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# Perspectives in syntheses, structures and bonding of acetylide-containing clusters of group 11 metals

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## Abstract

New aspects of chemistry and bonding have emerged from reactions of the anionic linear complexes $[M(C_2Ph)_2]^-$ with metal phenylacetylide polymers $[M(C_2Ph)]_n$ (M = Cu, Ag, Au). The reactions did not stop at depolymerization, but were followed by ethynylation and condensation of the formed cationic and anionic moieties into novel clusters. Thus the homonuclear $[Ag_5(C_2Ph)_6]^-$ and hetreonuclear $[Au_2Cu(C_2Ph)_4]^-$, $[Au_3M_2(C_2Ph)_6]^-$ (M = Cu, Ag), $[Ag_6Cu_7(C_2Ph)_{14}]^-$, and $[AuAg_6Cu_6(C_2Ph)_{14}]^-$ complexes were obtained. Extension of ethynylation reactions to neutral complexes resulted in the complexes $[Au_2Ag_2(C_2Ph)_4(PPh_3)_2]$, $[Ag_2Cu_2(C_2Ph)_4(PPh_3)_4]$, $[AuAg(C_2Ph)_2]_n$, $[AuCu(C_2Ph)_2]_n$, and $[AgCu(C_2Ph)_2]_n$. Aspects of syntheses, structures and bonding in these complexes are reviewed.

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## 1. Introduction

The linear complexes $[Q][M(C_2R)_2]$ (Q = Na, K; M = Cu; R = Me, Ph; Q = K; M = Ag; R = H, Me, Ph. Q = K; M = Au; R = Ph) discovered by Nast et al. [1–4] do not possess low energy d orbitals because of their anionic nature. They were described, particularly the gold derivatives, as being air-, light-, and moisture-sensitive and studies on their reactivities and properties were restricted to liquid ammonia solutions.

In our early investigations we employed the copper reagent $[(Ph_3P)_2N][Cu(C_2Ph)_2]$, which is more stable than its sodium or potassium analogues, with $[AuClPPh_3]$ hoping to obtain, as in the case with carbonylate anions, a complex with a copper gold bond. Instead, ethynylation took place, and the gold analogue of the copper reagent $[Au(C_2Ph)_2]^-$ was obtained in very high yield [5].

Earlier work showed that halide ions $X^-$ (X = Cl, Br, I) depolymerize $[Au(C_2Ph)]_n$ giving the linear anionic complexes $[XAuC_2Ph]^-$ [6]. However, when the same gold polymer was treated with the above copper reagent, ethynylation took place, giving $[Au(C_2Ph)_2]^-$ as the major product [5]. A small quantity of $[Au_2Cu(C_2Ph)_4]^-$ [**I**], however, was obtained as a second product.

$$[PhC_2CuC_2Ph]^- + 1/n\ [Au(C_2Ph)]_n$$

$$\rightarrow [PhC_2AuC_2Ph]^- + [Cu(C_2Ph)]_n$$

$$+ [Au_2Cu(C_2Ph)_4]^- \text{ is the minor product.}$$

In contrast to the above observation, that the linear gold complex does not react with $[Cu(C_2Ph)]_n$ (the reverse of the above equation) we found that the same reagent depolymerizes the analogous gold acetylide polymer, affording an anionic binuclear complex $[Au_2(C_2Ph)_3]^-$ (**II**) that is believed to have a gold–gold dative bond [7]. This latter result, and the formula of complex (**I**), prompted us to carry out a reaction between $[Au(C_2Ph)_2]^-$ and a mixture of $[Au(C_2Ph)]_n$ and $[Cu(C_2Ph)]_n$ in 1:1:1 mol ratio. The hope was to obtain the trinuclear complex (**I**) in high yield. This reaction, however, afforded the pentanuclear cluster $[Au_3Cu_2(C_2Ph)_6]^-$ (**III**) as the major product [8]. The desired product was obtained in very small yield just enough for $^1$H-NMR and IR spectra [9].

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## 2. Structure of complex (III)

Structural determination by Dr Knobler of complex (**III**) uncovered the mystery of these clusters [8] (Fig. 1).

The structure indicates that two ethynylation reactions took place, resulting in the three anionic linear gold moieties and the two copper cations, all condensed together to form the cluster. Both copper atoms are asymmetrically $\eta^2$-bonded to three alkyne ligands. The single $\nu$ (C≡C) band at ca. 2070 $cm^{-1}$ is only 30 $cm^{-1}$ lower than that of the un-coordinated alkyne of the linear gold complex $[Au(C_2Ph)_2]^-$.

The presence of appreciable metal-metal bonding was indicated by gold-copper bond distances (averaging 2.896 Å). These are comparable to the average Ir–Cu bond distances in the cluster $[Ir_2Cu_4(C_2Ph)_8(PPh_3)_2]$, in which metal-metal bonding is suggested to exist [10]. The intense yellow green color of the complex, in contrast with the colorless complexes of Cu(I) and Au(I), also suggests the presence of metal-metal interaction, as did the nature of the asymmetric $\pi$-interactions. The copper atoms were found to be pulled towards gold atoms, not pushed away. Although symmetric $\pi$-bonding, with a zwitterionic structure, is stronger than asymmetric $\pi$-bonding, the latter case of complex (**III**) was not obviously dictated by steric crowding. The metal-metal bonding observed apparently results from the stability acquired not only through metal-metal bonding but also via the several chelate rings that are generated as a result of such bonding.

The IR spectrum of complex (**I**) contained two $\nu$ (C≡C) bands, at 2100 and 2070 $cm^{-1}$, assigned to both uncoordinated and coordinated alkyne groups. In the light of the structure of (**III**), and from complex (**I**) IR spectrum, the following structure was suggested [9] (Fig. 2).

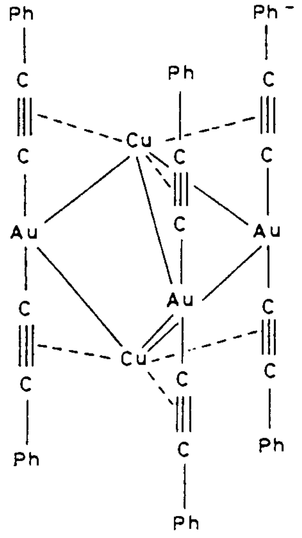

Fig. 1. Structure of complex (**III**).

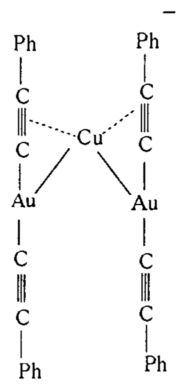

Fig. 2. Suggested structure of complex (**I**).

## 3. Stepwise synthesis of $[Au_3Cu_2(C_2Ph)_6]^-$ (III)

The stepwise synthesis was carried out of complex (**III**) starting from the linear anionic complex $[Au(C_2Ph)_2]^-$ through the binuclear complex $[Au_2(C_2Ph)_3]^-$ and the trinuclear cluster (**I**). The latter was obtained this time in high yield on addition of $[Cu(C_2Ph)]_n$ to $[Au_2(C_2Ph)_3]^-$ in a 1:1 mol ratio. Addition of $[Au(C_2Ph)]_n$ to complex (**I**) did not result in tetranuclear complex $[Au_3Cu(C_2Ph)_5]^-$, instead, complex (**III**) and $[AAfffu_2(C_2Ph)_3]^-$ (II) were obtained [9]. Complex (**III**), however, can be obtained alone by reacting complex (**I**) with a mixture of $[Au(C_2Ph)]_n$ and $[Cu(C_2Ph)]_n$ in 1:1:1 mol ratio.

In theory the anionic nature of complex (**III**) and the absence of steric crowding allow expansion of cluster (**III**) to higher nuclearity following similar steps as above. However, the reaction between complex (**III**) and the same mixture of polymers resulted in recovering complex (**III**) and formation of the mixed Au–Cu polymer $[AuCu(C_2Ph)_2]_n$ (see below) [11]. Apparently, basicity is not enough to hold atoms in a higher cluster and/or further $\pi$-interactions are not strong enough to give a stable cluster of higher nuclearity.

## 4. The pentanuclear clusters $[Au_3Ag_2(C_2Ph)_6]^-$, $[Ag_5(C_2Ph)_6]^-$ and $[Ag_{4.46}Cu_{0.54}(C_2Ph)_6]^-$

When $[Au_2(C_2Ph)_3]^-$ was employed with $[Ag(C_2Ph)]_n$ in 1:1 mol ratio, we did not get a gold–silver analogue to complex (**I**). Instead, $[Au_3Ag_2(C_2Ph)_6]^-$ (**IV**) and $[Au(C_2Ph)_2]^-$ were obtained [9,12]. The structure of (**IV**) was analogous to (**III**) with silver playing the role of copper [9,12,13].

Using $[Ag(C_2Ph)_2]^-$ and $[Ag(C_2Ph)]_n$ in 1:4 mol ratio afforded $[Ag_5(C_2Ph)_6]^-$ (**V**) in lower yields. It is believed that it has a structure similar to that of complex (**III**), implying that silver atoms are in two environments [12]. This is not the first time silver was found to exist in two environments i.e. cationic and anionic centres. We termed this feature, where silver atoms ethynylate other atoms in the same complex, auto ethynylation [12]. Cationic and anionic moieties are condensed to give the cluster. Silver complexes $[Ag(C_2R)PMe_3]_n$ (R = Ph, $SiMe_3$) [14,15] and $[Ag(C_2Ph)PPh_3]_4.3.5$ THF [15] exhibit the same phenomenon. The copper complex $[Cu(C_2Ph)PMe_3]_4$ [16] and the gold polymer complex $[Au(C_2Bu^t)]_6$ [17] also reveal similar properties. This feature is evidently an inherent property in alkynyl complexes of Group 11 metals. Although the structure of complex (**V**) was not elucidated by X-ray diffraction, structural determination for the complex obtained from the reaction between $[Cu(C_2Ph)_2]^-$ and $[Ag(C_2Ph)]_n$ in 1:4 mol ratio showed, however, that it is a copper disordered pentaargentate cluster with copper substituting silver atoms in some equatorial positions of the trigonal bipyramidal structure giving an Ag:Cu ratio 8.3:1 [18]. The formula of the complex is $[(Ph_3P)_2N]$ $[Ag_{4.46}Cu_{0.54}(C_2Ph)_6]$ (**VI**) (Fig. 3).

More routes were discovered for cluster (**IV**) involving the reactions of $[Ag(C_2Ph)]_n$ and $[XAu(C_2Ph)]^-$ (X = Cl, Br), of $[Au(C_2Ph)_2]^-$ and AgX (X = Cl, Br) or $[AuAg(C_2Ph)_2]_n$ (see below) and $X^-$ (X = Cl, Br, I) [19].

It is of interest to compare the reactivity of $[Au(C_2Ph)_2]^-$ and $[Pt(C_2Ph)_4]^{2-}$ with AgX. Whereas in the gold case, as mentioned above, the reaction resulted in cluster (**IV**), the reactions of MX (M = Ag; X = Cl, Br; M = Cu; X = Cl) with $[Pt(C_2Ph)_4]^{2-}$ resulted in addition products $[Pt(C_2Ph)_4(MX)_2]^{2-}$ in which the dianionic species is chelating two MX units through bridging alkyne ligands ($\mu-\eta^1$, $\eta^2$) [20].

Many alkynyl platinum(II) complexes having copper (I) and silver(I) $\pi$-coordinated to the alkyne ligand have been reported recently [21].

By using elemental analyses, IR spectra, and $^1$H-NMR, the product of the reaction of $[Au_3Cu_2(C_2Ph)_6]^-$ and a mixture of $[Au(C_2Ph)]_n$ and $[Ag(C_2Ph)]_n$, of $[Au_3Ag_2(C_2Ph)_6]^-$ with $[AuCu(C_2Ph)_2]_n$ or of $[Au_2Cu(C_2Ph)_4]^-$ with $[AuAg(C_2Ph)_2]_n$ was assigned the formula $[Au_3AgCu(C_2Ph)_6]^-$ (**VII**) [22]. However, recent single-crystal X-ray structural determination revealed that the product is composed of two bimetallic anionic clusters (**III**) and (**IV**) co-crystallized in one asymmetric unit [23].

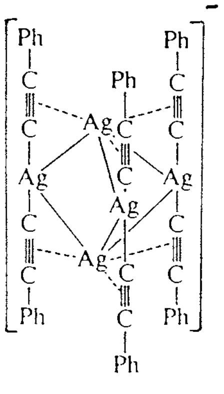

Fig. 3. Structure of comlex (**VI**) treated as $[Ag_5(C_2Ph)_6]^-$.

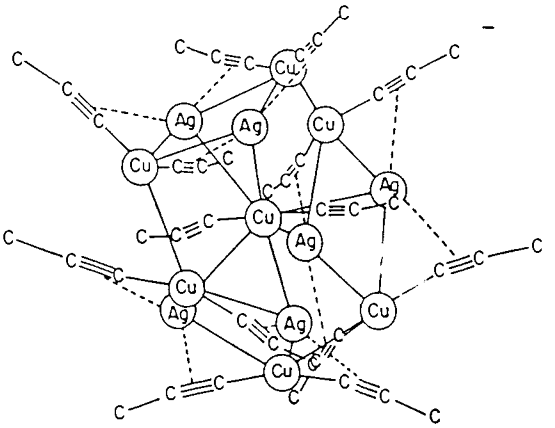

Fig. 4. Structure of complex (**VIII**).

## 5. The high polynuclear bimetallic $[Ag_6Cu_7(C_2Ph)_{14}]^-$ and the trimetallic $[AuAg_6Cu_6(C_2Ph)_{14}]^-$ clusters

When a reaction was carried out between $[Ag(C_2Ph)_2]^-$ and a mixture of $[Cu(C_2Ph)]_n$ and $[Ag(C_2Ph)]_n$ in 1:2:2 mol ratio, the high polynuclear cluster $[Ag_6Cu_7(C_2Ph)_{14}]^-$ (**VIII**) [24] was obtained. The same cluster formed when $[Cu(C_2Ph)_2]^-$ or QX [Q = $NBu^4_n$; X = Cl, Br, I; Q = $(Ph_3P)_2N$; X = Cl] and a mixture of $[Ag(C_2Ph)]_n$ and its copper analogue were employed [25]. Structural determination revealed that the complex exhibits new bonding features (Fig. 4) [24,26].

The central anion $[Cu(C_2Ph)_2]^-$, whether employed as a reactant or formed in situ by ethylynation, acts as a nucleus in building up the cluster. It is bonded through copper-silver interactions, to six silver atoms present in three tetranuclear subclusters $[Ag_2Cu_2(C_2Ph)_4]$ around the central linear moiety. Within the subcluster, each of the two copper atoms is end-on $\eta^1$-bonded in almost linear geometry to two alkynyl ligands, and each of the two silver atoms is asymmetrically side-on $\pi$-bonded to two alkyne groups. The structure can be viewed as three square pyramids sharing the apical atom.

When the linear gold complex $[Au(C_2Ph)_2]^-$ was employed with the same mixture of polymers, with different mol ratios, the trimetallic cluster $[AuAg_6Cu_6(C_2Ph)_{14}]^-$ (**IX**) was the sole product [25].

Apparently the relative high basicity of $[Cu(C_2Ph)_2]^-$ moieties in clusters(**VIII**) and (**IX**) are responsible for the high nuclearity of these two clusters. As mentioned above, when $[Au(C_2Ph)_2]^-$ or $[Ag(C_2Ph)_2]^-$ is employed in building up the clusters the nuclearity did not exceed five. IR spectra show that $\nu$ (C≡C) for linear complexes $[M(C_2Ph)_2]^-$ (M = Cu, Ag, Au) are at 2075, 2090, 2100 $cm^{-1}$, respectively. This confirms that the basicity decreases in the order $[Cu(C_2Ph)_2]^- > [Ag(C_2Ph)_2]^- > [Au(C_2Ph)_2]^-$. This reverses the trend amongst other transition metals [27]. The enhanced basicity transmitted throughout the cluster possibly helps to hold this relatively large number of metal atoms together.

A reaction between $[Au_3Cu_2(C_2Ph)_6]^-$ and a mixture of $[Ag(C_2Ph)]_n$ and $[Cu(C_2Ph)]_n$ in 1:4: mol ratio afforded the trimetallic $[AuAg_6Cu_6(C_2Ph)_{14}]^-$ (**IX**), the pentanuclear $[Au_3Ag_2(C_2Ph)_6]^-$ (**IV**) and $[Au(C_2Ph)_2]^-$. Similarly, when $[Au_3Ag_2(C_2Ph)_6]^-$ was employed instead of $[Au_3Cu_2(C_2Ph)_6]^-$, $[AuAg_6Cu_6C_2Ph)_{14}]$ (**IX**) and complex (**VII**) were obtained. Complex (**VI**) and $[AgCu(C_2Ph)_2]_n$ in 1:4 mol ratio gave complex (**VIII**) [22].

## 6. The neutral complexes $[Au_2Ag_2(C_2Ph)_4(PPh_3)_2]$, $[AuAg(C_2Ph)_2]_n$, $[AuCu(C_2Ph)_2]_n$, $[AgCu(C_2Ph)_2]_n$, and $[Ag_2Cu_2(C_2Ph)_4(PPh_3)_4]$

Depolymerization and ethynylation were not restricted to anionic complexes but were extended to neutral complexes giving neutral clusters. The fact that $[Au(C_2Ph)_2]^-$ does not react with $[Cu(C_2Ph)]_n$ but the dinuclear complex $[Au_2(C_2Ph)_3]$ (**II**) is ethynylated by the same copper reagent, forming $[Au_2Cu(C_2Ph)_4]^-$ [**I**], led us to believe that the 'AuC$_2$Ph' group in the dinuclear complex(**II**) is the reactive moiety. Considering the similarity between $[AuAuC_2Ph]^-$ and $[LAuC_2Ph]$ (L = neutral ligand), it was anticipated that $[L \rightarrow Au(C_2Ph)]$ would be ethynylated by $[Ag(C_2Ph)]_n$ and its copper analogue, leading in these cases, to neutral clusters [28].

Experimentation verified this prediction perfectly in the case of the silver derivative. Thus when the normally insoluble $[Ag(C_2Ph)]_n$ was added to a dichloromethane solution of $[Au(C_2Ph)PPh_3]$, it dissolved immediately and the tetranuclear cluster $[Au_2Ag_2(C_2Ph)_4(PPh_3)_2]$ (**X**) was isolated in very high yield. Single crystal structural determination confirmed that ethynylation took place [29] (Fig. 5).

The isolation of pure complex was hampered by the presence of the yellow polymer $[AuAg(C_2Ph)_2]_n$ formed by the reversible dissociation of $PPh_3$. The dimeric nature of the complex can be inferred from the nature of the IR spectrum. The latter showed a $\nu$ (C≡C) at $2075^{-1}$ cm assigned for coordinated alkyne ligand. A monomer would exhibit, as in complex (**I**), two $\nu$ (C≡C) for coordinated and uncoordinated alkyne ligands.

Since the ethynyl ligand of $[Ag(C_2Ph)]_n$ displaces $PPh_3$ in $[Au(C_2Ph)PPh_3]$, it was expected that it would displace both ligands in $[AuClPPh_3]$ with subsequent formation of the mixed gold–silver acetylide polymer complex. This was indeed the case, and the first mixed gold–silver alkynyl polymer $[AuAg(C_2Ph)_2]_n$ [**XI**] was obtained when the gold complex was reacted with the silver polymer in 1:2 mol ratio in toluene at room temperature (r.t.) [28]:

$$[AuClPPh_3] + 2/n\ [Ag(C_2Ph)]_n$$

$$\rightarrow 1/n\ [AuAg(C_2Ph)_2]_n + 1/4\ [AgClPPh_3]_4$$

Reaction between the same reagents in 1:1 mol ratio at r.t. in acetone resulted in quantitative precipitation of AgCl. The other product was $[Au(C_2Ph)PPh_3]$. When a further equivalent of $[Ag(C_2Ph)]_n$ was added to the reaction mixture prior to separation of AgCl, the latter formed $[AgClPPh_3]$ and complex (**XI**) 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 [28]. Evidently, the first step in the formation of the polymer complex (**XI**) 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 (**X**). The latter dissociates irreversibly in the presence of AgCl to give the polymer complex (**XI**) and $[AgClPPh_3]$ in high yields [28].

The same gold–silver polymer $[AuAg(C_2Ph)_2]$ (**XI**) was the sole product when $[Au(C_2Ph)L]$ (L = $AsPh_3$, $P(OPh)_3$) were employed with $[Ag(C_2Ph)]_n$ in 1:1 mol ratio. Here, dissociation of the ligand L was irreversible. The gold-copper analogue $[AuCu(C_2Ph)_2]_n$ (**XII**) was obtained when the same gold complexes were used with copper analogue of the silver polymer. The $\nu$ (C≡C) for (**XII**) is lower by ca. 40 $cm^{-1}$ than that of [**XI**] indicating stronger $\pi$-interaction between copper and alkyne. These findings are consistent with previous

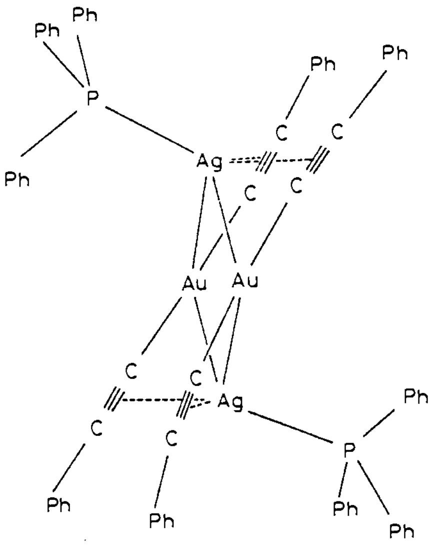

Fig. 5. Structure of complex [**X**].

observations [30]. When $[Au(C_2Ph)PPh_3]$, on the other hand, was employed with $[Cu(C_2Ph)]_n$, no reaction took place. These results were interpreted in terms of relative strengths of copper- and silver-acetylides as well as L–gold ($L = PPh_3$, $AsPh_3$, $P(OPh)_3$) bonds [28].

The bimetallic polymers, $[AgCu(C_2R)_2]_n$ (**XIII**, R = Ph; **XIV**, R = *p*-tolyl) were prepared by stirring a mixture of $[Ag(C_2R)]_n$ and $[Cu(C_2R)]_n$ in dichloromethane for several hours [31]. Treating both complexes with excess $PPh_3$ afforded the tetranuclear complexes $[Ag_2Cu_2(C_2R)_4(PPh_3)_4]$ (**XV**, R = Ph; **XVI**, R = *p*-tolyl). The structure of $[Ag_2Cu_2(C_2Ph)_4(PPh_3)_4]$ (**XV**) was determined by single crystal X-ray structural study [32].

The structure is similar to that of the tetranuclear $[Cu_4(C_2Ph)_4(PPh_3)_4]$ [33] having a tetrahedral skeleton of $Ag_2Cu_2$. Each metal atom is bonded to a phosphine ligand and to three phenylacetylide ligands; the latter being $\mu_3$-$\sigma$-bridging ligands. A series of cubane copper complexes of formulation $[Cu_4(C_2R)_4P'_4]$ (R = Ph, $SiMe_3$, PhOMe; $P' = PPh_2$(2-py), $P(p\text{-tolyl})_3$, $PMePh_2$) were also reported [34].

Recent examples of the latter mode of alkynyl bonding are also in the trinuclear complexes $[PtAg_2(C_6F_5)_2(C_2Ph)_2(PPh_3)_2]$ [35], $[Cu_3(\mu_3\text{-}\eta^1C_2Bu^t)(\mu_3\text{-}Cl)(\mu\text{-}dppm)_3]$ $[PF_6]$ [36], $[Cu_3(\mu_3\text{-}\eta^1\text{-}C_2Ph)(\mu\text{-}dppm)_3][BF_4]_2$, $[Cu_3(\mu_3\text{-}\eta^1\text{-}C_2Ph)_2(\mu\text{-}dppm)_3][BF_4]$, $[Cu_3(\mu_3\text{-}\eta^1\text{-}C_2Ph)[\mu_3Cl][\mu\text{-}dppm)_3][BF_4]$ [37,38], $[Ag_3(\mu_3\text{-}\eta^1\text{-}C_2C_6H_4\text{–}NO_2\text{–}p)(\mu\text{-}dppm)_3]^{2+}$ and $[Ag_3(\mu_3\text{-}\eta^1C_2C_6H_4\text{–}NO_2\text{–}p)_2\ (\mu\text{-}dppm)_3]^+$ [39], ($dppm = Ph_2PCH_2PPh_2$). Some more phosphine copper complexes containing bridging alkynyl ligands have been also reported [40].

## 7. Conclusion

The linear anionic complexes $[M(C_2Ph)_2]^-$ (M = Cu, Ag, Au) act as nuclei in building up the clusters, by virtue of their anionic nature and not being sterically crowded. The presence of the negative charge raises the energy of the d-electrons, which are usually low in energy, and therefore, renders them suitable for bonding. The relative high basicity of the linear copper moieties apparently allows clusters to proceed to high nuclearity. Cationic and anionic interaction is evidently an inherent feature of bonding in acetylide-containing Group 11 metal clusters. The likely existence of this property in alkynyl polymers of these metals, particularly of silver and copper, may be responsible for their ethynylating properties, that give rise not only to anionic but also to neutral clusters between these metals.

The alkynyl ligand has versatile modes of bonding. It remains to be seen if the chemistry described in this article would be useful in devising a systematic way for the synthesis of homo- and heteronuclear alkynyl transition metal clusters.

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