Mesitylgold Complexes: Synthesis and Reactivity; Crystal Structure of $[\{(Ph_3P)Au(\mu\text{-mes})Ag(tht)\}_2][SO_3CF_3]_2$ (mes = mesityl, tht = tetrahydrothiophene)†

María Contel,[a] Josefina Jiménez,[b] Peter G. Jones,[c] Antonio Laguna*,[b] and Mariano Laguna[b]
[a] *Departamento de Química, Universidad Pública de Navarra, E-31006 Pamplona, Spain*
[b] *Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza CSIC, E-50009 Zaragoza, Spain*
[c] *Institut für Anorganische und Analytische Chemie der Technischen Universität, Postfach 3329, D-38023 Braunschweig, Germany*

The complex $[AuCl(AsPh_3)]$ reacted with MgBr(mes) (mes = mesityl) to give the corresponding gold(I) derivative $[Au(mes)(AsPh_3)]$, which undergoes substitution reactions with neutral ligands to give the neutral complexes [Au(mes)L] ($L = Ph_2PCH_2PPh_2$, PPh_3 or PPh_2Me) or with QX to afford anionic complexes Q[Au(mes)X] [X = Cl, $Q = P(CH_2Ph)Ph_3$; X = Br, $Q = N(PPh_3)_2$]. The latter reacted with X_2 (X = Cl or Br) to give gold(III) complexes, $Q[Au(mes)X_3]$ [X = Cl, $Q = P(CH_2Ph)Ph_3$; X = Br, $Q = N(PPh_3)_2$]. The reaction of $[Au(mes)(PPh_3)]$ with $[Ag(OSO_2CF_3)L]$ [$L = PPh_3$ or tetrahydrothiophene (tht)] afforded $[\{(Ph_3P)Au(\mu\text{-mes})AgL\}_n][SO_3CF_3]_n$ ($L = PPh_3$, $n = 1$; L = tht, $n = 2$). The structure of $[\{(Ph_3P)Au(\mu\text{-mes})Ag(tht)\}_2][SO_3CF_3]_2$ has been determined by a single-crystal X-ray diffraction study, which shows an Au–Ag distance of 2.8245(6) Å.

Heteroleptic gold(I) compounds containing the mesityl group ($2,4,6\text{-}Me_3C_6H_2$, mes) as a simple (terminal) ligand have been obtained by addition of neutral or anionic ligands to solutions of $[\{Au(mes)\}_5]$[1,2] or by metathetical reactions between the chlorogold(I) precursor and $[\{Ag(mes)\}_5]$.[2] The first reaction type does not occur for N-, As- or S-donors, such as pyridine, $AsPh_3$ or tetrahydrothiophene (tht), under similar conditions.[2] In the chemistry of gold(III) only the complexes $[Au(mes)_2(L\text{–}L)]ClO_4$ (L–L = 2,2′-bipyridine, phenanthroline or 4,7-diphenylphenanthroline) have been described.[3]

It is also known that mesityl can act as a bridge between two metal centres, affording a three-centre two-electron bond.[4] In the chemistry of Group 11 metals this bridging mode has often been observed for homoleptic $(MR)_n$ (R = aryl) compounds.[1,5–9]

Mesityl is also found to function as a bridge in various heteroleptic copper compounds, for example $[Cu_4(mes)_4(tht)_2]$,[1,8] $[Cu_3(mes)(\mu\text{-}O_2CC_6H_4X\text{-}2)_2]$ (X = H, Cl or Br),[10,11] $[Cu_{10}O_2(mes)_6]$[12] and $[\{Cu(mes)\}_4\{\mu\text{-}SC_6H_4[CH(Me)NMe_2]\text{-}2\}_2\{MgSC_6H_4[CH(Me)NMe_2]\text{-}2\}_2]$.[13] However, no silver derivatives of this kind have been reported and only one of gold,[2] $[(Ph_3P)Au(\mu\text{-mes})Au(PPh_3)]ClO_4$, which was characterised solely by spectroscopic methods.

In this paper we describe the synthesis of neutral and anionic mononuclear gold complexes containing one simple (terminal) mesityl ligand, [Au(mes)L] [$L = AsPh_3$ **1**, dppm ($Ph_2PCH_2PPh_2$) **2**, PPh_3 **3** or PPh_2Me **4**], Q[Au(mes)X] [X = Cl, $Q = P(CH_2Ph)Ph_3$ **5**; X = Br, $Q = N(PPh_3)_2$ **6**] and $Q[Au(mes)X_3]$ [X = Cl, $Q = P(CH_2Ph)Ph_3$ **7**; X = Br, $Q = N(PPh_3)_2$ **8**], and heterobinuclear gold(I)–silver(I) complexes containing one mesityl acting as a bridge between the two metal centres, $[(Ph_3P)Au(\mu\text{-mes})Ag(PPh_3)][SO_3CF_3]$ **9** and $[\{(Ph_3P)Au(\mu\text{-mes})Ag(tht)\}_2][SO_3CF_3]_2$ **10**. The structure of **10** has been established by X-ray studies.

Results and Discussion

Mononuclear Derivatives.—The reaction in diethyl ether of $[AuCl(AsPh_3)]$ with MgBr(mes) in molar ratio 1:1.5 at 0 °C leads to the formation of $[Au(mes)(AsPh_3)]$ **1** [equation (1)]. In

$$[AuCl(AsPh_3)] + MgBr(mes) \longrightarrow [Au(mes)(AsPh_3)] + MgBrCl \quad (1)$$

the chemistry of gold(I) the compound $AsPh_3$ is weakly co-ordinating and can therefore be readily displaced by neutral and anionic ligands.[14] The complex $[Au(mes)(AsPh_3)]$ **1** behaves similarly and reacts with dppm, PPh_3 or PPh_2Me, in 1:1 ratio, to give the neutral complexes [Au(mes)L] (L = dppm **2**, PPh_3 **3** or PPh_2Me **4**) or with salts QX to give anionic complexes Q[Au(mes)X] [X = Cl, $Q = P(CH_2Ph)Ph_3$ **5**; X = Br, $Q = N(PPh_3)_2$ **6**] [see equations (2) and (3)].

$$[Au(mes)(AsPh_3)] + L \longrightarrow [Au(mes)L] + AsPh_3 \quad (2)$$

$$[Au(mes)(AsPh_3)] + QX \longrightarrow Q[Au(mes)X] + AsPh_3 \quad (3)$$

However, the reaction of **1** with dppe ($Ph_2PCH_2CH_2PPh_2$), even in molar ratio 1:1.5, leads to a mixture that contains dinuclear [(mes)Au(dppe)Au(mes)].[1] Complexes **3**–**5** have previously been prepared by other synthetic procedures.

The addition of Cl_2 or Br_2 to solutions of $[P(CH_2Ph)Ph_3][AuCl(mes)]$ **5** or $[N(PPh_3)_2][AuBr(mes)]$ **6**, in 1:1 ratio, gives the anionic gold(III) complexes $Q[Au(mes)X_3]$ [X = Cl, $Q = P(CH_2Ph)Ph_3$ **7**; X = Br, $Q = N(PPh_3)_2$ **8**].

All complexes are air- and moisture-stable solids at room temperature and are white (**1**–**6**), yellow (**7**) or red (**8**). Acetone solutions of **1**–**4** are non-conducting and those of **5**–**8** display conductivities typical of 1:1 electrolytes[15] (Table 1). The IR spectra show absorptions corresponding to the mesityl ligand at

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† *Supplementary data available:* Further details of the structure determination may be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für Wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany, on quoting the reference number CSD 400956, the names of the authors and the journal citation.

Table 1 Analytical and spectroscopic data for products

Complex	Yield (%)	Analysis (%)[a] C	H	N	Λ_M[b]/Ω^{-1} cm^2 mol^{-1}	^{1}H NMR,[c] δ(mes) o-CH_3	p-CH_3	m-H
1 [Au(mes)($AsPh_3$)]	87	51.9	4.05	—	1	2.59 (s)	2.25 (s)	6.91 (s)
		(52.1)	(4.2)	—				
2 [Au(mes)(dppm)]	91	58.35	4.8	—	1	2.53 (s)	2.27 (s)	6.90 (s)
		(58.3)	(4.75)	—				
3 [Au(mes)(PPh_3)]	80	55.70	4.6	—	7	2.59 (s)	2.26 (s)	6.92 (s)
		(56.05)	(4.55)	—				
4 [Au(mes)(PPh_2Me)]	51	51.15	4.5	—	1	2.60 (s)	2.28 (s)	6.94 (s)[d]
		(51.2)	(4.7)	—				
5 [P(CH_2Ph)Ph_3][AuCl(mes)]	76	58.3	4.8	—	118	2.31 (s)	2.16 (s)	6.69 (s)[e]
		(57.9)	(4.7)	—				
6 [N(PPh_3)$_2$][AuBr(mes)]	80	57.65	4.4	1.55	90	2.48 (s)	2.14 (s)	6.71 (s)
		(57.8)	(4.4)	(1.5)				
7 [P(CH_2Ph)Ph_3][AuCl_3(mes)]	70	52.3	4.0	—	124	2.44 (s)	2.19 (s)	6.57 (s)[e]
		(52.65)	(4.3)	—				
8 [N(PPh_3)$_2$][AuBr_3(mes)]	85	49.1	3.6	1.4	127	2.48 (s)	2.19 (s)	6.58 (s)
		(49.4)	(3.8)	(1.3)				
9 [(Ph_3P)Au(μ-mes)Ag(PPh_3)][SO_3CF_3]	70	49.9	3.6	—	116	2.45 (s)	2.26 (s)	6.95 (s)
		(50.3)	(3.7)	—				
10 [{(Ph_3P)Au(μ-mes)Ag(tht)}$_2$][SO_3CF_3]$_2$	72	41.3	3.75	—	103	2.54 (s)	2.28 (s)	6.99 (s)
		(41.6)	(3.7)	—				

[a] Calculated values are given in parentheses. [b] In acetone (5×10^{-4} mol dm^{-3}). [c] In $CDCl_3$, values in ppm. [d] δ(CH_3 of PPh_2Me) 2.12 (d) [$^2J_{PH}$ = 6.8 Hz]. [e] δ[CH_2 of P(CH_2Ph)$Ph_3{}^+$]: 5.07 (d, $^2J_{PH}$ 14.5) (**5**); 5.01 (d, $^2J_{PH}$ 13.9 Hz) (**7**).

1582, 840 (**1**), 1585, 849 (**2**), 1587, 840 (**3**), 1578, 851 (**4**), 1589, 852 (**5**), 1589, 845 (**6**), 1589, 852, 837 (**7**) or at 1590, 879, 849 cm^{-1} (**8**). Furthermore, complexes **5** and **7** show bands at 300m (**5**) and at 332m and 362m cm^{-1} (**7**), assigned to ν(Au–Cl).[16] For complexes **6** and **8** the ν(Au–Br) vibrations have not been observed, probably because they lie below 200 cm^{-1}, which is the limit of our spectrophotometer.

Their ^{1}H NMR spectra are as expected (Table 1) showing three singlets for the mesityl ligand. A multiplet at δ 3.24 is observed for the methylene protons of dppm in **2**. The ^{31}P-{^{1}H} NMR spectra show two doublets at δ 35.2 and −23.4 for dppm in **2** ($^2J_{PP}$ = 116 Hz) and a singlet for PR_3 in **3** and **4** (δ 44.9 and 30.9). For the anionic complexes, singlets assignable to the [P(CH_2Ph)Ph_3]$^+$ [δ 23.5 (**5** and **7**)] and [N(PPh_3)$_2$]$^+$ [δ 21.7 (**6** and **8**)] cations are also observed.

The mass spectra (positive-ion FAB for neutral complexes or negative ion FAB for anionic derivatives) show the parent ion for complexes **1** [m/z = 622 (11)], **3** [578 (28)], **5** [351 (25)], **6** [396 (7)], **7** [423 (100)] and **8** [556 (70%)].

Heteropolynuclear Derivatives of Gold and Silver.—The treatment of [Au(mes)(PPh_3)] with [Ag(OSO_2CF_3)L] (L = PPh_3 or tht), in molar ratio 1 : 1, in dichloromethane leads to the formation of complexes [{(Ph_3P)Au(μ-mes)AgL}$_n$][SO_3CF_3]$_n$ (L = PPh_3, n = 1 **9**; L = tht, n = 2 **10**) [equation (4)].

$$[\mathrm{Au(mes)(PPh_3)}] + [\mathrm{Ag(OSO_2CF_3)L}] \longrightarrow 1/n[\{\mathrm{(Ph_3P)Au(mes)AgL}\}_n][\mathrm{SO_3CF_3}]_n \quad (4)$$

These complexes are white solids, air- and moisture-stable at room temperature and their solutions in acetone show conductivities of *ca.* 100 ohm^{-1} cm^2 mol^{-1} (Table 1), corresponding to 1 : 1 electrolytes.[15] Their IR spectra show absorptions at 1265vs, 1240s, 1222m and 1140m (**9**) and 1260vs (br), 1223s and 1160s cm^{-1} (**10**) assignable to the triflate anion,[17] and absorptions corresponding to the mesityl ligand at 1597m, 846w (**9**) or at 1597m, 856w cm^{-1} (**10**). These latter bands are shifted to higher energy than in the starting product, as was observed for the complex [(Ph_3P)Au(μ-mes)Au(PPh_3)]ClO_4.[2]

Solutions of these complexes in chloroform show a singlet resonance in the ^{31}P-{^{1}H} NMR spectra at δ 43.9 (**9**), 43.5 (**10**) corresponding to the phosphorus atoms bonded to gold. In complex **9** the phosphorus atom bonded to silver appears at δ 10 as a broad band at room temperature. This signal splits at −55 °C into a doublet of doublets centred at δ 11.2 [J(^{107}Ag–P) = 416, J(^{109}Ag–P) = 473 Hz]. The ^{1}H NMR spectra show signals from the mesityl group (Table 1) and, for complex **10**, two multiplets at δ 2.95 and 1.91 assignable to the tetrahydrothiophene ligand are also observed. The mass spectra (FAB$^+$) show the parent ion only in the case of **9**, m/z = 949 (23%).

The structure of complex **10** has been determined by single-crystal X-ray diffraction, which shows a dimer, with the tetrahydrothiophene ligand acting as bridge between the two silver atoms. The structure of the cation is shown in Fig. 1; it possesses a crystallographic centre of inversion that relates the two [(Ph_3P)Au(μ-mes)Ag(tht)]$^+$ units.

As observed in other complexes with bridging mesityl ligands,[1,7–9] the planar mesitylene groups are nearly perpendicular to the plane through the atoms Au–Ag–C(11), the dihedral angles being 88°. The gold atoms are two-co-ordinate, with P–Au–C angles of 177.34(9)°, close to the linear stereochemistry preferred by Au^I. This contrasts with the angles observed in [{Au(mes)}$_5$] [148.3(7)–152.9(8)°][1,9] which show a deviation from linear stereochemistry attributable to Au^I–Au^I bonding interactions. The midpoint of the mesityl ring is approximately collinear with the *ipso*-carbon and the gold atom (170°), whereas the angle to the silver atom is 111°. The Au–C distances, 2.086(3) Å, are similar to those found in [{Au(mes)}$_5$] [2.13(2)–2.20(2) Å][1,9] and other compounds where two gold(I) atoms are bridged by an aromatic carbon such as [{Au(PPh_3)}$_2$(μ-$C_6F_3H_2$)]ClO_4 [2.162(8), 2.160(9) Å].[18] The Au–C bond distances seem to be substantially independent of the bonding mode displayed by the C-donor ligands.[1,9] The Au–P bond distances are 2.2886(9) Å, which are similar to those observed in [Au{2,6-(MeO)$_2C_6H_3$}(PPh_3)] (2.284 Å)[19] and [Au(C_6F_5)(PPh_2CHPPh_2Me)] [2.287(2) Å].[20]

The silver atom is bonded to a mesityl ligand and two sulfur atoms from tht molecules in a distorted-trigonal environment. The Ag–C bond distances [2.326(3) Å] are slightly longer than in [{Ag(mes)}$_4$] [average 2.20 Å].[1,7] The Ag–S bond

Table 2 Atomic coordinates (× 10^4) for compound **10**

Atom	*x*	*y*	*z*
Au	7 208.1(1)	2 682.0(1)	6 743.2(1)
Ag	5 995.7(3)	1 124.4(3)	8 784.1(2)
P	7 216.8(8)	2 787.2(8)	5 035.0(7)
C(11)	7 258(3)	2 648(3)	8 266(3)
C(12)	8 276(3)	1 999(3)	8 778(3)
C(13)	8 417(3)	2 125(3)	9 700(3)
C(14)	7 603(4)	2 930(3)	10 110(3)
C(15)	6 609(4)	3 565(3)	9 608(3)
C(16)	6 415(3)	3 437(3)	8 707(3)
C(17)	9 258(4)	1 181(4)	8 320(4)
C(18)	7 806(5)	3 090(5)	11 090(4)
C(19)	5 312(4)	4 169(4)	8 198(3)
C(21)	8 036(3)	4 003(3)	3 947(3)
C(22)	9 179(4)	4 231(4)	4 064(4)
C(23)	9 840(4)	5 131(4)	3 246(4)
C(24)	9 374(5)	5 818(4)	2 317(4)
C(25)	8 251(5)	5 600(4)	2 214(4)
C(26)	7 580(4)	4 693(3)	3 020(3)
C(31)	5 628(3)	2 960(3)	4 779(3)
C(32)	5 399(4)	2 529(4)	4 060(3)
C(33)	4 192(4)	2 639(4)	3 889(4)
C(34)	3 186(4)	3 195(4)	4 432(4)
C(35)	3 393(4)	3 624(4)	5 155(4)
C(36)	4 605(4)	3 511(4)	5 330(3)
C(41)	7 988(3)	1 480(3)	4 752(3)
C(42)	7 822(4)	389(3)	5 584(3)
C(43)	8 355(4)	−630(3)	5 379(4)
C(44)	9 057(4)	−557(4)	4 356(4)
C(45)	9 236(4)	525(4)	3 534(3)
C(46)	8 705(3)	1 557(3)	3 723(3)
S(1)	4 207.1(8)	76.2(8)	8 934.3(7)
C(51)	2 962(4)	1 112(4)	8 284(4)
C(52)	2 761(4)	645(4)	7 484(4)
C(53)	4 028(4)	126(4)	7 016(4)
C(54)	4 620(4)	−690(4)	7 977(3)
S(2)	7 662.7(9)	−1 853.3(8)	9 215.2(8)
O(1)	8 788(3)	−2 003(3)	9 617(3)
O(2)	6 496(3)	−2 048(3)	10 031(3)
O(3)	7 553(3)	−829(3)	8 243(2)
C(1)	7 884(5)	−3 085(4)	8 754(4)
F(1)	8 908(4)	−3 017(3)	7 965(3)
F(2)	6 889(4)	−3 097(3)	8 385(3)
F(3)	8 003(4)	−4 100(2)	9 557(3)

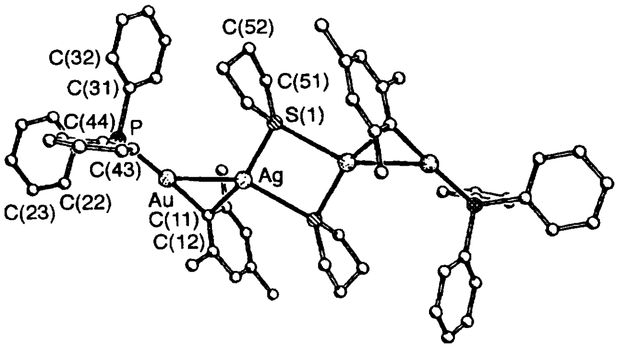

Fig. 1 The cation $[\{(Ph_3P)Au(\mu\text{-mes})Ag(tht)\}_2]^{2+}$ of complex **10** in the crystal. Hydrogen atoms are omitted for clarity

lengths are 2.4775(10) and 2.8392(11) Å; the former is similar to that found in $[\{AuAg(C_6F_5)_2(tht)\}_n]$ [2.454(4) Å][21] in which the tht ligand is monodentate and the latter is longer than in $[\{Ag(\mu\text{-tht})(tht)\}_n][BF_4]_n$ (2.554, 2.520 Å)[22] and $[NBu_4][Pt_2Ag(\mu\text{-tht})_2(C_6F_5)_6]$ [2.778(2), 2.547(2) Å].[23]

The Au–Ag distance, 2.8245(6) Å, indicates appreciable metal–metal bonding[24,25] (sum of covalent radii for gold and silver 2.89 Å) and is shorter than in $[(AuPPh_3)_2\{\mu\text{-}C(PPh_3)(C_5H_4N)\}\{\mu\text{-}Ag(O_2NO)(OClO_3)\}]$[26,27] [2.926(1), 3.006(1) Å], similar to those found in clusters such as $[Au_{13}Ag_{12}Cl_8\{P(C_6H_4Me\text{-}p)_3\}_{10}]PF_6$ (average 2.883 Å),[28] $[Pt(CO)(AgNO_3)\{Au(PPh_3)\}_8][NO_3]_2$ (average 2.8807 Å)[29] and slightly longer than those in $[\{AuAg(C_6F_5)_2(tht)\}_n]$ [2.726(2), 2.718(2) Å], $[\{AuAg(C_6F_5)_2(C_6H_6)\}_n]$ [2.702(2), 2.792(2) Å],[21] $[Pt(AgNO_3)\{Au(PPh_3)\}_8][NO_3]_2$ [2.786(5), 2.783(5), 2.714(5) Å][29] or $[Au_2Ag_2(CH_2PPh_3)_2(OClO_3)_4]$ [2.783(1), 2.760(1) Å].[30] The transannular Ag ⋯ Ag distance of 3.826 Å is too long to allow appreciable bonding interactions.

Experimental

Instrumentation and general experimental techniques were as described earlier.[31] The yields, C, H and N analyses, proton NMR and conductivity data are listed in Table 1. All the reactions were carried out at room temperature except that of $[AuCl(AsPh_3)]$ with MgBr(mes).

Table 3 Selected bond lengths (Å) and angles (°) for compound **10**

Au–C(11)	2.086(3)	Au–P	2.2886(9)
Au–Ag	2.8245(6)	Ag–C(11)	2.326(3)
Ag–S(1)	2.4775(10)	Ag–S(1^I)	2.8392(11)
P–C(41)	1.815(4)	P–C(21)	1.819(4)
P–C(31)	1.822(4)	S(1)–C(54)	1.828(4)
S(1)–C(51)	1.834(4)		
C(11)–Au–P	177.34(9)	C(11)–Au–Ag	54.06(9)
P–Au–Ag	128.60(3)	C(11)–Ag–S(1)	159.95(8)
C(11)–Ag–Au	46.54(8)	S(1)–Ag–Au	120.91(3)
C(11)–Ag–S(1^I)	106.02(9)	S(1)–Ag–S(1^I)	88.21(3)
Au–Ag–S(1^I)	150.83(2)	C(41)–P–C(21)	105.1(2)
C(41)–P–C(31)	103.9(2)	C(21)–P–C(31)	105.9(2)
C(41)–P–Au	113.97(12)	C(21)–P–Au	113.37(12)
C(31)–P–Au	113.66(12)	C(54)–S(1)–C(51)	94.6(2)
C(54)–S(1)–Ag	111.58(13)	C(51)–S(1)–Ag	111.0(2)
C(54)–S(1)–Ag^I	122.81(14)	C(51)–S(1)–Ag^I	125.4(2)
Ag–S(1)–Ag^I	91.79(3)		

Symmetry transformation used to generate equivalent atoms: I $-x + 1, -y, -z + 2$.

Preparations.—$[Au(mes)(AsPh_3)]$ **1**. To a solution of $[AuCl(AsPh_3)]$[32] (0.538 g, 1 mmol) in diethyl ether (30 cm^3) was added a solution of MgBr(mes) (1.5 mmol) in tetrahydrofuran (2 cm^3) at 0 °C under nitrogen. The mixture was stirred for 2 h at this temperature and then a drop of water was added. The solution was evaporated to dryness and complex **1** was recrystallised from dichloromethane–hexane.

[Au(mes)L] (L = dppm **2**, PPh_3 **3** *or* PPh_2Me **4**). To a solution of complex **1** (0.094 g, 0.15 mmol) in dichloromethane (20 cm^3) was added dppm (0.069 g, 0.18 mmol), PPh_3 (0.039 g, 0.15 mmol) or PPh_2Me (0.029 cm^3, 0.15 mmol). After stirring for 20 min the solvent was evaporated to *ca*. 5 cm^3. Addition of hexane (20 cm^3) led to the precipitation of complexes **2**–**4** as white solids.

Q[Au(mes)X] [X = Cl, Q = $P(CH_2Ph)Ph_3$ **5**; X = Br, Q = $N(PPh_3)_2$ **6**]. To a dichloromethane solution (25 cm^3) of complex **1** (0.187 g, 0.3 mmol) was added $[P(CH_2Ph)Ph_3]Cl$ (0.117 g, 0.3 mmol) or $[N(PPh_3)_2]Br$ (0.186 g, 0.3 mmol) and the mixture was stirred for 20 min. Partial concentration of the solution to *ca*. 5 cm^3 and addition of diethyl ether gave complexes **5** and **6** as white solids.

$Q[Au(mes)X_3]$ [X = Cl, Q = $P(CH_2Ph)Ph_3$ **7**; X = Br, Q = $N(PPh_3)_2$ **8**]. To a dichloromethane solution (20 cm^3) of complex **5** or **6** (0.106 g, 0.15 mmol of **5**; 0.140 g, 0.15 mmol of **6**) was added Cl_2 (0.6 cm^3 of a solution 0.25 mol dm^{-3} in CCl_4) or Br_2 (0.5 cm^3 of a solution 0.3 mol dm^{-3} in CCl_4), respectively. After stirring for 20 min the solution was evaporated to *ca.* 5 cm^3 and hexane (20 cm^3) added to precipitate complexes **7** and **8** as yellow and red solids, respectively.

$[\{(Ph_3P)Au(\mu\text{-mes})AgL\}_n][SO_3CF_3]_n$ (L = PPh_3, n = 1 **9**; L = tht, n = 2 **10**). To a solution of complex **3** (0.087 g, 0.15 mmol) in dichloromethane (20 cm^3) was added 0.15 mmol of $[Ag(OSO_2CF_3)L]$ [L = PPh_3 (0.078 g) or tht (0.052 g)], prepared in a similar way to $[Ag(OClO_3)L]$.[33] The solution was stirred for 20 min in the dark and the solvent was evaporated to *ca.* 5 cm^3. Addition of diethyl ether (20 cm^3) precipitated complexes **9** and **10** as white solids.

Crystal Structure Determination of Compound **10**.—*Crystal data.* $C_{64}H_{68}Ag_2Au_2F_6O_6P_2S_4$, M = 1847.04, triclinic, space group $P\bar{1}$, a = 10.946(2), b = 12.435(2), c = 13.701(2) Å, α = 66.37(1), β = 74.23(1), γ = 78.73(1)°, U = 1636.3(5) Å^3, Z = 1, D_c = 1.874 Mg m^{-3}, λ(Mo-Kα) = 0.710 73 Å, μ = 5.3 mm^{-1}, $F(000)$ = 900, T = -100 °C.

Data collection and reduction. A colourless prism *ca.* 0.75 × 0.45 × 0.4 mm was mounted in inert oil (type RS3000, donated by Fa. Riedel de Haën). 8818 Intensities were measured on a Siemens R3 diffractometer to $2\theta_{max}$ 55°, of which after absorption corrections (ψ scans) 6401 were unique (R_{int} 0.020).

Structure solution and refinement. The structure was solved by the heavy-atom method and refined anisotropically on F^2 (program SHELXL 93).[34] Hydrogen atoms were included using a riding model. The final $wR(F^2)$ was 0.061, with conventional $R(F)$ 0.024 for 392 parameters and 317 restraints; weighting scheme of the form $w^{-1} = \sigma^2(F^2) + (aP)^2 + bP$, where $P = (F_o^2 + 2F_c^2)/3$ and a and b are constants adjusted by the program; S 1.02, maximum Δ/σ 0.03, maximum $\Delta\rho$ 0.96 e Å^{-3}. Final atomic coordinates are given in Table 2, with derived bond lengths and angles in Table 3.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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