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Synthesis and Characterization of (*β*-Diketonato)silver Vinyltriethylsilane Compounds and Their Application to CVD of Silver Thin Films. Crystal Structure of the (2,2-Dimethyl-6,6,7,7,8,8,8-heptafluoro-3,5-octanedionato)silver Vinyltriethylsilane Dimer

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*Summary: New silver complexes of alkenes of empirical formula (β-diketonato)Ag(VTES), where β-diketonato = 1,1,1,5,5,5-hexafluoro-2,4-pentanedionato (hfac) (**1**), 1,1,1-trifluoro-2,4-pentanedionato (tfac) (**2**), and 2,2-dimethyl-6,6,7,7,8,8,8-heptafluoro-3,5-octanedionato (fod) (**3**) and VTES = vinyltriethylsilane, were prepared from reactions of Ag_2O with β-diketones in the presence of VTES. All compounds were characterized by elemental analyses and ^1H, ^{13}C, and ^{19}F NMR and IR spectra. The crystal structure of compound **3** determined by X-ray diffraction analysis showed a dimeric silver species with coordination of the C═C double bond of VTES, two oxygen atoms of a chelating fod ligand, and the methine C atom of another fod in the solid state. Hot-wall chemical vapor deposition experiments revealed that compound **1** is suitable as a precursor to deposit pure silver films in the temperature range 160−280 °C.*

Introduction

Metal-organic chemical vapor deposition (MOCVD) of metals attracts great research interest as the result of the important applications in the microelectronics industry.[1] For instance, CVD of aluminum and tungsten thin films can be used to deposit interconnected layers in microelectronic devices. Development of CVD of highly conductive coinage metals recently became crucial because of the reduction in dimensions of new generation microelectronic devices. Several organometallic compounds[2−7] including $[AgC(CF_3){=}CF(CF_3)]_4$, $[Ag(O_2CCF_3)]_n$, (*β*-diketonato)Ag(PR_3), and (hfac)Ag(C≡NMe) were used to deposit silver films under thermal or plasma conditions. In contrast to (*β*-diketonato)Cu(alkene) compounds being widely used as CVD precursors,[8] no silver analogue was reported to be suitable for CVD although such complexes have been known for years.[9,10] It is probably due to loss of alkene during or before these complexes are vaporized. In this paper, we report the synthesis and characterization of (*β*-diketonato)Ag(VTES) complexes, in which VTES = vinyltriethylsilane and *β*-diketonato = 1,1,1,5,5,5-hexafluoro-2,4-pentanedionato (hfac) (**1**), 1,1,1-trifluoro-2,4-pentanedionato (tfac) (**2**), and 2,2-dimethyl-6,6,7,7,8,8,8-heptafluoro-3,5-octanedionato (fod) (**3**), a unique single-crystal structure of compound **3**, and the results of hot-wall CVD experiments with compound **1** as a precursor.

Results and Discussion

Synthesis of (*β*-diketonato)Ag(VTES) Complexes. The title compounds were prepared from reactions of Ag_2O with the corresponding *β*-diketones in the presence of vinyltriethylsilane according to eq 1. The

$$Ag_2O + 2\beta\text{-diketone} + 2VTES \rightarrow 2(\beta\text{-diketonato})Ag(VTES) + H_2O \quad (1)$$

reactions were carried out in Et_2O solutions at room temperature, and products were isolated on extraction with hexane and removal of volatile species *in vacuo.* Similar methods were used to prepare other (*β*-diketonato)Ag complexes.[5,10−13] Compounds **1** and **2** are

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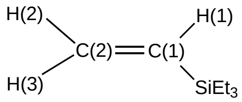
Table 1. Chemical Shifts[a] of Olefinic ^{1}H and ^{13}C NMR Resonances for VTES and Compounds 1−3

δ (Δδ[b]) (ppm)



	^{1}H			^{13}C	
	H(1)	H(2)	H(3)	C(1)	C(2)
VTES	6.11	5.98	5.68	132.7	136.5
1	5.12 (−0.99)	4.88 (−1.10)	4.69 (−0.99)	114.0 (−18.7)	124.0 (−12.5)
2	5.14 (−0.97)	5.02 (−0.96)	4.80 (−0.88)	112.9 (−19.8)	121.0 (−15.5)
3		4.92−4.49		109.9 (−22.8)	118.3 (−18.2)

[a] In C_6D_6. [b] $\Delta\delta = \delta_{\text{Ag complex}} - \delta_{\text{VTES}}$.

yellow liquids, and **3** is a white solid. They are moderately sensitive to air, moisture, and light. All compounds gave satisfactory elemental analyses and were characterized by solution ^{1}H, ^{13}C, and ^{19}F NMR and IR spectroscopic methods.

NMR Spectroscopic Studies of (β-diketonato)Ag(VTES) Complexes. The integrated ^{1}H and ^{13}C NMR spectra of the title compounds are consistent with the empirical formula (β-diketonato)Ag(VTES). Both ^{1}H and ^{13}C olefinic resonances are upfield relative to those of free vinyltriethylsilane. Comparisons of ^{1}H and ^{13}C chemical shifts for the free alkene and the alkene coordinating to the Ag(I) center were used to investigate the feature of olefin π-complexation to silver.[14,15] Variations of chemical shifts (Δδ) of olefinic protons and carbons for compounds **1**−**3** are listed in Table 1 and are larger than those for other (β-diketonato)Ag(alkene) compounds.[16] This feature implies the existence of relatively stronger bonding between the alkene and silver center in the title compounds.

Single-Crystal Structural Determination of Compound 3. Single-crystal X-ray diffraction analysis reveals that compound **3** is dimeric in the solid state. An ORTEP diagram showing the atomic labeling scheme of this molecule is presented in Figure 1. The crystal, collection, and refinement data are summarized in Table 2; selected bond lengths and bond angles are given in Table 3. The coordination geometry about silver is best described as a highly distorted tetrahedron. Each silver atom is coordinated by the C═C double bond of the VTES ligand, two oxygen atoms of a chelating fod ligand, and the methine carbon of another fod ligand. The same coordination mode for the β-diketonato ligand is reported in the structure of a dimeric trimethyl(4,6-nonanedionato)platinum complex.[17] The bond distances and angles within the β-diketonato ligand are similar to those of other (β-diketonato)silver(I) complexes according to previous reports.[5,7,12,13] The bond between Ag and methine C is relatively weak (Ag−C(4) distance = 2.423(7) Å) compared with those between silver and olefinic carbons in the same molecule (Ag−C(1) and Ag−C(2) bond distances are 2.320(8) and 2.337(9) Å, respectively). The bond distance of C═C in the coordinated olefin (C(1)−C(2) = 1.330(13) Å) similar to that of free alkene indicates weak π-back-bonding between the alkene and silver center in this compound. No other distances and angles within the VTES ligand are exceptional.

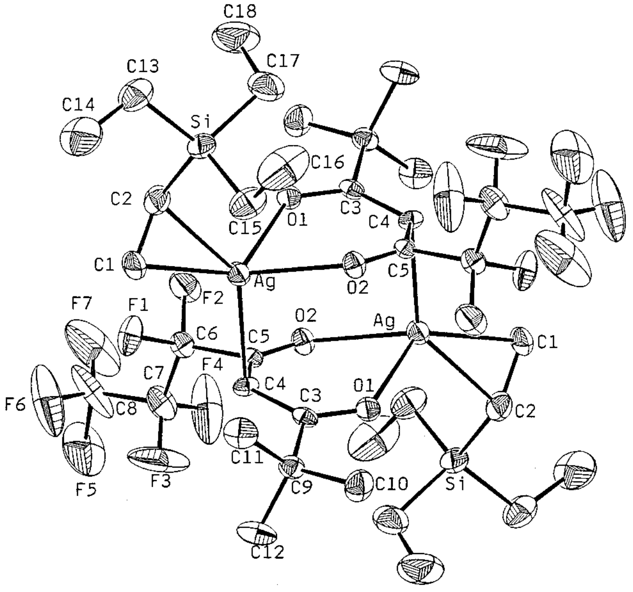


Figure 1. ORTEP diagram of the molecular structure of compound **3**.

Chemical Vapor Deposition of Silver from (hfac)Ag(VTES). Compound **1** was chosen to undertake CVD experiments since it can be evaporated at ambient temperature under reduced pressure. The experiments were carried out in the hot-wall system over the deposition temperature range 160−280 °C. The precursor was vaporized at 30 °C under reduced pressure (0.1 Torr) and was transferred through the deposition zone. Durations of deposition were 60−120 min, and the film thicknesses were about 1 μm. Continuous silver films with a metallic color and resistivities less than 5 μΩ·cm were deposited on both Si and SiO_2 substrates. All silver films had good adhesion according to the Scotch tape test. The surface morphology of the films was determined with SEM; a typical example deposited on a Si substrate at 220 °C appears in Figure 2. The films consist of continuous grains similar to those in previous reports.[4−7] The grain size increases with increasing deposition temperature. Needlelike crystals exist in the films shown in the SEM cross-

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[16] Δδ values of olefinic protons and carbons for (β-diketonato)Ag complexes of norbornadiene are −0.35 to −0.58 ppm and −0.6 to −5.6 ppm, respectively; for (β-diketonato)Ag complexes of 7-*t*-BuO-NBD the values are −0.57 to −0.66 ppm and −10.5 to −16.9 ppm, respectively. Chi, K.-M.; Chen, K.-H. Unpublished results.

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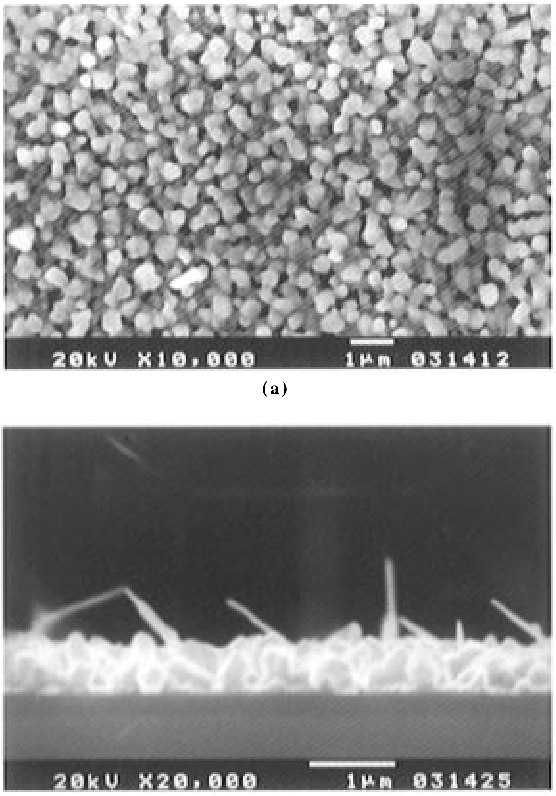
Table 2. Summary of Crystallographic Data for Compound 3

emp form	$C_{36}H_{54}O_4Ag_2F_{14}Si_2$
fw	1088.69
cryst size (mm^3)	0.10 × 0.40 × 0.50
space group	triclinic; $P\bar{1}$
a (Å)	9.943(3)
b (Å)	11.588(3)
c (Å)	11.802(5)
α (deg)	63.03(3)
β (deg)	81.30(3)
γ (deg)	89.56(3)
V (Å^3)	1195.0(7)
Z	1
d(calcd) (g/cm^3)	1.513
λ (Å)	0.7107
T (K)	298
F(000)	548
2θ range (deg)	16.82−24.16
scan type	$\theta/2\theta$
scan speed (deg/min)	3.30−8.24
scan width (deg)	$2(0.75 + 0.35 \tan \theta)$
$2\theta_{max}$	45.0
μ (cm^{-1})	9.456
transm	0.905; 1.000
index ranges	$-10 < h < 10$; $0 < k < 12$; $-10 < l < 12$
R_F; R_w[a]	0.051; 0.047
goodness-of-fit[b]	1.58
weighting scheme	$1/\sigma^2(F_o)$
refine prog	NRCVAX
no. of atoms	56
no. of params refined	263
largest Δ/σ	0.0319

[a] $R_F = \sum(F_o - F_c)/\sum F_o$. $R_w = (\sum[w(F_o - F_c)^2]/\sum(wF_o^2))^{1/2}$. [b] Goodness-to-fit = $(\sum[w(F_o - F_c)^2]/(\text{no. of reflcns} - \text{no. of params}))^{1/2}$.

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

	Bond Lengths		
Ag−O(1)	2.312(5)	Ag−O(2)	2.356(5)
Ag−C(1)	2.320(8)	Ag−C(2)	2.337(9)
Ag−C(4)	2.423(7)	O(1)−C(3)	1.251(9)
O(2)−C(5)	1.237(9)	C(1)−C(2)	1.330(13)
C(3)−C(4)	1.438(10)	C(4)−C(5)	1.402(10)
	Bond Angles		
O(1)−Ag−O(2)	77.90(17)	O(1)−Ag−C(1)	128.9(3)
O(1)−Ag−C(2)	99.5(3)	O(1)−Ag−O(4)	104.08(22)
O(2)−Ag−C(1)	130.3(3)	O(2)−Ag−C(2)	116.6(3)
O(2)−Ag−O(4)	99.27(22)	C(1)−Ag−C(2)	33.2(3)
C(1)−Ag−C(4)	109.9(3)	C(2)−Ag−C(4)	140.4(3)
Ag−O(1)−C(3)	130.5(5)	Ag−O(2)−C(5)	123.5(5)
Ag−C(1)−C(2)	74.1(5)	Ag−C(2)−C(1)	72.7(5)
Si−C(2)−C(1)	126.5(8)	O(1)−C(3)−C(4)	125.0(7)
C(3)−C(4)−C(5)	121.6(7)	O(2)−C(5)−C(4)	133.1(7)



(a)

(b)

Figure 2. Scanning electron micrographs of silver film deposited from (hfac)Ag(VTES) at 220 °C: (a) surface; (b) cross section.

section picture (Figure 2b). This crystallinity was confirmed by X-ray diffraction analyses. A diffraction pattern of a film deposited at 220 °C (Figure 3) corresponds to cubic silver. The compositions of the deposited films were characterized by Auger electron spectroscopic analyses. Purities of all silver films are greater than 96% with a trace of oxygen contamination.

In summary, we prepared new silver complexes of empirical formula (β-diketonato)Ag(VTES). All compounds were characterized by analytical and spectral methods. The structure of (fod)Ag(VTES) was determined by single-crystal X-ray diffraction analysis. CVD experiments using (hfac)Ag(VTES) as a precursor demonstrated deposition of pure silver films at temperatures above 160 °C.

Experimental Section

Syntheses and Characterization of (β-Diketonato)silver Vinyltriethylsilane Complexes. 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 techniques[18] in conjunction with a double-manifold vacuum line. Diethyl ether and hexane were dried and distilled from sodium benzophenone ketyl at atmospheric pressure before use. Silver(I) oxide, 1,1,1,5,5,5-hexafluoro-2,4-pentanedione, 1,1,1-trifluoro-2,4-pentanedione, 2,2-dimethyl-6,6,7,7,8,8,8-heptafluoro-3,5-octanedione, and vinyltriethylsilane (Aldrich Chemical Co.) were used without further purification. Elemental analyses were made 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 ^{1}H NMR and the ^{13}C signals of the solvents as references for ^{13}C NMR spectroscopies. ^{19}F NMR spectra were externally referred to $CFCl_3$. Infrared data were recorded on a Perkin-Elmer Model 16 PC FTIR spectrophotometer.

a. (hfac)Ag(VTES) (1). Vinyltriethylsilane (4.0 mL, 21.6 mmol) was transferred to a 250-mL Schlenk flask containing a suspended solution of Ag_2O (2.50 g, 10.8 mmol) in diethyl ether (50 mL). Then, a solution of hfacH (3.2 mL, 21.6 mmol) in Et_2O (20 mL) was added dropwise to the reaction flask with stirring and the reaction mixture turned yellow immediately. The mixture was stirred for 4 h at room temperature. The volatile components were removed *in vacuo* (0.1 Torr), and hexane (80 mL) was added to dissolve the product. After filtration and removal of hexane, a bright yellow liquid product was obtained in 82% yield (8.12 g).

Anal. Calcd for $C_{13}H_{19}O_2F_6AgSi$: C, 34.15; H, 4.19. Found: C, 33.77; H, 4.18. NMR data (C_6D_6, 18 °C): ^{1}H δ 6.09 (s, 1H, CH on hfac), 5.12 (dd, J_{H-H} = 19.1, 13.8 Hz, 1H, $CH_2{=}C(H)SiEt_3$ on VTES), 4.88 (dd, J_{H-H} = 13.8, 4.6 Hz, 1H,

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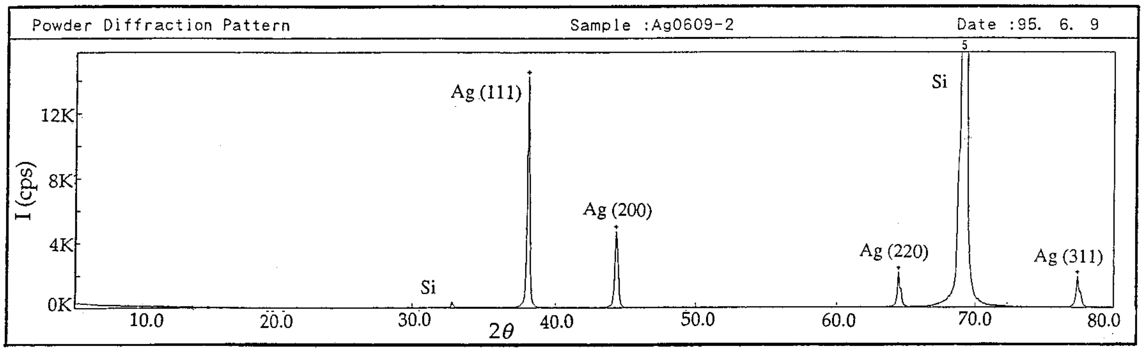

Figure 3. XRD pattern of silver film deposited from (hfac)Ag(VTES) at 220 °C.

C*H*=C(H)SiEt$_3$ on VTES), 4.69 (dd, J_{H-H} = 19.1, 4.6 Hz, 1H, C*H*=C(H)SiEt$_3$ on VTES), 0.80 (t, J_{H-H} = 7.8 Hz, 9H, C*H*$_3$ on VTES), 0.39 (q, J_{H-H} = 7.7 Hz, 6H, C*H*$_2$ on VTES) ppm. ^{13}C{^{1}H}: δ 177.8 (q, J_{F-C} = 32.3 Hz, CF$_3$*C*O on hfac), 124.0 (s, *C*H$_2$=C(H)SiEt$_3$ on VTES), 118.4 (q, J_{F-C} = 291.6 Hz, *C*F$_3$ on hfac), 114.0 (s, CH$_2$=*C*(H)SiEt$_3$ on VTES), 87.6 (s, *C*H on hfac), 7.1 (s, *C*H$_3$ on VTES), 3.4 (s, *C*H$_2$ on VTES) ppm. ^{19}F{^{1}H}: δ −76.8 (s) ppm. IR data (KBr disk) (ν_{CO}): 1663 (s), 1557 (m), 1536 (m), 1493 (s), 1473 (s) cm^{-1}.

(b). (tfac)Ag(VTES) (2). Pale yellow, liquid (tfac)Ag(VTES) was prepared in 85% yield with a procedure analogous to that of synthesis of compound **1**.

Anal. Calcd for $C_{13}H_{22}O_2F_3AgSi$: C, 38.72; H, 5.50. Found: C, 38.97; H, 5.33. NMR data (C_6D_6, 18 °C): ^{1}H δ 5.62 (s, 1H, C*H* on tfac), 5.14 (dd, J_{H-H} = 17.4, 13.8 Hz, 1H, CH$_2$=C(*H*)SiEt$_3$ on VTES), 5.02 (dd, J_{H-H} = 13.8, 6.0 Hz, 1H, C*H*=C(H)SiEt$_3$ on VTES), 4.80 (dd, J_{H-H} = 17.4, 6.0 Hz, 1H, C*H*=C(H)SiEt$_3$ on VTES), 1.82 (s, 3H, C*H*$_3$ on tfac), 0.84 (t, J_{H-H} = 7.7 Hz, 9H, C*H*$_3$ on VTES), 0.45 (q, J_{H-H} = 7.6 Hz, 6H, C*H*$_2$ on VTES) ppm. ^{13}C{^{1}H}: δ 198.4 (s, CH$_3$*C*O on tfac), 172.1 (q, J_{F-C} = 30.6 Hz, CF$_3$*C*O on tfac), 121.0 (s, *C*H$_2$=C(H)SiEt$_3$ on VTES), 119.6 (q, J_{F-C} = 285.9 Hz, *C*F$_3$ on tfac), 112.9 (s, CH$_2$=*C*(H)SiEt$_3$ on VTES), 91.8 (s, *C*H on tfac), 29.8 (s, *C*H$_3$ on tfac), 7.3 (s, *C*H$_3$ on VTES), 3.6 (s, *C*H$_2$ on VTES) ppm. ^{19}F{^{1}H}: δ −75.4 (s) ppm. IR data (KBr disk) (ν_{CO}): 1636 (s), 1530 (m), 1473 (s) cm^{-1}.

(c). (fod)Ag(VTES) (3). White, crystalline (fod)Ag(VTES) was prepared in 88% yield following a procedure similar to that of synthesis of compound **1**.

Anal. Calcd for $C_{18}H_{28}O_2F_7AgSi$: C, 39.64; H, 5.18. Found: C, 39.45; H, 5.14. NMR data (C_6D_6, 18 °C): ^{1}H δ 6.02 (s, 1H, C*H* on fod), 4.92−4.49 (m, 3H, C*H*$_2$=C(*H*)SiEt$_3$ on VTES), 1.16 (s, 9H, C(C*H*$_3$)$_3$ on fod), 0.83 (t, J_{H-H} = 7.8 Hz, 9H, C*H*$_3$ on VTES), 0.42 (q, J_{H-H} = 7.9 Hz, 6H, C*H*$_2$ on VTES) ppm. ^{13}C{^{1}H}: δ 206.7 (s, (CH$_3$)$_3$*C*O on fod), 173.0 (q, J_{F-C} = 21.2 Hz, C$_3$F$_7$*C*O on fod), 121.7−103.6 (m, *C*F$_2$*C*F$_2$*C*F$_3$ on fod), 118.3 (s, *C*H$_2$=C(H)SiEt$_3$ on VTES), 109.9 (s, CH$_2$=*C*(H)SiEt$_3$ on VTES), 89.5 (s, *C*H on fod), 42.9 (s, *C*(CH$_3$)$_3$ on fod), 28.1 (s, C(*C*H$_3$)$_3$ on fod), 7.3 (s, *C*H$_3$ on VTES), 3.4 (s, *C*H$_2$ on VTES) ppm. ^{19}F{^{1}H}: δ −80.7 (s), −118.6 (s), −126.3 (s) ppm. IR data (KBr disk) (ν_{CO}): 1631 (s), 1520 (m), 1478 (s) cm^{-1}. Mp: 70 °C (dec).

X-ray Single-Crystal Structural Determination of Compound 3. White crystals of (fod)Ag(VTES) were grown by crystallization from diethyl ether solution at −20 °C, and a single crystal of dimensions 0.10 × 0.40 × 0.50 mm^3 was selected for X-ray analysis. All diffraction data were collected on an Enraf-Nonius CAD-4 diffractometer with monochromated Mo Kα radiation (λ = 0.7107 Å) using $\theta/2\theta$ scan mode. Cell parameters were determined from 25 reflections (16.82 < 2θ < 24.16°). All data were corrected for Lorentz and polarization effects and for effects of absorption. A total of 3124 reflections were collected, but only 2094 unique reflections with $I > 2\sigma(I)$ were used for structural 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 atomic scattering factors were taken from ref 19. The final agreement factors are R_F = 0.051 and R_w = 0.047 with $w = 1/\sigma^2(F_o)$. Crystal, collection, and refinement data are summarized in Table 2.

Chemical Vapor Deposition of Silver Films from Compound 1. CVD experiments were conducted in a hot-wall reactor reported previously.[20] Silicon(100) wafers coated with 2000 Å of thermally grown SiO$_2$ were used as substrates. The substrates, typically 1.5 cm × 1.5 cm^2, were cleaned with deionized water, acetone, and 1,1,1-trichloroethane and then heated to 100 °C for 20 min before use. The CVD reactor was charged with approximately 0.5 g of (hfac)Ag(VTES) and a substrate in a glovebox with nitrogen atmosphere for each experiment. The assembled reactor was attached to a U-trap that was cooled with liquid N$_2$ and connected to a vacuum line. While the system was evacuated (0.1 Torr), the precursor was cooled with dried ice to prevent its evaporation and the deposition zone was preheated with a furnance for 1 h to attain the deposition temperature. The precursor remained at room temperature. The precursor was then warmed to 30 °C with a heating tape to transfer into the deposition zone, and deposition was continued until all precursor had evaporated. Deposition was undertaken over a temperature range 160−280 °C at 30 °C intervals. No carrier gas was used in these experiments.

Deposited films were characterized by surface analysis methods described as follows. Scanning electron micrographs were obtained on a JEOL JSM-5400 instrument. X-ray diffraction patterns were detected by a MAC Science MXP3 powder diffractometer with Cu Kα radiation (λ = 1.5045 Å). Auger electron spectroscopic analyses were made on a Fison Microlab 310D instrument at the National Science Council Southern Instrument Center (Department of Material Science, National Cheng Kung University). Film resistivities were measured with a four-point probe.

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Supporting Information Available: Crystallographic data for compound **3**, including tables of crystal data, atomic coordinates and *B* values, bond distances and angles, and anisotropic thermal parameters and text describing X-ray procedures (12 pages). Ordering information is given on any current masthead page.

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