# Mesitylgold Complexes: Synthesis and Reactivity; Crystal Structure of [{(Ph$_3$P)Au($\mu$-mes)Ag(tht)}$_2$][SO$_3$CF$_3$]$_2$ (mes = mesityl, tht = tetrahydrothiophene)†

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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$_2$PCH$_2$PPh$_2$, PPh$_3$ or PPh$_2$Me) or with QX to afford anionic complexes Q[Au(mes)X] [X = Cl, Q = P(CH$_2$Ph)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$_2$Ph)Ph$_3$; X = Br, Q = N(PPh$_3$)$_2$]. The reaction of [Au(mes)(PPh$_3$)] with [Ag(OSO$_2$CF$_3$)L] [L = PPh$_3$ or tetrahydrothiophene (tht)] afforded [{(Ph$_3$P)Au($\mu$-mes)AgL}$_n$][SO$_3$CF$_3$]$_n$ (L = PPh$_3$, $n$ = 1; L = tht, $n$ = 2). The structure of [{(Ph$_3$P)Au($\mu$-mes)Ag(tht)}$_2$][SO$_3$CF$_3$]$_2$ has been determined by a single-crystal X-ray diffraction study, which shows an Au–Ag distance of 2.8245(6) Å.

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Heteroleptic gold(I) compounds containing the mesityl group (2,4,6-Me$_3$C$_6$H$_2$, 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–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)($\mu$-O$_2$CC$_6$H$_4$X-2)$_2$] (X = H, Cl or Br),[10,11] [Cu$_{10}$O$_2$(mes)$_6$][12] and [{Cu(mes)}$_4${$\mu$-SC$_6$H$_4$[CH(Me)NMe$_2$]-2}$_2${MgSC$_6$H$_4$[CH(Me)NMe$_2$]-2}$_2$].[13] However, no silver derivatives of this kind have been reported and only one of gold,[2] [(Ph$_3$P)Au($\mu$-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$_2$PCH$_2$PPh$_2$) **2**, PPh$_3$ **3** or PPh$_2$Me **4**], Q[Au(mes)X] [X = Cl, Q = P(CH$_2$Ph)Ph$_3$ **5**; X = Br, Q = N(PPh$_3$)$_2$ **6**] and Q[Au(mes)X$_3$] [X = Cl, Q = P(CH$_2$Ph)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$_3$P)Au($\mu$-mes)Ag(PPh$_3$)][SO$_3$CF$_3$] **9** and [{(Ph$_3$P)Au($\mu$-mes)Ag(tht)}$_2$][SO$_3$CF$_3$]$_2$ **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

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

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$_2$Me, in 1 : 1 ratio, to give the neutral complexes [Au(mes)L] (L = dppm **2**, PPh$_3$ **3** or PPh$_2$Me **4**) or with salts QX to give anionic complexes Q[Au(mes)X] [X = Cl, Q = P(CH$_2$Ph)Ph$_3$ **5**; X = Br, Q = N(PPh$_3$)$_2$ **6**] [see equations (2) and (3)].

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

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

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

[a] Calculated values are given in parentheses. [b] In acetone ($5 \times 10^{-4}$ 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) |

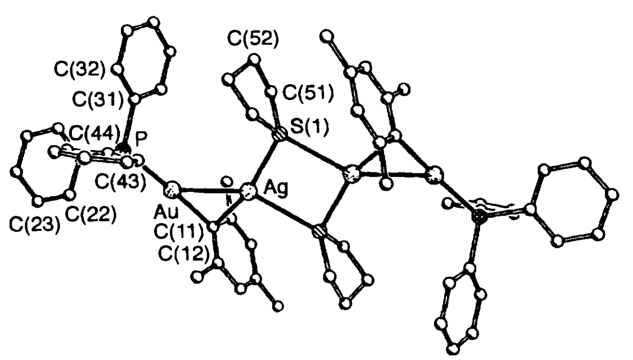

**Fig. 1** The cation $[\{(Ph_3P)Au(\mu\text{-mes})Ag(tht)\}_2]^{2+}$ of complex **10** in the crystal. Hydrogen atoms are omitted for clarity

**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 $-x + 1, -y, -z + 2$.

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).

*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, $\alpha$ = 66.37(1), $\beta$ = 74.23(1), $\gamma$ = 78.73(1)°, $U$ = 1636.3(5) $Å^3$, $Z$ = 1, $D_c$ = 1.874 Mg $m^{-3}$, $\lambda$(Mo-K$\alpha$) = 0.710 73 Å, $\mu$ = 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 ($\psi$ 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 $\Delta/\sigma$ 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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