

Synthesis and Characterization of a Bis(μ - β -diketonato)bis((1,2,5,6- η)-1,5-dimethyl-1,5-cyclooctadiene)disilver Complex. An Intermediate in the Synthesis of an Isomerically Pure (β -Diketonato)((1,2,5,6- η)-1,5-dimethyl-1,5-cyclooctadiene)copper(I) Complex

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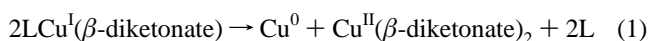
Dimethyl-1,5-cyclooctadiene (DMCOD) is synthesized by the Ni-catalyzed dimerization of isoprene and consists of 80% 1,5-dimethyl-1,5-cyclooctadiene (1,5-DMCOD) and 20% 1,6-dimethyl-1,5-cyclooctadiene (1,6-DMCOD). Reaction of Hhfac (1,1,1,5,5,5-hexafluoro-2,4-pentanedione) with Ag₂O in the presence of DMCOD results in the formation of isomeric Ag(I) species. Repeated recrystallizations yield an isomerically pure compound ((1,5-DMCOD)Ag(hfac))₂ that was characterized by X-ray crystallography and ¹H and ¹³C NMR and IR spectroscopy. X-ray crystallography revealed a dinuclear complex with a short Ag–Ag spacing (3.0134(3) Å at –150 °C and 3.0278(5) Å at –20 °C) and bridging hfac ligands (μ_2 bonding). The overall geometry around the Ag atoms is a deformed tetrahedron with two short Ag–O bonds (2.375 Å average) and two Ag–diene bonds. The methyl groups of the 1,5-DMCOD ligand are pointed toward the center of the molecule. Decomposition of the silver complex in a biphasic HCl (1 M)/CH₂Cl₂ mixture liberates isomerically pure 1,5-DMCOD; this diene is subsequently used to synthesize isomerically pure (1,5-DMCOD)Cu(hfac). The latter compound was characterized by ¹H and ¹³C NMR and IR spectroscopy and is a useful liquid precursor for Cu CVD. Crystallographic data: C₃₀H₃₄Ag₂F₁₂O₄, monoclinic, *P*2₁/*c* (No. 14), *Z* = 4; at –150 °C, *a* = 12.428(1) Å, *b* = 11.071(1) Å, *c* = 24.520(2) Å, β = 101.98(1)°; at –20 °C, *a* = 12.597(1) Å, *b* = 11.191(1) Å, *c* = 24.641(2) Å, β = 102.08(1)°.

Introduction

Chemical vapor deposition (CVD) processes¹ are increasingly important for VLSI metallization and interconnect. The deposition of pure, conformal metal films is required for multilevel devices with ≤ 0.25 μm features. As previously reported, the electrical resistivity of the interconnects may limit device performance.² Low-resistivity metals and low-dielectric-constant materials reduce the RC time constant and lead to improved device performance.³ Thus, CVD processes for the deposition of low-resistivity metals (i.e., gold, copper, and silver) require the identification and development of low-cost volatile precursors.

Earlier research has demonstrated the vast potential of Lewis-base-stabilized copper(I) β -diketonates as precursors for copper

CVD.^{4–10} The reactive copper(I) β -diketonate moiety can be ligated with various Lewis bases (i.e. phosphines, alkenes, dienes, and alkynes) to obtain a plethora of materials with varying physicochemical properties. The deposition of pure copper films occurs via the thermally-induced disproportionation of two Cu(I) species, as depicted in eq 1. In one of our studies,^{4a}



we used an isomeric mixture of dimethyl-1,5-cyclooctadiene (DMCOD) as the Lewis base to stabilize copper(I) 1,1,1,5,5,5-hexafluoroacetylacetonate (hfac). Commercially available DMCOD, synthesized via the nickel-catalyzed dimerization of isoprene,¹¹ consists of a mixture of 80% 1,5-dimethyl-1,5-cyclooctadiene (1,5-DMCOD) and 20% 1,6-dimethyl-1,5-cyclooctadiene (1,6-DMCOD). The synthesis of DMCOD Cu-

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(hfac) leads to an isomeric mixture of Cu(I) complexes when DMCOD is used in the synthesis. Although this isomeric mixture is a liquid with a useful vapor pressure, some uncertainty exists regarding the physical properties of the precursor, due to its isomeric identity. Initial attempts to separate the organic isomers (i.e., distillation) were unsuccessful, and thus, the majority of our copper CVD studies were performed using an isomeric mixture of copper(I) hfac complexes.^{4a}

In this paper, we report the preparation and purification of ((1,5-DMCOD)Ag(hfac))₂ from an isomeric mixture and its use as an intermediate in the synthesis of isomerically pure (1,5-DMCOD)Cu(hfac). Chemical isolation of the silver(I) isomer is easily achieved. Characterization of ((1,5-DMCOD)Ag(hfac))₂ was performed by X-ray crystallographic analyses at two temperatures and IR and NMR spectroscopies. Liberation of isomerically pure 1,5-DMCOD enables the synthesis and characterization of isomerically pure (1,5-DMCOD)Cu(hfac).

Experimental Section

All of the starting materials were commercially available and were used as received. Infrared spectra were obtained using an IBM IR44 single-beam spectrometer. The spectra were obtained by evaporating a pentane solution of the complex onto NaCl plates or using it neat between two NaCl plates. ¹H and ¹³C NMR spectra were recorded on a Bruker 250 MHz spectrometer. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

Synthesis of ((1,5-DMCOD)Ag(hfac))₂. An 11 g (0.047 mol) sample of Ag₂O (Aldrich) was stirred in 200 mL of spectroscopic grade methylene chloride (CH₂Cl₂). Then 18 g (0.086 mol) of 1,1,1,5,5,5-hexafluoroacetylacetone (Aldrich) was added dropwise to the stirred solution after the addition of 11.8 g (0.087 mole) of commercial dimethyl-1,5-cyclooctadiene (Aldrich). The black silver oxide was suspended in the clear solution and slowly dissolved as the reaction proceeded. Excess Ag₂O was filtered off upon completion of the reaction. Precipitation of a white solid occurred after cooling the filtrate for 1 h at -78 °C. The precipitate was filtered out, dried, and redissolved in 100 mL of CH₂Cl₂ at room temperature, and the solution was cooled to -78 °C again. Recrystallization was repeated twice with 80 and 60 mL of CH₂Cl₂, respectively. Pure ((1,5-DMCOD)Ag(hfac))₂ was obtained (25 g, 60%) as a white crystalline solid that is slightly light sensitive but can be stored for months at 23 °C in the absence of light. Anal. Calcd for C₃₀H₃₄F₁₂O₄Ag₂: C, 39.93; H, 3.80; F, 25.27; Ag, 23.91. Found: C, 39.99; H, 3.80; F, 24.70; Ag, 24.15. Mp = 107 °C. IR (thin film between two NaCl plates): 2915 (m), 1725 (w), 1636 (s), 1519 (s), 1483 (s), 1444 (m), 1384 (m), 1325 (w), 1255 (s), 1185 (s), 1137 (s), 849 (w), 792 (m), 765 (w), 737 (w), 660 (m), 577 (m), 524 (w) cm⁻¹. ¹H NMR (CDCl₃, 20 °C): δ 1.91 (s, CH₃), 2.48 (s, CH₂), 5.78 (s, C-H, hfac), 5.84 (t, C-H). ¹³C NMR: δ 26.72 (s, CH₃), 27.55 (s, CH₂), 33.77 (s, CH₂), 87.09 (s, C-H), 115.94 (s, C=C), 117.82 (q, 315 Hz, CF₃), 138.70 (s, C=C), 177.35 (q, 32 Hz, C=O).

Isolation of Pure 1,5-DMCOD. A solution consisting of 25 g (0.028 mol) of ((1,5-DMCOD)Ag(hfac))₂ in CH₂Cl₂ was reacted with an aqueous solution of HCl (1 M). Acidification led to a AgCl precipitate and liberation of isomerically pure 1,5-DMCOD. The organic layer was washed several times with water (five or six times) to eliminate "free" hexafluoroacetylacetone and was dried over anhydrous MgSO₄. The solvent was removed by vacuum distillation

Table 1. Abbreviated Crystallographic Data for ((1,5-DMCOD)Ag(hfac))₂

empirical formula	C ₃₀ H ₃₄ F ₁₂ O ₄ Ag ₂	C ₃₀ H ₃₄ F ₁₂ O ₄ Ag ₂
<i>a</i> , Å	12.428(1)	12.597(1)
<i>b</i> , Å	11.071(1)	11.191(1)
<i>c</i> , Å	24.520(2)	24.641(2)
β , deg	101.98(1)	102.08(1)
<i>V</i> , Å ³	3300.22(95)	3396.92(95)
<i>Z</i>	4	4
fw	902.32	902.32
space group	<i>P</i> 2 ₁ / <i>c</i> (No. 14)	<i>P</i> 2 ₁ / <i>c</i> (No. 14)
temp, °C	-150 ± 0.5	-20 ± 0.5
radiation/ λ , Å	Mo K α /0.710 73	Mo K α /0.710 73
<i>d</i> _{calc} , g cm ⁻³	1.816	1.765
abs coeff μ (Mo K α), cm ⁻¹	12.7	12.38
<i>R</i> ^a	0.033	0.045
<i>R</i> _w ^a	0.051	0.071

^a Relevant expressions are as follows, where *F*_o and *F*_c represent the observed and calculated structure factor amplitudes. Function minimized was $w(|F_o| - |F_c|)^2$, where $w = (\sigma(F))^{-2}$. $R = \sum(|F_o| - |F_c|) / \sum|F_o|$. $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$.

to yield 7.2 g (96%) of pure 1,5-DMCOD. IR (thin film between two NaCl slides): 2964 (m), 2928 (m), 2878 (m), 1727 (w), 1671 (w), 1533 (s), 1492 (s), 1260 (s), 1199 (m), 1144 (s), 1072 (w), 833(w), 800 (m), 740 (w), 665 (m), 582 (m), 496 (w) cm⁻¹. ¹H NMR (CDCl₃, 20 °C): δ 1.66 (s, CH₃), 2.3 (m, CH₂), 5.32 (t, C-H). ¹³C NMR of 1,5-dimethyl-1,5-cyclooctadiene measured in this study and referenced to CDCl₃ at δ 77.000: δ 26.22 (s, CH₃), 26.27 (s, CH₂), 33.32 (s, CH₂), 122.51 (s, C=C), 135.63 (s, C=C). Reported ¹³C NMR of 1,5-dimethyl-1,5-cyclooctadiene, referenced to TMS: δ 26.3, 26.5, 33.7, 122.8, 135.6.¹¹ ¹³C NMR of 1,6-dimethyl-1,5-cyclooctadiene measured in this study and referenced to CDCl₃ at δ : 77.000: δ 26.22 (s, CH₃), 27.44 (s, CH₂), 32.18 (s, CH₂), 122.35 (s, C=C), 135.72 (s, C=C). Reported ¹³C NMR of 1,6-dimethyl-1,5-cyclooctadiene, referenced to TMS: δ 26.3, 27.8, 32.5, 122.8, 135.6.¹¹

Synthesis of (1,5-DMCOD)Cu(hfac). The following reaction was carried out under a steady flow of nitrogen; although the complex is slightly O₂ sensitive, it is not necessary to purge the solution prior to initiation of the synthetic reaction. A three-neck round-bottom flask was charged with 5.5 g (38 mmol) of Cu₂O (Aldrich) and 50 mL of spectroscopic grade methylene chloride. 1,1,1,5,5,5-Hexafluoroacetylacetone (10.7 g, 51 mmol, Aldrich) was added dropwise to the magnetically stirred solution which contained 7 g (51 mmol) of purified 1,5-DMCOD. The reaction was stirred throughout the addition and for 30 min after the addition was completed. The brick-red cuprous oxide was suspended in the clear solution, which became yellow-green as the reaction proceeded. Excess Cu₂O was filtered off, and the methylene chloride solution was purified by flash chromatography using CH₂Cl₂ under nitrogen with a 1.3 in. (diameter) \times 5 in. (height) alumina column. After chromatography and distillation of the solvent, 17 g of yellow-orange liquid (1,5-DMCOD)Cu(hfac) was obtained (82% yield). IR (neat): 2945 (m), 2887 (m), 1642 (s), 1591 (w), 1550 (m), 1522 (m), 1486 (s), 1444 (s) 1379 (m), 1343 (m), 1260 (s), 1202 (s), 1148 (s), 1098 (m), 1037 (w), 1014 (w) 794 (m), 743 (m), 671 (s), 584 (m), 524 (w) cm⁻¹. ¹H NMR (CDCl₃, *T* = 23 °C): δ 1.72 (s, 6H), 2.39 (m, 8H), 5.34 (m, 2H), 5.92 ppm (s, 1H). ¹³C NMR: δ 177.1 (q, 34 Hz, CO), 128.4 (s, C=C-CH₃), 117.6 (q, 286 Hz, CF₃), 111.2 (s, C-H=C), 88.6 (s, CH), 33.5 (s, CH₂), 27.5 (s, CH₂), 26.2 (s, CH₃). Anal. Calcd for C₁₅H₁₇F₆O₂Cu: C, 44.28; H, 4.21; F, 28.02; Cu, 15.62. Found: C, 44.43; H, 4.35; F, 30.45; Cu 15.75.

Single-Crystal X-ray Diffraction. X-ray crystallographic analysis was performed on a single crystal of C₃₀H₃₄F₁₂O₄Ag₂, which was grown from a pentane solution at -20 °C. The crystal was attached to the tip of a glass fiber with grease and transferred into a cold nitrogen jet. Data were collected at -150 ± 0.5 °C (and -20 ± 0.5 °C) on an Enraf-Nonius CAD4 diffractometer using Mo K α radiation (λ = 0.710 73 Å) and a graphite monochromator. The crystal structure was refined and solved using the Enraf-Nonius MoLEN package. The compound crystallizes in space group *P*2₁/*c* (No. 14), with *a* = 12.428(1) Å, *b* = 11.071(1) Å, *c* = 24.520(2) Å, β = 101.98(1)°, and *V* = 3300(1) Å³ (at -20 °C, *a* = 12.597(1) Å, *b* = 11.191(1) Å, *c* =

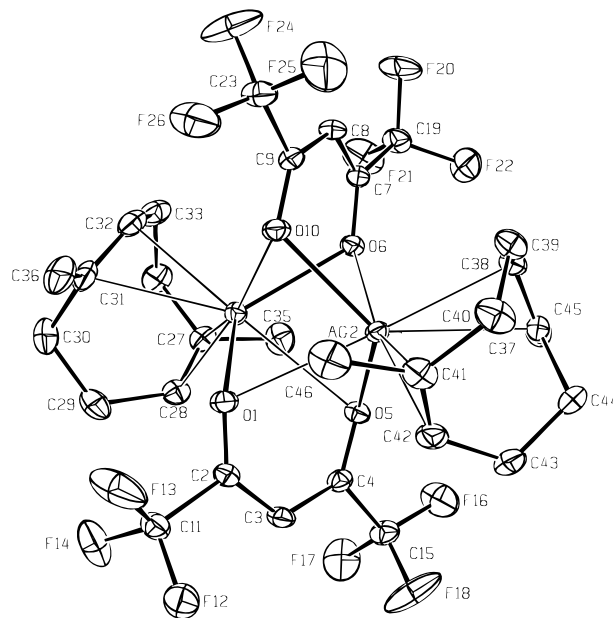
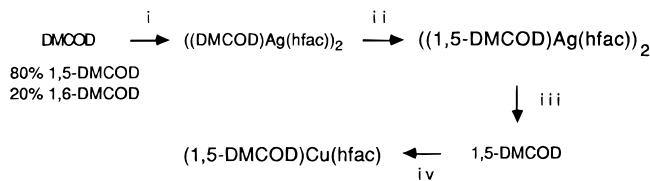
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Table 2. Positional Parameters and Equivalent Isotropic Displacement Parameters for the Non-Hydrogen Atoms of $((1,5\text{-DMCOD})\text{Ag}(\text{hfac}))_2$ at -150°C

atom	x	y	z	$B, \text{\AA}^2$
Ag1	0.73266(2)	0.13972(2)	0.31926(1)	2.137(3)
Ag2	0.75002(2)	0.24138(2)	0.43476(1)	2.003(3)
F12	1.1636(2)	0.2990(2)	0.3993(1)	5.87(6)
F13	1.1158(2)	0.1163(2)	0.4023(2)	8.04(7)
F14	1.1131(2)	0.2018(3)	0.3255(1)	5.65(6)
F16	0.7350(2)	0.6033(2)	0.3391(2)	7.15(7)
F17	0.8499(2)	0.5797(2)	0.2883(1)	6.07(6)
F18	0.9058(3)	0.6253(2)	0.3719(1)	8.07(8)
F20	0.3260(2)	0.0473(2)	0.3601(1)	4.96(5)
F21	0.3704(2)	0.1465(3)	0.2932(1)	5.60(6)
F22	0.3639(2)	0.2358(2)	0.3685(1)	5.29(6)
F24	0.5983(2)	-0.2335(2)	0.4330(2)	7.48(8)
F25	0.6495(3)	-0.1378(3)	0.5066(1)	7.23(8)
F26	0.7678(2)	-0.1929(2)	0.4608(1)	6.54(6)
O1	0.9073(2)	0.1731(2)	0.37770(8)	2.45(4)
O5	0.7555(2)	0.3719(2)	0.35766(8)	2.38(4)
O6	0.5774(1)	0.1849(2)	0.35626(8)	2.36(3)
O10	0.7364(2)	0.0277(2)	0.42125(9)	2.48(4)
C2	0.9716(2)	0.2557(2)	0.3715(1)	2.25(5)
C3	0.9487(2)	0.3774(3)	0.3606(1)	2.46(5)
C4	0.8423(2)	0.4247(2)	0.3537(1)	2.32(5)
C7	0.5146(2)	0.1067(3)	0.3698(1)	2.29(5)
C8	0.5425(2)	0.0031(2)	0.4017(1)	2.36(5)
C9	0.6515(2)	-0.0293(2)	0.4237(1)	2.31(5)
C11	1.0912(2)	0.2167(3)	0.3752(1)	2.87(6)
C15	0.8319(3)	0.5590(3)	0.3383(1)	3.06(6)
C19	0.3928(2)	0.1330(3)	0.3480(2)	3.13(6)
C23	0.6683(3)	-0.1489(3)	0.4555(2)	3.24(6)
C27	0.6665(3)	0.2040(3)	0.2125(1)	2.89(6)
C28	0.7744(3)	0.2183(3)	0.2282(1)	2.90(6)
C29	0.8655(3)	0.1333(4)	0.2222(1)	3.77(7)
C30	0.8418(3)	-0.0006(3)	0.2215(2)	3.92(7)
C31	0.7915(3)	-0.0479(3)	0.2686(1)	3.30(6)
C32	0.6825(3)	-0.0493(3)	0.2660(1)	3.29(6)
C33	0.5890(3)	-0.0073(3)	0.2203(2)	3.83(7)
C34	0.6123(3)	0.0937(3)	0.1818(1)	3.61(7)
C35	0.5875(3)	0.3020(3)	0.2214(2)	4.14(7)
C36	0.8704(3)	-0.1031(3)	0.3163(2)	4.34(8)
C37	0.6431(2)	0.3948(3)	0.4887(1)	2.57(5)
C38	0.6280(2)	0.2799(3)	0.5037(1)	2.87(5)
C39	0.6874(3)	0.2102(3)	0.5523(1)	3.58(6)
C40	0.8101(3)	0.2356(4)	0.5756(2)	4.14(8)
C41	0.8814(3)	0.2417(3)	0.5330(1)	3.19(6)
C42	0.8931(2)	0.3449(3)	0.5057(1)	3.13(6)
C43	0.8424(3)	0.4682(3)	0.5093(2)	3.95(7)
C44	0.7286(3)	0.4769(3)	0.5222(2)	3.56(7)
C45	0.5693(3)	0.4525(3)	0.4391(1)	3.50(6)
C46	0.9468(3)	0.1310(4)	0.5257(2)	4.21(8)

^a Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos \gamma)B(1,2) + ac(\cos \beta)B(1,3) + bc(\cos \alpha)B(2,3)]$.

24.641(2) Å, $\beta = 102.08(1)^\circ$, and $V = 3397(1) \text{ \AA}^3$; $Z = 4$; $d_{\text{calc}} = 1.816 \text{ g/cm}^3$ (at -20°C $d_{\text{calc}} = 1.765 \text{ g/cm}^3$); $\mu = 12.7 \text{ cm}^{-1}$ (at -20°C $\mu = 12.38 \text{ cm}^{-1}$); $F(000) = 1792$. A total of 10 557 unique reflections (10 312 at -20°C) were recorded in the range $2 \leq 2\theta \leq 60.0^\circ$, of which 3089 (4066) were considered as "unobserved" ($F^2 < 3.0\sigma(F^2)$), leaving 7468 (6246) for solution and refinement. The structure was solved by the Patterson method, yielding a solution for the silver atoms. The hydrogen atoms were included at their calculated positions with fixed B values (equal to 1.3 times that of the attached carbon atom) in the final stages of least-squares refinement, while using anisotropic temperature factors for all other atoms. A non-Poisson weighting scheme was applied with a p factor equal to 0.08. The final agreement factors were $R = 0.033$ and $R_w = 0.051$ (at -20°C , $R = 0.045$ and $R_w = 0.071$); $\text{GOF} = 1.06$ (1.41). The observed extinctions in the $h0l$ plane and on the $0k0$ axis unambiguously indicate the correct space group is $P2_1/c$.

**Figure 1.** ORTEP plot of $((1,5\text{-DMCOD})\text{Ag}(\text{hfac}))_2$ obtained by X-ray crystallographic analysis of a single crystal at -150°C , depicting the atomic numbering used throughout the text.**Scheme 1.** Synthesis of Isomerically Pure $(1,5\text{-DMCOD})\text{Cu}(\text{hfac})^a$ 

^a Key: (i) $\text{Ag}_2\text{O} + \text{Hhfac}$ in CH_2Cl_2 ; (ii) repeated crystallization in CH_2Cl_2 ; (iii) acidification in HCl (1 M)/ CH_2Cl_2 for 24 h at 23°C ; (iv) reaction with $\text{Cu}_2\text{O} + \text{Hhfac}$ in CH_2Cl_2 followed by column chromatography with deactivated alumina.

Results and Discussion

Syntheses of $((1,5\text{-DMCOD})\text{Ag}(\text{hfac}))_2$ and $(1,5\text{-DMCOD})\text{-Cu}(\text{hfac})$. As depicted in Scheme 1, the synthesis of isomerically pure $(1,5\text{-DMCOD})\text{Cu}(\text{hfac})$ relies upon the isolation of the corresponding isomerically pure silver complex as an intermediate. $\text{Ag}^I(\text{hfac})$ complexes were previously synthesized,^{12,13} and although relatively nonvolatile, they can be used for Ag CVD.^{14–16} Comparison of the Ag complexes to the analogous Cu species demonstrates dramatic changes in the observed physical properties. To better understand these physical property changes, we characterized the $\text{Ag}^I(\text{hfac})$ structure. As shown in Figure 1, the complex is dinuclear with $\mu\text{-}\eta^2\text{-hfac}$ ligands; the bridging nature of the β -diketonate ligands results in a dinuclear structure and explains the high melting point and observed vapor pressure.^{4a,13,16} The isolation of

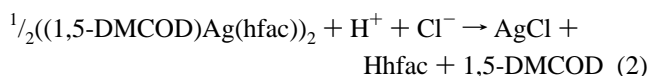
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Table 3. Selected Bond Distances (Å) As Determined by X-ray Crystallographic Analysis of ((1,5-DMCOD)Ag(hfac))₂ at -150 °C^a

Ag1–Ag2	3.0134(3)		
Ag1–O1	2.369(2)	Ag1–O5	2.731(2)
Ag1–O6	2.350(2)	Ag1–O10	2.783(2)
Ag1–C27	2.672(3)	Ag1–C28	2.548(3)
Ag1–C31	2.601(3)	Ag1–C32	2.476(3)
Ag2–O1	2.736(2)	Ag2–O5	2.392(2)
Ag2–O6	2.643(2)	Ag2–O10	2.390(2)
Ag2–C37	2.671(3)	Ag2–C38	2.530(3)
Ag2–C41	2.614(3)	Ag2–C42	2.493(3)

^a Numbers in parentheses are estimated standard deviations in the least significant digits.

isomerically pure ((1,5-DMCOD)Ag(hfac))₂ was achieved via repeated recrystallizations of the isomeric mixture. The purified silver complex was then acidified with a biphasic solution containing aqueous HCl and CH₂Cl₂. Acidification results in protonation of the hfac ligand and nearly quantitative liberation of pure 1,5-DMCOD, as depicted in eq 2. The liberated diene



was analyzed by NMR and IR spectroscopies and found to be isomerically pure 1,5-dimethyl-1,5-cyclooctadiene. The isomeric purity of the diene is easily checked by ¹³C NMR; the unique peaks attributed to 1,6-DMCOD are located at 26.22, 27.44, 32.18, 122.35, and 135.72 ppm. These peaks are observed in the spectrum of commercial DMCOD but are absent after purification using the Ag^I(hfac) intermediate. The isomerically pure diene was then reacted with Cu₂O and Hhfac to produce isomerically pure (1,5-DMCOD)Cu(hfac) after chromatography on deactivated alumina.

We attempted to isolate the second isomer of the silver complex, ((1,6-DMCOD)Ag(hfac))₂. However, 1,5-DMCOD is always present in the isolated samples. We, therefore, speculate that this second isolated species is a mixed-ligand material, such as (1,5-DMCOD)(1,6-DMCOD)((Ag(hfac))₂).

Crystal Structure of ((1,5-DMCOD)Ag(hfac))₂. The isomerically pure silver complex was characterized by X-ray crystallographic analysis of a single crystal. The ORTEP diagram (Figure 1) is similar to that reported for the nonmethylated analog, ((COD)Ag(hfac))₂.¹³ In the latter case, however, decomposition of the crystal during analysis resulted in extensive disorder and, therefore, large error in the data. These problems create some doubt about the ligand bonding and ligand geometry relative to the Ag(I) centers. The bond distances and bond angles for a crystal of ((1,5-DMCOD)Ag(hfac))₂ are listed in Tables 3 and 4, respectively. The two silver atoms display an identical environment: for Ag1, two Ag1–O bonds are short (Ag1–O1 = 2.369(2) and Ag1–O6 = 2.350(2) Å) and two Ag1–O distances are long (Ag1–O5 = 2.731(2) and Ag1–O10 = 2.783(2) Å). For Ag2, the short distances are Ag2–O5 = 2.392(2) and Ag2–O10 = 2.390(2) Å and the long distances are Ag2–O1 = 2.736(2) and Ag2–O6 = 2.643(2) Å.

Interestingly, the hfac ligands are bridging two silver(I) atoms and the two main planes, containing the β -diketonate atoms, form a dihedral angle of 23.44 ± 0.12°. The bonding of the bridging ligands is unclear; the long Ag–O distances (2.723 Å average) indicate only weak chemical bonding. Thus, we think that the best representation of the silver atomic environment is a modified tetrahedron, displaying a double μ_2 -hfac binding mode. We obtained data for ((1,5-DMCOD)Ag(hfac))₂ at -150 °C which are very different from that reported for ((COD)Ag(hfac))₂ at 20 °C.¹³ In the latter work, both μ_4 - η^2 -hfac and μ_2 -

Table 4. Selected Bond Angles (deg) As Determined from X-ray Analysis of ((1,5-DMCOD)Ag(hfac))₂^a

Ag2–Ag1–O1	59.69(5)	C31–Ag1–C32	30.5(1)
Ag2–Ag1–O5	48.90(4)	Ag1–Ag2–O1	48.36(4)
Ag2–Ag1–O6	57.46(5)	Ag1–Ag2–O5	59.39(5)
Ag2–Ag1–O10	48.51(4)	Ag1–Ag2–O6	48.56(4)
Ag2–Ag1–C27	140.22(7)	Ag1–Ag2–O10	60.71(5)
Ag2–Ag1–C28	135.10(8)	Ag1–Ag2–C37	139.22(7)
Ag2–Ag1–C31	140.74(8)	Ag1–Ag2–C38	139.00(7)
Ag2–Ag1–C32	140.55(8)	Ag1–Ag2–C41	140.87(8)
Ag2–C38–C37	80.8(2)	Ag1–Ag2–C42	136.77(8)
Ag2–C38–C39	100.5(2)	O1–Ag2–O5	67.79(6)
O1–Ag1–O10	71.56(6)	O1–Ag2–O6	96.91(6)
O1–Ag1–C27	127.46(9)	O1–Ag2–O10	72.13(6)
O1–Ag1–C28	98.58(9)	O1–Ag2–C37	155.63(8)
O1–Ag1–C31	95.8(1)	O1–Ag2–C38	168.25(9)
O1–Ag1–C32	123.3(1)	O1–Ag2–C41	95.50(9)
O5–Ag1–O6	72.66(6)	O1–Ag2–C42	90.10(9)
O5–Ag1–O10	97.39(6)	O5–Ag2–O6	73.70(6)
O5–Ag1–C27	94.34(8)	O5–Ag2–O10	120.07(7)
O5–Ag1–C28	87.45(9)	O5–Ag2–C37	96.09(9)
O5–Ag1–C31	153.69(9)	O5–Ag2–C38	123.07(9)
O5–Ag1–C32	166.77(9)	O5–Ag2–C41	127.78(9)
O6–Ag1–O10	67.04(6)	O5–Ag2–C42	98.1(1)
O6–Ag1–C27	102.17(9)	O6–Ag2–O10	68.97(6)
O6–Ag1–C28	126.78(9)	O6–Ag2–C37	95.70(8)
O6–Ag1–C31	133.51(9)	O6–Ag2–C38	91.02(8)
O6–Ag1–C32	104.3(1)	O6–Ag2–C41	158.22(9)
O10–Ag1–C27	160.58(8)	O6–Ag2–C42	166.0(1)
O10–Ag1–C28	166.17(9)	O10–Ag2–C37	132.08(8)
O10–Ag1–C31	96.82(9)	O10–Ag2–C38	102.97(9)
O10–Ag1–C32	93.01(9)	O10–Ag2–C41	98.2(1)
C27–Ag1–C28	29.3(1)	O10–Ag2–C42	124.9(1)
C27–Ag1–C31	78.8(1)	C37–Ag2–C38	29.9(1)
C27–Ag1–C32	73.5(1)	C37–Ag2–C41	79.8(1)
C28–Ag1–C31	74.1(1)	C37–Ag2–C42	73.6(1)
C28–Ag1–C32	84.3(1)	C38–Ag2–C41	74.4(1)
C38–Ag2–C42	84.1(1)	Ag1–C31–C30	106.8(2)
C41–Ag2–C42	30.5(1)	Ag1–C31–C32	69.6(2)
Ag1–O1–Ag2	71.95(5)	Ag1–C31–C36	99.1(2)
Ag1–O1–C2	124.9	Ag1–C32–C31	79.9(2)
Ag2–O1–C2	113.8	Ag1–C27–C28	70.2(2)
Ag1–O5–Ag2	71.71(5)	Ag1–C27–C34	106.6(2)
Ag1–O5–C4	116.4(2)	Ag1–C27–C35	97.4(2)
Ag2–O5–C4	120.7(2)	Ag2–C41–C40	107.2(2)
Ag1–O6–Ag2	73.98(5)	Ag2–C41–C42	69.8(2)
Ag1–O6–C7	124.1(2)	Ag2–C41–C46	98.0(2)
Ag2–O6–C7	115.3(2)	Ag2–C37–C38	69.3(2)
Ag1–O10–Ag2	70.78(5)	Ag2–C37–C44	106.7(2)
Ag1–O10–C9	114.4(2)	Ag2–C37–C45	98.7(2)
Ag2–O10–C9	122.2(2)	Ag2–C42–C41	79.8(2)
		Ag2–C42–C43	102.2(2)

^a Numbers in parentheses are estimated standard deviations in the least significant digits.

hfac with average Ag–O distances of 2.456 and 2.546 Å, respectively, were postulated as the β -diketonate bonding mode. In our study, the effect of temperature on the hfac bonding mode was checked by performing a second data collection with a second crystal at -20 °C. We obtained two very similar structures, and the geometry around the silver atoms is relatively unaffected by the temperature during the X-ray analysis.

The geometry of the diene ligand is similar to that expected for 1,5-cyclooctadiene (COD),¹⁹ and the Ag–C bond distances are similar to that reported in the literature.^{14,20} However, some subtle and interesting features can be observed in the crystal structure. First, the Ag–C(H) distances (2.512 Å average) are

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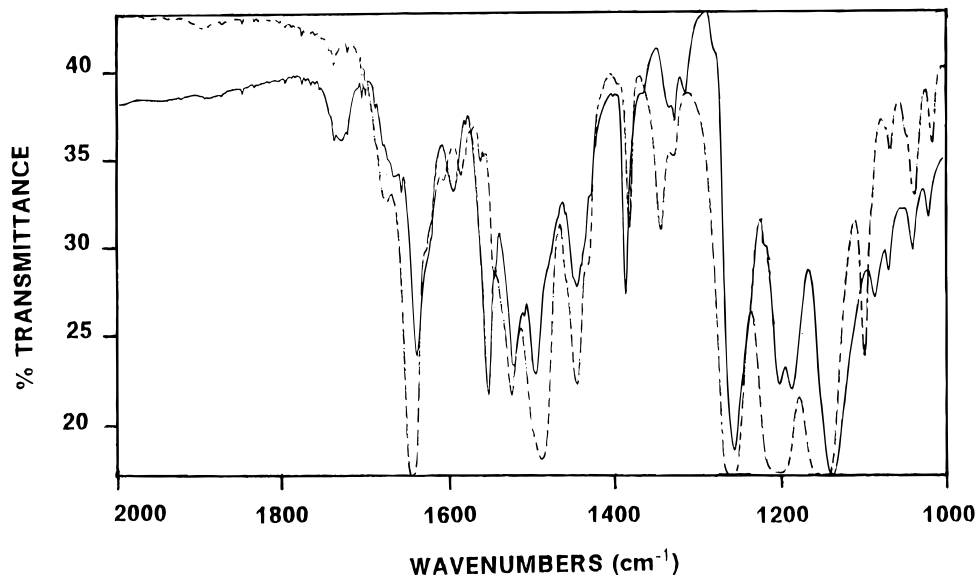


Figure 2. FTIR spectra obtained in the spectral region between 2000 and 1000 cm^{-1} from thin films of (a) isomerically pure (1,5-DMCOD)Cu(hfac) (—) and (b) ((1,5-DMCOD)Ag(hfac))₂ (---).

similar to those found in the nonmethylated analog, ((COD)-Ag(hfac))₂ (2.553 Å average). However, longer Ag—C(CH₃) distances (2.639 Å average) are also observed, indicative of a slightly weaker bond at the methyl-substituted, olefinic carbon. Second, the four methyl groups of the two 1,5-DMCOD ligands are oriented toward the center of the molecule. The carbon atoms are located only 3.2–3.6 Å away from the two silver atoms, thereby forming a methylated, hydrophobic cage around the two silver centers. Extending this structural information to the copper analog, (1,5-DMCOD)Cu(hfac) may be informative. Since the latter complex is a liquid below $-25\text{ }^{\circ}\text{C}$, no X-ray crystallographic data are available. Assuming an identical conformation of the 1,5-DMCOD ligand in the copper(I) analog, we can postulate that the methyl conformation is the origin of the enhanced volatility observed in (1,5-DMCOD)Cu(hfac) via elimination of the intermolecular interactions detected in (COD)-Cu(hfac).¹⁰ For example, at $62\text{ }^{\circ}\text{C}$, (COD)Cu(hfac) exhibits a vapor pressure of 56 mTorr, while (1,5-DMCOD)Cu(hfac) exhibits a vapor pressure of 135 mTorr at $62\text{ }^{\circ}\text{C}$.^{4e} This structural conformation may also explain the observed stability of the copper complex toward moisture in the environment. Last, the observed Ag—Ag distance (3.0134(3) Å) is similar to that reported for the corresponding ((COD)Ag(hfac))₂ (2.955(2) Å) complex. This internuclear distance is relatively short when compared to those of some oligomeric silver (I) complexes, but shorter Ag—Ag distances were previously reported in the literature.²⁰ No significant intermolecular interaction was detected in the crystal.

Spectroscopic Characterization of ((1,5-DMCOD)Ag(hfac))₂ and (1,5-DMCOD)Cu(hfac). Portions of the FTIR spectra of (1,5-DMCOD)Cu(hfac) and ((1,5-DMCOD)Ag(hfac))₂ are given in Figure 2. Although the hfac bonding modes are different, the spectra are very similar and the reported differences in the FTIR spectra of (COD)Cu(hfac) and ((COD)-Ag(hfac))₂¹³ are not observed here. The strong band located at 1642 cm^{-1} in the copper complex (C=O vibration) is shifted to 1636 cm^{-1} in the silver complex. Other spectral interpretations are not easily assigned since the IR absorptions of the β -diketonate ligand ($\nu_{\text{C=O}}$ and $\nu_{\text{C=C}}$) are intense and overlap in this region ($1800\text{--}1400\text{ cm}^{-1}$). Thus, we believe the IR data are of limited utility in identifying the complex structure and providing conclusive data on the hfac bonding mode.

Other information can be obtained from the NMR spectra presented in the Supporting Information. As previously reported,^{21,22} the extent of π and σ bonding can be “qualitatively” determined by comparative NMR and spectral shifts upon alkene–metal bonding. ¹H NMR spectra are determined by local diamagnetic effects and neighboring group anisotropy. Thus, proton chemical shift changes ($\Delta\delta$) are indicative of electronic environmental changes; σ bonding leads to a decreased electron density at the alkene and a net deshielding. Deshielding of the protons is observed upon comparison of “free” 1,5-DMCOD and ((1,5-DMCOD)Ag(hfac))₂. The protons neighboring the alkene shift downfield by $+0.46$ (=C—H) and $+0.25$ (=C—CH₃) ppm upon coordination to Ag^I(hfac). In (1,5-DMCOD)Cu(hfac), the chemical shift changes ($\Delta\delta$) are smaller ($+0.11$ ppm for =C—H and $+0.06$ ppm for =C—CH₃) than those observed for ((1,5-DMCOD)Ag(hfac))₂.²²

Comparative ¹³C NMR spectroscopy can also be used for analysis of the complexes. ¹³C NMR analysis of the “free” diene and the diene ligated to Ag^I(hfac) displayed discrete chemical shift changes ($\Delta\delta$) which are indicative of the metal–diene bonding mode.²¹ Larger spectral shifts are observed specifically for the alkene carbon atoms bound to the Ag(I) centers (C31 and C27, C32 and C28). For (1,5-DMCOD)Cu(hfac) the $\Delta\delta$ values are -7.2 and -11.3 ppm, while for the ((1,5-DMCOD)Ag(hfac))₂, the $\Delta\delta$ values are $+3.1$ and -6.6 ppm. For the alkene carbons, negative chemical shifts (shielding) are expected in all cases, except when the electron density decreases at the alkene carbons due to dominant σ bonding.^{21,22} In (1,5-DMCOD)Cu(hfac), the electron-donating CH₃ substituent leads to greater shielding of the =C(CH₃) carbons. In ((1,5-DMCOD)Ag(hfac))₂, a small shielding effect is noted for the =C(H) carbons (C32 and C28), but a positive chemical shift (deshielding) is observed for the =C(CH₃) carbons (C31 and C27). We believe that the NMR spectral shifts upon Ag(I) coordination are attributed to the dinuclear structure of ((1,5-DMCOD)Ag(hfac))₂. However, changing the HOMO–LUMO electronic energy, changing the conformational orientation of

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the methyl groups, or changing the metal center may be responsible for the observed NMR shifts.^{21,22}

Conclusion

In this paper, we have reported the synthesis, isolation, and X-ray structural characterization of the dinuclear complex ((1,5-DMCOD)Ag(hfac))₂. X-ray crystallography demonstrates that the β -diketonate ligands are μ_2 bridging the Ag(I) centers and the methyl substituents are oriented toward the center of the molecule. Acidification of the dinuclear Ag(I) complex liberates isomerically pure 1,5-DMCOD, which is used in the synthesis of the corresponding copper analog (1,5-DMCOD)Cu(hfac). A similar conformation of 1,5-DMCOD in the Cu(hfac) analog may lead to decreased intermolecular interactions between neighboring copper centers. Methyl substitution leads to

physical changes, such as the formation of a liquid with an increased vapor pressure, relative to the nonmethylated analog, (COD)Cu(hfac). However, our preliminary CVD experiments using isomerically pure (1,5-DMCOD)Cu(hfac) do **not** display significant process variations when compared to CVD from the isomeric mixture.

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Supporting Information Available: ¹³C NMR spectra and tables of the general displacement parameters for the non-hydrogen atoms and complete distances and angles at -150 and -20 °C and of atomic coordinates at -20 °C for ((1,5-DMCOD)Ag(hfac))₂ (20 pages). Ordering information is given on any current masthead page.

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