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Syntheses and reactivity of acetylide-containing clusters of Group IB metals. Preparation, structure, and reactions of the tetranuclear cluster $[Au_2Ag_2(C_2Ph)_4(PPh_3)_2]$. Syntheses and structure of the novel mixed-metal gold-silver and gold-copper phenylacetylide polymer complexes $[{AuM(C_2Ph)_2}_n]$ (M = Ag, Cu)

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Abstract

The tetranuclear cluster $[Au_2Ag_2(C_2Ph)_4(PPh_3)_2]$ has been made by reaction of $[Au(C_2Ph)PPh_3]$ with $[{Ag(C_2Ph)}_n]$ (1/1). Its structure and reactions are described. The novel mixed gold-silver and gold-copper phenylacetylide polymers $[{AuM(C_2Ph)}_n]$ (M = Ag, Cu) have been made by reaction of $[Au(C_2Ph)L]$ (L = AsPh₃, P(OPh)₃) with $[{Ag(C_2Ph)}_n]$ and $[{Cu(C_2Ph)}_n]$. The gold-silver polymer has also been made by reaction of $[AuClPPh_3]$ with $[{Ag(C_2Ph)}_n]$ (1/2). The structures of the polymers are discussed.

Monosubstituted alkynyl ligands show several modes of bonding in transition metal complexes. The coordination chemistry of metal alkynyl compounds has been reviewed [1]. We have recently reported the synthesis and structure of the novel cluster $[Au_3Cu_2(C_2Ph)_6]^-$ [2]. This cluster and two more members of the same class, namely the trinuclear $[Au_2Cu(C_2Ph)_4]^-$ and the pentanuclear $[Au_3Ag_2(C_2Ph)_6]^-$ complexes, were synthesized in a stepwise manner [3]. More recently the chemistry of Group IB metal arylacetylides has been extended by the synthesis of the high polynuclearity silver-copper cluster $[Ag_6Cu_7(C_2Ph)_{14}]^-$ and its trimetallic analogue $[AuAg_6Cu_6(C_2Ph)_{14}]^-$ [4,5].

Results and discussion

It was reported recently that the anionic complex $[Au(C_2Ph)_2]^-$ does not react with $[{Cu(C_2Ph)}_n]$ but that the binuclear anionic complex $[Au_2(C_2Ph)_3]^-$ does

react readily with the copper complex to give the trinuclear cluster $[Au_2Cu(C_2Ph)_4]^-$. It is thought that in this reaction the gold atom is ethynylated by the copper reagent [3]. It is apparent that the linear gold entity $[\rightarrow AuC_2Ph]$ is the reactive centre in the binuclear complex. We thought it of interest to examine the analogous reactions of the linear gold complexes $[Au(C_2Ph)L]$ (L = PPh₃, AsPh₃, P(OPh)₃) with silver phenylacetylide and its copper analogue. It was expected that ethynylation reactions would lead to the formation of interesting heteroatomic complexes between Group IB metal arylacetylides.

The tetranuclear cluster $[Au_2Ag_2(C_2Ph)_4(PPh_3)_2]$ (1)

The reaction of $[Au(C_2Ph)PPh_3]$ and $[{Ag(C_2Ph)}_n]$ in 1/1 mol ratio gave 1 in very high yield. Its synthesis and crystal structure have been reported in some detail [6]. The structure indicates that gold is ethynylated by the silver reagent in a way similar to the ethynylation of $[\rightarrow AuC_2Ph]$ by the copper polymer complex mentioned above. Two linear anionic gold moieties $[Au(C_2Ph)_2]^-$ and two cationic silver moieties $[AgPPh_3]^+$ are incorporated into complex 1. Complex 1 dissociates reversibly to give the polymer complex $[{AuAg(C_2Ph)_2}_n]$ (2) and PPh₃ [6].

The silver atoms, which are asymmetrically π -bonded to alkyne ligands, are closer to carbon bonded to gold than to carbon bonded to phenyl [6]. This is regarded, as suggested for the cluster $[Au_3Cu_2(C_2Ph)_6]^-$ [3], as an indication of the presence of gold-silver metal-metal bonding.

The structure of complex 1 is reminiscent of the structure of $[Ag(C_2Ph)PMe_3]$ [7]. The latter is a chain polymer involving anionic linear centres $[Ag(C_2Ph)_2]^-$ and cationic centres $[Ag(PMe_3)_2]^+$. The silver atoms are at bonding distances from each other. The cationic silver atoms are asymmetrically π -bonded to two alkyne ligands, one from each neighbouring silver atom. This cationic-anionic interaction in acetylide complexes containing Group IB metals is apparently an inherent feature in these



compounds [5]. The structure of complex 1 can be regarded as a manifestation of this feature.

Addition of Cl^- or Br^- to complex 1 in 2/1 mol ratio gives the linear complex anion $[Au(C_2Ph)_2]^-$ and silver complexes $[AgXPPh_3]$ (X = Cl or Br) in very high yields. We recently reported several methods for the preparation of the gold complex anion [8,9]. The present method represents a very convenient route to this complex since silver phenylacetylide, which is easy to prepare, is the only acetylide source required for the synthesis of complex 1 (see below).

The bimetallic gold-silver polymer complex $[{AuAg(C_2Ph)_2}_n]$ (2)

Since the ethynyl ligand of $[{Ag(C_2Ph)}_n]$ displaces triphenylphosphine in $[Au(C_2Ph)PPh_3]$, it was expected that it would displace both ligands in $[AuClPPh_3]$ with subsequent formation of a mixed gold-silver polymer complex. This was indeed the case, and first mixed gold-silver acetylide polymer was obtained. Thus interaction of $[AuClPPh_3]$ with $[{Ag(C_2Ph)}_2]_n]$ in 1/2 mol ratio in toluene at room temperature resulted in gradual formation of a yellow precipitate of the gold-silver polymer complex $[{AuAg(C_2Ph)}_2]_n]$ (2) and gradual disappearance of the silver polymeric reagent. The other product, which was $[AgClPPh_3]_4$, also separated out, and was washed away from the polymer with dichloromethane.

Complex 2 was identified by the usual methods. The elemental analysis for C and H agreed well with the above formula. The IR spectrum of the complex contained a weak band at ca. 2065, with a shoulder at ca. 2075 cm⁻¹, assigned to a π -bonded alkyne ligand. This frequency is close to that of the ν (C=C) band of the clusters $[Au_3Cu_2(C_2Ph)_6]^-$, $[Au_3Ag_2(C_2Ph)_6]^-$, and $[Au_2Ag_2(C_2Ph)_4(PPh_3)_2]$ [3,6]. It is likely that both alkynyl ligands are end-on bonded to gold, giving a linear moiety, as in the three clusters mentioned above, with subsequent π -bonding to silver. Polymerization takes place to give a higher coordination at silver. The same reasoning can be invoked to account for the dimeric nature of complex 1. Silver(I) and copper(I) are known to have a higher tendency than gold(I) to reach coordination numbers higher than two [10]. Reaction between the same reagents in 1/1 mol ratio in acetone at room temperature resulted in quantitative precipitation of silver chloride. The other product was $[Au(C_2Ph)PPh_3]$, identified by the usual methods [11]. When a further equivalent of silver phenylacetylide was added to the reaction mixture prior to separation of AgCl, the latter formed [AgClPPh₃] and complex 2 precipitated. The same result was achieved when $[{Ag(C_2Ph)}_n]$ was added to a mixture of $[Au(C_2Ph)PPh_3]$ and AgCl in 1/1/1 mol ratio.

Evidently, the first step in the formation of the polymer complex 2 is a metathesis affording AgCl and $[Au(C_2Ph)PPh_3]$. The second step involves ethynylation by a second molecule of silver phenylacetylide to give complex 1. The latter dissociates irreversibly in the presence of AgCl to give the polymer complex 2 and $[AgClPPh_3]$ in high yields.

We have recently devised a more convenient route for complex 2, and this route is also suitable for the preparation of the analogous gold-copper polymer complex $[{AuCu(C_2Ph)_2}_n]$ (3) (see below). It involves the reaction of the gold complex $[Au(C_2Ph)AsPh_3]$ and silver phenylacetylide in 1/1 mol ratio in acetone at room temperature. As the polymeric silver phenylacetylide dissolves gradually, the mixed-metal polymer complex 2 precipitates out gradually in high yield.

As mentioned above, PPh₃ dissociates reversibly from the cluster complex to give

the polymer complex 2, but the equilibrium lies on the side of cluster 1. With $AsPh_3$, on the other hand, the equilibrium lies on the side of the polymer complex 2, indicating that PPh_3 is a better donor towards silver than $AsPh_3$. This difference in donor properties is apparently crucial. Whether a cluster or a polymer is formed depends on how strongly the ligand replaced by the ethynyl group is bound to silver.

Similar results were obtained when $[Au(C_2Ph)P(OPh)_3]$ was employed with $[{Ag(C_2Ph)_n}]$ in 1/1 mol ratio under similar conditions as for the arsine derivative, and the polymer complex 2 was isolated in very high yield. Triphenylphosphite is a weaker donor than PPh₃. Complex 1 can be obtained in very high yield by treating a suspension of complex 2 in toluene at room temperature with more than a 1 molar proportion of PPh₃ [6].

The bimetallic gold-copper polymer complex $[{AuCu(C_2Ph)_2}_n]$ (3)

Addition of $[{Cu(C_2Ph)}_n]$ to a solution of $[Au(C_2Ph)PPh_3]$ in acetone at room temperature did not result in a reaction. On the other hand, use of the same copper reagent with $[Au(C_2Ph)L]$ (L = AsPh₃, P(OPh)₃) in acetone at room temperature gave a precipitate of a pale yellow polymer complex $[{AuCu(C_2Ph)_2}_n]$ (3) in high yield. The elemental analysis for C and H agreed well with this formulation. The IR spectrum contained a medium band at ca. 2034 cm⁻¹ assigned to a π -bonded alkyne. The alkyne band in the case of complex 3 is at lower frequency than that of complex 2, reflecting similar trends observed [12] for the polymer complexes $[{Cu(C_2Ph)}_n]$ and $[{Ag(C_2Ph)}_n]$ and implying stronger back-bonding in the case of copper.

Ethynylation of $[Au(C_2Ph)L] (L = PPh_3, AsPh_3, P(OPh)_3)$ by $[{Ag(C_2Ph)}_n]$ and $[Cu(C_2Ph)]_n]$ evidently depends on how strongly L is bound to gold and how strongly the ethynyl ligand is bound to silver or copper. Whereas $[{Ag(C_2Ph)}_n]$ ethynylates the three gold complexes to give either a cluster $(L = PPh_3)$ or a polymer $(L = AsPh_3, P(OPh)_3)$, the analogous copper reagent ethynylates only $[Au(C_2Ph)L] (L = AsPh_3, P(OPh)_3)$, to give a polymer. This probably indicates that the ethynyl ligand is more strongly bound to copper than silver. Ethynylation of $[AuCIPPh_3]$ and $[cis-PtCl_2(PPh_3)_2]$ by the anionic silver reagent $[Ag(C_2Ph)_2]^-$ and its copper analogue $[Cu(C_2Ph)_2]^-$ is consistent with the above observation [9]. Thus reactions involving the silver reagent resulted in the exchange of both ethynyl groups, whereas those involving the copper analogue ended in the transfer of one ethynyl ligand and formation of copper phenylacetylide.

Addition of PPh₃ to a suspension of complex 3 in acetone in 2/1 mol ratio at room temperature did not give the gold-copper complex analogous to complex 1. Instead, the complexes [Au(C₂Ph)PPh₃] and [Cu(C₂Ph)PPh₃] were obtained in high yield, and characterized by the usual methods.

Addition of $[Cu(C_2Ph)(PPh_3)]$ to a suspension of gold phenylacetylide in dichloromethane gave $[Au(C_2Ph)PPh_3]$ and a precipitate of the yellow-green $[\{Cu(C_2Ph)\}_n]$. These results are consistent with the above observation that ethynyl ligand is bound strongly to copper in $[\{Cu(C_2Ph)\}_n]$.

It seems likely that the mixed polymer complexes will give interesting organometallic compounds, since it is possible to introduce both metal atoms simultaneously to a reaction centre. The reactions of the complexes will be reported in the near future.

Experimental

Spectra were recorded with Beckman F.T. and Beckmann Acculab 4 (IR) spectrometers. Dichloromethane, pentane, and hexane were dried and distilled before use. Acetone (AnalaR grade) was kept over a molecular sieves and used without distillation. Toluene (AnalaR grade) was used without any further drying. Reactions and work-up were carried out at room temperature under nitrogen. The complexes $[{M(C_2Ph)}_n]$ (M = Ag, Au, Cu) were prepared as described elsewhere [3]. $[Au(C_2Ph)AsPh_3]$ was prepared by the method used for similar complexes $[Au(C_2Ph)L]$ [11]. Elemental analyses were carried out at Pascher's Microanalytical Laboratory, Remagen, West Germany and at Chem., Dep., King Fahd University of Petroleum and Minerals, Dhahran, Saudi Arabia.

Preparation of $[Au_2Ag_2(C_2Ph)_4(PPh_3)_2]$ (1)

(a) By reaction of $[Au(C_2Ph)PPh_3]$ with $[{Ag(C_2Ph)}_n]$. Silver phenylacetylide (0.105 g, 0.5 mmol) was added to a solution of $[Au(C_2Ph)PPh_3]$ (0.28 g, 0.5 mmol) in dichloromethane (15 cm³) containing PPh₃ (0.015 g, 0.06 mmol). A clear solution was formed within 5–10 min, and was filtered then diluted with pentane to give colourless crystals of $[Au_2Ag_2(C_2Ph)_4(PPh_3)_2]$ (1) (0.365 g, 95%), m.p. 190–192° C, ν_{max} (C=C) (Nujol) 2075w cm⁻¹. Anal. Found: C, 53.5; H, 3.25. $C_{68}H_{50}Ag_2Au_2P_2$ calcd.: C, 53.05; H, 3.25%.

(b) By reaction of $[\{AuAg(C_2Ph)_2\}_n]$ (2) with PPh₃. Triphenylphosphine (0.15 g, 0.57 mmol) was added to a stirred suspension of $[\{AuAg(C_2Ph)_2\}_n]$ (2) (0.254 g, 0.5 mmol) in toluene (20 cm³). Stirring was continued for 24 h, during which colourless crystals separated. These were filtered off, washed with toluene and hexane, and shown to be complex 1 (0.345 g, 90%), m.p. 190-192°C, $\nu_{max}(C \equiv C)$ (Nujol) 2075w cm⁻¹, identical in all respects to the sample described above.

Reaction of 1 and $[N(PPh_3)_2][Cl]$

Bis(triphenylphosphine)iminium chloride (1.147 g, 2.0 mmol) was added to a stirred suspension of complex $[Au_2Ag_2(C_2Ph)_4(PPh_3)_2]$ (1) (1.538 g, 1.0 mmol) in acetone (70 cm³). A white precipitate formed as complex 1 dissolved. Stirring was continued for 1 h, and the white precipitate was then filtered off. Recrystallization from CH₂Cl₂/hexane gave colourless crystals of [AgClPPh₃] (0.65 g, 80%), m.p. 295-298°C, lit. [13] 294°C. The filtrate was evaporated to dryness and the residue washed with toluene to remove any remaining silver complex. Recrystallization of the residue from acetone/hexane gave the linear gold complex [N(PPh_3)₂][Au(C₂-Ph)₂] (1.76 g, 94%), identical in all respects to a sample described previously [8,9,14].

A similar reaction between complex 1 and $[NBu_4^n][Br]$ also gave $[NBu_4^n][Au-(C_2Ph)_2]$ in very high yield.

Preparation of gold-silver polymer complex (2)

(a) By reaction of $[Au(C_2Ph)AsPh_3]$ with $[\{Ag(C_2Ph)\}_n]$. Silver phenylacetylide (0.105 g, 0.5 mmol) was added to stirred solution of $[Au(C_2Ph)AsPh_3]$ (0.302 g, 0.5 mmol) in acetone (25 cm³). The solution became yellow soon after addition. Stirring was continued for 24 h. The yellow precipitate of the polymer complex $[\{AuAg(C_2Ph)_2\}_n]$ (2) (0.235 g, 93%) was filtered off. Anal. Found: C, 37.25; H, 1.7. $C_{16}H_{10}$ AgAu calcd.: C, 37.85; H, 1.95%. ν_{max} (C=C) (Nujol) 2065w with a shoulder at 2075 cm⁻¹; changes colour at 235-240 and melts (decomp.) 280-285°C.

(b) By reaction of $[Au(C_2Ph)P(OPh)_3]$ with $[{Ag(C_2Ph)}_n]$. Triphenylphosphite (0.2 g, 0.64 mmol) was added to a stirred suspension of gold phenylacetylide (0.192 g, 0.64 mmol) in acetone (25 cm³). A clear solution was obtained within 5 min. Addition of $[{Ag(C_2Ph)}_n]$ (0.134 g, 0.64 mmol) produced an immediate yellow colouration and a yellow precipitate. Stirring was continued for 2 h. The yellow precipitate of complex 2 (0.25 g, 77%) was filtered off and shown to be identical to the sample described above.

(c) By reaction of $[AuClPPh_3]$ with $[{Ag(C_2Ph)}_n]$ in toluene. Silver phenylacetylide (0.418 g, 2.0 mmol) was added to solution of $[AuClPPh_3]$ (0.495 g, 1.0 mmol) in toluene (20 cm³). A yellow precipitate formed immediately. Stirring was continued for 2 h. A precipitate of a yellow species contaminated with a white one (0.9 g) was filtered off, and washed repeatedly with dichloromethane to leave the yellow complex 2 (0.49 g, 97%), identical to samples described in (a) and (b). The washings were combined, the volume was reduced, and hexane was added to give colourless crystals of [AgClPPh₃] (0.350 g, 86%).

Reaction between the reagents (1.0 mmol each) in acetone (25 cm³) gave a precipitate of silver chloride (0.143 g, 99%). The gold complex $[Au(C_2Ph)PPh_3]$ (0.45 g, 80%) was isolated from the filtrate and identified by the usual methods, m.p. 162–164, lit. [11] 164°C; ν_{max} (C=C) (Nujol) 2113m cm⁻¹.

(d) By reaction of $[{Ag(C_2Ph)}_n]$ with a mixture of $[Au(C_2Ph)PPh_3]$ and AgCl. Silver chloride (0.144 g, 1 mmol) was added to a stirred solution of $[Au(C_2Ph)PPh_3]$ (0.56 g, 1 mmol) in dichloromethane (15 cm³). No change was observed. Addition of silver phenylacetylide (0.209 g, 1.0 mmol) produced an immediate yellow colouration. Stirring was continued for 24 h and the yellow precipitate of complex 2 (0.49 g, 97%) was then filtered off and shown to be identical to samples prepared in (a), (b), and (c). The silver complex $[AgCl(PPh_3)]$ (0.352 g, 87%) was isolated from the filtrate and identified in the usual way.

Preparation of the gold-copper polymer complex (3)

(a) By reaction of $[Au(C_2Ph)AsPh_3]$ with $[\{Cu(C_2Ph)\}_n]$. Copper phenylacetylide (0.329 g, 2.0 mmol) was added to a stirred solution of $[Au(C_2Ph)AsPh_3]$ (1.208 g, 2.0 mmol) in acetone (30cm³). Stirring was continued for 18 h. The pale yellow precipitate of the polymer complex $[\{AuCu(C_2Ph)_2\}_n]$ (3) (0.89 g, 96%) was filtered off. Anal. Found: C, 41.75; H, 2.25. $C_{16}H_{10}AuCu$ calcd.: C, 41.5; H, 2.15%, ν_{max} (C=C) (Nujol) 2034m cm⁻¹; darkens at 190-195 and melts (decomp.) 215– 220 ° C.

(b) By reaction of $[Au(C_2Ph)P(OPh)_3]$ with $[\{Cu(C_2Ph)\}_n]$. Copper phenylacetylide (0.165 g, 1.0 mmol) was added to a solution of $[Au(C_2Ph)P(OPh)_3]$ (0.608 g, 1.0 mmol) in acetone (25 cm³). Stirring was continued for 35h. The pale yellow precipitate of complex 3 (0.44 g, 95%) was filtered off and shown to be identical to the sample described in (a) above.

Addition of copper phenylacetylide (0.082 g, 0.5 mmol) to a solution of $[Au(C_2Ph)PPh_3]$ (0.28 g, 0.5 mmol) in acetone (20 cm³) did not result in a reaction. The reagents were recovered unchanged (m.p. and IR evidence).

Reaction between $[{Au(C_2Ph)}_n]$ and $[Cu(C_2Ph)PPh_3]$

Gold phenylacetylide (0.149 g, 0.5 mmol) was added to a stirred solution of $[Cu(C_2Ph)PPh_3]$ (0.213 g, 0.5 mmol) in dichloromethane (20 cm³). A yellow green precipitate was formed immediately. Stirring was continued for 0.5h and the precipitate was filtered off and identified as copper phenylacetylide (0.08 g, 97%), and $[Au(C_2Ph)PPh_3]$ (0.25 g, 89%) was obtained by evaporating the filtrate to a small volume and adding hexane. It was identified as above.

Reaction between 3 and PPh₃

Triphenylphosphine (0.262 g, 1.0 mmol) was added to a stirred suspension of the polymer complex [{AuCu(C_2Ph_2 }_n] (0.232 g, 0.5 mmol) in acetone (20 cm³). The polymer dissolved and yellow green crystals began to separate. Stirring was continued for 10 min then hexane (10 cm³) was added to complete the precipitation. Filtration gave yellow crystals of [Cu(C_2Ph)PPh_3] (0.2 g, 94%), m.p. 210–212, lit. [12,15] 212–214°C; ν_{max} (C=C) (Nujol) 2021m cm⁻¹. Reducing the volume of the filtrate and addition of hexane gave white crystals of [Au(C_2Ph)PPh_3] (0.215 g, 77%) identified as above.

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