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Synthesis of Luminescent Trinuclear Silver(I) Acetylides of Bis(diphenylphosphino)methane and Bis(diphenylphosphino)-*n*-propylamine. X-ray Crystal Structures of $[Ag_3(\mu\text{-dppm})_3(\mu_3\text{-}\eta^1\text{-C}\equiv\text{C-C}_6H_4\text{-NO}_2\text{-}p)]^{2+}$ and $[Ag_3(\mu\text{-dppm})_3(\mu_3\text{-}\eta^1\text{-C}\equiv\text{C-C}_6H_4\text{-NO}_2\text{-}p)_2]^{+}$

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A series of soluble trinuclear silver(I) complexes containing monocapped and bicapped acetylides, $[Ag_3(LL)_3(\mu_3\text{-}\eta^1\text{-C}\equiv\text{CR})]^{2+}$ and $[Ag_3(LL)_3(\mu_3\text{-}\eta^1\text{-C}\equiv\text{C-C}_6H_4\text{-NO}_2\text{-}p)_2]^{+}$ [LL=$[(C_6H_5)_2P]_2CH_2$ (dppm), $[(C_6H_5)_2P]_2N^nPr$ (^{n}PrPNP)], have been synthesized. The X-ray crystal structures of $[Ag_3(\mu\text{-dppm})_3(\mu_3\text{-}\eta^1\text{-C}\equiv\text{C-C}_6H_4\text{-NO}_2\text{-}p)]^{2+}$ and $[Ag_3(\mu\text{-dppm})_3(\mu_3\text{-}\eta^1\text{-C}\equiv\text{C-C}_6H_4\text{-NO}_2\text{-}p)_2]^{+}$ have been determined.

Introduction

The photochemistry and photophysics of d^{10} polynuclear metal complexes have attracted increasing attention for the past decade,[1−9] the studies were mostly confined to Cu(I) and Au(I) complexes,[1−5,6a−h] with a few exceptions with Ag(I),[5e,6i,7] Zn(II), Cd(II), Hg(II),[8] Pd(0), and Pt(0).[9] Despite the remarkably rich and well-known photochemistry of silver(I) halides in photography, the photochemical and photophysical properties of polynuclear Ag(I) complexes are relatively less explored compared to those of its congeners.[5e,6i,7] Our recent efforts in using acetylide to bridge different metals such as Cu(I),[6a−g] Au(I),[4a−c] and Pt(II)[10] as well as the investigation of their rich photophysical and photochemical

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properties have prompted us to explore related studies on the Ag(I) acetylide complexes.

Moreover, there are only a few examples of the studies of alkynyl silver(I) complexes[11] owing to their sensitivity toward photodecomposition and low solubility in organic solvents. An example is $[RC{\equiv}CAg]_\infty$,[12] which is regarded as a coordination polymer with cross-linking between the ethynyls of adjacent $[RC{\equiv}CAg]$. The solubility of the alkynyl silver(I) complex can be improved by coordination of tertiary phosphine ligands. Examples included $[Me_3PAgC{\equiv}CPh]_\infty$[13a] and $[Me_3PAgC{\equiv}CSiMe_3]_\infty$.[13b] Examples of π-coordinated alkyne complexes have also been reported.[14] A recent report shows that a trinuclear Ag(I) complex with bicapped phenylacetylide groups exhibits luminescent behavior.[7h] Herein, we report the synthesis of a series of trinuclear silver(I) monocapped acetylide complexes and a bicapped analogue, which have been shown to exhibit luminescence in both the solid state and in fluid solution. The X-ray crystal structures of both the monocapped $[Ag_3(dppm)_3(C{\equiv}CC_6H_4\text{-}NO_2\text{-}p)]^{2+}$ and the bicapped $[Ag_3(dppm)_3(C{\equiv}CC_6H_4\text{-}NO_2\text{-}p)_2]^+$ complexes have been determined (dppm = $[(C_6H_5)_2P]_2CH_2$).

Experimental Section

Materials and Reagents. Phenylacetylene and $[Ag(MeCN)_4]BF_4$ were purchased from Aldrich Chemical Co. Ltd. (4-Methoxyphenyl)acetylene was obtained from Maybridge Chemical Co. Ltd. Bis(diphenylphosphino)methane was purchased from Strem Chemicals Inc. (4-Nitrophenyl)acetylene[15] and $[(C_6H_5)_2P]N^nPr$[16] were prepared by the literature procedures. $[Ag(MeCN)_4]PF_6$ was prepared according to literature procedure.[17] Tetra-*n*-butylammonium hexafluorophosphate (Aldrich) was recrystallized twice from absolute ethanol before use. All solvents were purified and distilled using standard procedures before use.[18] All other reagents were of analytical grade and were used as received.

Syntheses of Silver(I) Complexes. All reactions were carried out under anaerobic and anhydrous conditions using standard Schlenk techniques.

$[Ag_2(\mu\text{-}^nPrPNP)_2(MeCN)_4]X_2$ (1). [$^nPrPNP = [(C_6H_5)_2P]_2N(^nPr)$; X = BF_4, PF_6]. Complex **1** was prepared by a method similar to that for $[Ag_2(\mu\text{-dppm})_2(MeCN)_2](BF_4)_2$.[19] An acetonitrile solution (30 mL) of $[Ag(MeCN)_4]BF_4$ (0.36 g, 1 mmol) and ^nPrPNP (0.43 g, 1 mmol) was stirred at room temperature for 6 h, to give a colorless solution. The product was then filtered and reduced in volume. Subsequent diffusion of diethyl ether vapor into the concentrated solution gave colorless crystals of **1**. Yield, 0.42 g (60%). The hexafluorophosphate salt was similarly prepared using $[Ag(MeCN)_4]PF_6$ instead. ^1H NMR (CD_2Cl_2): δ 0.2 (6H, t, CH_3), 0.6 (4H, m, CH_2), 2.0 (12H, s, CH_3CN), 7.4−7.8 (40H, m, Ph). Positive FAB-MS: *m/z* 1157 {M − 2MeCN}$^+$. UV−Vis λ, nm (ϵ_{max}, $dm^3\ mol^{-1}\ cm^{-1}$) in CH_2Cl_2: 270 sh (17 360), 316 (24 090). Anal. Calcd for $C_{62}H_{66}N_6P_6F_{12}Ag_2$: C, 48.84; H, 4.36; N, 5.51. Found: C, 48.56; H, 4.30; N, 5.26.

$[Ag_3(\mu\text{-dppm})_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}C\text{-}Ph)](BF_4)_2$ (2). To a solution of phenylacetylene (21.9 μL, 0.2 mmol) in predried degassed THF (40 mL) under an inert atmosphere of nitrogen was added *n*-butyllithium (1.6 M, 0.13 mL, 0.20 mmol) at room temperature. A solid sample of $[Ag_2(\mu\text{-dppm})_2(MeCN)_2](BF_4)_2$ (0.37 g, 0.3 mmol) was added, and the resultant mixture was stirred at room temperature for 24 h. After evaporation to dryness, the resulting solid was extracted with acetone (3 × 8 mL), and the solution was filtered and reduced in volume. Subsequent diffusion of diether ether vapor into the concentrated solution gave **2** as air-stable colorless crystals. Yield, 0.14 g (40%). ^1H NMR (acetone-d_6): δ 3.7 (6 H, m, CH_2), 7.0−7.7 (65H, m, Ph). Positive FAB-MS: *m/z* 1664 {M$^+$}. UV−Vis λ, nm (ϵ_{max}, $dm^3\ mol^{-1}\ cm^{-1}$) in CH_2Cl_2: 254 sh (33 070), 280 sh (34 020), 288 (38 300). Anal. Calcd for $C_{83}H_{71}P_6B_2F_8Ag_3$: C, 56.92; H, 4.09. Found: C, 57.06; H, 4.24.

$[Ag_3(\mu\text{-dppm})_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}C\text{-}C_6H_4\text{-}OMe\text{-}p)](BF_4)_2$ (3). The procedure was similar to that of **2** except (4-methoxyphenyl)acetylene (26.4 mg, 0.2 mmol) was used instead. Colorless crystals were obtained. Yield, 0.12 g (35%). ^1H NMR (acetone-d_6): δ 3.8 (6H, m, CH_2), 4.0 (3H, s, OCH_3), 7.0−7.8 (64H, m, Ph). Positive FAB-MS: *m/z* 1694 {M$^+$}. UV−Vis λ, nm (ϵ_{max}, $dm^3\ mol^{-1}\ cm^{-1}$) in CH_2Cl_2: 254 sh (51 090), 312 sh (11 780). Anal. Calcd for $C_{84}H_{73}OP_6B_2F_8Ag_3$: C, 56.96; H, 4.14. Found: C, 56.69; H, 3.92.

$[Ag_3(\mu\text{-dppm})_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}C\text{-}C_6H_4\text{-}NO_2\text{-}p)](BF_4)_2$ (4). The procedure was similar to that of **2** except (4-nitrophenyl)acetylene (29.4 mg, 0.2 mmol) was used instead to give yellow crystals of **4**. Yield, 0.16 g (45%). ^1H NMR (acetone-d_6): δ 3.8 (6H, m, CH_2), 6.9−8.3 (64H, m, Ph). Positive FAB-MS: *m/z* 1709 {M$^+$}. UV−Vis λ, nm (ϵ_{max}, $dm^3\ mol^{-1}\ cm^{-1}$) in CH_2Cl_2: 262 (32 700), 352 (12 700). Anal. Calcd for $C_{83}H_{69}P_6NO_2B_2F_8Ag_3$: C, 55.49; H, 3.93; N, 0.78. Found: C, 55.53; H, 4.05; N, 0.77.

$[Ag_3(\mu\text{-}^nPrPNP)_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}C\text{-}Ph)](BF_4)_2$ (5). The procedure was similar to that of **2** except **1** (0.42 g, 0.3 mmol) was used instead of $[Ag_2(\mu\text{-dppm})_2(MeCN)_2](BF_4)_2$. Colorless crystals of **5** were obtained. Yield, 0.1 g (25%). ^1H NMR (acetone-d_6): δ 0.2 (9H, t, CH_3), 0.6 (6H, m, CH_2), 3.0 (6H, m, CH_2N), 6.6−7.9 (65H, m, Ph). Positive FAB-MS: *m/z* 1793 {M$^+$}. UV−Vis λ, nm (ϵ_{max}, $dm^3\ mol^{-1}\ cm^{-1}$) in CH_2Cl_2: 264 sh (43 870), 302 sh (24 100). Anal. Calcd for $C_{89}H_{86}N_3P_6B_2F_8Ag_3$: C, 56.84; H, 4.61; N, 2.23. Found: C, 56.81; H, 4.72; N, 2.18.

$[Ag_3(\mu\text{-dppm})_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}C\text{-}C_6H_4\text{-}NO_2\text{-}p)_2]PF_6$ (6). Complex **6** was prepared by the reaction of $[Ag_2(\mu\text{-dppm})_2(MeCN)_2](PF_6)_2$ (0.41 g, 0.3 mmol) with (4-nitrophenyl)acetylene (58.8 mg, 0.4 mmol) in the presence of excess KOH in CH_2Cl_2/MeOH (15 mL/5 mL) at room temperature under an inert atmosphere of nitrogen. ^1H NMR (acetone-d_6): δ 3.6 (6H, m, CH_2), 6.9−8.3 (68H, m, Ph). Positive FAB-MS: *m/z* 1772 {M$^+$}. UV−Vis λ, nm (ϵ_{max}, $dm^3\ mol^{-1}\ cm^{-1}$) in CH_2Cl_2: 260 sh (39 130), 326 (14 800). Anal. Calcd for $C_{91}H_{73}N_2O_4P_7F_6Ag_3$: C, 57.11; H, 3.90; N, 1.46. Found: C, 57.14; H, 3.95; N, 1.38.

Physical Measurements and Instrumentation. UV−visible spectra were obtained on a Hewlett-Packard 8452A diode array spectrophotometer, and steady-state excitation and emission spectra on a Spex Fluorolog 111 spectrofluorometer equipped with a Hamamatsu R-928 photomultiplier tube. Low-temperature (77 K) spectra were recorded by using an optical Dewar sample holder. ^1H NMR spectra were recorded on either a JEOL JNM-GSX270 or a Bruker DPX300 Fourier transform NMR spectrometer. Positive ion FAB mass spectra were recorded on a Finnigan MAT95 mass spectrometer. Elemental analyses of the new complexes were performed by Butterworth Laboratories Ltd.

Emission lifetime measurements were performed using a conventional laser system. The excitation source was the 355 nm output (third harmonic) of a Quanta-Ray Q-switched GCR-

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150 pulsed Nd−YAG laser (10 Hz). Luminescence decay signals were recorded on a Tektronix Model TDS-620A (500 MHz, 2 GS/s) digitial oscilloscope and analyzed using a program for exponential fits.

Cyclic voltammetric measurements were performed by using a CH Instruments Inc. Model CHI 620 electrochemical analyzer, which was interfaced to an IBM-compatible 486 personal computer. The electrolytic cell used was a conventional two-compartment cell. The salt bridge of the reference electrode was separated from the working electrode compartment by a Vycor glass. A Ag/AgNO$_3$ (0.1 mol dm^{-3} in CH$_3$CN) reference electrode was used. The ferrocenium−ferrocene couple was used as the internal standard in the electrochemical measurements in acetonitrile (0.1 M ^{n}Bu$_4$NPF$_6$). The working electrode was a glassy-carbon (Atomergic Chemetals V25) electrode with a platinum foil acting as the counter electrode. Treatment of the electrode surfaces was as reported elsewhere.[20]

Crystal Structure Determination. Crystal data for **4**: {[Ag$_3$C$_{83}$H$_{70}$NO$_2$P$_6$]$^{2+}$ 2 BF$_4$$^-$}; M_r = 1796.53, triclinic, space group $P\bar{1}$ (No. 2), a = 14.632(1) Å, b = 22.356(3) Å, c = 13.133(2) Å, α = 95.40(1)°, β = 111.981(8)°, γ = 89.28(1)°, V = 3965.0(9) Å^3, Z = 2, D_c = 1.505 g cm^{-3}, μ(Mo Kα) = 9.18 cm^{-1}, F(000) = 1808, T = 301 K. A yellow crystal of dimensions 0.20 × 0.15 × 0.25 mm was used for data collection at 28 °C on a Rigaku AFC7R diffractometer with graphite-monochromatized Mo Kα radiation (λ = 0.710 73 Å) using $\omega-2\theta$ scans with ω-scan angle (0.73 + 0.35 tan θ)° at a scan speed of 16.0 deg min^{-1} (up to six scans for reflection $I < 15\sigma(I)$). Intensity data (in the range of $2\theta_{\max}$ = 47°; h, 0 to 16; k, −24 to 24; l, −14 to 14 and three standard reflections measured after every 300 reflections showed decay of 1.50%), were corrected for decay and for Lorentz and polarization effects and empirical absorption corrections based on the Ψ-scan of four strong reflections (minimum and maximum transmission factors 0.820 and 1.000). A total of 12 244 reflections were measured, of which 11 713 were unique and $R_{\rm int}$ = 0.020. A total of 8129 reflections with $I > 3\sigma(I)$ were considered observed and used in the structural analysis. The space group was determined on the basis of statistical analysis of intensity distribution and the successful refinement of the structure solved by direct methods (SIR92[21a]) and a Fourier method and refined by full-matrix least squares using the software package TeXsan[21b] on a Silicon Graphics Indy computer. A crystallographic asymmetric unit consists of one complex cation and two BF$_4$$^-$ anions. With the exception of the B and F atoms, all the other 95 non-H atoms were refined anisotropically. A total of 70 H atoms at calculated positions with thermal parameters equal to 1.3 times that of the attached C atoms were not refined. Convergence for 896 variable parameters by least-squares refinement on F with $w = 4F_o^2/\sigma^2(F_o^2)$, where $\sigma^2(F_o^2) = [\sigma^2(I) + (0.025\ F_o^2)^2]$ for 8129 reflections with $I > 3\sigma(I)$ was reached at R = 0.043 and wR = 0.056 with a goodness of fit of 1.89. $(\Delta/\sigma)_{\max}$ = 0.03 for atoms of the complex cation. The final difference Fourier map was featureless, with maximum positive and negative peaks of 1.65 and 0.75 e Å^{-3}, respectively.

Crystal data for **6**: {[Ag$_3$C$_{91}$H$_{74}$N$_2$O$_4$P$_6$]$^+$ PF$_6$$^-$} M_r = 1914.01, monoclinic, space group $P2_1/n$ (No. 14), a = 15.658(6) Å, b = 23.718(3) Å, c = 23.860(3) Å, β = 107.97(2)°, V = 8428(4) Å^3, Z = 4, D_c = 1.508 g cm^{-3}, μ(Mo Kα) = 8.86 cm^{-1}, F(000) = 3864, T = 301 K. A yellow crystal of dimensions 0.20 × 0.15 × 0.25 mm was used for data collection at 28 °C on a Rigaku AFC7R diffractometer with graphite-monochromatized Mo Kα radiation (λ = 0.710 73 Å) using $\omega-2\theta$ scans with ω-scan angle (0.73 + 0.35 tan θ)° at a scan speed of 16.0 deg min^{-1} (up to six scans for reflection $I < 15\sigma(I)$). Intensity data (in the range of $2\theta_{\max}$ = 45°; h, 0 to 17; k, 0 to 26; l, −26 to 26 and three standard reflections measured after every 300 reflections showed decay of 2.35%) were corrected for decay and for Lorentz and polarization effects and empirical absorption corrections based on the Ψ-scan of four strong reflections (minimum and maximum transmission factors 0.883 and 1.000). A total of 11 833 reflections were measured, of which 11 347 were unique and $R_{\rm int}$ = 0.022. A total of 7547 reflections with $I > 3\sigma(I)$ were considered observed and used in the structural analysis. The space group was determined from systematic absences, and the structure was solved by Patterson methods and expanded by Fourier methods (PATTY[21c]) and refinement by full-matrix least squares using the software package TeXsan[21b] on a Silicon Graphics Indy computer. A crystallographic asymmetric unit consists of one complex cation and one PF$_6$$^-$ anion. With the exception of the six F atoms, all the other 107 non-H atoms were refined anisotropically. A total of 74 H atoms at calculated positions with thermal parameters equal to 1.3 times that of the attached C atoms were not refined. Convergence for 988 variable parameters by least-squares refinement on F with $w = 4\ F_o^2/\sigma^2(F_o^2)$, where $\sigma^2(F_o^2) = [\sigma^2(I) + (0.024F_o^2)^2]$ for 7547 reflections with $I > 3\sigma(I)$ was reached at R = 0.043 an wR = 0.055 with a goodness of fit of 1.96. $(\Delta/\sigma)_{\max}$ = 0.01. The final difference Fourier map was featureless, with maximum positive and negative peaks of 0.93 and 0.75 e Å^{-3}, respectively. Crystal and structure determination data as well as the selected bond distances and bond angles for **4** and **6** are collected in Tables 1−4, respectively.

Table 1. Crystal and Structure Determination Data for 4

formula	{[Ag$_3$C$_{83}$H$_{70}$NO$_2$P$_6$]$^{2+}$ 2BF$_4$$^-$}
fw	1796.53
T, K	301
a, Å	14.632(1)
b, Å	22.356(3)
c, Å	13.133(2)
α, deg	95.40(1)
β, deg	111.981(8)
γ, deg	89.28(1)
V, Å^3	3965.0(9)
cryst color and shape	yellow and prism
cryst syst	triclinic
space group	$P\bar{1}$ (No. 2)
Z	2
F(000)	1808
D_c, g cm^{-3}	1.505
cryst dimens, mm	0.20 × 0.15 × 0.25
λ, Å (graphite-monochromated Mo Kα)	0.71073
μ, cm^{-1}	9.18
collection range	$2\theta_{\max}$ = 47° (h, 0 to 16; k, −24 to 24; l, −14 to 14)
scan mode and scan speed, deg min^{-1}	$\omega-2\theta$, 16
scan width, deg	0.73 + 0.35 tan θ
no. of data collected	12 244
no. of unique data	11 713
no. of data used in refinement, m	8129
no. of parameters refined, p	896
R^a	0.043
wR^a	0.056
goodness of fit, S	1.89
maximum shift, $(\Delta/\sigma)_{\max}$	0.03
residual extremes in final difference map, e Å^{-3}	+1.65, −0.75

[a] $w = 4F_o^2/\sigma^2(F_o^2)$, where $\sigma^2(F_o^2) = [\sigma^2(I) + (0.025F_o^2)^2]$ with $I > 3\sigma(I)$.

Results and Discussion

The complexes [Ag$_3$(μ-dppm)$_3$(μ_3-η^1-C≡C-C$_6$H$_4$R-p)](BF$_4$)$_2$ [R = H **(2)**, OMe **(3)**, and NO$_2$ **(4)**] were prepared

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Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for 4

C(1)−C(2)	1.199(7)	Ag(1)···Ag(2)	2.9850(6)
C(1)−Ag(1)	2.224(5)	Ag(1)···Ag(3)	3.0877(6)
C(1)−Ag(2)	2.269(5)	Ag(2)···Ag(3)	3.4030(6)
C(1)−Ag(3)	2.349(6)		
Ag(1)−C(1)−C(2)	139.4(5)	Ag(3)−C(1)−C(2)	101.0(4)
Ag(2)−C(1)−C(2)	135.1(4)		

Table 3. Crystal and Structure Determination Data for 6

formula	$\{[Ag_3C_{91}H_{74}N_2O_4P_6]^+ PF_6^-\}$
fw	1914.01
T, K	301
a, Å	15.658(6)
b, Å	23.718(3)
c, Å	23.860(3)
β, deg	107.97(2)
V, Å^3	8428(4)
cryst color and shape	yellow and prism
cryst syst	monoclinic
space group	$P2_1/n$ (No. 14)
Z	4
F(000)	3864
D_c, g cm^{-3}	1.508
cryst dimens, mm	0.20 × 0.15 × 0.25
λ, Å (graphite-monochromated Mo Kα)	0.71073
μ, cm^{-1}	8.86
collection range	$2\theta_{max} = 45°$ (h, 0 to 17; k, 0 to 26; l, −26 to 26)
scan mode and scan speed, deg min^{-1}	$\omega-2\theta$, 16
scan width, deg	$0.73 + 0.35 \tan \theta$
no. of data collected	11 833
no. of unique data	11 347
no. of data used in refinement, m	7547
no. of parameters refined, p	988
R^a	0.043
wR^a	0.055
goodness of fit, S	1.96
maximum shift, $(\Delta/\sigma)_{max}$	0.01
residual extremes in final difference map, e Å^{-3}	+0.93, −0.75

[a] $w = 4F_o^2/\sigma^2(F_o^2)$, where $\sigma^2(F_o^2) = [\sigma^2(I) + (0.024F_o^2)^2]$ with $I > 3\sigma(I)$.

Table 4. Selected Bond Distances (Å) and Bond Angles (deg) for 6

C(1)−C(2)	1.04(1)	C(9)−Ag(2)	2.582(7)
C(9)−C(10)	1.025(10)	C(9)−Ag(3)	2.257(7)
C(1)−Ag(1)	2.417(8)	Ag(1)···Ag(2)	2.8946(8)
C(1)−Ag(2)	2.323(8)	Ag(1)···Ag(3)	3.1948(9)
C(1)−Ag(3)	2.981(8)	Ag(2)···Ag(3)	2.953(1)
C(9)−Ag(1)	2.692(8)		
Ag(1)−C(1)−C(2)	131.7(8)	Ag(1)−C(9)−C(10)	105.6(7)
Ag(3)−C(1)−C(2)	136.5(9)	Ag(2)−C(9)−C(10)	132.9(8)
Ag(2)−C(1)−C(2)	144.8(9)	Ag(3)−C(9)−C(10)	151.9(8)

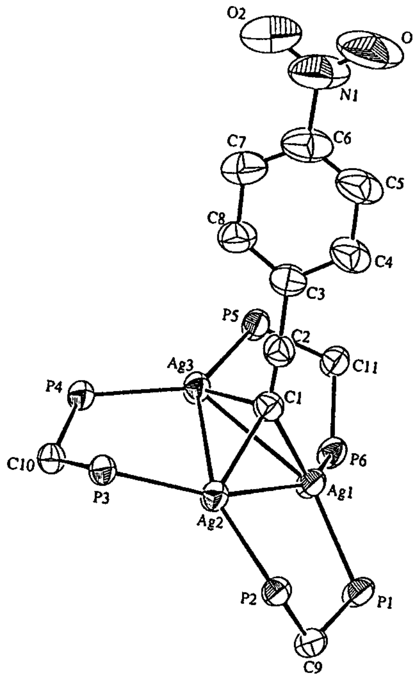

Figure 1. Perspective drawing of the complex cation of **4** with atomic numbering scheme. Hydrogen atoms and phenyl rings have been omitted for clarity. Thermal ellipsoids were drawn at the 40% probability level.

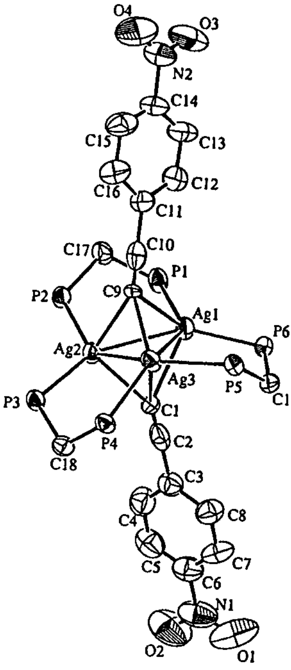

Figure 2. Perspective drawing of the complex cation of **6** with atomic numbering scheme. Hydrogen atoms and phenyl rings have been omitted for clarity. Thermal ellipsoids were drawn at the 40% probability level.

by the reaction of 3 equiv of $[Ag_2(\mu\text{-dppm})_2(MeCN)_2](BF_4)_2$ with 2 equiv of $HC{\equiv}CC_6H_4R\text{-}p$ in the presence of ^{n}BuLi in THF at room temperature under anaerobic and anhydrous conditions. $[Ag_3(\mu\text{-}^n\text{PrPNP})_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}C\text{-}C_6H_5)](BF_4)_2$ **(5)** was obtained by a similar method except $[Ag_2(\mu\text{-}^n\text{PrPNP})_2(MeCN)_4](BF_4)_2$ **(1)** was used instead [^{n}PrPNP = $[(C_6H_5)_2P]_2N^n$Pr]. $[Ag_3(\mu\text{-dppm})_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}C\text{-}C_6H_4NO_2\text{-}p)_2](PF_6)$ **(6)** was prepared by the reaction of 3 equiv of $[Ag_2(\mu\text{-dppm})_2(MeCN)_2](PF_6)$ with 4 equiv of $HC{\equiv}CC_6H_4NO_2\text{-}p$ in the presence of an excess of KOH in CH_2Cl_2/MeOH (3:1 v/v) at room temperature under an inert atmosphere of nitrogen. All complexes gave satisfactory elemental analyses and have been characterized by positive FAB-MS and ^{1}H NMR spectroscopy. The X-ray crystal structures for complexes **4** and **6** have also been determined.

The perspective drawings of the X-ray crystal structures of **4** and **6** with atomic numbering are depicted in Figures 1 and 2, respectively. Complex **4** consists of an isosceles triangular array of silver atoms with a dppm ligand bridging each edge to form a roughly planar $[Ag_3P_6]$ core. The acetylide unit is bonded to all three silver atoms to form a distorted trigonal pyramid. The Ag···Ag distances in the range of 2.9850(6)−3.4030(6) Å, which are comparable to the sum of van der Waals radii for silver (3.40 Å), are suggestive of very weak to no Ag···Ag bonding interaction. The bridging model of the alkynyl group is asymmetric with Ag−C bond distances in the range of 2.224(5)−2.349(6) Å and the bond angle between the alkynyl group and each silver atom (Ag−C(1)−C(2)) ranging from 101.0(4) to 139.4-(5)°. The bond distance of the C≡C bond (1.199(7) Å) is characteristic of typical metal acetylide σ bonding. A similar bonding mode has been observed in the related trinuclear copper(I) acetylide complexes.[6a,d,22] Monocapped triangular silver(I) complexes are scarce. An example of such a bonding mode in trinuclear silver(I) is the monomer of the α-trisilver amidoselenate polymeric network—Ag_3NSeO_3—where the $O_3SeN_3^-$ group is monocapped to three silver metal centers.[23] Despite a few reported examples of monocapped trinuclear copper(I) acetylide complexes,[6a,d,22] complex **4** represents the first example of a monocapped trinuclear silver(I) acetylide complex. On the other hand, complex **6** may be described as a triangular array of silver atoms bridged by two acetylide units and three dppm ligands. The central skeleton corresponds closely to a trigonal bipyramid with the silver atoms in the equatorial and the acetylide units in the axial positions. The edges of the triangle are not equivalent, with Ag···Ag separations in the range of 2.8946(8)−3.1948(9) Å, which are shorter than the sum of van der Waals radii for silver, suggesting that weak Ag···Ag interaction may exist. The alkynyl group is asymmetric with Ag−C bond distances falling within the range of 2.257(7)−2.981(8) Å and the bond angle between the alkynyl group and each silver atom (Ag−C(1)−C(2)) ranging from 131.7(8) to 144.8-(9)° and that of (Ag−C(9)−C(10)) in the range of 105.6-(7)−151.9(8)°. The bond distances of the C≡C bond (1.025(10)−1.04(1) Å) are characteristic of metal acetylide σ bonding. A similar bonding mode has been found in the analogous complex $[Ag_3(\mu\text{-dppm})_3(\mu_3\text{-}\eta^1\text{-C}{\equiv}\text{C-}C_6H_5)_2]Cl$,[7h] with Ag···Ag distances ranging from 2.866-(2) to 2.983(1) Å. Similar bonding modes have also been reported for the complexes $[Ag_3(\mu\text{-dppm})_3Br_2]^+$ [24a] and $[Ag_3(\mu\text{-dppm})_3Cl_2]^+$ [24b] with the two halogen atoms each bridging three silver atoms in the form of a distorted trigonal pyramid. Slightly longer Ag···Ag distances in the range of 3.192(3)−3.362(3) and 3.198(2)−3.540(2) Å have been found in the bromo- and chloro-capped complexes, respectively.

The luminescent behavior of the silver(I) complexes has been studied both at room temperature and at 77 K. The photophysical data are shown in Table 5. It is interesting to note that vibronic structures are observed for complexes **2**−**4** and **6** both at 77 K and at room temperature. The emission spectrum of **3** in MeOH/EtOH glass at 77 K is shown in Figure 3. Vibronically structured bands with vibrational progressional spacings of ~1880−2080 cm^{-1}, characteristic of the ν(C≡C) stretch were observed. Similar vibronic structures are observed in the solid state at 77 K and at room temperature. In some cases, at least two vibrational progressions were observed with spacings of about 1450−1600 and 1880−2080 cm^{-1}, respectively, the former being typical of the ν(C$\overset{...}{-}$C) stretching modes of the aromatic ring and the latter typical of the ν(C≡C) stretch. The observation of vibrational progressions is suggestive of the involvement of the aryl acetylide unit in the excited state. A comparison of the emission spectra of **2** and **3** with those of their trinuclear copper-(I) analogues showed that **2** and **3** occurred at higher energy than the corresponding $[Cu_3(\mu\text{-dppm})_3(\mu_3\text{-}\eta^1\text{-C}{\equiv}\text{C-Ph})](BF_4)_2$[6d] and $[Cu_3(\mu\text{-dppm})_3(\mu_3\text{-}\eta^1\text{-C}{\equiv}\text{C-}C_6H_4\text{-OMe-}p)](BF_4)_2$.[25] A possible assignment for the origin of the emission involves emissive states derived from ligand-to-metal charge-transfer (LMCT) transition mixed with d−s character. The red shifts in the 77 K solid state emission energy of ~0.29 and ~0.33 eV from **2** and **3**, respectively, to their corresponding Cu(I) analogues are comparable to the value of 0.31 eV reported for the related hexanuclear silver(I) and copper(I) thiocarbamate clusters, $Ag_6(mtc)_6$ and $Cu_6(mtc)_6$ (mtc = di-*n*-propyl monothiocarbamate), where an origin of mixed d → s and LMCT character has been suggested.[5e,g] Besides, a similar red shift in emission energy (~0.27 eV) on going from silver(I) to copper(I) chalcogenido clusters has been reported,[6h−j] in which a mixed d → s/LMCT origin has also been suggested and supported by molecular orbital calculations.[26] Another possible origin for the observed red shift in energy from Ag(I) to Cu(I) involves states derived from metal-to-ligand charge-transfer [MLCT d(M) → π* (acetylide)] transition. As

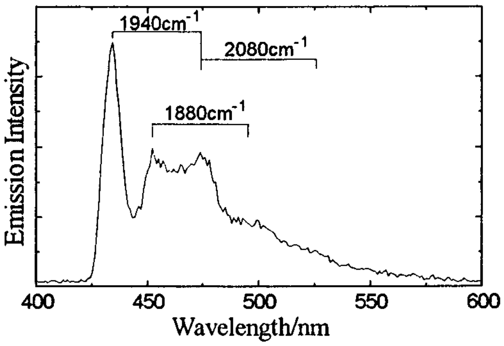

Figure 3. Emission spectrum of **3** in EtOH/MeOH (v/v 1:4) glass at 77 K.

Table 5. Photophysical Data for Ag(I) Complexes

complex	medium (*T*/K)	emission λ_{em}/nm (τ_0/μs)
2	solid (298)	430, 449, 467, 488 sh (93.0)
	solid (77)	428, 462, 469, 495, 515, 536 sh
	EtOH/MeOH (v/v 1:4) glass (77)	432, 453, 470, 496 sh
3	solid (298)	464 (5.2)
	solid (77)	443, 464, 482, 508 sh
	EtOH/MeOH (v/v 1:4) glass (77)	434, 452, 474, 494, 526 sh
4	solid (298)	526, 546 sh, 615 sh (48.0)
	solid (77)	535, 575
	EtOH/MeOH (v/v 1:4) glass (77)	508, 550 sh, 600 sh
5	solid (298)	512 (2.9)
	solid (77)	553
6	solid (298)	570, 627 sh (<0.1)
	solid (77)	532, 579
	$CHCl_3$ glass (77)	534, 598 sh

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Cu(I) is much more easily oxidized, given the higher energy of the Cu(I) 3d orbitals relative to those of the Ag(I) 4d orbitals,[27] the MLCT transition for copper(I) should also occur at lower energy than that for silver(I). In view of the fact that the ionization energy of Ag^+(g) is nearly 10^4 cm^{-1} larger than that for Cu^+(g),[27] an assignment of the emissive state as derived from a MLCT transition is less likely, given the relatively small energy difference for the emission of **2** and **3** with respect to their Cu(I) analogues, and the close resemblance of the observed energy shift with similar systems of LMCT origin.[5e,g,6h−j,26] Therefore, it is likely that the low-energy emission is derived from states of LMCT parentage mixed with a metal-centered $nd^9(n+1)s^1$ state. Such an assignment is also in agreement with our previous work on the trinuclear Cu(I) acetylide complexes.[6a,b,d] The long lifetime of the emissive state in the microsecond range is probably suggestive of a triplet parentage. However, the possibility of an involvement of an intraligand excited state of the acetylide should not be overlooked given the unusually long lifetime of the emissive state and the low-lying π^* orbital energy of the aryl acetylide unit.

Cyclic voltammetric studies of complexes **4** and **6** in MeCN (0.1 M $^n\mathrm{Bu_4NPF_6}$) showed the presence of a quasi-reversible reduction couple at ∼−1.40 V vs the ferrocenium−ferrocene couple, which coincides with the value found for the reduction of (4-nitrophenyl)acetylene. It is likely that the reduction couple observed in **4** and **6** is derived from a one-electron ligand-centered reduction. Moreover, a similar reduction couple also occurred in the analogous Cu(I) complexes, $[\mathrm{Cu_3}(\mu\text{-dppm})_3(\mu_3\text{-}\eta^1\text{-C}{\equiv}\text{C-}\mathrm{C_6H_4\text{-}NO_2}\text{-}p)](\mathrm{BF_4})_2$ and $[\mathrm{Cu_3}(\mu\text{-dppm})_3(\mu_3\text{-}\eta^1\text{-C}{\equiv}\text{C-}\mathrm{C_6H_4\text{-}NO_2}\text{-}p)_2]\mathrm{PF_6}$,[25] the potentials of which are found to be independent of the metal center, further supporting that they are ligand centered in origin. An additional irreversible reduction wave at ∼−1.10 V vs the ferrocenium−ferrocene couple has been observed in complex **4**, assignable to the reduction at the Ag(I) metal center. The absence of such a reduction wave in complex **6** is probably suggestive of its occurrence beyond the solvent window, as such a reduction would be expected to be more difficult in **6** than **4** given the lower overall positive charge of **6** relative to that of **4**. Attempts to investigate the electrochemical properties of complexes **2**, **3**, and **5** were unsuccessful as they were found to decompose readily in acetonitrile solution.

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Supporting Information Available: Tables of fractional coordinates and thermal parameters, general displacement parameter expressions (*U*), and all bond distances and bond angles for complexes **4** and **6** (41 pages). Ordering information is given on any current masthead page.

OM9609170

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