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π-Coordination of Silver and Copper to Mercury Bis-alkynyls: Synthesis and Structural Characterization

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The reactions between the mercury−dialkynyl complexes [Hg(C≡CR)$_2$] (R = C$_6$H$_5$, −C$_6$H$_4$−CH$_3$-4, and −C(CH$_3$)$_3$) and a series of Ag(I) and Cu(I) compounds are reported. Compounds with the general formula [Hg(C≡CR)$_2$Cu$_2$(CH$_3$CN)$_4$][PF$_6$]$_2$, [Hg(C≡CR)$_2$M$_2$(L)$_2$]X$_2$ (M = Ag, Cu; R = C$_6$H$_5$, −C$_6$H$_4$−CH$_3$-4, and −C(CH$_3$)$_3$; L = 2,2′-bipyridine, 1,10-phenanthroline; X = PF$_6$ or BF$_4$), and {[Hg(C≡CR)$_2$Ag][BF$_4$]}$_n$ (R = C$_6$H$_5$ and −C$_6$H$_4$−CH$_3$-4) resulted from these reactions. In these complexes the silver and copper atoms are π-coordinated to the alkynyls' triple bonds. Crystal structures of three of these complexes have been obtained, confirming the formulation and in two instances revealing weak anion···cation interactions. The structure of {[Hg(C≡CTol)$_2$Ag][BF$_4$]}$_n$ has been shown to be a polymer comprised of helices cross-linked by C−H···π interactions.

Introduction

The study of polynuclear metal−organic complexes has increased rapidly in recent years.[1] The interest in these mixed-metal systems stems not only from their structural variety but also from the possibility of forming extensively delocalized arrangements which could lead to metal−organic polymers exhibiting metal−metal communication.[2] Alkynyl groups are among the most widely used ligands for this purpose.

Metal−alkynyls are well known for most metals, and their chemistry has been developed extensively.[3] Partly this has been due to their application as reagents in organometallic transformations[4] and for the synthesis of polymetallic assemblies.[5] The chemistry of mercury−alkynyl compounds, however, has not been so thoroughly studied, even though they were first reported several decades ago.[6] One class of compounds that deserve particular attention are the mercury−dialkynyls, for which relatively few studies have been previously reported.[7] The linear coordination exhibited by the mercury(II) ion in organometallic complexes together with the evidence of weak Hg(II)···Hg(II) interactions[8] similar to the aurophilicity exhibited by gold suggests that mercury dialkynyls could be valuable building blocks for the synthesis of metal−organic polymers and supramolecular aggregates.

As part of our studies on mercury−alkynyl compounds, we were interested in exploring the possibility of coordinating metals in an η^2 fashion to the triple bonds of the mercury alkynyls. Extensive work by

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Fornies,[9] Lang,[10] Yam,[11] and others[12] has demonstrated that metals such as copper, silver, and gold can π-coordinate to alkynyl groups of organometallic compounds in an η^2 fashion, giving rise to interesting polymetallic species. Inspired by this chemistry and because of our interest in the supramolecular interactions of organometallic species, the reactions of $[Hg(C{\equiv}CR)_2]$ (R = $-C_6H_5$, $-C_6H_4-CH_3$-4, $-C(CH_3)_3$) with silver and copper compounds were studied. Here we report the synthesis and characterization of $[Hg(C{\equiv}CR)_2Cu_2(CH_3CN)_4][PF_6]_2$ (R = C_6H_5, $-C_6H_4-CH_3$-4, $-C(CH_3)_3$), $[Hg(C{\equiv}CR)_2M_2(L)_2]X_2$ (R = C_6H_5, $-C_6H_4-CH_3$-4, $-C(CH_3)_3$; M = Ag, Cu; L = bipyridine, phenanthroline; X = PF_6^- or BF_4^-), and the polymeric compounds $\{[Hg(C{\equiv}CR)_2Ag][BF_4]\}_n$ (R = C_6H_5, $-C_6H_4-CH_3$-4). The X-ray crystal structures of three of these species are presented.

Results and Discussion

Synthesis of $[Hg(C{\equiv}CR)_2Cu_2(CH_3CN)_4][PF_6]_2$ and $\{[Hg(C{\equiv}CR)_2Ag][BF_4]\}_n$. When the mercury−dialkynyl compounds $[Hg(C{\equiv}CR)_2]$ (R = C_6H_5, $-C_6H_4-CH_3$-4, $-C(CH_3)_3$) are reacted with 2 equiv of $[Cu(CH_3CN)_4][PF_6]$ in organic solvents, white precipitates are formed. On the basis of IR, ^{1}H NMR, and elemental analyses the new products obtained can be formulated as $[Hg(C{\equiv}CR)_2Cu_2(CH_3CN)_4][PF_6]_2$ (R = C_6H_5, **1**; $-C_6H_4-CH_3$-4, **2**; $-C(CH_3)_3$, **3**) (see Scheme 1). This formulation is also consistent with the mass spectrometric results.

Compared with the corresponding starting materials, the IR spectra of these compounds show a shift of the ν(C≡C) stretch toward lower frequencies (see Table 1), suggesting a π-bonding mode of copper to the alkynyl ligands. Two bands in the region around 2320 and 2290 cm^{-1} are consistent with the presence of coordinated acetonitrile. The ^{1}H NMR spectra of **1**−**3** show only one set of signals for the R groups on the alkynyl ligand. In all three cases these signals are shifted slightly compared with those of the parent compounds. This formulation has been confirmed by a single-crystal X-ray analysis of compound **1**.

Scheme 1. Synthesis of 1−5

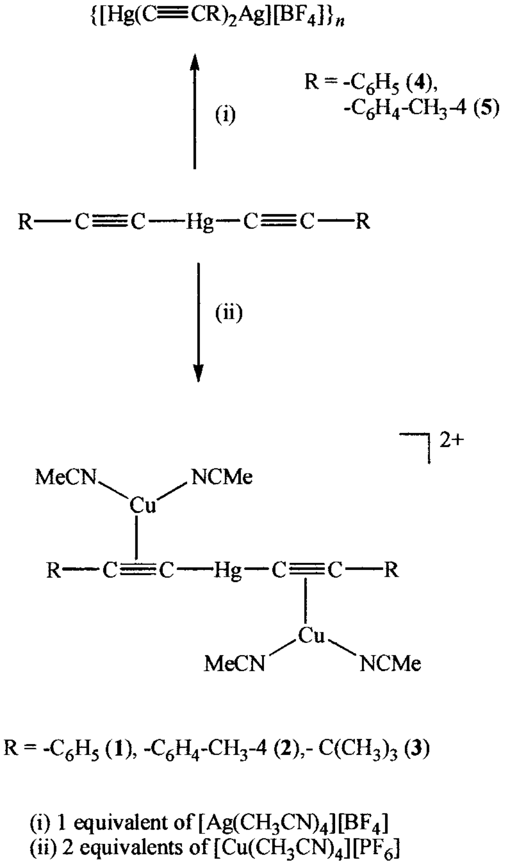

Table 1. ν(C≡C) Stretches (cm^{-1}) for Compounds 1−17 and for the Corresponding Starting Materials $[Hg(C{\equiv}CR)_2]$

compound	IR (cm^{-1}) ν(C≡C)
$[Hg(C{\equiv}CPh)_2]^a$	2146, 2113
$[Hg(C{\equiv}CTol)_2]^a$	2140
$[Hg(C{\equiv}C^tBu)_2]^a$	2175, 2142
$[Hg(C{\equiv}CPh)_2Cu_2(CH_3CN)_4][PF_6]_2$ (**1**)	2022, 1981
$[Hg(C{\equiv}CTol)_2Cu_2(CH_3CN)_4][PF_6]_2$ (**2**)	1981
$[Hg(C{\equiv}C^tBu)_2Cu_2(CH_3CN)_4][PF_6]_2$ (**3**)	2011
$[Hg(C{\equiv}CPh)_2Cu_2(bipy)_2][PF_6]_2$ (**6**)	1967, 1951
$[Hg(C{\equiv}CTol)_2Cu_2(bipy)_2][PF_6]_2$ (**7**)	1968, 1941
$[Hg(C{\equiv}C^tBu)_2Cu_2(bipy)_2][PF_6]_2$ (**8**)	1947
$[Hg(C{\equiv}CPh)_2Cu_2(phen)_2][PF_6]_2$ (**9**)	1983, 1963
$[Hg(C{\equiv}CTol)_2Cu_2(phen)_2][PF_6]_2$ (**10**)	1958, 1937
$[Hg(C{\equiv}C^tBu)_2Cu_2(phen)_2][PF_6]_2$ (**11**)	1964
$\{[Hg(C{\equiv}CPh)_2Ag][BF_4]\}_n$ (**4**)	2094
$\{[Hg(C{\equiv}CTol)_2Ag][BF_4]\}_n$ (**5**)	2090
$[Hg(C{\equiv}CPh)_2Ag_2(bipy)_2][BF_4]_2$ (**12**)	2049, 1995
$[Hg(C{\equiv}CTol)_2Ag_2(bipy)_2][BF_4]_2$ (**13**)	2063, 1997
$[Hg(C{\equiv}C^tBu)_2Ag_2(bipy)_2][BF_4]_2$ (**14**)	2053
$[Hg(C{\equiv}CPh)_2Ag_2(phen)_2][BF_4]_2$ (**15**)	2058
$[Hg(C{\equiv}CTol)_2Ag_2(phen)_2][BF_4]_2$ (**16**)	2051, 2038
$[Hg(C{\equiv}C^tBu)_2Ag_2(phen)_2][BF_4]_2$ (**17**)	2049

[a] Starting materials for the synthesis of species **1**−**17**.

Since both silver(I) and copper(I) show a similar tendency to π-coordinate to alkenes and alkynes, the analogous reactions with silver have been studied. In contrast with the reactions with copper, when the mercury bis-alkynyl complexes $[Hg(C{\equiv}CR)_2]$ (R = C_6H_5, $-C_6H_4-CH_3$-4) are reacted with $[Ag(CH_3CN)_4][BF_4]$, the expected $[Hg(C{\equiv}CR)_2Ag_2(CH_3CN)_4][BF_4]_2$ compounds are not formed. Instead, on the basis of elemental analyses and IR and NMR spectroscopy, the white solids obtained can be formulated as $\{[Hg(C{\equiv}CR)_2Ag][BF_4]\}_n$ (R = C_6H_5, **4**; $-C_6H_4-CH_3$-4, **5**) in which all the acetonitrile ligands have been replaced. This formulation is consistent with either a molecular square or a

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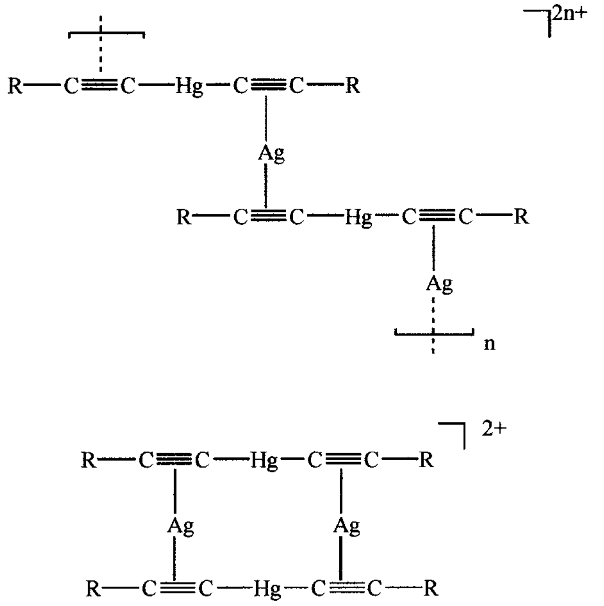
Scheme 2



polymeric arrangement (see Scheme 2). The structure of compound **5** has been established by a single-crystal X-ray analysis, demonstrating to be the polymeric arrangement (*vide infra*).

The IR spectra of compounds **4** and **5** show a shift of the ν(C≡C) stretches to lower frequencies (see Table 1) compared with those of the parent mercury bis-alkynyl complexes, thus suggesting a π-coordination of the silver ions to the triple bonds of the alkynyl groups. These spectra also indicate that all the acetonitrile ligands have been substituted since no bands are observed in the region between 2320 and 2290 cm^{-1}. The molecular peak in the FAB-mass spectrum has been assigned to the $[Hg(C{\equiv}CR)_2Ag]^+$ fragment. The ^1H NMR spectra of the three complexes show a small change in the chemical shifts of the R groups on the alkynyl ligands, suggesting a new chemical environment around the bis-alkynyl moieties. Interestingly, the reactions between $[Hg(C{\equiv}CR)_2]$ and the simple silver salt $AgBF_4$ yield the same compounds as those obtained with $[Ag(CH_3CN)_4][BF_4]$, confirming that the acetonitrile is not retained in the coordination sphere of the silver ion.

The different reactivities of $[Hg(C{\equiv}CR)_2]$ with $[Cu(CH_3CN)_4][PF_6]$ and $[Ag(CH_3CN)_4][BF_4]$ are somewhat unexpected. The larger shift of the ν(C≡C) bond stretch to lower frequencies in the copper derivatives compared to those of the silver complexes suggests a stronger coordination of the copper ion to the alkynyl bonds. The presence of the coordinated acetonitrile molecules on the copper centers in **1**−**3** is surprising compared with the silver derivatives, where all the solvent molecules have been replaced, especially since there is evidence in the literature that the four acetonitrile groups in $[Cu(CH_3CN)_4][PF_6]$ can be displaced by coordination to two metal−alkynyl groups (see for example the platinum−alkynyl−copper compounds reported by Yam[11b]).

Several attempts to synthesize the copper analogues of the polymeric species **4** and **5** have been made but without success. This lack of success suggests that the two remaining acetonitrile molecules are probably too strongly coordinated to the copper center to be replaced by the relatively weakly coordinating alkynyl ligand. Stronger ligands would seem to be needed to displace these coordinated solvent molecules (see next section).

Synthesis of $[Hg(C{\equiv}CR)_2M_2(bipy)_2][PF_6]_2$ and $[Hg(C{\equiv}CR)_2M_2(phen)_2][PF_6]_2$ (M = Ag or Cu; R = C_6H_5, $-C_6H_4-CH_3$-4, $-C(CH_3)_3$). After the unsuccessful attempts to substitute the acetonitrile molecules from compounds **1**−**3**, reactions between these complexes and the strongly chelating ligands 2,2′-bipyridine and 1,10-phenanthroline have been investigated. When 2 equiv of 2,2′-bipyridine are added to solutions of $[Hg(C{\equiv}CR)_2Cu_2(CH_3CN)_4][PF_6]_2$ in CH_2Cl_2, pale yellow precipitates are obtained which can be formulated as $[Hg(C{\equiv}CR)_2Cu_2(bipy)_2][PF_6]_2$ (R = C_6H_5, **6**; $-C_6H_4-CH_3$-4, **7**; $-C(CH_3)_3$, **8**) on the basis of elemental analyses, FAB-mass spectrometry, and ^1H NMR and IR spectroscopy.

The IR spectra of compounds **6**−**8** show two ν(C≡C) bands which are shifted to lower frequencies compared with those of the corresponding starting materials (see Table 1). Strong bands in the region around 1600 cm^{-1} are attributed to the C=N stretching of the bipyridine molecules. No ν(C≡N) absorptions are observed in any of the spectra of the three products, indicating that substitution of the acetonitrile molecules has occurred. Additionally, the signals in the ^1H NMR spectra are compatible with the presence of coordinated bipyridine. The presence of only one set of signals indicates the equivalence of the protons on the two rings of the bipyridine, suggesting that free rotation around the Cu−η^2-alkynyl bond occurs in solution. The compounds are insoluble in chlorinated solvents and THF. They are slightly soluble in acetone, but they quickly decompose (even under a N_2 atmosphere) to a blue solution, suggesting the presence of Cu(II) species. Thus, NMR spectra in acetone must be run quickly on freshly made solutions and, even then, good integration of the signals is always hard to achieve (this is possibly due to the presence of small amounts of paramagnetic Cu(II) species). The instability of these compounds has prevented us from undertaking further ^{13}C and ^{199}Hg NMR spectroscopic studies in solution.

In an analogous series of reactions, compounds **1**−**3** have been reacted with 1,10-phenanthroline to yield the new species $[Hg(C{\equiv}CR)_2Cu_2(phen)_2][PF_6]_2$ (R = C_6H_5, **9**; $-C_6H_4-CH_3$-4, **10**; $-C(CH_3)_3$, **11**) as pale yellow solids. The IR spectra of these compounds also show two ν(C≡C) absorptions shifted to lower frequencies than those of the corresponding starting materials (see Table 1). The ν(C≡N) bands for coordinated acetonitrile molecules are not observed. Compounds **9**−**11** are insoluble in most common solvents but slightly soluble in acetone, allowing for their study in solution. The ^1H NMR spectra in acetone show signals due to the R groups on the alkynyls and to the coordinated phenanthroline. These compounds behave similarly to the bipyridine complexes **6**−**8** and also decompose quickly in solution.

The analogous silver compounds are obtained by reacting the mercury−dialkynyl species $[Hg(C{\equiv}CR)_2]$ with silver(I) salts in the presence of bipyridine or phenanthroline.

Reaction of the mercury bis-alkynyl compounds with 2 equiv of $AgBF_4$ and 2 equiv of 2,2′-bipyridine in THF produces $[Hg(C{\equiv}CR)_2Ag_2(bipy)_2][BF_4]_2$ (R = C_6H_5, **12**;

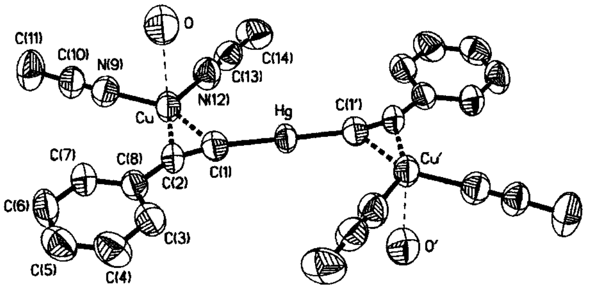


Figure 1. Molecular structure of **1**, showing also the weakly coordinated water molecules (50% probability ellipsoids).

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 1

Hg−C(1)	2.006(8)	Hg−C(1′)	2.006(8)
Cu−C(1)	1.991(8)	Cu−C(2)	2.037(8)
Cu−N(9)	1.938(7)	Cu−N(12)	1.967(8)
Cu−O	2.70(2)	C(1)−C(2)	1.246(11)
C(2)−C(8)	1.436(8)		
C(1)−Hg−C(1′)	180.0	C(1)−Cu−C(2)	36.0(3)
C(1)−Cu−N(9)	151.7(3)	C(1)−Cu−N(12)	105.7(3)
C(2)−Cu−N(9)	115.8(3)	C(2)−Cu−N(12)	141.6(3)
N(9)−Cu−N(12)	102.0(3)	C(1)−Cu−O	100.5(4)
C(2)−Cu−O	99.8(4)	N(9)−Cu−O	85.5(4)
N(12)−Cu−O	89.3(4)	C(2)−C(1)−Cu	74.0(5)
C(2)−C(1)−Hg	165.7(7)	Cu−C(1)−Hg	120.3(4)
C(1)−C(2)−C(8)	158.3(7)	C(1)−C(2)−Cu	70.0(5)
C(8)−C(2)−Cu	131.7(4)		

p-C_6H_4Me, **13**; $-C(CH_3)_3$, **14**) as white precipitates. The compounds have been characterized on the basis of elemental analyses, mass spectrometry, IR and NMR spectroscopy, and, in the case of the phenyl derivative, an X-ray single-crystal structural determination (vide infra). The IR spectra show a shift of the C≡C stretching mode to lower frequencies, which is indicative of a π-coordination of silver to the triple bond. The ^1H NMR spectra in acetone show the signals of the alkynyl groups and the coordinated bipyridine in the expected ratio. Further studies in solution have been prevented by the insolubility of these compounds.

Analogous reactions between mercury−dialkynyls, $AgBF_4$, and phenanthroline yield the expected $[Hg(C{\equiv}CR)_2Ag_2(phen)_2][BF_4]_2$ (R = C_6H_5, **15**; *p*-C_6H_4Me, **16**; $-C(CH_3)_3$, **17**) compounds in good yields. They have been characterized on the basis of elemental analyses, mass spectrometry, and IR and NMR spectroscopy.

X-ray Crystallography of Compounds 1, 5, and 12. The X-ray analysis of $[Hg(C{\equiv}CPh)_2Cu_2(CH_3CN)_4][PF_6]_2$ (**1**) reveals the molecule to be on a crystallographic inversion center and an almost planar geometry for the cation (Figure 1); the mean deviation from planarity for all the atoms excluding the included water molecules and the anions is 0.056 Å.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for 5

Hg−C(1)	2.00(2)	Hg−C(11)	2.02(2)
Ag−C(1)	2.29(2)	Ag−C(2)	2.42(2)
Ag−C(11′)	2.27(2)	Ag−C(12′)	2.43(2)
C(1)−C(2)	1.22(3)	C(2)−C(8)	1.44(3)
C(1)−Hg−C(11)	177.9(10)	C(1)−Ag−C(2)	29.9(7)
C(1)−Ag−C(11′)	172.2(8)	C(2)−Ag−C(11′)	153.8(7)
C(11′)−Ag−C(12′)	29.9(7)	C(1)−Ag−C(12′)	148.5(6)
C(2)−Ag−C(12′)	125.6(6)	Hg−C(1)−Ag	106.2(8)
Hg−C(1)−C(2)	173(2)	Ag−C(1)−C(2)	81.0(13)
Ag−C(2)−C(1)	69.2(12)	Ag−C(2)−C(8)	114.7(13)
C(1)−C(2)−C(8)	174(2)		

Table 4. Selected Bond Lengths (Å) and Angles (deg) for 12

Hg−C(1)	2.017(7)	Hg−C(1′)	2.017(7)
Ag−C(1)	2.235(7)	Ag−C(2)	2.351(7)
Ag−N(1)	2.252(6)	Ag−N(2)	2.306(7)
C(1)−C(2)	1.209(11)	C(2)−C(8)	1.465(8)
C(1)−Hg−C(1′)	180.0	C(1)−Ag−C(2)	30.4(3)
C(1)−Ag−N(1)	164.0(3)	C(1)−Ag−N(2)	121.9(2)
C(2)−Ag−N(1)	134.7(2)	C(2)−Ag−N(2)	152.3(2)
N(1)−Ag−N(2)	72.7(2)	Hg−C(1)−C(2)	167.8(7)
Ag−C(1)−C(2)	80.1(5)	Hg−C(1)−Ag	112.1(4)
Ag−C(2)−C(1)	69.5(5)	Ag−C(2)−C(8)	125.3(4)
C(1)−C(2)−C(8)	165.0(7)		

Table 5. Selected $^{13}C\{^1H\}$ NMR Chemical Shifts (ppm) for Compounds 1−5, 14, and for the Corresponding Starting Materials $[Hg(C{\equiv}CR)_2]$

compound	$^{13}C\{^1H\}$ NMR (ppm) δ(C≡C)
$[Hg(C{\equiv}CPh)_2]$[a]	C_β: 107.0; C_α: 121.0
$[Hg(C{\equiv}CTol)_2]$[a]	C_β: 104.1; C_α: 120.5
$[Hg(C{\equiv}C^tBu)_2]$[a]	C_β: 116.3; C_α: 108.3
$[Hg(C{\equiv}CPh)_2Cu_2(CH_3CN)_4][PF_6]_2$ (**1**)	C_β: 108.4; C_α: 115.6
$[Hg(C{\equiv}CTol)_2Cu_2(CH_3CN)_4][PF_6]_2$ (**2**)	C_β: 108.4; C_α: 114.8
$[Hg(C{\equiv}C^tBu)_2Cu_2(CH_3CN)_4][PF_6]_2$ (**3**)	C_β: 104.8; C_α: 90.4
$\{[Hg(C{\equiv}CPh)_2Ag][BF_4]\}_n$ (**4**)	C_β: 107.7; C_α: 110.9
$\{[Hg(C{\equiv}CTol)_2Ag][BF_4]\}_n$ (**5**)	C_β: 108.6; C_α: 108.8
$\{[Hg(C{\equiv}C^tBu)_2Ag_2(bipy)_2][BF_4]_2$ (**8**)	C_β: 121.7; C_α: 94.6

[a] Starting materials for the synthesis of species **1**−**17**.

The geometry at copper is essentially trigonal planar, the metal being covalently bonded to two acetonitrile ligands and π-bonded to the ethyne bond of the mercury dialkynyl unit. The Cu−C(1) and Cu−C(2) distances are slightly asymmetric at 1.991(8) and 2.037(8) Å, respectively (Table 2). Accompanying this side-bonding are distinct nonlinearities in the angles at C(1) [165.7(7)°] and C(2) [158.3(7)°], the bending being away from the copper center. There is also a small (ca. 6°) torsional twist about the C(2)−C(8) bond. The Hg−C(1) distance of 2.006(8) Å is unexceptional, but the C≡C bond length of 1.246(11) Å is noticeably longer then those observed in other mercury dialkynyls;[13] this elongation is probably a consequence of the π-bonding, though in a platinum dialkynyl complex with a “side-bonding” of a mercury to the ethynyl bond the C≡C distances were still less than 1.2 Å.[14] The partial occupancy included water molecules located in an apical position with respect to the trigonal copper coordination planes. The Cu···O distance [2.70(2) Å] is consistent with a weak, out of plane, $Cu-OH_2$ linkage.

The molecules pack to form parallel sheets, though with only marginal $\pi-\pi$ overlap. Although the mean interplanar separations between symmetry-related aryl rings are 3.29 Å, only the edges of the ring systems overlap each other, the ring centroid···ring centroid separations being 4.42 Å. There are no close intermolecular contacts to the mercury centers, the shortest F···Hg distance being 3.24 Å, and the shortest Hg···Hg and Hg···Cu nonbonded contacts are 8.48 and 3.47 Å, respectively.

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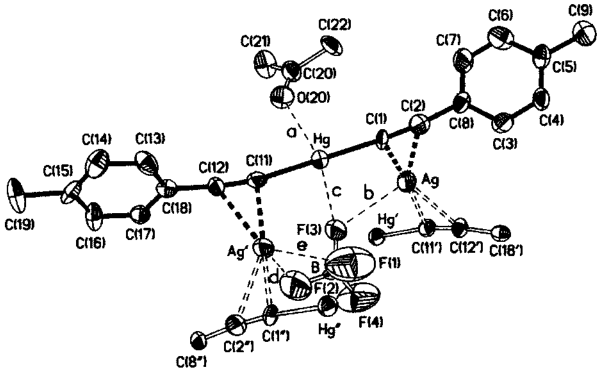

Figure 2. Molecular structure of **5**, showing the π-linking of adjacent ethynyl units by the silver atoms, and also the anion and the included acetone molecule. The contact distances (Å) are (a) 2.75, (b) 2.71, (c) 2.97, (d) 2.97, and (e) 3.05 (50% probability ellipsoids).

The single-crystal X-ray analysis shows compound $\{[Hg(C{\equiv}CTol)_2Ag][BF_4]\}_n$ (**5**) to be polymeric with the silver atom π-bonding approximately linearly between the ethyne linkages of adjacent molecules (Figure 2).

Here the mercury dialkynyl complex does not have inversion symmetry, and hence there are two unique ethynyl units. The Ag−C bonds are, in each case, asymmetric, with distances to C(1) and C(2) of 2.29(2) and 2.42(2) Å, and to C(11) and C(12) of 2.27(2) and 2.43(2) Å, respectively. The bending of the Hg−C≡C−Ar linkage is less pronounced than in **1**, with angles at C(1), C(2), C(11), and C(12) of 173(2)°, 174(2)°, 172(2)°, and 173(2)° respectively, and the aryl rings are rotated substantially out of the C(1), C(2), C(8) and C(11), C(12), C(18) planes by ca. 24° and 44° respectively. The Hg−C distances of 2.00(2) and 2.02(2) Å do not differ significantly from those in **1**, and the C≡C bond lengths [both 1.22(3) Å] are again toward the high side of the lengths observed in other mercury−dialkynyl complexes.[13]

In this complex there are notable short contacts involving both the BF_4 anions and the included acetone solvent molecules. The oxygen atom of the acetone makes a short [2.75 Å] near-orthogonal (ca. 85°) approach to the C−Hg−C moiety. One of the fluorine atoms [F(3)] makes a similar approach at 2.97 Å and a significantly shorter approach to the silver atom of 2.71 Å (a distance comparable to intramolecular Ag⋯F distances[15] but shorter than those normally observed for anion−cation contact). Two of the other fluorine atoms [F(1) and F(2)] make longer approaches of 3.05 and 2.97 Å, respectively, to a symmetry-related silver center. These intermolecular interactions probably contribute to the pitch of the helical polymer chain that is created by the 2_1 screw axis. Adjacent helices interleave with each other and are cross-linked by C−H⋯π interactions (a in Figure 3). The structure is chiral, and hence all of the chains have a common helicity. The shortest Hg⋯Hg and Hg⋯Ag nonbonded contacts are 5.66 and 3.44 Å, respectively.

The crystallographic analysis of compound $[Hg(C{\equiv}CR)_2Ag_2(bipy)_2][BF_4]_2$ (**12**) showed that as in **1** the cations have crystallographic C_i symmetry (Figure 4) and a near-planar geometry in the solid state (the mean deviation from planarity is 0.14 Å).

The silver atoms of the 2,2′-*N*,*N*′-bipyridylsilver(I) units are π-bonded to the ethynyl bonds of the mercury−dialkynyl moieties; the Ag−C(1) and Ag−C(2) distances are significantly asymmetric at 2.235(7) and 2.351(7) Å, respectively. The Hg−C(1)−C(2)−C(8) chain is bent away from the “trigonal planar” silver center, the angles at C(1) and C(2) being 167.8(7) and 165.0(7) Å, respectively. There is only a small (ca. 5°) torsional twist about the C(2)−C(8) bond. The Hg−C distances [2.017(7) Å] do not differ significantly from those observed in **1** and **5**. In contrast, the C≡C distance [1.209(11) Å] is noticeably shorter than seen in **1** and **5**, though it is still longer than those observed in other mercury dialkynyl species.[13] The Ag−N(1) and Ag−N(2) bond lengths are noticeably asymmetric at 2.252(6) and 2.306(7) Å, respectively, though this appears to be commonplace in 2,2′-*N*,*N*′-bipyridylsilver complexes.

As in **5**, the BF_4 anions play an integral role in the structure, “bridging” between the mercury and silver centers (Figure 4). One of the fluorine atoms [F(1)] makes a near orthogonal (ca. 82°) approach to the C(1)−Hg−C(1′) fragment. The F⋯Hg distance of 2.80(2) Å is comparable to (if not shorter than) the shortest recorded approach of a BF_4 anion to a mercury center of 2.829 Å in the structure of (η^5-cyclopentadienyl)tricarbonyltriphenylphosphinomercury−molybdenum(II) tetrafluoroborate.[16a] However a contact of 2.814 Å to a fluorine atom of an AsF_6 anion has been reported.[16b] The Ag⋯F distance is significantly longer at 3.092(2) Å and longer than the analogous contact in **5**.

The complexes pack to form continuous π−π stacks utilizing all three unique aromatic rings in the molecule (Figure 5).

The shortest Hg⋯Hg and Hg⋯Ag nonbonded contacts are 9.53 and 3.53 Å, respectively. We believe that the bridging role played by the BF_4^- anions inhibits a more regular stacking of the ring systems, which could facilitate intermolecular Hg⋯Hg and Ag⋯Ag interactions.

IR and ^{13}C NMR Spectroscopy. In addition to the structural characterization of compounds **1**, **5**, and **12**, IR and ^{13}C NMR spectroscopy of the species presented in this paper are consistent with an η^2 coordination of the Cu(I) and Ag(I) ions to the alkynyl groups of $[Hg(C{\equiv}CR)_2]$. This is demonstrated by the shift of the C≡C stretch of all the compounds **1**−**17** to lower frequencies as compared with those of the corresponding starting materials $[Hg(C{\equiv}CR)_2]$ (see Table 1). The M−η^2-(RC≡CR) bond can be described in terms of the Chatt−Duncanson−Dewar model with σ-donation from a filled π-orbital of the triple bond to an empty orbital of the metal center and a back-donation from a filled metal d-orbital to the empty π^* of the C≡C moiety. As has been discussed elsewhere, this leads to a decrease in the covalent character of the triple bond and, as a consequence, to a shift of the ν(C≡C) to lower frequencies.[17]

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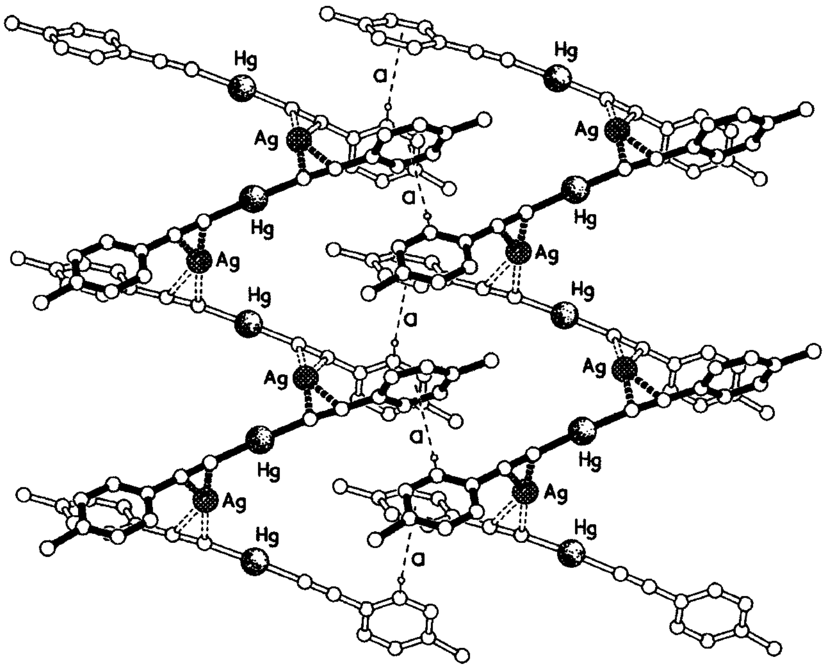

Figure 3. Cross-linking of a pair of adjacent helical chains in the structure of **5** by C−H⋯π interactions (a). The H⋯π distance is 2.83 Å, and the C−H⋯π angle is 146°.

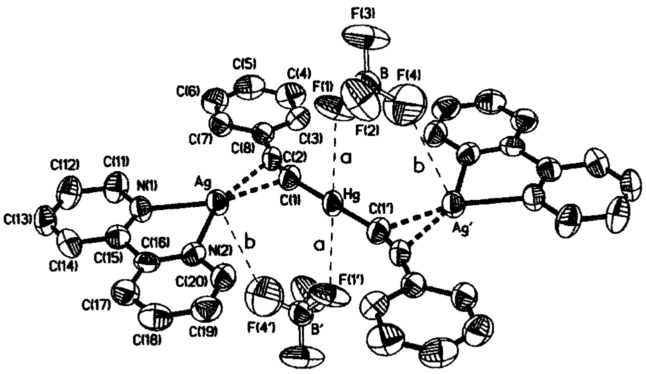

Figure 4. Solid-state structure of **12** showing the planar conformation of the cation and the "bridging" role of the BF_4 anions. The distances of the nonbonded F⋯M contacts are (a) 2.80(2); (b) 3.09(2) Å (50% probability ellipsoids).

A comparison between the IR spectra of the Cu(I) and Ag(I) complexes shows that the copper compounds have consistently lower C≡C stretching frequencies than the corresponding silver species, suggesting that Cu(I) binds more strongly to the alkynyl groups than Ag(I). This observation is consistent with previously reported experimental[9b] and theoretical results.[18]

Because of insolubility and stability problems, only some of the metal−alkynyl species have been studied by $^{13}C\{^1H\}$ NMR spectroscopy (see Table 5). Sharp and well-defined peaks are observed for the carbon atoms belonging to the R groups of the alkynyl moieties and for the carbon atoms in the co-ligands. The most important changes in chemical shift upon coordination to Cu(I) and Ag(I) are obviously for the carbon atoms in the C≡C triple bonds. It has been previously established that (with the exception of ^{t}Bu derivative) the chemical shift for the C_α (directly bonded to the mercury) appears at a lower field than the C_β (carbon directly linked to the R group).[19] The simple bis-alkynyl compounds $[Hg(C{\equiv}CR)_2]$ have chemical shifts between 108.7 and 121.0 ppm for C_α and between 104.1 and 116.6 for C_β.[19] Upon coordination of these species to Cu(I) and Ag(I), the chemical shift of C_β remains practically unchanged (except for the ^{t}Bu-containing compounds **3** and **14**), while that for C_α is shifted to higher field. This suggests that the η^2 interaction between M(I) and the triple bond is not symmetrical (which was demonstrated by the X-ray crystallographic studies). The change in chemical shift of C_α is larger upon coordination to silver (10.1 ppm, R = C_6H_5, and 11.7 ppm, R = p-C_6H_4Me) than to copper (5.4 ppm, R = C_6H_5, and 4.9 ppm, R = p-C_6H_4Me). This difference is also consistent with the crystallographic observations: the η^2 bond in the silver complexes is more asymmetric than in the copper complexes.

Conclusions

The mercury bis-alkynyl complexes $[Hg(C{\equiv}CR)_2]$ have been successfully used as building blocks for the synthesis of polymetallic arrangements when they are π-coordinated to Cu(I) and Ag(I). Spectroscopic and structural characterization suggest that Cu(I) centers coordinate more strongly to the triple bonds than the Ag(I) ones, which is consistent with previously reported data. The structural characterization of three of these species (i.e., $[Hg(C{\equiv}CPh)_2Cu_2(CH_3CN)_4][PF_6]_2$, $\{[Hg(C{\equiv}CTol)_2Ag][BF_4]\}_n$, and $[Hg(C{\equiv}CPh)_2Ag_2(bipy)_2][BF_4]_2$) has shown the presence of interesting supramolecular interactions. The extended planar metal−organic arrangement exhibited by $[Hg(C{\equiv}CPh)_2Ag_2(bipy)_2][BF_4]_2$ is potentially a valuable system to study nonbonding Hg⋯Hg and Ag⋯Ag interactions. In the current structure a more regular π-stacking between the molecules seems to be inhibited by the presence of the BF_4^- counterions, which consequently prevents it from exhibiting intermolecular metal−metal interactions. We

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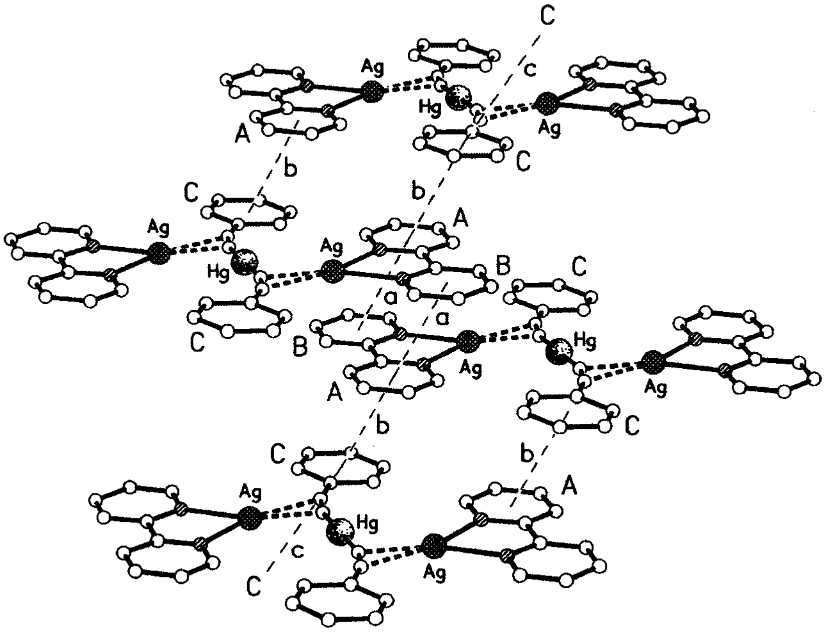

Figure 5. Part of the 3D-dimensional $\pi-\pi$ stacking arrangement of the cations in **12**. The centroid···centroid and mean interplanar separations (Å) are (a) 3.87, 3.46; (b) 3.89, 3.46; (c) 4.09, 3.56.

are currently studying the possibility of using different anions (planar) or ligands (negatively charged) to favor an appropriate arrangement of the molecules to show such interactions. Also interesting is the novel polymeric structure $\{[Hg(C{\equiv}CTol)_2Ag][BF_4]\}_n$. In this species the BF_4^- anions also play an important structural role since they help in keeping the mercury and silver atoms in a fixed relative position. The variation of anions will define the extent of their structural influence in this polymeric arrangement. In summary the results presented in this paper demonstrate the variety of structures that can be obtained upon π-coordination of Ag(I) and Cu(I) ions to the $[Hg(C{\equiv}CR)_2]$ compounds. This geometrically rigid species seems to be a good and relatively unexplored building block for the design of polymetallic aggregates.

Experimental Section

Instrumentation. Infrared spectra were recorded on a Perkin-Elmer FTIR1720 spectrometer as KBr disks or Nujol mulls between 4000 and 400 cm^{-1}, while polyethylene plates were used between 400 and 180 cm^{-1}. NMR spectra were recorded on a JEOL GS 270 MHz spectrometer. ^1H spectra were referenced internally to the residual ^1H impurity present in the deuterated solvent. Chemical shifts in the ^1H spectra were reported in parts per million (ppm) relative to TMS. FAB(+) mass spectra were recorded on a VG Autospec spectrometer using 3-NBA for the sample matrix. The ionizing radiation was 35 keV Cs^+ primary ion beam. All the reactions were carried out under an inert atmosphere of nitrogen using standard Schlenk techniques. The reactions with silver compounds were carried out with exclusion of light. $[Hg(C{\equiv}CR)_2]$ (R = C_6H_5, p-C_6H_4Me, $-C(CH_3)_3$,)[6] and $[Cu(CH_3CN)_4][PF_6]$[20] were synthesized according to literature procedures. PhC≡CH, TolC≡CH, $(CH_3)_3C{\equiv}CH$, 2,2'-bipyridine, 1,10-phenanthroline, $HgCl_2$, $[Ag(CH_3CN)_4][BF_4]$, and $AgBF_4$ were purchased from Aldrich and used as received.

Synthesis of $[Hg(C{\equiv}CPh)_2Cu_2(CH_3CN)_4][PF_6]_2$ (1). $[Cu(CH_3CN)_4][PF_6]$ (1.14 g, 3.06 mmol) was dissolved in CH_2Cl_2 (15 mL) and added to a solution of $[Hg(C{\equiv}CPh)_2]$ (0.62 g, 1.54 mmol) in toluene (30 mL). A white microcrystalline precipitate formed immediately. The mixture was stirred for 1 h to ensure completion of the reaction. The white precipitate was filtered off, washed with toluene and diethyl ether, and dried in vacuo. Evaporation of the mother liquor and addition of diethyl ether rendered additional complex (yield 1.30 g, 86%). Anal. Found: C, 29.43; H, 2.16; N, 5.49. Calcd for $[C_{24}Cu_2F_{12}H_{22}HgN_4P_2]$: C, 29.28; H, 2.24; N, 5.69. IR (Nujol): ν_{max}/cm^{-1} 2318s, 2291s ($CH_3\mathit{CN}$), 2022m, 1981s (C≡C), 845vs (PF_6). FAB$^+$-MS: m/z 549 $\{[Hg(C{\equiv}CPh)_2Cu(CH_3CN)_2]^+\}$. ^1H NMR $[(CD_3)_2CO]$: δ 7.55−7.52 (m, 2H), 7.44−7.38 (m, 3H), 2.21 (s, 6H, $\mathit{CH_3}CN$). $^{13}C\{^1H\}$ NMR $[(CD_3)_2CO]$: δ 1.0 ($\mathit{C}H_3CN$), 108.4 ($HgC{\equiv}\mathit{C}$), 115.6 ($Hg\mathit{C}{\equiv}C$), 122.4 ($^i\mathit{C}-C_6H_5$), 128.9, 129.5 and 131.9 ($\mathit{C_6}H_5$), $CH_3\mathit{C}N$ signal was not observed.

Synthesis of $[Hg(C{\equiv}CTol)_2Cu_2(CH_3CN)_4][PF_6]_2$ (2). $[Cu(CH_3CN)_4][PF_6]$ (0.93 g, 2.50 mmol) was dissolved in CH_2Cl_2 (15 mL) and added to a solution of $[Hg(C{\equiv}CTol)_2]$ (0.54 mg, 1.25 mmol) in toluene (20 mL) with a few drops of THF. A white microcrystalline precipitate formed immediately. The mixture was stirred for 1 h to ensure completion of the reaction. The white precipitate was filtered off, washed with toluene and diethyl ether, and dried in vacuo. Evaporation of the mother liquor and addition of diethyl ether rendered additional complex (yield 0.89 g, 70%). Anal. Found: C, 30.97; H, 2.34; N, 4.95. Calcd for $[C_{26}Cu_2H_{26}HgF_{12}N_4P_2]$: C, 30.84; H, 2.57; N, 5.53. IR (Nujol): ν_{max}/cm^{-1} 2321m, 2294m ($CH_3\mathit{CN}$), 1981m (C≡C), 843vs (PF_6). FAB$^+$-MS: m/z 577 $\{[Hg(C{\equiv}CTol)_2Cu(CH_3CN)_2]^+\}$. ^1H NMR (CD_2Cl_2): δ 7.42 (d, ^3J = 8.2 Hz, 2H), 7.20 (d, ^3J = 7.9 Hz, 2H), 2.36 (s, 3H, $C_6H_4-\mathit{CH_3}$), 2.22 (s, 6H, $\mathit{CH_3}CN$). $^{13}C\{^1H\}$ NMR $[(CD_3)_2CO]$: δ 0.9 ($\mathit{C}H_3CN$), 20.8 ($C_6H_4-\mathit{C}H_3$), 108.8 ($HgC{\equiv}\mathit{C}$), 114.8 ($Hg\mathit{C}{\equiv}C$), 119.3 ($^i\mathit{C}-C_6H_4-CH_3$), 129.5, 131.9, and 139.9 ($\mathit{C_6}H_4-CH_3$), $CH_3\mathit{C}N$ signal was not observed.

Synthesis of $[Hg(C{\equiv}C^tBu)_2Cu_2(CH_3CN)_4][PF_6]_2$ (3). $[Cu(CH_3CN)_4][PF_6]$ (0.47 g, 1.27 mmol) was added in one portion to a solution of $[Hg(C{\equiv}C^tBu)_2]$ (0.23 mg, 0.63 mmol) in THF (20 mL). The pale yellow solution was stirred for 1 h. Evaporation of most of the solvent under reduced pressure and addition of diethyl ether yielded an off-white complex (yield 0.407 g, 68%). Anal. Found: C, 25.47; H, 3.10; N, 5.57. Calcd for $[C_{20}Cu_2H_{30}HgF_{12}N_4P_2]$: C, 25.43; H, 3.18; N, 5.93. IR (Nujol): ν_{max}/cm^{-1} 2321s, 2289s ($CH_3\mathit{CN}$), 2011m (C≡C), 836vs (PF_6). FAB$^+$-MS: m/z 591 $\{[Hg(C{\equiv}C^tBu)_2Cu(CH_3CN)_4]^+\}$, 509

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$\{[\mathrm{Hg(C{\equiv}C^tBu)_2Cu(CH_3CN)_2}]^+\}$. ^{1}H NMR $[(\mathrm{CD_3})_2\mathrm{CO}]$: δ 2.26 (s, 6H, CH_3CN), 1.29 (s, 9H, C(CH_3)$_3$). ^{13}C{^{1}H} NMR $[(\mathrm{CD_3})_2\mathrm{CO}]$: δ 0.9 (CH$_3$CN), 30.4 (C(CH$_3$)$_3$), 30.8 (C(CH$_3$)$_3$), 90.4 (HgC$\equiv$$C$), 104.9 (Hg$C$$\equiv$C), 121.0 (CH$_3$$C$N).

Synthesis of $\{[\mathrm{Hg(C{\equiv}CPh)_2Ag}][\mathrm{BF_4}]\}_n$ (4). $\mathrm{AgBF_4}$ (0.10 g, 0.51 mmol) was added in one portion to a solution of $[\mathrm{Hg(C{\equiv}CPh)_2}]$ (0.21 g, 0.52 mmol) in THF (10 mL). The colorless solution was stirred in the dark for 1 h, then filtered on a Celite pad. The solution was concentrated under reduced pressure and diethyl ether added, yielding a white compound (yield 0.16 g, 52%). Anal. Found: C, 32.03; H, 1.49. Calcd for $[\mathrm{AgBC_{16}F_4H_{10}Hg}]$: C, 32.15; H, 1.67. IR (Nujol): $\nu_{\max}$/cm^{-1} 2094vs, (C$\equiv$C), 1074br (BF$_4$). FAB$^+$-MS: *m/z* 511 $\{[\mathrm{Hg(C{\equiv}CPh)_2Ag}]^+\}$. ^{1}H NMR $[(\mathrm{CD_3})_2\mathrm{CO}]$: δ 7.54−7.50 (m, 2H), 7.43−7.35 (m, 3H). ^{13}C{^{1}H} NMR $[(\mathrm{CD_3})_2\mathrm{CO}]$ δ 107.7 (HgC$\equiv$$C$), 110.9 (Hg$C$$\equiv$C), 120.9 (^{i}$C$−C$_6H_5$), 128.9, 129.9, and 132.7 (C_6H$_5$).

Synthesis of $\{[\mathrm{Hg(C{\equiv}CTol)_2Ag}][\mathrm{BF_4}]\}_n$ (5). $\mathrm{AgBF_4}$ (0.094 g, 0.480 mmol) was added in one portion to a solution of $[\mathrm{Hg(C{\equiv}CTol)_2}]$ (0.209 g, 0.485 mmol) in THF (10 mL). The colorless solution was stirred in the dark for 1 h, then filtered on a Celite pad. The solution was concentrated under reduced pressure and diethyl ether added, yielding a white compound (yield 0.186 g, 61%). Anal. Found: C, 34.39; H, 2.12. Calcd for $[\mathrm{AgBC_{18}F_4H_{14}Hg}]$: C, 34.54; H, 2.24. IR (Nujol): $\nu_{\max}$/cm^{-1} 2090vs, (C$\equiv$C), 1077br (BF$_4$). FAB$^+$-MS: *m/z* 539 $\{[\mathrm{Hg(C{\equiv}CTol)_2Ag}]^+\}$. ^{1}H NMR $[(\mathrm{CD_3})_2\mathrm{CO}]$: δ 7.42 (d, ^3J = 8.2 Hz, 2H), 7.18 (d, ^3J = 7.9 Hz, 2H), 2.34 (s, 3H, C$_6$H$_4$−CH_3). ^{13}C{^{1}H} NMR $[(\mathrm{CD_3})_2\mathrm{CO}]$: δ 20.7 (C$_6H_4$−CH$_3$) 108.7 (HgC$\equiv$$C$) 108.8 (Hg$C$$\equiv$C), 117.3 (^{i}$C$−C$_6H_4$−CH$_3$), 129.5, 132.9, and 140.6 (C_6H$_4$−CH$_3$).

Synthesis of $[\mathrm{Hg(C{\equiv}CPh)_2Cu_2(bipy)_2}][\mathrm{PF_6}]_2$ (6). 2,2′-Bipyridine (0.05 g, 0.320 mmol) was dissolved in $\mathrm{CH_2Cl_2}$ (15 mL) and added dropwise to a solution of $[\mathrm{Hg(C{\equiv}CPh)_2Cu_2(CH_3CN)_4}][\mathrm{PF_6}]_2$ (0.16 g, 0.163 mmol) in $\mathrm{CH_2Cl_2}$ (15 mL). A pale orange solution formed, which, after ca. 15 min, yielded a white precipitate. The suspension was stirred for 1 h. The precipitate was then filtered off and washed with $\mathrm{CH_2Cl_2}$ and diethyl ether (yield 0.11 g, 59%). Anal. Found: C, 37.90; H, 2.12; N, 4.85. Calcd for $[\mathrm{C_{36}Cu_2F_{12}H_{26}HgN_4P_2}]$: C, 38.17; H, 2.30; N, 4.95. IR (Nujol): $\nu_{\max}$/cm^{-1} 1967w, 1951w (C$\equiv$C), 1604m, 1594m (C=N), 844vs (PF$_6$). FAB$^+$-MS: *m/z* 987 $\{[\mathrm{Hg(C{\equiv}CPh)_2Cu_2(bipy)_2}][\mathrm{PF_6}]\}^+$, 623 $\{[\mathrm{Hg(C{\equiv}CPh)_2Cu(bipy)}]^+\}$. ^{1}H NMR $[(\mathrm{CD_3})_2\mathrm{CO}]$: δ 8.73 (d, ^3J = 8.2 Hz, 2H), 8.65 (d, ^3J = 4.7 Hz, 2H), 8.43−8.34 (m, 2H), 7.83−7.74 (m, 4H), 7.55−7.64 (m, 3H).

Synthesis of $[\mathrm{Hg(C{\equiv}CTol)_2Cu_2(bipy)_2}][\mathrm{PF_6}]_2$ (7). 2,2′-Bipyridine (0.13 g, 0.8 mmol) was dissolved in $\mathrm{CH_2Cl_2}$ (5 mL) and added to a solution of $[\mathrm{Hg(C{\equiv}CTol)_2Cu_2(CH_3CN)_4}][\mathrm{PF_6}]_2$ (0.41 g, 0.4 mmol) in $\mathrm{CH_2Cl_2}$ (20 mL). The purple solution was stirred for 1 h. Evaporation of the solvent under reduced pressure and addition of diethyl ether yielded an off-white compound (yield 0.42 g, 90%). Anal. Found: C, 39.12; H, 2.52; N, 4.62. Calcd for $[\mathrm{C_{38}Cu_2F_{12}H_{30}HgN_4P_2}]$: C, 39.32; H, 2.59; N, 4.83. IR (Nujol): $\nu_{\max}$/cm^{-1} 1968m, 1941m (C$\equiv$C), 1600vs, 1567w (C=N), 842vs (PF$_6$). FAB$^+$-MS: *m/z* 1017 $\{[\mathrm{Hg(C{\equiv}CTol)_2Cu_2(bipy)_2}][\mathrm{PF_6}]\}^+$, 651 $\{[\mathrm{Hg(C{\equiv}CTol)_2Cu(bipy)}]^+\}$. ^{1}H NMR $[(\mathrm{CD_3})_2\mathrm{CO}]$: δ 8.71 (d, ^3J = 8.2 Hz, 2H), 8.65 (d, ^3J = 4.4 Hz, 2H), 8.40−8.34 (m, 2H), 7.80−7.76 (m, 2H), 7.63 (d, ^3J = 8.2 Hz, 2H), 7.38(d, ^3J = 7.9 Hz, 2H), 2.42 (s, 3H, C$_6$H$_4$−CH_3).

Synthesis of $[\mathrm{Hg(C{\equiv}C^tBu)_2Cu_2(bipy)_2}][\mathrm{PF_6}]_2$ (8). 2,2′-Bipyridine (0.081 g, 0.52 mmol) was dissolved in $\mathrm{CH_2Cl_2}$ (5 mL) and added to a solution of $[\mathrm{Hg(C{\equiv}C^tBu)_2Cu_2(CH_3CN)_4}][\mathrm{PF_6}]_2$ (0.25 g, 0.26 mmol) in $\mathrm{CH_2Cl_2}$ (20 mL). A white precipitate formed immediately. This was stirred for 1 h to ensure completion of the reaction. It was then filtered off, washed with $\mathrm{CH_2Cl_2}$, and dried in vacuo (yield 0.17 g, 60%). Anal. Found: C, 35.09; H, 2.91; N, 5.00. Calcd for $[\mathrm{C_{32}Cu_2F_{12}H_{34}HgN_4P_2}]$: C, 35.16; H, 3.11; N, 5.13. IR (Nujol): $\nu_{\max}$/cm^{-1} 1947s (C$\equiv$C), 1600vs, 1568w (C=N), 838vs (PF$_6$). FAB$^+$-MS: *m/z* 583 $\{[\mathrm{Hg(C{\equiv}C^tBu)_2Cu(bipy)}]^+\}$. ^{1}H NMR ($\mathrm{CD_2Cl_2}$): δ 8.84 (d, ^3J = 4.7 Hz, 2H), 8.36 (d, ^3J = 8.2 Hz, 2H), 8.26−8.20 (m, 2H), 7.74−7.69 (m, 2H), 1.44 (s, 9H, C(CH_3)$_3$).

Synthesis of $[\mathrm{Hg(C{\equiv}CPh)_2Cu_2(phen)_2}][\mathrm{PF_6}]_2$ (9). 1,10-Phenanthroline (0.05 g, 0.277 mmol) in $\mathrm{CH_2Cl_2}$ (10 mL) was added dropwise to a solution of $[\mathrm{Hg(C{\equiv}CPh)_2Cu_2(CH_3CN)_4}][\mathrm{PF_6}]_2$ (0.137 g, 0.139 mmol) in $\mathrm{CH_2Cl_2}$ (10 mL). An off-white precipitate formed immediately. The mixture was left to stir for 1 h, then the precipitate was filtered off, washed with $\mathrm{CH_2Cl_2}$ and with diethyl ether, and dried in vacuo (yield 0.107 g, 65%). Anal. Found: C, 39.44; H, 1.94; N, 4.55. Calcd for $[\mathrm{C_{40}Cu_2F_{12}H_{26}HgN_4P_2{\cdot}1/2CH_2Cl_2}]$: C, 39.77; H, 2.21; N, 4.58. IR (Nujol): $\nu_{\max}$/cm^{-1} 1983m, 1963m (C$\equiv$C), 1623m, 1603m, 1580m (C=N), 844vs (PF$_6$). FAB$^+$-MS: *m/z* 1035 $\{[\mathrm{Hg(C{\equiv}CPh)_2Cu_2(phen)_2}][\mathrm{PF_6}]\}^+$, 647 $\{[\mathrm{Hg(C{\equiv}CPh)_2Cu(bipy)}]^+\}$. ^{1}H NMR $[(\mathrm{CD_3})_2\mathrm{CO}]$: δ 9.05 (d, ^3J = 3.4 Hz, 2H), 8.97 (d, ^3J = 8.2 Hz, 2H), 8.34 (s, 2H), 8.18−8.12 (m, 2H), 7.78−7.75 (m, 2H), 7.58−7.55 (m, 3H).

Synthesis of $[\mathrm{Hg(C{\equiv}CTol)_2Cu_2(phen)_2}][\mathrm{PF_6}]_2$ (10). 1,10-Phenanthroline (0.06 g, 0.33 mmol) in $\mathrm{CH_2Cl_2}$ (10 mL) was added dropwise to a solution of $[\mathrm{Hg(C{\equiv}CTol)_2Cu_2(CH_3CN)_4}][\mathrm{PF_6}]_2$ (0.169 g, 0.167 mmol) in $\mathrm{CH_2Cl_2}$ (10 mL). An off-white precipitate formed immediately. The mixture was left to stir for 1 h, and then the precipitate was filtered off, washed with $\mathrm{CH_2Cl_2}$ and with diethyl ether, and dried in vacuo (yield 0.136 g, 67%). Anal. Found: C, 38.74; H, 2.18; N, 4.24. Calcd for $[\mathrm{C_{42}Cu_2F_{12}H_{30}HgN_4P_2{\cdot}1/2CH_2Cl_2}]$: C, 39.09; H, 2.47; N, 4.19. IR (Nujol): $\nu_{\max}$/cm^{-1} 1958m, 1937m (C$\equiv$C), 1625m, 1605m, 1588m (C=N), 840vs (PF$_6$). FAB$^+$-MS: *m/z* 675 $\{[\mathrm{Hg(C{\equiv}CTol)_2Cu(phen)}]^+\}$. ^{1}H NMR $[(\mathrm{CD_3})_2\mathrm{CO}]$: δ 9.06 (d, ^3J = 3.5 Hz, 2H), 8.95 (d, ^3J = 8.2 Hz, 2H), 8.33 (s, 2H), 8.11−8.06 (m, 2H), 7.75 (d,^3J = 7.9 Hz, 2H), 7.45 (d,^3J = 8.1 Hz, 2H), 2.47 (s, 3H, C$_6$H$_4$−CH_3).

Synthesis of $[\mathrm{Hg(C{\equiv}C^tBu)_2Cu_2(phen)_2}][\mathrm{PF_6}]_2$ (11). 1,10-Phenanthroline (0.17 g, 0.94 mmol) in $\mathrm{CH_2Cl_2}$ (10 mL) was slowly added to a solution of $[\mathrm{Hg(C{\equiv}C^tBu)_2Cu_2(CH_3CN)_4}][\mathrm{PF_6}]_2$ (0.44 g, 0.47 mmol) in $\mathrm{CH_2Cl_2}$ (10 mL). A purple solution formed immediately, which then turned pale, yielding a white precipitate. The mixture was left to stir for 1 h, and then the precipitate was filtered off, washed with $\mathrm{CH_2Cl_2}$ and with diethyl ether, and dried in vacuo (yield 0.38 g, 71%). Anal. Found: C, 37.77; H, 2.85; N, 4.82. Calcd for $[\mathrm{C_{36}Cu_2F_{12}H_{34}HgN_4P_2}]$: C, 37.89; H, 2.98; N, 4.91. IR (Nujol): $\nu_{\max}$/cm^{-1} 1964m (C$\equiv$C), 1625m, 1605m, 1582m (C=N), 843vs (PF$_6$). FAB$^+$-MS: *m/z* 995 $\{[\mathrm{Hg(C{\equiv}C^tBu)_2Cu_2(phen)_2}][\mathrm{PF_6}]\}^+$, 607 $\{[\mathrm{Hg(C{\equiv}C^tBu)_2Cu(bipy)}]^+\}$. ^{1}H NMR $[(\mathrm{CD_3})_2\mathrm{CO}]$: δ 9.51 (s, br, 2H), 9.46 (d, ^3J = 8.2 Hz, 2H), 8.34 (s, 2H), 8.20−8.14 (m, 2H), 1.51 (s, 9H, C(CH$_3$)$_3$).

Synthesis of $[\mathrm{Hg(C{\equiv}CPh)_2Ag_2(bipy)_2}][\mathrm{BF_4}]_2$ (12). $\mathrm{AgBF_4}$ (0.20 g, 1.04 mmol) was added to a solution of $[\mathrm{Hg(C{\equiv}CPh)_2}]$ (0.21 g, 0.522 mmol) in THF (10 mL). The pale yellow solution was stirred in the dark for 1 h. 2,2′-Bipyridine (0.162 g, 1.04 mmol) was then added in one portion, yielding a pale yellow solid, which was stirred for 15 min, filtered, and washed with THF (yield 0.51 g, 88%). Anal. Found: C, 39.18; H, 2.38; N, 5.23. Calcd for $[\mathrm{Ag_2B_2C_{36}F_8H_{26}HgN_4}]$: C, 39.12; H, 2.35; N, 4.87. IR (Nujol): $\nu_{\max}$/cm^{-1} 2049m, 1995w (C$\equiv$C), 1592m, 1567w (C=N), 1058br (BF$_4$). FAB$^+$-MS: *m/z* 667 $\{[\mathrm{Hg(C{\equiv}CPh)_2Ag(bipy)}]^+\}$. ^{1}H NMR $[(\mathrm{CD_3})_2\mathrm{CO}]$: δ 8.83 (d, ^3J = 4.4 Hz, 2H), 8.56 (d, ^3J = 8.1 Hz, 2H), 8.28−8.18 (m, 2H), 7.78−7.68 (m, 2H), 7.61−7.51 (br, 2H), 7.44−7.37 (m, 3H).

Synthesis of $[\mathrm{Hg(C{\equiv}CTol)_2Ag_2(bipy)_2}][\mathrm{BF_4}]_2$ (13). $\mathrm{AgBF_4}$ (0.106 g, 0.54 mmol) was added to a solution of $[\mathrm{Hg(C{\equiv}CTol)_2}]$ (0.117 g, 0.27 mmol) in THF (10 mL). The pale yellow solution was stirred in the dark for 1 h. 2,2′-Bipyridine (0.084 g, 0.54 mmol) was then added, yielding a pale yellow solid, which was stirred for 15 min, filtered, and washed with THF (yield 0.24 g, 78%). Anal. Found: C, 40.43; H, 2.72; N, 4.96. Calcd for $[\mathrm{Ag_2B_2C_{38}F_8H_{30}HgN_4}]$: C, 40.27; H, 2.65; N, 4.94. IR (Nujol): $\nu_{\max}$/cm^{-1} 2063m, 1997w (C$\equiv$C), 1590m, 1574w (C=N), 1051br (BF$_4$). FAB$^+$-MS: *m/z* 1047 $\{[\mathrm{Hg(C{\equiv}CTol)_2Ag_2(bipy)_2}][\mathrm{BF_4}]\}^+$, 695 $\{[\mathrm{Hg(C{\equiv}CTol)_2Ag(bipy)}]^+\}$. ^{1}H NMR $[(\mathrm{CD_3})_2\mathrm{CO}]$: δ 8.84

(br, 2H), 8.60 (br, 2H), 8.26 (br, 2H), 7.75 (br, 2H), 7.45 (d, ^3J = 8.2 Hz, 2H), 7.22 (d, ^3J = 7.9 Hz, 2H), 2.35 (s, 3H).

Synthesis of $[Hg(C\equiv C^tBu)_2Ag_2(bipy)_2][BF_4]_2$ (14). $AgBF_4$ (0.34 g, 1.75 mmol) was added to a solution of $[Hg(C\equiv C^tBu)_2]$ (0.32 g, 0.88 mmol) in $CHCl_3$ (10 mL). The pale yellow solution was stirred in the dark for 15 min. 2,2'-Bipyridine (0.27 g, 1.74 mmol) was then added, yielding a white solid, which was stirred for 15 min, filtered, and washed with $CHCl_3$ and then with diethyl ether (yield 0.68 g, 73%). Anal. Found: C, 36.25; H, 3.08; N, 5.41. Calcd for $[Ag_2B_2C_{32}F_8H_{34}HgN_4]$: C, 36.08; H, 3.19; N, 5.26. IR (Nujol): ν_{max}/cm^{-1} 2053m (C≡C), 1590m, 1576w (C═N), 1062br (BF_4) FAB$^+$-MS: m/z 979 $\{[Hg(C\equiv C^tBu)_2Ag_2(bipy)_2][BF_4]\}^+$, 627 $\{[Hg(C\equiv C^tBu)_2Ag(bipy)]^+\}$. ^{1}H NMR ($CD_2Cl_2$): δ 8.75 (d, ^3J = 4.4 Hz, 2H), 8.25 (d, ^3J = 8.2 Hz, 2H), 8.11−8.04 (m, 2H), 7.61−7.58 (m, 2H), 1.43 (s, 9H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 29.9 ($C(CH_3)_3$), 32.1 ($C(CH_3)_3$) 94.6 (HgC≡*C*), 121.7 (Hg*C*≡C), 122.9, 126.2, 139.9, 151.1, 151.1, and 151.1 (bipy).

Synthesis of $[Hg(C\equiv CPh)_2Ag_2(phen)_2][BF_4]_2$ (15). $AgBF_4$ (0.28 g, 1.4 mmol) was added to a solution of $[Hg(C\equiv CPh)_2]$ (0.29 g, 0.72 mmol) in THF (10 mL). The pale yellow solution was stirred in the dark for 1 h. 1,10-Phenanthroline (0.25 g, 1.4 mmol) was then added, yielding a pale yellow solid, which was stirred for 15 min, filtered, and washed with THF (yield 0.62 g, 75.0%). Anal. Found: C, 41.51; H, 2.07; N, 4.86. Calcd for $[Ag_2B_2C_{40}F_8H_{26}HgN_4]$: C, 41.65; H, 2.25; N, 4.86. IR (Nujol): ν_{max}/cm^{-1} 2058m (C≡C), 1621m, 1591w, 1574w (C═N), 1057br (BF_4). FAB$^+$-MS: m/z 691 $\{[Hg(C\equiv CPh)_2Ag(phen)]^+\}$. ^{1}H NMR [$(CD_3)_2CO$]: δ 9.19 (d, ^3J = 3.5 Hz, 2H), 8.77 (d, ^3J = 8.2 Hz, 2H), 8.2 (s, 2H), 8.04−7.99 (m, 2H), 7.59−7.56 (m, 2H), 7.43−7.38 (m, 3H).

Synthesis of $[Hg(C\equiv CTol)_2Ag_2(phen)_2][BF_4]_2$ (16). $AgBF_4$ (0.78 g, 4 mmol) was added to a solution of $[Hg(C\equiv CTol)_2]$ (0.86 g, 2 mmol) in THF (10 mL). The pale yellow solution was stirred in the dark for 1 h. 1,10-Phenanthroline (0.72 g, 4 mmol) was then added, yielding a pale yellow solid, which was stirred for 15 min, filtered, and washed with THF (yield 2.14 g, 90%). Anal. Found: C, 42.88; H, 2.59; N, 4.68. Calcd for $[Ag_2B_2C_{42}F_8H_{30}HgN_4]$: C, 42.70; H, 2.54; N, 4.74. IR (Nujol): ν_{max}/cm^{-1} 2051w, 2038w (C≡C), 1621m, 1590w, 1574w (C═N), 1055br (BF_4). FAB$^+$-MS: m/z 1093 $\{[Hg(C\equiv CTol)_2Ag_2(phen)_2][BF_4]^+\}$, 719 $\{[Hg(C\equiv CTol)_2Ag(phen)]^+\}$. ^{1}H NMR [$(CD_3)_2CO$]: δ 9.21 (d, ^3J = 3.5 Hz, 2H), 8.82 (d, ^3J = 8.2 Hz, 2H), 8.24 (s, 2H), 8.09−8.04 (m, 2H), 7.47 (d, ^3J = 7.9 Hz, 2H), 7.22 (d, ^3J = 7.9 Hz, 2H), 2.36 (s, 3H).

Synthesis of $[Hg(C\equiv C^tBu)_2Ag_2(phen)_2][BF_4]_2$ (17). $AgBF_4$ (0.35 g, 1.8 mmol) was added to a solution of $[Hg(C\equiv C^tBu)_2]$ (0.326 g, 0.9 mmol) in THF (10 mL). The pale yellow solution was stirred in the dark for 1 h. 1,10-Phenanthroline (0.324 g, 1.8 mmol) was then added, yielding a pale yellow solid, which was stirred for 15 min, filtered, and washed with THF (yield 0.83 g, 83%). Anal. Found: C, 38.76; H, 2.85; N, 5.15. Calcd for $[Ag_2B_2C_{36}F_8H_{34}HgN_4]$: C, 38.84; H, 3.05; N, 5.03. IR (Nujol): ν_{max}/cm^{-1} 2049m (C≡C), 1620m, 1590m, 1573m (C═N), 1065br (BF_4).

Crystal data for 1: $[C_{24}H_{22}N_4Cu_2Hg][PF_6]_2\cdot 1.3H_2O$, M = 1007.5, triclinic, space group $P\bar{1}$ (no. 2), a = 8.482(1), b = 8.706(1), c = 12.081(1) Å, α = 87.67(1)°, β = 74.93(1)°, γ = 83.03(1)°, V = 855.0(2) Å^3, Z = 1 (the complex has crystallographic C_i symmetry), D_c = 1.957 g cm^{-3}, μ(Cu Kα) = 11.1 mm^{-1}, $F(000)$ = 483, T = 293 K; clear needles, 0.67 × 0.04 × 0.03 mm, Siemens P4/RA diffractometer, graphite-monochromated Cu Kα radiation, ω-scans, 2698 independent reflections. The structure was solved by the heavy atom method, and the non-hydrogen atoms were refined anisotropically using full-matrix least-squares based on F^2 to give R_1 = 0.042, wR_2 = 0.104 for 2502 independent observed absorption corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta \le 128°$] and 257 parameters. CCDC 149436.

Crystal data for 5: $\{[C_{18}H_{14}AgHg][BF_4]\cdot Me_2CO\}_n$, M = 683.6, monoclinic, space group $P2_1$ (no. 4), a = 10.472(2), b = 8.927(2), c = 11.806(2) Å, β = 97.04(1)°, V = 1095.3(4) Å^3, Z = 2, D_c = 2.073 g cm^{-3}, μ(Mo Kα) = 7.94 mm^{-1}, $F(000)$ = 644, T = 203 K; clear platy prisms, 0.37 × 0.17 × 0.07 mm, Siemens P4/PC diffractometer, graphite-monochromated Mo Kα radiation, ω-scans, 1932 independent reflections. The structure was solved by the heavy atom method, and the non-hydrogen atoms were refined anisotropically using full-matrix least-squares based on F^2 to give R_1 = 0.041, wR_2 = 0.088 for 1640 independent observed absorption corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta \le 50°$] and 262 parameters. The absolute chirality of **5** was determined by a combination of R-factor tests [R_1^+ = 0.0405, R_1^- = 0.0504] and by use of the Flack parameter [x^+ = −0.03(3)]. CCDC 149437.

Crystal data for 12: $[C_{36}H_{26}N_4Ag_2Hg][BF_4]_2$, M = 1104.6, triclinic, space group $P\bar{1}$ (no. 2), a = 9.525(2), b = 10.051(2), c = 10.775(2) Å, α = 72.75(1)°, β = 84.61(1)°, γ = 62.09(1)°, V = 869.3(3) Å^3, Z = 1 (the complex has crystallographic C_i symmetry), D_c = 2.110 g cm^{-3}, μ(Mo Kα) = 5.60 mm^{-1}, $F(000)$ = 526, T = 293 K; clear platy prisms, 0.23 × 0.17 × 0.08 mm, Siemens P4/PC diffractometer, graphite-monochromated Mo Kα radiation, ω-scans, 3012 independent reflections. The structure was solved by the heavy atom method, and the non-hydrogen atoms were refined anisotropically using full-matrix least-squares based on F^2 to give R_1 = 0.036, wR_2 = 0.069 for 2268 independent observed absorption corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta \le 50°$] and 265 parameters. CCDC 149438.

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Supporting Information Available: Details about the X-ray crystal structures, including ORTEP diagrams, and tables of crystal data and structure refinement, atomic coordinates, bond lengths and angles, and anisotropic displacement parameters for **1**, **5**, and **12**. This material is available free of charge via the Internet at http://pubs.acs.org.

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