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Rhombic Dodecahedral Ag_8M_6 (M = Cu, Ag, Au) Cluster Complexes of Ferrocenylethynyl Prepared by Reaction of $(AgC{\equiv}CFc)_n$ with $[M_2(Ph_2PNHPh_2)_2(MeCN)_2]^{2+}$ (M = Cu, Ag, Au)

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Summary: Reaction of the polymeric silver ferrocenylacetylide $(AgC{\equiv}CFc)_n$ with $[M_2(Ph_2PNHPPh_2)_2(MeCN)_2]^{2+}$ (M = Cu, Ag, Au) gave rise to the isolation of rhombic dodecahedral $Ag^I_8M^I_6$ cage complexes together with the unusual 1,2,5-azadiphospholium product $[FcC{=}CH(Ph_2PNPPh_2)](BF_4)$ by the cyclic addition of $FcC{\equiv}C$ to $Ph_2PNHPPh_2$. Distinct redox wave splitting occurs in the $Ag^I_8Cu^I_6$ cage complex with $\Delta E_{1/2} = 0.15$ V due to successive oxidation of the Fc groups, induced probably by electronic interactions between iron centers in the ferrocenylacetylides.

Great effort has been devoted to the chemistry of metal alkynyl complexes because of their intriguing spectroscopic, redox, and optical properties and their potential applications in molecular electronics.[1,2] As a redox-active alkynyl ligand, ferrocenylethynyl ($FcC{\equiv}CH$) has been used widely in the design of [D]−[M]−[A] ([D] = donor, [M] = metal or cluster, [A] = acceptor) compounds to explore electronic communication between ferrocenyl groups across a metal or cluster-containing spacer.[3−10] The [M] spacers are mononuclear Ru^{II} and Pt^{II} components in the complexes *trans*-$[Ru^{II}(P\text{-}P)_2(C{\equiv}CFc)_2]$ (P-P = diphosphine)[3] and *trans*-$[Pt^{II}(PR_3)_2(C{\equiv}CFc)_2]$ (R = aryl, alkyl).[4] They can also be binuclear Pt^I_2 and Ru^{III}_2, trinuclear Cu^I_3, and M^{II}_3 cluster units in the complexes $[Pt_2(dppm)_2(C{\equiv}CFc)_2]$ (dppm = bis(diphenylphosphino)methane),[5] $[Ru_2(Y\text{-}DMBA)_4(C{\equiv}CFc)_2]$ (Y-DMBA = meta-substituted dimethylbenzamidinates),[6] $[Cu_3(\mu\text{-}dppm)_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}CFc)_2](PF_6)$,[7] and $[M_3(dpa)_4(C{\equiv}CFc)_2]$ (dpa = 2,2′-dipyridylamide, M = Co,[8] Ru[9]), respectively. It has been demonstrated that the electronic nature of the [M] connectors, including metal centers and their ancillary ligands, plays a vital role in the electronic coupling and, hence, electron delocalization in these species.[3−10] Recently, the bis(ferrocenylethynyl)-capped hexanuclear platinum compound $[Pt_6(\mu\text{-}PtBu_2)_4(CO)_4(C{\equiv}CFc)_2]$ has been reported,[11] which reveals the presence of intramolecular electron transfer from the $\{Pt_6\}$ cluster to the peripheral ferrocenyl subunits.

During our studies on group 11 metal alkynyl chemistry, a series of $Ag^I{-}Cu^I$ and $Ag^I{-}Au^I$ heterometallic cluster complexes with various nuclearities have been prepared by reaction of $[M_2(Ph_2PXPPh_2)_2(MeCN)_2]^{2+}$ (X = CH_2, NH; M = Cu^I, Ag^I, Au^I) with polymeric silver acetylides,[12] which exhibit rich spectroscopic and luminescent properties. These studies prompted us to attempt the depolymerization of polymeric silver ferrocenylacetylide $(AgC{\equiv}CFc)_n$ with $[M_2(Ph_2PXPPh_2)_2(MeCN)_2]^{2+}$. Interestingly, while the reactions gave octahedral hexanuclear Ag^I_6 and Cu^I_6 complexes when X = CH_2,[13] rhombic dodecahedral $Ag^I_8M^I_6$ (M = Cu, Ag, Au) cage complexes and a 1,2,5-azadiphospholium product were isolated when X = NH (Scheme 1).

Slow addition of 2 equiv of polymeric $(AgC{\equiv}CFc)_n$ to a 1,2-dichloroethane−methanol−dichloromethane (2/2/1 v/v/v) solution of $[M_2(Ph_2PNHPPh_2)_2(MeCN)_2](BF_4)_2$ with stirring gave a clear red solution, from which the purple product **1** and red Ag_8M_6 cluster complex (M = Cu (**2**), Ag (**3**), Au (**4**)) were separated by silica gel column chromatography.[14] These compounds have been characterized by ESI-MS spectrometry, microanalyses, ^{1}H NMR and IR spectroscopy (Supporting Information), and X-ray crystallography.[15]

The compound $[FcC{=}CH(Ph_2PNPPh_2)](BF_4)$ (**1**) (Figure 1) is a 1,2,5-azadiphospholium species originating probably from a cyclic addition reaction of PPh_2NHPPH_2 with ferrocenylethynyl. The curved array FcC=CH (C3−C2−C1 = 126.6(4)°)

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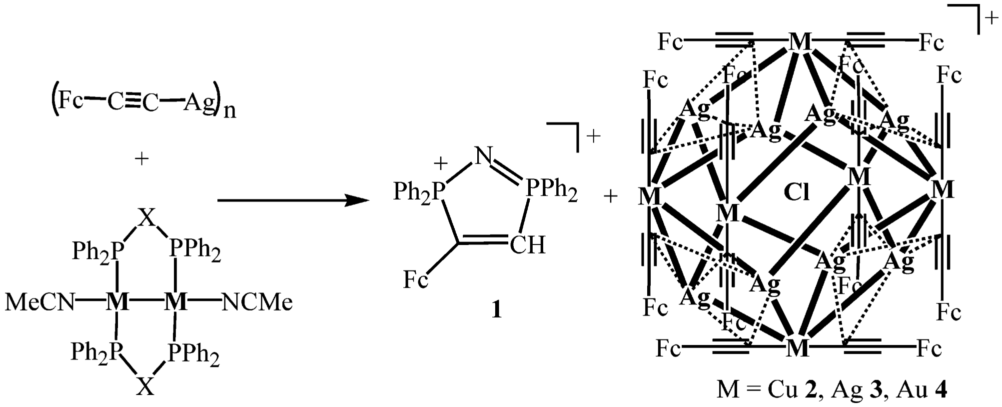
Scheme 1. Synthetic Routes to Complexes 1−4



instead of linearity in FcC≡CH suggests sp^2-hybridized character for C1 and C2 atoms. The C1−C2 length (1.341(6) Å) is typical of a C═C double bond, which was also confirmed by the IR spectrum, with a strong *ν*(C═C) band occurring at 1618 cm^{-1}. The P−N (1.601(4) and 1.612(4) Å) distances are close to those in the deprotonated $[Ph_2PNPPh_2]^-$ [16] but obviously shorter than those in PPh_2NHPPH_2.[17] The related bonding parameters are comparable to those in the phenyl counterpart $[PhC{=}CH(Ph_2PNPPh_2)]Br$, which was formed by direct reaction of PPh_2NHPPh_2 with PhC≡CBr.[18]

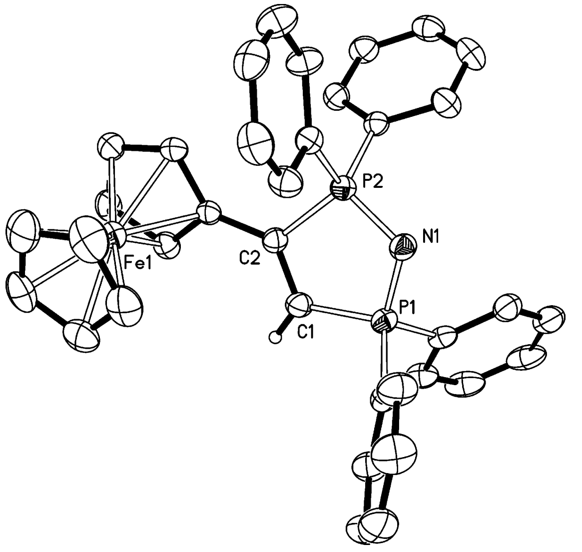


Figure 1. ORTEP drawing of the cation of **1** with atom-labeling scheme showing 30% thermal ellipsoids.

The Ag_8M_6 cluster complexes exhibit a cage structure composed of 8 Ag^I and 6 M^I (M = Cu (**2**), Ag (**3**), Au (**4**)) centers linked by 12 ferrocenylacetylides, in which a chloride ion is located at the center of the cage. The Ag_8M_6 cluster (Figure 2) forms a rhombic dodecahedron[19] made up of 14 Ag_2M_2 quadrangles. Eight Ag^I centers are arranged at the 8 apices of a cube, whereas 6 M^I centers are oriented at the 6 apices of an octahedron. Interestingly, each of the 6 square planes in the Ag^I_8 cube is capped with a M^I atom.[19] Likewise, each of the 8 triangular planes in the M^I_6 octahedron is capped with a Ag^I atom (Figure 2). The Ag−Cu (2.82−3.07 Å for **2**), Ag−Ag (2.89−3.086 Å for **3**), and Ag−Au (2.92−3.31 Å for **4**) distances lie within the ranges found in other Ag^I−Cu^I, Ag^I−Ag^I, and Ag^I−Au^I alkynyl complexes.[2,12,19,20] These distances are shorter than the sum of Ag^I and M^I van der Waals radii (3.06 Å for Ag^I−Cu^I and 3.40 Å for Ag^I−Ag^I and Ag^I−Au^I), indicating unambiguously the presence of metal−metal contacts.[12,20] It is noteworthy that each Ag^I atom is associated with 3 adjacent M^I atoms, whereas each M^I atom is connected to 4 adjacent Ag^I atoms via Ag^I−M^I contacts. The acetylides adopt an asymmetric μ_3-η^1 or μ_3-η^1:η^1:η^2 bonding mode to link one M^I and two/three Ag^I centers, in which the M−C length is much shorter than those of the Ag−C bonds. The M−C≡C−Fc arrays are quasi-linear, whereas those of Ag−C≡C−Fc are curved.

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(14) Synthetic procedure for **1** and **2**: to 10 mL of a 1,2-dichloroethane−methanol−dichloromethane (2/2/1 v/v/v) solution of $[Cu_2(Ph_2PNHPPh_2)_2(MeCN)_2](BF_4)_2$ (115.3 mg, 0.10 mmol) was added slowly $(AgC{\equiv}CFc)_n$ (63.3 mg, 0.20 mmol) with stirring for 12 h to give a clear deep red solution. The solvents were removed in vacuo to afford a red residue, which was dissolved in 5 mL of dichloromethane. The solution was then chromatographed on a silica gel column (100−200 mesh). The first band was eluted using dichloromethane−acetone (50/3) to afford a small quantity of unidentified species. Elution of the second band using dichloromethane−acetone (5/1) gave the mauve compound **1**. Yield: 18% (based on AgC≡CFc). The third band was eluted using dichloromethane−acetone (1/1), affording compound **2** as a red product. Yield: 47% (based on AgC≡CFc). Detailed characterization data for compounds **1**−**4** is provided in the the Supporting Information.

(15) Crystal data for **1**: $C_{36}H_{30}BF_4FeNP_2$, $M_r = 681.21$, triclinic, space group $P\bar{1}$, $a = 10.3467(3)$ Å, $b = 10.9956(1)$ Å, $c = 14.9663(4)$ Å, $\alpha = 96.362(1)^\circ$, $\beta = 107.810(1)^\circ$, $\gamma = 93.639(1)^\circ$, $V = 1602.54(6)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.412$ g cm^{-3}, $\mu = 0.621$ mm^{-1}, $T = 293(2)$ K, R1 = 0.0637, wR2 = 0.1554 for 3984 reflections with $I > 2\sigma(I)$, GOF = 1.091. Crystal data for **2**·CH_2Cl_2·$8H_2O$: $C_{145}H_{127}Ag_8Cl_3Cu_6Fe_{12}O_9$, $M_r = 4034.22$, triclinic, space group $P\bar{1}$, $a = 16.261(5)$ Å, $b = 18.153(7)$ Å, $c = 27.627(9)$ Å, $\alpha = 87.950(11)^\circ$, $\beta = 75.424(10)^\circ$, $\gamma = 74.763(7)^\circ$, $V = 7611(5)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.760$ g cm^{-3}, $\mu = 3.025$ mm^{-1}, $T = 293(2)$ K, R1 = 0.0867, wR2 = 0.2629 for 15 304 reflections with $I > 2\sigma(I)$, GOF = 1.078. Crystal data for **3**·$10H_2O$: $C_{144}H_{129}Ag_{14}ClFe_{12}O_{11}$, $M_r = 4251.3$, triclinic, space group $P\bar{1}$, $a = 15.6539(3)$ Å, $b = 16.7787(2)$ Å, $c = 17.6979(2)$ Å, $\alpha = 79.829(1)^\circ$, $\beta = 69.036(1)^\circ$, $\gamma = 62.276(1)^\circ$, $V = 3842.09(10)$ Å^3, $Z = 1$, $\rho_{calcd} = 1.837$ g cm^{-3}, $\mu = 2.897$ mm^{-1}, $T = 293(2)$ K, R1 = 0.1053, wR2 = 0.2644 for 7426 reflections with $I > 2\sigma(I)$, GOF = 1.292. Crystal data for **4**·$10H_2O$: $C_{144}H_{129}Ag_8Au_6ClFe_{12}O_{11}$, $M_r = 4785.88$, triclinic, space group $P\bar{1}$, $a = 15.6892(1)$ Å, $b = 16.7712(3)$ Å, $c = 17.7327(3)$ Å, $\alpha = 81.126(1)^\circ$, $\beta = 68.883(1)^\circ$, $\gamma = 62.678(1)^\circ$, $V = 3866.7(1)$ Å^3, $Z = 1$, $\rho_{calcd} = 2.055$ g cm^{-3}, $\mu = 7.803$ mm^{-1}, $T = 293(2)$ K, R1 = 0.0986, wR2 = 0.2530 for 7146 reflections with $I > 2\sigma(I)$, GOF = 1.228.

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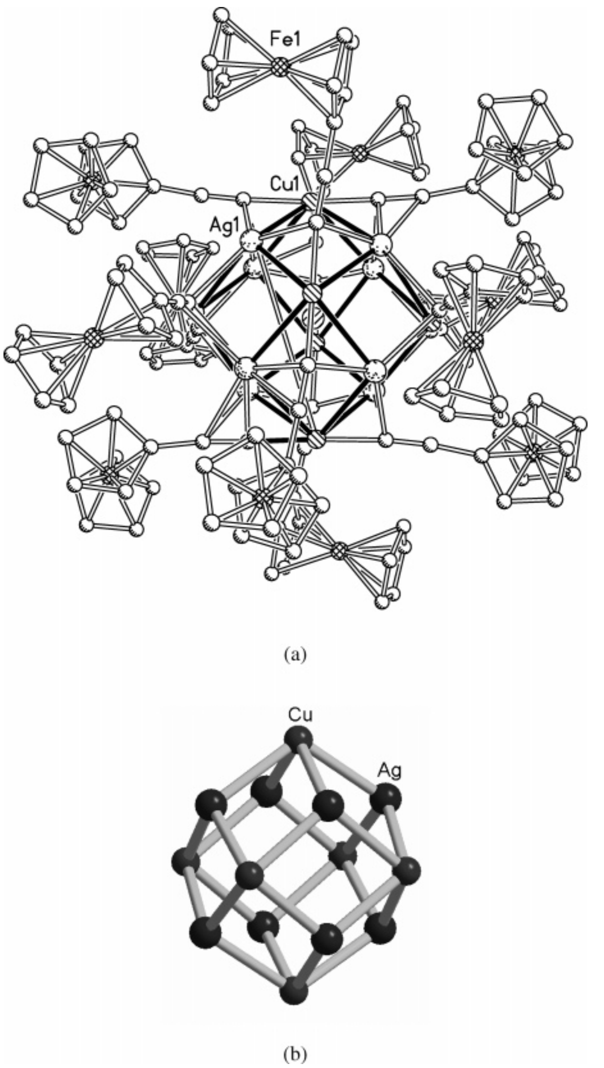

(a)

(b)

Figure 2. (a) Perspective view of the complex cation of **2**. (b) Ag_8Cu_6 cluster core showing a rhombic dodecahedral structure.

While the Ag center is located in a distorted-triangular-planar environment built from three C donors, the M center exhibits a quasi-linear arrangement, with the C−M−C angle being close to 180°. As depicted in Scheme S1 (Supporting Information), Fc−C≡C−M−C≡C−Fc arrays are likely oriented in three different conformations, of which the trans mode is most frequently found in the [D]−[M]−[A] compounds of ferrocenylethynyl.[3,4,6,7,9,11] The cis and gauche orientations, however, occur only in a few cases. Four examples with cis conformations are $Cu_6(dppm)_2(C\equiv CFc)_4(ClO_4)_2$,[13] $Pt_2(dppm)_2(C\equiv CFc)_2$,[5] $Co_3(dpa)_4(C\equiv CFc)_2$,[8] and $Ir_2Cu_4(C\equiv CFc)_8$.[10] Two examples with gauche orientations are $[Ag_6(dppm)_2(C\equiv CFc)_4(CH_3OH)_2](BF_4)_2$[13] and *trans*-$Mn(dmpe)_2(C\equiv CFc)_2$.[21] In contrast with the all-trans orientations in Ag_{14} complex **3** and Ag_8Au_6 complex **4**, of the six Fc−C≡C−Cu−C≡C−Fc arrays in Ag_8Cu_6 complex **2**, three are cis-oriented and other three are gauche-arranged. Average intramolecular Fe···Fe separations in the bridging Fc−C≡C−M−C≡C−Fc arrays are 11.55, 12.28, and 12.25 Å for compounds **2** (M = Cu), **3** (M = Ag), and **4** (M = Au), respectively, which are comparable to those in the trinuclear complex $[Cu^I_3(dppm)_3(\mu_3\text{-}\eta^1\text{-}C\equiv CFc)_2](PF_6)$ (11.78 Å)[7] and octahedral hexanuclear complex $[Ag_6(dppm)_2(C\equiv CFc)_4(CH_3OH)_2](BF_4)_2$ (11.85 Å)[13] but obviously longer than those in $Cu_6(dppm)_2(C\equiv CFc)_4(ClO_4)_2$ (11.08 Å).[13] It is noticeable that, for the Ag_8Cu_6 complex **2**, the Fe···Fe separations in the gauche-oriented (average 11.45 Å) Fc−C≡C−Cu−C≡C−Fc arrays are obviously shorter than those in the cis-arranged (average 11.75 Å) ones.

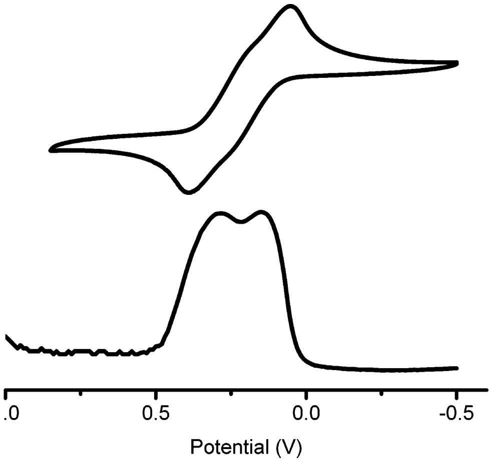

Figure 3. Cyclic and differential pulse voltammograms (CV and DPV) of **2** in a 0.1 M dichloromethane solution of $(Bu_4N)(PF_6)$. The scan rate is 100 mV s^{-1} for CV and 20 mV s^{-1} for DPV.

Redox properties of **1**−**4** were investigated by cyclic and pulse differential voltammetry in a 0.1 M dichloromethane solution of $(Bu_4N)(PF_6)$. A reversible redox wave occurs at $E_{1/2} = 0.34$ V (vs Fc^+/Fc) for **1** due to the oxidation of ferrocenyl, which is more positive compared with that for ferrocenylethynyl (0.14 V),[4b] indicating that cyclic formation of 1,2,5-azadiphospholium makes oxidation of the iron center much more difficult. As shown in Figure 3, **2** exhibits two separate reversible redox waves at 0.29 and 0.14 V, respectively, ascribed to the successive oxidation of ferrocenyls. The wave separation $\Delta E_{1/2}$ of two stepwise redox processes is 0.15 V, which corresponds to the comproportionation constant $K_c = 343$. The distinct redox wave splitting indicates that intramolecular electronic communication is likely operative between ferrocenyls and is mediated across the quasi-linear pathway Fc−C≡C−Cu−C≡C−Fc.[22,23] It is noteworthy that redox wave splitting in **2** ($\Delta E_{1/2} = 0.15$ V, Fe···Fe = 11.60 Å) is more obvious than that in the triangular trinuclear complex $[Cu^I_3(\mu\text{-dppm})_3(\mu_3\text{-}\eta^1\text{-}C\equiv CFc)_2]^+$ ($\Delta E_{1/2} = 0.11$ V, Fe···Fe = 11.78 Å)[7] and octahedral hexanuclear complexes $Cu_6(dppm)_2(C\equiv CFc)_4(ClO_4)_2$[13] ($\Delta E_{1/2} < 0.07$ V, Fe···Fe = 11.85 Å) and $[Ag_6(dppm)_2(C\equiv CFc)_4(CH_3OH)_2](BF_4)_2$[13] ($\Delta E_{1/2} < 0.07$ V, Fe···Fe = 11.08 Å), although their Fe···Fe separations in the Fc−C≡C−M−C≡C−Fc arrays are similar. This is likely elucidated by the better linearity in the Fc−C≡C−M−C≡C−Fc arrays for **2** compared with those for tri- and hexanuclear Cu^I or Ag^I complexes.[7,13] In striking contrast with the reversible redox properties of **2**, the electrochemical behavior of **3** and **4** is irreversible, with a broad oxidation peak (0.42 V for **3** and 0.40 V for **4**) in the anodic region and a small reduction peak (0.07 V for **3** and 0.08 V for **4**) on the cathodic side, probably because of their instability in the electrochemical measurement, which induces dissociation of the Ag_8M_6 (M = Ag, Au) cluster species.

In summary, depolymerization of silver ferrocenylacetylide $(AgC\equiv CFc)_n$ with $[M_2(Ph_2PNHPh_2)_2(MeCN)_2]^{2+}$ (M = Cu, Ag,

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Au) induced isolation of rhombic dodecahedral heteronuclear $Ag^{I}_{8}M^{I}_{6}$ cage complexes together with the unusual 1,2,5-azadiphospholium product $[FcC{=}CH(Ph_2PNPPh_2)](BF_4)$ by a cyclic addition reaction of $FcC{\equiv}C$ with $Ph_2PNHPPh_2$. Intramolecular electronic communication is likely operative between Fc groups and is mediated by the pathways $Fc{-}C{\equiv}C{-}M{-}C{\equiv}C{-}Fc$ (M = Cu, Ag) in the $Ag^{I}_{8}Cu^{I}_{6}$ cage complex.

Supporting Information Available: Text giving experimental details, figures giving additional views of the compounds prepared and additional characterization data, and CIF files giving crystal data for **1**−**4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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