Syntheses and reactivity of acetylide-containing clusters of Group 1B Metals

VII *. Preparation and possible structures of the novel pentanuclear [Au$_3$Ag$_2$(C$_2$Ph)$_6$]$^-$, [Ag$_5$(C$_2$Ph)$_6$]$^-$, and [Ag$_4$Cu(C$_2$Ph)$_6$]$^-$ clusters. The reactivity of the polymer complexes [{AuAg(C$_2$Ph)$_2$}$_n$] and [{AuCu(C$_2$Ph)$_2$}$_n$]

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Abstract

The stepwise synthesis of the gold-silver pentanuclear cluster [Au$_3$Ag$_2$(C$_2$Ph)$_6$]$^-$ is described. The pentanuclear clusters [Ag$_5$(C$_2$Ph)$_6$]$^-$ and [Ag$_4$Cu(C$_2$Ph)$_6$]$^-$ are obtained by the reactions of silver phenylacetylide with, respectively, the linear silver complex anion [Ag(C$_2$Ph)$_2$]$^-$ and with its copper analogue. Their possible structures are discussed. Depending on the molar ratio of the reactants, the reaction of [Cu(C$_2$Ph)$_2$]$^-$ and [{AuCu(C$_2$Ph)$_2$}$_n$] affords the cluster [Au$_2$Cu(C$_2$Ph)$_4$]$^-$ or the complex [Au$_3$Cu$_2$(C$_2$Ph)$_6$]$^-$. Whereas the reaction of [Cu(C$_2$Ph)$_2$]$^-$ and [{AuAg(C$_2$Ph)$_2$}$_n$] gives [Au$_3$Ag$_2$(C$_2$Ph)$_6$]$^-$ and the trimetallic complex [AuAg$_6$Cu$_6$(C$_2$Ph)$_{14}$]$^-$, that between [Ag(C$_2$Ph)$_2$]$^-$ and the same polymer complex affords only [Au$_3$Ag$_2$(C$_2$Ph)$_6$]$^-$.

New aspects of Group 1B metal arylacetylides chemistry have been developed recently. The most interesting of these was the synthesis of several heteronuclear bimetallic and trimetallic clusters [1–6]. The preparation and crystal structure of the pentanuclear cluster [Au$_3$Cu$_2$(C$_2$Ph)$_6$]$^-$ have been reported recently [1]. That complex, the trinculear [Au$_2$Cu(C$_2$Ph)$_4$]$^-$, and the pentanuclear [Au$_3$Ag$_2$(C$_2$Ph)$_4$]$^-$ clusters were synthesized in stepwise procedures [2]. All these complexes belong to the same class of clusters. The neutral tetranuclear complex [Au$_2$Ag$_2$(C$_2$Ph)$_4$-

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* For part VI see ref. 4.

$(PPh_3)_2$], which was prepared through the reaction between [$Au(C_2Ph)PPh_3$] and [$\{Ag(C_2Ph)\}_n$], belongs to a second class of clusters between Group 1B Metals [3], and the polymer complexes [$\{AuAg(C_2Ph)_2\}_n$] and [$\{AuCu(C_2Ph)_2\}_n$] can be regarded as belonging to the same class [4]. The synthesis and crystal structure of the high polynuclear cluster [$Ag_6Cu_7(C_2Ph)_{14}$]$^-$, which was prepared by the reaction of [$Ag(C_2Ph)_2$]$^-$ or its copper analogue with a mixture of [$\{Ag(C_2Ph)\}_n$] and [$\{Cu(C_2Ph)\}_n$], have been reported [5]. This complex and the trimetallic analogue [$AuAg_6Cu_6(C_2Ph)_{14}$]$^-$ exhibit new bonding features, and so belong to a third class of clusters beween these metals [5,6].

Results and discussion

The heteronuclear cluster [$N(PPh_3)_2$][$Au_3Ag_2(C_2Ph)_6$] (1). The synthesis of complex **1** has been briefly reported [2], and we now give details of that synthesis. In contrast to copper phenylacetylide [2], addition of the silver analogue to [$N(PPh_3)_2$][$Au_2(C_2Ph)_3$] in 1/1 mol ratio did not give an isolable trinuclear cluster, but instead the pentanuclear cluster **1** and the linear gold complex [$N(PPh_3)_2$][$Au(C_2Ph)_2$].

$$[N(PPh_3)_2][Au_2(C_2Ph)_3] + [AgC_2Ph] \rightarrow$$
$$\tfrac{1}{2}[N(PPh_3)_2][Au_3Ag_2(C_2Ph)_6] + \tfrac{1}{2}[N(PPh_3)_2][Au(C_2Ph)_2]$$
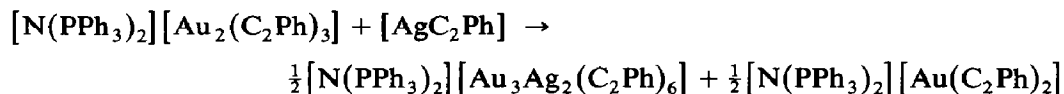
It seems that the gold–silver analogue of [$Au_2Cu(C_2Ph)_4$]$^-$ is not stable, disproportionating into complex **1** and the linear gold complex:

$$2[Au_2Ag(C_2Ph)_4]^- \rightarrow [Au_3Ag_2(C_2Ph)_6]^- + [Au(C_2Ph)_2]^-$$
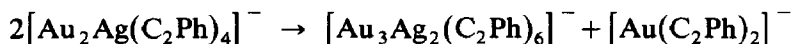
Similar results were obtained when the analogous tetrabutylammonium salt of the binuclear gold complex was treated with silver phenylacetylide or its copper analogue i.e. pentanuclear and not trinuclear complexes were isolated. It seems that the bulky bis(triphenylphosphine)iminium cation stabilizes the trinuclear cluster [$Au_2Cu(C_2Ph)_4$]$^-$. The trinuclear gold–silver analogue is apparently not stable with either cation.
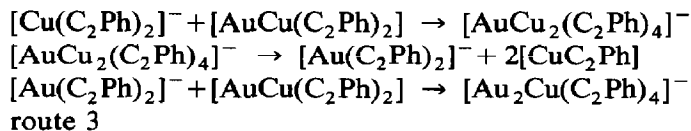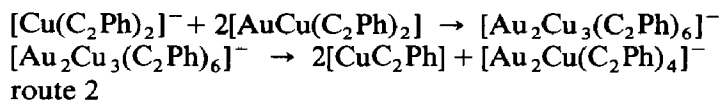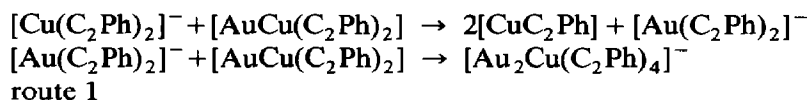
The separation of complex **1** from the linear complex [$Au(C_2Ph)_2$]$^-$ was hampered by their similar solubilities. We thus attempted to achieve high conversion to complex **1** by adding amounts of gold phenylacetylide and its silver analogue equivalent to the amount of [$Au(C_2Ph)_2$]$^-$ produced. The intention was to generate [$Au_2(C_2Ph)_3$]$^-$, which would then react with [$\{Ag(C_2Ph)\}_n$] to give **1**. However, quantitative conversion into complex **1** was not achieved, probably, because of reversible dissociation of **1** to the linear complex and the polymer complex [$\{AuAg(C_2Ph)_2\}_n$].

The homonuclear cluster [$Ag_5(C_2Ph)_6$]$^-$ (2). It was reported [2] recently that [$Au(C_2Ph)_2$]$^-$ depolymerizes [$\{Au(C_2Ph)\}_n$] to give a binuclear complex [$Au_2(C_2Ph)_3$]$^-$, believed to contain a gold–gold dative bond. The reaction of [$N(PPh_3)_2$][$Ag(C_2Ph)_2$] and [$\{Ag(C_2Ph)\}_n$] in 1/4 mole ratio in dichloromethane at room temperature afforded the white pentanuclear cluster [$N(PPh_3)_2$][$Ag_5(C_2Ph)_6$] (**2**) in moderate yield. The elemental analysis and ^{1}H NMR spectrum agree very well with the above formula. The spectrum showed two complex resonances (as in the case of [$N(PPh_3)_2$][$Au_3Cu_2(C_2Ph)_6$] and [$N(PPh_3)_2$][$Au_3Ag_2(C_2Ph)_6$]) at δ 7.66

(1) (2) (3)

and 7.11, with integration ratio 1/1, and these were assigned to the phenylphosphine and phenylacetylide protons, respectively. The IR spectrum contained a weak band at ca. 2064 cm^{-1}, assigned to asymmetrically π-bonded alkyne groups. This frequency is lower by ca. 20 cm^{-1} than that for the linear complex [Ag(C$_2$Ph)$_2$]$^-$. This lowering of ν(C≡C) is comparable to that observed (as a result of asymmetric π-bonding of silver) in the clusters [Au$_3$Ag$_2$(C$_2$Ph)$_6$]$^-$ (1) and [Au$_2$Ag$_2$(C$_2$Ph)$_4$(PPh$_3$)$_2$] [2,3]. We believe that complex 2 has a trigonal bipyramidal arrangement of silver atoms. Each one of the equatorial silver atoms is linearly coordinated end-on to two ethynyl ligands. The other two silver atoms are in apical positions, and each is asymmetrically π-bonded to three alkyne groups. The structure suggested for complex 2 is similar to that reported for the pentanuclear clusters [Au$_3$Cu$_2$(C$_2$Ph)$_6$]$^-$ and [Au$_3$Ag$_2$(C$_2$Ph)$_6$]$^-$ [1,2]. In the reaction used to prepare 2, two silver atoms are forced to ethynylate the other two atoms, a process that can be regarded as an 'autoethynylation'. Cationic and anionic moieties are condensed into the cluster, with the cationic entities taking up apical positions and anionic equatorial positions. The presence of two types of silver atoms in one complex is not unprecedented; the structure of [Ag(C$_2$Ph)PMe$_3$] involves cationic centres [Ag(Me$_3$P)$_2$]$^+$ as well as linear anionic moieties [Ag(C$_2$Ph)$_2$]$^-$ [7]. The silver atoms are at bonding distances from each other forming a linear chain of metal atoms. Each cationic silver is asymmetrically bonded side-on to two alkynyl ligands, one from each adjacent anion. The same kind of 'autoethynylation' can be considered to be involved in formation of this phosphine complex. Compared with those of gold(I), silver(I) and copper(I) complexes have a greater tendency to achieve a coordination number higher than two [8]. This is probably the reason for the low stability of homonuclear high nuclearity gold complexes of this kind, e.g. [Au$_3$(C$_2$Ph)$_4$]$^-$, [Au$_5$(C$_2$Ph)$_6$]$^-$ [2].

The heteronuclear silver-copper cluster [Ag$_4$Cu(C$_2$Ph)$_6$]$^-$ (3). The reaction between [Cu(C$_2$Ph)$_2$]$^-$ and [{Ag(C$_2$Ph)}$_n$] was carried out in 1/4 mole ratio under conditions similar to those used for 2. It gave the straw-coloured pentanuclear

silver-copper cluster $[Ag_4Cu(C_2Ph)_6]^-$ (3). Elemental analyses for C, H, Ag, and Cu and ^{1}H NMR agree very well with the above formula. The IR spectrum contained a weak band at ca. 2064 cm^{-1} assigned for asymmetric π-bonded alkyne. It is believed that the structure of 3 is similar to that of other pentanuclear clusters described above, with two silver atoms and the copper atom occupying equatorial positions and the other two silver atoms in apical positions. The structure implies that 'autoethynylation' of silver has taken place. This structure is favoured over the other possibility in which the copper and one silver are in apical positions, with the other three silver atoms in equatorial positions. The structure of the cluster $[Ag_6Cu_7(C_2Ph)_{14}]^-$ mentioned above reveals that silver phenylacetylide ethynylates copper phenylacetylide, i.e. it is the phenylethynyl ligand of silver which is transferred to copper and not the opposite [5,6]. Furthermore, in ethynylation reactions using the copper anionic complex $[Cu(C_2Ph)_2]^-$ and its silver analogue, one ethynyl ligand is transferred from the copper reagent while both ethynyl ligands are transferred from silver [9]. It is unlikely, therefore, that copper would lose both ethynyl ligands to two silver atoms and consequently be in an apical position.

The same copper anionic reagent $[Cu(C_2Ph)_2]^-$ did not react with $[\{Cu(C_2Ph)\}_n]$. Apparently, copper phenylacetylide is too a strong polymer to be deploymerized by the anionic reagent. Likewise, no reaction was observed when the gold reagent $[Au(C_2Ph)_2]^-$ was treated with the same copper polymer complex or the analogous p-tolylacetylide derivative [1,2].

The reaction between $[Cu(C_2Ph)_2]^-$ and gold-copper polymer complex $[\{AuCu-(C_2Ph)_2\}_n]$. We tried the reaction between $[Cu(C_2Ph)_2]^-$ and the mixed-metal polymer complex in 1/2 mol ratio in the hope of obtaining the cluster $[Au_2Cu_3(C_2Ph)_6]^-$, in which copper atoms are in different environments, i.e. two in apical positions and one in an equatorial position. Under the conditions used to give complexes 2 and 3, the reaction did not give the $[Au_2Cu_3(C_2Ph)_6]^-$ complex, but instead the copper complex polymer $[\{Cu(C_2Ph)\}_n]$ and the trinuclear cluster $[Au_2Cu(C_2Ph)_4]^-$ reported previously [2]. Both products were formed in very high yield. Three routes to the two products can be envisaged:

$[Cu(C_2Ph)_2]^- + [AuCu(C_2Ph)_2] \rightarrow 2[CuC_2Ph] + [Au(C_2Ph)_2]^-$
$[Au(C_2Ph)_2]^- + [AuCu(C_2Ph)_2] \rightarrow [Au_2Cu(C_2Ph)_4]^-$
route 1

$[Cu(C_2Ph)_2]^- + 2[AuCu(C_2Ph)_2] \rightarrow [Au_2Cu_3(C_2Ph)_6]^-$
$[Au_2Cu_3(C_2Ph)_6]^- \rightarrow 2[CuC_2Ph] + [Au_2Cu(C_2Ph)_4]^-$
route 2

$[Cu(C_2Ph)_2]^- + [AuCu(C_2Ph)_2] \rightarrow [AuCu_2(C_2Ph)_4]^-$
$[AuCu_2(C_2Ph)_4]^- \rightarrow [Au(C_2Ph)_2]^- + 2[CuC_2Ph]$
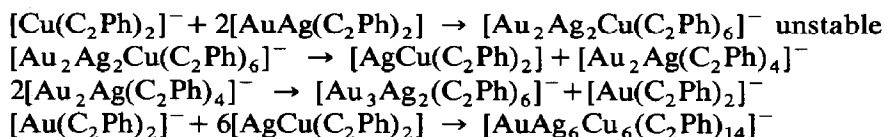$[Au(C_2Ph)_2]^- + [AuCu(C_2Ph)_2] \rightarrow [Au_2Cu(C_2Ph)_4]^-$
route 3

In route 1, the anionic copper complex is suggested to ethynylate the copper of one equivalent of the polymer, causing dissociation of copper from the mixed polymer as copper phenylacetylide and producing the anionic gold complex $[Au(C_2Ph)_2]^-$. The latter complex then reacts with the remaining one equivalent of the mixed

polymer to afford the trinuclear cluster $[Au_2Cu(C_2Ph)_4]^-$. In route 2, on the other hand, the expected complex $[Au_2Cu_3(C_2Ph)_6]^-$ dissociates irreversibly, giving two equivalents of copper phenylacetylide and the trinuclear cluster. We have reported [2] previously that neither $[Au(C_2Ph)_2]^-$ nor $[Au_2Cu(C_2Ph)_4]^-$ react with copper phenylacetylide, and that is why we have represented the dissociation of the suggested pentanuclear complex $[Au_2Cu_3(C_2Ph)_6]^-$ as being irreversible. An alternative path (route 3) related to both routes and involving the formation of an unstable trinuclear complex $[AuCu_2(C_2Ph)_4]^-$, which dissociates irreversibly into $[Au(C_2Ph)_2]^-$ and $2CuC_2Ph$, cannot be ruled out.

When the reaction between both reagents was carried out in 1/3 mole ratio, the pentanuclear cluster $[Au_3Cu_2(C_2Ph)_6]^-$ was the major product. In this case the presence of an additional equivalent of the polymer converted the trinuclear cluster into the pentanuclear cluster.

The reaction between $[Cu(C_2Ph)_2]^-$ and gold-silver polymer complex $[\{AuAg-(C_2Ph)_2\}_n]$. The aim of this reaction was to obtain a trimetallic cluster containing the three coinage metals in one complex, with gold and copper playing similar roles. When the reaction between both reagents in 1/2 mole ratio was carried out under the conditions described above, the bimetallic cluster $[Au_3Ag_2(C_2Ph)_6]^-$ (1) and the high nuclearity trimetallic complex $[AuAg_6Cu_6(C_2Ph)_{14}]^-$ were formed. Both products were identified by the usual method including comparison with authentic samples [2,6].

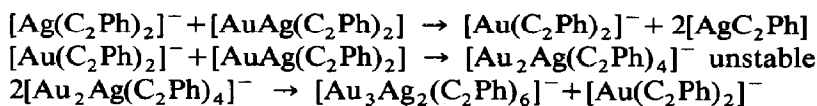A sequence similar to that in route 2 above can account for the formation of the two products, as follows:

$[Cu(C_2Ph)_2]^- + 2[AuAg(C_2Ph)_2] \rightarrow [Au_2Ag_2Cu(C_2Ph)_6]^-$ unstable
$[Au_2Ag_2Cu(C_2Ph)_6]^- \rightarrow [AgCu(C_2Ph)_2] + [Au_2Ag(C_2Ph)_4]^-$
$2[Au_2Ag(C_2Ph)_4]^- \rightarrow [Au_3Ag_2(C_2Ph)_6]^- + [Au(C_2Ph)_2]^-$
$[Au(C_2Ph)_2]^- + 6[AgCu(C_2Ph)_2] \rightarrow [AuAg_6Cu_6(C_2Ph)_{14}]^-$

We have noted above that $[Au_2Ag(C_2Ph)_4]^-$ is a possible intermediate during the formation of complex 1. It has also been shown that the reaction of $[Au(C_2Ph)_2]^-$ and silver-copper polymer complex $[\{AgCu(C_2Ph)_2\}_n]$, which we have recently prepared, affords the trimetallic cluster $[AuAg_6Cu_6(C_2Ph)_{14}]^-$ in very high yield [10].

The reaction between $[Ag(C_2Ph)_2]^-$ and gold-silver polymer complex $[\{AuAg(C_2 Ph)_2\}_n]$. Carrying out the reaction between the anionic silver complex and the mixed-metal polymer complex in 1/3 mol ratio resulted in the isolation of the pentanuclear cluster $[Au_3Ag_2(C_2Ph)_6]^-$ (1) in good yield.

This reaction may proceed through routes similar to those suggested above for related reactions:
$[Ag(C_2Ph)_2]^- + [AuAg(C_2Ph)_2] \rightarrow [Au(C_2Ph)_2]^- + 2[AgC_2Ph]$
$[Au(C_2Ph)_2]^- + [AuAg(C_2Ph)_2] \rightarrow [Au_2Ag(C_2Ph)_4]^-$ unstable
$2[Au_2Ag(C_2Ph)_4]^- \rightarrow [Au_3Ag_2(C_2Ph)_6]^- + [Au(C_2Ph)_2]^-$

In an independent reaction, it was found [10] that the reaction of $[Au(C_2Ph)_2]^-$ and $[\{AuAg(C_2Ph)_2\}_n]$ in 1/1 or 1/2 mole ratio afforded the pentanuclear cluster $[Au_3Ag_2(C_2Ph)_6]^-$.

Experimental

Spectra were recorded on Beckman Acculab 4 (IR) and JEOL JNM FX-100 (^{1}H NMR) spectrometers. Dichloromethane and hexane were dried and distilled before use. Acetone (AnalaR grade) was kept over molecular sieves and used without distillation. Reactions and work-up were carried out at room temperature under nitrogen. The complexes [{AuAg(C$_2$Ph)$_2$}$_n$], [{AuCu(C$_2$Ph)$_2$}$_n$], [Au(C$_2$Ph)$_2$]$^-$, [Ag(C$_2$Ph)$_2$]$^-$, and [Cu(C$_2$Ph)$_2$]$^-$ were prepared by published methods [4,9,11]. Elemental analyses were carried out at the Pascher's Microanalytical Laboratory, Remagen, West Germany.

Preparation of complex 1, [N(PPh$_3$)$_2$][Au$_3$Ag$_2$(C$_2$Ph)$_6$]. (a) Silver phenylacetylide (0.209 g, 1.0 mmol) was added to a solution of [Au$_2$(C$_2$Ph)$_3$]$^-$ prepared [2] in situ by adding gold phenylacetylide (0.298 g, 1.0 mmol) to a stirred solution of [N(PPh$_3$)$_2$][Au(C$_2$Ph)$_2$] (0.937 g, 1.0 mmol) in acetone (50 cm^3) containing pyridine (1.0 cm^3). The silver phenylacetylide dissolved within 2–3 min. More of the gold phenylacetylide and its silver analogue were added alternately to the reaction mixture with stirring, in amounts equivalent to the amount of [Au(C$_2$Ph)$_2$]$^-$ produced (0.5, 0.25, 0.125, 0.063 mmol). Stirring was continued for 10 min after the last addition. A yellow residue (0.307 g) was filtered off and identified as [{AuAg(C$_2$Ph)$_2$}$_n$], identical to an authentic sample described previously [4]. Addition of hexane to the filtrate gave pale yellow crystals of complex 1 (1.27 g, 65%) m.p. 175°C(decomp.), $\nu_{max.}$ (Nujol) 2082w cm^{-1}, identical in all respects to an authentic sample described previousely [2].

(b) Silver phenylacetylide (0.14 g, 0.666 mmol) was added with stirring to a solution of [Au$_2$(C$_2$Ph)$_3$]$^-$ (0.666 mmol), prepared as described above in acetone (20 cm^3) in the presence of pyridine (1.0 cm^3). The acetylide dissolved within 2–3 min. Filtration and addition of hexane resulted in precipitation of pale yellow flakes and white woolly crystals. Tedious manual separation followed by repeated recrystallization (acetone/hexane) of each type of crystals afforded pale yellow flakes of complex [1] (0.41 g, 31%) and white woolly crystals of [N(PPh$_3$)$_2$][Au(C$_2$Ph)$_2$] (0.175 g, 28%) identical in all respects to authentic samples.

Preparation of complex 2, [N(PPh$_3$)$_2$][Ag$_5$(C$_2$Ph)$_6$]. Silver phenylacetylide (0.418 g, 2.0 mmol) was added to [N(PPh$_3$)$_2$][Ag(C$_2$Ph)$_2$] (0.424 g, 0.5 mmol) in dichloromethane (25 cm^3). Stirring was continued for 30 min and the solvent then removed under vacuum. The residue was redissolved in acetone (20 cm^3) to leave uncharged silver phenylacetylide (0.125 g, 0.6 mmol). Addition of hexane (10 cm^3) to the filtrate gave white woolly crystals (0.60 g). Recrystallization from acetone/ hexane afforded white woolly crystals of complex 2, [N(PPh$_3$)$_2$][Ag$_5$(C$_2$Ph)$_6$] (0.450 g, 53%), m.p. 151–153°C (Found: C, 59.95; H, 3.6; Ag, 32.1. C$_{84}$H$_{60}$Ag$_5$NP$_2$ calcd.: C, 59.85; H, 3.55; Ag, 32.05%), $\nu_{max.}$ (Nujol) 2064w cm^{-1} (C≡C); the ^{1}H NMR spectrum [(CD$_3$)$_2$CO] showed two complex resonances at δ 7.66 and 7.11 with intensity ratio 1/1.

Preparation of complex 3, [N(PPh$_3$)$_2$][Ag$_4$Cu(C$_2$Ph)$_6$]. Silver phenylacetylide (0.836 g, 4.0 mmol) was added to [N(PPh$_3$)$_2$][Cu(C$_2$Ph)$_2$] (0.804 g, 1.0 mmol) in dichloromethane (25 cm^3). The colour changed to orange. Stirring was continued for 10 min and the solvent then evaporated to dryness. Crystallization from acetone/ hexane afforded straw-yellow woolly crystals of complex 3, [N(PPh$_3$)$_2$][Ag$_4$Cu-(C$_2$Ph)$_6$] (1.210 g, 74%), m.p. 145–147°C (Found: C, 61.25; H, 3.70; Ag, 27.9; Cu, 2.75. C$_{84}$H$_{60}$Ag$_4$CuNP$_2$ calcd.: C, 61.50; H, 3.65; Ag, 26.3; Cu, 3.85%), $\nu_{max.}$ (Nujol)

2064w cm^{-1} (C≡C); the ^{1}H NMR spectrum showed two complex resonances at δ 7.68 and 7.11 with intensity ratio 1/1.

Reaction between [N(PPh$_3$)$_2$][Cu(C$_2$Ph)$_2$] *and* [{AuCu(C$_2$Ph)$_2$}$_n$]. (a) The gold-copper polymer complex (0.463 g, 1.0 mmol) was added to a stirred solution of [N(PPh$_3$)$_2$][Cu(C$_2$Ph)$_2$] (0.402 g, 0.5 mmol) in dichloromethane (20 cm^3). Stirring was continued for 15 min and the mixture then evaporated to dryness. The residue was extracted with acetone (20 cm^3) to leave a yellow precipitate identified as [{Cu(C$_2$Ph)}$_n$] (0.163 g, 99%). Addition of hexane (12 cm^3) to the filtered extract gave yellow woolly crystals of [N(PPh$_3$)$_2$][Au$_2$Cu(C$_2$Ph)$_4$] (0.500 g, 71.5%), m.p. 145°C lit. [2] 143–145°C, $\nu_{max.}$ (Nujol) 2105m (sh) and 2070w cm^{-1} (C≡C). The ^{1}H NMR [(CD$_3$)$_2$CO] showed two complex resonances at δ 7.68 and 7.08 with intensity ratio 3/2.

(b) The gold-copper polymer (0.347 g, 0.75 mmol) was added to a stirred solution of [N(PPh$_3$)$_2$][Cu(C$_2$Ph)$_2$] (0.201 g, 0.25 mmol) in dichloromethane (20 cm^3). Stirring was continued for 2 h and the solvent then removed. Acetone (20 cm^3) was added to the residue, and the solution filtered and treated with hexane (20 cm^3), to give yellow crystals (0.315 g). Recrystallization from acetone/hexane afforded yellow crystals of [N(PPh$_3$)$_2$][Au$_3$Cu$_2$(C$_2$Ph)$_6$] (0.230 g, 49%), $\nu_{max.}$ (Nujol) 2075w cm^{-1} (C≡C), m.p. 170–172°C identical in all respects to an authentic sample described previousely [2].

Reaction between [N(PPh$_3$)$_2$][Cu(C$_2$Ph)$_2$] *and* [{AuAg(C$_2$Ph)$_2$}$_n$]. The gold-silver polymer complex (0.507 g, 1.0 mmol) was added to a stirred solution of [N(PPh$_3$)][Cu(C$_2$Ph)$_2$] (0.402 g, 0.5 mmol) in dichloromethane (20 cm^3). The colour changed immediately from yellow to orange. The solution was stirred for 5 min and the solvent then removed under vacuum. Crystallization from acetone/hexane gave a yellow-orange solid (0.520 g). Recrystallization from acetone/hexane afforded pale yellow crystals, identified as [N(PPh$_3$)$_2$][Au$_3$Ag$_2$(C$_2$Ph)$_6$] (1) (0.300 g, 61%) m.p. 175°C lit. [2] 175–177°C (Found: C, 52.25; H, 3.15. C$_{854}$H$_{60}$Ag$_2$Au$_3$NP$_2$ calcd.: C, 51.4; H, 3.1%), $\nu_{max.}$ (Nujol) 2082w cm^{-1} (C≡C). The ^{1}H NMR spectrum [(CD$_3$)$_2$CO] showed two complex resonances at δ 7.70 and 7.04 with intensity ratio 1/1. Orange red blocks were obtained as a second crop, and identified as [N(PPh$_3$)$_2$][AuAg$_6$Cu$_6$(C$_2$Ph)$_{14}$] (0.040 g, 15%) (Found: C, 56.1; H, 3.2, Au, 6.1. C$_{148}$H$_{100}$Ag$_6$AuCu$_6$NP$_2$ calcd.: C, 55.9; H, 3.15, Au, 6.2%), $\nu_{max.}$ (Nujol) 2039w cm^{-1} (C≡C). The ^{1}H NMR spectrum in [(CD$_3$)$_2$CO] showed two complex resonances at δ 7.68 and 7.1 with integration ratio 3/7, identical with that of an authentic sample [6].

Reaction between [N(PPh$_3$)$_2$][Ag(C$_2$Ph)$_2$] *and* [{AuAg(C$_2$Ph)$_2$}$_n$]. The gold-silver polymer [{AuAg(C$_2$Ph)$_2$}$_n$] (0.38 g, 0.75 mmol) was added to a stirred solution of [N(PPh$_3$)$_2$][Ag(C$_2$Ph)$_2$] (0.212 g, 0.25 mmol) in dichloromethane (20 cm^3). Stirring was continued for 2 h and the solvent then removed under reduced pressures. Acetone was added to the resulting residue, and the solution filtered and treated with hexane to give pale yellow crystals of [N(PPh$_3$)$_2$][Au$_3$Ag$_2$(C$_2$Ph)$_6$] (1) (0.31 g, 64%) m.p. 175–177°C (decomp.) identical with authentic sample [2].

Acknowledgements

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