

# Trinuclear Au<sub>2</sub>Ag and Au<sub>2</sub>Cu Complexes with Mesityl Bridging Ligands. X-ray Structure of the Chain Polymer [Au( $\mu$ -mes)AsPh<sub>3</sub>]<sub>2</sub>Ag](ClO<sub>4</sub>)

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The reaction of the complex [Au(mes)L] (mes = mesityl, L = PPh<sub>3</sub>, AsPh<sub>3</sub>) with Ag(OSO<sub>2</sub>-CF<sub>3</sub>), Ag(OCIO<sub>3</sub>), or [Cu(CNMe)<sub>4</sub>]PF<sub>6</sub>, in molar ratio 2:1, affords trinuclear derivatives [Au( $\mu$ -mes)L]<sub>2</sub>M]A [M = Ag, L = PPh<sub>3</sub>, A = SO<sub>3</sub>CF<sub>3</sub><sup>-</sup> (**1**); L = AsPh<sub>3</sub>, A = ClO<sub>4</sub><sup>-</sup> (**2a**), SO<sub>3</sub>CF<sub>3</sub><sup>-</sup> (**2b**); M = Cu, A = PF<sub>6</sub><sup>-</sup>, L = PPh<sub>3</sub> (**3**), AsPh<sub>3</sub> (**4**)]. Complexes **1** and **2** react further with various ligands in a 1:1 molar ratio to give the dinuclear compounds [AuAg( $\mu$ -mes)-(PPh<sub>3</sub>)L]SO<sub>3</sub>CF<sub>3</sub> (L = PPh<sub>3</sub>, tetrahydrothiophene, 2,2'-bipyridine, or SPPH<sub>3</sub>) or [AuAg( $\mu$ -mes)(AsPh<sub>3</sub>)L]A (L = AsPh<sub>3</sub>, A = SO<sub>3</sub>CF<sub>3</sub><sup>-</sup>; L = <sup>1</sup>/<sub>2</sub> Ph<sub>2</sub>AsCH<sub>2</sub>AsPh<sub>2</sub>, A = ClO<sub>4</sub><sup>-</sup>). The structure of [Au( $\mu$ -mes)AsPh<sub>3</sub>]<sub>2</sub>Ag](ClO<sub>4</sub>) (**2a**) has been determined by a single-crystal X-ray diffraction study, which shows an Au–Ag distance of 2.7758(8) Å; the trinuclear species are connected by short Au...Au contacts of 3.132 Å to form a chain polymer.

## Introduction

Recent studies of hypercoordinated derivatives of representative elements with Au(PR<sub>3</sub>) fragments have shown that weak gold–gold interactions,<sup>1</sup> frequently observed in gold clusters and in some gold(I) complexes, contribute significantly to the stability of these species and are indeed the sole explanation for the formation of some of them (e.g. [N(AuPMe<sub>3</sub>)<sub>5</sub>·AuClPMe<sub>3</sub>]<sup>2</sup>). These interactions, which can be compared in strength to a typical hydrogen bond (29–33 kJ mol<sup>-1</sup>)<sup>3</sup> and are brought about by relativistic effects,<sup>4</sup> have also been observed recently in heteronuclear gold–silver<sup>5–18</sup> and gold–copper<sup>18–22</sup> derivatives. Most of these heteronuclear complexes have been obtained by reacting acidic

silver(I) or copper(I) centers with gold complexes that are nucleophilic either at the gold atoms (e.g. [AuAg-(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(C<sub>6</sub>H<sub>6</sub>)]<sub>n</sub>),<sup>8</sup> [Au<sub>13</sub>Ag<sub>12</sub>Cl<sub>8</sub>{P(C<sub>6</sub>H<sub>4</sub>Me-p)<sub>3</sub>}<sub>10</sub>]PF<sub>6</sub>,<sup>9</sup> [Pt(AgNO<sub>3</sub>){Au(PPh<sub>3</sub>)<sub>3</sub>]<sub>8</sub>][NO<sub>3</sub>]<sub>2</sub>,<sup>10</sup> [Pt(CuCl){Au(PPh<sub>3</sub>)<sub>3</sub>]<sub>8</sub>][NO<sub>3</sub>]<sub>2</sub><sup>19</sup>) or at other donor atoms such as phosphorus (e.g. [Au(mes)]<sub>2</sub>( $\mu$ -dppm)<sub>2</sub>Ag]ClO<sub>4</sub><sup>17</sup>), nitrogen (e.g. [(AuPPh<sub>3</sub>)<sub>2</sub>{ $\mu$ -C(PPh<sub>3</sub>)(C<sub>5</sub>H<sub>4</sub>N)}{ $\mu$ -Ag(O<sub>2</sub>NO)(OCIO<sub>3</sub>)}]<sub>5</sub>),<sup>6</sup> or carbon (e.g. [(Ph<sub>3</sub>P)Au( $\mu$ -mes)Ag(tht)]<sub>2</sub>][SO<sub>3</sub>-CF<sub>3</sub>]<sub>2</sub>,<sup>7</sup> NBu<sub>4</sub>[Au<sub>3</sub>Cu<sub>3</sub>(C<sub>2</sub>Ph)<sub>6</sub>]<sub>20</sub>). The former type gives heteronuclear complexes with unbridged gold–metal bonds, whereas the latter forms heteronuclear complexes with bridging ligands and with short contacts between the metallic centers.

In this paper we report the synthesis of trinuclear Au<sub>2</sub>Ag and Au<sub>2</sub>Cu derivatives obtained by the reaction of [Au(mes)L] (mes = mesityl, L = PPh<sub>3</sub>, AsPh<sub>3</sub>) with

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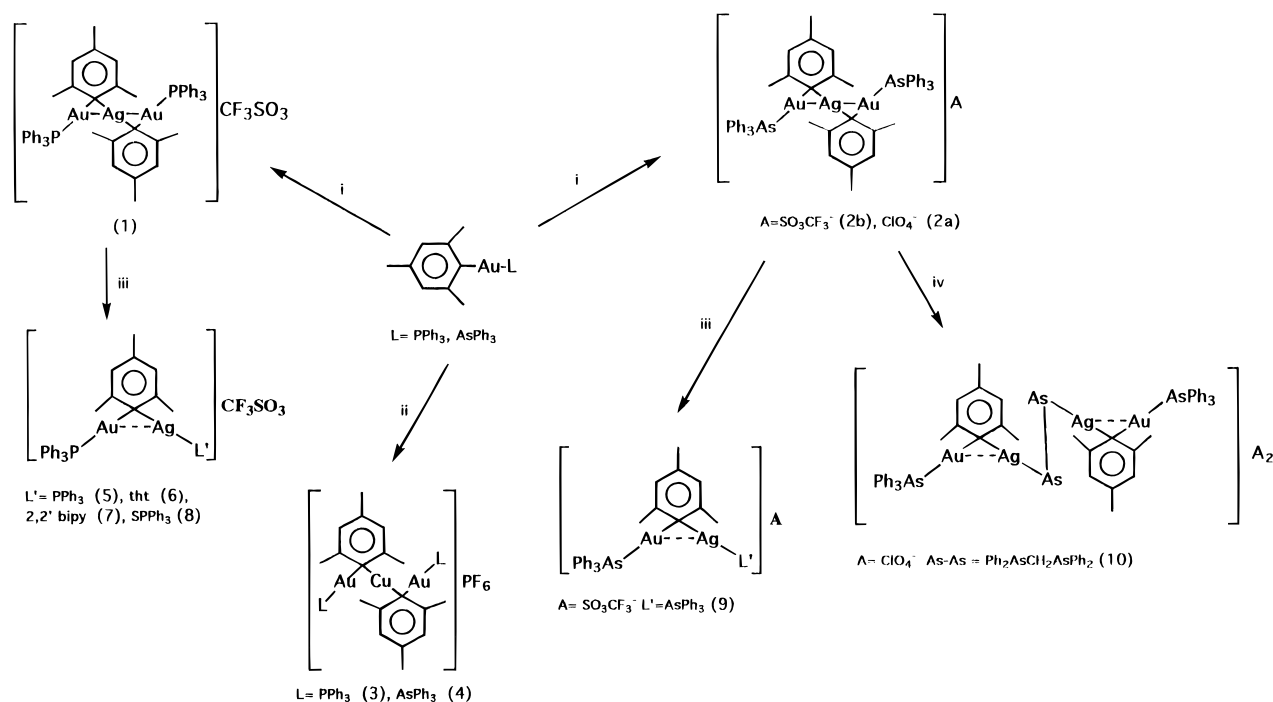
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Scheme 1



i)  $\text{AgOCIO}_3$  or  $\text{AgOSO}_2\text{CF}_3$ ; ii)  $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{PF}_6$ ; iii)  $\text{L}'$ ,  $-\text{[Au}(\text{mes})\text{L}]$ ; iv)  $\text{dppa}$ ,  $-\text{[Au}(\text{mes})\text{L}]$

weakly coordinated silver or copper compounds such as  $\text{Ag}(\text{OSO}_2\text{CF}_3)$ ,  $\text{Ag}(\text{OCIO}_3)$ , or  $[\text{Cu}(\text{CNMe})_4]\text{PF}_6$  in molar ratio 2:1. The X-ray diffraction analysis of  $[\{\text{Au}(\mu\text{-mes})\text{-AsPh}_3\}_2\text{Ag}](\text{ClO}_4^-)$  shows the central silver atom to be coordinated to two Au–Ag-bridging mesityl groups. The trinuclear molecules are connected through intermolecular gold–gold contacts of 3.132 Å, giving rise to a chain polymer. The reaction of the trinuclear  $\text{Au}_2\text{Ag}$  derivatives  $[\{\text{Au}(\mu\text{-mes})\text{L}\}_2\text{Ag}](\text{A})$  with various neutral ligands in 1:1 ratio affords dinuclear complexes  $[\text{AuAg}(\mu\text{-mes})(\text{PPh}_3)\text{L}']\text{SO}_3\text{CF}_3$  ( $\text{L}' = \text{PPh}_3$ , tetrahydrothiophene, 2,2'-bipyridine, or SPPH<sub>3</sub>) or  $[\text{AuAg}(\mu\text{-mes})(\text{AsPh}_3)\text{L}']\text{A}$  ( $\text{L}' = \text{AsPh}_3$ ,  $\text{A} = \text{SO}_3\text{CF}_3^-$ ;  $\text{L}' = \frac{1}{2} \text{Ph}_2\text{AsCH}_2\text{AsPh}_2$ ,  $\text{A} = \text{ClO}_4^-$ ).

## Results and Discussion

Recently<sup>7</sup> we have shown that mesityl in mononuclear derivatives  $[\text{Au}(\text{mes})\text{L}]$  ( $\text{mes} = \text{mesityl}$ ,  $\text{L} = \text{PPh}_3$ ,  $\text{AsPh}_3$ ) can replace poorly coordinated ligands such  $\text{OCIO}_3$  or  $\text{OSO}_2\text{CF}_3$  in  $\text{Ag}(\text{OCIO}_3)\text{L}$  and  $\text{Ag}(\text{OSO}_2\text{CF}_3)\text{L}$  affording dinuclear  $[\text{AuAg}(\mu\text{-mes})(\text{PPh}_3)\text{L}']\text{SO}_3\text{CF}_3$  ( $\text{L} = \text{PPh}_3$ , tetrahydrothiophene). The mass spectrum of the bis(triphenylphosphine) derivative showed, besides the parent ion peak  $[\text{M} - \text{SO}_3\text{CF}_3]^+$ , an ion at  $m/z$  1266 (11%) assignable to  $[\text{Au}_2\text{Ag}(\text{mes})_2(\text{PPh}_3)_2]^+$ . This indicates that an ion of this type could be stable, and thus a similar reaction involving  $[\text{Au}(\text{mes})\text{PPh}_3]$  and  $\text{Ag}(\text{OSO}_2\text{CF}_3)$  in a 2:1 ratio is a potential method of synthesis of this complex. The reaction works well in diethyl ether, affording bright yellow solutions from which the trinuclear  $\text{Au}_2\text{Ag}$  derivative  $[\{\text{Au}(\mu\text{-mes})\text{PPh}_3\}_2\text{Ag}]\text{SO}_3\text{CF}_3$  (**1**) (see reaction i, Scheme 1) can be obtained. However,  $[\{\text{Au}(\mu\text{-mes})\text{PPh}_3\}_2\text{Ag}](\text{ClO}_4^-)$  cannot be isolated in pure form using  $\text{Ag}(\text{OCIO}_3)$ , because the final solid also contains  $[\text{AuAg}(\mu\text{-mes})(\text{PPh}_3)_2](\text{ClO}_4^-)$ . The novel complexes  $[\{\text{Au}(\mu\text{-mes})\text{AsPh}_3\}_2\text{Ag}](\text{A})$  ( $\text{A} = \text{ClO}_4^-$  (**2a**) and

$\text{SO}_3\text{CF}_3^-$  (**2b**)) can be synthesized starting from  $[\text{Au}(\text{mes})\text{AsPh}_3]$ .

Complexes **1** and **2** are air- and moisture-stable yellow (**2a**) or pale yellow solids. Acetone solutions display conductivities typical of 1:1 electrolytes,<sup>23</sup> and the IR spectra show absorptions arising from the  $\text{SO}_3\text{CF}_3^-$  counterions<sup>24</sup> at 1275 (vs, br), 1221 (m), and 1142 (s)  $\text{cm}^{-1}$  (**1**) and 1292 (vs, br), 1223 (s), and 1152 (s)  $\text{cm}^{-1}$  (**2b**). Absorptions assigned<sup>25</sup> to  $\text{ClO}_4^-$  appear at 1094 (vs, br) and 623  $\text{cm}^{-1}$  (**2a**). The absorptions from the mesityl groups are present at 1596 (m), 847 (m)  $\text{cm}^{-1}$  (**1**), 1596 (m), 855 (m)  $\text{cm}^{-1}$  (**2a**), and 1594 (w), 851 (m)  $\text{cm}^{-1}$  (**2b**). These signals are shifted to higher energy than in the starting products, as was observed in other mesityl-bridged complexes.<sup>7,26</sup> Their  $^1\text{H}$  NMR spectra show three singlets for the mesityl ligand, slightly displaced from the resonances of the starting material, and in a consistent ratio with the phenyl resonances of the ancillary ligands. The singlet at 43.4 ppm in the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **1** is high-field displaced from the signal of the starting material, as in other polynuclear gold complexes with mesityl bridges. The mass spectra (FAB+) show, for all the compounds, the ion peak  $[\text{M} - \text{SO}_3\text{CF}_3]^+$  at  $m/z$  1266 (23%, **1**) and 1352 (27%, **2b**) or  $[\text{M} - \text{ClO}_4]^+$  at  $m/z$  1352 (52%, **2b**).

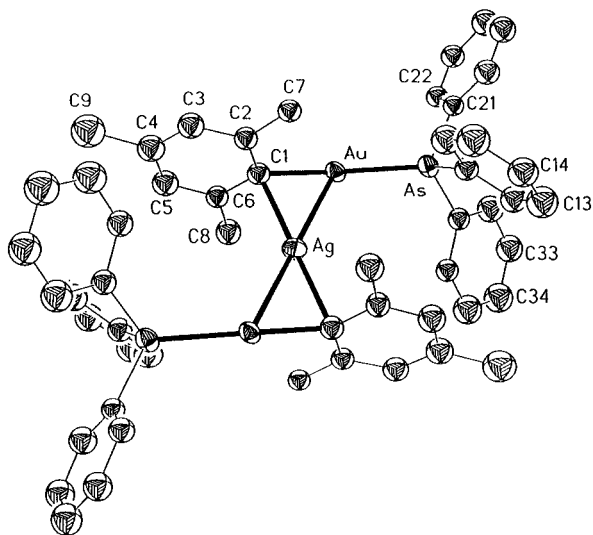
The structure of complex **2a** has been determined by an X-ray diffraction study (Figures 1 and 2); selected bond lengths and angles are given in Table 1. The molecule exhibits inversion symmetry with the silver atom on the special position (0.5, 0.5, 0.5). The silver center is bonded to the ipso carbon atoms of the mesityl

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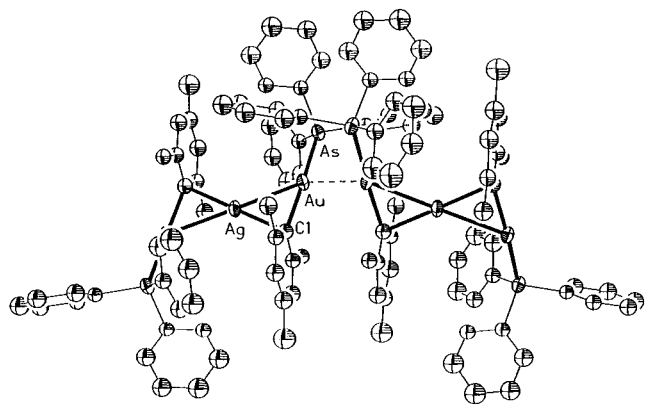
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**Figure 1.** Perspective view of the individual molecule of complex **2a** showing the atom-numbering scheme. Displacement parameter ellipsoids represent 50% probability surfaces. H atoms are omitted for clarity.



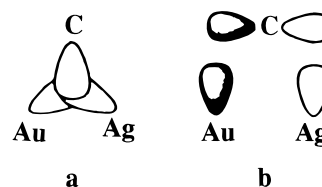
**Figure 2.** Part of the polymeric chain of complex **2a**.

**Table 1. Selected Bond Lengths (Å) and Angles (deg) for 2a<sup>a</sup>**

Au–C(1)	2.09(2)	Au–As	2.425(2)
Au–Ag	2.7758(8)	Au–Au <sup>1</sup>	3.132(2)
Ag–C(1)	2.27(2)	As–C(31)	1.927(11)
As–C(11)	1.928(11)	As–C(21)	1.941(10)
C(1)–Au–As	166.8(4)	C(1)–Au–Ag	53.5(5)
As–Au–Ag	120.14(6)	C(1)–Au–Au <sup>1</sup>	90.2(5)
As–Au–Au <sup>1</sup>	100.13(6)	Ag–Au–Au <sup>1</sup>	136.08(4)
C(1)–Ag–C(1) <sup>2</sup>	180.0	C(1)–Ag–Au	47.6(6)
C(1) <sup>2</sup> –Ag–Au	132.4(6)	Au–Ag–Au <sup>2</sup>	180.0
C(31)–As–C(11)	103.2(7)	C(31)–As–C(21)	104.2(6)
C(11)–As–C(21)	104.0(6)	C(31)–As–Au	118.7(5)
C(11)–As–Au	106.9(5)	C(21)–As–Au	118.0(5)
C(2)–C(1)–C(6)	119(2)	C(2)–C(1)–Au	116.4(12)
C(6)–C(1)–Au	122.1(13)	C(2)–C(1)–Ag	105.4(9)
C(6)–C(1)–Ag	100.2(11)	Au–C(1)–Ag	78.9(7)

<sup>a</sup> Symmetry transformations used to generate equivalent atoms: (1)  $-x + 1, y, -z + 3/2$ ; (2)  $-x + 1, -y + 1, -z + 1$ .

groups and also bridges the two gold fragments with an Ag–Au distance of 2.7758(8) Å. This distance is shorter than those found in complexes where a formally nonbonding Ag···Au interaction has been proposed, e.g. [Ag( $\mu$ -dppm)<sub>2</sub>{Au(mes)}<sub>2</sub>]ClO<sub>4</sub> [2.944(2) and 2.946(2) Å],<sup>17</sup> [(AuPPh<sub>3</sub>)<sub>2</sub>{ $\mu$ -C(PPh<sub>3</sub>)(C<sub>5</sub>H<sub>4</sub>N)}]{ $\mu$ -Ag(O<sub>2</sub>NO)(OClO<sub>3</sub>)}] [2.926(1), 3.006(1) Å],<sup>5</sup> or [{(Ph<sub>3</sub>P)Au( $\mu$ -mes)Ag(tht)}<sub>2</sub>](SO<sub>3</sub>CF<sub>3</sub>)<sub>2</sub> [2.8245(6) Å],<sup>7</sup> but is of the same order as those found in complexes with formal silver–gold



**Figure 3.** Representation of the two-electron three-center Au–C(mesityl)–Ag bond.

bonds, such as [Au<sub>13</sub>Ag<sub>12</sub>Cl<sub>8</sub>{P(C<sub>6</sub>H<sub>4</sub>Me-4)<sub>3</sub>}<sub>10</sub>]PF<sub>6</sub> (average 2.883 Å),<sup>9</sup> [{AuAg(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(C<sub>6</sub>H<sub>6</sub>)<sub>n</sub>] [2.702(2), 2.792(2) Å],<sup>8</sup> or [Pt(AgNO<sub>3</sub>){Au(PPh<sub>3</sub>)<sub>3</sub>}<sub>8</sub>](NO<sub>3</sub>)<sub>2</sub> [2.714(5)–2.786(5) Å].<sup>10</sup> Thus an appreciable silver–gold bonding interaction should be postulated in **2a**. Short, presumably bonding, interactions also exist in other complexes with bridging mesityl groups, e.g. [Au<sub>5</sub>(mes)<sub>5</sub>]<sup>27</sup> where the gold–gold contacts are 2.692(1) and 2.708(2) Å and there is great deviation from linearity at the gold atoms. In [Ag<sub>4</sub>(mes)<sub>4</sub>]<sup>27</sup> the silver–silver interactions are 2.733(3) and 2.755(3) Å with angles of 169.0(9)° at the silver center. Short Au–Au contacts have been found in complexes with other bridging aromatic groups such as [C<sub>5</sub>H<sub>5</sub>FeC<sub>5</sub>H<sub>4</sub>(AuPPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup> [2.768(2) Å]<sup>28</sup> or [C<sub>6</sub>F<sub>5</sub>H<sub>2</sub>(AuPPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup> [2.759(1) Å].<sup>29</sup> The deviation from linearity at the gold atom [C(1)–Au–As 166.8(4)°] is only moderate.

The M–C bond lengths were not determined with high precision, but the values Au–C(1) 2.09(2) Å and Ag–C(1) 2.27(2) Å are similar to those found in the complexes mentioned above. The Ag–C–Au angle at the bridging carbon is acute [78.9(7)°] as has been observed in complexes for which 3c,2e<sup>−</sup> bonding is postulated: [Al<sub>2</sub>Ph<sub>6</sub>],<sup>30</sup> 77°; [Al<sub>2</sub>Ph<sub>2</sub>Me<sub>4</sub>],<sup>31</sup> 77.8°; [Cu<sub>4</sub>R<sub>4</sub>]<sup>32</sup> (R = C<sub>6</sub>H<sub>4</sub>NMe<sub>2</sub>), 71.35°, and related complexes.

The most important orbital interactions for the Au–C–Ag bridge are shown in Figure 3a,b. The former shows that there is a bond not only between C and Ag but also between the metal atoms. The latter (Figure 3b), displays a nonbonding contribution between the gold and silver atoms, but it is responsible for the commonly found orientation of a bridging aryl perpendicular to the metal···metal vector as occurs in complex **2a**. It is noteworthy that the mesityl bridge it is not symmetrically disposed [Au–C(1)–C(4) 163.3°, Ag–C(1)–C(4) 110.7°] in contrast to the usual symmetrical disposition of the aryl ligand in the examples above mentioned. Preliminary extended Hückel calculations<sup>33</sup> show not very important changes in energy depending on this angle, the lowest energy being at the Au–C(1)–C(4) angle of 150°. The small deviation between the observed and theoretical values could be due to the crystal packing to form a unidimensional chain polymer parallel to the *y* axis by intermolecular gold–gold contacts (related by a 2-fold axis) of 3.132(2) Å.

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Reactions of  $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{PF}_6$  with  $[\text{Au}(\text{mes})\text{L}]$  ( $\text{L} = \text{PPh}_3$ ,  $\text{AsPh}_3$ ) in a 1:2 ratio afford trinuclear gold–copper complexes  $[\{\text{Au}(\mu\text{-mes})\text{L}\}_2\text{Cu}](\text{PF}_6)$  ( $\text{L} = \text{PPh}_3$  (**3**),  $\text{AsPh}_3$  (**4**)) as white solids in good yield (reaction ii). They are air- and moisture-stable solids, and their acetone solutions show conductivity values for a 1:1 electrolyte. Their  $^1\text{H}$  NMR spectra are very similar to those of the silver–gold complexes, and again the resonance assigned to  $\text{PPh}_3$  ligand in **3** appears very close to that in **1**, 43.7 ppm. Their IR spectra, besides the  $\text{PF}_6$  absorptions<sup>34</sup> at 839 (vs, br) (**3**) and 838 (vs, br)  $\text{cm}^{-1}$  (**4**), show bands at 1597 (m) (**3**) and 1595 (m)  $\text{cm}^{-1}$  (**4**) assignable to the mesityl ligand; the band at ca. 840  $\text{cm}^{-1}$  is presumably overlapped by the  $\text{PF}_6$  absorption. The mass spectra show the parent ion peak  $[\text{M} - \text{PF}_6]^+$  at  $m/z$  1218 (27%, **3**) and 1307 (15%, **4**). All these data indicate a structure for these complexes similar to that of the silver–gold derivative **2a**, but the lack of color could imply a different packing. Unfortunately, we were not able to obtain suitable single crystals of these materials.

Complex **1** reacts with triphenylphosphine and tetrahydrothiophene (reaction iii) to give in nearly quantitative yield the previously reported complexes  $[\text{AuAg}(\mu\text{-mes})(\text{PPh}_3)\text{L}]\text{SO}_3\text{CF}_3$  ( $\text{L} = \text{PPh}_3$ , tht) and  $[\text{Au}(\text{mes})\text{-PPh}_3]$ , which can be easily separated because of the solubility of the latter in diethyl ether. The same reaction starting from **2a,b** gives a mixture of complexes, probably due to ligand exchange between silver and gold. Similar results have been achieved using complexes **3** and **4** as starting materials, and in these cases disproportionation of the copper(I) complexes also occurs. These substitution reactions can be used to synthesize novel di- or polynuclear derivatives, depending on the chosen ligand. Thus, complex **1** reacts with 2,2'-bipyridine and  $\text{SPPH}_3$  to give, besides  $[\text{Au}(\text{mes})\text{-PPh}_3]$ ,  $[\text{AuAg}(\mu\text{-mes})(\text{PPh}_3)\text{L}]\text{SO}_3\text{CF}_3$  ( $\text{L} = \text{bipy}$  (**7**),  $\text{SPPH}_3$  (**8**)). Complex **2a** reacts with  $\text{AsPh}_3$  affording  $[\text{AuAg}(\mu\text{-mes})(\text{AsPh}_3)_2]\text{SO}_3\text{CF}_3$  (**9**), and complex **2b** reacts with  $\text{Ph}_2\text{AsCH}_2\text{AsPh}_2$  (dpam), in a 2:1 ratio, to give  $[\text{Au}_2\text{Ag}_2(\mu\text{-mes})_2(\text{AsPh}_3)_2(\text{dpam})](\text{SO}_3\text{CF}_3)_2$  (**10**). In both cases  $[\text{Au}(\text{mes})\text{AsPh}_3]$  can be recovered from the mother liquors.

Complexes **7–10** are white solids that are conducting in acetone solution, showing values characteristic of 1:1 electrolytes (complexes **7–9**) or 2:1 in the case of **10**. The infrared spectra show absorptions at 1273 (vs, br), 1223 (vs, br), 1146 (s) (**7**), 1266 (vs, br), 1223 (s, br), 1106 (s) (**8**), and 273 (vs, br), 1225 (s), 1154 (s)  $\text{cm}^{-1}$  (**9**) assignable to  $\text{SO}_3\text{CF}_3^-$  and 1094 (vs, br), 623  $\text{cm}^{-1}$  (**10**) assignable to perchlorate anion, as well as absorptions at 1588 (w), 857 (m) (**7**), 1596 (w), 1586 (w), 859 (m), 847 (m) (**8**), 1596 (w, br), 1581 (w, br), 851 (w, br) (**9**), and 1594 (w), 1580 (w), 851 (w, br)  $\text{cm}^{-1}$  (**10**) characteristic of mesityl bridging groups.  $^1\text{H}$  and  $^{31}\text{P}\{^1\text{H}\}$  spectra are in accordance with the proposed formulation, both by the position of the resonances and by their ratio, the most notable features being the low-field position, 7.13 ppm, of the *meta* H of **7** (which may indicated a bridging position for the mesityl group) and the existence of coupling between the P atom of  $\text{SPPH}_3$  and the silver atoms in **8** (which shows that the new

ligand is bonded to the silver atom). The latter appears at 37.17 ppm as a broad doublet ( $^3J_{\text{Ag-P}} = 78.1$  Hz) because the coupling with  $^{107}\text{Ag}$  and  $^{109}\text{Ag}$  is not resolved. The mass spectra show the parent ion peak  $[\text{M} - \text{SO}_3\text{CF}_3]^+$  at  $m/z$  841 (79%, **7**), 981 (31%, **8**), or 1037 (13%, **9**). The mass spectra of **10** do not show the parent ion peak, probably because of its dicationic character. It is noteworthy that the mass spectra of **7–9** contain the trinuclear ions  $[\{\text{Au}(\mu\text{-mes})\text{L}\}_2\text{Ag}]^+$  which have been formed under mass spectral conditions, as reported for  $[\text{AuAg}(\mu\text{-mes})(\text{PPh}_3)_2]\text{SO}_3\text{CF}_3$ .

## Experimental Section

The starting materials  $[\text{AgOClO}_3]$ ,<sup>35</sup>  $[\text{AgOSO}_2\text{CF}_3]$ ,<sup>35</sup>  $[\text{Au}(\text{mes})\text{PPh}_3]$ ,<sup>7</sup>  $[\text{Au}(\text{mes})\text{AsPh}_3]$ ,<sup>7</sup> and  $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{PF}_6$ <sup>36</sup> were prepared as described previously. All other reagents were commercially available. All reactions were performed by avoiding light exposure.

The C, H, N, and S analyses were carried out on a Perkin-Elmer Model 2400 microanalyzer. Conductivities were measured in approximately  $5 \times 10^{-4}$  mol  $\text{dm}^{-3}$  acetone solutions, with a Jenway Model 4010 conductimeter. The infrared spectra were recorded (4000–400  $\text{cm}^{-1}$ ) on a Nicolet 510 FT-IR spectrometer using Nujol mulls between polyethylene sheets. The  $^1\text{H}$  NMR spectra were recorded on a Varian Unity 200 spectrometer, whereas  $^{31}\text{P}$  NMR spectra were recorded on a Varian Unity 300 and Bruker ARX 300 spectrometer, in  $\text{CDCl}_3$ . Chemical shifts are cited relative to  $\text{SiMe}_4$  ( $^1\text{H}$ ) and 85%  $\text{H}_3\text{PO}_4$  (external  $^{31}\text{P}$ ). Mass spectra were recorded on a VG Autospec with FAB technique using 3-nitrobenzyl alcohol as matrix.

Caution: Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of material should be prepared and all samples handled with great caution.

**Syntheses.**  $[\{\text{Au}(\mu\text{-mes})\text{L}\}_2\text{Ag}]\text{A}$  [ $\text{L} = \text{PPh}_3$ ,  $\text{A} = \text{SO}_3\text{CF}_3^-$  (**1**);  $\text{L} = \text{AsPh}_3$ ,  $\text{A} = \text{ClO}_4^-$  (**2a**),  $\text{A} = \text{SO}_3\text{CF}_3^-$  (**2b**)]. To a dichloromethane (30  $\text{cm}^3$ ) solution of  $[\text{Au}(\text{mes})\text{PPh}_3]$  (0.1157 g, 0.2 mmol) or  $[\text{Au}(\text{mes})\text{AsPh}_3]$  (0.1245 g, 0.2 mmol) was added a solution of  $\text{AgOClO}_3$  (0.0207 g, 0.1 mmol) or  $\text{AgOSO}_2\text{CF}_3$  (0.0257 g, 0.1 mmol) in diethyl ether (10  $\text{cm}^3$ ). The reactions were instantaneous. The resulting bright yellow solutions were concentrated to ca. 5  $\text{cm}^3$ . Addition of *n*-hexane (20  $\text{cm}^3$ ) led to the precipitation of complexes **1** and **2b** as pale yellow solids, whereas by addition of diethyl ether (20  $\text{cm}^3$ ) compound **2a** was obtained as a yellow solid. Yield (%): 88 (**1**), 78 (**2a**), 97 (**2b**). Data for **1** are as follow. Anal. Calcd for  $\text{C}_{55}\text{H}_{52}\text{Au}_2\text{AgP}_2\text{F}_3\text{SO}_3$ : C, 46.70; H, 3.70; S, 2.25. Found: C, 46.40; H, 3.35; S, 2.00.  $\Lambda_{\text{M}}$ : 122  $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ .  $^1\text{H}$  NMR:  $\delta = 7.6$ –7.2 (m, 30H, Ph), 6.88 (s, 4H, H-*m*), 2.36 (s, 12H, *o*-me), and 2.18 (s, 6H, *p*-me).  $^{31}\text{P}$  NMR:  $\delta = 43.4$  (s). Data for **2a** are as follow. Anal. Calcd for  $\text{C}_{54}\text{H}_{52}\text{Au}_2\text{AgAs}_2\text{ClO}_4$ : C, 44.65; H, 3.60. Found: C, 44.25; H, 3.70.  $\Lambda_{\text{M}}$ : 126  $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ .  $^1\text{H}$  NMR:  $\delta = 7.6$ –7.2 (m, 30H, Ph), 6.91 (s, 4H, H-*m*), 2.44 (s, 12H, *o*-me) and 2.22 (s, 6H, *p*-me). Data for **2b** are as follow. Anal. Calcd for  $\text{C}_{55}\text{H}_{52}\text{Au}_2\text{AgAs}_2\text{F}_3\text{SO}_3$ : C, 44.00; H, 3.50; S, 2.15. Found: C, 43.80; H, 3.10; S, 1.95.  $\Lambda_{\text{M}}$ : 127  $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ .  $^1\text{H}$  NMR:  $\delta = 7.6$ –7.2 (m, 30H, Ph), 6.91 (s, 4H, H-*m*), 2.45 (s, 12H, *o*-me), and 2.23 (s, 6H, *p*-me).

$[\{\text{Au}(\mu\text{-mes})\text{L}\}_2\text{Cu}]\text{PF}_6$  [ $\text{L} = \text{PPh}_3$  (**3**),  $\text{AsPh}_3$  (**4**)]. To a dichloromethane (30  $\text{cm}^3$ ) solution of  $[\text{Au}(\text{mes})\text{PPh}_3]$  (0.1157 g, 0.2 mmol) or  $[\text{Au}(\text{mes})\text{AsPh}_3]$  (0.1245 g, 0.2 mmol) was added a solution of  $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{PF}_6$  (0.0372 g, 0.1 mmol) in dichloromethane (10  $\text{cm}^3$ ). The reactions were carried out at 0  $^\circ\text{C}$ . After 15 min of stirring, the slightly yellow solutions

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were concentrated to ca. 5 cm<sup>3</sup>. Addition of *n*-hexane (20 cm<sup>3</sup>) gave **3** and **4** as white solids. Yield (%): 62 (**3**), 82 (**4**). Data for **3** are as follow. Anal. Calcd for C<sub>54</sub>H<sub>52</sub>P<sub>2</sub>Au<sub>2</sub>CuPF<sub>6</sub>: C, 47.50; H, 3.85. Found: C, 47.15; H, 3.65.  $\Lambda_M$ : 129  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>. <sup>1</sup>H NMR:  $\delta$  = 7.6–7.2 (m, 30H, Ph), 6.80 (s, 4H, H-*m*), 2.35 (s, 12H, *o*-me), and 2.12 (s, 6H, *p*-me). <sup>31</sup>P NMR:  $\delta$  = 43.7 (s) (Au–P) and –144.1 (sep, <sup>1</sup>J<sub>P–F</sub> = 713.3 Hz). Data for **4** are as follow. Anal. Calcd for C<sub>54</sub>H<sub>52</sub>As<sub>2</sub>Au<sub>2</sub>CuPF<sub>6</sub>: C, 44.65; H, 3.60. Found: C, 44.15; H, 3.65.  $\Lambda_M$ : 135  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>. <sup>1</sup>H NMR:  $\delta$  = 7.6–7.2 (m, 30H, Ph), 6.84 (s, 4H, H-*m*), 2.38 (s, 12H, *o*-me) and 2.28 (s, 6H, *p*-me). <sup>31</sup>P NMR:  $\delta$  = –144.1 (sep, <sup>1</sup>J<sub>P–F</sub> = 713.3 Hz).

[AuAg( $\mu$ -mes)(PPh<sub>3</sub>)L]SO<sub>3</sub>CF<sub>3</sub> [L = PPh<sub>3</sub> (**5**), tht (**6**), bipy (**7**), SPPPh<sub>3</sub> (**8**)]. To dichloromethane solutions of **1** (0.1414 g, 0.1 mmol) were added PPh<sub>3</sub> (0.0262 g, 0.1 mmol), tht (8.82  $\mu$ L, 0.1 mmol), bipy (0.0156 g, 0.1 mmol), and SPPPh<sub>3</sub> (0.0294 g, 0.1 mmol). The mixtures were stirred for 20 min and the solutions concentrated to ca. 5 cm<sup>3</sup>. Addition of *n*-hexane (20 cm<sup>3</sup>) (**5**, **6**) or diethyl ether (20 cm<sup>3</sup>) (**7**, **8**) gave the corresponding complexes as white solids. Yields (%): 82 (**5**), 95 (**6**), 73 (**7**), 56 (**8**). Data for **5** are as follow. Anal. Calcd for C<sub>38</sub>H<sub>34</sub>AuAgN<sub>2</sub>PF<sub>3</sub>SO<sub>3</sub>: C, 46.05; H, 3.45; N, 2.80; S, 3.25. Found: C, 45.85; H, 3.40; N, 2.85; S, 3.05.  $\Lambda_M$  = 122  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>. <sup>1</sup>H NMR:  $\delta$  = 8.39 (dd, 2H, H<sub>3</sub> bipy), 8.18 (dd, 2H, H<sub>6</sub> bipy), 8.05 (td, 2H, H<sub>5</sub> bipy); 7.6–7.2 (m, 15H, Ph); td, 2H, H<sub>4</sub> bipy); 7.13 (s, 2H, H-*m*), 2.70 (s, 6H, *o*-me), 2.37 (s, 3H, *p*-me). <sup>31</sup>P NMR:  $\delta$  = 44.1 (s). Data for **8** are as follow. Anal. Calcd for C<sub>46</sub>H<sub>41</sub>AuAgP<sub>2</sub>S<sub>2</sub>F<sub>3</sub>O<sub>3</sub>: C, 48.90; H, 3.65; S, 5.70. Found: C, 49.10; H, 3.50; S, 5.20.  $\Lambda_M$  = 105  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>. <sup>1</sup>H NMR:  $\delta$  = 7.6–7.2 (m, 30H, Ph); 6.89 (s, 2H, H-*m*), 2.46 (s, 6H, *o*-me), and 2.25 (s, 3H, *p*-me). <sup>31</sup>P NMR at –55 °C:  $\delta$  = 45.8 (s) (Au–P) and 37.17 (d, br) (Ag–SP) <sup>3</sup>J<sub>Ag–P</sub> = 78.1 Hz.

[AuAg( $\mu$ -mes)(AsPh<sub>3</sub>)<sub>2</sub>]SO<sub>3</sub>CF<sub>3</sub> (**9**). To a dichloromethane solution of **2b** (0.1502 g, 0.1 mmol) was added AsPh<sub>3</sub> (0.0306 g, 0.1 mmol). After 20 min of stirring, the transparent solution was concentrated to ca. 5 cm<sup>3</sup>. Addition of *n*-hexane (20 cm<sup>3</sup>) gave **9** as a white solid. Yield (%): 99 (**9**). Anal. Calcd for C<sub>46</sub>H<sub>41</sub>AuAgAs<sub>2</sub>F<sub>3</sub>SO<sub>3</sub>: C, 46.60; H, 3.50; S, 2.70. Found: C, 46.20; H, 3.30; S, 2.20.  $\Lambda_M$  = 110  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>. <sup>1</sup>H NMR:  $\delta$  = 7.6–7.2 (m, 30H, Ph); 6.92 (s, 2H, H-*m*), 2.55 (s, 6H, *o*-me) and 2.26 (s, 3H, *p*-me).

[Au<sub>2</sub>Ag<sub>2</sub>( $\mu$ -mes)<sub>2</sub>(AsPh<sub>3</sub>)<sub>2</sub>(Ph<sub>2</sub>AsCH<sub>2</sub>AsPh<sub>2</sub>)](ClO<sub>4</sub>)<sub>2</sub> (**10**). To a dichloromethane solution of **2a** (0.2179 g, 0.15 mmol) was added Ph<sub>2</sub>AsCH<sub>2</sub>AsPh<sub>2</sub> (0.0345 g, 0.075 mmol). After being stirred for 30 min, the solution was concentrated to 5 cm<sup>3</sup>. Addition of diethyl ether (20 cm<sup>3</sup>) resulted in the precipitation of **10** as a white solid. Yield (%): 85 (**10**). Anal. Calcd for C<sub>79</sub>H<sub>74</sub>Au<sub>2</sub>Ag<sub>2</sub>As<sub>4</sub>Cl<sub>2</sub>O<sub>8</sub>: C, 44.50; H, 3.50. Found: C, 44.95; H, 3.40.  $\Lambda_M$  = 206  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>. <sup>1</sup>H NMR:  $\delta$  = 7.6–7.2 (m, 45H, Ph); 6.99 (s, 4H, H-*m*), 2.63 (s, 12H, *o*-me), 2.31 (s, 6H, *p*-me); 4.01 (s, 2H, CH<sub>2</sub>).

**X-ray Structure Determination.** Numerical data are summarized in Table 2. The crystal was mounted in inert oil on a glass fiber. Data were collected using monochromated Mo K $\alpha$  radiation ( $\lambda$  = 0.710 73 Å). A Siemens P4 diffractometer with LT-2 low-temperature attachment was used with scan type  $\omega$ . Cell constants were refined from the setting angles of 61 reflections in the  $2\theta$  range 6–25°. An absorption correction was applied on the basis of  $\psi$ -scans. The structure was solved by the heavy-atom method and refined on  $F^2$  (program SHELXL-93)<sup>37</sup> anisotropically for the heaviest atoms.

**Table 2.** Details of Data Collection and Structure Refinement for Complex **2a**

compd	<b>2a</b> : CH <sub>2</sub> Cl <sub>2</sub>
chem formula	C <sub>55</sub> H <sub>54</sub> AgAs <sub>2</sub> Au <sub>2</sub> Cl <sub>3</sub> O <sub>4</sub>
cryst habit	monoclinic
cryst size/mm	0.45 × 0.30 × 0.20
space group	C2/c
<i>a</i> /Å	20.634(2)
<i>b</i> /Å	21.431(2)
<i>c</i> /Å	15.7216(11)
$\beta$ /deg	121.992(5)
<i>V</i> /Å <sup>3</sup>	5896.2(7)
<i>Z</i>	4
<i>D<sub>c</sub></i> /Mg m <sup>-3</sup>	1.731
<i>M</i>	1536.97
<i>F</i> (000)	2952
<i>T</i> /°C	–100
$2\theta_{\max}$ /deg	50
$\mu$ (Mo K $\alpha$ )/mm <sup>-1</sup>	6.58
transm	0.785–0.937
no. of reflns measd	5208
no. of unique reflns	5059
<i>R</i> <sub>int</sub>	0.084
<i>R</i> <sup>a</sup> ( <i>F</i> , <i>F</i> > 4 $\sigma$ ( <i>F</i> ))	0.085
<i>wR</i> <sup>b</sup> ( <i>F</i> <sup>2</sup> , all reflns)	0.223
no. of params	125
no. of restraints	67
<i>S</i> <sup>c</sup>	1.089
max $\Delta\rho$ /e Å <sup>-3</sup>	2.24

<sup>a</sup>  $R(F) = \sum ||F_o| - |F_c|| / \sum |F_o|$ . <sup>b</sup>  $wR(F^2) = [\sum \{w(F_o^2 - F_c^2)^2\} / \sum \{w(F_o^2)^2\}]^{0.5}$ ;  $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$ , where  $P = [F_o^2 + 2F_c^2] / 3$  and *a* and *b* are constants adjusted by the program. <sup>c</sup>  $S = [\sum \{w(F_o^2 - F_c^2)^2\} / (n - p)]^{0.5}$ , where *n* is the number of data and *p* the number of parameters.

The (assumed) perchlorate and two assumed chlorines of dichloromethane were assigned occupation factors of 0.5. They form part of an extensive region of featureless electron density and are probably completely disordered (except for the perchlorate chlorine). The perchlorate Cl–O bonds are far too short. An alternative refinement in *Cc* revealed one independent perchlorate chlorine only, with full occupation, but the refinement suffered from near-singularity effects (nonequality of chemically equivalent bonds, etc.). It is unlikely that X-ray methods alone can distinguish either the space group or the chemical nature of the disorder regions.

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**Supporting Information Available:** Tables of crystal data, data collection, and solution and refinement parameters, positional and *U* parameters, bond distances and angles, and anisotropic thermal parameters (7 pages). Ordering information is given on any current masthead page.

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