C_6F_3H_2$-2,4,6) as metal centre M and have tried to form an M→M′ bond. For M′ we have selected Ag, since only a few heterobinuclear Au–Ag derivatives, such as $[Au_2Ag_2R_4]$ and $[Au_2Ag_4R_4X_2]$ [2–5] [X = Br, I, or CF_3SO_3; R = $C_6H_4(CH_2NMe_2)$-2, or $C_6H_4(NMe_2)$-2] or $[\{(C_6F_5)_2Au(CN)_2Ag\}_n]$ [6] are known, and none has been characterized by *X*-ray structure analysis.

In the present paper we describe the preparation and properties of complexes $[\{AuAgR_2\}_n]$ (R = $C_6F_3H_2$-2,4,6) and $[\{AuAgR_2L\}_n]$ (R = C_6F_5 or $C_6F_3H_2$-2,4,6; L = N-, O-, S-, or P-donor ligands, alkenes, alkynes, or arenes). Some of these results have been the subject of a preliminary communication.[7]

Results and Discussion

The reaction between $Q[Au(C_6F_3H_2\text{-}2,4,6)_2]$ (Q = $NBu^n_4{}^+$) and $Ag[ClO_4]$ in CH_2Cl_2 leads to the precipitation of a yellow solid of general formula $[\{AuAg(C_6F_3H_2\text{-}2,4,6)_2\}_n]$ (1) [equation (i)]; $QClO_4$ can be isolated upon evaporation of the solution.

$$Q[AuR_2] + AgClO_4 \longrightarrow QClO_4 + \underset{(1)}{[\{AuAgR_2\}_n]} \quad \text{(i)}$$

If the process is carried out in Et_2O, in which the solubilities are reversed, $QClO_4$ precipitates quantitatively, and the remaining yellow solution renders, upon vacuum evaporation, the yellow complex (1) (Table 1).

If process (i) is carried out with the pentafluorophenyl derivative $Q[Au(C_6F_5)_2]$ the following results are achieved: (*a*) in dichloromethane, mixing of the reactants gives no precipitate, whilst vacuum evaporation of the solution affords solid residues which seem to be a mixture of $[\{AuAgR_2\}_n]$, starting materials, and $QClO_4$; (*b*) in Et_2O, a mixture of $QClO_4$, $[\{AuAgR_2\}_n]$, and $Q[AuR_2]$ precipitates, which cannot be separated even by repeated fractional crystallization.

Therefore, in both solvents reaction (i) can be regarded as an equilibrium [equation (ii)], which for R = $C_6F_3H_2$-2,4,6

$$Q[AuR_2] + Ag[ClO_4] \rightleftharpoons QClO_4 + [\{AuAgR_2\}_n] \quad \text{(ii)}$$

is completely displaced towards the right, but for R = C_6F_5 is only partially displaced.

If solid mixtures of $[\{AuAg(C_6F_5)_2\}_n]$ and $Q[Au(C_6F_5)_2]$ are dissolved in dichloromethane and treated with a neutral ligand L (for example, pyridine) a precipitate of $[\{AuAg(C_6F_5)_2L\}_n]$ is formed, $Q[Au(C_6F_5)_2]$ remaining in solution [equation (iii)].

$$[\{AuAgR_2\}_n] + nL \longrightarrow [\{AuAgR_2L\}_n] \quad \text{(iii)}$$

Correspondingly, addition of a variety of neutral ligands L to the yellow dichloromethane solutions of $[\{AuAg(C_6F_5)_2\}_n]$ leads to the precipitation of the respective adducts $[\{AuAg(C_6F_5)_2L\}_n]$. Ten complexes of this general formula have been obtained (see Table 1) with L = tetrahydrothiophene (tht) (2), pyridine (py) (3), 2,2′-bipyridyl (bipy) (4), 1,10-phenanthroline (phen) (5), ethylenediamine (en) (6), 1,3-propylenediamine (pn) (7), and pyridine *N*-oxide (pyo) (8). Addition of $OPPh_3$, $SPPh_3$, or PPh_2Me does not give rise to any precipitate, but evaporation to dryness, extraction of the residue with Et_2O,

† *catena*-Di-μ-(tetrahydrothiophene)argentio-bis[bis(perfluorophenyl)gold] and *catena*-di-μ-(η^2-benzene)argentio-bis[bis(perfluorophenyl)gold] respectively.

Supplementary data available (No. SUP 23783, 49 pp.): structure factors, thermal parameters, H-atom co-ordinates. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii–xix.

Table 1. Analytical and physical data for complexes (1)—(33)

Complex	Yield (%)	Found (calc.) (%) C	H	N	Au + Ag	Λ_M [a]/ ohm^{-1} cm^2 mol^{-1}	M.p.[b]/°C
(1) $[\{AuAg(C_6F_3H_2)_2\}_n]$	74	25.4	0.9	—	54.95	7	208—210
		(25.4)	(0.7)		(53.75)		
(2) $[\{AuAg(C_6F_5)_2(tht)\}_n]$	94	26.25	1.2	—	42.05	76	190
		(26.4)	(1.1)		(41.9)		
(3) $[\{AuAg(C_6F_5)_2(py)\}_n]$	84	28.35	0.75	2.0	42.75	64	205
		(28.45)	(0.7)	(1.95)	(42.45)		
(4) $[\{AuAg(C_6F_5)_2(bipy)\}_n]$	90	33.35	1.05	3.55	38.0	77	208—210
		(33.25)	(1.0)	(3.5)	(38.35)		
(5) $[\{AuAg(C_6F_5)_2(phen)\}_n]$	90	35.3	1.05	3.3	37.6	71	160—162
		(35.2)	(1.0)	(3.4)	(37.2)		
(6) $[\{AuAg(C_6F_5)_2(en)\}_n]$	71	23.6	1.1	4.0	44.2	74	162—164
		(24.05)	(1.15)	(4.0)	(43.6)		
(7) $[\{AuAg(C_6F_5)_2(pn)\}_n]$	60	24.85	1.7	3.75	43.1	71	150—152
		(25.25)	(1.4)	(3.9)	(42.75)		
(8) $[\{AuAg(C_6F_5)_2(pyo)\}_n]$	72	27.5	0.8	2.05	41.6	70	199—201
		(27.8)	(0.7)	(1.9)	(41.5)		
(9) $[\{AuAg(C_6F_5)_2(OPPh_3)\}_n]$	45	39.85	1.8	—	34.05	76	140
		(39.3)	(1.65)		(33.25)		
(10) $[\{AuAg(C_6F_5)_2(SPPh_3)\}_n]$	52	39.05	1.8	—	32.9	83	75
		(38.6)	(1.6)		(32.65)		
(11) $[\{AuAg(C_6F_5)_2(PPh_2Me)\}_n]$	60	35.9	1.7	—	36.55	80	174—178
		(35.8)	(1.55)		(36.3)		
(12) $[\{AuAg(C_6F_3H_2)_2(tht)\}_n]$	74	29.9	2.0	—	47.1	12	208—210
		(29.35)	(1.85)		(46.55)		
(13) $[\{AuAg(C_6F_3H_2)_2(py)\}_n]$	57	31.95	1.6	2.15	47.6	12	178—180
		(31.6)	(1.4)	(2.15)	(47.2)		
(14) $[\{AuAg(C_6F_3H_2)_2(bipy)\}_n]$	74	36.65	1.75	3.8	42.1	15	234—235
		(36.55)	(1.65)	(3.85)	(42.15)		
(15) $[\{AuAg(C_6F_3H_2)_2(phen)\}_n]$	72	38.85	2.05	3.8	40.85	15	180
		(38.6)	(1.6)	(3.75)	(40.8)		
(16) $[\{AuAg(C_6F_3H_2)_2(4Me\text{-}pyo)\}_n]$	55	31.7	1.9	2.05	45.2	8	153—155
		(31.95)	(1.65)	(2.05)	(45.1)		
(17) $[\{AuAg(C_6F_3H_2)_2(OPPh_3)\}_n]$	63	42.8	2.45	—	36.45	7	170—172
		(42.6)	(2.25)		(36.05)		
(18) $[\{AuAg(C_6F_3H_2)_2(SPPh_3)\}_n]$	74	42.2	2.75	—	34.75	20	124—125
		(41.85)	(2.2)		(35.4)		
(19) $[\{AuAg(C_6F_3H_2)_2(PPh_3)\}_n]$	36	43.65	2.8	—	35.1	3	123—125
		(43.45)	(2.3)		(36.75)		
(20) $[Ag(py)_2][Au(C_6F_5)_2]$	50	33.5	1.65	3.75	38.05	87	150
		(33.15)	(1.25)	(3.5)	(38.25)		
(21) $[Ag(phen)(PPh_3)][Au(C_6F_5)_2]$	75	46.15	2.05	2.75	26.9	72	178—180
		(46.65)	(2.15)	(2.6)	(28.2)		
(22) $[Ag(bipy)(PPh_3)][Au(C_6F_5)_2]$	90	45.75	2.15	2.75	28.95	68	176—177
		(45.45)	(2.2)	(2.65)	(28.8)		
(23) $[\{AuAg(C_6F_5)_2(C_8H_{14})\}_n]$ [c]	61	31.75	1.8	—	41.55	80	172—175
		(32.05)	(1.9)		(40.7)		
(24) $[\{AuAg(C_6F_5)_2(C_8H_8)\}_n]$ [d]	40	33.0	1.25	—	40.25	82	162—165
		(32.3)	(1.1)		(41.0)		
(25) $[\{AuAg(C_6F_5)_2(C_8H_{12})\}_n]$ [e]	46	32.8	1.6	—	39.8	80	179—180
		(32.15)	(1.6)		(40.8)		
(26) $[\{AuAg(C_6F_5)_2(C_7H_8)\}_n]$ [f]	60	31.4	1.15	—	41.55	76	216
		(31.2)	(1.1)		(41.7)		
(27) $[\{AuAg(C_6F_5)_2(C_6H_{10})\}_n]$ [g]	69	30.55	1.4	—	42.5	75	188—190
		(30.0)	(1.4)		(42.3)		
(28) $[\{AuAg(C_6F_5)_2{\cdot}0.5C_2Ph_2\}_n]$	63	31.15	0.9	—	42.05	84	175—177
		(31.5)	(0.7)		(41.85)		
(29) $[\{AuAg(C_6F_5)_2(OCMe_2)\}_n]$	77	26.15	0.95	—	43.2	66	164—165
		(25.85)	(0.85)		(43.75)		
(30) $[\{AuAg(C_6F_5)_2(C_6H_6)\}_n]$	63	30.3	1.15	—	42.05	75	202—204
		(30.15)	(0.85)		(42.5)		
(31) $[\{AuAg(C_6F_5)_2(C_6H_5CH_3)\}_n]$	65	31.25	1.25	—	41.6	72	176—178
		(31.2)	(1.1)		(41.7)		
(32) $[\{AuAg(C_6F_5)_2[C_6H_5(OCH_3)]\}_n]$	60	30.65	1.15	—	40.55	72	180
		(30.55)	(1.1)		(40.8)		
(33) $[\{AuAg(C_6F_5)_2(C_6H_{10})\}_n]$ [h]	46	30.25	1.8	—	41.5	66	138—140
		(30.0)	(1.4)		(42.25)		

[a] In acetone. [b] With decomposition. [c] C_8H_{14} = cyclo-octene. [d] C_8H_8 = styrene. [e] C_8H_{12} = cyclo-octa-1,3-diene. [f] C_7H_8 = norbornadiene. [g] C_6H_{10} = hex-3-yne. [h] C_6H_{10} = cyclohexene.

Table 2. Some i.r. bands due to C_6F_5 groups

Complex	ν (cm^{-1})	
$[NBu^n_4][Au(C_6F_5)_2]$	780s	950vs, br
(2) $[\{AuAg(C_6F_5)_2(tht)\}_n]$	786s	969vs, 955 (sh)
(3) $[\{AuAg(C_6F_5)_2(py)\}_n]$	789s	965vs
(4) $[\{AuAg(C_6F_5)_2(bipy)\}_n]$	785s	965vs, br
(5) $[\{AuAg(C_6F_5)_2(phen)\}_n]$	784s	965vs, br
(6) $[\{AuAg(C_6F_5)_2(en)\}_n]$	792s	960vs, br
(7) $[\{AuAg(C_6F_5)_2(pn)\}_n]$	785s	965vs, 955vs
(8) $[\{AuAg(C_6F_5)_2(pyo)\}_n]$	789s	971vs, 961 (sh)
(9) $[\{AuAg(C_6F_5)_2(OPPh_3)\}_n]$	785s	968vs
(10) $[\{AuAg(C_6F_5)_2(SPPh_3)\}_n]$	785s	960vs, br
(11) $[\{AuAg(C_6F_5)_2(PPh_2Me)\}_n]$	787s	965vs, 961 (sh)
(23) $[\{AuAg(C_6F_5)_2(C_8H_{14})\}_n]$	796s	967vs, 962vs
(24) $[\{AuAg(C_6F_5)_2(C_8H_8)\}_n]$	794s	965vs, br
(25) $[\{AuAg(C_6F_5)_2(C_8H_{12})\}_n]$	793s	964vs, 968vs
(26) $[\{AuAg(C_6F_5)_2(C_7H_8)\}_n]$	794s	965vs, br
(27) $[\{AuAg(C_6F_5)_2(C_6H_{10})\}_n]$	794s	967vs, br
(28) $[\{AuAg(C_6F_5)_2{\cdot}0.5C_2Ph_2\}_n]$	780s	970vs, 958vs
(29) $[\{AuAg(C_6F_5)_2(OCMe_2)\}_n]$	786s	970vs, 962s
(30) $[\{AuAg(C_6F_5)_2(C_6H_6)\}_n]$	790s	962vs, br
(31) $[\{AuAg(C_6F_5)_2(C_6H_5CH_3)\}_n]$	793s	968vs, 963vs
(32) $[\{AuAg(C_6F_5)_2[C_6H_5(OCH_3)]\}_n]$	791s	964vs, br
(33) $[\{AuAg(C_6F_5)_2(C_6H_{10})\}_n]$	791s	962vs, 958vs

followed by removal of the undissolved $QClO_4$ and concentration of the filtrate leads to complexes of the same general formula with L = $OPPh_3$ (9), $SPPh_3$ (10), and PPh_2Me (11).

For R = $C_6F_3H_2$-2,4,6, complexes of general formula $[\{AuAg(C_6F_3H_2\text{-}2,4,6)_2L\}_n]$ are obtained either by treating suspensions of (1) in CH_2Cl_2 with L and partially evaporating the solutions, or by addition of L to ether solutions of (1) and isolating the precipitate; L = tht (12), py (13), bipy (14), or phen (15). The complexes with L = 4-methylpyridine *N*-oxide (4Me-pyo) (16), $OPPh_3$ (17), $SPPh_3$ (18), and PPh_3 (19) do not spontaneously precipitate, but separate upon partial evaporation of the solution and addition of hexane.

The colour of complexes (1)—(19) varies from pale yellow to red, those with R = C_6F_5 being deeper in colour than those with R = $C_6F_3H_2$. All are air-, light-, and moisture-stable at room temperature. They are soluble in EtOH, Me_2CO, and CH_3NO_2. The colour of the solutions is less intense than that of the solids; those of complexes with R = C_6F_5 are colourless whilst those for R = $C_6F_3H_2$ remain pale yellow.

The i.r. absorption bands characteristic of the anions $[AuR_2]^-$ [8] are displaced towards higher energies upon formation of the binuclear complexes (1)—(19). For $[Au(C_6F_5)_2]^-$ the bands at 780s and 950vs are shifted in the bimetallic complexes by 6—14 cm^{-1} and 10—26 cm^{-1} respectively. For $[Au(C_6F_3H_2\text{-}2,4,6)_2]^-$ similar shifts of the bands at 830 and 985 cm^{-1} can be observed for the corresponding binuclear complexes (see Tables 2 and 3).

Acetone solutions of the C_6F_5 derivatives show higher conductivities (Λ_M = 75 ohm^{-1} cm^2 mol^{-1}) than those of the $C_6F_3H_2$ derivatives (Λ_M = 7—15 ohm^{-1} cm^2 mol^{-1}). This is presumably due to an equilibrium in the presence of the solvent S [equation (iv)], which, in accordance with our observations, lies further towards the right for R = C_6F_5.

$$[\{AuAgR_2L\}_n] + nS \rightleftharpoons n[L{-}Ag{-}S]^+[AuR_2]^- \quad \text{(iv)}$$

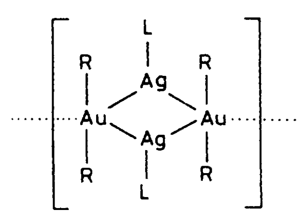
To determine the structure of the $[\{AuAgR_2L\}_n]$ complexes, orange crystals of (2) (L = tht), obtained by slow evaporation of acetone solutions, have been the subject of a single-crystal *X*-ray study. The structure is shown in Figure 1.

The compound forms polymeric chains by repetition of the

Table 3. Some i.r. bands due to $C_6F_3H_2$-2,4,6 groups

Complex	ν (cm^{-1})	
$[NBu^n_4][Au(C_6F_3H_2)_2]$	830s	985vs, 995vs
(1) $[\{AuAg(C_6F_3H_2)_2\}_n]$	847vs	1 000vs, 1 006 (sh)
(12) $[\{AuAg(C_6F_3H_2)_2(tht)\}_n]$	844s	1 002vs, 1 012vs
(13) $[\{AuAg(C_6F_3H_2)_2(py)\}_n]$	831vs	1 003vs, 1 006 (sh)
(14) $[\{AuAg(C_6F_3H_2)_2(bipy)\}_n]$	840s	1 005vs, 1 012vs
(15) $[\{AuAg(C_6F_3H_2)_2(phen)\}_n]$	840s	1 000s, br
(16) $[\{AuAg(C_6F_3H_2)_2(4Me\text{-}pyo)\}_n]$		1 000vs, 1 007vs
(17) $[\{AuAg(C_6F_3H_2)_2(OPPh_3)\}_n]$	842s	994vs, 1 006vs
(18) $[\{AuAg(C_6F_3H_2)_2(SPPh_3)\}_n]$	833s	1 000s, 1 008vs
(19) $[\{AuAg(C_6F_3H_2)_2(PPh_3)\}_n]$	838s	990vs, 995vs

structural unit (A) through short Au $\cdots$ Au contacts (2.889 Å). Such contacts are well known for Au^I compounds,[9] although this distance is the shortest yet observed in the absence of bridging ligands. The gold atoms lie on the two-fold axes $\frac{1}{4}$, $\frac{1}{4}$, *z*, thus giving rise to systematic weakness of reflections with odd *l*.



(A)

The $(AuAg)_2$ rings involve short Au–Ag distances (2.726 and 2.718 Å); these must represent some degree of metal–metal bonding and are thus the first reported Au–Ag bonds. A feasible bonding model is that the silver atom is sp^2 hybridized, electron density being withdrawn from the gold atom. This is consistent with ^{197}Au Mössbauer studies of a series of such complexes,[10] and with our i.r. studies, in which the bands due to C_6F_5 (sensitive to the electron density at gold) are displaced towards higher energies relative to $[Au(C_6F_5)_2]^-$ [8] (Table 2).

The geometry of the $Au(C_6F_5)_2$ groups is little distorted (C–Au–C 176 and 177°) with respect to the free anion; [11] the C–Au–C moieties are rotated by 51° relative to each other. The tht ligands show high thermal motion of C(2) and C(3), possibly involving disorder of these atoms, and the reliability of tht dimensions is thus limited.

Addition of another mol equivalent of a neutral ligand L′ to suspensions of $[\{AuAg(C_6F_5)_2L\}_n]$ in CH_2Cl_2 leads to the formation of colourless solutions which upon partial evaporation and addition of n-hexane precipitate the complexes $[AgLL'][AuR_2]$ [L = py, L′ = py (20); L = phen, L′ = PPh_3 (21); L = bipy, L′ = PPh_3 (22)]. These complexes are probably formed according to equation (v) since they are

$$[\{AuAgR_2L\}_n] + nL' \longrightarrow n[AgLL']^+[AuR_2]^- \quad \text{(v)}$$

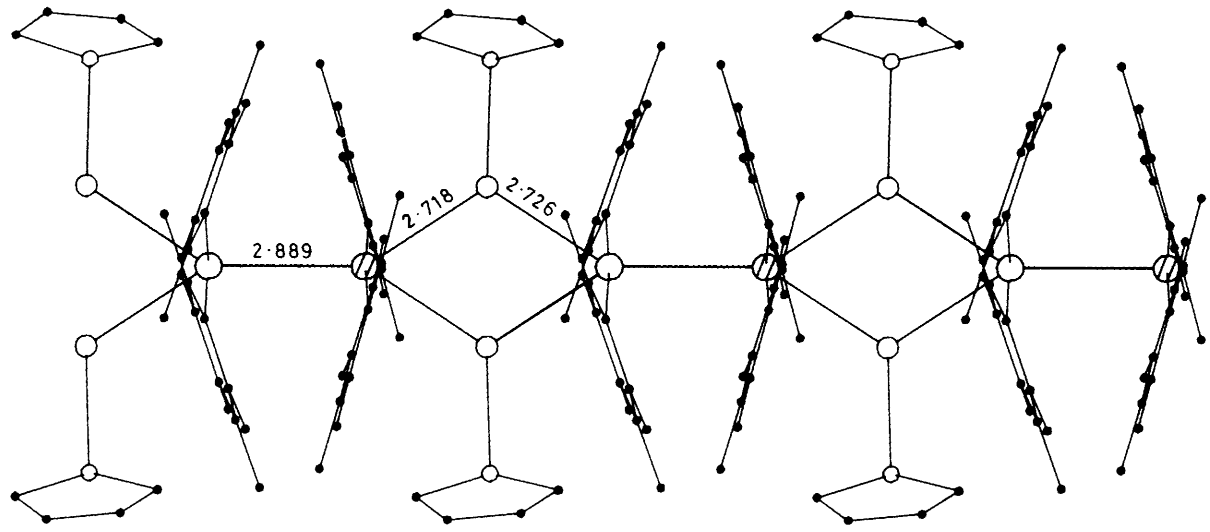


Figure 1. The polymeric structure of [{$AuAg(C_6F_5)_2(SC_4H_8)$}$_n$] (2) projected down the *b* axis. Key to atom types: black dots, C or F; open circles, S (small), Ag (medium), Au(1) (large); hatched circles, Au(2)

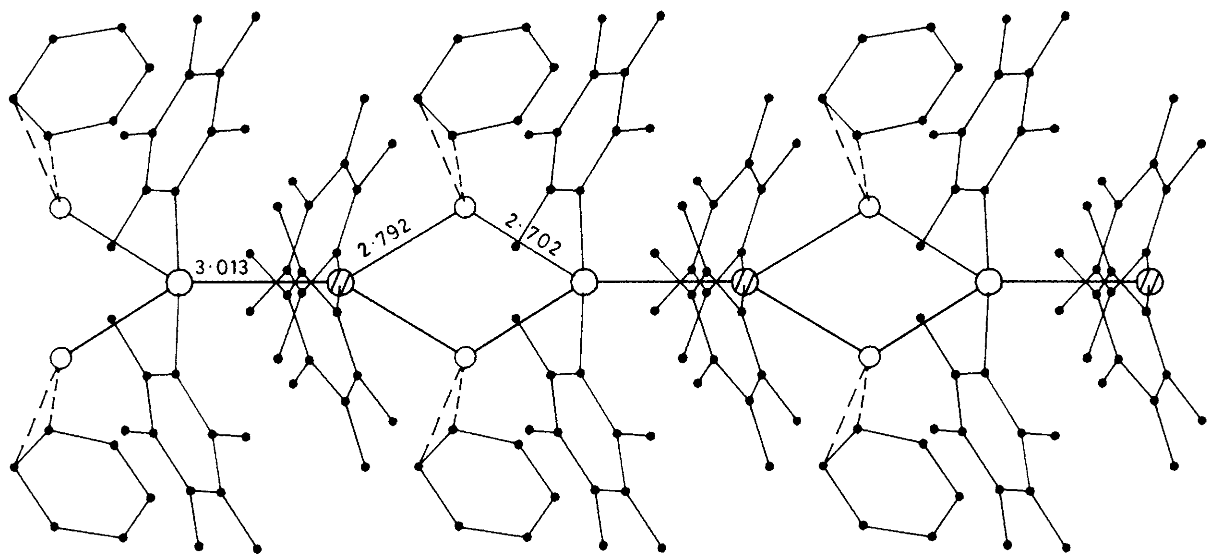


Figure 2. The polymeric structure of [{$AuAg(C_6F_5)_2(C_6H_6)$}$_n$] (30) projected down the *c* axis. Atom key: see Figure 1

conducting in acetone (Table 1) and show the same i.r. absorption bands as [$NBu^n{}_4$][$Au(C_6F_5)_2$] (Table 2). However, the reactions of [{$AuAg(C_6F_3H_2$-2,4,6$)_2L$}$_n$] with another mol equivalent of the neutral ligand either do not occur or lead to mixtures of non-conducting products, *e.g.* the reaction of [{$AuAg(C_6F_3H_2)_2(PPh_3)$}$_n$] with PPh_3 gives a mixture from which [$Au(C_6F_3H_2)(PPh_3)$] [12] and [$Ag(C_6F_3H_2)(PPh_3)_2$] can be isolated.

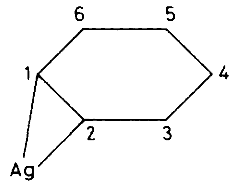
Different types of neutral ligands, such as olefins and acetylenes, can also react according to equation (iii). For R = C_6F_5 the corresponding [{$AuAgR_2L$}$_n$] can be prepared with L = cyclo-octene (23), styrene (24), cyclo-octa-1,3-diene (25), norbornadiene (26), and hex-3-yne (27); for R = $C_6F_3H_2$-2,4,6 a reaction can be observed with L = cyclo-octa-1,5-diene and norbornadiene but precipitation of the compounds, filtering, and washing with n-hexane leads to dissociation of the diolefin and reformation of the starting complex [{$AuAgR_2$}$_n$]. With L = arene no reaction could be observed in either case.

For R = C_6F_5 and L = diphenylacetylene the complex [{$AuAgR_2{\cdot}0.5C_2Ph_2$}$_n$] (28) is obtained, which in acetone undergoes dissociation since [{$AuAgR_2(OCMe_2)$}$_n$] (29) can be isolated after vacuum evaporation: *i.e.* C_2Ph_2 is so weakly attached that it can be displaced irreversibly by acetone (in all other cases, evaporation of the acetone yields the starting complex). This lability of C_2Ph_2 can be exploited for the indirect preparation of arene complexes. Thus [equation (vi)] if complex (28) is suspended in arene and carefully warmed

$$[\{AuAg(C_6F_5)_2{\cdot}0.5C_2Ph_2\}_n] + \text{arene} \longrightarrow [\{AuAg(C_6F_5)_2(\text{arene})\}_n] + 0.5C_2Ph_2 \quad \text{(vi)}$$

(60 °C), it goes into solution; if the colourless solutions are allowed to cool to room temperature, the complexes [{$AuAg(C_6F_5)_2$(arene)}$_n$] [arene = C_6H_6 (30), $C_6H_5CH_3$ (31), or $C_6H_5(OCH_3)$ (32)] crystallize. Some olefin complexes, unobtainable by the general method [equation (iii)], could also be obtained in this way, *e.g.* (33) (L = cyclohexene).

Table 4. Selected bond lengths (Å) in silver(I)–benzene and related complexes



Complex	C–C average	C^1–C^2	C^2–C^3	C^3–C^4	C^4–C^5	C^5–C^6	C^6–C^1	Ag–C^1	Ag–C^2	Ref.
$[Ag\{(C_6H_5)C_6H_{11}\}_2]ClO_4$	1.41	1.42	1.44	1.34	1.44	1.43	1.38	2.48	2.68	*a*
$[Ag(C_6H_4Me_2\text{-}1,3)_2]ClO_4$	1.41	1.37	1.39	1.44	1.42	1.42	1.44	2.45	2.61	*b*
$[\{Ag(\text{indene})(ClO_4)\}_2]$	1.42	1.47	1.37	1.46	1.44	1.41	1.36	2.76	2.47	*c*
$[Ag(C_6H_6)]ClO_4$		1.35	1.43				1.43	2.63	2.50	*d*
$[Ag(C_6H_6)AlCl_4]$	1.40	1.47	1.47	1.21	1.42	1.31	1.52	2.92	2.47	*e*
$[\{AuAg(C_6F_5)_2(C_6H_6)\}_n]$	1.36	1.35	1.33	1.32	1.35	1.39	1.49	2.50	2.48	*f*

[a] E. A. H. Griffith and E. L. Amma, *J. Am. Chem. Soc.*, 1971, **93**, 3167. [b] I. F. Taylor, jun., E. A. Hall, and E. L. Amma, *J. Am. Chem. Soc.*, 1969, **91**, 5745. [c] P. F. Rodesiler, E. A. H. Griffith, and E. L. Amma, *J. Am. Chem. Soc.*, 1972, **94**, 761. [d] H. G. Smith and R. E. Rundle, *J. Am. Chem. Soc.*, 1958, **80**, 5075. [e] R. W. Turner and E. L. Amma, *J. Am. Chem. Soc.*, 1966, **88**, 3243. [f] This work.

Crystals of (30), obtained as orange prisms by slow cooling of warm (60 °C) benzene solutions, lose benzene slowly in air and were thus sealed in glass capillaries for an *X*-ray study. The structure of (30) is shown in Figure 2.

The structure type is the same as (2), with $(AuAg)_2$ rings and polymeric metal-atom chains. The metal–metal bond lengths are somewhat different from (2); Au(1) · · · Au(2) is appreciably longer (3.013 Å) and Au–Ag more asymmetric (2.702 and 2.792 Å). The gold atoms again lie on a two-fold axis, but this has no systematic effect on reflection intensities in $C2/c$. The torsion angle between Au(1)–C(11) and Au(2)–C(21) is 41°.

The silver atom is η^2-bonded symmetrically by the benzene ring (Ag–C 2.48 and 2.50 Å), with a dihedral angle of 80° between the ring plane (r.m.s. deviation <0.01 Å) and the AgC_2 moiety. The appreciable thermal motion of the ring makes its dimensions somewhat unreliable, but there are some notable features: C(31)–C(32), the bond between the atoms bonded to silver, is short (1.35 Å), while one neighbouring bond is extremely long [C(31)–C(36) 1.49 Å]. A survey of structures containing the $Ag(\eta^2\text{-}C_6H_6)$ unit (Table 4) reveals no clear pattern of bond lengths, although none of the structures is of high accuracy.

Several of the above complexes [(2), (3), (5), (6), (7), (11)] can also be prepared by a second general method [equation (vii)], the addition of $[Au(C_6F_5)L]$ to ether solutions of $[Ag(C_6F_5)]$.[13]

$$[Au(C_6F_5)L] + [Ag(C_6F_5)] \longrightarrow [\{AuAg(C_6F_5)_2L\}_n] \quad \text{(vii)}$$

This process however is not of great preparative importance, since its yields are similar to those of equation (iii) and it presupposes the existence of the gold(I) complex.

Attempts to prepare isomers of the above complexes according to equation (viii) did not succeed; the same com-

$$[Au(OClO_3)(tht)] + [NBu_4][Ag(C_6F_5)_2] \longrightarrow [\{AuAg(C_6F_5)_2(tht)\}_n] \quad \text{(viii)}$$

plex (2) was obtained. Though migrations of the C_6F_5 group are known in the chemistry of gold,[11,14] this is the first case involving another Group 1B metal.

Experimental

Infrared spectra were recorded on a Perkin-Elmer 599 spectrophotometer using Nujol mulls between polyethylene sheets. Conductivities were measured in *ca.* 5×10^{-4} mol dm^{-3} solution with a Philips PW 9501/01 conductimeter. Carbon, H, and N analyses were carried out with a Perkin-Elmer 240 microanalyzer. Gold and silver were jointly determined by ashing the samples with an aqueous solution of hydrazine. The yields, melting points, C, H, N, and Au + Ag analyses are listed in Table 1.

Table 5. Atom co-ordinates ($\times 10^4$) for complex (2)

Atom	*X/a*	*Y/b*	*Z/c*
Au(1)	2 500	2 500	2 487(1)
Au(2)	2 500	2 500	535(1)
Ag	1 162(1)	2 374(1)	4 014(1)
C(11)	1 619(10)	1 697(5)	2 534(7)
C(12)	461(11)	1 603(5)	2 240(7)
C(13)	−67(10)	1 052(5)	2 149(8)
C(14)	567(11)	567(5)	2 358(8)
C(15)	1 736(11)	611(5)	2 656(8)
C(16)	2 222(10)	1 169(5)	2 748(8)
F(12)	−222(7)	2 077(3)	2 022(5)
F(13)	−1 195(6)	1 008(3)	1 848(5)
F(14)	109(7)	22(3)	2 240(5)
F(15)	2 363(7)	133(3)	2 828(6)
F(16)	3 366(6)	1 207(3)	3 041(6)
C(21)	3 212(10)	1 656(4)	497(7)
C(22)	2 452(12)	1 174(4)	331(8)
C(23)	2 848(14)	594(6)	436(10)
C(24)	3 974(14)	476(5)	703(8)
C(25)	4 752(12)	934(5)	845(8)
C(26)	4 355(11)	1 513(5)	731(7)
F(22)	1 314(6)	1 273(3)	105(6)
F(23)	2 048(8)	145(3)	304(6)
F(24)	4 328(7)	−95(3)	820(5)
F(25)	5 885(7)	808(3)	1 102(6)
F(26)	5 175(6)	1 936(3)	885(5)
S	−955(3)	2 660(1)	3 975(2)
C(1)	−1 236(12)	3 227(5)	3 123(9)
C(2)	−1 624(26)	3 750(7)	3 588(11)
C(3)	−1 736(21)	3 705(7)	4 508(12)
C(4)	−1 348(11)	3 145(5)	4 898(8)

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

$[\{AuAg(C_6F_3H_2\text{-}2,4,6)_2\}_n]$ (1). (*a*) To a solution of $[NBu^n_4][Au(C_6F_3H_2)_2]$[8] (0.1754 g, 0.25 mmol) in dichloromethane (30 cm^3), $Ag[ClO_4]$ (0.0518 g, 0.25 mmol) was added and

Table 6. Bond lengths (Å) and angles (°) for complex (2)

Au(1)–Au(2)	2.889(2)	Au(1)–C(11)	2.057(12)
Ag–Au(1)	2.726(2)	Au(2)–C(21)	2.059(11)
Ag–S	2.454(4)	Ag–Au(2^{i})	2.718(2)
C(11)–C(12)	1.383(18)	C(11)–C(16)	1.401(16)
C(12)–C(13)	1.379(17)	C(12)–F(12)	1.349(14)
C(13)–C(14)	1.337(18)	C(13)–F(13)	1.341(15)
C(14)–C(15)	1.383(18)	C(14)–F(14)	1.339(14)
C(15)–C(16)	1.374(18)	C(15)–F(15)	1.308(15)
C(16)–F(16)	1.353(14)	C(21)–C(22)	1.398(16)
C(21)–C(26)	1.362(17)	C(22)–C(23)	1.386(17)
C(22)–F(22)	1.335(16)	C(23)–C(24)	1.346(23)
C(23)–F(23)	1.362(17)	C(24)–C(25)	1.363(20)
C(24)–F(24)	1.355(15)	C(25)–C(26)	1.386(17)
C(25)–F(25)	1.353(17)	C(26)–F(26)	1.341(14)
C(1)–S	1.820(14)	C(1)–C(2)	1.430(23)
C(2)–C(3)	1.372(26)	C(3)–C(4)	1.450(22)
C(4)–S	1.804(13)		
Au(1)–Ag–Au(2^{i})	111.9(2)		
Au(2)–Au(1)–C(11)	91.9(4)	Ag–Au(1)–C(11)	67.5(4)
C(11)–Au(1)–Ag	109.0(4)	Au(2)–Au(1)–Ag	146.0(2)
Ag–Au(1)–Ag^{ii}	68.0(2)	C(11)–Au(1)–C(11^{ii})	176.1(6)
Au(1)–Au(2)–Ag^{iii}	145.9(2)	Au(1)–Au(2)–C(21)	91.6(4)
C(21)–Au(2)–Ag	70.6(4)	C(21)–Au(2)–Ag	106.6(4)
Ag^{iii}–Au(2)–Ag^{iv}	68.2(2)	C(21)–Au(2)–C(21^{ii})	176.8(7)
Au(1)–Ag–S	118.9(2)	S–Ag–Au(2^{i})	121.6(2)
Au(1)–C(11)–C(12)	124.9(9)	Au(1)–C(11)–C(16)	121.3(9)
C(12)–C(11)–C(16)	113.1(11)	C(11)–C(12)–C(13)	124.7(12)
C(11)–C(12)–F(12)	119.1(11)	C(13)–C(12)–F(12)	116.3(11)
C(12)–C(13)–C(14)	118.8(12)	C(12)–C(13)–F(13)	120.1(11)
C(14)–C(13)–F(13)	121.0(12)	C(13)–C(14)–C(15)	121.2(12)
C(13)–C(14)–F(14)	120.8(12)	C(15)–C(14)–F(14)	117.9(11)
C(14)–C(15)–C(16)	118.0(12)	C(14)–C(15)–F(15)	120.7(12)
C(16)–C(15)–F(15)	121.2(12)	C(11)–C(16)–C(15)	124.1(12)
C(11)–C(16)–F(16)	118.2(11)	C(15)–C(16)–F(16)	117.7(11)
Au(2)–C(21)–C(22)	118.9(9)	Au(2)–C(21)–C(26)	125.0(9)
C(22)–C(21)–C(26)	115.6(11)	C(21)–C(22)–C(23)	121.0(13)
C(21)–C(22)–F(22)	119.7(10)	C(23)–C(22)–F(22)	119.3(12)
C(22)–C(23)–C(24)	121.1(14)	C(22)–C(23)–F(23)	118.1(14)
C(24)–C(23)–F(23)	120.7(12)	C(23)–C(24)–C(25)	119.6(13)
C(23)–C(24)–F(24)	119.8(13)	C(25)–C(24)–F(24)	120.6(14)
C(24)–C(25)–C(26)	119.0(13)	C(24)–C(25)–F(25)	118.9(12)
C(26)–C(25)–F(25)	122.0(12)	C(21)–C(26)–C(25)	123.6(12)
C(21)–C(26)–F(26)	121.2(10)	C(25)–C(26)–F(26)	115.3(11)
Ag–S–C(1)	111.5(5)	Ag–S–C(4)	112.0(5)
C(1)–S–C(4)	93.4(7)	S–C(1)–C(2)	107.1(11)
C(1)–C(2)–C(3)	116.4(16)	C(2)–C(3)–C(4)	115.6(16)
S–C(4)–C(3)	107.2(11)		

Symmetry operators: i *x*, 0.5 − *y*, 0.5 + *z*; ii 0.5 − *x*, 0.5 − *y*, *z*; iii 0.5 − *x*, *y*, −0.5 + *z*; iv *x*, 0.5 − *y*, −0.5 + *z*.

Table 7. Atom co-ordinates (× 10^4) for complex (30)

Atom	*X/a*	*Y/b*	*Z/c*
Au(1)	0	4 097(1)	2 500
Au(2)	0	116(1)	2 500
Ag	661(1)	7 035(1)	3 084(1)
C(11)	802(4)	4 193(9)	2 398(4)
C(12)	1 331(4)	3 292(10)	2 819(4)
C(13)	1 844(4)	3 086(11)	2 714(5)
C(14)	1 829(5)	3 842(14)	2 160(6)
C(15)	1 318(5)	4 754(13)	1 717(5)
C(16)	816(4)	4 918(9)	1 849(4)
F(12)	1 354(3)	2 463(7)	3 354(3)
F(13)	2 344(3)	2 193(8)	3 141(4)
F(14)	2 319(3)	3 642(10)	2 034(4)
F(15)	1 296(3)	5 459(9)	1 161(3)
F(16)	316(2)	5 785(7)	1 385(2)
C(21)	260(4)	206(8)	1 756(4)
C(22)	816(4)	−294(10)	1 825(4)
C(23)	1 045(4)	12(11)	1 382(4)
C(24)	681(5)	893(13)	813(4)
C(25)	110(5)	1 432(12)	696(4)
C(26)	−93(4)	1 068(9)	1 160(4)
F(22)	1 222(2)	−1 164(7)	2 399(2)
F(23)	1 622(3)	−479(9)	1 507(3)
F(24)	889(3)	1 296(10)	371(3)
F(25)	−254(4)	2 353(8)	137(3)
F(26)	−669(2)	1 666(7)	1 015(2)
C(31)	1 619(7)	8 200(16)	4 046(5)
C(32)	1 292(5)	7 346(18)	4 308(5)
C(33)	1 424(6)	5 724(21)	4 556(5)
C(34)	1 891(9)	4 831(17)	4 552(7)
C(35)	2 244(5)	5 515(21)	4 292(6)
C(36)	2 144(8)	7 210(31)	4 027(6)

stirred for 2 h. The precipitated pale yellow complex (1) was filtered off and washed with dichloromethane.

(*b*) To a suspension of $[NBu^n_4][Au(C_6F_3H_2)_2]$ [8] (0.1754 g, 0.25 mmol) in diethyl ether (30 cm^3) was added $Ag[ClO_4]$ (0.0518 g, 0.25 mmol). After 1 h stirring $[NBu^n_4]ClO_4$ was filtered off. Evaporation of the filtrate followed by addition of hexane allowed the isolation of (1) (56% yield).

$[\{AuAg(C_6F_5)_2L\}_n]$ (2)—(11), (23)—(27) *and* $[\{AuAg(C_6F_5)_2\cdot 0.5C_2Ph_2\}_n]$ (28). (*a*) To a solution of $[NBu^n_4][Au(C_6F_5)_2]$ [15] (0.1934 g, 0.25 mmol) in dichloromethane (30 cm^3) was added $Ag[ClO_4]$ (0.0518 g, 0.25 mmol). After 45 min the yellow solution was filtered through diatomaceous earth. The clear filtrate was stirred with the ligand L (0.25 mmol) for 30 min, which in most cases gave rise to the formation of a precipitate [complexes (2)—(8), (23), and (26)—(28)], which was filtered off.

In the case of L = $OPPh_3$, $SPPh_3$, and PPh_2Me no precipitate was formed. Evaporation to dryness, washing with diethyl ether (3 × 20 cm^3), followed by evaporation and addition of hexane led to complexes (9)—(11). In the case of L = styrene (C_8H_8) (24) and cyclo-octa-1,3-diene (C_8H_{12}) (25) the dichloromethane solution was concentrated to 10 cm^3 and the precipitate which formed was filtered off.

(*b*) To an ether solution of $[Ag(C_6F_5)]$ [13] (0.25 mmol) was added $[Au(C_6F_5)L]$.[10,15] A coloured precipitate was formed within a few minutes. After stirring for 30 min the complex was filtered off and washed with ether. Yields: L = tht (2) 87%; py (3) 85%; phen (5) 99%; en (6) 70%; pn (7) 69%.

In the case of L = PPh_2Me the ether solution was concentrated to 5 cm^3, hexane (20 cm^3) was added, and the precipitate (11) was filtered off (80%).

(*c*) To a dichloromethane solution of [AuCl(tht)] [15] (0.0801 g, 0.25 mmol) at −20 °C, $Ag[ClO_4]$ (0.0518 g, 0.25 mmol) was added and stirred for 2 h at this temperature. The AgCl formed, together with a small amount of metallic gold, was removed by filtration through diatomaceous earth, and $[NBu^n_4][Ag(C_6F_5)_2]$ [13] (0.1711 g, 0.25 mmol) was added to the filtrate. The orange coloured precipitate which formed was identified as (2) (40%). Evaporation of the filtrate rendered a white solid identified as unreacted $[NBu^n_4][Ag(C_6F_5)_2]$ (47%).

$[\{AuAg(C_6F_3H_2\text{-}2,4,6)_2L\}_n]$ (12)—(19). (*a*) To ether solutions of (1) (1 mmol) was added 1 mmol of the respective ligand L and the mixture stirred for 30 min. Complexes (12)—(15) precipitated spontaneously; they were filtered off and washed with ether. For (16)—(19) the solutions were partially evaporated, and hexane was added to precipitate the complexes.

(*b*) To a suspension of (1) (0.1417 g, 0.25 mmol) in dichloromethane was added 0.25 mmol of the respective ligand L. After 2 h stirring, during which time (1) gradually dissolved, the reaction mixture was filtered through diatomaceous earth. The filtrate was concentrated to 5 cm^3 and hexane added to

Table 8. Bond lengths (Å) and angles (°) for complex (30)

Au(1)–C(11)	2.063(11)	Au(1)–C(21)	2.051(11)
Ag–Au(1)	2.702(2)	Ag–C(31)	2.498(12)
Ag–C(32)	2.480(10)	Ag–Au(2^{i})	2.792(2)
Au(1)–Au(2)	3.013(2)	C(11)–C(12)	1.374(11)
C(11)–C(16)	1.372(15)	C(12)–C(13)	1.379(17)
C(12)–F(12)	1.340(13)	C(13)–C(14)	1.361(20)
C(13)–F(13)	1.333(11)	C(14)–C(15)	1.366(15)
C(14)–F(14)	1.352(19)	C(15)–C(16)	1.385(19)
C(15)–F(15)	1.344(16)	C(16)–F(16)	1.351(9)
C(21)–C(22)	1.338(14)	C(21)–C(26)	1.382(10)
C(22)–C(23)	1.371(17)	C(22)–F(22)	1.381(9)
C(23)–C(24)	1.352(13)	C(23)–F(23)	1.344(13)
C(24)–C(25)	1.347(18)	C(24)–F(24)	1.346(17)
C(25)–C(26)	1.377(17)	C(25)–F(25)	1.354(10)
C(26)–F(26)	1.356(12)	C(31)–C(32)	1.353(23)
C(31)–C(36)	1.494(29)	C(32)–C(33)	1.326(21)
C(33)–C(34)	1.323(28)	C(34)–C(35)	1.346(27)
C(35)–C(36)	1.389(28)		

Au(2)–Au(1)–C(11)	92.0(3)	Ag–Au(1)–C(11)	69.5(3)
Ag–Au(1)–C(11^{ii})	107.0(3)	C(11)–Au(1)–C(11^{ii})	176.0(5)
Au(1)–Ag–Au(2^{i})	112.0(2)	Au(1)–Au(2)–C(21)	88.1(3)
C(21)–Au(2)–Ag^{iii}	95.1(3)	C(21)–Au(2)–Ag^{iv}	88.0(3)
Au(2)–Au(1)–Ag	145.4(2)	C(21)–Au(2)–C(21^{ii})	176.2(5)
Au(1)–Ag–C(31)	145.0(4)	Au(1)–Ag–C(32)	123.0(4)
C(31)–Ag–C(32)	31.6(6)	C(31)–Ag–Au(2^{i})	102.5(4)
C(32)–Ag–Au(2^{i})	111.9(4)	Ag–Au(1)–Ag^{ii}	69.2(2)
Au(1)–Au(2)–Ag^{iii}	146.7(2)	Au(1)–C(11)–C(12)	122.0(8)
Au(1)–C(11)–C(16)	122.3(6)	C(12)–C(11)–C(16)	115.0(10)
C(11)–C(12)–C(13)	124.2(10)	C(11)–C(12)–F(12)	119.7(10)
C(13)–C(12)–F(12)	116.0(8)	C(12)–C(13)–C(14)	117.8(9)
C(12)–C(13)–F(13)	121.5(11)	C(14)–C(13)–F(13)	120.7(12)
C(13)–C(14)–C(15)	121.3(14)	C(13)–C(14)–F(14)	119.5(10)
C(15)–C(14)–F(14)	119.2(14)	C(14)–C(15)–C(16)	118.4(13)
C(14)–C(15)–F(15)	121.3(14)	C(16)–C(15)–F(15)	120.4(9)
C(11)–C(16)–C(15)	123.3(8)	C(11)–C(16)–F(16)	120.6(10)
C(15)–C(16)–F(16)	116.0(10)	Au(2)–C(21)–C(22)	124.7(6)
Au(2)–C(21)–C(26)	121.9(8)	C(22)–C(21)–C(26)	112.6(10)
C(21)–C(22)–C(23)	126.4(8)	C(21)–C(22)–F(22)	119.0(10)
C(23)–C(22)–F(22)	114.5(9)	C(22)–C(23)–C(24)	118.1(11)
C(22)–C(23)–F(23)	122.1(8)	C(24)–C(23)–F(23)	119.8(12)
C(23)–C(24)–C(25)	119.8(13)	C(23)–C(24)–F(24)	120.9(12)
C(25)–C(24)–F(24)	119.2(9)	C(24)–C(25)–C(26)	119.1(9)
C(24)–C(25)–F(25)	120.5(12)	C(26)–C(25)–F(25)	120.5(11)
C(21)–C(26)–C(25)	124.0(10)	C(21)–C(26)–F(26)	119.9(10)
C(25)–C(26)–F(26)	116.0(8)	Ag–C(31)–C(32)	73.5(8)
Ag–C(31)–C(36)	105.0(9)	C(32)–C(31)–C(36)	116.9(14)
Ag–C(32)–C(31)	75.0(7)	Ag–C(32)–C(33)	106.8(9)
C(31)–C(32)–C(33)	123.5(15)	C(32)–C(33)–C(34)	120.6(17)
C(33)–C(34)–C(35)	121.7(14)	C(34)–C(35)–C(36)	121.6(16)
C(31)–C(36)–C(35)	115.6(18)	Ag^{iii}–Au(2)–Ag^{iv}	66.7(2)

Symmetry operators: i $x, 1 + y, z$; ii $-x, y, 0.5 - z$; iii $x, -1 + y, z$; iv $-x, -1 + y, 0.5 - z$.

precipitate the complexes: (13) 56%, (14) 65%, (15) 83%, (16) 89%, (18) 39%, and (19) 64%.

$[AgLL'][Au(C_6F_5)_2]$ (20)—(22). To a suspension of (3), (4), or (5) (0.25 mmol) in dichloromethane (30 cm^3) was added L′ (0.25 mmol) (L′ = py or PPh_3); a clear solution was formed. After 30 min stirring, concentration to ~5 cm^3 and addition of hexane (20 cm^3) precipitated a white solid, which was identified as (20)—(22).

In the case of L = L′ = py (20) an excess of py had to be used to prevent formation of (3).

$[\{AuAg(C_6F_5)_2(OCMe_2)\}_n]$ (29). Complex (28) (0.3640 g, 0.5 mmol) was dissolved in acetone (40 cm^3), and the solvent was evaporated to ~10 cm^3. Addition of hexane (20 cm^3) precipitated a greenish yellow solid (29), which was filtered off. Evaporation of the filtrate to dryness gave further (29). The complex was washed with hexane (3 × 10 cm^3) containing a few drops of acetone.

$[\{AuAg(C_6F_5)_2(arene)\}_n]$ (30)—(32) *and* $[\{AuAg(C_6F_5)_2(C_6H_{10})\}_n]$ (33). A suspension of (28) (0.1820 g, 0.25 mmol) in 15 cm^3 benzene, toluene, anisole, or cyclohexene was warmed in a water-bath at 60 °C for 15 min, during which time the starting compound went into solution. After filtering through diatomaceous earth, the solution was allowed to cool to room temperature, and crystalline (30)—(33) were filtered off.

Crystal Data for (2).—$(C_{16}H_8AgAuF_{10}S)_n$, M (monomer) = 727.13, orthorhombic, space group $Pccn$, a = 11.185(3), b = 22.475(6), c = 14.802(4) Å, U = 3 721 Å^3, Z = 8, D_c = 2.60 g cm^{-3}, Mo-K_α radiation (λ = 0.710 69 Å), μ = 91 cm^{-1}, $F(000)$ = 2 688. 3 265 Unique profile-fitted [16] reflections in the range $7 < 2\theta < 50°$ were measured on a Stoe four-circle diffractometer. Reflections with l odd were systematically weak. After Lorentz, polarization, and semi-empirical absorption corrections (crystal size 0.5 × 0.2 × 0.15 mm), 2 005 reflections with $F > 4\sigma(F)$ were used for all calculations. Cell constants were refined from 2θ values of 40 reflections in the range $20 < 2\theta < 24°$.

The structure was solved by the heavy-atom method and refined to R = 0.041, R' = 0.037 [all atoms except H anisotropic; H atoms included with a riding model C–H 0.96 Å, H–C–H 109.5°, U(H) = 1.2 $U_{equiv.}$(C); weighting scheme $w^{-1} = \sigma^2(F) + 0.0002\ F^2$]. Final atomic co-ordinates and derived parameters are given in Tables 5 and 6. A final difference map showed no peaks >0.75 e Å^{-3}.

Crystal Data for (30).—$(C_{18}H_6AgAuF_{10})_n$, M (monomer) = 717.07, monoclinic, space group $C2/c$, a = 24.231(5), b = 7.570(1), c = 22.613(5) Å, β = 117.49(2)°, U = 3 680 Å^3, Z = 8, D_c = 2.59 g cm^{-3}, Mo-K_α radiation (λ = 0.710 69 Å), μ = 91 cm^{-1}, $F(000)$ = 2 640. 3 740 Profile-fitted [16] reflections were measured in the range $7 < 2\theta < 55°$; after Lorentz, polarization, and semi-empirical absorption corrections (crystal size 0.6 × 0.35 × 0.2 mm), merging equivalents gave 3 655 unique reflections, of which 3 008 with $F > 4\sigma(F)$ were used for all calculations. Cell constants were refined from 2θ values of 32 reflections in the range $20 < 2\theta < 24°$.

The structure was solved by the heavy-atom method and refined anisotropically to R = 0.035, R' = 0.036 [H atoms not located; $w^{-1} = \sigma^2(F) + 0.000\,25\ F^2$; extinction correction $x = 5.0(2) \times 10^{-7}$, where F is divided by $(1 + xF^2/\sin 2\theta)^{0.25}$]. Final atomic co-ordinates and derived parameters are given in Tables 7 and 8. A final difference map showed only one peak >0.8 e Å^{-3} (1.3, near Ag).

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