

Syntheses and Reactivity of Acetylide-containing Clusters of Group 1B Metals. Stepwise Syntheses of Trinuclear $[\text{Au}_2\text{Cu}(\text{C}_2\text{Ph})_4]^-$ and Pentanuclear $[\text{Au}_3\text{Cu}_2(\text{C}_2\text{Ph})_6]^-$ and $[\text{Au}_3\text{Ag}_2(\text{C}_2\text{Ph})_6]^-$ Clusters

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The pentanuclear cluster $[\text{Au}_3\text{Cu}_2(\text{C}_2\text{Ph})_6]^-$ was obtained from the reaction between $[\{\text{Au}(\text{C}_2\text{Ph})\}_n]^-$ and a mixture of $[\text{Au}(\text{C}_2\text{Ph})_2]^-$ and $[\{\text{Cu}(\text{C}_2\text{Ph})\}_n]^-$. Its structure is described. The same cluster has been synthesized in a stepwise manner starting with $[\text{Au}(\text{C}_2\text{Ph})_2]^-$ through the binuclear complex $[\text{Au}_2(\text{C}_2\text{Ph})_3]^-$ and the trinuclear cluster $[\text{Au}_2\text{Cu}(\text{C}_2\text{Ph})_4]^-$. The synthesis of the analogous gold-silver cluster $[\text{Au}_3\text{Ag}_2(\text{C}_2\text{Ph})_6]^-$ was achieved by a slightly modified method.

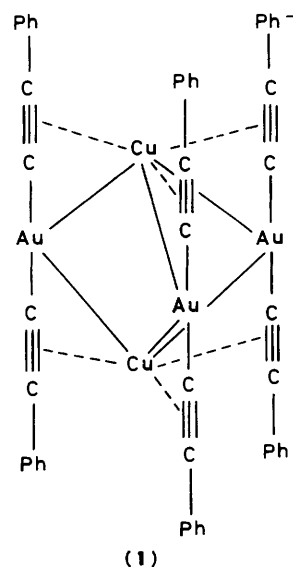
We have recently reported¹ the synthesis and single-crystal X-ray structure of the pentanuclear cluster $[\text{Au}_3\text{Cu}_2(\text{C}_2\text{Ph})_6]^-$ (1), which is the main product of the reaction between $[\{\text{Au}(\text{C}_2\text{Ph})\}_n]^-$ and a mixture of $[\text{Au}(\text{C}_2\text{Ph})_2]^-$ and $[\{\text{Cu}(\text{C}_2\text{Ph})\}_n]^-$ in 1:1:1 mol ratio in tetrahydrofuran at room temperature. Complex (1) is yellow with a green tinge. An interesting feature of this reaction is the transfer of the phenylethynyl ligand from copper to gold with subsequent π bonding of copper atoms to alkyne groups as well as bonding to gold atoms. The metal atoms have a trigonal-bipyramidal arrangement with the three gold atoms forming an equilateral triangle and the two copper atoms occupying apical positions.

Each gold atom is σ bonded to two phenylethynyl ligands in a linear co-ordination. Each copper atom is asymmetrically π bonded to three alkyne groups. The gold-gold distances lie in the range 3.44–3.53 Å, indicating the lack of metal-metal bonding (in the metal, Au-Au is 2.889 Å). Average Au-Cu distances (2.896 Å) suggest appreciable metal-metal bonding (sum of covalent radii for gold and copper is 2.72 Å).

The gold-copper metal-metal bonding can be inferred from the nature of the copper-alkyne interaction, which is asymmetric with copper being closer to carbon bonded to gold (Cu-C 2.0–2.15 Å) than to carbon bonded to phenyl (Cu-C 2.35–2.65 Å). This indicates that cationic copper is pulled towards anionic gold with subsequent metal-metal bonding. The gold atoms could use their *d* electrons, which are expected to be of suitable energy by virtue of the anionic nature of gold, for bonding purposes. An alternative zwitterionic structure, which lacks metal-metal interaction, requires a trigonal copper with symmetric π bonding. This manner of copper-alkyne interaction is similar to the bonding of copper, each to two alkyne groups, in the cluster $[\text{Ir}_2\text{Cu}_4(\text{C}_2\text{Ph})_8(\text{PPh}_3)_2]$, in which metal-metal bonding is suggested to exist.² The intense colour of the complex, compared to colourless or white for complexes of Cu^I and Au^I , also suggests the presence of metal-metal interaction.

The i.r. spectrum showed one $\nu(\text{C}\equiv\text{C})$ absorption band at *ca.* 2 075 cm^{-1} , only 25 cm^{-1} lower than $\nu(\text{C}\equiv\text{C})$ in $[\text{Au}(\text{C}_2\text{Ph})_2]^-$, consistent with weak asymmetric π bonding. Molecular weight determination by ebullioscopic methods gave a value characteristic of a 1:1 electrolyte (see Table). Proton n.m.r. spectroscopy showed resonances having intensities in the ratio 30:8:8:8:12 for $[\text{NBu}_4][\text{Au}_3\text{Cu}_2(\text{C}_2\text{Ph})_6]^-$.

A minor product, which was obtained as the second crop from the above reaction, is believed to be $[\text{NBu}_4][\text{Au}_2\text{Cu}(\text{C}_2\text{Ph})_4]^-$ (3) (only i.r. and ¹H n.m.r. evidence). The i.r. spectrum showed two $\nu(\text{C}\equiv\text{C})$ bands at *ca.* 2 110 and 2 070 cm^{-1}



(see below). The ¹H n.m.r. spectrum contained resonances at δ 7.13, 3.48, 1.79, 1.45, and 0.96 with intensity ratio 20:8:8:8:12.

The fact that complex (1) is obtained from the above reaction mixture and that $[\text{Au}(\text{C}_2\text{Ph})_2]^-$ depolymerises $[\{\text{Au}(\text{C}_2\text{Ph})\}_n]^-$ and not $[\{\text{Cu}(\text{C}_2\text{Ph})\}_n]^-$ led us to expect the existence of some reactive species that could react with the copper reagent to give complex (1). We set out, therefore, to examine this possibility by attempting the stepwise synthesis of complex (1).

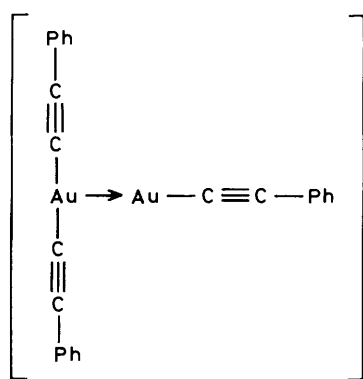
Results

The Binuclear Complex $[\text{Au}_2(\text{C}_2\text{Ph})_3]^-$ (2).—It was reported recently³ that $[\text{Au}(\text{C}_2\text{Ph})_2]^-$ depolymerises $[\{\text{Au}(\text{C}_2\text{Ph})\}_n]^-$ (1:2) in acetone affording complex (2) in moderate yields. Another product from the reaction was an isomer of the well known starting material, $[\{\text{Au}(\text{C}_2\text{Ph})\}_n]^-$.⁴ Excess of $[\{\text{Au}(\text{C}_2\text{Ph})\}_n]^-$ was used in the above reaction because complex (2) was anticipated to compete for $[\{\text{Au}(\text{C}_2\text{Ph})\}_n]^-$ giving homonuclear complexes with higher nuclearity, *e.g.* $[\text{Au}_3(\text{C}_2\text{Ph})_4]^-$, which decompose giving the less reactive isomeric $[\{\text{Au}(\text{C}_2\text{Ph})\}_n]^-$ and $[\text{Au}(\text{C}_2\text{Ph})_2]^-$. The above procedure has been modified by using a 1:1 mol ratio and carrying out the reaction in the presence of an excess of pyridine (py). This ligand is the only tertiary amine that depolymerises $[\{\text{Au}(\text{C}_2\text{Ph})\}_n]^-$.⁴ Apparently, $[\text{Au}(\text{C}_2\text{Ph})_2]^-$ displaces pyridine from the substi-

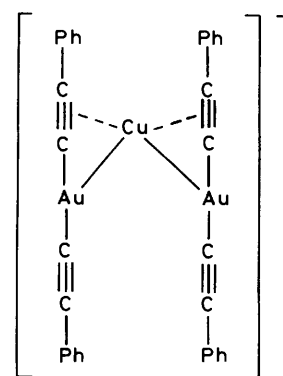
Table. M.p. and analytical data

	Complex	M.p. (°C)	Analysis ^a (%)					M(acetone) ^b
			C	H	N	Au	Cu or Ag	
(1)	[NBu ₄][Au ₃ Cu ₂ (C ₂ Ph) ₆]	170—173 ^c	48.7 (49.05)	4.3 (4.2)	0.85 (0.9)	38.3 (37.75)	8.4 (8.1)	968 (1 566)
(2)	[N(PPh ₃) ₂][Au ₂ (C ₂ Ph) ₃]	135—137 ^c	58.05 (58.3)	3.8 (3.65)	0.9 (1.15)	30.4 (31.9)		665 (1 235)
(3)	[N(PPh ₃) ₂][Au ₂ Cu(C ₂ Ph) ₄]	143—145	58.2 (58.3)	3.7 (3.55)	0.9 (1.0)			
(4)	[N(PPh ₃) ₂][Au ₂ Cu(C ₂ Ph) ₃ (C ₂ C ₆ H ₄ Me- <i>p</i>)]	160—162 ^c	57.65 (58.55)	3.75 (3.7)	1.15 (1.0)	27.2 (27.85)	4.8 (4.5)	854 (1 414.5)
(5)	[N(PPh ₃) ₂] ₂ [Au ₂ CuCl(C ₂ Ph) ₄]	175—180 ^c	63.55 (63.25)	4.35 (4.05)	1.3 (1.4)			6.15 (6.3)
(6)	[N(PPh ₃) ₂][Au ₃ Ag ₂ (C ₂ Ph) ₆]	175—177 ^c	51.4 (51.4)	3.35 (3.05)	0.6 (0.7)	29.7 (30.3)	10.9 (11.05)	

^a Calculated values in parentheses. ^b Molecular weight determination by ebullioscopic methods. ^c Melts with decomposition.



(2)



(3)

tution labile complex [Au(C₂Ph)(py)]⁻ affording complex (2), and possibly reducing competition from the above reaction. The i.r. spectrum of complex (2) showed one medium $\nu(\text{C}\equiv\text{C})$ band at 2 110 cm^{-1} assigned to unco-ordinated alkyne ligand. Analytical data showed it to be a 1:1 adduct and molecular weight determination (see Table) indicated a 1:1 electrolyte.

The Trinuclear Cluster [Au₂Cu(C₂Ph)₄]⁻ (3).—Complex (2) reacts readily with [$\{\text{Cu}(\text{C}_2\text{Ph})\}_n$] in acetone at room temperature giving the trinuclear cluster [Au₂Cu(C₂Ph)₄]⁻ (3) in very high yield. Thus, the copper complex dissolves within 1 h when added (1:1) to an acetone solution of complex (2). Yellow crystals of complex (3) are obtained on addition of hexane to the filtrate from the reaction mixture. The analogous cluster [Au₂Cu(C₂Ph)₃(C₂C₆H₄Me-*p*)]⁻ (4) was obtained by a similar method.³ Analytical data for both complexes showed a 1:1 adduct, and molecular weight determination for complex (4) indicated a 1:1 electrolyte. The i.r. spectra for both complexes contained bands at *ca.* 2 105 and 2 070 cm^{-1} . The above data coupled with the fact that in complex (1) the acetylide ligands are bonded end-on to gold and side-on to copper suggest that the most likely structure for complex (3) is as shown. A similar structure is expected for complex (4). The bonding features in this structure are similar to those of complex (1) except that only half of the acetylide ligands are engaged in π bonding due to the presence of only one copper atom in the complex. The bands in the i.r. spectra at *ca.* 2 105 and 2 070 cm^{-1} could be assigned to unco-ordinated and asymmetrically co-ordinated alkyne groups respectively.

Complex (3) can also be obtained, stepwise in very high yield

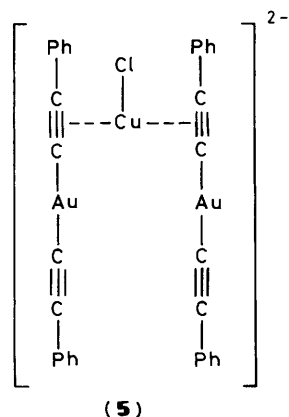
(90%) starting with the linear complex [Au(C₂Ph)₂]⁻ by carrying out the reaction as above but without separating complex (2).

The yellow colour of complex (3) disappeared when [N(PPh₃)₂]Cl was added (1:1) to a solution of it in acetone. The complex [N(PPh₃)₂]₂[Au₂CuCl(C₂Ph)₄]⁻ (5) is obtained in high yield on addition of hexane to the filtrate. Its i.r. spectrum contained bands at *ca.* 2 100 and 1 950 cm^{-1} . A possible structure for this complex is as shown.

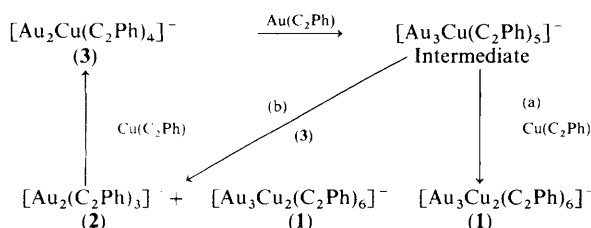
In this complex the gold atoms retain their linear co-ordination. On the other hand, copper is trigonal and symmetrically π bonded to two alkyne groups. There is no longer a metal-metal bonding. The dramatic decrease in $\nu(\text{C}\equiv\text{C})$ for the co-ordinated alkyne groups is probably due to stronger symmetrical interaction between copper and the ethynyl ligands. The white colour of the complex is consistent with the lack of metal-metal bonding.

The Pentanuclear Cluster [Au₃Cu₂(C₂Ph)₆]⁻ (1).—Copper phenylacetylide did not react with complex (3) when it was added (1:1) to a solution of it in acetone. However, when [$\{\text{Au}(\text{C}_2\text{Ph})\}_n$] was added (1:1) to the previous mixture complex (1) was obtained in very high yield. It was isolated as its tetrabutylammonium and bis(triphenylphosphine)iminium salts.

We could not isolate the tetranuclear complex [Au₃Cu(C₂Ph)₅]⁻ when [$\{\text{Au}(\text{C}_2\text{Ph})\}_n$] was added (1:1) to complex (3) in acetone. Instead, complexes (1) and (2) were obtained. Complex (2) was treated with [$\{\text{Cu}(\text{C}_2\text{Ph})\}_n$], giving (3) as expected. Apparently, the tetranuclear complex is very reactive



and reacts with complex (3), which is trinuclear, affording the pentanuclear cluster, (1), and the binuclear complex, (2). In the presence of $[\{\text{Cu}(\text{C}_2\text{Ph})\}_n]$, the pentanuclear cluster is formed by one or by both routes depicted in the Scheme. In route (a) the



Scheme. Possible routes for the formation of complex (1) from (3)

tetranuclear intermediate reacts directly with $[\{\text{Cu}(\text{C}_2\text{Ph})\}_n]$ giving complex (1) in a way similar to the reaction of complex (2) with the same copper reagent. In route (b) the tetranuclear intermediate reacts with complex (3) affording complexes (1) and (2). The latter reacts with $[\{\text{Cu}(\text{C}_2\text{Ph})\}_n]$ present regenerating complex (3), etc.

The Pentanuclear Cluster $[\text{Au}_3\text{Ag}_2(\text{C}_2\text{Ph})_6]^-$ (6).—This cluster is analogous to the gold-copper cluster (1). Silver phenylacetylide dissolved readily when added (1:1) to complex (2) in acetone at room temperature. Then gold phenylacetylide was added to the above solution (2:1) and stirring was continued for 15 h. Addition of hexane to the filtrate gave the pale yellow cluster $[\text{Au}_3\text{Ag}_2(\text{C}_2\text{Ph})_6]^-$ (6). It was characterized by the usual methods. The i.r. spectrum contained a weak band at *ca.* $2\,082\text{ cm}^{-1}$ assigned to co-ordinated $\nu(\text{C}\equiv\text{C})$. It is about 10 cm^{-1} higher than that of the analogous gold-copper cluster (1). In the fingerprint area, the spectra of the two complexes were identical. There is no doubt that complex (6) has a similar structure to that of (1), with silver playing a role similar to that of copper in these reactions.

We are currently investigating the reactions of these clusters.

Experimental

Spectra were obtained using Beckman Acculab 4 (i.r.) and JEOL JNM FX-100 (^1H n.m.r.) spectrometers. Dichloromethane, hexane, and tetrahydrofuran (thf) 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 in a nitrogen atmosphere. The complexes $[\{\text{Au}(\text{C}_2\text{Ph})\}_n]$ and $[\text{Au}(\text{C}_2\text{Ph})_2]^-$ were prepared by the literature methods,^{4,5} $[\{\text{Ag}(\text{C}_2\text{Ph})\}_n]$,

$[\{\text{Cu}(\text{C}_2\text{Ph})\}_n]$, and $[\{\text{Cu}(\text{C}_2\text{C}_6\text{H}_4\text{Me-}p)\}_n]$ by treating aqueous ammoniacal solutions of AgNO_3 or Cu_2I_2 with the appropriate arylacetylene. Elemental analyses and molecular weight determinations were done at Pascher's Microanalytical Laboratory, Remagen, West Germany.

Reaction between $[\text{NBu}^n_4][\text{Au}(\text{C}_2\text{Ph})_2]$ and a Mixture of $[\{\text{Au}(\text{C}_2\text{Ph})\}_n]$ and $[\{\text{Cu}(\text{C}_2\text{Ph})\}_n]$.—Gold phenylacetylide (0.149 g, 0.5 mmol) was added to a mixture of $[\text{NBu}^n_4][\text{Au}(\text{C}_2\text{Ph})_2]$ (0.321 g, 0.5 mmol) and $[\{\text{Cu}(\text{C}_2\text{Ph})\}_n]$ (0.082 g, 0.5 mmol) in thf (15 cm^3) with stirring. The colour changed from yellow to yellow-green. After 1.5 h the reaction mixture was filtered and the filtrate evaporated to dryness. Crystallisation from CH_2Cl_2 -hexane afforded yellow crystals with a green tinge, $[\text{NBu}^n_4][\text{Au}_3\text{Cu}_2(\text{C}_2\text{Ph})_6]$ (1) [0.216 g, 55% based on $\text{Au}(\text{C}_2\text{Ph})/\text{Cu}(\text{C}_2\text{Ph})$ used]. ν_{max} (KBr disc) $2\,075\text{ w cm}^{-1}$ ($\text{C}\equiv\text{C}$). Proton n.m.r. spectrum $[(\text{CD}_3)_2\text{CO}]$ δ 7.05, 3.48, 1.78, 1.45, and 0.96 with intensity ratio 30:8:8:8:12. A yellow product obtained from a second crop is believed to be $[\text{NBu}^n_4][\text{Au}_2\text{Cu}(\text{C}_2\text{Ph})_4]$ (0.060 g). ν_{max} (KBr disc) $2\,108\text{ m (sh)}$ and $2\,071\text{ w cm}^{-1}$ ($\text{C}\equiv\text{C}$). Proton n.m.r. spectrum δ 7.13, 3.48, 1.79, 1.45, and 0.96 with intensity ratio 20:8:8:8:12.

Reaction between $[\text{N}(\text{PPh}_3)_2][\text{Au}(\text{C}_2\text{Ph})_2]$ and $[\{\text{Au}(\text{C}_2\text{Ph})\}_n]$.—(a) *In the absence of pyridine.* Slow addition of $[\{\text{Au}(\text{C}_2\text{Ph})\}_n]$ (0.298 g, 1 mmol) to a stirred solution of $[\text{N}(\text{PPh}_3)_2][\text{Au}(\text{C}_2\text{Ph})_2]$ (0.469 g, 0.5 mmol) in acetone (22 cm^3) produced a yellow solution and a yellowish pale green residue. The latter (0.145 g) was obtained by filtration and identified as a structural isomer of the starting material $[\{\text{Au}(\text{C}_2\text{Ph})\}_n]$ (Found: C, 32.35; H, 1.85. $\text{C}_8\text{H}_5\text{Au}$ requires C, 32.2; H, 1.65%), m.p. 145–150 °C (decomp.), ν_{max} (Nujol) $2\,030$ (sh) and $1\,985$ (sh) cm^{-1} ($\text{C}\equiv\text{C}$). Addition of hexane (60 cm^3) to the filtrate gave a pale yellow precipitate (0.525 g). Repeated recrystallisation from acetone-hexane gave an off-white solid of complex (2), $[\text{N}(\text{PPh}_3)_2][\text{Au}_2(\text{C}_2\text{Ph})_3]$ (0.310 g, 50%), ν_{max} (Nujol) $2\,110\text{ m cm}^{-1}$ ($\text{C}\equiv\text{C}$); the ^1H n.m.r. spectrum showed two complex resonances at δ 7.69 and 7.13 with intensity ratio 2:1 for the phenylphosphine and phenylacetylide protons respectively.

(b) *In the presence of pyridine.* Gold phenylacetylide (0.596 g, 2 mmol) was added to a solution of $[\text{N}(\text{PPh}_3)_2][\text{Au}(\text{C}_2\text{Ph})_2]$ (1.874 g, 2 mmol) in acetone (35 cm^3) containing pyridine (2 cm^3). Stirring was continued for 0.5 h, then the reaction mixture was filtered off. Addition of hexane (60 cm^3) gave an oil which solidified on stirring giving an off-white product (2.25 g). Recrystallisation from acetone-hexane afforded complex (2) (1.66 g, 67%) (Found: C, 58.05; H, 3.8; N, 0.9. $\text{C}_{60}\text{H}_{45}\text{Au}_2\text{NP}_2$ requires C, 58.3; H, 3.65; N, 1.15%) identical in all respects to the sample described above.

Reaction between $[\text{N}(\text{PPh}_3)_2][\text{Au}_2(\text{C}_2\text{Ph})_3]$ and $[\{\text{Cu}(\text{C}_2\text{Ph})\}_n]$.—Copper phenylacetylide (0.188 g, 1.142 mmol) was added to $[\text{N}(\text{PPh}_3)_2][\text{Au}_2(\text{C}_2\text{Ph})_3]$ (1.41 g, 1.142 mmol) in acetone (70 cm^3). Stirring was continued for 1.5 h. Filtration and addition of hexane (45 cm^3) gave yellow woolly crystals of complex (3), $[\text{N}(\text{PPh}_3)_2][\text{Au}_2\text{Cu}(\text{C}_2\text{Ph})_4]$ (1.415 g, 89%), ν_{max} (Nujol) $2\,105\text{ m (sh)}$ and $2\,070\text{ w cm}^{-1}$ ($\text{C}\equiv\text{C}$); the ^1H n.m.r. spectrum showed two complex resonances at δ 7.68 and 7.08 with intensity ratio 3:2.

Preparation of Complex (3) without Isolation of Complex (2).—Gold phenylacetylide (0.298 g, 1 mmol) was added to a solution of $[\text{N}(\text{PPh}_3)_2][\text{Au}(\text{C}_2\text{Ph})_2]$ (0.937 g, 1 mmol) in acetone (55 cm^3) containing pyridine (1 cm^3). The reaction mixture was stirred for 15 min, then filtered and $[\{\text{Cu}(\text{C}_2\text{Ph})\}_n]$ (0.165 g, 1 mmol) added to the filtrate. A clear yellow solution

was obtained after stirring for 30 min. Filtration and addition of hexane (80 cm³) gave complex (3) (1.230 g, 88%), m.p. 143–145 °C, identical in all respects to the sample prepared as above.

Preparation of Complex (4), [N(PPh₃)₂][Au₂Cu(C₂Ph)₃-(C₂C₆H₄Me-*p*)].—Copper *p*-tolylacetylide (0.052 g, 0.29 mmol) was added to solution of [N(PPh₃)₂][Au₂(C₂Ph)₃] (0.178 g, 0.145 mmol) in acetone (15 cm³). Stirring was continued for 2 h. Yellow crystals of complex (4), [N(PPh₃)₂][Au₂Cu(C₂Ph)₃-(C₂C₆H₄Me-*p*)] (0.145 g, 71%) were obtained on addition of hexane (30 cm³) to the filtrate, ν_{\max} (Nujol) 2 110m (sh) and 2 070w cm⁻¹ (C≡C).

Preparation of Complex (5), [N(PPh₃)₂]₂[Au₂CuCl(C₂Ph)₄].—Bis(triphenylphosphine)iminium chloride (0.16 g, 0.28 mmol) was added to [N(PPh₃)₂][Au₂Cu(C₂Ph)₄] (0.39 g, 0.3 mmol) in acetone (35 cm³). The yellow colour disappeared within 5 min. Addition of hexane (35 cm³) to the filtrate gave white crystals of complex (5), [N(PPh₃)₂]₂[Au₂CuCl(C₂Ph)₄] (0.44 g, 80%), ν_{\max} (Nujol) 2 105m (sh) and 1 955w,br cm⁻¹ (C≡C).

Reaction of Complex (3) and a Mixture of [Cu(C₂Ph)]_n and [Au(C₂Ph)]_n.—Gold phenylacetylide (0.063 g, 0.214 mmol) was added to a mixture of [N(PPh₃)₂][Au₂Cu(C₂Ph)₄] (0.3 g, 0.214 mmol) and [Cu(C₂Ph)]_n (0.035 g, 0.214 mmol) in acetone (25 cm³). Stirring was continued till a clear solution was obtained (1.25 h). Filtration and addition of hexane gave yellow crystals with a green tinge of complex (1), [N(PPh₃)₂]-[Au₃Cu₂(C₂Ph)₆] (0.340 g, 85%), m.p. 168–170 °C (decomp.) (Found: C, 54.7; H, 3.35; N, 0.85. C₈₄H₆₀Au₃Cu₂NP₂ requires C, 54.2; H, 3.2, N, 0.75%), ν_{\max} (Nujol) 2 075w cm⁻¹ (C≡C); the ¹H n.m.r. spectrum [(CD₃)₂CO] showed two complex resonances at δ 7.68 and 7.08 with intensity ratio 1:1.

Reaction between [N(PPh₃)₂][Au₂Cu(C₂Ph)₄] and [Au(C₂Ph)]_n.—Gold phenylacetylide (0.170 g, 0.571 mmol) was added to [N(PPh₃)₂][Au₂Cu(C₂Ph)₄] (0.800 g, 0.571 mmol) in acetone (30 cm³). Stirring was continued for 1 h, and a yellow residue of [Au(C₂Ph)]_n (0.083 g) was recovered. Addition of hexane (30 cm³) to the filtrate resulted in the formation of

complex (1) (0.425 g, 80%), m.p. 168–170 °C (decomp.), ν_{\max} (Nujol) 2 075w cm⁻¹ (C≡C) (Found: C, 53.90; H, 3.45; N, 0.85%). Reducing the volume of the remaining filtrate afforded pale yellow solid complex (2), [N(PPh₃)₂][Au₂(C₂Ph)₃] (0.215 g, 61%). Reaction of the latter complex (0.195 g, 0.158 mmol) and [Cu(C₂Ph)]_n (0.026 g, 0.158 mmol) in acetone gave complex (3) (0.19 g, 86%) identical in all respects to the sample described above.

Preparation of Complex (6), [N(PPh₃)₂][Au₃Ag₂(C₂Ph)₆].—Silver phenylacetylide (0.105 g, 0.5 mmol) was added to [N(PPh₃)₂][Au₂(C₂Ph)₃] (0.618 g, 0.5 mmol) in acetone (40 cm³). A clear solution was obtained within 15 min. Then [Au(C₂Ph)]_n (0.298 g, 1 mmol) was added to the previous solution. Stirring was continued for 17 h. Filtration and addition of hexane (30 cm³) resulted in the formation of pale yellow crystals of complex (6), [N(PPh₃)₂][Au₃Ag₂(C₂Ph)₆] (0.32 g, 66%), ν_{\max} (Nujol) 2 082w cm⁻¹; the ¹H n.m.r. spectrum [(CD₃)₂CO] showed two complex resonances at δ 7.67 and at 7.02 with intensity ratio 1:1.

Acknowledgements

We are grateful to Professor M. F. Hawthorne for providing X-ray facilities, Mr. M. K. Mahmoud and Mr. M. H. Ja'far for technical assistance, and Research Centre, College of Science, King Saud University for financial support (project Chem/1406/05).

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Received 30th September 1987; Paper 7/1750