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# Luminescent $Ag^I$–$Cu^I$ Heterometallic Hexa-, Octa-, and Hexadecanuclear Alkynyl Complexes

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A series of $Ag^I$–$Cu^I$ heteronuclear alkynyl complexes were prepared by reaction of polymeric $(MC{\equiv}CC_6H_4R\text{-}4)_n$ (M = $Cu^I$ or $Ag^I$; R = H, $CH_3$, $OCH_3$, $NO_2$, $COCH_3$) with $[M'_2(\mu\text{-}Ph_2PXPPh_2)_2(MeCN)_2](ClO_4)_2$ (M′ = $Ag^I$ or $Cu^I$; X = NH or $CH_2$). Heterohexanuclear complexes $[Ag_4Cu_2(\mu\text{-}Ph_2PNHPPh_2)_4(C{\equiv}CC_6H_4R\text{-}4)_4](ClO_4)_2$ (R = H, **1**; $CH_3$, **2**) were afforded when X = NH, and heterooctanuclear complexes $[Ag_6Cu_2(\mu\text{-}Ph_2PCH_2PPh_2)_3(C{\equiv}CC_6H_4R\text{-}4)_6(MeCN)](ClO_4)_2$ (R = H, **3**; $CH_3$, **4**; $OCH_3$, **5**; $NO_2$, **6**) were isolated when X = $CH_2$. Self-assembly reaction between $(MC{\equiv}CC_6H_4COCH_3\text{-}4)_n$ and $[M'_2(\mu\text{-}Ph_2PCH_2PPh_2)_2(MeCN)_2](ClO_4)_2$, however, gave heterohexadecanuclear complex $[Ag_6Cu_2(\mu\text{-}Ph_2PCH_2PPh_2)_3(C{\equiv}CC_6H_4COCH_3\text{-}4)_6]_2(ClO_4)_4$ (**7**). The heterohexanuclear complexes **1** and **2** show a bicapped cubic skeleton ($Ag_4Cu_2C_4$) consisting of four $Ag^I$ and two $Cu^I$ atoms and four acetylide C donors. The heterooctanuclear complexes **3**–**6** exhibit a waterwheel-like structure that can be regarded as two $Ag_3Cu(C{\equiv}CC_6H_5)_3$ components put together by three bridging $Ph_2PCH_2PPh_2$ ligands. The heterohexadecanuclear complex **7** can be viewed as a dimer of heterooctanuclear complex $[Ag_6Cu_2(\mu\text{-}Ph_2PCH_2PPh_2)_3(C{\equiv}CC_6H_4COCH_3\text{-}4)_6](ClO_4)_2$ through the silver and acetyl oxygen (Ag–O = 2.534 (4) Å) linkage between two waterwheel-like $Ag_6Cu_2$ units. All of the complexes show intense luminescence in the solid states and in fluid solutions. The microsecond scale of lifetimes in the solid state at 298 K reveals that the emission is phosphorescent in nature. The emissive state in compounds **1**–**5** is likely derived from a $^3$LMCT ($C{\equiv}CC_6H_4R\text{-}4 \rightarrow Ag_4Cu_2$ or $Ag_6Cu_2$) transition, mixed with a metal cluster-centered ($d \rightarrow s$) excited state. The lowest lying excited state in compounds **6** and **7** containing electron-deficient 4-nitrophenylacetylide and 4-acetylphenylacetylide, respectively, however, is likely dominated by an intraligand $^3[\pi \rightarrow \pi^*]$ character.

## Introduction

Interest in metal alkynyl complexes has been stimulated by their rich electronic and luminescent properties and potential applications in molecular electronics.[1] Relative to numerous homonuclear group 11 metal alkynyl complexes,[2−15] the chemistry of heterometallic alkynyl complexes has comparatively been neglected because of synthetic difficulty in controlling the heterometallic arrays.[5b,16−18] It has been demonstrated that group 11 metal alkynyl complexes exhibit

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rich photophysical properties due to the manifold origins of excited states such as metal-centered, ligand-to-metal (LMCT), metal-to-ligand (MLCT), and intra- and interligand transitions.[1a,4,5]

It has been shown that reactions of $[M_2(\mu\text{-}Ph_2PXPPh_2)_2(MeCN)_2]^{2+}$ (X = $CH_2$ or NH; M = $Cu^I$, $Ag^I$, or $Au^I$) with alkynyl or depolymerizing polymeric group 11 metal acetylides utilizing phosphine usually give di-, tri-, and tetranuclear cluster complexes that exhibit rich photoluminescence properties.[4−6,11,14] Depolymerizing silver or copper ferrocenylacetylide $(MC{\equiv}CFc)_n$ (M = $Cu^I$, $Ag^I$) with $[M_2(\mu\text{-}Ph_2PCH_2PPh_2)_2(MeCN)_2]^{2+}$ affords octahedral hexanuclear complexes.[15] In order to attain heterometallic molecular materials, one of the possible synthetic strategies is to incorporate two different metal components by self-assembly.[19] We describe herein a feasible approach to synthesize group 11 heterometallic alkynyl complexes by reaction of polymeric metal alkynyl $(MC{\equiv}CC_6H_4R\text{-}4)_n$ (M = $Cu^I$ or $Ag^I$; R = H, $CH_3$, $OCH_3$, $NO_2$, $COCH_3$) with $[M'_2(\mu\text{-}Ph_2PXPPh_2)_2(MeCN)_2](ClO_4)_2$ (M′ = $Ag^I$ or $Cu^I$; X = NH or $CH_2$). Interestingly, while the reaction gave heterohexanuclear complexes $[Ag_4Cu_2(\mu\text{-}Ph_2PNHPPh_2)_4(C{\equiv}CC_6H_4R\text{-}4)_4](ClO_4)_2$ (R = H, **1**; $CH_3$, **2**) when X = NH, heterooctanuclear complexes $[Ag_6Cu_2(\mu\text{-}Ph_2PCH_2PPh_2)_3(C{\equiv}CC_6H_4R\text{-}4)_6(MeCN)](ClO_4)_2$ (R = H, **3**; $CH_3$, **4**; $OCH_3$, **5**; $NO_2$, **6**) and heterohexadecanuclear complex $[Ag_6Cu_2(\mu\text{-}Ph_2PCH_2PPh_2)_3(C{\equiv}CC_6H_4COCH_3\text{-}4)_6]_2(ClO_4)_4$ (**7**) were isolated when X = $CH_2$.

## Experimental Section

**Materials and Reagents.** All synthetic operations were performed under dry argon atmosphere by using Schlenk techniques. Solvents were dried by standard methods and distilled prior to use. The reagents bis(diphenylphosphino)amine ($Ph_2PNHPPh_2$), bis(diphenylphospino)methane ($Ph_2PCH_2PPh_2$), silver perchlorate ($AgClO_4$), phenylacetylene ($HC{\equiv}CC_6H_5$), 4-ethynyltoluene ($HC{\equiv}CC_6H_4CH_3$-4), and 1-ethynyl-4-methoxybenzene ($HC{\equiv}CC_6H_4$-$OCH_3$-4) were available commercially (from Acros, Fluka, Alfa Aesar, or Aldrich Chemical Co.). 4-Nitrophenylacetylene ($HC{\equiv}CC_6H_4NO_2$-4) and 4-acetylphenylacetylene ($HC{\equiv}CC_6H_4COCH_3$-4) were prepared by the literature procedures.[20] The polymeric metal alkynyl compounds $(MC{\equiv}CC_6H_4R\text{-}4)_n$ (M = $Cu^I$ or $Ag^I$; R = H, $CH_3$, $OCH_3$, $NO_2$, $COCH_3$) were obtained by the described methods.[21] The precursor compounds $[M_2(Ph_2PXPPh_2)_2(MeCN)_2](ClO_4)_2$

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(M = Cu or Ag; X = NH or $CH_2$) were prepared by similar synthetic procedures described in the literature.[22]

**CAUTION!** *Silver or copper acetylides and perchlorate salts are potentially explosive and should be handled with care and in small amounts.*

**$[Ag_4Cu_2(\mu\text{-}Ph_2PNHPPh_2)_4(C\equiv CC_6H_5)_4](ClO_4)_2$ 1**. $(AgC\equiv CC_6H_5)_n$ (41.8 mg, 0.20 mmol) was added to an acetonitrile (20 mL) solution of $[Cu_2(Ph_2PNHPPh_2)_2(MeCN)_2](ClO_4)_2$ (118.0 mg, 0.10 mmol). The suspended solution was then stirred at room temperature for 1 day to afford a clear yellow solution. Diffusion of diethyl ether vapor onto the concentrated acetonitrile solution gave yellow crystals of **1**. Yield: 90.6 mg (65%). Elemental analysis calcd (%) for $C_{128}H_{104}Ag_4Cl_2Cu_2N_4O_8P_8\cdot 2CH_3CN$: C, 56.92; H, 3.98; N, 3.02. Found: C, 57.04; H, 3.77; N, 3.02. ES-MS: *m/z* (%) 1253 (82) $[M]^{2+}$, 866 (100) $[Ag_4Cu_2(PPh_2NHPPh_2)_2(C\equiv CC_6H_5)_4]^{2+}$. IR (KBr, $cm^{-1}$): $\nu$ 2009 (w, C≡C), 1967 (w, C≡C), 1890 (w, C≡C), 1099 (s, $ClO_4$). $^{31}P$ NMR (202.3 MHz, $CD_3CN$, ppm): 63.8 (d, $J_{Ag-P} = 401$ Hz, NH*P*AgPNH), 63.0 (d, $J_{Ag-P} = 348$ Hz, NH*P*AgPNH), 60.8 (d, $J_{Ag-P} = 317$ Hz, NH*P*AgPNH), 59.8 (d, $J_{Ag-P} = 360$ Hz, NH*P*AgPNH), 53.0 (m, $J_{Ag-P} = 378$ Hz, $J_{Ag-P} = 366$ Hz Ag*P*NHPAg), 46.4 (s, AgPNH*P*Cu), 45.5 (s, AgPNH*P*Cu). UV−vis (MeCN): $\lambda_{max}$ ($\epsilon$) = 239 (209940), 285 nm (196070).

**$[Ag_4Cu_2(\mu\text{-}Ph_2PNHPPh_2)_4(C\equiv CC_6H_4CH_3\text{-}4)_4](ClO_4)_2$ 2.** The same synthetic procedure as for **1** was utilized except using $(AgC\equiv CC_6H_4CH_3\text{-}4)_n$ instead of $(AgC\equiv CC_6H_5)_n$. Yield: 80 mg (58%). Elemental analysis calcd (%) for $C_{132}H_{112}Ag_4Cl_2Cu_2N_4O_8P_8$: C, 57.45; H, 4.09; N, 2.03. Found: C, 57.04; H, 3.89; N, 2.27. ES-MS: *m/z* (%) 1280 (100) $[M]^{2+}$, 894 (93) $[Ag_4Cu_2(Ph_2PNHPPh_2)_2(C\equiv CC_6H_4CH_3\text{-}4)_4]^{2+}$. IR (KBr, $cm^{-1}$): $\nu$ 2004 (w, C≡C), 1896 (w, C≡C), 1811 (w, C≡C), 1099 (s, $ClO_4$). $^{31}P$ NMR (202.3 MHz, $CD_3CN$, ppm): 64.5 (d, $J_{Ag-P} = 369$ Hz, NH*P*AgPNH), 63.6 (d, $J_{Ag-P} = 372$ Hz, NH*P*AgPNH), 61.1 (d, $J_{Ag-P} = 346$ Hz, NH*P*AgPNH), 60.2(d, $J_{Ag-P} = 400$ Hz, NH*P*AgPNH), 53.3 (m, $J_{Ag-P} = 370$ Hz, $J_{Ag-P} = 368$ Hz Ag*P*NHPAg), 46.5 (s, AgPNH*P*Cu), 45.7 (s, AgPNH*P*Cu). UV−vis (MeCN): $\lambda_{max}$ ($\epsilon$) = 239 (216021), 302 (216980), 331 nm (114690).

**$[Ag_6Cu_2(\mu\text{-}Ph_2PCH_2PPh_2)_3(C\equiv CC_6H_5)_6(MeCN)](ClO_4)_2$ 3.** $(AgC\equiv CC_6H_5)_n$ (62.8 mg, 0.30 mmol) was added to an acetonitrile−dichloromethane (v/v 1:1) solution of $[Cu_2(Ph_2PCH_2PPh_2)_2(MeCN)_2](ClO_4)_2$ (117.2 mg, 0.10 mmol). The suspended solution was stirred at room temperature for 1 day to give a clear pale yellow solution. Diffusion of diethyl ether vapor into the concentrated solution afforded yellow crystals of the product. Yield: 83 mg (63%). Elemental analysis calcd (%) for $C_{125}H_{99}Ag_6Cl_2Cu_2NO_8P_6$: C, 54.12; H, 3.60; N, 0.50. Found: C, 54.25; H, 3.61; N, 0.51. ES-MS: *m/z* (%) 1268 (12) $[(M - CH_3CN)]^{2+}$, 1083 (16) $[Ag_6Cu_2(Ph_2PCH_2PPh_2)_2(C\equiv CC_6H_5)_6(H_2O)]^{2+}$, 701 (10) $[Ag_6Cu_2(C\equiv CC_6H_5)_6(H_2O)]^{2+}$, 865 (100) $[Ag_3Cu(Ph_2PCH_2PPh_2)_3(C\equiv CC_6H_5)_2]^{2+}$. IR (KBr, $cm^{-1}$): $\nu$ 2019 (w, C≡C), 1892 (w, C≡C), 1809 (w, C≡C), 1097 (s, $ClO_4$). $^{31}P$ NMR (202.3 MHz, $CD_3CN$, ppm): 9.9 (m, $J_{Ag-P} = 772$ Hz, $C_2$NAg*P*$CH_2$PAg; $J_{Ag-P} = 577$ Hz, $C_2$Ag*P*$CH_2$PAg; $^2J_{P-P} = 43$ Hz, Ag*P*$CH_2$*P*Ag). UV−Vis (MeCN): $\lambda_{max}$ ($\epsilon$) = 256 (44160), 288 (39660), 322 nm (33780).

**$[Ag_6Cu_2(\mu\text{-}Ph_2PCH_2PPh_2)_3(C\equiv CC_6H_4CH_3\text{-}4)_6(MeCN)](ClO_4)_2$ 4.** This complex was prepared by the same procedure as **3** except for the use of $(AgC\equiv CC_6H_4CH_3\text{-}4)_n$ instead of $(AgC\equiv CC_6H_5)_n$. Yield: 92 mg (63%). Elemental analysis calcd (%) for $C_{131}H_{111}Ag_6Cl_2Cu_2NO_8P_6\cdot{}^1/_4CH_2Cl_2\cdot CH_3OH\cdot H_2O$: C, 54.24; H, 4.01; N, 0.48. Found: C, 54.17; H, 3.85; N, 0.41. ES-MS: *m/z* (%) 1310 (63) $[(M - CH_3CN)]^{2+}$, 1117 (14) $[Ag_6Cu_2(Ph_2PCH_2PPh_2)_2(C\equiv CC_6H_4CH_3\text{-}4)_6]^{2+}$, 937 (50) $[Ag_6Cu_2(Ph_2PCH_2PPh_2)(C\equiv CC_6H_4CH_3\text{-}4)_6(H_2O)]^{2+}$, 893 (100) $[Ag_3Cu(Ph_2PCH_2PPh_2)_3(C\equiv CC_6H_4CH_3\text{-}4)_2(H_2O)]^{2+}$. IR (KBr, $cm^{-1}$): $\nu$ 2013 (w, C≡C), 1905 (w, C≡C), 1813 (w, C≡C), 1092 (s, $ClO_4$). $^{31}P$ NMR (202.3 MHz, $CD_3CN$, ppm): 10.1 (m, $J_{Ag-P} = 772$ Hz, $C_2$NAg*P*$CH_2$PAg; $J_{Ag-P} = 574$ Hz, $C_2$Ag*P*$CH_2$PAg; $J_{Ag-P} = 409$ Hz, $C_3$Ag*P*$CH_2$PAg; $^2J_{P-P} = 43$ Hz, Ag*P*$CH_2$PAg). UV−vis (MeCN): $\lambda_{max}$ ($\epsilon$) = 263 (46190), 320 (50050), 343 nm (35180).

**$[Ag_6Cu_2(\mu\text{-}Ph_2PCH_2PPh_2)_3(C\equiv CC_6H_4OCH_3\text{-}4)_6(MeCN)](ClO_4)_2$ 5.** This complex was prepared by the same procedure as **3** except for the use of $(AgC\equiv CC_6H_4OCH_3\text{-}4)_n$ instead of $(AgC\equiv CC_6H_5)_n$. Yield: 55 mg (39%). Elemental analysis calcd (%) for $C_{131}H_{111}Ag_6Cl_2Cu_2NO_{14}P_6$: C, 53.26; H, 3.79; N, 0.47. Found: C, 53.17; H, 3.85; N, 0.41. ES-MS: *m/z* (%) 1546 (16) $[Ag_3Cu(Ph_2PCH_2PPh_2)_2(C\equiv CC_6H_4OCH_3\text{-}4)_3]^+$, 1357 (62) $[(M - CH_3CN)]^{2+}$, 1165 (15) $[Ag_6Cu_2(Ph_2PCH_2PPh_2)_2(C\equiv CC_6H_4OCH_3\text{-}4)_6]^{2+}$, 923 (100) $[Ag_3Cu(Ph_2PCH_2PPh_2)_3 (C\equiv CC_6H_4OCH_3\text{-}4)_2(MeCN)]^{2+}$, 731 (21) $[Ag_3Cu(Ph_2PCH_2PPh_2)_2(C\equiv CC_6H_4OCH_3\text{-}4)_2(MeCN)]^{2+}$. IR (KBr, $cm^{-1}$): $\nu$ 2001 (w, C≡C), 1088 (s, $ClO_4$). $^{31}P$ NMR (202.3 MHz, $CD_3CN$, ppm): 9.0 (m, $J_{Ag-P} = 769$ Hz, $C_2$NAg*P*$CH_2$PAg; $J_{Ag-P} = 574$ Hz, $C_2$Ag*P*$CH_2$PAg; $J_{Ag-P} = 397$ Hz, $C_3$Ag*P*$CH_2$PAg; $^2J_{P-P} = 43$ Hz, Ag*P*$CH_2$PAg). UV−vis (MeCN): $\lambda_{max}$ ($\epsilon$) = 256 (80927), 321 (66911), 335 nm (50113).

**$[Ag_6Cu_2(\mu\text{-}Ph_2PCH_2PPh_2)_3(C\equiv CC_6H_4NO_2\text{-}4)_6(MeCN)](ClO_4)_2$ 6.** This complex was prepared by the same procedure as **3** except for the use of $(AgC\equiv CC_6H_4NO_2\text{-}4)_n$ instead of $(AgC\equiv CC_6H_5)_n$ and acetonitrile as the solvent. Yield: 78 mg (50%). Elemental analysis calcd (%) for $C_{125}H_{93}Ag_6Cl_2Cu_2N_7O_{20}P_6\cdot{}^1/_2CH_3CN\cdot 2H_2O$: C, 48.89; H, 3.03; N, 3.39. Found: C, 48.80; H, 2.91; N, 3.62. ES-MS: *m/z* (%) 1592 (47) $[Ag_3Cu(Ph_2PCH_2PPh_2)_2(C\equiv CC_6H_4NO_2\text{-}4)_3]^+$, 1546 (100) $[Ag_3Cu(Ph_2PCH_2PPh_2)_2(C\equiv CC_6H_4NO_2\text{-}4)_2(ClO_4)]^+$, 1403 (15) $[(M\text{-}CH_3CN)]^{2+}$, 1163 (38) $[Ag_3Cu(Ph_2PCH_2PPh_2)(C\equiv CC_6H_4NO_2\text{-}4)_2(ClO_4)]^+$, 1021 (38) $[Ag_6Cu_2(Ph_2PCH_2PPh_2) (C\equiv CC_6H_4NO_2\text{-}4)_6]^{2+}$, 955 (100) $[Ag_3(Ph_2PCH_2PPh_2)(C\equiv CC_6H_4NO_2\text{-}4)(ClO_4)]^+$. IR (KBr, $cm^{-1}$): $\nu$ 2017 (w, C≡C), 1088 (s, $ClO_4$). $^{31}P$ NMR (202.3 MHz, $CD_3CN$, ppm): 10.0 (d, $J_{Ag-P} = 577$ Hz, Ag*P*$CH_2$PAg). UV−vis (MeCN): $\lambda_{max}$ ($\epsilon$) = 266 (42550), 368 (33380), 410 nm (29174).

**$[Ag_6Cu_2(\mu\text{-}Ph_2PCH_2PPh_2)_3(C\equiv CC_6H_4COCH_3\text{-}4)_6]_2(ClO_4)_4$ 7**. This complex was prepared by the same procedure as **3** except for the use of $(AgC\equiv CC_6H_4COCH_3\text{-}4)_n$ instead of $(AgC\equiv CC_6H_5)_n$ and acetonitrile as the solvent. Yield: 125 mg (42%). Elemental analysis calcd (%) for $[C_{135}H_{108}Ag_6Cl_2Cu_2O_{14}P_6]_2\cdot(C_2H_5)_2O\cdot 4H_2O$: C, 53.80; H, 3.86. Found: C, 53.40; H, 3.86. IR (KBr, $cm^{-1}$): $\nu$ 2020 (w, C≡C), 1682 (s, C=O),1096 (s, $ClO_4$). $^{31}P$ NMR (202.3 MHz, $CD_3CN$, ppm): 9.2 (m, $J_{Ag-P} = 868$ Hz, OAg*P*$CH_2$PAg; $J_{Ag-P} = 580$ Hz, $C_2$Ag*P*$CH_2$PAg; $J_{Ag-P} = 409$ Hz, $C_3$Ag*P*$CH_2$PAg; $^2J_{P-P} = 43$ Hz, Ag*P*$CH_2$PAg). UV−vis (MeCN): $\lambda_{max}$ ($\epsilon$) = 256 (51599), 304 (74890), 360 (59528), 389 nm (40802).

**Crystal Structural Determination.** Crystals coated with epoxy resin or sealed in capillaries with mother liquors were measured on a SIEMENS SMART CCD diffractometer by the $\omega$ scan technique at room temperature using graphite-monochromated Mo Kα ($\lambda$ = 0.71073 Å) radiation. An absorption correction by SADABS was applied to the intensity data. The structures were solved by direct methods or the Patterson procedure, and the heavy atoms were located from the *E*-map. The remaining non-hydrogen atoms were determined from the successive difference Fourier syntheses. All non-hydrogen atoms were refined anisotropically except those mentioned otherwise. The hydrogen atoms were generated geometrically with isotropic thermal parameters. The

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[22] (a) Diez, J.; Gamasa, M. P.; Gimeno, J.; Tiripicchio, A.; Camellini, M. T. *J. Chem. Soc., Dalton Trans*. **1987**, 1275. (b) Ho, D. M.; Bau, R. *Inorg. Chem.* **1983**, *22*, 4073. (c) Sekabunga, E. J.; Smith, M. L.; Webb, T. R.; Hill, W. E. *Inorg. Chem.* **2002**, *41*, 1205.

**Table 1.** Crystallographic Data for Compounds **1**−**4**, **6**, and **7**

| | **1**·$2CH_3CN$ | **2**·$^1/_2(C_2H_5)_2O$·$3CH_3CN$·$H_2O$ | **3** | **4**·$CH_3OH$·$^1/_4CH_2Cl_2$·$H_2O$ | **6**·$^1/_2CH_3CN$·$2H_2O$ | **7**·$(C_2H_5)_2O$·$4H_2O$ |
|---|---|---|---|---|---|---|
| empirical formula | $C_{132}H_{110}Ag_4Cl_2Cu_2N_6O_8P_8$ | $C_{140}H_{126}Ag_4Cl_2Cu_2N_7O_{9.5}P_8$ | $C_{125}H_{99}Ag_6Cl_2Cu_2NO_8P_6$ | $C_{132.25}H_{116.5}Ag_6Cl_{2.5}Cu_2NO_{10}P_6$ | $C_{126}H_{98.5}Ag_6Cl_2Cu_2N_{7.5}O_{22}P_6$ | $C_{213.5}H_{120}Ag_6Cl_2Cu_2O_{17}P_6$ |
| fw | 2785.48 | 2935.70 | 2774.07 | 2928.51 | 3100.64 | 3988.11 |
| space group | $C2/c$ | $P\bar{1}$ | $P2_1/c$ | $P2_1/n$ | $P\bar{1}$ | $P\bar{1}$ |
| $a$, Å | 54.4811(2) | 15.4263(3) | 11.9077(2) | 25.2670(4) | 15.6499(4) | 15.440(7) |
| $b$, Å | 16.0616(3) | 17.2100(3) | 33.3697(4) | 20.2672(4) | 17.0264(4) | 17.120(8) |
| $c$, Å | 30.1341(5) | 26.7899(5) | 28.8849(2) | 26.9231(4) | 27.1874(8) | 26.736(12) |
| $\alpha$, deg | | 103.52(0) | | | 84.185(1) | 93.457(6) |
| $\beta$, deg | 107.98(0) | 90.287(1) | 96.050(1) | 90.02(0) | 89.496(1) | 91.477(4) |
| $\gamma$, deg | | 91.40(0) | | | 69.957(1) | 109.051(6) |
| $V$, Å$^3$ | 25081.1(6) | 6912.8(2) | 11413.7(2) | 13787.1(4) | 6768.0(3) | 6660(5) |
| $Z$ | 8 | 2 | 4 | 4 | 2 | 2 |
| $\rho_{calcd}$, g/cm$^3$ | 1.475 | 1.410 | 1.614 | 1.411 | 1.521 | 1.989 |
| $\mu$, mm$^{-1}$ | 1.148 | 1.046 | 1.560 | 1.306 | 1.333 | 1.376 |
| radiation ($\lambda$, Å) | 0.71073 | 0.71073 | 0.71073 | 0.71073 | 0.71073 | 0.71073 |
| temp, K | 293(2) | 293(2) | 293(2) | 293(2) | 293(2) | 293(2) |
| R1$^a$ ($F_o$) | 0.0760 | 0.0655 | 0.0765 | 0.0879 | 0.0892 | 0.0636 |
| wR2$^b$ ($F_o^2$) | 0.1762 | 0.1574 | 0.1555 | 0.2220 | 0.2116 | 0.1684 |
| GOF | 1.262 | 1.174 | 1.320 | 1.229 | 1.214 | 1.054 |

[a] $R1 = \Sigma|F_o - F_c|/\Sigma F_o$. [b] $wR2 = \Sigma[w(F_o^2 - F_c^2)_2]/\Sigma[w(F_o^2)]^{1/2}$.

structures were refined on $F^2$ by full-matrix least-squares methods using the SHELXTL-97 program package.[23] Crystallographic parameters and the details for data collections and refinements are summarized in Table 1 for **1**·$2CH_3CN$, **2**·$^1/_2(C_2H_5)_2O$·$3CH_3CN$·$H_2O$, **3**, **4**·$CH_3OH$·$^1/_4CH_2Cl_2$·$H_2O$, **6**·$^1/_2CH_3CN$·$2H_2O$, and **7**·$(C_2H_5)_2O$·$4H_2O$. Full crystallographic data are provided in the Supporting Information.

**Physical Measurements.** Elemental analyses (C, H, N) were carried out on a Perkin-Elmer model 240C automatic instrument. Electrospray mass spectra (ES-MS) were recorded on a Finnigan LCQ mass spectrometer using dichloromethane−methanol or acetonitrile−methanol as mobile phase. UV−vis absorption spectra in acetonitrile and dichloromethane solutions were measured on a Perkin-Elmer Lambda 25 UV−vis spectrometer. Infrared spectra were recorded on a Magna750 FT-IR spectrophotometer with KBr pellets. $^{31}P$ NMR spectra were measured on a Varian UNITY-500 spectrometer using 85% $H_3PO_4$ as external standard. Emission and excitation spectra were recorded on a Perkin-Elmer LS 55 luminescence spectrometer with a red-sensitive photomultiplier type R928. Emission lifetimes were determined on an Edinburgh Analytical Instruments F900 fluorescence spectrometer using an LED laser at 397 nm excitation, and the resulting emission was detected by a thermoelectrically cooled Hamamatsu R3809 photomultiplier tube. The instrument response function at the excitation wavelength was deconvolved from the luminescence decay.

## Results and Discussion

As shown in Scheme 1, the complexes were prepared by reaction of $[Cu_2(\mu\text{-}Ph_2PXPPh_2)_2(MeCN)_2](ClO_4)_2$ with $(AgC{\equiv}CC_6H_4R\text{-}4)_n$ in acetonitrile or dichloromenthane. The suspended solution became a clear yellow or orange-yellow solution after being stirred at room temperature for several hours. Diffusion of diethyl ether or layering of hexane onto the solutions afforded well-shaped crystals. It is noteworthy that reaction of $[Ag_2(\mu\text{-}Ph_2PXPPh_2)_2(MeCN)_2](ClO_4)_2$ with $(CuC{\equiv}CC_6H_4R\text{-}4)_n$ gave the same product as that of $[Cu_2(\mu\text{-}Ph_2PXPPh_2)_2(MeCN)_2](ClO_4)_2$ with $(AgC{\equiv}CC_6H_4R\text{-}4)_n$, but afforded lower yields of the products.

The positive ES-MS showed a high abundance of molecular ion peaks $[M]^{2+}$ (**1** and **2**) or $[M - CH_3CN]^{2+}$ (**3**−**6**). The IR spectra displayed weak $\nu(C{\equiv}C)$ stretching vibrations in the range 1800−2030 cm$^{-1}$. In the $^{31}P$ NMR spectra of heterohexanuclear compounds **1** (Figure S1, Supporting Information) and **2**, the P donors bound to $Cu^I$ centers display two singlets, whereas those bonded to $Ag^I$ centers afford a multiplet (composed of one doublet and one triplet with different Ag−P couplings) and four doublets. Thus, it is suggested that the eight P donors in the heterohexanuclear complexes are inequivalent in acetonitrile solutions. The $^{31}P$ NMR spectra (Figure S2, Supporting Information) of **3**−**7** with $Ag_6Cu_2$ cluster cores show clearly three couples of inequivalent Ag−P couplings, compatible with the presence of three types of $Ag^I$ centers with $C_2P$, $C_3P$, or $C_2NP$ ($C_2OP$ for **7**) chromophores, respectively, as revealed by the X-ray crystallography (vide infra).

The structures of compounds **1**−**4**, **6**, and **7** were determined by X-ray crystallography. Selected atomic distances and bonding angles are presented in Table 2. The perspective views of the coordination cations of complexes **1**, **3**, and **7** are depicted in Figure 1, 2, and 3, respectively.

In the complexes $[Ag_4Cu_2(\mu\text{-}Ph_2PNHPPh_2)_4(C{\equiv}CC_6H_4R\text{-}4)_4](ClO_4)_2$ (R = H, **1**; $CH_3$, **2**), the coordination cation (Figure 1) displays a bicapped cubic skeleton ($Ag_4Cu_2C_4$) consisting of four $Ag^I$ and two $Cu^I$ atoms and four acetylide C donors. The bicapped cubic apices are occupied by $Ag^I$ (Ag1 and Ag3) atoms, and the cubane ($Cu_2Ag_2C_4$) is composed of two $Cu^I$ (Cu1 and Cu2) and two $Ag^I$ (Ag2 and Ag4) centers bridged by four alkynyl C (C1, C11, C21, and C31) donors. It has been shown that tetrameric $Cu^I$ alkynyl complexes with monodentate phosphine as coligand afford $Cu_4C_4$ cuboidal cores,[24] but the $Cu_2Ag_2C_4$ cubane described herein represents heterometallic alkynyl cuboidal assembly. Within the $Ag_4Cu_2$ cluster core, Cu1Cu2Ag2Ag4 forms a $Cu_2Ag_2$ cluster tetrahedron. The alkynyl ligands adopt $\mu_3$- and $\mu_4$-$\eta^1$ bonding modes, in which the former is only coordinated to three metal centers in the cubane, whereas

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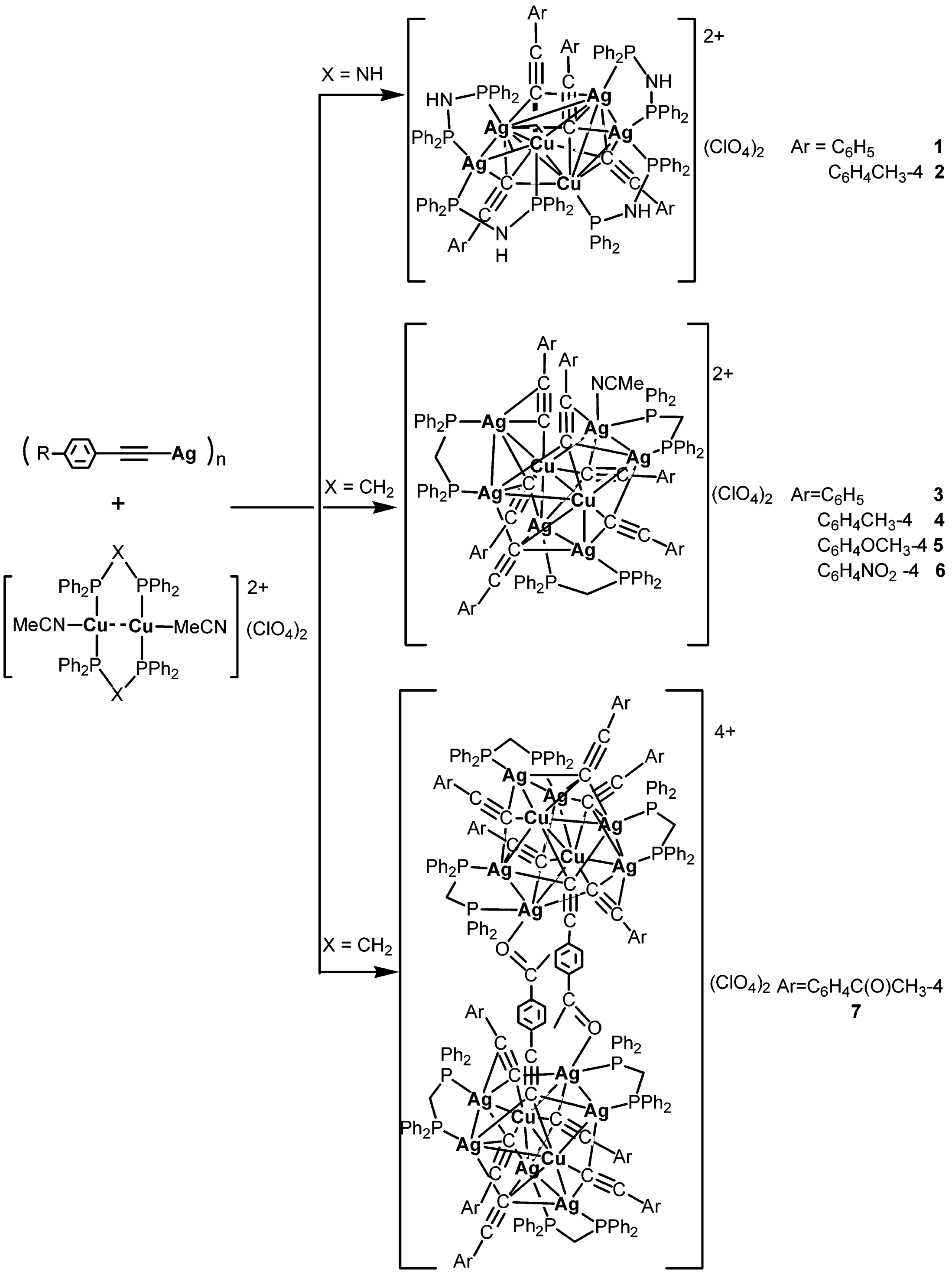
(23) Sheldrick, G. M. *SHELXL-97, Program for the Refinement of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1997.

Scheme 1



the latter also bridged one $Ag^I$ center outside the cubane. The heterohexanuclear molecule is likely regarded as a dimer of trigonal planar species $[Ag_2Cu(\mu\text{-}Ph_2PNHPPh_2)_2(C\equiv CC_6H_4R\text{-}4)_2]^+$, incorporating with each other in an almost perpendicular mode, in which the dihedral angle between two $Ag_2Cu$ planes (Ag1Ag2Cu2 and Ag3Ag4Cu1) is 86.2° and 82.9° for **1** and **2**, respectively. The $Cu^I$ and $Ag^I$ centers in the cubane apices display tetrahedral coordination environments with $C_3P$ chromophores, while the $Ag^I$ centers in the bicapped cubic apices are located in severely distorted trigonal planar geometry with $CP_2$ donors. The $Cu^I-Cu^I$ distances are 2.5733(18) and 2.5315(12) Å for **1** and **2**,

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(24) (a) Naldini, L.; Demartin, F.; Manassero, M.; Sansoni, M.; Rassu, G.; Zoroddu, M. A. *J. Organomet. Chem.* **1985**, *279*, C42. (b) Gamasa, M. P.; Gimeno, J.; Lastra, E.; Solans, X. *J. Organomet. Chem.* **1988**, *346*, 277. (c) Osakada, K.; Takizawa, T.; Yamamoto, T. *Organometallics* **1995**, *14*, 3531. (d) Yam, V. W. W.; Lee, W. K.; Cheung, K. K. *J. Chem. Soc., Dalton Trans.* **1996**, 2335. (e) Yam, V. W. W.; Fung, W. K. M.; Cheung, K. K. *J. Cluster Sci.* **1999**, *10*, 37. (f) Yam, Y. W. W.; Lam, C. H.; Zhu, N. *Inorg. Chim. Acta* **2002**, *331*, 239.

**Table 2.** Selected Bond Distances (Å) and Angles (deg) of Compounds **1**−**4**, **6**, and **7**

| | **1** | **2** | | **3** | **4** | **6** | **7** |
|---|---|---|---|---|---|---|---|
| Cu1−Cu2 | 2.5733(18) | 2.5315(12) | Cu1−Cu2 | 2.960(2) | 3.424(2) | 3.277(2) | 3.181(1) |
| Ag2−Cu1 | 2.7514(15) | 2.6997(10) | Ag1−Cu1 | 2.7140(19) | 2.687(2) | 2.650(2) | 2.5916(12) |
| Ag3−Cu1 | 2.8673(15) | 2.8846(10) | Ag3−Cu1 | 2.5959(18) | 2.575(2) | 2.663(2) | 2.6777(14) |
| Ag4−Cu1 | 2.8774(16) | 2.9243(11) | Ag5−Cu1 | 2.7090(18) | 2.780(2) | 2.698(2) | 2.6875(12) |
| Ag1−Cu2 | 2.8194(16) | 2.7570(10) | Ag2−Cu2 | 2.8317(18) | 2.641(2) | 2.804(2) | 2.7751(11) |
| Ag2−Cu2 | 3.1071(17) | 2.9950(11) | Ag4−Cu2 | 2.6451(18) | 2.676(2) | 2.754(2) | 2.6203(14) |
| Ag4−Cu2 | 2.7841(18) | 2.7625(11) | Ag6−Cu2 | 2.7776(18) | 2.668(2) | 2.663(2) | 2.7735(12) |
| Ag1−Ag2 | 3.0638(14) | 3.0778(9) | Ag1−Ag2 | 3.0246(16) | 3.1407(18) | 3.0560(19) | 2.9826(14) |
| Ag2−Ag4 | 3.1336(15) | 3.2652(10) | Ag3−Ag4 | 3.0689(17) | 2.980(2) | 3.0436(17) | 2.9970(12) |
| Ag3−Ag4 | 2.9783(13) | 2.9973(9) | Ag5−Ag6 | 3.0070(15) | 3.0787(19) | 3.0982(19) | 3.0425(11) |
| Ag1−P3 | 2.482(3) | 2.492(2) | Ag1−P1 | 2.389(4) | 2.371(5) | 2.403(5) | 2.3655(18) |
| Ag1−P6 | 2.460(3) | 2.457(2) | Ag1−C1 | 2.246(13) | 2.270(15) | 2.527(16) | 2.254(5) |
| Ag1−C21 | 2.563(12) | 2.566(7) | Ag1−C21 | 2.789(3) | 2.507(16) | 2.365(17) | 2.583(5) |
| Ag2−C1 | 2.373(11) | 2.374(8) | Ag2−P2 | 2.446(3) | 2.430(4) | 2.429(4) | 2.4266(17) |
| Ag2−C11 | 2.393(12) | 2.392(8) | Ag2−C11 | 2.544(12) | 2.399(15) | 2.399(13) | 2.667(5) |
| Ag2−P5 | 2.402(3) | 2.395(2) | Ag2−C21 | 2.571(13) | 2.663(14) | | 2.482(5) |
| Ag3−P2 | 2.487(3) | 2.4869(19) | Ag2−C31 | 2.454(13) | 2.570(14) | 2.673(17) | 2.378(5) |
| Ag3−P8 | 2.481(3) | 2.480(2) | Ag3−P3 | 2.392(4) | 2.403(4) | 2.414(4) | 2.4158(14) |
| Ag3−C31 | 2.604(12) | 2.661(7) | Ag3−C1 | 2.414(13) | 2.390(16) | 2.587(16) | 2.484(5) |
| Ag4−C21 | 2.331(11) | 2.369(8) | Ag3−C51 | 2.431(12) | 2.451(17) | 2.330(15) | 2.538(5) |
| Ag4−P7 | 2.372(3) | 2.384(2) | Ag4−P4 | 2.403(3) | 2.409(4) | 2.390(4) | 2.3760(15) |
| Ag4−C31 | 2.418(12) | 2.429(7) | Ag4−C11 | 2.685(11) | 2.535(13) | 2.479(13) | 2.526(5) |
| Ag4−C1 | 2.519(11) | 2.548(8) | Ag4−C41 | 2.271(12) | 2.346(15) | 2.321(14) | 2.261(5) |
| Cu1−C1 | 2.142(12) | 2.129(8) | Ag5−P5 | 2.415(3) | 2.436(4) | 2.429(4) | 2.4183(14) |
| Cu1−C11 | 2.172(14) | 2.204(8) | Ag5−C21 | 2.471(13) | 2.423(16) | 2.545(17) | 2.653(5) |
| Cu1−C31 | 2.053(14) | 2.040(7) | Ag5−C31 | 2.383(13) | 2.496(15) | 2.455(15) | 2.506(5) |
| Cu1−P1 | 2.283(3) | 2.264(2) | Ag5−C51 | 2.567(12) | 2.657(15) | 2.532(15) | |
| Cu2−C11 | 2.171(13) | 2.110(8) | Ag6−P6 | 2.431(3) | 2.411(4) | 2.407(4) | 2.3774(14) |
| Cu2−C21 | 2.101(13) | 2.065(8) | Ag6−C31 | 2.459(13) | 2.485(15) | 2.535(17) | 2.450(5) |
| Cu2−C31 | 2.258(12) | 2.235(7) | Ag6−C41 | 2.407(11) | 2.368(15) | 2.310(13) | 2.316(5) |
| Cu2−P4 | 2.277(3) | 2.263(2) | Ag6−N1 | 2.635(14) | 2.55(2) | 2.512(19) | |
| C1−C2 | 1.192(15) | 1.178(10) | Cu1−C1 | 2.001(13) | 2.013(18) | 1.952(18) | 2.004(5) |
| C11−C12 | 1.178(16) | 1.210(10) | Cu1−C21 | 1.951(14) | 1.954(16) | 2.024(16) | 1.944(4) |
| C21−C22 | 1.133(15) | 1.175(10) | Cu1−C51 | 1.962(13) | 2.000(19) | 1.949(16) | 1.961(5) |
| C31−C32 | 1.225(16) | 1.213(10) | Cu2−C11 | 2.007(14) | 2.003(17) | 1.996(15) | 1.974(5) |
| P6−Ag1−P3 | 123.29(11) | 122.27(7) | Cu2−C31 | 2.031(14) | 1.970(17) | 1.98(2) | 1.991(4) |
| P6−Ag1−C21 | 116.4(3) | 114.18(18) | Cu2−C41 | 2.021(14) | 2.010(18) | 2.005(14) | 2.000(5) |
| P3−Ag1−C21 | 104.6(3) | 106.79(17) | C1−C2 | 1.219(16) | 1.21(2) | 1.24(2) | 1.203(6) |
| C1−Ag2−C11 | 97.6(4) | 99.8(3) | C11−C12 | 1.192(16) | 1.22(2) | 1.235(19) | 1.204(7) |
| C1−Ag2−P5 | 123.9(3) | 124.68(19) | C21−C22 | 1.225(18) | 1.23(2) | 1.18(2) | 1.217(6) |
| C11−Ag2−P5 | 128.9(3) | 124.5(2) | C31−C32 | 1.204(16) | 1.20(2) | 1.22(2) | 1.199(6) |
| P8−Ag3−P2 | 126.42(10) | 126.97(7) | C41−C42 | 1.228(16) | 1.18(2) | 1.211(19) | 1.226(7) |
| P8−Ag3−C31 | 116.8(3) | 119.00(17) | C51−C52 | 1.232(16) | 1.18(2) | 1.25(2) | 1.215(7) |
| P2−Ag3−C31 | 104.9(3) | 101.05(17) | C1−Ag1−P1 | 153.7(3) | 159.4(5) | 128.9(4) | 146.35(13) |
| C21−Ag4−P7 | 116.5(3) | 120.48(19) | C1−Ag1−C21 | 82.4(3) | 88.3(6) | 90.1(6) | 89.71(17) |
| C21−Ag4−C31 | 97.6(4) | 96.9(2) | P1−Ag1−C21 | 122.9(3) | 111.5(4) | 134.0(4) | 123.65(11) |
| C11−Cu1−P1 | 101.9(3) | 100.7(2) | C21−Cu1−C51 | 125.6(5) | 123.3(7) | 114.1(6) | 126.2(2) |
| C31−Cu1−C1 | 107.4(5) | 107.9(3) | C21−Cu1−C1 | 115.4(5) | 114.2(6) | 121.3(7) | 120.0(2) |
| C31−Cu1−C11 | 107.8(5) | 105.0(3) | C51−Cu1−C1 | 117.1(5) | 120.6(6) | 124.2(6) | 113.2(2) |
| C1−Cu1−C11 | 112.5(4) | 114.5(3) | C11−Cu2−C41 | 121.7(5) | 113.7(6) | 111.4(5) | 120.5(2) |

respectively, which are comparable to those observed in cuboidal complexes [Cu(C≡CR)(PR′$_3$)]$_4$.[24] The Cu$^I$−Ag$^I$ and Ag$^I$−Ag$^I$ separations are in the ranges 2.7514(15)−3.1071(17) and 2.9783(13)−3.2652(15) Å, respectively. Of four Ph$_2$PNHPPh$_2$ ligands, two bridge Ag$^I$−Ag$^I$ centers whereas other two join Ag$^I$−Cu$^I$ atoms.

The heterooctanuclear coordination cations in the complexes [Ag$_6$Cu$_2$($\mu$-Ph$_2$PCH$_2$PPh$_2$)$_3$(C≡CC$_6$H$_4$R-4)$_6$(MeCN)](ClO$_4$)$_2$ (R = H, **3**; CH$_3$, **4**; OCH$_3$, **5**; NO$_2$, **6**) exhibit a waterwheel-like structure that can be regarded as two Ag$_3$Cu(C≡CC$_6$H$_5$)$_3$ components joined together by three bridging Ph$_2$PCH$_2$PPh$_2$ ligands as shown in Figure 2 (compound **3**). The six Ag$^I$ centers compose a twisting triangular prism with the Cu$^I$ atoms located at the centers of two trigonal basal planes. Twist of the triangular prism is revealed by the dihedral angles between the planes Cu1Cu2Ag1 and Cu1Cu2Ag2 (36.7°), between Cu1Cu2Ag3 and Cu1Cu2Ag4 (5.3°), and between Cu1Cu2Ag5 and Cu1Cu2Ag6 (21.4°). The dihedral angle between the basal planes Ag1Ag3Ag5 and Ag2Ag4Ag6 is 10.1°, and Cu1 and Cu2 atoms deviate from the planes 0.503 and 0.240 Å, respectively. The alkynyl adopts three types of bonding modes $\mu_3$-$\eta^1$, $\mu_4$-$\eta^1$, and $\mu_3$-$\eta^1$,$\eta^1$,$\eta^2$ to join Ag$^I$ and Cu$^I$ centers. The Cu$^I$ centers exhibit distorted C-bonded trigonal-planar geometry. For Ag$^I$ centers, Ag1, Ag3, and Ag4 afford an approximately trigonal-planar environment with C$_2$P donors while Ag2, Ag5, and Ag6 display distorted tetrahedral surroundings with C$_3$P or C$_2$NP chromophores. The Cu$^I$−Cu$^I$ distances are in the range 2.960(2)−3.424(2) Å for **3**−**6**. The Ag$^I$−Cu$^I$ and Ag$^I$−Ag$^I$ separations are in the ranges 2.5959(18)−2.8317(18) and 3.0070(15)−3.0689(17) Å, respectively.

For compound **7**, the heterohexadecanuclear complex cation [Ag$_6$Cu$_2$($\mu$-Ph$_2$PCH$_2$PPh$_2$)$_3$(C≡CC$_6$H$_4$COCH$_3$-4)$_6$]$_2^{4+}$ (Figure 3) results from dimerization of the heteroctanuclear

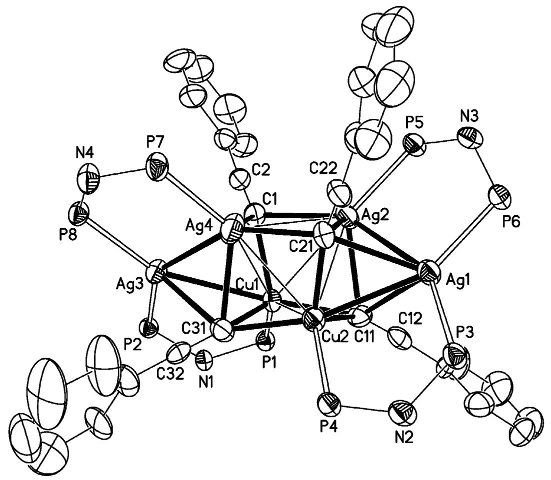

**Figure 1.** ORTEP drawing of the complex cation of **1** with atom labeling scheme showing 30% thermal ellipsoids. Phenyl rings on the phosphorus atoms are omitted for clarity.

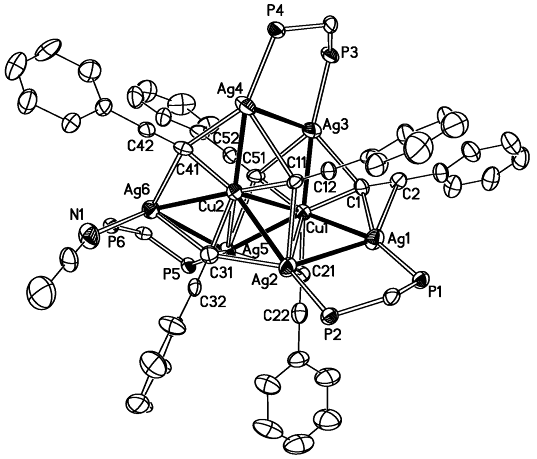

**Figure 2.** ORTEP drawing of the complex cation of **3** with atom labeling scheme showing 30% thermal ellipsoids. Phenyl rings on the phosphorus atoms are omitted for clarity.

complex $[Ag_6Cu_2(\mu\text{-}Ph_2PCH_2PPh_2)_3(C\equiv CC_6H_4COCH_3\text{-}4)_6]^{2+}$ through the Ag4−O2A (2.534 (4) Å) bonding interaction between the acetyl O2A in 4-acetylphenylacetylide and the Ag4 atom. It is observed that a weakly coordinated acetonitrile always occurs in the heterooctanuclear complexes $[Ag_6Cu_2(\mu\text{-}Ph_2PCH_2PPh_2)_3(C\equiv CC_6H_4R\text{-}4)_6(MeCN)](ClO_4)_2$ (R = H, **3**; $CH_3$, **4**; $OCH_3$, **5**; $NO_2$, **6**). The formation of the **7** is likely related to substitution of the coordinated acetonitrile by acetyl oxygen donor from 4-acetylphenylacetylide. The metal···metal separations between the two $Ag_6Cu_2$ units through the bridging 4-acetylphenylacetylide are beyond 10.0 Å.

The electronic absorption spectra of **1**−**7** in dichloromethane or acetonitrile solutions are characterized by absorption bands at ca. 218−255, 280−340 nm and low-energy shoulders tailing to ca. 450 nm. The high-energy bands at ca. 218−255 and 280−340 nm are typical for ligand-centered $\pi-\pi^*$ (diphosphine) and $\pi-\pi^*$ ($C\equiv CC_6H_4R$-4) transitions, respectively. It is noted that **6** and **7** containing electron-deficient 4-acetylphenylacetylide and 4-nitrophenylacetylide show distinguishable lower-energy absorption at ca. 350−390 and 350−410 nm, repectively, in acetonitrile. It is likely that the absorption bands are related to a metal perturbed ligand-centered $\pi-\pi^*$ ($C\equiv CC_6H_4R$-4) transition.[5a,25]

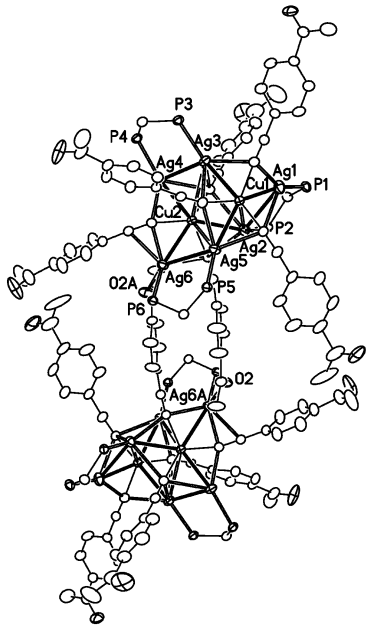

**Figure 3.** ORTEP drawing of the complex cation of **7** with atom labeling scheme showing 30% thermal ellipsoids. Phenyl rings on the phosphorus atoms are omitted for clarity.

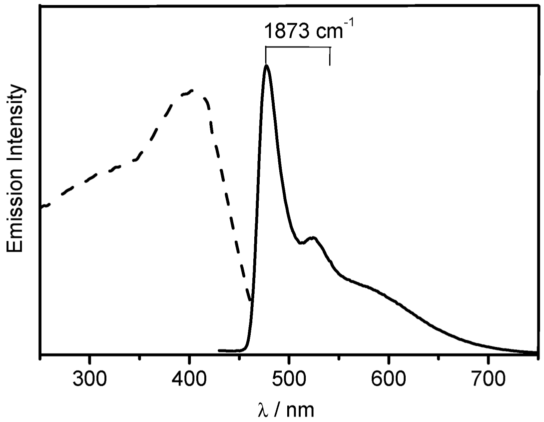

**Figure 4.** Excitation (− − −) and emission (−) spectra of complex **1** in the solid state at 77 K.

The photophysical data of complexes **1**−**7** are summarized in Table 3. Excitations of solid samples and fluid solutions of **1**−**7** at room temperature or 77 K with $\lambda_{ex}$ > 350 nm produce intense luminescence. The solid samples at 298 K afford lifetimes in the microsecond range, indicating that the luminescence is most likely associated with a spin-forbidden triplet parentage. Vibronic-structured emission bands with vibrational progressional spacings of 1800−2100 $cm^{-1}$ are observed in the complexes at 77 K, which is typical for the $\nu(C\equiv C)$ stretching modes of the acetylides in the ground states. The appearance of vibronic progressions is indicative of the involvement of the acetylide in the excited state. The emission spectrum of complex **1** in the solid state at 77 K is shown in Figure 4.

Comparing the emission bands of **1** and **2** in solid states or in fluid solutions, a slight red-shift in energy is observed on going from the phenylacetylide complex **1** to 4-methyl-

**Table 3.** Photophysical Data for Compounds **1**−**7**

| complex | absorption[a] $\lambda_{abs}$ (nm) ($\epsilon$/dm$^3$ mol$^{-1}$ cm$^{-1}$) | medium | $\lambda_{em}$/nm ($\tau_{em}$/$\mu$s)[b] (298 K) | $\lambda_{em}$/nm (77 K) |
|---|---|---|---|---|
| **1** | 239 (209940), 285 (196070) | solid | 480 (1.2) | 478, 525 (sh) |
| | | $CH_2Cl_2$ | 453 ($<$0.1), 616 (sh) | 464, 507 (sh) |
| | | MeCN | 436, 613 | 472, 530 (sh) |
| **2** | 239 (216021), 302 (216980), 331 (114690) | solid | 483 (1.3), 531 (sh) | 484, 531 (sh) |
| | | $CH_2Cl_2$ | 458 ($<$0.1), 620 (sh) | 468, 515 (sh) |
| | | MeCN | 442, 626 | 473 |
| **3** | 256 (44160), 288 (39660), 322 (33780) | solid | 478 (5.6) | 478, 524 (sh) |
| | | $CH_2Cl_2$ | 458 ($<$0.1) | 467 |
| | | MeCN | 452 | 468 |
| **4** | 263 (46190), 320 (50050), 343 (35180) | solid | 484 (5.1), 600 (sh) | 481, 533 (sh) |
| | | $CH_2Cl_2$ | 463 ($<$0.1) | 464, 505 (sh) |
| | | MeCN | 452 | 462,505 (sh) |
| **5** | 256 (80927), 321 (66911), 335 (50113) | solid | 498 (1.5), 606 | 579 |
| | | $CH_2Cl_2$ | 546 ($<$0.1) | 463, 502 (sh) |
| | | MeCN | 550 | 465, 506 (sh) |
| **6** | 266 (42550), 368 (33380), 410 (29174) | solid | 601 (3.4) | 610 |
| | | $CH_2Cl_2$ | 534 ($<$0.1) | 574 |
| | | MeCN | 548 | 585 |
| **7** | 256 (51599), 304 (74890), 360 (59528), 389 (40802) | solid | 532 (1.8) | 526 |
| | | $CH_2Cl_2$ | 516 ($<$0.1) | 525 |
| | | MeCN | 520 | 521 |

[a] In $CH_3CN$ at 298 K. [b] The excitation wavelength in the lifetime measurement is 397 nm.

phenylacetylide **2** counterparts. The emission energy trend in the heterooctanuclear complexes is **3** > **4** > **5**. This is in line with the order of $\sigma$-donating properties of phenylacetylide, 4-methylphenylacetylide, and 4-methoxyphenylacetylide. Therefore, the emissive state of **1**−**5** is likely derived from a $^3$LMCT ($C{\equiv}CC_6H_4R\text{-}4 \rightarrow Ag_4Cu_2$ or $Ag_6Cu_2$) transition, mixed with a metal cluster-centered (d → s) excited state modified by metal−metal interactions in view of the short Cu−Cu, Cu−Ag, and Ag−Ag contacts observed. This assignment also agrees with the proposed emission origin in homotri-, tetra-, and hexanuclear $Cu^I$ and $Ag^I$ alkynyl complexes described in the literature.[5] It is noteworthy that heterooctanuclear complex **6** and hexadecanuclear complex **7** containing electron-deficient 4-nitrophenylacetylide and 4-acetylphenylacetylide, respectively, show an emission at a much lower energy relative to those in **3**−**5**. It is likely that this emission originates from the ligand-centered 4-nitrophenylacetylide or 4-acetylphenylacetylide, mixed possibly with some metal cluster-centered character, because the emission energy is close to that in the free alkynyl ligand. Similar assignment was also proposed for the trinuclear $Cu^I$ and $Ag^I$ complexes of 4-nitrophenylacetylide with the lowest lying excited state dominated by an intraligand $^3[\pi \rightarrow \pi^*]$ character.[5a,25]

## Conclusions

A feasible synthetic route was developed to attain heterometallic alkynyl arrays by self-assembly incorporation of metal components $(AgC{\equiv}CC_6H_4R\text{-}4)_n$ with $[Cu_2(\mu\text{-}Ph_2PXPPh_2)_2(MeCN)_2]^{2+}$ (X = NH, $CH_2$). It is revealed that the $Cu^I-Ag^I$ alkynyl complexes adopt different structural topologies depending on the X group in the diphosphine $Ph_2PXPPh_2$. While heterohexanuclear complexes $[Ag_4Cu_2(\mu\text{-}Ph_2PNHPPh_2)_4(C{\equiv}CC_6H_4R\text{-}4)_4](ClO_4)_2$ (R = H, **1**; $CH_3$, **2**) with bicapped cubic structures were afforded when X = NH, heterooctanuclear complexes $[Ag_6Cu_2(\mu\text{-}Ph_2PCH_2PPh_2)_3(C{\equiv}CC_6H_4R\text{-}4)_6(MeCN)](ClO_4)_2$ (R = H, **3**; $CH_3$, **4**; $OCH_3$, **5**; $NO_2$, **6**) with waterwheel-like $Ag_6Cu_2$ cluster arrays and heterohexadecanuclear complex $[Ag_6Cu_2(\mu\text{-}Ph_2PCH_2PPh_2)_3(C{\equiv}CC_6H_4COCH_3\text{-}4)_6]_2(ClO_4)_4$ (**7**) were isolated when X = $CH_2$. The $Cu^I-Ag^I$ heterometallic alkynyl complexes display intense luminescence with emissive lifetimes in the microsecond scale. The synthetic strategy described herein may open a significant approach for design of luminescent heteronuclear group 11 metal alkynyl arrays.

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**Supporting Information Available:** $^{31}$P NMR spectra of compounds **1** (Figure S1), **4** (Figure S2), and **7** (Figure S3). X-ray crystallographic files in CIF format for the structure determinations of compounds $\mathbf{1}\cdot 2CH_3CN$, $\mathbf{2}\cdot {}^1/_2(C_2H_5)_2O\cdot 3CH_3CN\cdot H_2O$, **3**, $\mathbf{4}\cdot CH_3OH\cdot {}^1/_4CH_2Cl_2\cdot H_2O$, $\mathbf{6}\cdot {}^1/_2CH_3CN\cdot 2H_2O$, and $\mathbf{7}\cdot (C_2H_5)_2O\cdot 4H_2O$. This material is available free of charge via the Internet at http://pubs.acs.org.

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