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## Syntheses and reactivity of acetylide-containing clusters of Group 1B metals

### VIII \* Preparation, characterization and possible structure of a novel pentanuclear trimetallic cluster $[\text{Au}_3\text{AgCu}(\text{C}_2\text{Ph})_6]^-$ . Reactions of pentanuclear and trinuclear acetylide complexes

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#### Abstract

The novel pentanuclear trimetallic cluster  $[\text{Au}_3\text{AgCu}(\text{C}_2\text{Ph})_6]^-$  has been prepared by the reactions of  $[\text{Au}_3\text{Cu}_2(\text{C}_2\text{Ph})_6]^-$  with a mixture of gold phenylacetylide and silver phenylacetylide, of  $[\text{Au}_3\text{Ag}_2(\text{C}_2\text{Ph})_6]^-$  with  $[\{\text{AuCu}(\text{C}_2\text{Ph})_2\}_n]$ , or of  $[\text{Au}_2\text{Cu}(\text{C}_2\text{Ph})_4]^-$  with  $[\{\text{AuAg}(\text{C}_2\text{Ph})_2\}_n]$ . Its possible structure is discussed. The conversion of the pentanuclear clusters  $[\text{Au}_3\text{Cu}_2(\text{C}_2\text{Ph})_6]^-$  and  $[\text{Au}_3\text{Ag}_2(\text{C}_2\text{Ph})_6]^-$  into the high polynuclearity trimetallic cluster  $[\text{AuAg}_6\text{Cu}_6(\text{C}_2\text{Ph})_{14}]^-$  and of  $[\text{Ag}_4\text{Cu}(\text{C}_2\text{Ph})_6]^-$  into the complex  $[\text{Ag}_6\text{Cu}_7(\text{C}_2\text{Ph})_{14}]^-$  is described. The reactions of  $[\text{Au}_2\text{Cu}(\text{C}_2\text{Ph})_4]^-$  with  $\text{PPh}_3$ ,  $\text{P}(\text{OMe})_3$ , and  $\text{CuCl}$ , and those of  $[\text{Au}_2\text{CuCl}(\text{C}_2\text{Ph})_4]^{2-}$  with  $[\{\text{AuCu}(\text{C}_2\text{Ph})_2\}_n]$ , a mixture of  $[\{\text{Ag}(\text{C}_2\text{Ph})\}_n]$  and  $[\{\text{Cu}(\text{C}_2\text{Ph})\}_n]$ , and  $\text{CuCl}$  are reported.

#### Introduction

We previously described [1] the syntheses and characterization of the novel pentanuclear clusters  $[\text{Ag}_5(\text{C}_2\text{Ph})_6]^-$  and  $[\text{Ag}_4\text{Cu}(\text{C}_2\text{Ph})_6]$ . Both species, the mixed-metal polymer complexes  $[\{\text{AuAg}(\text{C}_2\text{Ph})_2\}_n]$  and  $[\{\text{AuCu}(\text{C}_2\text{Ph})_2\}_n]$ , and the trimetallic cluster  $[\text{AuAg}_6\text{Cu}_6(\text{C}_2\text{Ph})_{14}]^-$ , represent the most recent development in the chemistry of arylacetylide-containing clusters of Group 1B metals [2,3]. We now describe some further advances in this field.

\* Part VII: ref. 1

## Results and discussion

### *Trimetallic pentanuclear cluster $[Au_3AgCu(C_2Ph)_6]^-$*

The role of  $[M(C_2Ph)_2]^-$  ( $M = Au, Cu$ ) in the formation of the high polynuclearity clusters  $[MAg_6Cu_6(C_2Ph)_{14}]^-$  was ascribed [3,4] to the anionic nature of the linear complex and to the absence of sterical crowding. The pentanuclear clusters  $[Au_3M_2(C_2Ph)_6]^-$  ( $M = Ag, Cu$ ) are suitable, at least in theory, to serve as starting points for clusters of higher nuclearity. Both are anionic, and their gold moieties are linear, thus leaving ample room for expansion of the cluster. We found that the reaction of  $[Au_3Cu_2(C_2Ph)_6]^-$  with a mixture of  $[\{Au(C_2Ph)\}_n]$  and  $[\{Ag(C_2Ph)\}_n]$  in 1:1:1 mol ratio in acetone at room temperature in the presence of pyridine did not give a cluster of higher nuclearity, and instead, we obtained the novel (yellow with a green tinge) trimetallic pentanuclear cluster  $[Au_3AgCu(C_2Ph)_6]^-$  in high yield. It was characterized by the usual methods. Its elemental analysis and  $^1H$  NMR spectrum are wholly consistent with the assigned formula. The IR spectrum contained two unresolved weak bands at ca 2084 and 2074  $cm^{-1}$ . The  $\nu(C\equiv C)$  band for the cluster  $[Au_3Ag_2(C_2Ph)_6]^-$  appears at ca 2082  $cm^{-1}$ , a frequency higher by ca 10  $cm^{-1}$  than, that of the corresponding band in the analogous cluster  $[Au_3Cu_2(C_2Ph)_6]^-$  [5]. The two bands in the IR spectrum of the complex can be assigned to asymmetrical alkyne groups  $\pi$ -bonded to silver and copper, respectively. It is well known that gold has a greater tendency to show linear coordination than silver and copper [6]. It is likely, therefore, that the complex has a trigonal bipyramidal structure, similar to that of  $[Au_3Cu_2(C_2Ph)_6]^-$  and  $[Au_3Ag_2(C_2Ph)_6]^-$ , with gold atoms occupying equatorial positions and silver and copper in apical positions playing similar roles. This complex and the cluster  $[AuAg_6Cu_6(C_2Ph)_{14}]^-$  are the only trimetallic complexes containing the three coinage metals to be reported to date.

It is likely that the pentanuclear cluster  $[Au_3Cu_2(C_2Ph)_6]^-$  expands into an unstable intermediate of higher nuclearity. The latter then dissociates into the trimetallic pentanuclear cluster. An alternative route, involving the dissociation of  $[Au_3Cu_2(C_2Ph)_6]^-$  into the trinuclear complex  $[Au_2Cu(C_2Ph)_4]^-$  in the presence of pyridine, with subsequent reaction of the latter complex with  $[\{Au(C_2Ph)\}_n]$  and  $[\{Ag(C_2Ph)\}_n]$  to give the trimetallic complex, cannot be ruled out.

The same complex can also be obtained by reaction of the analogous gold-silver pentanuclear cluster  $[Au_3Ag_2(C_2Ph)_6]^-$  with the polymer complex  $[\{AuCu(C_2Ph)_2\}_n]$  in 1:1 mol ratio in the absence of pyridine.

A third method for the preparation of the same cluster involves the reaction between the trinuclear cluster  $[Au_2Cu(C_2Ph)_4]^-$  and the polymer complex  $[\{AuAg(C_2Ph)_2\}_n]$  in 1:1 mol ratio in the absence of pyridine. In all cases the product was identified by the usual methods.

### *Reaction between the bimetallic pentanuclear cluster $[Au_3Cu_2(C_2Ph)_6]^-$ and a mixture of $[\{Ag(C_2Ph)\}_n]$ and $[\{Cu(C_2Ph)\}_n]$*

The reaction between the above compounds in 1:4:4 mol ratio in acetone at room temperature afforded the orange-red trimetallic cluster  $[AuAg_6Cu_6(C_2Ph)_{14}]^-$ , the pentanuclear cluster  $[Au_3Ag_2(C_2Ph)_6]^-$ , and the linear complex  $[Au(C_2Ph)_2]^-$ . All these complexes were identified by the usual methods and by comparison with

authentic samples [3,5,7]. In this reaction the bimetallic gold–copper cluster is converted into a high polynuclearity trimetallic cluster, which belongs to another class of clusters between Group 1B metal arylacetylides [2,3].

Addition of copper phenylacetylide alone to the pentanuclear cluster  $[\text{Au}_3\text{Cu}_2(\text{C}_2\text{Ph})_6]^-$  did not result in reaction. On the other hand, addition of silver phenylacetylide alone to the same cluster caused an immediate change of colour from yellow to orange-red. Apparently,  $[\text{Au}_3\text{Cu}_2(\text{C}_2\text{Ph})_6]^-$  is not stable in the presence of  $[\{\text{Ag}(\text{C}_2\text{Ph})\}_n]$ . The latter complex is likely to ethynylate the copper in the cluster, causing its breakdown. This could result in the formation of copper phenylacetylide, the linear complex  $[\text{Au}(\text{C}_2\text{Ph})_2]^-$ , and the gold silver polymer complex  $[\{\text{AuAg}(\text{C}_2\text{Ph})_2\}_n]$ . The linear anionic complex could then react with the added silver phenylacetylide and the copper phenylacetylide produced to form the trimetallic cluster  $[\text{AuAg}_6\text{Cu}_6(\text{C}_2\text{Ph})_{14}]^-$  [3]. The reaction of the linear gold complex with the Au–Ag polymer complex results in the formation of the pentanuclear cluster  $[\text{Au}_3\text{Ag}_2(\text{C}_2\text{Ph})_6]^-$  [1]. The objective of using a high molar ratio of copper and silver polymers was to obtain higher yields of the high polynuclearity cluster. The structure of the complex  $[\text{Ag}_6\text{Cu}_7(\text{C}_2\text{Ph})_{14}]^-$  indicates [4] that silver ethynylates copper, and is consistent with above suggestion.

*Reaction between the bimetallic pentanuclear cluster  $[\text{Au}_3\text{Ag}_2(\text{C}_2\text{Ph})_6]^-$  and  $[\{\text{Ag}(\text{C}_2\text{Ph})\}_n]$  and  $[\{\text{Cu}(\text{C}_2\text{Ph})\}_n]$*

Addition of copper phenylacetylide to the above pentanuclear cluster did not result in reaction. On the other hand, the reaction between the above three reagents in 1 : 6 : 6 mol ratio afforded the two trimetallic clusters  $[\text{AuAg}_6\text{Cu}_6(\text{C}_2\text{Ph})_{14}]^-$  and  $[\text{Au}_3\text{AgCu}(\text{C}_2\text{Ph})_6]^-$ . We concluded that the presence of silver phenylacetylide is essential for the conversion of the  $\text{Au}_3\text{Ag}_2$  cluster into the  $\text{AuAg}_6\text{Cu}_6$  complex. Both clusters were identified by the usual methods and comparison with authentic samples. We suggest that in this case decomposition of the pentanuclear cluster into  $[\text{Au}(\text{C}_2\text{Ph})_2]^-$  and  $[\{\text{AuAg}(\text{C}_2\text{Ph})_2\}_n]$  in the presence of  $[\{\text{Ag}(\text{C}_2\text{Ph})\}_n]$  and  $[\{\text{Cu}(\text{C}_2\text{Ph})\}_n]$  leads to the formation of  $[\text{AuAg}_6\text{Cu}_6(\text{C}_2\text{Ph})_{14}]^-$ . An alternative route for this reaction and an additional path for the preceding one can be envisaged as involving expansion of the pentanuclear cluster about gold. The anionic nature of the complex and the ample space available allow such expansion, which could lead ultimately to formation of the  $[\text{AuAg}_6\text{Cu}_6(\text{C}_2\text{Ph})_{14}]^-$  complex. Furthermore, the conditions required for formation of a trimetallic pentanuclear cluster are available, i.e. the gold complexes, pentanuclear cluster, silver, and copper phenylacetylides are present in excess in the reaction mixture.

*Reaction between the bimetallic pentanuclear cluster  $[\text{Ag}_4\text{Cu}(\text{C}_2\text{Ph})_6]^-$  and the silver–copper polymer complex  $[\{\text{AgCu}(\text{C}_2\text{Ph})_2\}_n]$*

We tried to expand the cluster by using the recently obtained polymer complex  $[\{\text{AgCu}(\text{C}_2\text{Ph})_2\}_n]$  [8] in 1 : 4 molar ratio in order to get a high polynuclearity cluster with a stoichiometry different from that of  $[\text{Ag}_6\text{Cu}_7(\text{C}_2\text{Ph})_{14}]^-$ . When the reaction was carried out in dichloromethane  $[\text{Ag}_6\text{Cu}_7(\text{C}_2\text{Ph})_{14}]^-$  was formed along with four equivalents of silver phenylacetylide. We could not decide whether expansion of the pentanuclear cluster was followed by release of silver phenylacetylide or silver phenylacetylide was first lost to leave  $[\text{Cu}(\text{C}_2\text{Ph})_2]^-$ . The latter is known to react with the mixed polymer to give  $[\text{Ag}_6\text{Cu}_7(\text{C}_2\text{Ph})_{14}]^-$  [8].

*Reactions of the trinuclear cluster  $[Au_2Cu(C_2Ph)_4]^-$*

The reaction of the trinuclear cluster with  $PPh_3$  in 1 : 2 mol ratio in acetone gave three products. The first one separated out during the reaction and was identified as  $[Cu(C_2Ph)PPh_3]$ . The second product was the linear complex  $[N(PPh_3)_2][Au(C_2Ph)_2]$  and the third  $[Au(C_2Ph)PPh_3]$ . It is noteworthy that the reaction of  $[AuCu(C_2Ph)_n]$  with  $PPh_3$  in 1 : 2 mol ratio afforded  $[Cu(C_2Ph)PPh_3]$  as the first crop and  $[Au(C_2Ph)PPh_3]$  as the second product [2]. These results are consistent with the view that  $[Au_2Cu(C_2Ph)_4]^-$  is composed of the moieties  $[Au(C_2Ph)_2]^-$  and  $[AuCu(C_2Ph)_2]$ .

The reaction of the trinuclear cluster with  $P(OMe)_3$  proceeded in a way more or less similar way to the previous reaction, but the complex  $[Au(C_2Ph)_2]^-$  was the only isolable product. Several attempts to obtain other products from the residual sticky solid failed.

When copper(I) chloride was employed with the same cluster in 1 : 1 molar ratio, the pentanuclear cluster  $[Au_3Cu_2(C_2Ph)_6]^-$  was the only product isolated.

*Reactions of the trinuclear complex  $[Au_2CuCl(C_2Ph)_4]^{2-}$*

The reaction of this complex, which was reported recently [5], with the polymer complex  $[AuCu(C_2Ph)_2]_n$  in 1 : 2 molar ratio gave the cluster  $[Au_3Cu_2(C_2Ph)_6]^-$  in very high yield. When a mixture of silver phenylacetylide and copper phenylacetylide was employed, the trimetallic cluster  $[AuAg_6Cu_6(C_2Ph)_{14}]^-$  was isolated in good yields and identified by the usual methods.

Use of copper(I) chloride with the same trinuclear complex in 1 : 1 molar ratio afforded the complex  $[Au_3Cu_2(C_2Ph)_6]^-$  and off-white woolly crystals, which could not be identified.

## Experimental

Experimental procedures were as described previously [1]. The complexes  $[Au_3Cu_2(C_2Ph)_6]^-$ ,  $[Au_2Cu(C_2Ph)_4]^-$ ,  $[Au_3Ag_2(C_2Ph)_6]^-$ ,  $[Au_2CuCl(C_2Ph)_4]^{2-}$ ,  $[AuAg(C_2Ph)_2]_n$ ,  $[AuCu(C_2Ph)_2]_n$ ,  $[Ag_4Cu(C_2Ph)_6]^-$  were prepared by published methods 1,2,5.

*Preparation of complex  $[Au_3AgCu(C_2Ph)_6]^-$*

(a) *By reaction between  $[NBu^*_4][Au_3Cu_2(C_2Ph)_6]$  and a mixture of  $[Au(C_2Ph)]_n$  and  $[Ag(C_2Ph)]_n$ .* Gold phenylacetylide (0.060 g, 0.2 mmol) was added to a solution of  $[NBu^*_4][Au_3Cu_2(C_2Ph)_6]$  (0.313 g, 0.2 mmol) in acetone (15 cm<sup>3</sup>) containing pyridine (0.1 cm<sup>3</sup>). A clear solution was obtained. Silver phenylacetylide (0.042 g, 0.2 mmol) was added with stirring and a yellow precipitate separated within two minutes. The solution was filtered after 1 h to leave a yellow precipitate (0.070 g). Addition of hexane (30 cm<sup>3</sup>) to the filtrate gave a yellow-green solid (0.285 g). Recrystallization from acetone/hexane afforded  $[NBu^*_4][Au_3AgCu(C_2Ph)_6]$  (0.180 g, 56%), m.p. 165–168°C. (Found: C, 47.45; H, 3.65; Ag, 7.1;  $C_{64}H_{66}AgAu_3CuN$  requires C, 47.7; H, 4.1; Ag, 6.7%.)  $\nu_{max}$  (Nujol) 2084w and 2074w cm<sup>-1</sup> (C≡C). The <sup>1</sup>H spectrum [(CD<sub>3</sub>)<sub>2</sub>CO] showed complex resonances at  $\delta$  7.06, 3.47, 1.85, 1.45, and 0.96 with integration ratio 30 : 8 : 8 : 8 : 12.

(b) *By reaction of  $[NBu^*_4][Au_3Ag_2(C_2Ph)_6]$  with  $[AuCu(C_2Ph)_2]_n$ .* Gold-copper polymer complex (0.102 g, 0.22 mmol) was added to a solution of

[NBu<sup>n</sup><sub>4</sub>][Au<sub>3</sub>Ag<sub>2</sub>(C<sub>2</sub>Ph)<sub>6</sub>] (0.364 g, 0.22 mmol) in acetone (30 cm<sup>3</sup>). Stirring was continued for 1 h. Filtration left a yellow solid (0.095 g). Addition of hexane (20 cm<sup>3</sup>) to the filtrate gave yellow-green crystals of [NBu<sup>n</sup><sub>4</sub>][Au<sub>3</sub>AgCu(C<sub>2</sub>Ph)<sub>6</sub>] (0.265 g, 75%), m.p. 165 °C,  $\nu_{\max}$  (Nujol) 2084w and 2074w cm<sup>-1</sup> (C≡C). (Found: C, 47.5; H, 4.2; Cu, 2.55. C<sub>64</sub>H<sub>66</sub>AgAu<sub>3</sub>CuN requires Cu, 3.95%.)

(c) *By reaction of [N(PPh<sub>3</sub>)<sub>2</sub>][Au<sub>2</sub>Cu(C<sub>2</sub>Ph)<sub>4</sub>] with the polymer complex [{AuAg(C<sub>2</sub>Ph)<sub>2</sub>]<sub>n</sub>].* The gold-silver polymer complex (0.127 g, 0.25 mmol) was added to a solution of [N(PPh<sub>3</sub>)<sub>2</sub>][Au<sub>2</sub>Cu(C<sub>2</sub>Ph)<sub>4</sub>] (0.350 g, 0.25 mmol) in acetone (20 cm<sup>3</sup>). Stirring was continued for 2 h. Filtration and addition of hexane to the filtrate gave the yellow complex [N(PPh<sub>3</sub>)<sub>2</sub>][Au<sub>3</sub>AgCu(C<sub>2</sub>Ph)<sub>6</sub>] (0.385 g, 81%). m.p. 170 °C,  $\nu_{\max}$  (Nujol) 2084w and 2074w cm<sup>-1</sup> (C≡C). (Found: C, 52.7; H, 3.25; Ag, 6.85. C<sub>84</sub>H<sub>60</sub>AgAu<sub>3</sub>CuNP<sub>2</sub> requires C, 52.85; H, 3.15; Ag, 5.65%.)

*Reaction between [Au<sub>3</sub>Cu<sub>2</sub>(C<sub>2</sub>Ph)<sub>6</sub>]<sup>-</sup> and a mixture of [{Ag(C<sub>2</sub>Ph)}<sub>n</sub>] and [{Cu(C<sub>2</sub>Ph)}<sub>n</sub>]*

A mixture of silver phenylacetylide (0.209 g, 1.0 mmol) and copper phenylacetylide (0.165 g, 1.0 mmol) was added to a stirred solution of [NBu<sup>n</sup><sub>4</sub>][Au<sub>3</sub>Cu<sub>2</sub>(C<sub>2</sub>Ph)<sub>6</sub>] (0.392 g, 0.25 mmol) in acetone (30 cm<sup>3</sup>). The colour changed from yellow to orange and a yellow precipitate was formed. Stirring was continued for 2 h. The yellow precipitate was filtered off (0.33 g) (a mixture of polymers) and hexane (20 cm<sup>3</sup>) added to the filtrate to give orange-red crystals of [NBu<sup>n</sup><sub>4</sub>][AuAg<sub>6</sub>Cu<sub>6</sub>(C<sub>2</sub>Ph)<sub>14</sub>] (0.16 g, 33%), m.p. 180 °C (decomp.). (Found: C, 52.35; H, 3.39; Au, 6.9. C<sub>128</sub>H<sub>106</sub>Ag<sub>6</sub>AuCu<sub>6</sub>N requires C, 53.25; H, 3.7; Au, 6.85%) IR  $\nu_{\max}$  (Nujol) 2039w cm<sup>-1</sup> (C≡C). The second crop consisted of pale yellow crystals (0.145 g). Recrystallization gave crystals of [NBu<sup>n</sup><sub>4</sub>][Au<sub>3</sub>Ag<sub>2</sub>(C<sub>2</sub>Ph)<sub>6</sub>] (0.09 g, 33%), m.p. 175 °C (decomp.),  $\nu_{\max}$  (Nujol) 2082 cm<sup>-1</sup> (C≡C). (Found: C, 46.9; H, 3.8. C<sub>64</sub>H<sub>66</sub>Ag<sub>2</sub>Au<sub>3</sub>N requires C, 46.4; H, 4.0%.) Concentration of the filtrate from the second crop and addition of hexane gave white crystals of [NBu<sup>n</sup><sub>4</sub>][Au(C<sub>2</sub>Ph)<sub>2</sub>] (0.03 g, 28%),  $\nu_{\max}$  (Nujol) 2100s cm<sup>-1</sup> (C≡C), m.p. 125–127 °C, identical to an authentic sample [7].

*Reaction between [Au<sub>3</sub>Ag<sub>2</sub>(C<sub>2</sub>Ph)<sub>6</sub>]<sup>-</sup> and a mixture of [{Ag(C<sub>2</sub>Ph)}<sub>n</sub>] and [{Cu(C<sub>2</sub>Ph)}<sub>n</sub>]*

A mixture of the polymers (1.0 mmol each) was added to a stirred solution of [N(PPh<sub>3</sub>)<sub>2</sub>][Au<sub>3</sub>Ag<sub>2</sub>(C<sub>2</sub>Ph)<sub>6</sub>] (0.324 g, 0.166 mmol) in acetone (20 cm<sup>3</sup>). The colour changed from yellow to orange within 5 min. The mixture was stirred for 18 h and the yellow precipitate (0.328 g) then filtered off. Addition of hexane to the filtrate gave orange-red crystals (0.15 g). Recrystallization from acetone/hexane afforded [N(PPh<sub>3</sub>)<sub>2</sub>][AuAg<sub>6</sub>Cu<sub>6</sub>(C<sub>2</sub>Ph)<sub>14</sub>] (0.115 g, 22%) (found: C, 55.75; H, 2.9; Au, 6.1; C<sub>148</sub>H<sub>100</sub>Ag<sub>6</sub>AuCu<sub>6</sub>NP<sub>2</sub> requires C, 55.9; H, 3.15; Au, 6.2%), identical in all respects to an authentic sample [3]. Addition of hexane to the filtrate from the first crop precipitated a yellow solid (0.075 g). Recrystallization from acetone/hexane gave yellow crystals of [N(PPh<sub>3</sub>)<sub>2</sub>][Au<sub>3</sub>AgCu(C<sub>2</sub>Ph)<sub>6</sub>] (0.05 g, 15.8%),  $\nu_{\max}$  (Nujol) 2084, 2074 cm<sup>-1</sup> (C≡C), m.p. 170 °C (decomp.) (found: C, 52.5; H, 3.0; C<sub>84</sub>H<sub>60</sub>AgAu<sub>3</sub>CuNP<sub>2</sub> requires C, 52.85; H, 3.15%), identical to the authentic sample described above.

*Reaction between [CuAg<sub>4</sub>(C<sub>2</sub>Ph)<sub>6</sub>]<sup>-</sup> and [{AgCu(C<sub>2</sub>Ph)<sub>2</sub>]<sub>n</sub>]*

The complex polymer [{AgCu(C<sub>2</sub>Ph)<sub>2</sub>]<sub>n</sub> (0.374 g, 1.0 mmol) was added to a

stirred solution of the complex  $[\text{N}(\text{PPh}_3)_2][\text{CuAg}_4(\text{C}_2\text{Ph})_6]$  (0.41 g, 0.25 mmol) in dichloromethane (25 cm<sup>3</sup>). Stirring was continued for 1 h. The solvent was removed under vacuum and the residue was redissolved in acetone (30 cm<sup>3</sup>). The white solid residue of  $[\{\text{Ag}(\text{C}_2\text{Ph})\}_n]$  (0.135 g, 97%) was filtered off  $\nu_{\text{max}}$  (Nujol) 2054 cm<sup>-1</sup> (C≡C), identical in all respects to an authentic sample. Addition of hexane to the filtrate gave orange-red blocks of  $[\text{N}(\text{PPh}_3)_2][\text{Au}_6\text{Cu}_7(\text{C}_2\text{Ph})_{14}]$  (0.38 g, 75%) (found: C, 57.5; H, 3.29; C<sub>148</sub>H<sub>100</sub>Ag<sub>6</sub>Cu<sub>7</sub>NP<sub>2</sub> requires C, 58.35; H, 3.28%), IR  $\nu_{\text{max}}$  (Nujol) 2045 cm<sup>-1</sup>, identical to an authentic sample [3].

*Reactions of the trinuclear cluster  $[\text{Au}_2\text{Cu}(\text{C}_2\text{Ph})_4]^-$ .*

(a) *With triphenylphosphine.* The phosphine ligand (0.131 g, 0.5 mmol) was added to a stirred solution of  $[\text{N}(\text{PPh}_3)_2][\text{Au}_2\text{Cu}(\text{C}_2\text{Ph})_4]$  (0.35 g, 0.25 mmol) in acetone (20 cm<sup>3</sup>). A change in colour occurred and yellow green crystals separated within 5 min. Stirring was continued for 3 h. The precipitate was filtered off and identified as  $[\text{Cu}(\text{C}_2\text{Ph})\text{PPh}_3]$  (0.05 g, 46.9%), m.p. 205–208, lit. [9] 210–212 °C,  $\nu_{\text{max}}$  (Nujol) 2021 cm<sup>-1</sup> (C≡C). Addition of hexane (15 cm<sup>3</sup>) to the filtrate afforded white crystals of  $[\text{N}(\text{PPh}_3)_2][\text{Au}(\text{C}_2\text{Ph})_2]$  (0.23 g, 98%), which was identified in the usual way [7]. A third product was obtained by concentrating the filtrate from the second crop and adding hexane, and was identified as  $[\text{Au}(\text{C}_2\text{Ph})\text{PPh}_3]$  (0.065 g, 46%), m.p. 160–162, lit. [10] 164 °C,  $\nu_{\text{max}}$  (Nujol) 2113 cm<sup>-1</sup> (C≡C).

(b) *With (MeO)<sub>3</sub>P.* Trimethylphosphite (0.3 cm<sup>3</sup>) was added to a stirred solution of  $[\text{N}(\text{PPh}_3)_2][\text{Au}_2\text{Cu}(\text{C}_2\text{Ph})_4]$  (0.35 g, 0.25 mmol) in acetone (25 cm<sup>3</sup>). The mixture immediately became colourless. Stirring was continued for 10 min. Filtration and addition of hexane to the filtrate gave colourless crystals of  $[\text{N}(\text{PPh}_3)_2][\text{Au}(\text{C}_2\text{Ph})_2]$  (0.22 g, 94%) which was identified in the usual way. Several attempts to isolate additional product from the sticky material obtained as a second crop were unsuccessful.

(c) *With CuCl.* Copper(I) chloride (0.025 g, 0.25 mmol) was added to a solution of  $[\text{N}(\text{PPh}_3)_2][\text{Au}_2\text{Cu}(\text{C}_2\text{Ph})_4]$  (0.35 g, 0.25 mmol) in acetone (25 cm<sup>3</sup>). Stirring was continued for 18 h. A yellow precipitate (0.08 g) was filtered off. Addition of hexane (30 cm<sup>3</sup>) to the filtrate gave a yellow solid (0.125 g). Recrystallization using acetone/hexane afforded yellow crystals of  $[\text{N}(\text{PPh}_3)_2][\text{Au}_3\text{Cu}_2(\text{C}_2\text{Ph})_6]$  (0.09 g, 19%), which was identified in the usual way [5].

*Reactions of the trinuclear complex  $[\text{Au}_2\text{CuCl}(\text{C}_2\text{Ph})_4]^{2-}$*

(a) *With  $[\{\text{AuCu}(\text{C}_2\text{Ph})_2\}_n]$ .* The gold–copper polymer complex  $[\{\text{AuCu}(\text{C}_2\text{Ph})_2\}_n]$  (0.116 g, 0.25 mmol) was added to a suspension of  $[\text{N}(\text{PPh}_3)_2]_2[\text{Au}_2\text{CuCl}(\text{C}_2\text{Ph})_4]$  (0.247 g, 0.125 mmol) in acetone (35 cm<sup>3</sup>). Stirring was continued for 1 h, during which the colourless solution became yellow. Filtration and addition of hexane (26 cm<sup>3</sup>) gave yellow crystals of  $[\text{N}(\text{PPh}_3)_2][\text{Au}_3\text{Cu}_2(\text{C}_2\text{Ph})_6]$  (0.217 g, 93%), m.p. 173–175 °C,  $\nu_{\text{max}}$  (Nujol) 2075 cm<sup>-1</sup> (C≡C). The <sup>1</sup>H NMR spectrum  $[(\text{CD}_3)_2\text{CO}]$  showed two complex resonances at  $\delta$  7.68 and 7.08 with integration ratio 1 : 1. The product was identical with an authentic sample [5].

(b) *With a mixture of  $[\{\text{Ag}(\text{C}_2\text{Ph})\}_n]$  and  $[\{\text{Cu}(\text{C}_2\text{Ph})\}_n]$ .* A mixture of silver phenylacetylide (0.25 g, 1.195 mmol) and copper phenylacetylide (0.2 g, 1.22 mmol) was added to a suspension of  $[\text{N}(\text{PPh}_3)_2]_2[\text{Au}_2\text{CuCl}(\text{C}_2\text{Ph})_4]$  (0.2 g, 0.1 mmol) in acetone (25 cm<sup>3</sup>). Stirring was continued for 14 h. Filtration and addition of hexane to the filtrate gave  $[\text{N}(\text{PPh}_3)_2][\text{AuAg}_6\text{Cu}_6(\text{C}_2\text{Ph})_{14}]$  (0.15 g, 47%) (found: C, 55.55;

H, 3.1; N, 0.35;  $C_{148}H_{100}Ag_6AuCu_6NP_2$  requires C, 55.85; H 3.15; N, 0.45 %), identical with an authentic sample [3].

(c) *With CuCl*. Copper(I) chloride (0.025 g, 0.25 mmol) to a suspension of  $[N(PPh_3)_2]_2[Au_2CuCl(C_2Ph)_4]$  (0.493 g, 0.25 mmol). Stirring was continued for 18 h. Filtration and addition of hexane to the filtrate gave yellow crystals (0.245 g). Recrystallization from acetone/hexane afforded  $[N(PPh_3)_2][Au_3Cu_2(C_2Ph)_6]$  (0.16 g, 34%), identical with an authentic sample. The second crop from the reaction mixture was an off-white solid (0.13 g). Recrystallization gave woolly white crystals (0.05 g) (found: C, 62.25; H, 4.05%), IR  $\nu_{max}$  (Nujol) 2027w, 1989w  $cm^{-1}$  (C≡C), which developed a colour on standing, indicating there was some decomposition. The product could not be identified.

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