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Synthesis and Structure of Polymeric Networks of Silver Hexafluoroacetylacetonate Complexes of THF, Toluene, and Vinyltrimethylsilane

William J. Evans,*[†] Dimitrios G. Giarikos,[†] Daniel Josell,[§] and Joseph W. Ziller[†]

Department of Chemistry, University of California, Irvine, California 92697-2025 and
Metallurgy Division, National Institute of Standards and Technology, Gaithersburg, Maryland
20899-8554

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The reaction of 1,1,1,5,5,5-hexafluoroacetylacetone (Hhfac) with Ag_2O in the presence of L = THF, toluene, and $Me_3SiCH{=}CH_2$ was studied to obtain $[Ag(hfac)L]_x$ complexes for use as chemical vapor deposition precursors. The structures and volatilities of these three complexes were compared to those of the previously synthesized $Ag(hfac)(Me_3SiC{\equiv}CSiMe_3)$, **1**, which was also crystallographically characterized for comparison. The reaction of Ag_2O with Hhfac in THF forms the polymeric complex $[Ag_4(hfac)_4(THF)_2]_\infty$, **2**, which has tetrametallic subunits with hfac ligands that bridge via oxygen and carbon. Both 4- and 5-coordinate silver metal centers are found in **2**. Ag_2O reacts with Hhfac in toluene to form a complex with a similar tetrametallic unit $[Ag_4(hfac)_4(toluene)_2]_\infty$, **3**. In this case, the tetrametallic subunits are assembled via bridging toluene molecules, and each silver is 6-coordinate. In the presence of excess vinyltrimethylsilane (vtms), Ag_2O and Hhfac form $[Ag_3(hfac)_3(vtms)]_\infty$, **4**, which contains trimetallic subunits assembled via oxygen atoms of bridging hfac ligands and 5- and 6-coordinate silver.

Introduction

Efficient and controlled deposition of metals onto substrates is an important aspect of constructing new electronic devices. Chemical vapor deposition (CVD) techniques have been used extensively for this purpose.[1−6] Among the commonly investigated molecular precursors for CVD are complexes of perfluorinated β-diketonates.[7] Recent work has demonstrated superconformal iodine-catalyzed chemical vapor deposition of copper in submicrometer dimension trenches and vias from copper hexafluoroacetylacetonate ($CF_3COCHCOCF_3$, hfac) precursors.[8−13] As a first step in attempting to extend this bottom-up feature-filling process to silver, several silver hfac precursors have been synthesized.

To fully define these compounds and to gain information on their relative volatilities, X-ray crystallographic data have been collected on four base adduct complexes of Ag(hfac) with THF, toluene, vinyl-trimethylsilane, and bis-trimethylsilyl acetylene. These studies show the propensity for Ag(hfac) units to aggregate into extended polymeric structures with these ligands, a factor that may limit volatility. Previous structural studies of Ag(hfac)L complexes have shown that most are monomeric[14−26] and that the few aggregates that exist are primarily tetramers.[14,27,28]

Results

Ag_2O reacts readily with 2 equiv of 1,1,1,5,5,5-hexafluoroacetylacetone (Hhfac) in the presence of Lewis bases to make adducts of general formula $[Ag(hfac)L_x]_y$ (eq 1). Reactions typically occurred in 4 h and were conducted at

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* E-mail: wevans@uci.edu.
[†] University of California.
[§] National Institute of Standards and Technology.

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$$Ag_2O + 2Hhfac \xrightarrow{L} 2[Ag(hfac)L_x]_y + H_2O$$

$$L = Me_3SiC{\equiv}CSiMe_3,\ \mathbf{1};\ THF,\ \mathbf{2};\ toluene,\ \mathbf{3};\ Me_3SiHC{=}CH_2,\ \mathbf{4} \quad (1)$$

subambient temperatures because of their exothermicity. Complexes **2**−**4** were made with L as the solvent. Ag(hfac)($Me_3SiC{\equiv}CSiMe_3$), **1**, was previously synthesized in this way with a 2 equiv $Me_3SiC{\equiv}CSiMe_3$ excess.

Although the synthesis and isolation of products **2**−**4** was facile, they were not readily characterized by elemental analysis and their volatilities were not similar. Complexes **2**−**4** did not show any signs of volatility at 100 °C and 4 × 10^{-6} Torr (5 × 10^{-4} Pa). Complex **1**, on the other hand, sublimes at 40 °C and 4 × 10^{-6} Torr.[28] Elemental analysis of the reaction products with L = THF, toluene, and vinyltrimethylsilane consistently gave values in which the Ag/F ratio was higher than anticipated for a 1:1 Ag:hfac adduct. In addition, the CH analysis did not indicate a 1:1 ratio of Ag/L.

To gain more definitive information about these reaction products, their X-ray crystal structures were determined. These experiments revealed that only complex **1** was monomeric and had a 1:1 Ag/L ratio. This explained in part the observed volatility differences and the analytical data.

Structural Aspects. Ag(hfac)($Me_3SiC{\equiv}CSiMe_3$), 1. The structure of **1** is the least complicated of the four complexes since it crystallizes as a monomer, as shown in Figure 1. The structure is very similar to that of Ag($PhCOCHCOCF_3$)($Me_3SiCCSiMe_3$).[29] In **1**, the two oxygen atoms of hfac, the two alkyne carbon atoms, and Ag are coplanar to 0.0283 Å. If the alkyne moiety is considered to occupy one coordination site, the complex is trigonal planar. The 1.222(6) Å C(1)−C(2) bond is in the triple bond region,[28−30] and the SiCC angles are 170.8(4)° and 173.6(4)° (Table 2), which indicate little back-bonding from silver. The hfac ligand functions as a nonbridging bidentate chelate with 2.245(3) Å Ag−O(1) and 2.251(3) Å Ag−O(2) distances in the normal range[14,27,28,31] (Table 2). These distances are shorter than the Ag−O(hfac) distances in complexes **2**−**4** which are all bridging (Tables 2 and 3). The Ag−C ($Me_3SiC{\equiv}CSiMe_3$) distances are 2.255(4) and 2.267(4) Å.

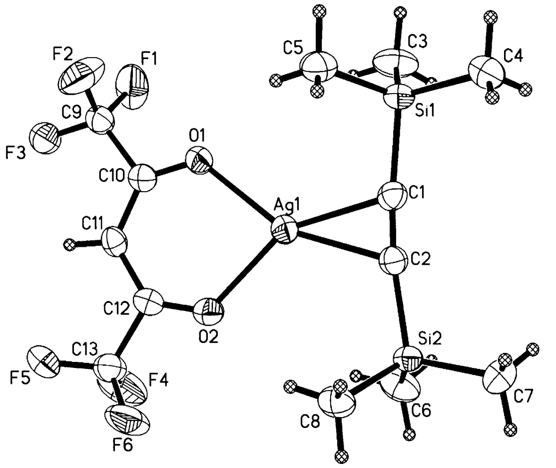

Figure 1. Thermal ellipsoid plot of Ag(hfac)($Me_3SiC{\equiv}CSiMe_3$), **1**, shown at the 50% probability level.

$[Ag_4(hfac)_4(THF)_2]_\infty$, 2. The Ag_2O/Hhfac/THF reaction product crystallizes as a polymeric material comprised of chains of tetrametallic subunits of formula $[Ag_4(hfac)_4L_2]$ in which L = THF. The chain structure is shown in Figure 2, and the tetrasilver repeat unit is in Figure 3.

In the tetrametallic unit, the four silver atoms are coplanar by symmetry and describe a parallelogram with sides of 3.617(10) Å [Ag(1)−Ag(2)] and 3.779(10) Å [Ag(1)−Ag(2A)]. The Ag−Ag−Ag angles are 59.1(2)° at Ag(1) and 120. 9(2)° at Ag(2). The four metals are connected by four bridging hfac ligands. One pair of hfac ligands uses both oxygen atoms to bridge Ag(1) and Ag(2) (O(1) and O(2) donor atoms) with 2.373(2)−2.474(2) Å Ag−O distances. The other pair of hfac ligands uses only O(3) as a bridge (2.416(2) and 2.456(2) Å) with O(4) bound only to Ag(2) at 2.352(2) Å. This arrangement places three oxygen donor atoms around each Ag(1) and four around each Ag(2).

However, each silver is further ligated. Each Ag(1) position is additionally bound by a THF with a 2.228(3) Å Ag−O distance. The extra ligation to each Ag(2) involves carbon atoms of the hfac ligands and generates the chain structure of **2** (Figure 2). This interaction occurs with the backside of the hfac ligands containing O(3) and O(4), i.e., with the part of these ligands away from the oxygen donor atoms. The closest approach of the Ag(2) sites to these bridging hfac ligands is to C(8) at a distance of 2.624(3) Å. This is a distance much longer than the Ag−C(alkyne) dis-

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Table 1. X-ray Data Collection Parameters[a] for Ag(hfac)($Me_3SiC{\equiv}CSiMe_3$), **1**; $[Ag_4(hfac)_4(THF)_2]_\infty$, **2**; $[Ag_4(hfac)_4(toluene)_2]_\infty$, **3**; and $[Ag_3(hfac)_3(vtms)]_\infty$, **4**

empirical formula	$C_{13}H_{19}F_6O_2Si_2Ag$ **1**	$[C_{28}H_{20}F_{24}O_{10}Ag_4]_\infty$ **2**	$[C_{34}H_{20}F_{24}O_8Ag_4]_\infty$ **3**	$[C_{20}H_{15}F_{18}O_6SiAg_3]_\infty$ **4**
fw	485.33	1403.92	1443.98	1045.02
T (K)	165(2)	161(2)	186(2)	165(2)
cryst syst	monoclinic	triclinic	monoclinic	triclinic
space group	$P2_1/n$	$P\bar{1}$	$C2/c$	$P\bar{1}$
a (Å)	13.1679(10)	8.0252(3)	41.271(3)	11.3415(5)
b (Å)	9.4922(7)	11.2091(4)	12.5725(10)	11.7534(5)
c (Å)	16.3439(12)	12.5306(5)	16.4444(13)	13.3836(5)
α (deg)	90	109.0870(10)	90	93.6360(10)
β (deg)	100.8260(10)	106.2580(10)	91.7670(10)	103.6640(10)
γ (deg)	90	94.9270(10)	90	114.4510(10)
V (Å^3)	2006.5(3)	1002.88(7)	8528.7(12)	1551.66(11)
Z	4	1	8	2
ρ_{calcd} (Mg/m^3)	1.607	2.325	2.249	2.237
μ (mm^{-1})	1.179	2.088	1.964	2.056
R1[b] (all data)	0.0625	0.0386	0.0441	0.0365
wR2[c] (all data)	0.1181	0.0895	0.0767	0.0865

[a] Radiation: Mo Kα ($\mu = 0.71073$ Å). Monochromator: highly oriented graphite. [b] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/[\sum[w(F_o^2)^2]]^{1/2}$.

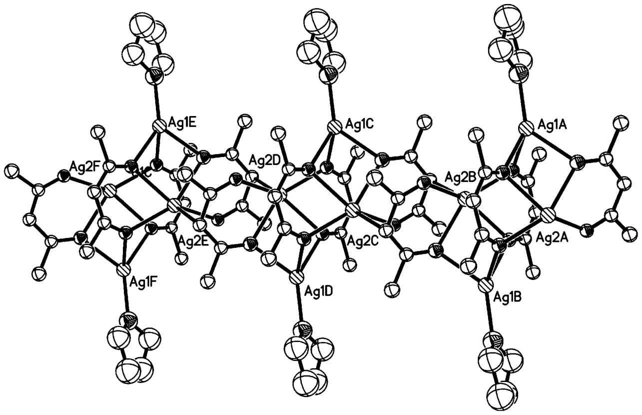

Figure 2. Chain thermal ellipsoid plot of $[Ag_4(hfac)_4(THF)_2]_\infty$, **2**, shown at the 50% probability level.

Table 2. Bond Distances (Å) in Ag(hfac)($Me_3SiC{\equiv}CSiMe_3$), **1** and $[Ag_4(hfac)_4(THF)_2]_\infty$, **2**

Bond (Å)			
1		**2**	
Ag(1)−O(1)	2.245(3)	Ag(1)−O(1)	2.373(2)
Ag(1)−O(2)	2.251(3)	Ag(1)−O(3)	2.416(2)
Ag(1)−C(1)	2.255(4)	Ag(1)−O(5)	2.228(3)
Ag(1)−C(2)	2.267(4)	Ag(1)−O(2A)	2.416(3)
C(1)−C(2)	1.222(6)	Ag(2)−O(1)	2.474(2)
		Ag(2)−O(2)	2.391(2)
		Ag(2)−O(3)	2.456(2)
		Ag(2)−O(4)	2.352(2)
		Ag(2)−C(8B)	2.624(3)
Angles for 1			
C(2)−C(1)−Si(1)	173.6(4)	C(1)−C(2)−Si(2)	170.8(4)

tances in **1**. The bridging to every Ag(2) and symmetry-related Ag(2A) located diagonally in the parallelogram generates the chain in which the Ag(2) positions are located along the long direction of the chain. Since the Ag(1) and Ag(1A) positions are oriented crossways to the Ag(2)−Ag(2A) axis and since a THF is ligated to each Ag(1), the THF ligands point out from either side of the chain perpendicular to the length of the chain, as shown in the end view (Figure 4).

$[Ag_4(hfac)_4(toluene)_2]_\infty$, 3. The Ag_2O/Hhfac/toluene reaction product is similar to **2** in that it crystallizes as a polymer of tetrametallic subunits of formula $[Ag_4(hfac)_4L_2]$ (Figure 5). Within each tetrametallic subunit shown in Figure 6, the four silver atoms are planar to only 0.30 Å and describe a distorted parallelogram with sides of 3.369(12) Å [Ag(3)−Ag(4)], 3.478(10) Å [Ag(1)−Ag(2)], 3.670(10) Å [Ag(2)−Ag(3)], and 3.733(10) Å [Ag(1)−Ag(4)]. The Ag−Ag−Ag angles are 84.7(2)°, 87.2(3)°, 90.4(2)°, and 91.0(2)°. The four bridging hfac ligands that connect the four Ag atoms all use both oxygen atoms to bridge the silver atoms. This places four oxygens around each silver at distances of 2.348(2)−2.572(2) Å.

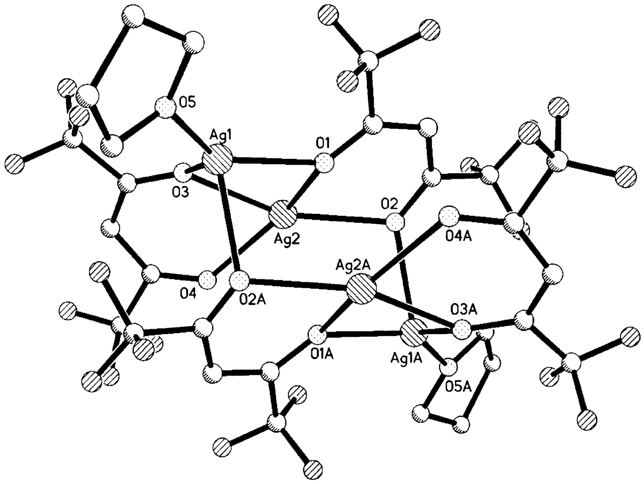

Figure 3. Ball-and-stick diagram of the subunit of $[Ag_4(hfac)_4(THF)_2]_\infty$, **2**.

However, in this L = toluene system, the polymeric structure differs from **2** in that the subunits are connected by toluene bridges and not by hfac ligands. Moreover, each Ag in the tetrametallic unit of **3** interacts with a bridging toluene, which is shared between two silver positions. As a result, all of the silver atoms are bridged and a layer structure is generated as shown in Figure 6 in a top view and in Figure 7 in a side view.

Ag(1) and Ag(3) are oriented toward carbons meta and para to the methyl group. As in **2**, the Ag−C distances in **3** are much longer than the Ag−C(alkyne) distances in **1**. Each

Table 3. Bond Distances (Å) in $[Ag_4(hfac)_4(toluene)_2]_\infty$, **3** and $[Ag_6(hfac)_6(vtms)_2]_\infty$, **4**

bond	**3**	bond	**3**	bond	**4**	bond	**4**
Ag(1)−O(1)	2.475(2)	Ag(3)−O(3)	2.572(2)	Ag(1)−O(1)	2.534(2)	Ag(3)−O(2)	2.571(2)
Ag(1)−O(2)	2.388(2)	Ag(3)−O(4)	2.436(2)	Ag(1)−O(3)	2.418(3)	Ag(3)−O(4)	2.533(3)
Ag(1)−O(6)	2.403(2)	Ag(3)−O(5)	2.386(2)	Ag(1)−O(4)	2.359(3)	Ag(3)−O(5)	2.373(3)
Ag(1)−O(8)	2.423(2)	Ag(3)−O(7)	2.348(2)	Ag(1)−C(1)	2.308(4)	Ag(3)−O(6)	2.434(3)
Ag(1)−C(30C)	2.640(4)	Ag(3)−C(21)	2.487(3)	Ag(1)−C(2)	2.365(7)	Ag(3)−O(6B)	2.372(3)
Ag(1)−C(31C)	2.455(4)	Ag(3)−C(22)	2.565(4)	Ag(1)−C(2B)	2.337(12)		
Ag(2)−O(1)	2.431(2)	Ag(4)−O(2)	2.364(2)	Ag(2)−O(1)	2.579(2)		
Ag(2)−O(4)	2.380(2)	Ag(4)−O(3)	2.383(2)	Ag(2)−O(2)	2.496(3)		
Ag(2)−O(7)	2.400(2)	Ag(4)−O(5)	2.531(2)	C(1)−C(2)	1.254(8)		
Ag(2)−O(8)	2.425(2)	Ag(4)−O(6)	2.420(2)	Ag(2)−O(5)	2.390(3)		
Ag(2)−C(28)	2.462(3)	Ag(4)−C(25)	2.503(3)	Ag(2)−O(1A)	2.404(2)		
Ag(2)−C(29)	2.699(3)	Ag(4)−C(26)	2.813(3)	Ag(2)−O(3A)	2.522(3)		

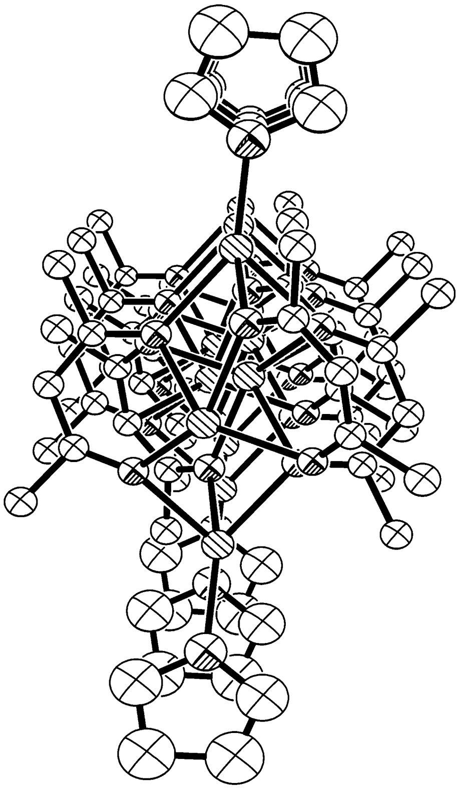

Figure 4. End view thermal ellipsoid plot of $[Ag_4(hfac)_4(THF)_2]_\infty$, **2**, shown at the 50% probability level.

has a long Ag−C distance, 2.455(4) and 2.487(3) Å, and an even longer one, 2.640(4) and 2.565(4) Å, for Ag(1) and Ag(3), respectively, but there is no pattern with respect to the meta or para positions. Ag(2) and Ag(4) have 2.462(3) and 2.503(3) Å distances to the ortho carbon and much longer 2.699(3) and 2.813(3) Å distances, respectively, to the meta carbon. These distances are typical of those in the many Ag arene structures cited in the literature.[32] The C−C distances in the toluene molecules fall in the narrow range 1.378(6)−1.402(5) Å.

$[Ag_3(hfac)_3(vtms)]_\infty$, 4. The Ag_2O/Hhfac/vinyltrimethylsilane (vtms) reaction product crystallizes as a polymeric material similar to **2** in that it is a chain structure. However, in **4**, the repeat unit is trimetallic, $[Ag_3(hfac)_3(vtms)]$, and the chain is generated by bridging hfac oxygen atoms (Figure 8).

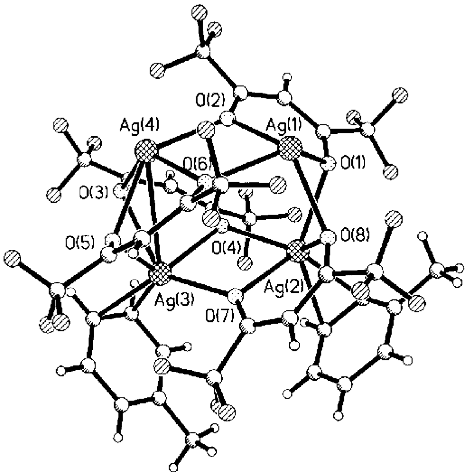

Figure 5. Ball-and-stick diagram of a subunit of $[Ag_4(hfac)_4(toluene)_2]_\infty$, **3**.

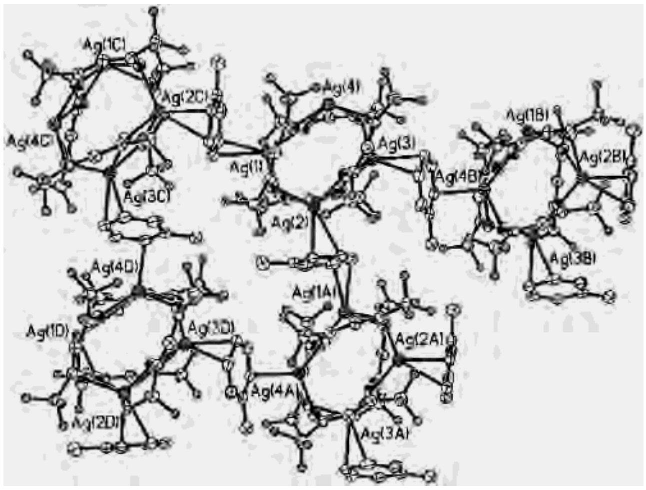

Figure 6. Thermal ellipsoid plot of the chain in $[Ag_4(hfac)_4(toluene)_2]_\infty$, **3**, shown at the 50% probability level.

The three crystallographically independent silver positions describe a distorted triangle with Ag−Ag distances of 3.341(10), 3.500(12), and 3.943(10) Å and Ag−Ag−Ag angles of 52.9(2)°, 56.7(2)°, and 70.4(3)°. Each hfac in the subunit uses one oxygen atom to connect the silver atoms within the triangle with Ag−O distances of 2.359(3)−2.571(2) Å and one oxygen to connect to another triangle with the same broad range of distances. Each Ag(1) position is bound to vinyl trimethylsilane via 2.308(4) and 2.365(7) Å Ag−C bonds. The 1.254(8) Å C(1)−C(2) bond of the vinyl substituent is in the double bond region. It is equivalent

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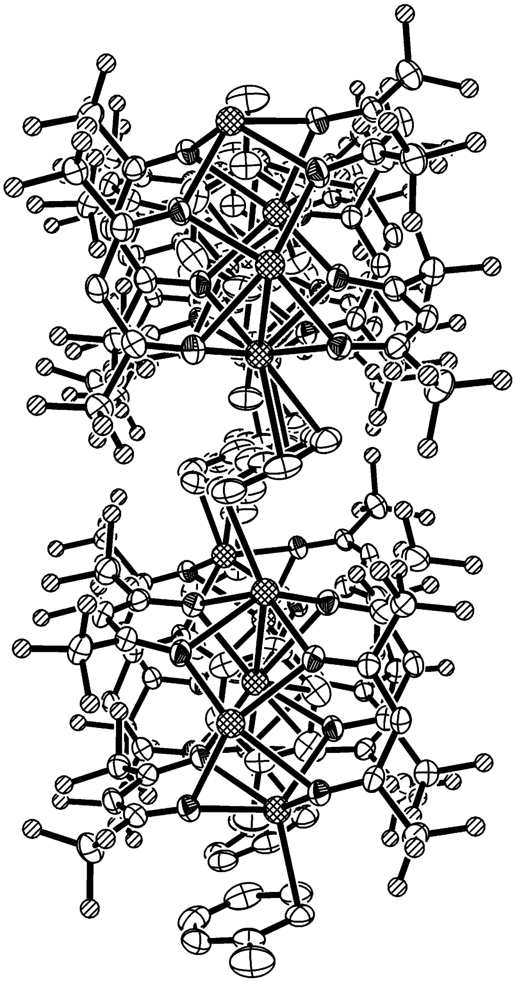

Figure 7. Edge view thermal ellipsoid plot of $[Ag_4(hfac)_4(toluene)_2]_\infty$, **3**, shown at the 50% probability level.

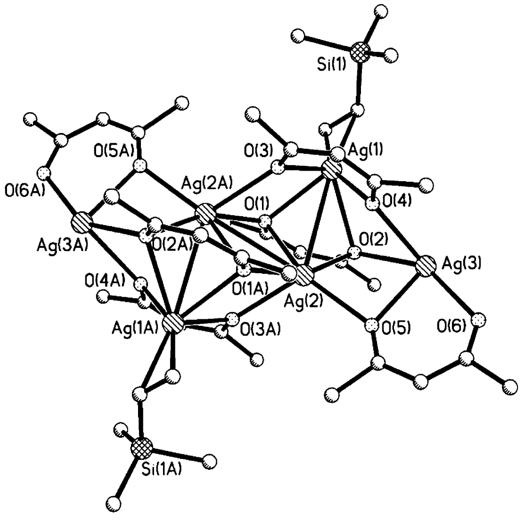

Figure 8. Ball-and-stick diagram of two units of $[Ag_3(hfac)_3(vtms)]_\infty$, **4**. Fluorine atoms are omitted for the sake of clarity.

within the error limits to the 1.330(13) Å C−C distance in $Ag(fod)(Et_3SiCH_2CH)$[33] (fod = 2,2-dimethyl-6,6,7,7,8,8,8-heptafluoro-3,5-octanedionato). As in **1,** little back-bonding from silver is found.

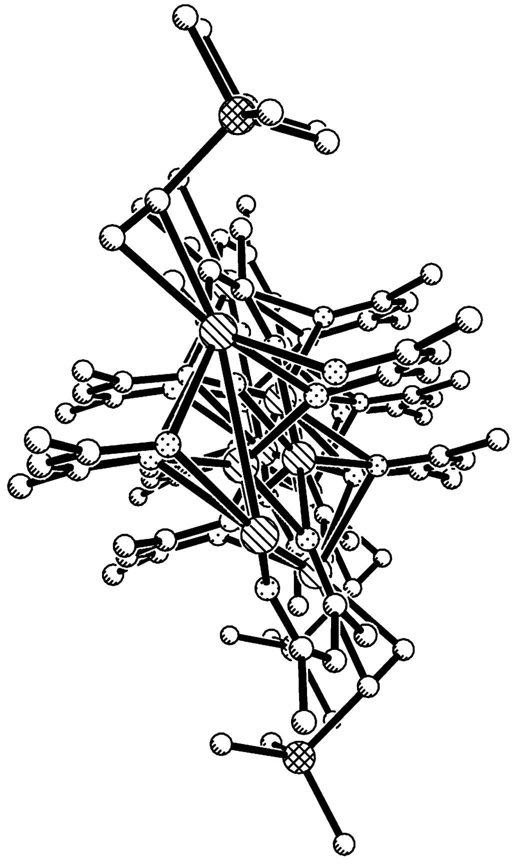

Figure 9. Edge view ball-and-stick diagram of $[Ag_3(hfac)_3(vtms)]_\infty$, **4**. Fluorine atoms are omitted for the sake of clarity.

The triangles in **4** are oriented along the chain such that Ag(1A) and Ag(2A) are bridged to the next triangle via Ag(2B) and Ag(1B) in a (triangle side) to (triangle side) fashion and Ag(3A) is bridged to the Ag(3) in the previous triangle with a (triangle point) to (triangle point) orientation. The terminal vtms ligands point out from the chain as the THF ligands do in **2** except that they are located at 1/3 of the Ag positions instead of 1/2 due to the stoichiometry. Their location is shown in the end view (Figure 9), analogous to Figure 4 for **2**.

Discussion

A variety of Ag(hfac)L complexes have been investigated for purposes of chemical vapor deposition and related processes. Monomeric complexes are typically observed with the following ligands: L = 1,4-oxathiane-S,[14] trimethylphosphine,[15] triphenylphosphine,[16] pentamethyldiethylenetriamine,[17] hexamethyltriethylenetetraamine,[33] η^2-7-*tert*-butoxynorbornadiene,[18] tetraglyme,[19,20] 4,5-η-3,3,6,6-tetramethyl-1-thia-4-cycloheptyne-1,1-dioxide,[21] diphenylacetylene,[28] and methyl isocyanide.[22] Five examples of bimetallic complexes have been observed with L = η^2,η^2-1,5-cyclooctadiene,[24] water,[14] diglyme,[16] bis(dimethylphosphino)methane,[25] and 1,5-dimethylcyclo-octa-1,5-diene.[26] To our knowledge, in the Cambridge Crystallographic Data Base, there are no trimetallic structures but there are five tetrametallic structures with L = norbornadiene,[14] *p*-iodotoluene,[27] 1,2-di-iodobenzene,[27] diethylthiol,[23] and 4-octyne.[28] For L = 1,2-di-iodobenzene

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(33) Chi, K. M.; Chen, K. H. *Organometallics* **1996**, *15*, 2575.

and Et_2S, the complexes exist as extended systems in the solid state.[27] Given this prospensity for forming monomeric complexes, it was surprising to see that three of the complexes examined here had polymeric structures despite the fact that the L ligands seemed rather innocuous with respect to bridging. In fact, only for L = toluene did the L function as the bridge.

The structural details on **3** and **4** do not reveal any particularly unusual bonding for Ag, hfac, or L. However, structure **2** is unusual in that the hfac ligand rarely bonds via the backside carbon portion. To our knowledge, this is the first Ag−C(hfac) interaction reported in the literature, although this type of bonding has been seen in $Pd(hfac)_2L$ complexes where L = dimethylamide[34] and diethylthiol.[23]

Conclusions

Although earlier studies of Ag(hfac)L complexes suggest that a wide variety of primarily monometallic complexes are accessible, the current results show that even with simple nonbridging L ligands, Ag(hfac)L compounds can form extended systems of low volatility. The hfac ligand can be sufficiently bridging via both O and C components to unexpectedly form extended networks. Hence, careful choice of ligand and solvent are likely to be crucial in obtaining the properties needed for CVD.

Experimental Section

All complexes were synthesized and handled in air. Ag(hfac)($Me_3SiC{\equiv}CSiMe_3$) was prepared as previously described.[28] Ag_2O, vinyltrimethylsilane, Hhfac, bis-trimethylsilylacetylene, toluene, diethyl ether, tetrahydrofuran, and deuterated benzene were purchased from Aldrich and used without further purification. ^1H and ^{13}C NMR spectra were obtained using Omega 500 MHz and GN 500 MHz NMR spectrometers at 23 °C. IR spectra were obtained using an ASI ReactIR 1000 spectrometer.[35] Elemental analyses were performed by Desert Analytics, Tuscon, AZ.

Synthesis of $[Ag_4(hfac)_4(THF)_2]_\infty$, 2. Hhfac (3.78 g, 18.2 mmol) was added dropwise via syringe to a suspension of silver oxide (2.11 g, 9.1 mmol) in THF (50 mL) which had been cooled to −10 °C. The mixture was stirred for 4 h and filtered through a medium filter frit to remove any insoluble unreacted Ag_2O material. Removal of solvent under vacuum yielded a white solid (5.18 g, 81%). X-ray quality crystals were grown from a diethyl ether solution during slow evaporation at room temperature. Calcd. for $Ag_4C_{28}H_{20}F_{24}O_{10}$: Ag, 30.7; C, 24.0; H, 1.4. Found: Ag, 29.3; C, 23.4; H, 1.3. ^1H NMR (C_6D_6, 23 °C): δ 6.14 (s, 4, CO*CH*CO), 3.57 (t, 8H), 1.42 (p, 8H). ^{13}C NMR (C_6D_6, 23°C): δ 177.68, 177.42, 128.89, 120.08, 117.78, 87.39, 68.23, 26.16. IR (thin film): 2961 m, 1648 s, 1548 s, 1521 s, 1482 s, 1386 m, 1324 m, 1251 s, 1200 s, 1150 s, 1081 s, 997 w, 998 w, 942 m, 845 m, 795 m, 764 w, 737 w, 699 w, 664 m cm^{-1}.

Synthesis of $[Ag_4(hfac)_4(toluene)_2]_\infty$, 3. Complex **3** (6.2 g, 84%) was prepared as described for **2** from Ag_2O (2.37 g, 10.2 mmol), Hhfac (4.25 g, 20.4 mmol), and toluene (70 mL). X-ray quality crystals were grown from a diethyl ether solution during slow evaporation at room temperature. Calcd. for $Ag_4C_{34}H_{20}F_{24}O_8$: Ag, 29.9; C, 28.3; H, 1.4. Found: Ag, 28.4; C, 27.5; H, 1.4. ^1H NMR (C_6D_6, 23 °C): δ 6.14 (s, 4, CO*CH*CO), 3.57 (t, 8H), 1.42 (p, 8H). ^{13}C NMR (C_6D_6, 23 °C): δ 138.3, 129.7, 128.9, 128.7, 128.0, 126.0, 120.0, 117.8, 32.2, 21.8. IR (thin film): 2281 m, 1640 s, 1602 w, 1548 m, 1525 s, 1482 s, 1386 w, 1324 m, 1251 s, 1204 s, 1185 s, 1158 s, 1119 s, 1081 s, 942 m, 849 w, 795 m, 756 w, 695 w, 660 m cm^{-1}.

Synthesis of $[Ag_3(hfac)_3(vtms)]_\infty$, 4. Vinyltrimethylsilane (2.66 g, 26.5 mmol) was added dropwise via syringe to a suspension of silver oxide (1.54 g, 6.65 mmol) in ether (40 mL). Hhfac (2.77 g, 13.3 mmol) was added dropwise via syringe to the suspension which was cooled to −30 °C. The solution was stirred for 4 h and filtered through a medium filter frit to remove any insoluble unreacted Ag_2O materials. Removal of solvent under vacuum yielded a white solid (3.8 g, 83%). X-ray quality crystals were grown from a diethyl ether solution during slow evaporation at room temperature. Calcd. for $Ag_3C_{20}H_{15}F_{18}Si$: Ag, 31.0; C, 23.0; H, 1.5. Found: Ag, 30.0; C, 22.7; H, 1.4. ^1H NMR (C_6D_6, 23 °C): δ 6.17 (s, 6, CO*CH*CO), 5.09, (s, 0.5H) 5.06, (s, 0.5H) 5.05, (s, 0.5H) 5.02 (s, 0.5H), 4.72, 4.71 (d, 1H), 4.69, 4.68 (d, 1H), 4.58, 4.57 (d, 1H), 4.54, 4.53 (d, 1H), −0.10 (s, 18H). ^{13}C NMR (C_6D_6, 23 °C): δ 286.8, 255.4, 177.9, 177.7, 177.4, 122.4, 120.0, 117.8, 113.7, 87.7, 26.16, −1.31. IR (thin film): 2980 m, 2887 m, 1648 s, 1556 s, 1529 s, 1482 m, 1444 s, 1386 m, 1332 m, 1251 s, 1189 s, 1162 s, 1127 s, 1085 s, 1050 m, 1000 m, 998 m, 942 m, 842 s, 803 m, 760 m, 699 w, 664 m cm^{-1}.

X-ray Data Collection, Structure Determination, and Refinement for 1−4. X-ray crystallographic data were obtained by mounting a crystal on a glass fiber and transferring it to a Bruker CCD platform diffractometer. X-ray data collection parameters for **1**−**4** are shown in Table 1. The SMART[36] program package was used to determine the unit cell parameters and for data collection (20 s/frame scan time for a sphere of diffraction data for **1**, **2**, and **4**, 30 s/frame scan time for a sphere of diffraction data for **3**). The raw frame data was processed using SAINT[37] and SADABS[38] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL[39] program. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors[40] for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model.

Ag(hfac)($Me_3SiCCSiMe_3$), 1. A colorless crystal grown by sublimation of approximate dimensions 0.13 × 0.18 × 0.24 mm^3 was mounted on a glass fiber and transferred to a Bruker CCD platform diffractometer. The diffraction symmetry was $2/m$, and the systematic absences were consistent with the centrosymmetric monoclinic space group $P2_1/n$ which was later determined to be correct. At convergence, wR2 = 0.1181 and GOF = 1.091 for 217 variables refined against 4110 data (0.80 Å). As a comparison for refinement on F, R1 = 0.0416 for those 3176 data with $I > 2.0\sigma(I)$.

$[Ag_4(hfac)_4(THF)_2]_\infty$, 2. A colorless crystal of approximate dimensions 0.12 × 0.26 × 0.29 mm^3 showed that diffraction symmetry was $2/m$ and the systematic absences were consistent with the monoclinic space groups Cc and $C2/c$. It was later

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(34) Siedle, A. R.; Pignolet, L. H. *Inorg. Chem.* **1981**, *20*, 1849.

(35) Product names are provided for completeness of experimental description. They do not imply NIST endorsement.

(36) *SMART Software Users Guide*, Version 5.1; Bruker Analytical X-ray Systems, Inc.: Madison, WI, 1999.

(37) *SAINT Software Users Guide*, Version 6.0; Bruker Analytical X-ray Systems, Inc.: Madison, WI, 1999.

(38) Sheldrick, G. M. *SADABS*; Bruker Analytical X-ray Systems, Inc.: Madison, WI, 1999.

(39) Sheldrick, G. M. *SHELXTL*, version 5.10; Bruker Analytical X-ray Systems, Inc.: Madison, WI, 1999.

(40) *International Tables for X-ray Crystallography*; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1992; Vol. C.

determined that the centrosymmetric space group *C*2/*c* was correct. At convergence, wR2 = 0.0767 and GOF = 1.021 for 631 variables refined against 10 336 data. As a comparison for refinement on *F*, R1 = 0.0306 for those 8371 data with $I > 2.0\sigma(I)$.

$[Ag_4(hfac)_4(toluene)_2]_\infty$, 3. A colorless crystal of approximate dimensions 0.09 × 0.17 × 0.31 mm^3 showed that there were no systematic absences nor any diffraction symmetry other than the Friedel condition. The centrosymmetric triclinic space group $P\bar{1}$ was assigned and later determined to be correct. The THF carbon atoms (C11)−C(14) were disordered and included using multiple components with partial site occupancy factors. At convergence, wR2 = 0.0895 and GOF = 1.039 for 295 variables refined against 4713 data. As a comparison for refinement on *F*, R1 = 0.0329 for those 4133 data with $I > 2.0\sigma(I)$.

$[Ag_6(hfac)_6(vtms)_2]_\infty$, 4. A colorless crystal of approximate dimensions 0.22 × 0.30 × 0.30 mm^3 showed that there were no systematic absences nor any diffraction symmetry other than the Friedel condition. The centrosymmetric triclinic space group $P\bar{1}$ was assigned and later determined to be correct. Several atoms were disordered and were included using multiple components with partial site occupancy factors. At convergence, wR2 = 0.0865 and GOF = 1.037 for 425 variables refined against 7252 data. As a comparison for refinement on *F*, R1 = 0.0333 for those 6654 data with $I > 2.0\sigma(I)$.

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Supporting Information Available: Tables of crystal data, positional parameters, bond distances and angles, and thermal parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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