Synthesis and Characterization of New Silver Complexes of Alkynes. Single-Crystal Structures of (1,1,1,5,5,5-Hexafluoro-2,4-pentanedionato)-(diphenylacetylene)silver and Tetrakis(1,1,1,5,5,5hexafluoro-2,4-pentanedionato)bis(4-octyne)tetrasilver

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Summary: Novel silver alkyne complexes of the empirical formula $[(hfac)Ag]_{n}L$, where hfac = 1, 1, 1, 5, 5, 5-hexafluoro-2,4-pentanedionato and n = 1 for L = diphenylacetylene(1) and bis(trimethylsilyl)acetylene (2) and n = 2 for L = 2-butyne (3), 2-hexyne (4), 3-hexyne (5), and 4-octyne (6), were prepared from reactions of Ag_2O with hfach in the presence of the corresponding alkynes. X-ray single-crystal diffraction analyses reveal that compound 1 is a mononuclear silver complex with a coordination number of 3 and compound $\mathbf{\hat{6}}$ is a tetranuclear silver species in which each silver atom is four-coordinate.

Introduction

It has been shown that $(\beta$ -diketonato)copper(I) complexes of alkynes are suitable for chemical vapor deposition (CVD) of pure copper films.¹ The synthesis and structural characterization of the analogous compounds of silver have not been reported, although they have been mentioned in the patent literature.² As a matter of fact, relatively few examples of silver complexes of alkynes have been reported.³ Most of these compounds contain silver centers asymmetrically π -coordinated with acetylenic C=C bonds which σ -bond to other metals.⁴⁻⁹ The only two examples of symmetrically

502

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 π -coordinated alkyne complexes are [Ag(TBC)₂]⁺, where TBC = 1,2:5,6:9,10-tribenzocyclododeca-1,5,9-triene-3,7,11-trivne,¹⁰ and the polymeric species [(CF₃SO₃)- $AgL_{I_{II}}$, where L = 1.6-cyclodecadiyne, 1.7-cyclododecadiyne, and 1,8-cyclotetradecadiyne.11 Thus, it is valuable to investigate the preparation and structural properties of (β -diketonato)silver alkyne compounds and their potential as CVD precursors. Here we report the synthesis and characterization of several (hfac)Ag alkyne complexes (hfac = 1,1,1,5,5,5-hexafluoro-2,4-pentanedionato) and single-crystal structures of two of these compounds.

Experimental Section

General Procedures and Starting Materials. All operations were performed under an atmosphere of nitrogen purified by passage through columns of activated BASF catalyst and molecular sieves and using standard Schlenk techniques¹² in conjunction with a double-manifold vacuum line. All hydrocarbon and ethereal solvents were dried and distilled from sodium benzophenone ketyl at atmospheric pressure before use. Silver(I) oxide, 1,1,1,5,5,5-hexafluoro-2,4pentanedione, diphenylacetylene, bis(trimethylsilyl)acetylene, 2-butyne, 2-hexyne, 3-hexyne, and 4-octyne (Aldrich Chemical Co.) were used without further purification. Elemental analyses were carried out at the National Science Council Southern Instrument Center (Department of Chemistry, National Cheng Kung University). NMR data were recorded on a Varian Gemini-200 NMR spectrometer by using the protio impurities of deuterated solvents as references for the ¹H NMR and the ¹³C signals of the solvents as references for ¹³C NMR spectroscopy. ¹⁹F NMR spectra were externally referenced to CFCl₃. Infrared data were recorded on a Perkin-Elmer Model 16 PC FTIR spectrophotometer. Melting points were measured in sealed capillaries on a Thomas-Hoover Unimelt instrument without calibration.

Synthesis and Characterization of the (hfac)Ag Complexes of Alkynes. a. (hfac)Ag(PhC=CPh) (1). A solution of diphenylacetylene (0.77 g, 4.32 mmol) in 20 mL of Et₂O was transferred to a 250-mL Schlenk flask containing a slurry

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solution of Ag₂O (0.50 g, 2.16 mmol) in Et₂O (30 mL). After the solution was stirred for 30 min and cooled to -30 °C, a solution of hfacH (0.61, 4.32 mmol) in Et₂O (30 mL) was added to the reaction flask dropwise. The solution mixture was stirred for 4 h and slowly warmed to room temperature. After filtration and removal of the volatile components *in vacuo* (0.1 Torr), a pale yellow powder was obtained. Recrystallization of the compound from hexane (10 mL) at 0 °C afforded 1.66 g (78% yield) of analytically pure, white product.

Anal. Calcd for $C_{19}H_{11}O_2F_6Ag$: C, 46.28; H, 2.25. Found: C, 46.06; H, 2.27. NMR data (C_6D_6 , 18 °C): ¹H δ 7.49 (m, 4H, *H* on diphenylacetylene), 7.02 (m, 6H, *H* on diphenylacetylene), 6.12 (s, 1H, *CH* on hfac) ppm; ¹³C{¹H} δ 177.9 (q, $J_{F-C} = 31.7$ Hz, CF₃CO on hfac), 132.8 (s), 129.4 (s), 129.2 (s), 124.3 (s) (phenyl *C*s on diphenylacetylene), 119.3 (q, $J_{F-C} = 287.3$ Hz, *C*F₃ on hfac), 90.6 (s, Ph*C*=*C*Ph), 88.1 (s, *C*H on hfac) ppm; ¹⁹F{¹H} δ -76.5 (s) ppm. IR data (KBr disk): $\nu_{C=C}$ 1963 (w), ν_{CO} 1659 (s), 1558 (m), 1524 (s), 1498 cm⁻¹. Mp: 113 °C dec.

b. (hfac)Ag(Me₃SiC=CSiMe₃) (2). White, crystalline compound 2 was prepared in 82% yield with a procedure analogous to that for the synthesis of compound 1.

Anal. Calcd for $C_{13}H_{19}O_2F_6Si_2Ag$: C, 32.17; H, 3.95. Found: C, 32.15; H, 3.95. NMR data $(C_6D_6, 18 \text{ °C})$: ¹H δ 6.17 (s, 1H, *CH* on hfac), 0.12 (s, 18H, $(CH_3)_3SiC=CSi(CH_3)_3$) ppm; ¹³C{¹H} δ 178.5 (q, $J_{F-C} = 32.2$ Hz, CF_3CO on hfac), 119.2 (q, $J_{F-C} = 287.3$ Hz, CF_3 on hfac), 108.7 (s, $(CH_3)_3SiC=CSi(CH_3)_3$), 88.4 (s, *C*H on hfac), 0.6 (s, $(CH_3)_3SiC=CSi(CH_3)_3$) ppm; ¹⁹F{¹H} δ -76.5 (s) ppm. IR data (KBr disk): $\nu_{C=C}$ 2009 (w), ν_{CO} 1655 (s), 1540 (s), 1498 (s), 1420 (m) cm⁻¹. Mp: 67 °C dec; sublima-

tion temperature 40 °C/0.1 Torr.

c. [(hfac)Ag]₂(MeC≡CMe) (3). Pale yellow, crystalline compound **3** was prepared in 78% yield following a procedure similar to that for the synthesis of compound **1**.

Anal. Calcd for $C_{14}H_8O_4F_{12}Ag_2$: C, 24.59; H, 1.18. Found: C, 24.38; H, 1.19. NMR data (C_6D_6 , 18 °C): ¹H δ 6.13 (s, 2H, CH on hfac), 1.40 (s, 6H, $H_3CC \equiv CCH_3$) ppm; ¹³C{¹H} δ 178.6 (q, $J_{F-C} = 31.9$ Hz, CF_3CO on hfac), 119.6 (q, $J_{F-C} = 292.2$ Hz, CF_3 on hfac), 89.3 (s, CH on hfac), 75.3 (s, $H_3CC \equiv CCH_3$), 5.1 (s, $H_3CC \equiv CCH_3$) ppm; ¹⁹F{¹H} δ –76.8 (s) ppm. IR data (KBr disk): $\nu_{C} \equiv C 2166$ (w), ν_{CO} 1673 (s), 1609 (s), 1530 (s) cm⁻¹. Mp: 73 °C dec.

d. $[(hfac)Ag]_2(MeC \equiv C^n Pr)$ (4). Pale yellow, crystalline compound 4 was prepared in 71% yield by using a procedure analogous to that for the synthesis of compound 1.

Anal. Calcd for $C_{16}H_{12}O_4F_{12}Ag_2$: C, 26.99; H, 1.70. Found: C, 26.53; H, 1.94. NMR data (C_6D_6 , 18 °C): ¹H δ 6.10 (s, 2H, methine *CH* on hfac), 1.80 (m, 4H, $CH_2CH_2CH_3$ on 2-hexyne), 1.42 (s, 6H, *CH*₃ on 2-hexyne), 1.27 (m, 4H, $CH_2CH_2CH_3$ on 2-hexyne), 0.74 (m, 6H, $J_{H-H} = 7.33$ Hz, $CH_2CH_2CH_2CH_3$ on 2-hexyne) ppm; ¹³C{¹H} δ 178.3 (q, $J_{F-C} = 33.0$ Hz, CF_3CO on hfac), 119.5 (q, $J_{F-C} = 288.0$ Hz, *CF*₃ on hfac), 88.5 (s, *CH* on hfac), 79.7 (s, acetylenic *C* on 2-hexyne), 76.0 (s, acetylenic *C* on 2-hexyne), 24.0 (s, $CH_2CH_2CH_3$ on 2-hexyne), 22.7 (s, $CH_2CH_2CH_3$ on 2-hexyne), 14.1 (s, $CH_2CH_2CH_3$ on 2-hexyne), 5.1 (s, *CH*₃ on 2-hexyne) ppm; ¹⁹F{¹H} δ –76.4 (s) ppm. IR data (KBr disk): $\nu_{C=C}$ 2175 (w), ν_{CO} 1658 (s), 1650 (s), 1565 (s), 1530 (s), 1493 (s) cm⁻¹. Mp: 66 °C dec.

e. [(hfac)Ag]₂(EtC≡CEt) (5). Pale yellow, crystalline compound 5 was prepared in 71% yield by using a procedure analogous to that of synthesis of compound 1.

Anal. Calcd for $C_{16}H_{12}O_4F_{12}Ag_2$: C, 26.99; H, 1.70. Found: C, 27.25; H, 2.00. NMR data (C_6D_6 , 18 °C): ¹H δ 6.13 (s, 2H, methine *CH* on hfac), 1.69 (q, 4H, $J_{H-H} = 7.50$ Hz, *CH*₂ on 3-hexyne), 0.87 (t, 6H, $J_{H-H} = 7.43$ Hz, *CH*₃ on 3-hexyne) ppm; ¹³C{¹H} δ 178.6 (q, $J_{F-C} = 31.9$ Hz, *CF*₃*CO* on hfac), 119.5 (q, $J_{F-C} = 288.0$ Hz, *CF*₃ on hfac), 88.8 (s, *CH* on hfac), 81.5 (s, $-C \equiv C-$ on 3-hexyne), 15.6 (s, *CH*₂ on 3-hexyne), 14.8 (s, *CH*₃ on 3-hexyne) ppm; ¹⁹F{¹H} δ -76.7 (s) ppm. IR data (KBr disk): $\nu_{C=C} = 2147$ (w) ν_{CO} 1655 (s), 1567 (s), 1540 (s), 1513 (s) cm⁻¹. Mp: 55 °C dec.

 Table 1.
 Summary of Crystallographic Data for Compounds 1 and 6

	1	6	
emp formula	C ₁₉ H ₁₁ O ₂ AgF ₆	C ₃₆ H ₃₂ O ₈ Ag ₄ F ₂₄	
fw	493.15	1480.06	
cryst size (mm ³)	$0.20\times0.40\times0.45$	$0.08\times0.30\times0.60$	
space group	triclinic; <i>P</i> 1	monoclinic; $P2_1/c$	
a (Å)	12.335(3)	11.475(3)	
b (Å)	12.387(3)	26.924(6)	
<i>c</i> (Å)	14.509(3)	16.549(5)	
α (deg)	68.945(17)		
β (deg)	87.751(20)	105.58(3)	
γ (deg)	66.324(20)		
$V(Å^3)$	1880.3(7)	4924.9(23)	
Ζ	4	4	
d(calcd) (g/cm ³)	1.742	1.996	
λ (Å)	0.7107	0.7107	
<i>T</i> (K)	298.00	298.00	
<i>F</i> (000)	968	2849	
2θ range (deg)	15.52 - 25.60	16.66 - 30.52	
scan type	$\theta/2\theta$	$\theta/2\theta$	
scan speed (deg/min)	2.06 - 8.24	2.06 - 8.24	
scan width (deg)	$2(0.60 + 0.35 \tan \theta)$	$2(0.70 + 0.35 \tan \theta)$	
$2 heta_{ m max}$	45.0	45.0	
$\mu ({\rm cm}^{-1})$	11.266	16.848	
transmissn	0.864; 1.000	0.749; 1.000	
index ranges	-12 < h < 13	-12 < h < 11	
_	0 < k < 13	0 < k < 28	
	-14 < l < 15	0 < <i>l</i> < 17	
R_{F} ; R_{w}^{a}	0.037; 0.040	0.047; 0.049	
goodness of fit ^b	2.00	1.11	
weights scheme	$1/\sigma^2(F_0)$	$1/\sigma^2(F_0)$	
refinement program	NRCVAX	NRCVAX	
no. of atoms	78	104	
no. of params refined	506	650	
largest Δ/σ	0.0243	0.0298	

 ${}^{a}R_{F} = \sum (F_{0} - F_{c})/\sum F_{0}$. $R_{w} = (\sum [w(F_{0} - F_{c})^{2}]/\sum (wF_{0}^{2}))^{1/2}$. b Goodness of fit = $[\sum [w(F_{0} - F_{c})^{2}]/[(no. of reflections) - (no. of parameters)]]^{1/2}$.

f. $[(hfac)Ag]_2(^{n}PrC \equiv C^{n}Pr)$ (6). White, crystalline compound **6** was prepared in 70% yield by using a procedure analogous to that of synthesis of compound **1**.

Anal. Calcd for $C_{18}H_{16}O_4F_{12}Ag_2$: C, 29.21; H, 2.18. Found: C, 28.86; H, 2.08. NMR data (C_6D_6 , 18 °C): ¹H δ 6.15 (s, 2H, methine *CH* on hfac), 1.86 (t, 4H, $J_{H-H} = 7.04$ Hz, CH_2CH_2 -CH₃ on 4-octyne), 1.27 (m, 4H, CH₂CH₂CH₃ on 4-octyne), 0.76 (t, 6H, $J_{H-H} = 7.27$ Hz, *CH*₃ on 4-octyne) ppm; ¹³C{¹H} δ 177.4 (q, $J_{F-C} = 32.0$ Hz, CF₃*C*O on hfac), 118.7 (q, $J_{F-C} = 287.6$ Hz, *CF*₃ on hfac), 87.3 (s, *C*H on hfac), 80.0 (s, $-C \equiv C -$ on 4-octyne), 23.1 (s, *C*H₂CH₂CH₃ on 4-octyne), 21.7 (s, CH₂CH₂CH₃ on 4-octyne), 13.3 (s, *C*H₃ on 4-octyne) ppm; ¹⁹F{¹H} δ -76.4 (s) ppm. IR data (KBr disk): $\nu_{C=C} = 2176$ (w), ν_{CO} 1682 (s), 1659 (s), 1563 (s) 1513 (s) cm⁻¹. Mp: 67 °C dec.

X-ray Single-Crystal Structure Determination. Two examples of the title compounds were characterized structurally in the solid state by single-crystal X-ray diffraction. All diffraction data were collected on an Enraf-Nonius CAD-4 diffractometer with monochromated Mo K α radiation ($\lambda = 0.709$ 30 Å) using the $\theta/2\theta$ scan mode. Crystal, collection, and refinement data are summarized in Table 1.

a. (hfac)Ag(PhC=CPh) (1). White cubic crystals of compound 1 were grown by crystallization from a hexane–diethyl ether mixed solution at -20 °C, and a single crystal of dimensions $0.20 \times 0.40 \times 0.45$ mm³ was selected for X-ray analysis. Cell parameters were determined from the fit of 25 reflections (15.52 < 2θ < 25.60°). All data were corrected for Lorentz and polarization effects and for effects of absorption. A total of 4900 reflections was collected, but only 3441 unique reflections with $I > 2\sigma(I)$ were used for structure solution and refinement. The structure was solved by the heavy-atom method and refined by full-matrix least squares based on F values. All non-hydrogen atoms were refined with anisotropic thermal parameters. The final agreement factors are $R_F =$

0.037 and $R_w = 0.040$ with $w = 1/\sigma^2(F_o)$. The atomic scattering factors were taken from ref 13.

b. [(hfac)Ag]₂("**PrC**=**C**"**Pr**) (6). White needlelike crystals of compound 6 were grown by crystallization from hexane solution at -20 °C, and a single crystal of dimensions $0.08 \times 0.30 \times 0.60$ mm³ was selected for X-ray analysis. Cell parameters were determined from the fit of 25 reflections (16.66 < 2θ < 30.52°). All data were corrected for Lorentz and polarization effects and for effects of absorption. A total of 6414 reflections was collected, but only 3397 unique reflections with $I > 2\sigma(I)$ were used for structure solution and refinement. The structure was solved by the heavy-atom method and refined by full-matrix least squares based on F values. All non-hydrogen atoms were refined with anisotropic thermal parameters. The final agreement factors are $R_F = 0.047$ and $R_w = 0.049$ with $w = 1/\sigma^2(F_0)$. The atomic scattering factors were taken from ref 13.

Results and Discussion

The title compounds were prepared from reactions of Ag₂O with hfacH in the presence of the corresponding alkyne according to eq 1. These reactions were carried

$$Ag_{2}O + 2hfacH + excess RC≡CR' \rightarrow$$

$$[(hfac)Ag]_{n}(RC≡CR') + H_{2}O (1)$$

$$1-6$$

$$n = 1: R = R' = Ph (1); R = R' = Me_{3}Si (2)$$

$$n = 2$$
: R = R' = Me (**3**); R = Me, R' = ⁿPr (**4**);

$$R = R' = Et$$
 (5): $R = R' = {}^{n}Pr$ (6)

out in Et₂O solutions, and products were isolated by extraction with hexane and removal of volatile species in vacuo. Two kinds of compounds were obtained. The integrated ¹H NMR spectra of these compounds show that they have the empirical formula $[(hfac)Ag]_{n}L$, in which n = 1 for L = diphenylacetylene (1) and bis-(trimethylsilyl)acetylene (**2**) and n = 2 for L = 2-butyne (3), 2-hexyne (4), 3-hexyne (5), and 4-octyne (6). Elemental analyses of these compounds are consistent with the formula. They are thermally stable at ambient temperature and moderately sensitive to air, moisture, and light. Examination of the volatility of these compounds has been carried out by sublimation under reduced pressure (about 100 mTorr). Compound 2 can be sublimed without decomposition at 40 °C; the others decomposed before sublimination occurred. The ¹³C NMR resonances of the acetylenic carbons for compounds 1-6 are slightly upfield (0.1-5.9 ppm) relative to these for the free alkynes. This feature implies weak interaction between the $C \equiv C$ triple bond and silver center in the title compounds.

The molecular structures of compounds **1** and **6** were determined in the solid state by single-crystal X-ray diffraction analyses. The crystal, collection, and refinement data are summarized in Table 1. Selected bond lengths and bond angles are given in Tables 2 and 3 for compounds **1** and **6**, respectively. Two independent molecules of compound **1** exist in the unit cell. An ORTEP plot of one molecule is shown in Figure 1. This compound is mononuclear in the solid state, and the coordination geometry about the silver center is approximately trigonal-planar and resembles those of (β -

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

(4		ompound -		
Bond Lengths				
Ag(1a) - O(1a)	2.234(4)	Ag(b) - O(1b)	2.229(4)	
Ag(1a) - O(2a)	2.228(4)	Ag(1b) - O(2b)	2.231(4)	
Ag(1a) - C(1a)	2.261(6)	Ag(1b)-C(1b)	2.272(5)	
Ag(1a) - C(2a)	2.263(6)	Ag(1b) - C(2b)	2.278(5)	
O(1a)-C(16a)	1.238(7)	O(1b) - C(16b)	1.258(7)	
O(2a)-C(18a)	1.243(7)	O(1b)-C(18b)	1.231(7)	
C(1a)-C(2a)	1.208(8)	C(1b)-C(2b)	1.201(8)	
C(16a)-C(17a)	1.393(8)	C(16b)-C(17b)	1.372(8)	
C(17a)-C(18a)	1.380(8)	C(17b)-C(18b)	1.389(8)	
Bond Angles				
O(1a) - Ag(1a) - O(2a)	84.22(14)	O(1b) - Ag(1b) - O(2b)	83.97(14)	
O(1a) - Ag(1a) - C(1a)	121.37(18)	O(1b) - Ag(1b) - C(1b)	119.80(17)	
O(1a) - Ag(1a) - C(2a)	152.32(18)	O(1b) - Ag(1b) - C(2b)	150.42(17)	
O(2a) - Ag(1a) - C(1a)	154.36(18)	O(2b) - Ag(1b) - C(1b)	156.18(17)	
O(2a) - Ag(1a) - C(2a)	123.46(18)	O(2b) - Ag(1b) - C(2b)	125.61(17)	
C(1a) - Ag(1a) - C(2a)	30.98(21)	C(1b)-Ag(1b)-C(2b)	30.62(20)	
Ag(1a) - C(1a) - C(2a)	74.6(4)	Ag(1b)-C(1b)-C(2b)	75.0(4)	
Ag(1a)-C(1a)-C(3a)	119.7(4)	Ag(1b)-C(1b)-C(3b)	117.8(4)	
Ag(1a) - C(2a) - C(1a)	74.4(4)	Ag(1b)-C(2b)-C(1b)	74.4(4)	
Ag(1a) - C(2a) - C(9a)	119.7(4)	Ag(1b)-C(2b)-C(9b)	117.2(4)	
C(2a)-C(1a)-C(3a)	167.5(6)	C(2b) - C(1b) - C(3b)	167.2(6)	
C(1a)-C(2a)-C(9a)	165.9(6)	C(1b) - C(2b) - C(9b)	168.4(6)	

Table 3. Selected Bond Lengths (Å) and Angles (deg) for Compound 6

Bond Lengths Ag(1) - O(1)2.383(9)2.347(15) Ag(1) - C(4)Ag(1)-O(3) Ag(1) - C(5)2.332(15) 2.418(9)Ag(1) - O(5)2.506(9)C(4) - C(5)1.12(3)Ag(4)-C(12) Ag(2) - O(3)2.500(9)2.305(15)Ag(2)-O(4) 2.424(8)Ag(4)-C(13) 2.328(20)Ag(2) - O(5)2.419(9) C(12) - C(13)1.13(3)O(1)-C(18) O(2)-C(20) Ag(2)-O(6) 2.360(8) 1.240(15) Ag(3)-O(1) 2.421(8) 1.254(15) Ag(3)-O(2) O(3)-C(23) 2.534(9)1.248(15)Ag(3) - O(7)2.391(9) O(4)-C(25) 1.257(16) Ag(3) - O(8)2.389(8) O(5)-C(28) 1.239(15) Ag(4)-O(2) O(6)-C(30) 2.417(9)1.216(15)Ag(4) - O(4)2.387(9)O(7)-C(33) 1.237(16) Ag(4)-O(8) 2.499(8) O(8)-C(35) 1.257(15) Bond Angles O(1)-Ag(3)-(2) O(1)-Ag(1)-O(3) 77.0(3) 70.0(3) O(1) - Ag(1) - O(5)81.5(3) O(1) - Ag(3) - (7)130.6(3)O(1)-Ag(3)-(8) O(3) - Ag(1) - O(5)81.0(3) 151.0(3) C(4) - Ag(1) - C(5)27.8(6) O(2) - Ag(3) - (7)147.6(3) $Ag(1) - \bar{C}(4) - C(5)$ 75.4(11) O(2)-Ag(3)-(8) 81.2(3) Ag(1) - C(5) - C(4)O(7) - Ag(3) - (8)76.6(3) 76.8(11) C(3) - C(4) - C(5)168.4(17)O(2) - Ag(4) - O(4)75.4(3) C(4) - C(5) - C(6)O(2) - Ag(4) - O(8)166.8(19) 81.4(3)O(3)-Ag(2)-O(4) 70.9(3) O(4) - Ag(4) - O(8)79.6(3) O(3)-Ag(2)-O(5) 81.1(3) C(12)-Ag(4)-C(13) 28.1(8)Ag(4) - C(12) - C(13)O(3) - Ag(2) - O(6)146.3(3) 77.1(13) O(4) - Ag(2) - O(5)151.4(3) Ag(4) - C(13) - C(12)74.8(13) O(4)-Ag(2)-O(6) C(11) - C(12) - C(13)131.6(3) 169.0(20)O(5) - Ag(2) - O(6)75.8(3) C(12)-C(13)-C(14)166.3(22)

diketonato)copper alkyne complexes.¹⁴ The atoms O(1), O(2), C(1), and C(2) are mutually coplanar, and the silver atom lies slightly above the plane (0.011(3) Å and 0.017(3) Å for molecules **a** and **b**, respectively). The Ag–O bond distances, the O–Ag–O bite angle, and other bond lengths and angles within the hfac ligand are similar to those observed for other examples of (hfac)Ag complexes.^{15–17} The coordinated alkyne shows

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Figure 1. ORTEP diagram of the molecular structure of compound **1**.

a C–C bond distance similar to that of free alkyne, C–C–Ph deformation angles of 167°, and long Ag–C bond distances (about 2.26 Å). These structural features are in agreement with poor π -back-donation from silver to the alkyne ligand.

Compound 6 is a tetranuclear species in the solid state that is similar to the analogous complex of norbornadiene [(hfac)Ag]₄(nbd)₂.¹⁷ An ORTEP diagram showing the atomic labeling scheme of this compound is presented in Figure 2. Four silver atoms lie on a plane and are bound together with bridging hfac ligands. There are two kinds of silver atoms in the molecule: Ag(1) and Ag(4) are coordinated with C=C of alkyne and three O atoms of different hfac ligands; Ag(2) and Ag(3) are coordinated with four O atoms of two chelating hfac ligands. Each silver center is four-coordinate with the coordination geometry of a distorted tetrahedron. The hfac ligands exhibit two types of coordination modes: one bridges two Ag atoms (Ag(1), Ag(2) or Ag(3), Ag(4))in a μ_2 fashion and the other bridges three Ag atoms $(Ag(1), Ag(2), Ag(4) \text{ or } Ag(1), Ag(3), Ag(4)) \text{ in a } \mu_3$



Figure 2. ORTEP diagram of the molecular structure of compound **6**.

fashion. The C \equiv C bond distances of alkynes are unusually short and not accurate because of decomposition of the compound during the data collection. Bond lengths between Ag and C of alkynes longer than those in the molecule of compound **1** indicate the weaker interaction between silver and alkyne in compound **6**.

In summary, we prepared two kinds of new silver complexes of alkynes. All compounds were characterized by analytical and spectroscopic methods. Structural properties of two compounds were determined by single-crystal X-ray diffraction analysis. Among these compounds, compound **2** is volatile and can be sublimed at 40 °C under reduced pressure (about 100 mTorr). Examination of the application of this species to chemical vapor deposition is in process.

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Supporting Information Available: Crystallographic data for compounds **1** and **6**, including tables of crystal data, atomic coordinates, bond distances bond angles, and anisotropic thermal parameters (29 pages). Ordering information is given on any current masthead page.

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