Organometallics **2002,** *21,* 2275−2282

Luminescent Tetranuclear Silver(I) Arylacetylide Complexes Bearing Tricyclohexylphosphine Ligands: Synthesis, Molecular Structures, and Spectroscopic Comparison with Gold(I) and Copper(I) Arylacetylides

Yong-Yue Lin,[†] Siu-Wai Lai,*[,†] Chi-Ming Che,*[,†] Kung-Kai Cheung,[†] and Zhong-Yuan Zhou[‡]

Department of Chemistry and the HKU-CAS Joint Laboratory on New Materials,
The University of Hong Kong, Pokfulam Road, Hong Kong,
and Department of Applied Biology and Chemical Technology,
The Hong Kong Polytechnic University, Hunghom, Hong Kong

Received September 19, 2001

A series of luminescent tetranuclear silver(I) arylacetylides $[Ag_4\{\mu\text{-}(C\equiv C)_xC_6H_4R\text{-}p)_4\}(PCy_3)_y]$ ($x = 1$, $y = 2$, R = H (**1**), CH_3 (**2**), OCH_3 (**3**), $C\equiv CPh$ (**5**); $x = 2$, $y = 4$, R = H (**4**)) were synthesized by treatment of tricyclohexylphosphine (PCy_3) with $[Ag\{(C\equiv C)_xC_6H_4R\text{-}p\}]_\infty$ in dichloromethane in the absence of light, and their spectroscopic and photophysical properties have been investigated. The X-ray structure of **1** exhibits a planar parallelogram-like Ag_4 core and consists of $[Ag(C\equiv CPh)_2]$ and $[Ag(PCy_3)]$ fragments with phenylacetylide σ-coordinated to silver atoms in a μ_2-bonding mode (mean asymmetric Ag−C(α) distances are 2.05 and 2.33 Å). For **2**, **3**, and **5**, with different *para* substituents in the arylacetylide units, similar tetranuclear structures are observed. In contrast, the structure of **4** can be described as two interpenetrating tetrahedra of four silver atoms and four phenylbutadiynyl moieties forming a twisted cubane structure, with each silver atom further coordinated to a PCy_3 ligand. The electronic absorption spectra of **1**−**5** in CH_2Cl_2 are dominated by strong, vibronically structured absorptions at 250−332 nm (ϵ 10^4−10^5 $dm^3\ mol^{-1}\ cm^{-1}$) with vibrational spacings of 1420−2160 cm^{-1} which are attributed to $\nu(C\equiv C)$ or admixtures of acetylenic and aryl stretching frequencies. The solid-state emission spectra of **1**−**3** at 298 and 77 K show intense vibronically structured bands at 422−607 nm which are attributed to $^3(\pi\pi^*)$ excited states of the arylacetylide ligands. For **4**, the solid-state emission is slightly red-shifted in energy from the $^3(\pi\pi^*)$ emission of the corresponding mononuclear $[Au(PCy_3)(C\equiv C-C\equiv CPh)]$ congener, whereas for **5**, a red-shift in its emission is observed from that of **1**−**4**. A comparison between the emission of Cu(I), Ag(I), and Au(I) arylacetylides is made.

Introduction

The versatile coordination behavior of acetylide ligands has been aptly demonstrated by recent studies on the structural diversity of coinage metal derivatives.[1] Concomitantly, $d^{10}-d^{10}$ closed-shell metallophilic interactions[2] and ligand functionality have resulted in the formation and isolation of multinuclear aggregates and three-dimensional networks with novel and diverse structures; examples are some binuclear, polymeric, and catenane-like gold(I) complexes,[3,4] copper(I) alkynyl clusters,[1d,5] and silver(I) aggregates.[1e,6] Among these three classes of coinage metal acetylide compounds, silver(I) derivatives are less studied in the literature. Presumably this is due to their extreme instabilities with regard to light-induced decomposition reactions. The tendency of forming polymeric chains confers difficulties in obtaining species with well-defined stoichiometry. Reports on the employment of N, P, O, and S donor ligands yielding d^{10}-metal aggregates with lower nuclearity have recently appeared.[5c−g,6d] By varying the

---

* Corresponding author. Fax: +852 2857 1586. E-mail: cmche@hku.hk.

[†] The University of Hong Kong.

[‡] The Hong Kong Polytechnic University.

(1) (a) van Koten, G.; James, S. L.; Jastrzebski, J. T. B. H. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, 1995; Vol. 3, p 57. (b) Lang, H.; Köhler, K.; Blau, S. *Coord. Chem. Rev.* **1995**, *143*, 113. (c) Janssen, M. D.; Köhler, K.; Herres, M.; Dedieu, A.; Smeets, W. J. J.; Spek, A. L.; Grove, D. M.; Lang, H.; van Koten, G. *J. Am. Chem. Soc.* **1996**, *118*, 4817. (d) Yam, V. W. W.; Fung, W. K. M.; Cheung, K. K. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1100. (e) Guo, G. C.; Zhou, G. D.; Mak, T. C. W. *J. Am. Chem. Soc.* **1999**, *121*, 3136.

(2) Pyykkö, P. *Chem. Rev.* **1997**, *97*, 597.

(3) (a) Jia, G.; Puddephatt, R. J.; Scott, J. D.; Vittal, J. J. *Organometallics* **1993**, *12*, 3565. (b) Schmidbaur, H. *Chem. Soc. Rev.* **1995**, 391. (c) Irwin, M. J.; Jia, G.; Payne, N. C.; Puddephatt, R. J. *Organometallics* **1996**, *15*, 51. (d) McArdle, C. P.; Irwin, M. J.; Jennings, M. C.; Puddephatt, R. J. *Angew. Chem., Int. Ed.* **1999**, *38*, 3376. (e) McArdle, C. P.; Vittal, J. J.; Puddephatt, R. J. *Angew. Chem., Int. Ed.* **2000**, *39*, 3819.

(4) (a) Li, D.; Xiao, H.; Che, C. M.; Lo, W. C.; Peng, S. M. *J. Chem. Soc., Dalton Trans.* **1993**, 2929. (b) Shieh, S. J.; Xiao, H.; Peng, S. M.; Che, C. M. *J. Chem. Soc., Dalton Trans.* **1994**, 3067. (c) Yam, V. W. W.; Choi, S. W. K.; Cheung, K. K. *Organometallics* **1996**, *15*, 1734. (d) Xiao, H.; Cheung, K. K.; Che, C. M. *J. Chem. Soc., Dalton Trans.* **1996**, 3699. (e) Irwin, M. J.; Vittal, J. J.; Puddephatt, R. J. *Organometallics* **1997**, *16*, 3541. (f) Hunks, W. J.; MacDonald, M. A.; Jennings, M. C.; Puddephatt, R. J. *Organometallics* **2000**, *19*, 5063.

10.1021/om010835y CCC: $22.00
Publication on Web 05/02/2002

electronic and steric demands of ancillary ligands, the control over the generation of particular aggregates can be elucidated.

Recent studies by various groups have highlighted the rich photoluminescent properties and potential device applications of polynuclear copper(I)[7] arylacetylide complexes which display long-lived and emissive excited states in solution at room temperature. Assignment of these electronic excited states remains elusive in the literature,[8] but the effect of metallophilicity in red-shifting the $^3(\pi\pi^*)$ emissions of arylacetylides has been noted in several examples of polynuclear Au(I) and Cu(I) arylacetylide complexes. On the other hand, investigations on spectroscopic properties of polynuclear $[\mathrm{Ag(C{\equiv}CR)}]_n$ aggregates remain sparse and the question as to the effect of Ag(I)−Ag(I) and alkynyl−Ag(I) interactions upon the spectroscopic and photophysical properties of the excited states derived from $[\mathrm{Ag(C{\equiv}CR)}]_n$ aggregates remains to be addressed.

This present account reports the synthesis, crystal structures, and photophysical properties of a series of tetranuclear Ag(I) arylacetylide compounds bearing tricyclohexylphosphine ligand ($\mathrm{PCy_3}$). Compared to arylphosphines, $\mathrm{PCy_3}$ does not exhibit low-lying ligand-localized excited states, and this will facilitate spectroscopic assignments of the $[\mathrm{Ag(C{\equiv}CR)}]_n$ aggregates. This paper focuses on the effect of modifying (1) the nature of substituents on the arylacetylide moiety and (2) the steric demand from arylacetylide to phenylbutadiynyl, upon the stoichiometry and structural conformation adopted by the Ag(I) arylacetylide complexes. The spectroscopic properties of Cu(I), Ag(I), and Au(I) arylacetylides are compared and the involvement of arylacetylide-to-metal charge transfer in the emissions of $\mathrm{d^{10}}$ metal arylacetylides is discussed.

Experimental Section

General Procedures. All starting materials were used as received. 4-Phenyl-1,3-butadiyne[9] and $[\mathrm{Ag(C{\equiv}CPh)}]_\infty$[10] were prepared by literature methods (**Caution**: silver acetylides in the dry state detonate easily by mechanical shock and should be handled with care in small amounts). 4-(Phenylethynyl)phenylacetylene was synthesized via Pd/Cu-catalyzed carbon−carbon coupling of (trimethylsilyl)(4-iodophenyl)acetylene[11] and phenylacetylene followed by the desilylation reaction.[12] Dichloromethane for synthesis and photophysical studies was washed with concentrated sulfuric acid, 10% sodium hydrogen carbonate, and water, dried by calcium chloride, and distilled over calcium hydride. All other solvents were of analytical grade and purified according to conventional methods.[13] All reactions were carried out in the absence of light using standard Schlenk techniques.

Fast atom bombardment (FAB) mass spectra were obtained on a Finnigan Mat 95 mass spectrometer with a 3-nitrobenzyl alcohol matrix. ^{1}H (in MHz, 500), ^{13}C (126), and ^{31}P (202) NMR measurements were performed on a Bruker DPX 500 FT-NMR spectrometer with tetramethylsilane (^{1}H and ^{13}C) and $\mathrm{H_3PO_4}$ (^{31}P) as references. Elemental analysis was performed by the Institute of Chemistry at the Chinese Academy of Sciences, Beijing. Infrared spectra were recorded on a BIO RAD FT-IR spectrophotometer. UV−vis spectra were recorded on a Perkin-Elmer Lambda 19 UV/vis spectrophotometer.

Emission and Lifetime Measurements. Steady-state emission spectra were recorded on a SPEX 1681 Fluorolog-2 series F111AI spectrophotometer. Low-temperature (77 K) emission spectra for glasses and solid-state samples were recorded in 5 mm diameter quartz tubes, which were placed in a liquid nitrogen Dewar equipped with quartz windows. The emission spectra were corrected for monochromator and photomultiplier efficiency and for xenon lamp stability.

Emission lifetime measurements were performed with a Quanta Ray DCR-3 pulsed Nd:YAG laser system (pulse output 355 nm, 8 ns). The emission signals were detected by a Hamamatsu R928 photomultiplier tube and recorded on a Tektronix model 2430 digital oscilloscope. Errors for λ values (±1 nm), τ (±10%), and ϕ (±10%) are estimated. Details of emission quantum yield determinations using the method of Demas and Crosby[14] have been provided previously.[15]

Synthesis. $[\mathbf{Ag_4(\mu\text{-}C{\equiv}CPh)_4(PCy_3)_2}]$, 1. To a stirred suspension of $[\mathrm{Ag(C{\equiv}CPh)}]_\infty$ (0.10 g, 0.48 mmol) in dichloromethane (30 mL) at room temperature was added tricyclohexylphosphine, $\mathrm{PCy_3}$ (0.073 g, 0.26 mmol). Upon stirring for 2 h, the color of the mixture changed to light yellow and the mixture was filtered and evaporated to dryness. Recrystallization by slow diffusion of diethyl ether into a dichloromethane solution of the crude product afforded colorless crystals. Yield: 0.11 g, 66%. Anal. Calcd for $\mathrm{C_{68}H_{86}P_2Ag_4}$: C, 58.47; H, 6.21. Found: C, 58.41; H, 6.20. FAB-MS: *m/z* 1397 [M$^+$], 1314 [M$^+$ − Cy]. ^{1}H NMR ($\mathrm{CD_2Cl_2}$): 1.15−1.29 (m, 18H, Cy), 1.40−1.45 (m, 12H, Cy), 1.65 (m, 6H, Cy), 1.75−1.77 (m, 12H, Cy), 1.86−1.93 (m, 18H, Cy), 7.09−7.17 (m, 12H, Ph), 7.31−7.33 (m, 8H, Ph). ^{13}C{^{1}H} NMR ($\mathrm{CD_2Cl_2}$): 26.4 (Cy), 27.7 (d, $^2J_{\mathrm{PC}}$ = 11.5 Hz, Cy), 31.5 (d, $^3J_{\mathrm{PC}}$ = 4.0 Hz, Cy), 32.4 (d, $^1J_{\mathrm{PC}}$ = 13.5 Hz, Cy), 111.2 (Ag−C≡*C*), 113.5 (Ag−*C*≡C), 125.4, 127.2, 128.3, 132.5 (Ph). ^{31}P{^{1}H} NMR ($\mathrm{CD_2Cl_2}$): 35.74 (br d). IR (KBr): ν 2076 (C≡C) cm^{-1}.

$[\mathbf{Ag_4(\mu\text{-}C{\equiv}CC_6H_4CH_3\text{-}\mathit{p})_4(PCy_3)_2}]$, 2. $[\mathrm{Ag(C{\equiv}CC_6H_4CH_3\text{-}\mathit{p})}]_\infty$ was prepared by a procedure similar to that described for $[\mathrm{Ag(C{\equiv}CPh)}]_\infty$ except 4-ethynyltoluene was used. Reaction of $[\mathrm{Ag(C{\equiv}CC_6H_4CH_3\text{-}\mathit{p})}]_\infty$ (0.11 g, 0.49 mmol) with $\mathrm{PCy_3}$ (0.070 g, 0.25 mmol) using the method described for **1** afforded colorless crystals. Yield: 0.16 g, 89%. Anal. Calcd for $\mathrm{C_{72}H_{94}P_2Ag_4}$: C, 59.52; H, 6.52. Found: C, 59.29; H, 6.74. FAB-MS: *m/z* 1453 [M$^+$]. ^{1}H NMR ($\mathrm{CD_2Cl_2}$): 1.20−1.30 (m, 18H, Cy), 1.41−1.43 (m, 12H, Cy), 1.67 (m, 6H, Cy), 1.76−1.78 (m, 12H, Cy), 1.90−1.92 (m, 18H, Cy), 2.28 (s, 12H, $\mathrm{CH_3}$), 6.92 (d, 8H, $^3J_{\mathrm{HH}}$ = 7.9 Hz, $\mathrm{C_6H_4}$), 7.20 (d, 8H, $^3J_{\mathrm{HH}}$ = 8.0 Hz, $\mathrm{C_6H_4}$). ^{13}C{^{1}H} NMR ($\mathrm{CD_2Cl_2}$): 21.5 ($\mathrm{CH_3}$), 26.4 (Cy), 27.7 (d, $^2J_{\mathrm{PC}}$ = 11.4 Hz, Cy), 31.5 (d, $^3J_{\mathrm{PC}}$ = 3.6 Hz, Cy), 32.3 (d, $^1J_{\mathrm{PC}}$ = 14.1 Hz, Cy), 109.5 (Ag−C≡*C*), 114.1 (Ag−*C*≡C), 122.3, 129.0, 132.4,

---

(5) (a) Corfield, P. W. R.; Shearer, H. M. M. *Acta Crystallogr.* **1966**, *21*, 957. (b) Naldini, L.; Demartin, F.; Manassero, M.; Sansoni, M.; Rassu, G.; Zoroddu, M. A. *J. Organomet. Chem.* **1985**, *279*, C42. (c) Knotter, D. M.; Spek, A. L.; van Koten, G. *J. Chem. Soc., Chem. Commun.* **1989**, 1738. (d) Reger, D. L.; Huff, M. F. *Organometallics* **1992**, *11*, 69. (e) Knotter, D. M.; Spek, A. L.; Grove, D. M.; van Koten, G. *Organometallics* **1992**, *11*, 4083. (f) Munakata, M.; Kitagawa, S.; Kawada, I.; Maekawa, M.; Shimono, H. *J. Chem. Soc., Dalton Trans.* **1992**, 2225. (g) Diez, J.; Gamasa, M. P.; Gimeno, J.; Lastra, E.; Aguirre, A.; García-Granda, S. *Organometallics* **1993**, *12*, 2213.

(6) (a) Wang, C. F.; Peng, S. M.; Chan, C. K.; Che, C. M. *Polyhedron* **1996**, *15*, 1853. (b) Yam, V. W. W.; Fung, W. K. M.; Cheung, K. K. *Organometallics* **1997**, *16*, 2032. (c) Wang, Q. M.; Mak, T. C. W. *J. Am. Chem. Soc.* **2001**, *123*, 7594. (d) Wang, Q. M.; Mak, T. C. W. *Angew. Chem., Int. Ed.* **2001**, *40*, 1130.

(7) (a) Ma, Y. G.; Chan, W. H.; Zhou, X. M.; Che, C. M. *New J. Chem.* **1999**, *23*, 263. (b) Ma, Y.; Che, C. M.; Chao, H. Y.; Zhou, X.; Chan, W. H.; Shen, J. *Adv. Mater.* **1999**, *11*, 852.

(8) Che, C. M.; Chao, H. Y.; Miskowski, V. M.; Li, Y. Q.; Cheung, K. K. *J. Am. Chem. Soc.* **2001**, *123*, 4985.

(9) Kende, A. S.; Smith, C. A. *J. Org. Chem.* **1988**, *53*, 2655.

(10) Blake, D.; Calvin, G.; Coates, G. E. *Proc. Chem. Soc.* **1959**, 396.

(11) Hsung, R. P.; Chidsey, C. E. D.; Sita, L. R. *Organometallics* **1995**, *14*, 4808.

(12) Lavastre, O.; Cabioch, S.; Dixneuf, P. H.; Vohlidal, J. *Tetrahedron* **1997**, *53*, 7595.

(13) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*, 2nd ed.; Pergamon: Oxford, 1980.

(14) Demas, J. N.; Crosby, G. A. *J. Phys. Chem.* **1971**, *75*, 991.

(15) Lai, S. W.; Chan, M. C. W.; Cheung, T. C.; Peng, S. M.; Che, C. M. *Inorg. Chem.* **1999**, *38*, 4046.

Table 1. Crystal Data

	1	**4**·0.5Et$_2$O	**5**
formula	C$_{68}$H$_{86}$P$_2$Ag$_4$	C$_{114}$H$_{157}$O$_{0.5}$P$_4$Ag$_4$	C$_{100}$H$_{102}$P$_2$Ag$_4$
fw	1396.79	2090.76	1797.24
cryst size, mm	0.14 × 0.10 × 0.08	0.20 × 0.16 × 0.14	0.40 × 0.35 × 0.15
cryst syst	triclinic	monoclinic	triclinic
space group	$P\bar{1}$	$C2/c$	$P\bar{1}$
a, Å	10.100(3)	27.750(6)	10.149(2)
b, Å	13.455(4)	14.851(2)	12.649(3)
c, Å	13.856(4)	55.998(9)	16.909(3)
α, deg	62.796(5)	90	78.91(3)
β, deg	76.059(6)	96.274(7)	82.26(3)
γ, deg	72.428(7)	90	88.80(3)
V, Å^3	1584.7(8)	22940(7)	2110.7(8)
Z	1	8	1
D_c, g cm^{-3}	1.464	1.211	1.414
μ, cm^{-1}	13.06	7.71	9.98
$2\theta_{\max}$, deg	55.4	55.1	50.7
no. unique data	7212	26126	6984
no. obsd data	3285 ($I > 2\sigma(I)$)	12348 ($I > 2\sigma(I)$)	5263 ($I \geq 2\sigma(I)$)
no. variables	335	1102	478
R,[a] R_w[b]	0.043, 0.11	0.065, 0.20	0.027, 0.065
residual ρ, e Å^{-3}	+0.50, −0.60	+0.94, −1.05	+0.32, −0.64

[a] $R = \sum||F_o| - |F_c|| / \sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$.

137.3 (C$_6$H$_4$). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): 36.72 (br d). IR (KBr): ν 2064 (C≡C) cm^{-1}.

[Ag$_4$(μC≡CC$_6$H$_4$OCH$_3$-*p*)$_4$(PCy$_3$)$_2$], 3. [Ag(C≡CC$_6$H$_4$OCH$_3$-*p*)]$_\infty$ was prepared by a procedure similar to that described for [Ag(C≡CPh)]$_\infty$ except 1-ethynyl-4-methoxybenzene was used. Reaction of [Ag(C≡CC$_6$H$_4$OCH$_3$-*p*)]$_\infty$ (0.12 g, 0.50 mmol) with PCy$_3$ (0.070 g, 0.25 mmol) using the method described for **1** afforded colorless crystals. Yield: 0.14 g, 74%. Anal. Calcd for C$_{72}$H$_{94}$O$_4$P$_2$Ag$_4$: C, 57.01; H, 6.25. Found: C, 56.65; H, 6.56. FAB-MS: *m/z* 1517 [M$^+$]. ^{1}H NMR (CD$_2$Cl$_2$): 1.22−1.31 (m, 18H, Cy), 1.39−1.44 (m, 12H, Cy), 1.66−1.67 (m, 6H, Cy), 1.77−1.79 (m, 12H, Cy), 1.86−1.93 (m, 18H, Cy), 3.74 (s, 12H, OCH$_3$), 6.63 (d, 8H, $^3J_{\rm HH}$ = 8.6 Hz, C$_6$H$_4$), 7.24 (d, 8H, $^3J_{\rm HH}$ = 8.8 Hz, C$_6$H$_4$). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): 26.4 (Cy), 27.7 (d, $^2J_{\rm PC}$ = 11.5 Hz, Cy), 31.5 (d, $^3J_{\rm PC}$ = 3.9 Hz, Cy), 32.4 (d, $^1J_{\rm PC}$ = 14.1 Hz, Cy), 55.6 (OCH$_3$), 108.7 (Ag−C≡*C*), 113.4 (Ag−*C*≡C), 113.9, 117.8, 133.9, 159.1 (C$_6$H$_4$). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): 36.03 (br s). IR (KBr): ν 2056 (C≡C) cm^{-1}.

[Ag$_4$(μ-C≡C−C≡C−Ph)$_4$(PCy$_3$)$_4$], 4. [Ag(C≡C−C≡C−Ph)]$_\infty$ was prepared by a procedure similar to that described for [Ag(C≡CPh)]$_\infty$ except 4-phenyl-1,3-butadiyne was used. To a suspension of [Ag(C≡C−C≡C−Ph)]$_\infty$ (0.14 g, 0.60 mmol) in dichloromethane (20 mL) was added PCy$_3$ (0.17 g, 0.61 mmol). The mixture was heated under reflux for 2 h, and the resultant dark green mixture was filtered and evaporated to dryness to give a yellow solid. Recrystallization by slow diffusion of diethyl ether into a dichloromethane solution of the crude product afforded yellow crystals. Yield: 0.16 g, 52%. Anal. Calcd for C$_{112}$H$_{152}$P$_4$Ag$_4$: C, 65.50; H, 7.46. Found: C, 65.65; H, 7.85. FAB-MS: *m/z* 2053 [M$^+$]. ^{1}H NMR (CD$_2$Cl$_2$): 1.22−1.40 (m, 60H, Cy), 1.71−1.73 (m, 12H, Cy), 1.82−1.91 (m, 60H, Cy), 7.26−7.29 (m, 12H, Ph), 7.40−7.43 (m, 8H, Ph). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): 26.4 (Cy), 27.7 (d, $^2J_{\rm PC}$ = 9.2 Hz, Cy), 31.6 (Cy), 32.2 (d, $^1J_{\rm PC}$ = 15.6 Hz, Cy), 68.2 (Ag−C≡C−C≡*C*), 77.2 (Ag−C≡C−*C*≡C), 88.8 (Ag−C≡*C*), 123.9 (Ph), 125.7 (Ag−*C*≡C), 128.2, 128.6, 132.7 (Ph). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): 39.28 (br s). IR (KBr): ν 2169, 2001 (C≡C) cm^{-1}.

[Ag$_4$(μ-C≡C−C$_6$H$_4$−C≡C−Ph)$_4$(PCy$_3$)$_2$], 5. [Ag(C≡C−C$_6$H$_4$−C≡C−Ph)]$_\infty$ was prepared by a procedure similar to that described for [Ag(C≡CPh)]$_\infty$ except 4-(phenylethynyl)phenylacetylene was used. Reaction of [Ag(C≡C−C$_6$H$_4$−C≡C−Ph)]$_\infty$ (0.15 g, 0.49 mmol) with PCy$_3$ (0.070 g, 0.25 mmol) using the method described for **1** afforded colorless crystals. Yield: 0.12 g, 55%. Anal. Calcd for C$_{100}$H$_{102}$P$_2$Ag$_4$: C, 66.83; H, 5.72. Found: C, 67.05; H, 6.03. FAB-MS: *m/z* 1797 [M$^+$]. ^{1}H NMR (CD$_2$Cl$_2$): 1.21−1.33 (m, 18H, Cy), 1.36−1.42 (m, 12H, Cy), 1.71−1.73 (m, 6H, Cy), 1.82−1.84 (m, 12H, Cy), 1.91−1.92 (m, 18H, Cy), 7.31−7.52 (m, 36H, aryl H). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): 26.4 (Cy), 27.6 (d, $^2J_{\rm PC}$ = 11.5 Hz, Cy), 31.6 (Cy), 32.2 (d, $^1J_{\rm PC}$ = 16.7 Hz, Cy), 89.9 (C≡*C*Ph), 90.4 (*C*≡CPh), 120.8 (Ag−C≡*C*), 123.7 (Ag−*C*≡C), 128.6, 128.8, 131.6, 131.9, 132.0 (aryl C). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): 38.97 (br d). IR (KBr): ν 2215, 2069 (C≡C) cm^{-1}.

X-ray Crystallography. Crystals of **1**−**3**, **4**·0.5Et$_2$O, and **5** were grown by slow diffusion of diethyl ether into dichloromethane solutions. Crystal data and details of data collection and refinement for **1**, **4**·0.5Et$_2$O, and **5** are summarized in Table 1 (see Supporting Information for **2** and **3**).

Data for complexes **1** and **4**·0.5Et$_2$O were collected at 294 K on a Bruker CCD area detector diffractometer by the φ and ω scan technique using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). For both complexes, the coordinates of the metal atoms were determined by direct methods, and the remaining non-hydrogen atoms were located from successive Fourier difference syntheses. The structures were refined by full-matrix least-squares techniques with an anisotropic thermal parameter for all the non-hydrogen atoms. The calculations were performed on a COMPUCON PC/586 computer with the Bruker AXS SHELXTL/PC program package.[16] For **1**, a crystallographic asymmetric unit consists of half of one molecule. For **4**·0.5Et$_2$O, a crystallographic asymmetric unit consists of one molecule, with half of one diethyl ether molecule as solvent of crystallization.

Diffraction experiments for **2**, **3**, and **5** were performed at 301 K on a MAR diffractometer with graphite-monochromatized Mo Kα radiation (λ = 0.71073 Å). The structures of **2** and **5** were solved by direct methods (SIR92 or SIR97),[17] whereas that of **3** was done by Patterson methods and expanded by Fourier methods (PATTY).[18] Refinement of structures was performed by full-matrix least-squares using the software package TeXsan[19] on a Silicon Graphics Indy computer (for **2** and **3**) or using the SHELXL-97 program

---

(16) Sheldrick, G. M. *SHELXL 97*, A Program for Crystal Structure Determination; University of Göttingen, 1997.

(17) (a) SIR92: Altomare, A.; Cascarano, M.; Giacovazzo, C.; Guagliardi, A.; Burla, M. C.; Polidori, G.; Camalli, M. *J. Appl. Crystallogr.* **1994**, *27*, 435. (b) SIR97: Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, M.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. *J. Appl. Crystallogr.* **1998**, *32*, 115.

(18) PATTY: Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; Garcia-Granda, S.; Gould, R. O.; Smits, J. M. M.; Smykalla, C. The DIRDIF program system; Technical Report of the Crystallography Laboratory; University of Nijmegen: The Netherlands, 1992.

(19) TeXsan: Crystal Structure Analysis Package, Molecular Structure Corporation: The Woodlands, TX, 1985 and 1992.

package (for **5**) on PC. For **5**, a crystallographic asymmetric unit consists of half of a formula unit. All non-H atoms were refined anisotropically and H atoms were generated by the program SHELXL-97.

Results and Discussion

Synthesis and Characterization. Treatment of PCy_3 with 1 or 2 equiv of $[Ag(C{\equiv}CC_6H_4R\text{-}p)]_\infty$ (R = H, CH_3, OCH_3, and $C{\equiv}CPh$) in dichloromethane afforded the colorless complexes $[Ag_4(\mu\text{-}C{\equiv}CC_6H_4R\text{-}p)_4(PCy_3)_2]$ (**1**−**3** and **5**, respectively) in moderate to high yields (55−90%). Attempts to synthesize derivatives with electron-withdrawing aryl substituents (R = Cl, F) resulted in extremely unstable complexes. The reaction between equimolar amounts of PCy_3 and $[Ag(C{\equiv}C{-}C{\equiv}CPh)]_\infty$ in dichloromethane gave the yellow complex **4**, $[Ag_4(\mu\text{-}C{\equiv}C{-}C{\equiv}CPh)_4(PCy_3)_4]$. This class of compounds is stable in solid state, but in solution, they are stable only in the absence of light.

The parent molecular ions M^+ of complexes **1**−**5** can be located in their FAB mass spectra. The IR spectra of **1**−**3** reveal weak $\nu(C{\equiv}C)$ absorption at 2056−2076 cm^{-1}; similar $\nu(C{\equiv}C)$ stretching frequencies were found in $[Cu_6(C_6H_4NMe_2\text{-}2)_4(\mu_2\text{-}\eta^1\text{-}C{\equiv}CR)_2]$ (R = Ph, 2040 cm^{-1}; R = C_6H_4Me-4, 2042 cm^{-1})[20] and $[Cu_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}CPh)_2\text{-}(\mu\text{-}Ph_2PCH_2PPh_2)_3]BF_4$ (2027 cm^{-1}).[21] In the IR spectrum of **4**, the two observed frequencies at 2001 and 2169 cm^{-1} are similar to those found in the copper analogue, $[Cu(C{\equiv}C{-}C{\equiv}CPh)PMe_3]_n$ (1981 and 2161 cm^{-1}).[22] The IR spectrum of **5** shows two weak $\nu(C{\equiv}C)$ absorptions at 2069 and 2215 cm^{-1}.

The ^1H NMR spectra of **1**−**5** show multiplets at δ 1.15−1.93 and 6.63−7.52 due to the cyclohexyl and aryl protons, respectively. For **2** and **3**, the ^1H NMR spectra show the methyl and methoxy resonances as a singlet at δ 2.28 and 3.74, respectively. The integrated intensities for these signals are in good agreement with that deduced from the chemical formulation.

The $^{13}C\{^1H\}$ NMR spectra of **1**−**5** display collections of peaks at δ 26.4−32.4 and 113.9−159.1 corresponding to the cyclohexyl carbons of the PCy_3 and aryl ligands, respectively. Two broad singlets at δ 113.4−114.1 and 108.7−111.2 in the $^{13}C\{^1H\}$ NMR spectra of **1**−**3** are assigned to the α- and β-acetylide carbon atoms. The broad nature of these peaks is due to unresolved coupling with ^{107}Ag and ^{109}Ag nuclides. In the $^{13}C\{^1H\}$ NMR spectra of **4**, singlets at 125.7, 88.8, 77.2, and 68.2 ppm are assigned to the α, β, γ, and δ butadiynyl atoms. The $^{31}P\{^1H\}$ NMR spectra of **1**−**5** show a broad doublet centered at δ 35.74−39.28 with averaged coupling to ^{107}Ag and ^{109}Ag nuclides.

Crystal Structures. X-ray structural determinations of **1**−**3**, **4**·0.5Et_2O, and **5** have been performed (Figures 1−3; perspective views for **2** and **3** are available in the Supporting Information); selected bond lengths and angles are listed in Table 2. The molecular structures of **1**−**3** and **5** can be visualized as being constructed from two *trans*-$[Ag(C{\equiv}CC_6H_4R\text{-}p)_2]$ and $[Ag(PCy_3)]$ units (i.e., 2:1 arylacetylide to PCy_3 ratio). The core of each molecule consists of four silver atoms arranged in a parallelogram-like array forming a Ag_4 plane. This differs remarkably from the tetranuclear copper analogue $[Cu_4(\mu_3\text{-}\eta^1\text{-}C{\equiv}CPh)_4\{P(C_6H_4Me\text{-}p)_3\}_4]$,[23] which bears a 1:1 phenylacetylide to phosphine stoichiometry and adopts a cubane structure. The observed silver−silver distances are 2.9367(9) and 2.9819(9) Å for **1**, 2.8670(4) and 3.0707(5) Å for **2**, and 2.9450(9) and 2.9891(9) Å for **5**. These Ag−Ag separations are longer than the sum of van der Waals radii for silver (2.89 Å),[24] and they may be considered as weakly interacting.[25] The Ag(1)−Ag(2)−Ag(1A) and Ag(2)−Ag(1)−Ag(2A) angles in **1** (76.55(1)° and 103.45(1)°) deviate from 90°, like a parallelogram (82.98(1) and 97.02(1)° for **2**; 79.00(3) and 101.00(3)° for **5**).

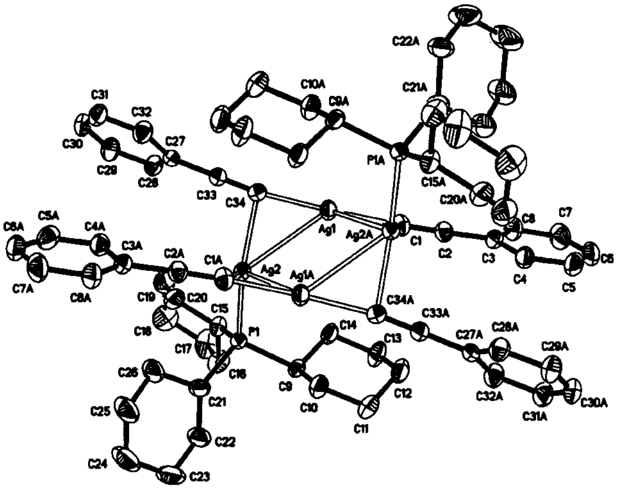

Figure 1. Perspective view of **1** (30% probability ellipsoids).

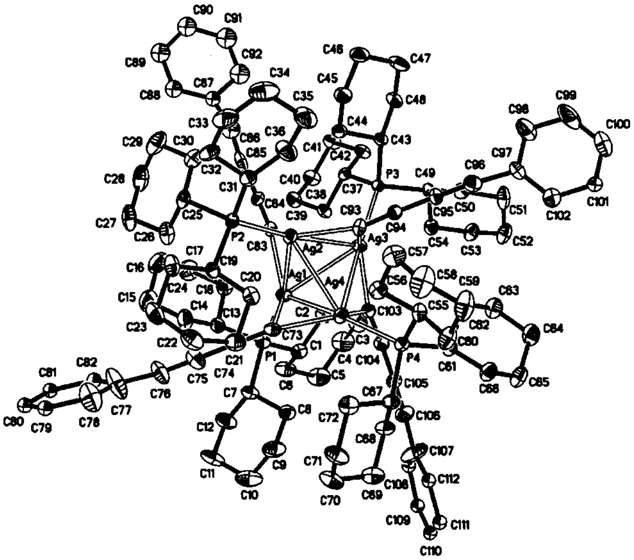

Figure 2. Perspective view of **4** (40% probability ellipsoids).

Each of the silver atoms in the *trans*-$[Ag(C{\equiv}CC_6H_4R\text{-}p)_2]$ fragments in **1**−**3** and **5** is σ-bonded to two arylacetylide ligands, with Ag−C bond distances ranging from 2.048(3) to 2.083(3) Å. An approximately linear

---

(20) ten Hoedt, R. W. M.; van Koten, G.; Noltes, J. G. *J. Organomet. Chem.* **1977**, *133*, 113.

(21) Diéz, J.; Gamasa, M. P.; Gimeno, J.; Aguirre, A.; García-Granda, S. *Organometallics* **1991**, *10*, 380.

(22) Coates, G. E.; Parkin, C. *J. Inorg. Nucl. Chem.* **1961**, *22*, 59.

(23) Yam, V. W. W.; Lee, W. K.; Cheung, K. K. *J. Chem. Soc., Dalton Trans.* **1996**, 2335.

(24) Emsley, J. *The Elements*; Clarendon: Oxford, 1998; p 192.

(25) Jansen, M. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1098.

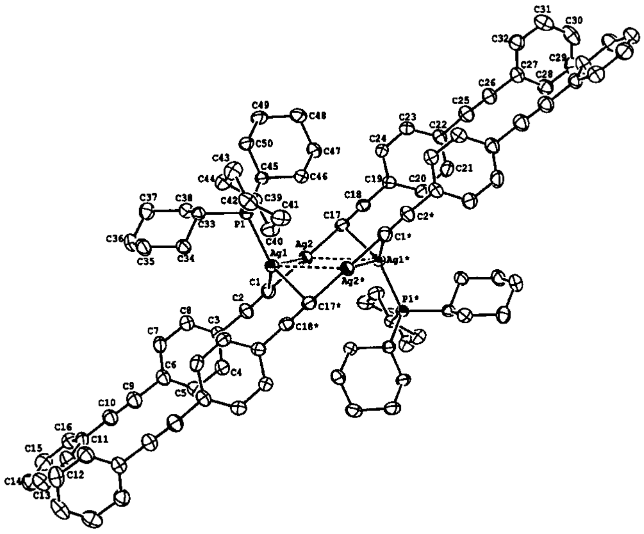

Figure 3. Perspective view of **5** (30% probability ellipsoids).

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

Complex **1**			
Ag(1)−Ag(2)	2.9367(9)	Ag(2)−P(1)	2.4100(8)
Ag(2)−Ag(1A)	2.982(1)	C(1)−C(2)	1.203(4)
Ag(1)−Ag(2A)	2.9819(9)	C(2)−C(3)	1.438(4)
Ag(1)−C(1)	2.048(3)	C(5)−C(6)	1.364(7)
Ag(1)−C(34)	2.055(3)	C(33)−C(34)	1.204(4)
Ag(2)−C(34)	2.285(3)	C(27)−C(33)	1.437(4)
Ag(2)−C(1A)	2.377(4)	P(1)−C(9)	1.850(3)
Ag(2A)−C(1)	2.377(4)	C(11)−C(12)	1.494(6)
Ag(1)−Ag(2)−Ag(1A)	76.55(1)	C(2)−C(1)−Ag(1)	173.5(3)
Ag(2)−Ag(1)−Ag(2A)	103.45(1)	C(34)−Ag(2)−C(1A)	109.2(1)
C(1)−Ag(1)−C(34)	176.2(2)	P(1)−Ag(2)−Ag(1A)	109.28(2)
Ag(1)−C(1)−Ag(2A)	84.4(1)	C(34)−Ag(2)−Ag(1A)	106.77(8)
C(1)−Ag(1)−Ag(2A)	52.5(1)	C(21)−P(1)−Ag(2)	110.0(1)
Complex **4**·0.5Et$_2$O			
Ag(1)−Ag(2)	3.0462(5)	Ag(2)−C(93)	2.176(3)
Ag(1)−Ag(3)	2.9295(6)	Ag(3)−C(93)	2.521(3)
Ag(1)−Ag(4)	2.9962(5)	Ag(3)−C(103)	2.151(3)
Ag(2)−Ag(3)	3.2067(5)	Ag(4)−C(103)	2.559(3)
Ag(2)−Ag(4)	2.9482(6)	C(73)−C(74)	1.207(5)
Ag(3)−Ag(4)	3.2005(5)	C(74)−C(75)	1.388(6)
Ag(1)−C(73)	2.444(3)	C(75)−C(76)	1.179(6)
Ag(4)−C(73)	2.175(4)	C(76)−C(77)	1.387(5)
Ag(1)−C(83)	2.194(3)	Ag(1)−P(1)	2.432(1)
Ag(2)−C(83)	2.421(3)	P(2)−C(19)	1.854(3)
Ag(1)−C(73)−Ag(4)	80.7(1)	C(73)−Ag(1)−C(83)	111.3(1)
Ag(2)−C(93)−Ag(3)	85.8(1)	C(83)−Ag(2)−C(93)	109.0(1)
Ag(1)−C(83)−Ag(2)	82.4(1)	C(93)−Ag(3)−C(103)	106.8(1)
Ag(3)−C(103)−Ag(4)	85.2(1)	C(73)−Ag(4)−C(103)	108.3(1)
C(73)−C(74)−C(75)	178.4(4)	C(93)−C(94)−C(95)	176.4(4)
C(75)−C(76)−C(77)	173.4(5)	C(95)−C(96)−C(97)	175.0(4)
Complex **5**			
Ag(1)−Ag(2)	2.9450(9)	Ag(1)−P(1)	2.427(1)
Ag(1)−Ag(2*)	2.9891(9)	C(1)−C(2)	1.198(4)
Ag(2)−C(1)	2.061(4)	C(2)−C(3)	1.443(5)
Ag(2)−C(17)	2.057(3)	C(25)−C(26)	1.194(5)
Ag(1)−C(1)	2.335(4)	C(26)−C(27)	1.435(5)
Ag(1*)−C(17)	2.414(3)	P(1)−C(33)	1.840(3)
Ag(2)−Ag(1)−Ag(2*)	79.00(3)	C(2)−C(1)−Ag(2)	169.5(3)
Ag(1)−Ag(2)−Ag(1*)	101.00(3)	C(9)−C(10)−C(11)	177.4(4)
C(1)−Ag(2)−C(17)	179.8(1)	C(1)−Ag(1)−C(17*)	105.5(1)
Ag(1)−C(1)−Ag(2)	83.9(1)	P(1)−Ag(1)−Ag(2)	111.32(3)
C(17)−Ag(2)−Ag(1*)	53.35(9)		

coordination geometry (C−Ag−C angles range from 176.2(2)° to 179.8(1)°) is therefore evident. These four arylacetylide groups do not lie coplanar with the central Ag$_4$ plane, but are slanted in a parallel fashion at an angle of ca. 50°. The acetylide groups further coordinate to adjacent Ag atoms with average Ag−C(α) and Ag−C(β) distances of 2.35 and 2.85 Å, respectively. Thus, the bonding mode of the acetylide group is similar to that previously reported for the arylphosphine congener, [Ph$_3$PAgC≡CPh]$_4$·3.5THF (asymmetric Ag−C(α) distances: 2.05 and 2.45 Å, respectively).[26] The C≡C bond distances (average 1.20 Å) are normal for a carbon−carbon triple bond.

The Ag(I) in the [Ag(PCy$_3$)] units of **1**−**3** and **5** are covalently bonded to one PCy$_3$ ligand, argentophilically interacting with two adjacent silver centers, and asymmetrically bonded to two arylacetylide units. The bond angles around these Ag(I) range from 50.1° to 119.1°. The two PCy$_3$ ligands are orientated in a *trans* fashion out of the Ag$_4$ plane. The Ag−P bond distances (mean 2.43 Å) are typical of those reported for silver(I)−phosphine complexes such as [(Ph$_3$P)$_2$Ag]BF$_4$ (average 2.42 Å).[27]

For **2**, **3**, and **5**, in which different *p*-substituents at the arylacetylide but the same phosphine ligand are adopted, tetranuclear structures similar to that of **1** are observed. It is evident that different *p*-substituents in the arylacetylide units (CH$_3$ in **2**, OCH$_3$ in **3**, and C≡CPh in **5**) do not impose any significant influence on the molecular structure of the complexes. The aryl C$_6$H$_4$ rings in the [Ag(C≡CC$_6$H$_4$R-*p*)$_2$] strands orientate in a coplanar fashion, allowing intramolecular π-stacking interaction with interplanar separations of ~3.5 Å. However, the phenyl rings at both ends of the [Ag(C≡CC$_6$H$_4$C≡CPh)$_2$] units in **5** show no additional π-stacking interaction. Replacing the arylacetylide by the phenylbutadiynyl ligand has yielded a different aggregate, complex **4**, with a higher phosphine-to-arylacetylide ratio than **1**−**3** and **5**. The molecular structure of **4** depicts two interpenetrating tetrahedra of four silver atoms and four phenylbutadiynyl ligands situated on alternate corners of a twisted cubane structure, with each silver atom further coordinated to a PCy$_3$ ligand. Such a cubane-type structure is similar to those observed for the tetrameric [Ag$_4$(PPh$_3$)$_4$X$_4$][28] complexes (X = Cl, Br, I) and the copper analogues.[29]

The Ag−Ag distances in **4** range from 2.9295(6) to 3.2067(5) Å and are longer than those in the analogous [Cu$_4$(μ_3-η^1-C≡CPh)$_4${P(C$_6$H$_4$Me-*p*)$_3$}$_4$] complex (2.567(2)−2.607(2) Å).[23] The silver atoms cause a significant expansion of the inner M$_4$ tetrahedron when compared to the structure of its Cu$_4$ analogue. Other vertexes in the cubane core of **4** are occupied by four C(α) atoms of the phenylbutadiynyl ligands, which are σ-bonded to the silver atoms. The asymmetric Ag−C(short) and Ag−C(long) contacts lie in the 2.151(3)−2.194(3) Å and 2.421(3)−2.559(3) Å ranges, respectively, and are partially longer than those observed in **1**−**3** and **5**. The Ag−C−Ag angles, ranging from 80.7(1)° to 85.8(1)°, and the C−Ag−C angles, varying from 106.8(1)° to 111.3(1)°, deviate from the ideal value of 90°. The mean of two alternating C≡C distances is 1.205 Å, while the carbon−

---

(26) Brasse, C.; Raithby, P. R.; Rennie, M. A.; Russell, C. A.; Steiner, A.; Wright, D. S. *Organometallics* **1996**, *15*, 639.

(27) Bachman, R. E.; Andretta, D. F. *Inorg. Chem.* **1998**, *37*, 5657.

(28) (a) Teo, B. K.; Calabrese, J. C. *Inorg. Chem.* **1976**, *15*, 2467. (b) Teo, B. K.; Calabrese, J. C. *J. Chem. Soc., Chem. Commun.* **1976**, 185.

(29) (a) Churchill, M. R.; Kalra, K. L. *Inorg. Chem.* **1974**, *13*, 1065. (b) Barron, P. F.; Dyason, J. C.; Engelhardt, L. M.; Healy, P. C.; White, A. H. *Inorg. Chem.* **1984**, *23*, 3766.

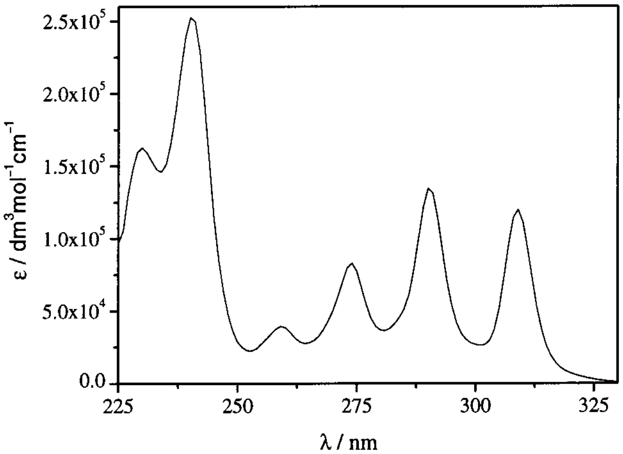

Figure 4. UV−vis absorption spectrum of **4** in dichloromethane at 298 K.

Table 3. UV−Visible Absorption Data of Complexes 1−5 in Dichloromethane

complex	λ_{max}/nm (ϵ/dm^3 mol^{-1} cm $^{-1}$)
1	226 (58700), 237 (59100), 248 (66100), 262 (82000), 275 (83800), 291 (sh, 34400)
2	242 (28700), 253 (38800), 265 (49100), 278 (48200), 300 (sh, 14200)
3	261 (56200), 272 (54400), 283 (53000), 303 (sh, 24800)
4	240 (252000), 259 (39500), 274 (82800), 290 (135000), 309 (120000)
5	298 (sh, 113000), 310 (132000), 317 (sh, 127000), 332 (120000)

carbon bond distance between them is 1.386 Å, which reflects partial multiple bond character. The phenylbutadiynyl ligands are not significantly distorted from linearity, as indicated by the angles C(73)−C(74)−C(75) (178.4(4)°), C(75)−C(76)−C(77) (173.4(5)°), C(93)−C(94)−C(95) (176.4(4)°), and C(95)−C(96)−C(97) (175.0(4)°). The four Ag−P bond distances (mean 2.43 Å) fall in the same range as **1**−**3** and **5**, whereas the P−Ag−C angles vary from 103.98(8)° to 138.11(9)°.

Absorption Spectroscopy. All complexes in solutions are sensitive toward photodecomposition, and all photophysical measurements have been taken using freshly prepared samples. The UV−visible spectral data of complexes **1**−**5** in dichloromethane (Table 3; see Figure 4 for **4**) show the intense, vibronically structured absorptions at 250−332 nm (ϵ 10^4−10^5 dm^3 mol^{-1} cm^{-1}), which are attributed to ligand-localized transitions. Since the aliphatic PCy$_3$ ligands are optically transparent in the UV region $\lambda \geq 250$ nm, the high-energy absorptions in **1**−**5** are assigned as singlet intraligand $\pi \rightarrow \pi^*$(arylacetylide) transitions. For **1**, the well-resolved structured absorption bands at 226−291 nm exhibit vibrational spacings of 1804−2155 cm^{-1}, which are typical for ν(C≡C) stretching frequencies of the phenylacetylide group. These spacings show disparity to that of 1098−1865 cm^{-1} observed for [Au(C≡CPh)(PCy$_3$)][30] at 249−290 nm, which involve mixing between $^1(\pi\pi^*)$ acetylenic and $^1(\pi\pi^*)$ aryl states. Absorption bands in a similar range have been reported for the silver(I) [Ag$_3$(C≡CPh)$_2$(dppm)$_3$]Cl[6a] and gold(I) phenylacetylide complexes, namely, [Au(L)(C≡CPh)] (L = PPh$_3$,[4a] PMe$_3$[31]) and [{Au(C≡CPh)}$_2$(μ-dppe)] (dppe = 1,2-bis(diphenylphosphino)ethane).[4a] On the contrary, the copper analogues such as [Cu$_4$(μ_3-η^1-C≡CPh)$_4$-{P(C$_6$H$_4$R)$_3$}$_4$] (R = H, F, Me, OMe),[23] which contain weak Cu−Cu interactions and arylacetylides π-coordinated to the Cu(I) centers, exhibit a variety of excited states (see below).

The electronic absorption spectrum of **2** exhibits similar vibronically structured bands at 242−278 nm with progressional spacings of 1765−1796 cm^{-1}, attributable to the ν(C≡C) stretching frequencies of the arylacetylide. In the absorption spectrum of **3**, structured bands at 261−283 nm with progressional spacings of 1429−1549 cm^{-1} are not as well resolved as those in **1** and **2**. These spacings are significantly lowered from that expected for ν(C≡C) in the acetylenic excited state. We suggest that the transition has both $^1(\pi\pi^*)$ acetylenic and $^1(\pi\pi^*)$ aryl characteristics. Complex **4** shows intense vibronically structured absorption at 259−309 nm with progressional spacings of 2114, 2013, and 2121 cm^{-1} respectively. These spacings are comparable to those observed in the absorption spectrum of the free HC≡C−C≡CPh in dichloromethane (ca. 2000 cm^{-1} at 243−285 nm). Only one vibrational progression attributed to ν(C≡C) is evident in the absorption of **4** at 259−309 nm, suggesting that the electronic transition is localized on the acetylenic C≡C−C≡C unit and assigned to the intraligand [^{1}IL: $\pi \rightarrow \pi^*$(C≡C−C≡CPh)] transition. The absorption spectrum of **5** shows two peaks at 310 and 332 nm and two shoulders at 298 and 317 nm; these transitions are slightly red-shifted from that observed in **1**−**4**. This corresponds to lowering of the $\pi \rightarrow \pi^*$ transition energy resulting from the extended conjugation system of the arylacetylide moieties in **5**.

Solid-State and Solution Emission Spectroscopy. Excitation of complexes **1**−**5** at $\lambda > 350$ nm in solid state at 298 and 77 K produces blue-white luminescence (Table 4). The room-temperature solid-state emission spectra show well-resolved vibronic structures at 415−623 nm with vibrational spacings of ca. 1100, 1600, and 2100 cm^{-1} (see Figure 5 for **1**). Such spacings are attributed to a combination of vibrational modes of the C≡C groups and aryl moieties. Upon cooling to 77 K, these emission bands are better resolved. Similar observation for [Pt(PEt$_3$)$_2$(C≡CPh)$_2$][32] was reported by Sacksteder et al. The large Stokes shift of these emissions from the corresponding singlet intraligand transitions is indicative of their triplet parentage, and they are attributed to the $^3(\pi\pi^*)$ excited states with an admixture of phenyl and acetylenic character. Comparison has been made with the mononuclear gold(I) complex [Au(PCy$_3$)(C≡CPh)],[30] in which the [Au(PCy$_3$)]$^+$ unit is isolobal to H$^+$ and does not have strong absorption at $\lambda > 250$ nm. The solid-state emission spectrum of [Au(PCy$_3$)(C≡CPh)] at 298 K displays a vibronically structured band at 421−511 nm (see Figure 5), which is at similar energy to the emission of complex **1**. This reveals the solid-state emissions of **1**−**3** to be purely intraligand in character, and the interaction(s) within the Ag$_4$ core together with the interaction(s) between the Ag$_4$ core and arylacetylides do not have any significant perturbation on the $^3(\pi\pi^*)$ emission energy of the

---

[30] Chao, H. Y. Ph.D. Thesis, The University of Hong Kong, 2001.

[31] Yam, V. W. W.; Choi, S. W. K. *J. Chem. Soc., Dalton Trans.* **1996**, 4227.

[32] Sacksteder, L. A.; Baralt, E.; DeGraff, B. A.; Lukehart, C. M.; Demas, J. N. *Inorg. Chem.* **1991**, *30*, 2468.

Table 4. Emission Data of Complexes 1−5 (λ_{ex} 350 nm)

	solid state		fluid (concentration 5×10^{-5} M)	
	298 K: λ_{max}/nm; τ_o/μs	77 K: λ_{max}/nm	298 K:[a] λ_{max}/nm; τ_o/μs; ϕ_o	77 K: λ_{max}/nm
1	422 (max), 443, 460, 497, 514, 541; 7.52	424, 442 (max), 455, 465, 477, 480, 501, 515, 547, 559 (sh), 576 (sh), 592 (sh)	418 (max), 434, 455, 480 (sh); 0.31; 0.025	426 (max), 448, 465, 490 (sh)[b]
2	428, 479 (max), 509, 516, 532 (sh), 550 (sh), 565 (sh); 0.93	427, 438, 456, 478 (max), 498, 507, 518, 530, 551, 565, 579, 607 (sh)	unstable	399, 413, 419, 426 (max), 434, 441, 449, 457, 466, 483 (sh), 495 (sh), 505 (sh)[c]
3	428, 448, 473, 496 (max), 523, 527, 542 (sh), 578 (sh); 0.88	425, 435, 451, 458, 471 (max), 496, 526, 539, 553, 575, 591, 606 (sh)	399, 435 (max), 487 (sh), 540 (sh); 0.22; 5.13×10^{-3}	401, 414, 420, 428, 436, 442, 451, 459, 469, 486 (sh), 496 (sh)[c]
4	489 (max), 547, 623 (sh); 0.30	489 (max), 510, 528, 547, 620 (sh)	464 (max), 491, 514, 543 (sh), 579 (sh); 0.29; 0.033	442 (max), 452, 462, 475, 490, 499, 514, 531, 548[b]
5	515 (max), 547; 0.50	515, 544 (max), 570, 592, 612	510 (very weak)	520, 542 (max), 567[b]

[a] In dichloromethane; decomposition observed after data collection. [b] In MeOH/EtOH (4:1). [c] In butyronitrile.

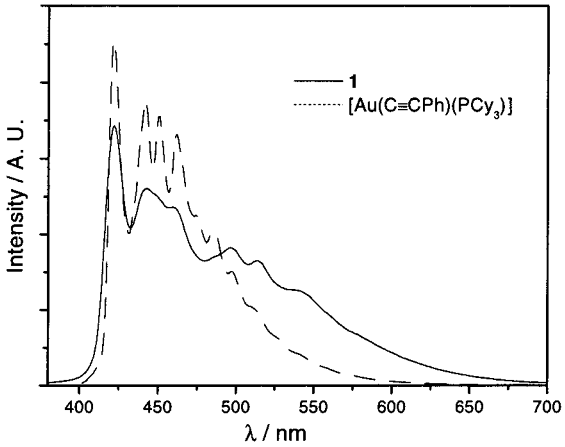

Figure 5. Solid-state emission spectra of **1** and $[Au(PCy_3)(C{\equiv}CPh)]$ at 298 K (λ_{ex} 350 nm).

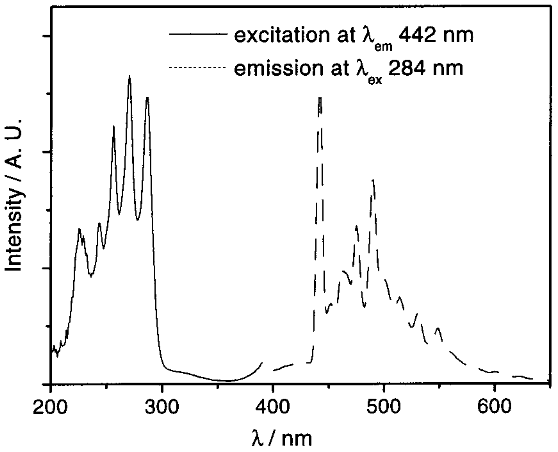

Figure 6. Normalized excitation and emission spectra (λ_{em} 442 nm; λ_{ex} 284 nm) of **4** in MeOH/EtOH (4:1) at 77 K.

arylacetylides. The room-temperature solid-state emission of **4** with peak maxima at 489 and 547 nm is slightly red-shifted in energy from the emission of $[Au(PCy_3)(C{\equiv}C{-}C{\equiv}CPh)]$ with peak maxima at 466 and 519 nm;[30] both emissions display similar progressional spacings (2168 cm^{-1} in **4**, 2191 cm^{-1} in $[Au(PCy_3)(C{\equiv}C{-}C{\equiv}CPh)]$). The solid-state emission of **5** (λ_{max} 515 nm at 298 K; 544 nm at 77 K) is comparable in energy to that of the mononuclear gold(I) congener $[Au(PCy_3)(C{\equiv}CC_6H_4C{\equiv}CPh)]$ (λ_{max} 516 nm at 298 K; 541 nm at 77 K) but red-shifts from the emissions of **1**−**4**. We tentatively suggest that the decrease in energy is a consequence of the extended π-conjugation in the $[Ag(C{\equiv}CC_6H_4C{\equiv}CPh)_2]$ units. Unlike gold(I) and silver(I) arylacetylides, the copper(I) analogues such as $[Cu_4(\mu_3\text{-}\eta^1\text{-}C{\equiv}CPh)_4\{P(C_6H_4R)_3\}_4]$ (R = H, F, Me, OMe)[23] usually display broad and unstructured emission with peak maxima at 510−550 nm, which are at similar or lower energy than the emissions of **1**−**3**. This suggests that the visible emission of polynuclear Cu(I) arylacetylide is unlikely to have ligand-to-metal charge transfer (LMCT) character since LMCT for Ag(I) should be at lower energy than Cu(I). For polynuclear Cu(I) arylacetylide complexes, π-coordination of arylacetylide ligands to Cu(I), and weak intramolecular Cu−Cu interactions are usually evident, and these structural features are responsible for the red-shift in emission energy from the $^3(\pi\pi^*)$ emissions of arylacetylide ligands. In this work, π-coordination of arylacetylides to Ag(I) is not evident in the crystal structures of **1**−**5** and the arylacetylides adopt a σ-μ_2 coordination mode. Unlike the copper(I) arylacetylide compounds, coordination of $[RC{\equiv}C]^-$ to Ag(I) has virtually little effect on the intraligand $^3(\pi\pi^*)$ emission energy. For those Au(I) arylacetylides without Au−Au interaction, only σ-coordination of arylacetylide to Au(I) dominates, and this causes no significant perturbation on the intraligand $\pi \rightarrow \pi^*$ transition. For $[\{Au(C{\equiv}CPh)\}_2(\mu\text{-dppe})]$,[4a] its solid-state emission occurs at 550 nm and this was previously attributed to arise from intramolecular Au−Au interaction in the crystal lattice, which causes a red-shift in emission energy from the intraligand $^3(\pi\pi^*)$ emission.

Emission data for complexes **1**−**5** in dichloromethane at 298 K and in glassy MeOH/EtOH (4:1) or butyronitrile solutions at 77 K are listed in Table 4. The room-temperature emissions in dichloromethane solutions are very weak (λ_{max} 360−550 nm) and slowly change against time of measurement. Weak emission observed in dichloromethane solution of **1** at 418−480 nm is virtually at the same wavelength range as that in the mononuclear $[Au(PCy_3)(C{\equiv}CPh)]$[30] counterpart, suggesting that the emissions are attributed to the $^3(\pi\pi^*)$ excited states of the phenylacetylide ligands. Compound **5** emits weakly in dichloromethane at 510 nm, which is similarly attributed to come from the $^3(\pi\pi^*)$ excited state localized on the acetylenic unit.

Complexes **1**−**5** in 77 K glassy solutions display intense vibronically structured emissions at 399−567 nm with progressional spacings of ~1100−2000 cm^{-1}. The excitation and emission spectra of **4** (Figure 6) in 77 K glassy MeOH/EtOH solution illustrate the large

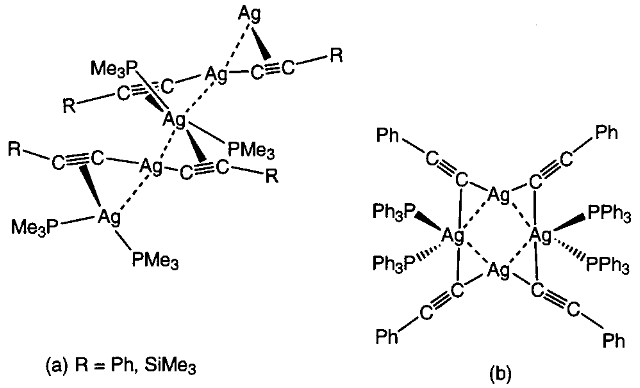

Figure 7. Examples of Ag(I) acetylide aggregates bearing phosphine ligands: (a) polymeric chains of $[Me_3PAgC{\equiv}CR]_\infty$ (R = Ph,[33] $SiMe_3$[26]) and (b) $[Ph_3PAgC{\equiv}CPh]_4$.[26]

Stokes shift of the emission, and hence $^3(\pi\pi^*)$ excited states of the arylacetylide ligands are assigned.

General Remarks

An early example of silver(I) acetylide compounds with phosphine ligands, namely, $[Me_3PAgC{\equiv}CPh]_\infty$,[33] shows infinite polymeric chains of silver atoms. A similar chain-like structure is also found for $[Me_3PAgC{\equiv}CSiMe_3]_\infty$[26] (Figure 7a), showing that alternation of phenyl- to trimethylsilylacetylide does not influence the structure of these polymeric chains. However, when the PMe_3 is replaced by the more bulky PPh_3 unit, the tetrameric $[Ph_3PAgC{\equiv}CPh]_4{\cdot}3.5THF$[26] with a “flat-butterfly” geometry is observed (Figure 7b). Undoubtedly, the nature of the phosphine auxiliaries plays an important role in the formation of the $[Ag(C{\equiv}CR)]_n$ aggregate. In this work, we have employed tricyclohexylphosphine ligand, which has a large cone angle (170°).[34] The molecular structures of $[Ag_4(\mu\text{-}C{\equiv}CC_6H_4R\text{-}p)_4(PCy_3)_2]$ (R = H (**1**), CH_3 (**2**), OCH_3 (**3**), and $C{\equiv}CPh$ (**5**)) reveal that these tetranuclear assemblies are constructed from $[Ag(C{\equiv}CC_6H_4R\text{-}p)_2]$ and $[Ag(PCy_3)]$ units with a phosphine-to-arylacetylide ratio of 1:2. This is in contrast to the 1:1 ratio found for $[Ph_3PAgC{\equiv}CPh]_4{\cdot}3.5THF$ and $[Me_3PAgC{\equiv}CPh]_\infty$. This decrease in ratio originates from the bulkiness of the PCy_3 ligand. Furthermore, steric repulsion between the cyclohexyl and aryl moieties in **1**−**3** and **5** results in two kinds of Ag(I), one with σ-coordination to two arylacetylides and the other with σ-coordination to a PCy_3 group. The Ag(PCy_3) and $[Ag(C{\equiv}CR)_2]$ fragments are held together via σ-coordination of arylacetylide to Ag(I) and weak Ag(I)−Ag(I) interactions.

The molecular structure of **4** bearing phenylbutadiynyl ligands depicts a twisted cubane-type aggregate with 1:1 PCy_3-to-[Ph−C≡C−C≡C] ratio, which is similar to the tetrameric copper(I) complex $[Ph_3PCuC{\equiv}CPh]_4$[5b] and related derivatives.[23] Compared to **1**−**3** and **5**, the extended butadiynyl ligand apparently alleviates steric strain between the Cy and aryl groups and facilitates coordination of a PCy_3 ligand per Ag atom. In summary, the structural variations in these tetranuclear silver(I) complexes can be rationalized in terms of intramolecular repulsion involving the bulky PCy_3 and the arylacetylide ligands. The adoption of differing structural motifs appears to be controlled by the steric influence of both phosphine and acetylide auxiliaries.

Employment of the aliphatic PCy_3 ligand makes spectroscopic assignments less complicated. The large cone angle of PCy_3 maintains its steric bulkiness as that in PPh_3. Absorption spectra of the complexes in this work are dominated by the vibronically structured singlet $\pi \rightarrow \pi^*$ transition(s) of the arylacetylides in the UV region; the metal-centered, Ag(I)-to-arylacetylide and/or arylacetylide-to-Ag(I) charge-transfer transitions have not been located at $\lambda \geq 250$ nm despite the structural data revealing that both arylacetylide-to-Ag(I) and Ag(I)−Ag(I) interactions are evident in the crystal structures of the complexes. When comparing the emission data of these Ag(I) arylacetylides with that of the mononuclear gold(I) counterparts, the emission is characteristic of the triplet intraligand $^3(\pi\pi^*)$ excited state. Upon coordinating arylacetylide to Au(I) or Ag(I), the triplet intraligand emission is enhanced and readily tuned by varying the π-conjugation along the arylacetylide unit. Previously studied Cu(I) arylacetylides usually display long-lived, intense, and lower energy emission which show significant disparity in photophysical properties from that of Ag(I) and Au(I) congeners. Since the LMCT excited states of Ag(I) are expected to occur at lower energy than that of Cu(I), the triplet emission from polynuclear Cu(I)−arylacetylides is unlikely to have LMCT character in view of the present findings. For the Ag_4 complexes studied in this work, the Ag−Ag and arylacetylide-to-Ag(I) interactions have little effect upon the intraligand $^3(\pi\pi^*)$ emission energy. Whether this would mean that Ag(I) functions merely as a Lewis acid like a monovalent cation within the $[Ag(C{\equiv}CR)]_n$ aggregates would require more studies to validate.

Acknowledgment. We are grateful for financial support from The University of Hong Kong, the HKU Large Item Equipment Grant, and the Research Grants Council of the Hong Kong SAR, China [HKU 7298/99P]. We thank Dr. N. Zhu for the structural determination.

Supporting Information Available: Listings of crystal data, atomic coordinates, calculated coordinates, anisotropic displacement parameters, and bond lengths and angles for **1**−**3**, **4**·$0.5Et_2O$, and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM010835Y

---

[33] Corfield, P. W. R.; Shearer, H. M. M. *Acta Crystallogr.* **1966**, *20*, 502.

[34] Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.