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Journal of Organometallic Chemistry 641 (2002) 126–133

Journal of Organometallic Chemistry

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Recent studies on alkynyl complexes of the Group 11 and 12 metals

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Received 27 June 2001; accepted 22 August 2001

Abstract

Although alkynyl complexes of Group 11 and 12 metals have been known for many years, recent crystallographic studies have revealed some interesting and novel structural features. These result from the combination of the alternative bonding modes available to the alkynyl ligand and the occurrence of weak metal–metal interactions. These come together to favour the formation of polynuclear ring and polyhedral structures. For example, the seemingly simple isoleptic compound [Au(C_2^tBu)] has a catenane structure based on two interweaving Au_6 rings and within each ring the alkynyl ligands displaying a range of bonding modes which involve σ- and π-bonding. The study of the reactions of the corresponding silver compound has revealed the formation of a complex with a cation which has a regular rhombohedral structure which is based on a halide anion encapsulated by 14 silver atoms. This compound results from the incorporation of halide anions in the interstitial site in the work-up process. The reactions between the mercury–dialkynyl complexes [$Hg(C_2R)_2$] (R = Ph, Tol or ^{t}Bu) and silver(I) and copper(I) ions have led to complexes where the Group 11 metal ions are π-coordinated to the alkynyl π-bonds. This leads to an interesting series of structures and, for example, $\{[Hg(C_2Tol)_2Ag][BF_4]\}_n$ has a polymeric structure with helices cross linked by C–H···π-interactions. © 2002 Elsevier Science B.V. All rights reserved.

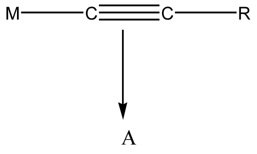
Keywords: Alkynes; Alkynyls; Group 11; Mercury; Catenanes; Anion recognition

1. Introduction

Although the organometallic chemistries of the Group 11 metals with alkynyl ligands can be traced back nearly 40 years ago to Nast [1], recent work in this field has shown that it can still generate novel chemistries and results. The alkynyl ligand has proved to be remarkably versatile in its coordinating abilities. Specifically, the triple bond of the alkynyl ligand may coordinate to other Lewis acid centres in a π-fashion as shown below and this can result in the generation of novel hydrogen bonded and polynuclear metal complexes (Scheme 1).

The electronic characteristics of alkynyl ligands have been investigated in some detail using spectroscopic and structural techniques [2] and it is generally agreed that the alkynyl ligand is a good σ-donor and a weak π-acceptor. These conclusions have been supported by molecular orbital calculations on bis(alkynyl) complexes of platinum [3]. The alkynyl ligand also appears to be a good π-donor and consequently the triple bond is able to either coordinate to another metal atom in a π-fashion or form unusual T-shaped hydrogen bonds.

There are several extensive reviews which discuss the chemistry of metal–alkynyl complexes in detail [4–9]. It is not our intention to provide another exhaustive review of this area but to describe recent developments in our laboratory which illustrate the way in which the versatility of the alkynyl ligand may be exploited to



A = Lewis acid

Scheme 1. Metal alkynyls can easily interact with Lewis acids.

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PII: S0022-328X(01)01305-5

build up some novel structures. Specifically, the following types of interactions are discussed. The π-donor ability of alkynyl ligands has long been utilised to coordinate additional metal atoms, however, we recently illustrated that the donor ability of this multiple bond may also be used to coordinate organic molecules with acidic C–H bonds, e.g. $CHCl_3$. We have also shown that in the absence of Lewis acids the metal–alkynyl complexes polymerise to form interesting polymeric structures. In the case of gold these interactions lead to a novel catenane structure and for silver a polyhedral structure which is capable of incorporating halide anions into a complex rhombohedral structure.

2. π-Coordination of coinage metals to mercury–(bis)alkynyl complexes

The ability of the alkynyl moiety to readily display both σ and π coordination modes has been extensively exploited for the synthesis of polymetallic assemblies in which more than one type of metal is present [4–9]. Fornies and co-workers, for example, have used the $[Pt(C{\equiv}CR)_4]^{2+}$ unit to prepare a wide range of multimetallic assemblies [10]. Some of these multimetallic species are based on the π-coordination of Cu(I), Ag(I) or Au(I) centres to the alkynyl groups of the platinum unit. Another extensively studied system is Lang's $\{[Ti](C{\equiv}CR)_2\}$ in which the alkynyl groups are σ-bonded to the titanium centre {where $[Ti] = (\eta^5\text{-}C_5H_4SiMe_3)_2Ti$} [11]. This complex can then form strong π-bonds (in a chelating fashion) to a second metal centre acting as a kind of π-*tweezer*. Yam et al. have extensively studied the luminescent properties of polynuclear metal–alkynyl complexes based on copper(I), silver(I) and gold(I) among other metals [12]. The flexibility on the bonding modes of the alkynyl fragment has been successfully used by this group to produce a wide range of polynuclear structures which exhibit rich photophysical and photochemical properties.

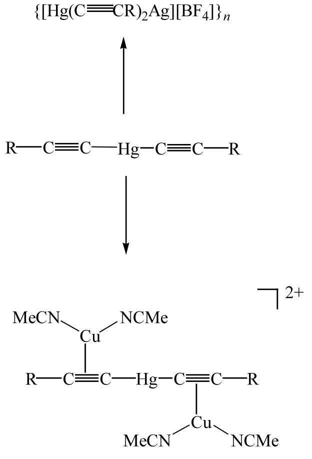
Most of our interest in metal–alkynyl complexes has been concentrated on the coinage metals. This is partly due to the potential ability of these metals to display non-covalent McM interactions which could be used to form polymetallic assemblies (in addition to the π-coordination of the metal centres to the alkynyl moiety). At this point it was of interest to study systems based on mercury(II)–alkynyls and compare their chemistry to one of the alkynyl complexes of the coinage metals. Mercury(II) can also display non-covalent Hg···Hg or Hg···M interactions, although only few examples showing these interactions have been clearly identified [13–15,17]. Moreover, the possibility of having neutral $Hg(C{\equiv}CR)_2$ species which could use the alkynyl groups to further coordinate other metals (such as copper, silver and gold) was an attractive alternative. Our most recent results in this area together with the latest examples reported in the literatures are described in the following sections.

2.1. Hg(II)···Hg(II) interactions

It has been suggested that, similar to the metallophilic interactions displayed by Au(I), Ag(I) and Cu(I), complexes based on Hg(II) should display mercurophilicity [13]. However, only few complexes displaying short Hg(II)···Hg(II) separations have been reported to date. The discussion on whether or not these short distances have to be considered as clear indications of metallophilic interactions is still open to debate, especially in those cases where bridging ligands might be responsible for the proximity of the metal centres [14]. In 1997, Zamora et al. [15] reported the synthesis of $[L_3Hg_3O]^+$ (L = 1,3-dimethyluracil-5-yl). The trimercury cations dimerise in the solid state through short intercationic Hg···Hg contacts to give hexanuclear compounds, showing a remarkable similarity to the trigold oxonium salts $[(LAu)_3O]^+$ (L = non-bulky phosphine) which display intra- and inter-cationic Au···Au interactions again leading to dimerisation [16]. A clear example of intermolecular Hg···Hg interaction can be found in the complex $[MeHg(SC_4H_2N_2Me)]$ where two mercury atoms are separated by a distance of 3.10 Å [17]. This distance is clearly shorter than twice the van der Waals radius of mercury (~4 Å). Besides the Hg···Hg interactions, there is also interest in establishing the strength of Hg···M attractive interactions (where M is another d^{10} metal). During the last few years some structural evidence has been reported on Hg(II)···Au(I) interactions [18–20].

2.2. Mercury(II)–alkynyl complexes

Even though mercury alkynyls have been widely used as reagents for organometallic transformations [21], compared to other metal alkynyls, they have not been so thoroughly studied. Their main application has been as alkynyl transfer reagents [21,22] and, to a far lesser extent, for the synthesis of polymetallic assemblies [23]. Mercury bisalkynyls $Hg(C{\equiv}CR)_2$ are generally prepared by mixing K_2HgI_4 with the corresponding $RC{\equiv}CH$ in the presence of KOH [24], while monoalkynyls with formula $Hg(C{\equiv}CR)X$ can be obtained from different synthetic routes [25]. To date there are around 50 mercury–bisalkynyl complexes reported in the literature [26]. Most of them have been characterised by IR and NMR spectroscopies. The $\nu(C{\equiv}C)$ stretches for these compounds appear normally around 2150 cm^{-1}. ^{13}C-NMR spectroscopy has also been used to determine the presence of the mercury–alkynyl bond [27]. Due to



R = $-C_6H_5$, $-C_6H_4-CH_3-4$, $-C(CH_3)_3$

Scheme 2. Reaction scheme for the synthesis of $\{[Hg(C{\equiv}CTol)_2Ag][BF_4]\}_n$ and $[Hg(C{\equiv}CR)_2Cu_2(MeCN)_4][PF_6]_2$.

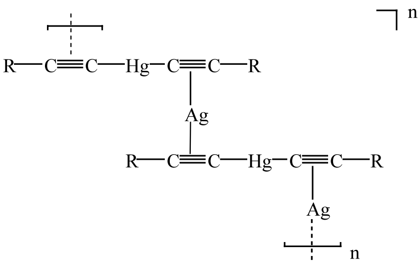


Fig. 1. Schematic representation of the structure of $\{[Hg(C{\equiv}CTol)_2Ag][BF_4]\}_n$.

the low solubility of these compounds in common organic solvents, long collection times are generally needed to record ^{13}C-NMR spectra, in particular for the observation of the ^{199}Hg satellites of the alkynyl carbon atoms. A thorough investigation of the ^{13}C- and ^{199}Hg-NMR spectra of alkynyls with formula $Hg(C{\equiv}CR)_2$, $R'Hg(C{\equiv}CR)$ and $R'HgC{\equiv}CHgR'$ has demonstrated that the values of the coupling constants $^1J(^{199}Hg-^{13}C{=}C_4H_9^n)$ vary within a very wide range, going from 3875 Hz for $ClHg(C{\equiv}CH)$ to 880 Hz for $(C_6H_{11})HgC{\equiv}CHg(C_6H_{11})$. The δ (^{199}Hg) values for the compounds $Hg(C{=}CR)_2$ change according to the polarisation of the Hg–C= bond with increasing shielding of ^{199}Hg going from electron-donating groups to electron-withdrawing substituents (e.g. δ (^{199}Hg) = −837.3 for R = ^{t}Bu, δ (^{199}Hg) = −975.3 for R = Cl).

In spite of the well-established synthetic procedures developed to prepare mercury–bisalkynyls and of their systematic spectroscopic characterisation, the structural data available for these compounds are very scarce. As a consequence, little is known about their potential mercurophilic interactions and about their ability to use the alkynyl moiety for further coordination. To date, only $Hg(C{\equiv}CPh)_2$ and $Hg(C{\equiv}CSiMe_3)_2$ have been structurally characterised [28]. The X-ray crystallographic study of these organometallic species confirmed the linear arrangement of the alkynyl ligands about the metal centre. Weak mercurophilic interactions are found in this structure together with π-interactions between the mercury centres and the C≡C moiety.

The linear coordination exhibited by mercury(II), the weak Hg(II)···Hg(II) interactions and the π-interactions between the mercury centres and the alkynyl moieties shown in the two reported crystal structures, suggested that $Hg(C{\equiv}CR)_2$ could be a good building block for the synthesis of multimetallic assemblies. This stimulated us to start a thorough study of the ability of these species to interact with other metals and examine the possibility of enhancing metallophilicity by a combination of non-covalent interactions (e.g. π–π interactions exhibited by the ligands). Specifically, the spectroscopic and structural studies of the products resulting from the reactions between $Hg(C{\equiv}CR)_2$ (R = C_6H_5, p-C_6H_4Me, $-C(CH_3)_3$) and coinage metals were undertaken [29]. Here we discuss some of these results and compare them with relevant data previously reported in the literature.

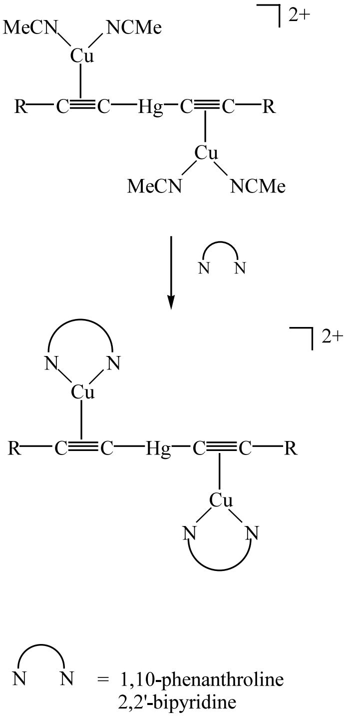
2.3. The $Hg(C{\equiv}CR)_2$ unit as building block for multimetallic systems

The reaction of $Hg(C{\equiv}CR)_2$ with two equivalents of $[Cu(MeCN)_4][PF_6]$ leads to the facile formation of the trimetallic compounds $[Hg(C{\equiv}CR)_2Cu_2(MeCN)_4][PF_6]_2$ (see Scheme 2).

These mixed-metal complexes have been spectroscopically and, in one case when R = Ph, structurally characterised showing that the alkynyl moiety is σ-bonded to the mercury centre and π-bonded to the copper atoms [29]. Even though this type of coordination has been previously suggested to be present in the polymeric compound $[Hg(C{\equiv}CPh)_2(CuCl_2)_2]_n$ [30], this is the first structurally characterised example of a copper(I) complex π-coordinated to a mercury–alkynyl species. In this complex the π-bonded copper centres retain in their coordination sphere the acetonitrile groups present in the starting material preventing the further coordination of a second $Hg(C{\equiv}CR)_2$ unit to the copper which would lead to the formation of a mixed-metal polymer.

In contrast to the reactivity of the copper(I) salts, when $Hg(C{\equiv}CR)_2$ (R = C_6H_5, p-C_6H_4Me, $-C(CH_3)_3$) are reacted with $[Ag(MeCN)_4][BF_4]$ the polymeric species $\{[Hg(C{\equiv}CR)_2Ag][BF_4]\}_n$ (R = Ph, Tol) are obtained. One of these species (when R = Tol) has been structurally characterised showing the polymeric arrangement with the silver atoms π-bonding approximately linearly between the ethyne linkages of adjacent molecules (see Fig. 1).

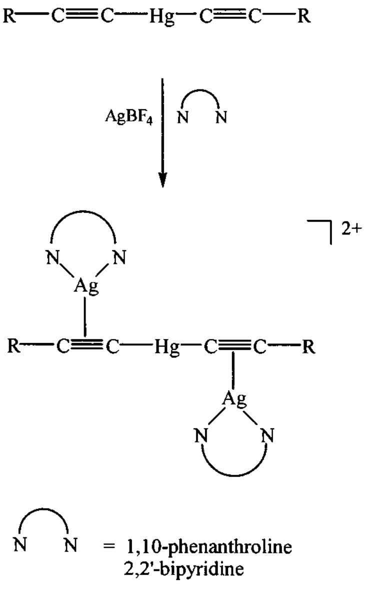
This polymeric organometallic compound is chiral and hence all the chains have a common helicity. The twist of this helical structure seems to be in good measure determined by the presence of the anion (BF_4^-) which interacts strongly with the silver and mercury centres. Unfortunately, no short contacts between the metals (to suggest metallophilic interactions) were observed.



N N = 1,10-phenanthroline
2,2′-bipyridine

R = $-C_6H_5$, $-C_6H_4-CH_3-4$, $-C(CH_3)_3$

Scheme 3. Reaction scheme for the synthesis of $[Hg(C{\equiv}CR)_2Cu_2(L_2)_2][PF_6]_2$.



N N = 1,10-phenanthroline
2,2′-bipyridine

R = $-C_6H_5$, $-C_6H_4-CH_3-4$, $-C(CH_3)_3$

Scheme 4. Reaction scheme for the synthesis of $[Hg(C{\equiv}CR)_2Ag_2(L_2)_2][BF_4]_2$.

As has already been pointed out part of the interest in studying these multimetallic systems, is the potential appearance of metallophilic interactions such as Hg(II)···Hg(II), Ag(I)···Ag(I) or the mixed Hg(II)···Ag(I). A possibility to favour these interactions is to enhance the π-stacking ability of the complexes' ligands. In order to do this, the reaction between the complexes $[Hg(C{\equiv}CR)_2Cu_2(MeCN)_4][PF_6]_2$ and planar chelating ligands, which could displace the acetonitrile groups, were studied. When $[Hg(C{\equiv}CR)_2Cu_2(MeCN)_4][PF_6]_2$ is reacted with either 1,10-phenanthroline or 2,2′-bipyridine, the formation of $[Hg(C{\equiv}CR)_2Cu_2(L_2)_2][PF_6]_2$ (where L_2 = 1,10-phenanthroline or 2,2′-bipyridine) is observed (see Scheme 3).

Similarly, the reactions between $AgBF_4$ and $Hg(C{\equiv}CR)_2$ in the presence of either 2,2′-bipyridine or 1,10-phenanthroline (L_2), lead to the formation of the planar system $[Hg(C{\equiv}CR)_2Ag_2(L_2)_2][BF_4]_2$ (see Scheme 4). One of them (for R = Ph and L_2 = bipyridine) has been structurally characterised showing the Ag(bipy) moieties π-bonding to the alkynyl units. All the metal centres and ligands are located in the same plane giving a perfectly planar structure.

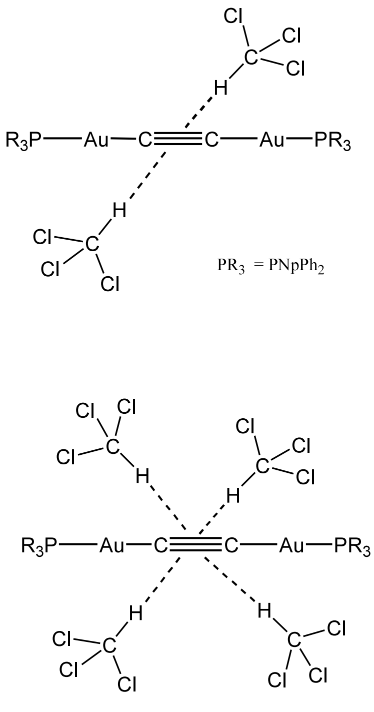
However, the presence of BF_4^- above and below the plane of the molecules, forbids two units to approach each other preventing them from proper π-stacking and hindering any potential metallophilic interaction.

The examples presented in this section have demonstrated the ability of the alkynyl moiety to act as a σ and π ligand bringing together several metal centres. These are among the first examples in which mercury–bisalkynyl species are used for this purpose leading to the formation of either molecular species or polymeric assemblies.

3. Interactions of M–alkynyl with acidic C–H groups

The interactions between the π-bonds of the alkynyl ligand and a cationic metallic Lewis acid has many precedents in the chemical literature. However, the interactions between an acidic C–H group of a chloroform molecule and a triple C–C bond is much more unusual. These were observed for the first time in ethynyl complexes of gold with polyphenyl–phosphine ligands, notably $R_3P{-}Au(C{\equiv}C)Au{-}PR_3{\cdot}nCHCl_3$ (where $PR_3 = PPh_2Naphthyl$ or $PR(Naphthyl)_2$) [31].

The geometries of these complexes resemble a dumbbell with the Au–C≡C–Au fragment representing the bar and two large spherical triarylphosphine ligands representing the spheres. The C–C and Au–C bonds have bond lengths which fall in the range expected for



Scheme 5. Schematic representation of the H-bonding interaction between R_3P–Au(C≡C)Au–PR_3 and $CHCl_3$.

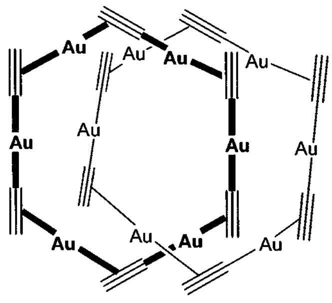
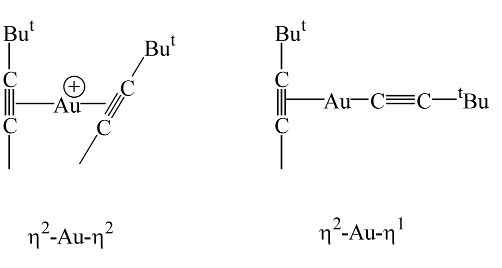


Fig. 2. Schematic representation of the gold catenane [{Au(C≡C^{t}Bu)$_6$}$_2$].



Scheme 6.

gold–alkynyl complexes. Centro-symmetrically related pairs of $CHCl_3$ molecules are positioned with their C–H bonds directed orthogonally towards the centre of the C–C bond. The structures are represented in Scheme 5.

The distance between the H of the C–H bond and the middle of the C–C bond is 2.42 Å in the first example and 2.54 Å in the second compound. The C–H hydrogen atom is ca. 2.50 Å from each carbon atom of the C–C bond in the first example and 2.60–2.70 Å in the second compound. The Cl_3CH–π(C–C) interactions are very close to the optimal T-shaped geometry predicted theoretically.

Clearly, the dumbbell shape of these molecules provides an ideal cavity for the chloroform molecules to dock into and interact with the ethyne bond. We have performed detailed ab initio and density functional calculations on ethyne and ethynyl complexes with organic molecules which have acidic C–H bonds [32]. The residual charge on the ethynyl fragment was found to be a very important consideration and for example the triple bond in Na_2C_2 was found to be a much stronger electron-donating group than that in H_2C_2 and the calculated interaction energy to $CHCl_3$ rises from 10 to 60 kJ mol^{-1}. For the model compound H_3PAuC_2-$AuPH_3$ the binding energy to a $CHCl_3$ molecule was calculated to be ca. 25 kJ mol^{-1}. However, the calculations suggest that it is not only electrostatic interactions that are responsible for the strength of the hydrogen bond but also the overlap between the 1s orbital of the hydrogen atom and the carbon 2p orbitals which gives rise to a significant covalent contribution.

4. Gold(I) alkynyls: synthesis of a gold catenane

Coates and Parkin first synthesised $[\mathrm{AuC}_2^t\mathrm{Bu}]_n$ nearly 40 years ago and suggested in the absence of structural data, it had a polymeric structure. When we prepared the same compound using an alternative route from the labile $[\mathrm{Au(NH_3)_2}]^+$ complex we were able to isolate yellow crystals which were amenable to a single-crystal X-ray crystallographic analysis [33]. The analysis demonstrated that the compound had the novel catenane structure illustrated in Fig. 2.

The structure is based on two interlocking six-membered rings of gold atoms and therefore the compound is more correctly formulated as $[\{\mathrm{Au(C_2^tBu)}\}_6]_2$. The adoption of this novel structure may be attributed to two important factors. First, the flexibility of the alkynyl ligand since each ring contains pairs of gold atoms with the three coordination modes shown in Scheme 6.

Since these three moieties bear different formal charges on the gold atoms this requires some migrations of alkynyl ligands to occur in the formation of the catenane rings. Within each ring the gold atoms form an almost regular hexagon (Au···Au contacts lie in the narrow range of 3.30–3.60 Å) and define a plane where the maximum deviations of the gold atoms are no more than 0.10 Å. These contacts suggest that aurophilic interactions may also contribute to the adoption of the structure observed.

5. Anion templated synthesis of silver alkynyl cage-type compounds

The synthesis of the catenane $[\{Au(C{\equiv}C^tBu)_6\}_2]$ discussed in Section 4, stimulated us to undertake analogous studies with silver(I). The possibility of forming polymetallic assemblies in which non-covalent Ag···Ag interactions were displayed was particularly attractive since, in contrast to the well-defined aurophilic interactions, the analogous argentophilicity has only recently been properly studied. Since short Ag(I)···Ag(I) distances (shorter than 3.4 Å which is the sum of the van der Waals radii) in bi- and poly-nuclear bridged complexes are typically induced or favoured by the ligand's framework, examples of ligand-unsupported Ag···Ag contacts are extremely important in elucidating the extent of stabilisation lent to the system by the argentophilic attraction. Among the most interesting examples of argentophilicity are a series of silver(I) double, triple and quadruple salts recently reported by Mak and co-workers [34–36]. In these systems argentophilic interactions promote the aggregation of the Ag(I) centres into polyhedral cage-type compounds with Ag···Ag distances normally comparable to the interatomic contact of 2.89 Å observed in silver metal [37].

Ligand-unsupported Ag···Ag interactions have also been suggested in $[Ag_3(2\text{-}(3(5)\text{-}pz)py)_3]_2\cdot 2py$ (where pz = pyrazine and py = pyridine) [38], where these distances are closer to the upper van der Waals limit; they are still thought to be due to genuine metallophilic interactions. Omary et al. have recently reported evidence of ligand-unsupported metallophilicity in $Tl[Ag(CN)_2]$, which is particularly important since the attractive interactions occur in a mononuclear compound with no bridging ligand [39]. On the other hand, spectroscopic evidence for argentophilicity has been obtained from the study of a series of binuclear silver(I) complexes reported by Che et al. [40]. The $4d\sigma^*$–$5p\sigma$ transition, originating from Ag(I)···Ag(I) interactions, has been studied by means of UV and Raman spectroscopies in the ground and excited states and has been confirmed to be predominantly localised in the Ag···Ag *bond*. A theoretical approach to the study of metallophilic interactions for the three coinage metals has been developed by Pyykkö et al. [41] and Laguna and co-workers [42], concluding that 'metallophilic attraction is indeed present for all the coinage metals as a correlation effect, strengthened by the relativistic effect for gold'.

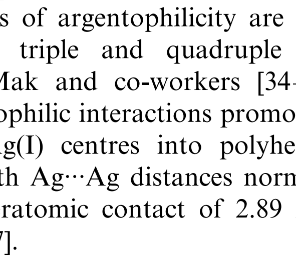


Fig. 3. Schematic representation of the rhombohedral core of the silver cage $[Ag_{14}(C{\equiv}C^tBu)_{12}Cl][OH]$.

Structural evidence for the existence of argentophilic attractions in silver alkynyl complexes is extremely poor, probably due to the photosensitivity of these complexes and their low solubility in common solvents. Three structures of simple silver acetylides are known, $[Ph_3PAg(C{=}CPh)]_4\cdot 3.5THF$, $[Me_3PAg(C{=}CSiMe_3)]_8$ and $[Me_3PAg(C{=}CPh)]_8$ [43,44]. An analysis of the structures reveals that the compounds, despite aggregating in a different fashion, can be considered as made up of similar $[Ag(alkynyl)_2]^-$ and $[Ag(PR_3)_2]^+$ units with Ag···Ag separations again comparable with the distances found in silver metal. In a series of trinuclear silver(I) acetylides recently reported by Yam et al. [45,46], the Ag···Ag distances range from 2.895(8) to 3.403(6) Å and are comparable to the sum of the van der Waals radii of silver (3.44 Å).

In our own efforts to understand the nature of the Ag···Ag interactions and by analogy to the synthesis of the gold catenane described in Section 4, $AgBF_4$ was reacted with $^tBuC{\equiv}CH$ in the presence of NEt_3 and a white precipitate was obtained which has been formulated as $[Ag(C{\equiv}C^tBu)]_n$ [47]. Coates and Parkin have suggested that compounds with this general formula are polymers in which the silver(I) centres coordinate via σ and π bonds to the alkynyl groups [48]. However, little is known about the real structure of these organometallic polymers. This white solid is insoluble in common solvents which has prevented us from structurally characterising it. However, we have now established that if it is treated with $CHCl_3$, $[Ag(C{\equiv}C^tBu)]_n$ undergoes a reaction (most probably involving the HCl present in chloroform) to yield the novel cage-type cationic species $[Ag_{14}(C{\equiv}C^tBu)_{12}Cl]^+$. The X-ray crystallographic characterisation of this cage has shown that the silver atoms are arranged so as to form a near-regular rhombic dodecahedron with Ag···Ag distances for the 'edges' in the 2.953(2)–2.986(2) Å range (see Fig. 3).

These distances are comparable with those seen, for example, in the silver double salts reported by Mak and co-workers [34–36] attributed to Ag···Ag argentophilic interactions (see Table 1 for a summary of silver–silver contacts).

Table 1
Ag···Ag contacts in silver complexes

Complex	Ag···Ag (Å)	References
$2Ag_2C_2 \cdot 3AgCN \cdot 15CF_3CO_2$-$Ag \cdot 2AgBF_4 \cdot 9H_2O$	2.839(2)–3.316(1)	[36]
$Ag_2C_2 \cdot AgF \cdot 4CF_3SO_3Ag \cdot CH_3CN$	2.878(1)–3.003(1)	[35]
$Ag_2C_2 \cdot 8AgF$	2.8441(4)–3.0863(5)	[34b]
$[Ag_3(2\text{-}(3(5)\text{-pz})py)_3]_2 \cdot 2py$	3.227(2)	[38]
$Tl[Ag(CN)_2]$	3.110(3)	[39]
$[Ag_2(\mu\text{-dcpm})(\mu\text{-}O_2CCF_3)_2]$	2.8892(9)	[40]
$[Ag(Pcy_3)](O_2CCF_3)]_2$	3.095(1)	[40]
$[Ph_3PagC{=}CPh]_4 \cdot 3.5THF$	2.921(1)–3.084(1)	[43]
$[Ag_3(\mu\text{-dppm})_3(\mu_3\text{-}\eta^1\text{-}C{=}C\text{–}C_6H_4\text{–}NO_2\text{-}p)_2]PF_6$	2.8946(8)–3.1948(9)	[45]
$[Ag_3(\mu\text{-dppm})_3(\mu_3\text{-}\eta^1\text{-}C{=}C\text{–}C_6H_4\text{–}NO_2\text{-}p)](BF_4)_2$	2.9850(6)–3.4030(6)	[45]

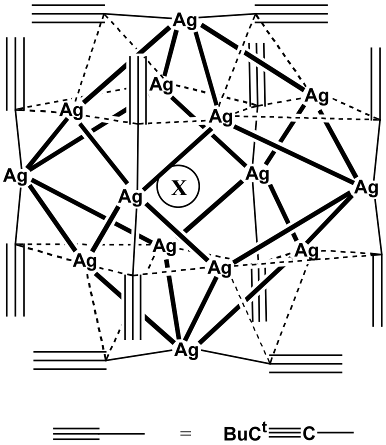


Fig. 4. Schematic representation of the molecular structure of $[Ag_{14}(C{\equiv}C^tBu)_{12}Cl][OH]$.

Six of the silver atoms in this cage can be envisaged as forming an octahedron (with the anion at its centre) which interpenetrates a cubic array made up of the remaining eight silver atoms. Each of the 'octahedral' site silver atoms bears two σ-bonded alkynyl groups which in turn bridges pairs of silver atoms that form the edges of the 'cube' (see Fig. 4).

This results suggest that the conversion of $[Ag(C{\equiv}C^tBu)]_n$ to the cationic cage $[Ag_{14}(C{\equiv}C^tBu)_{12}Cl]^+$ is partly directed (or templated) by the chloride anions present in $CHCl_3$. In order to test this hypothesis, the reaction between $AgBF_4$, $^tBuC{\equiv}CH$ and NEt_3 was repeated but this time in the presence of stoichiometric amounts of chloride (e.g. $[NEt_4]Cl$). In this case, the formation of the insoluble material (i.e. $[Ag(C{\equiv}C^tBu)]_n$) was not observed and instead high yields of the cage compound $[Ag_{14}(C{\equiv}C^tBu)_{12}Cl]^+$ were obtained (which has been spectroscopically and structurally characterised). In order to explore the generality of this anion-templated synthesis, the reaction was repeated but this time in the presence of a bromide source (e.g. $[NBu_4]Br$). As expected, the formation of the bromide-containing cationic cage $[Ag_{14}(C{\equiv}C^tBu)_{12}Br]^+$ was observed (which has also been structurally characterised). Attempts to prepare the analogous iodide cage compound have not yet been successful. Our preliminary results indicate that a bigger cage-type compound might be formed.

6. Conclusions

The combination of the alternative bonding modes available to the alkynyl ligand and the occurrence of weak metal–metal interactions come together to favour the formation of polynuclear ring and polyhedral structures. Even seemingly simple isoleptic compounds turn out to have novel and interesting structures. Furthermore, the compounds in solutions can provide precursors for interesting templating reactions involving halide anions.

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