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Copper(I) Precursors for Chemical Vapor Deposition of Copper Metal[1]

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Several copper(I) complexes are compared as precursors for deposition of Cu metal from the vapor phase in H_2 carrier gas. The best of these, (hfac)Cu^{I}(COD) (hfacH = 1,1,1,5,5,5-hexafluoro-2,4-pentanedione; COD = 1,5-cyclooctadiene), yields films of low resistivity (3–4 $\mu\Omega$ cm) and high purity (96%, by Auger electron spectroscopy); these are similar to films produced by H_2 reduction of the more familiar copper(II) complex Cu(hfac)$_2$. (Hfac)Cu^{I}(1,3-butadiene) and [(hfac)Cu^{I}]$_2$(μ-1,3,5,7-cyclooctatetraene) produce films of only slightly higher resistivity (4–6 $\mu\Omega$ cm), but films from CpCu^{I}(PR$_3$) (R = CH_2CH_3, OCH_3, OCH_2CH_3) are noticeably inferior ($\rho > 10$ $\mu\Omega$ cm). (hfac)Cu^{I}(COD) has also been studied by X-ray crystallography. (Hfac)Cu^{I}(COD), monoclinic, space group $P2_1/c$; a = 10.042 (2), b = 9.878 (2), c = 15.756 (3) Å; β = 108.64 (2)°; Z = 4; R = 0.044 (R_w = 0.051) for 1790 reflections ($I > 3\sigma(I)$) and 233 parameters. The structure contains a 2-fold disorder in the Cu atom position, corresponding to η^2 and η^4 bonding modes of the COD ligand.

Introduction

There has been increasing interest recently in low-temperature chemical vapor deposition (CVD) of copper and other highly conducting metals for use as interconnects in integrated circuits.[2] The most extensively investigated precursors for deposition of Cu are copper(II) complexes of β-diketones and related Schiff-base ligands. As early as 1965, Van Hemert and co-workers reported CVD of metal films using Cu^{II}(hfac)$_2$ (see ligand abbreviations in Experimental Section) and other volatile β-diketone complexes in H_2.[3] More recently, Cu^{II}(hfac)$_2$ has been used in laser-induced[4] and plasma-assisted[5] copper CVD experiments, and a mechanistic study of the deposition process with Cu^{II}(hfac)$_2$ and H_2 has been described.[6] Other precursors have been explored; among these are the highly fluorinated Schiff-base complex Cu^{II}(nona-F)$_2$[7] and the copper(I) species [Cu^{I}(O-t-Bu)]$_4$[8] and CpCu^{I}(PEt$_3$).[9] These species still suffer from several disadvantages: the (nona-F)H ligand in Cu(nona-F)$_2$, for example, is not commercially available; and [Cu^{I}(O-t-Bu)]$_4$ and CpCu^{I}(PEt$_3$) are restricted to CVD at low pressure.

In our studies of other copper complexes as precursors for CVD, we were especially interested in copper(I) complexes, for two reasons. First, the lower oxidation state might result in easier reduction to the metal. Second, the lower affinity of Cu(I) for O- and N-containing ligands might lead to less contamination by these elements in the deposited films. We were also intrigued by several reports of neutral copper(I) complexes that are either oils or low-melting solids,[10] because this suggested that their vapor pressures might be sufficient for CVD. Indeed, volatile precursors for CVD of Rh,[11] Pd,[12] Pt,[13–15] and Au[16] melt at low temperatures. With copper, the β-diketone/alkene complexes prepared by Doyle and co-workers[17] seemed among the most promising. We have now performed CVD experiments with several of these Cu(I) species under mild conditions. The results, including an X-ray structural study of the best precursor, (hfac)Cu^{I}(COD), are reported herein.

Since we began this inquiry, Hampden-Smith and co-workers have described CVD of copper metal using CpCu^{I}(PMe$_3$),[18] (hfac)Cu^{I}(PR$_3$),[19,20] and (hfac)Cu^{I}(COD).[21] They have shown that several of these complexes disproportionate, forming Cu^{II} complexes and Cu metal, at high temperatures, and that the disproportionations can be

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Table I. Properties of CVD Precursors and Deposited Films[a]

complex	temp/°C				Cu $\rho/\mu\Omega$ cm	auger analysis[b]/%		
	melt	evap/subl[c]	decomp	source[d]		Cu	C	O
$(hfac)Cu^I(COD)$	100–105	<30	150	70	3.6 ± 1.5	96	2	2
$(hfac)Cu^I(C_4H_6)$	*e*	*e*	30–40	*e*	4.4			
$[(hfac)Cu^I]_2(\mu\text{-COT})$	102		100–110	105	5.9			
$CpCu^IP(OCH_3)_3$	–10	60	90–100	90	>20	75	23	2
$CpCu^IP(OC_2H_5)_3$	–10	65	120	105	>100	64	32	4
$CpCu^IP(C_2H_5)_3$[f]	110	70		95	13	94	4	2
$Cu^{II}(hfac)_2 \cdot H_2O$	115–120	<30		80–85	4.0 ± 1.5	96	2	2

[a] For deposition on borosilicate glass disk under standard conditions: H_2 flow, 80–100 mL min^{-1} at 1 atm; substrate temperature 200 ± 5 °C. Resistivities reproducible within ±20% unless otherwise noted. [b] Analyzed after Ar sputtering to remove surface impurities; detection limit 2%. [c] Temperature of sublimation (for solids) or evaporation (liquids), at 0.4–0.5 mmHg. [d] Minimum precursor temperature required for deposition of opaque film (thickness $\gtrsim$0.2 μm) within 1 h. [e] Could not be measured due to decomposition of precursor. [f] Deposition required reduced pressure of H_2; no deposition observed at atmospheric pressure.

utilized as routes for Cu CVD. A recent report from Reynolds and co-workers[22] also describes Cu CVD via disproportionation of $(hfac)Cu^I(COD)$. The work described herein complements these CVD studies: our depositions are nearly all carried out with H_2 as the carrier gas and reducing agent, in contrast to the disproportionation route (in the absence of carrier gas) chosen by the other groups for Cu formation. Our approach allows for lower deposition temperatures, leads to different selectivity, and is potentially capable of higher yields of Cu while maintaining high film quality.

The present work includes a single-crystal X-ray analysis of $(hfac)Cu^I(COD)$. This portion of the study also complements that recently reported by Hampden-Smith and co-workers:[21] Our analysis was conducted at a different temperature, and it encompasses crystallographic disorder not included in the previous report. One aspect of this disorder suggests an equilibrium between η^2 and η^4 coordination modes for the bound COD ligand.

Experimental Section

Materials and Procedures. Metal complexes (hfac)Cu(L) (L = COD, 1,3-butadiene), $[(hfac)Cu]_2(\mu\text{-COT})$,[17] and $CpCu^I(PR_3)$ (R = CH_2CH_3, OCH_3, OCH_2CH_3)[23] were prepared according to literature methods. $(hfac)Cu^I(COD)$ was purified by sublimation under 1 atm N_2 at 85 °C. $CpCu^I(PEt_3)$ was purified by dissolution in pentane, passage through a short Celite column to remove colored impurities, and cooling to produce white needles (mp <–10 °C). $Cu^{II}(hfac)_2$ was obtained as the hydrate from the Aldrich Chemical Co. and used as received. Solvents for use with air-sensitive materials were degassed and dried according to standard procedures. [Ligand abbreviations are as follows: hfacH = hexafluoroacetylacetone, or 1,1,1,5,5,5-hexafluoro-2,4-pentanedione; COD = 1,5-cyclooctadiene; COT = 1,3,5,7-cyclooctatetraene; Cp = η^5-cyclopentadienyl; (nona-F)H = 1,1,1,5,5,5-hexafluoro-4-(2,2,2,-trifluoroethyl)nitrilo-2-pentanone, or hexafluoroacetylacetone (2,2,2-trifluoroethyl)imine.]

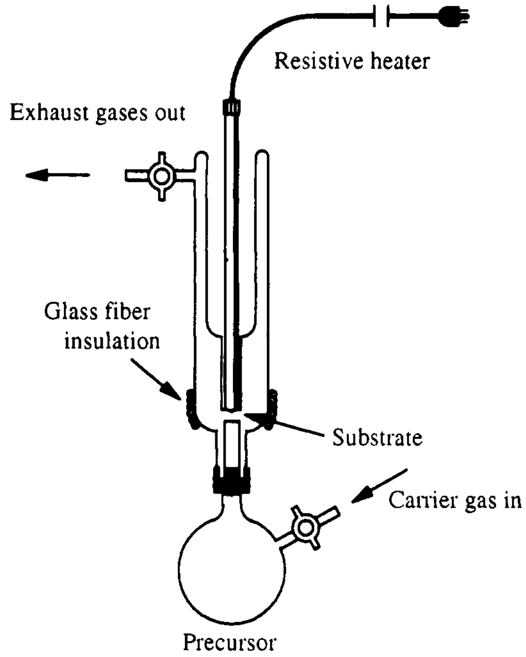

Figure 1. Sketch of cold-wall glass CVD reactor.

CVD was carried out in a vertical cold-wall reactor (see drawing in Figure 1); most experiments utilized a constant flow of hydrogen gas (80–100 mL min^{-1}) at atmospheric pressure. Substrates were wafers of Si ((100); polygons ca. 10 mm dia. × 0.6 mm thick) or borosilicate glass (disks 13 mm dia. × 0.05 mm thick). These were attached to a resistively heated metal probe, using conducting silver paint (SPI Supplies Inc.), and warmed to 200 ± 10 °C. (A small amount of fiberglass insulation was used to wrap the outer glass tube just outside the heated probe tip, in order to make the deposited films as uniform as possible; the wall temperature was approximately 140–145 °C during operation.) The precursor was heated to 70–105 °C as needed for evaporation in the carrier gas stream (see Table I). Some of the precursors decomposed significantly in the evaporation chamber during deposition experiments. For $(hfac)Cu^I(COD)$ and $Cu^{II}(hfac)_2$, on the other hand, no such decomposition was evident; with these precursors, a charge of ca. 0.15 g was sufficient for two or three deposition experiments with no discernible loss in film quality. The reactor was allowed to cool to room temperature, under a flow of H_2, before it was opened after a run; this minimized tarnishing of the films.

Resistivity measurements were made on the films by using a four-point probe (Veeco FPP-100). Film thicknesses determined with a Tencor Alpha-Step 200 stylus profilometer were used to convert sheet resistivity to bulk resistivity. Auger spectra were measured on a Perkin-Elmer Model CXL-1000 instrument. Pure copper films are readily contaminated when exposed to air; therefore, the films were cleaned by argon sputtering prior to Auger analysis. Volatile products from the CVD experiments were trapped by passing the exhaust gases through CH_2Cl_2, and analyzed by mass spectroscopy (Hewlett-Packard direct-probe or GC-MS instruments).

X-ray Analysis. Crystals of $(hfac)Cu^I(COD)$ were obtained by layering a solution of the complex in CH_2Cl_2 with hexane at ca. –5 °C. The density of the crystals was estimated by flotation ($CHCl_3$–CH_2Br_2), but the resulting value is only approximate: the measurement had to be made quickly because the crystals dissolve slowly in the solvent mixture. Diffraction data were collected on an Enraf-Nonius CAD4 diffractometer fitted with Mo Kα source and graphite monochromator, using the ω–2θ scan method. Final unit cell constants were determined from the orientations of 25 centered high-angle reflections. The intensities were corrected for absorption (using ψ scan data for five reflections) and linear decay during data collection. Additional crystallographic data are summarized in Table II.

The structure was solved by direct methods and refined by full-matrix least-squares, using the VAXSDP[24] set of programs.

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Table II. Crystallographic Data for (hfac)Cu^I(COD)[a]

formula	$CuC_{13}H_{13}F_6O_2$	space group	$P2_1/c$
formula wt	378.8	temp/°C	23 ± 2
color	yellow	λ/Å	0.71073 (Mo Kα)
a/Å	10.042 (2)	ρ_m, ρ_x/g cm^{-3}	1.74 (5), 1.699
b/Å	9.878 (2)	μ/cm^{-1}	15.4
c/Å	15.756 (3)	transm coeff	0.833–0.999
β/deg	108.64 (2)	$R(F_o)$[b]	0.044
V/Å^3	1481 (1)	$R_w(F_o)$[c]	0.051
Z	4		

[a] In Tables II–V, estimated standard deviations in the least significant digits of the values are given in parentheses. [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $R_w = (\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)^{1/2}$; $w = 4F_o^2/(\sigma^2(I) + (0.02F_o^2)^2)$.

Table III. Atomic Coordinates for (hfac)Cu^I(COD)

	x	y	z	U_{eq}/Å^2 [a]
Cu[b]	0.07298 (6)	0.15087 (7)	0.09680 (5)	0.0603 (2)
Cu′[c]	0.0946 (2)	0.1870 (3)	0.1159 (1)	0.1237 (7)
O1	0.1959 (2)	0.2117 (3)	0.0261 (2)	0.0703 (8)
O2	0.2282 (2)	0.0490 (3)	0.1847 (2)	0.0720 (8)
C1	0.3236 (3)	0.1804 (4)	0.0467 (2)	0.052 (1)
C2	0.4014 (3)	0.1031 (4)	0.1161 (2)	0.055 (1)
C3	0.3497 (3)	0.0445 (4)	0.1795 (2)	0.056 (1)
C4	0.3925 (4)	0.2361 (4)	−0.0188 (3)	0.068 (1)
C5	0.4491 (4)	−0.0426 (5)	0.2515 (3)	0.088 (2)
C6	−0.1306 (4)	0.1725 (4)	0.0233 (3)	0.068 (1)
C7	−0.1256 (4)	0.1103 (4)	0.1010 (3)	0.064 (1)
C8	−0.1574 (4)	0.1755 (4)	0.1786 (3)	0.077 (1)
C9	−0.0340 (5)	0.2437 (5)	0.2479 (3)	0.085 (2)
C10	0.0632 (4)	0.3229 (4)	0.2117 (3)	0.070 (1)
C11	0.0306 (4)	0.3969 (4)	0.1389 (3)	0.065 (1)
C12	−0.1132 (4)	0.4207 (4)	0.0750 (3)	0.078 (1)
C13	−0.1598 (4)	0.3177 (5)	−0.0028 (3)	0.078 (1)
F1[d]	0.3290 (4)	0.2050 (6)	−0.0980 (2)	0.192 (2)
F2[d]	0.5231 (3)	0.2000 (4)	−0.0013 (2)	0.128 (1)
F3[d]	0.4030 (4)	0.3691 (4)	−0.0120 (3)	0.143 (1)
F4[d]	0.5798 (3)	−0.0350 (4)	0.2589 (2)	0.138 (1)
F5[d]	0.4321 (4)	−0.0330 (5)	0.3278 (2)	0.170 (2)
F6[d]	0.4161 (5)	−0.1757 (4)	0.2278 (3)	0.168 (2)
F1′[e]	0.500 (2)	0.305 (2)	0.017 (1)	0.064 (4)
F2′[e]	0.323 (1)	0.317 (1)	−0.0759 (8)	0.043 (3)
F3′[e]	0.437 (2)	0.141 (2)	−0.055 (1)	0.070 (5)
F4′[e]	0.532 (2)	−0.112 (2)	0.231 (1)	0.067 (4)
F5′[e]	0.408 (1)	−0.104 (1)	0.2982 (9)	0.048 (3)
F6′[e]	0.534 (2)	0.061 (2)	0.322 (1)	0.070 (5)

[a] $U_{eq} = {}^1/_3(a^2a^{*2}U_{11} + b^2b^{*2}U_{22} + c^2c^{*2}U_{33} + 2aca^*c^*U_{13}\cos\beta)$. [b] Occupancy 0.7. [c] Occupancy 0.3. [d] Occupancy 0.87. [e] Occupancy 0.13; refined isotropically (displacement parameter given is U_{iso}).

Positional and anisotropic displacement parameters were refined for all non-hydrogen atoms (except for F1′–F6′, which were refined isotropically); hydrogen atoms were placed in calculated positions, with fixed isotropic displacement parameters. Refined atomic coordinates are listed in Table III, and bond distances and angles are given in Tables IV and V. A packing diagram, additional data collection and refinement parameters, calculated hydrogen atom coordinates, anisotropic displacement parameters, and observed and calculated structure factors are available as supplementary material (see paragraph at end of paper).

Results and Discussion

Choice of Complexes. A small number of types of neutral copper(I) complexes offered potentially volatile candidates for CVD experiments. Many Cu(I) complexes are ionic and therefore likely to be highly involatile; others (such as $[Cu^I(O\text{-}t\text{-}Bu)]_4$[8]) are oligomeric or polymeric and therefore also have relatively low vapor pressures. Representative members of several of the mononuclear and binuclear groups were chosen for the present study.

Table IV. Interatomic Distances/Å for (hfac)Cu^I(COD)

Cu–Cu′	0.472 (7)	Cu′–C11	2.235 (8)	C5–F5	1.272 (6)
Cu–O1	2.001 (4)	Cu′–C1011	2.076	C5–F6	1.378 (8)
Cu–O2	1.995 (4)	O1–C1	1.257 (4)	C5–F4′	1.20 (2)
Cu–C6	2.013 (5)	O2–C3	1.249 (4)	C5–F5′	1.13 (2)
Cu–C7	2.056 (5)	C1–C2	1.357 (5)	C5–F6′	1.56 (2)
Cu–C67	1.918[a]	C1–C4	1.519 (6)	C6–C7	1.356 (6)
Cu···C10	2.508 (5)	C2–C3	1.391 (5)	C6–C13	1.496 (6)
Cu···C11	2.590 (5)	C3–C5	1.516 (6)	C7–C8	1.504 (6)
Cu···C1011	2.464	C4–F1	1.244 (6)	C8–C9	1.522 (7)
Cu′–O1	2.004 (8)	C4–F2	1.301 (5)	C9–C10	1.499 (6)
Cu′–O2	1.976 (8)	C4–F3	1.320 (6)	C10–C11	1.311 (6)
Cu′–C6	2.270 (8)	C4–F1′	1.25 (2)	C11–C12	1.492 (6)
Cu′–C7	2.277 (7)	C4–F2′	1.24 (2)	C12–C13	1.545 (7)
Cu′–C67	2.170	C4–F3′	1.26 (2)		
Cu′–C10	2.117 (9)	C5–F4	1.282 (6)		

[a] Distances involving the calculated centroids C67 and C1011 are given without estimated standard deviations.

Table V. Bond Angles/deg for (hfac)Cu^I(COD)

O1–Cu–O2	93.1 (2)	C2–C3–C5	117.7 (4)
O1–Cu–C6	110.0 (2)	C1–C4–F1	113.1 (4)
O1–Cu–C7	148.6 (2)	C1–C4–F2	113.8 (4)
O1–Cu···C10	111.8 (2)	C1–C4–F3	110.3 (4)
O1–Cu···C11	92.4 (2)	C1–C4–F1′	114 (1)
O1–Cu–C67	129.6[a]	C1–C4–F2′	117.0 (8)
O1–Cu···C1011	102.2	C1–C4–F3′	110 (1)
O2–Cu–C6	151.3 (2)	F1–C4–F2	107.7 (5)
O2–Cu–C7	115.5 (2)	F1–C4–F3	109.3 (6)
O2–Cu···C10	92.4 (2)	F2–C4–F3	101.9 (5)
O2–Cu···C11	116.8 (2)	F1′–C4–F2′	101 (1)
O2–Cu–C67	133.7	F1′–C4–F3′	103 (2)
O2–Cu···C1011	105.0	F2′–C4–F3′	111 (1)
C6–Cu–C7	38.9 (2)	C3–C5–F4	116.5 (5)
C6–Cu···C10	94.4 (2)	C3–C5–F5	114.2 (5)
C6–Cu···C11	80.1 (2)	C3–C5–F6	107.1 (5)
C7–Cu···C10	81.2 (2)	C3–C5–F4′	118 (1)
C7–Cu···C11	86.2 (2)	C3–C5–F5′	120 (1)
C10···Cu···C11	29.7 (1)	C3–C5–F6′	104.0 (8)
C67–Cu···C1011	85.0	F4–C5–F5	110.6 (6)
O1–Cu′–O2	93.6 (3)	F4–C5–F6	103.3 (5)
O1–Cu′–C6	100.4 (4)	F5–C5–F6	103.5 (7)
O1–Cu′–C7	131.5 (4)	F4′–C5–F5′	108 (2)
O1–Cu′–C10	130.6 (4)	F4′–C5–F6′	108 (1)
O1–Cu′–C11	103.8 (4)	F5′–C5–F6′	97 (1)
O1–Cu′–C67	116.2	Cu–C6–C7	72.2 (3)
O1–Cu′–C1011	117.4	Cu–C6–C13	109.5 (3)
O2–Cu′–C6	132.2 (4)	Cu′–C6–C7	72.9 (3)
O2–Cu′–C7	107.1 (3)	Cu′–C6–C13	100.6 (3)
O2–Cu′–C10	106.0 (4)	C7–C6–C13	129.1 (4)
O2–Cu′–C11	137.0 (4)	Cu–C7–C6	68.9 (3)
O2–Cu′–C67	120.4	Cu–C7–C8	113.8 (3)
O2–Cu′–C1011	122.3	Cu′–C7–C6	72.4 (3)
C6–Cu′–C7	34.7 (2)	Cu′–C7–C8	103.0 (3)
C6–Cu′–C10	98.8 (3)	C6–C7–C8	125.7 (4)
C6–Cu′–C11	83.3 (3)	C7–C8–C9	115.9 (4)
C7–Cu′–C10	85.6 (3)	C8–C9–C10	116.0 (4)
C7–Cu′–C11	90.3 (3)	Cu···C10–C9	95.8 (3)
C10–Cu′–C11	34.9 (2)	Cu···C10–C11	78.6 (3)
C67–Cu′–C1011	89.4	Cu′–C10–C9	101.7 (4)
Cu–O1–C1	122.8 (3)	Cu′–C10–C11	77.4 (4)
Cu′–O1–C1	119.6 (3)	C9–C10–C11	127.8 (4)
Cu–O2–C3	122.3 (3)	Cu···C11–C10	71.6 (3)
Cu′–O2–C3	119.7 (3)	Cu···C11–C12	100.2 (3)
O1–C1–C2	128.6 (4)	Cu′–C11–C10	67.6 (3)
O1–C1–C4	112.6 (3)	Cu′–C11–C12	107.6 (3)
C2–C1–C4	118.8 (3)	C10–C11–C12	126.6 (4)
C1–C2–C3	124.1 (3)	C11–C12–C13	114.5 (4)
O2–C3–C2	129.0 (4)	C6–C13–C12	115.5 (4)
O2–C3–C5	113.2 (4)		

[a] Angles involving the calculated centroids C67 and C1011 are given without estimated standard deviations.

Stability and Physical Characteristics. The copper(I) complexes are all stable at room temperature in the absence of air, but most are somewhat sensitive to O_2. (Hfac)Cu^I(COD), for example, is a pale yellow solid which

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(24) Frenz, B. A. *Enraf-Nonius Structure Determination Package*; Enraf-Nonius: Delft, The Netherlands, 1985.

can be stored in air at room temperature for several days without decomposition. Exposure to air for longer periods leads to loss of COD (readily detectable by its odor) and formation of a green powdery solid. (The green decomposition product is probably a Cu^{II} hydroxo or carbonato complex, since it is much less soluble in organic solvents than $Cu^{II}(hfac)_2$.) (Hfac)Cu^{I}(1,3-butadiene), on the other hand, although similar in appearance to the COD complex, is much more reactive. (Hfac)Cu^{I}(1,3-butadiene) is stable in the solid state to ca. 30 °C, but solutions in hexane disproportionate (giving a copper mirror and $Cu^{II}(hfac)_2$) at room temperature unless they are saturated with 1,3-butadiene. Attempts to sublime (hfac)Cu^{I}(1,3-butadiene) under reduced pressure also gave a green sublimate and a reddish brown residue. The green complex was characterized by infrared spectroscopy as $Cu^{II}(hfac)_2$. The greater stability of (hfac)Cu^{I}(COD) compared to the butadiene complex may be due to the less flexible, more strongly chelating nature of the cyclooctadiene ligand. This would be true especially if the η^4 coordination mode of the COD ligand is significant; see below.

$[(Hfac)Cu^{I}]_2(\mu\text{-}COT)$ is purer than (hfac)Cu^{I}(COD) when first prepared, and it is obtained in higher yield: whereas substantial quantities of unreacted Cu_2O and COD remain following the synthesis of (hfac)Cu^{I}(COD), the preparation of the binuclear COT complex is nearly quantitative. However, the COT complex is sensitive to heat: it begins to decompose (under N_2 or H_2) when heated to ca. 100 °C.

The cyclopentadienyl complexes $CpCu^{I}(PR_3)$ (R = CH_2CH_3, OCH_3, OCH_2CH_3) react more readily with O_2 than the β-diketone species mentioned above. The phosphite complexes are low-melting colorless solids which can be stored under N_2 for several days without decomposition. $CpCu^{I}(PEt_3)$ is an air-sensitive off-white solid, also stable for several days when stored under nitrogen. Temperatures of melting, sublimation (or evaporation), and decomposition for these complexes are listed in Table I.

Crystal-Structure Analysis. An ORTEP[25] drawing of (hfac)Cu^{I}(COD) is shown in Figure 2. The molecule shows two types of crystallographic disorder. First, the Cu atom is disordered between two positions, represented by Cu and Cu′. At an early stage in the refinement, the occupancies for these two Cu atoms were refined, while their displacement parameters were fixed. The ratio of the resulting occupancies was approximately 0.7:0.3; therefore, in the remainder of the refinement, the occupancies of Cu and Cu′ were fixed at 0.70 and 0.30, respectively.

Both Cu and Cu′ are within reasonable bonding distance of the two β-diketone O atoms and the C6=C7 double bond (see Table IV). Cu′ is approximately symmetrically placed between the C6=C7 and C10=C11 double bonds, making its coordination environment roughly tetrahedral (as judged by the midpoints "C67" and "C1011" of the two double bonds; see Table V). On the other hand, Cu is clearly coordinated to C6=C7 but much farther away from C10=C11, suggesting approximate three-coordination. C6=C7 is significantly longer than C10=C11; this is consistent with the predominance of Cu and the η^2 structure.

The second type of disorder present in the model is a 2-fold rotational disorder in the CF_3 groups. The majority of the electron density was successfully modeled by the unprimed atoms (F1–F6, occupancy 0.87), which were refined anisotropically; those named with primes (F1′–F6′, occupancy 0.13) were refined isotropically.

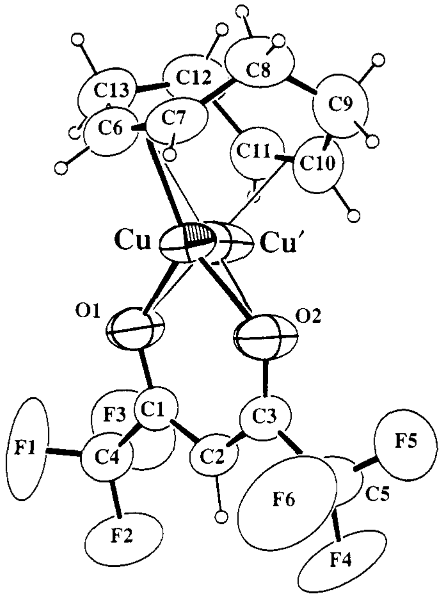

Figure 2. ORTEP[25] illustration of (hfac)Cu^{I}(COD), with ellipsoids at the 50% probability level (H atoms shown as spheres of 0.3 Å radius). Both Cu (one octant shaded) and Cu′ (no shading on ellipsoid) are shown. Cu is within reasonable bonding distance only of C6=C7, whereas Cu′ is close to both C6=C7 and C10=C11. Of the disordered F atoms, only F1–F6 are shown; F1′–F6′ (occupancy 0.13) are omitted for clarity.

Adjacent molecules in the crystal are loosely associated in pairs, with the closest intermolecular Cu···Cu distance 4.181 (4) Å. (The Cu′ atoms are farther apart: Cu′···Cu′ 5.11 (1) Å). Other significant intermolecular contacts within these "pairs" of molecules involve the close approach of C6 and C7 to the Cu–O1–C1–C2–C3–O2 chelate ring of the adjacent molecule; the shortest distance is O1···O7, 3.704 (5) Å.

Comparison of (Hfac)Cu^{I}(COD) with Other Structures. Hampden-Smith and co-workers[21] have recently reported the structure of (hfac)Cu^{I}(COD), determined at −30 °C; our results, from a room-temperature data set, are similar in many respects. We originally solved the structure is space group $P2_1/n$, which is the slightly more orthogonal setting for the crystals at room temperature. However, we have now transformed the data and parameters and relabeled the atoms to match the $P2_1/c$ solution of Hampden-Smith and co-workers as closely as possible.

The most significant differences between these two solutions for (hfac)Cu^{I}(COD) involve disorder in the CF_3 groups and the Cu atom. (This disorder may have been responsible for the difficulties noted by Doyle and co-workers[17] in their attempts to solve the structure at room temperature.) With our data set, we found that modeling the CF_3 groups as two partially occupied sets (87% and 13%) of F atoms with a common C atom center gave improved results. Refinement of a model containing only one set of F atoms converged; however, at this stage, a difference Fourier synthesis revealed peaks near all of the F atoms which were in the proper orientation about C4 and C5 to represent a second set of partially occupied CF_3 groups. The occupancies for the two sets were chosen by a method similar to that for Cu and Cu′, using the difference peak heights as a guide.

Our use of two partially occupied metal atoms (Cu and Cu′) to model the observed electron density has been mentioned above. The model of Hampden-Smith and

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[25] Johnson, C. K. ORTEP-II: *A Fortran Thermal-Ellipsoid Plot Program for Crystal-Structure Illustrations*; Report ORNL-5138; National Technical Information Service; U.S. Department of Commerce: Springfield, VA, 1976.

co-workers[21] included only one Cu site. We initially also adopted the simpler model; however, this refinement converged with $R = 0.082$, and a difference Fourier synthesis revealed a peak with height 2.09 e Å^{-3} 1.12 Å from the Cu atom. Similarly, in the work of Hampden-Smith and co-workers,[21] the largest difference peak, 1.70 e Å^{-3}, is 0.99 Å away from Cu.

On the basis of the observation of a significant quantity of electron density near the Cu atom in the simpler refinements (both in our case and in that of Hampden-Smith et al.) and on our successful refinement of a model with two independent, partially occupied Cu sites, we believe it is likely that some of the molecules in the crystal have COD bound in an η^4 fashion. (Alternatively, a dynamic process is possible, in which all of the molecules interconvert between the η^2 and η^4 forms.) There is no evidence for distinct η^2 and η^4 isomers in solution NMR studies (either ours or those of Hampden-Smith et al.[21]): only one olefinic ^{1}H resonance is observed even at the lowest temperatures (−80 °C, in CD_2Cl_2). (In the coldest solutions, the COD CH_2 resonance splits into a very broad doublet. However, this does not help to determine whether the COD is bound in the η^2 or η^4 fashion.) Addition of excess COD to these solutions still leads to only one olefinic ^{1}H resonance, at a chemical shift intermediate between those for free COD and pure (hfac)Cu^I(COD). These NMR spectra appear to be in the fast-exchange limit even in cold solution; therefore, the question of contributing quantities of the η^2 and η^4 isomers, suggested by the crystal-structure data, is difficult to answer directly.

The structure of [(hfac)Cu^I]$_2$(μ-COT), reported by Doyle and co-workers,[17] also includes a disorder model for Cu, with the different partially occupied Cu atoms coordinated to different double bonds in the COT molecule. However, neither of the Cu sites in this structure is within reasonable bonding distance of more than one C=C bond. Therefore, in [(hfac)Cu^I]$_2$(μ-COT), only η^2 coordination of the olefin to Cu appears to be important.

Several other copper(I)–olefin complexes have been structurally characterized. Examples in which the Cu atoms are three-coordinate include [CuCl(η^2-norbornadiene)]$_4$,[26] [(μ-Cl)Cu(COD)]$_n$,[27] and [(NN)Cu(η^2-C_2H_4)](ClO$_4$) (NN = 2,2′-bipyridine, 1,10-phenanthroline).[28] In [(COD)Cu(μ-Cl)]$_2$,[29] (η^2-C_6H_6)Cu(μ-Cl)$_3$AlCl,[30] and (HB(Me$_2$pz)$_3$)Cu(η^2-C_2H_4),[31] on the other hand, the Cu atoms are four-coordinate, with geometry close to tetrahedral. Finally, in the structure of Cu$_2$(μ-Cl)$_2$(cyclooctene)$_3$,[32] both three- and four-coordinate Cu atoms are found. (The distances and angles in the Cu–COD moiety in the present structure are similar to those in the above copper(I) complexes; the Cu–O distances are also only slightly longer than those in several five-coordinate adducts of Cu^{II}(hfac)$_2$.[33]) Thus, copper(I) is relatively stable in either the trigonal or tetrahedral geometry, and the η^2 and η^4 isomers of (hfac)Cu^I(COD) may be approximately equal in energy.

Hampden-Smith and co-workers have prepared complexes of general formula (β-diketonato)Cu^I(PMe$_3$)$_n$ = (n = 1, 2) as stable solids.[34] The stability of the four-coordinate species (i.e., n = 2) in this series also supports our proposal that the η^4-COD structure can be important for (hfac)Cu^I(COD).

Metal Film Deposition. A glass cold-wall reactor (Figure 1), with a substrate temperature of 200 ± 10 °C, was used for all experiments. Most of the complexes shown in Table I could be used as precursors for deposition of copper in reasonably pure form, as judged by both resistivity and Auger analyses. The smallest detectable concentration of impurities in the Auger analyses was ca. 2%. No N or F impurities could be seen by this method in any of the films we prepared. The highest-quality data were obtained only after argon sputtering; this suggests that surfaces of freshly prepared samples were readily contaminated on contact with air even at room temperature. Deposition rates were ca. 0.5 μm h^{-1} at the tabulated threshold source temperatures. Higher rates could be achieved at higher source temperatures, but a quantitative study of rates was not possible with this apparatus.

(Hfac)Cu^I(COD) gave the best results, producing Cu films at least as pure as those from Cu^{II}(hfac)$_2$, at comparable rates, at the same deposition temperature, and a slightly lower evaporation temperature. Scanning electron micrographs of the films produced from (hfac)Cu^I(COD) reveal irregular, closely knit granules of size $\lesssim$0.5 μm. These films could be deposited under almost identical conditions on borosilicate glass (as shown in Table I) or on silicon (with native oxide coating). Growth rates were approximately the same for (hfac)Cu^I(COD) with the two substrates. (This contrasts with Cu^{II}(hfac)$_2$, which requires much higher substrate temperatures for Cu deposition on silicon than on glass, even in the presence of H_2.) Cu films deposited on Si showed resistivities similar (ρ = 3.9 ± 2.0 $\mu\Omega$ cm) to those grown on glass.

High-quality films were also obtained starting with (hfac)Cu^I(1,3-butadiene). However, the source temperature needed for deposition (85–90 °C) is higher than the decomposition temperature of the precursor. In separate experiments, decomposition of (hfac)Cu^I(1,3-butadiene) even in the absence of H_2 produced copper metal and a low-melting volatile green material whose IR spectrum is identical to that of freshly prepared Cu^{II}(hfac)$_2$. These observations indicate that the principal route to Cu formation with this complex is disproportionation:

$$2(\text{hfac})\text{Cu}^{\text{I}}(\text{butadiene}) \rightarrow \text{Cu} + 2\text{butadiene} + \text{Cu}^{\text{II}}(\text{hfac})_2 \quad (1)$$

[(Hfac)Cu^I]$_2$(μ-COT) also gave Cu films of high quality. Furthermore, these experiments did not appear to produce Cu^{II}(hfac)$_2$, suggesting that disproportionation is less favorable than direct reduction by H_2 under our conditions. This observation is of interest because disproportionation of [(Hfac)Cu^I]$_2$(μ-COT) could occur by a unimolecular reaction, since the two required Cu atoms are present in the same precursor molecule. However, heating [(hfac)Cu^I]$_2$(μ-COT) to ca. 100 °C, as required for reasonable deposition rates, resulted in slow decomposition: the solid turned dark brown over a period of ca. 0.5 h under atmospheres of either N_2 or H_2. (Some metallic copper formed in the source chamber during these experiments,

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(33) These show a range of ca. 1.91–1.97 Å. Belford, R. C. E.; Fenton, D. E.; Truter, M. R. *J. Chem. Soc., Dalton Trans.* **1974**, 17. Durley, R. C. E.; Fenton, D. E.; Truter, M. R. *Acta Crystallogr., Sect. B* **1980**, *36B*, 2991. Dickman, M. H.; Doedens, R. J. *Inorg. Chem.* **1981**, *20*, 2677. Gatteschi, D.; Laugier, J.; Rey, P.; Zanchini, C. *Inorg. Chem.* **1987**, *26*, 938.

(34) Shin, H.-K.; Chi, K. M.; Farkas, J.; Hampden-Smith, M. J.; Kodas, T. T.; Duesler, E. N. *Inorg. Chem.* **1992**, *31*, 424.

suggesting the type of disproportionation mentioned above for (hfac)Cu^I(butadiene).) Because of the higher source temperatures required and the relatively facile decomposition, [(hfac)$Cu^I]_2(\mu$-COT) was also not studied extensively as a precursor.

$CpCu^I(PEt_3)$ gave reasonably good films, with Cu content ca. 85%. However, deposition under 1 atm of H_2 was unsuccessful; films could only be obtained under reduced pressures. (The relatively low purity of the films we produced from $CpCu^I(PEt_3)$ was surprising, since Beach and co-workers[9] have reported device-quality Cu CVD using the same precursor. However, the high-vacuum conditions of Beach et al. are not achievable with our reactor; also, Reynolds and co-workers[22] recently cited difficulties in reproducible film formation with $CpCu^I(PEt_3)$ as precursor.) $CpCu^I(P(OEt)_3)$ and $CpCu^I(P(OMe)_3)$ gave less pure films: these contained high percentages of carbon and showed high resistivities.

All of the above precursors, except (hfac)Cu^I(butadiene), appear to require H_2 in the carrier gas for optimum formation of Cu at these relatively low deposition temperatures. For example, films obtained using $Cu^{II}(hfac)_2$ as the precursor and pure N_2 as the carrier gas were less metallic in appearance. Auger analysis revealed a high percentage of oxygen (suggesting the formation of copper oxides rather than Cu metal) in these films even after prolonged argon sputtering.

Disproportionation vs Direct Reduction of Cu^I. Two other groups[21,22] have reported CVD of copper from (hfac)Cu^I(COD) at somewhat higher temperatures in the absence of hydrogen. They have shown that this occurs by disproportionation:

$$2(\mathrm{hfac})\mathrm{Cu^I}(\mathrm{COD}) \rightarrow \mathrm{Cu} + 2\mathrm{COD} + \mathrm{Cu^{II}}(\mathrm{hfac})_2 \quad (2)$$

We considered the possibility that this reaction might also be responsible for deposition in our experiments. (This reaction is analogous to reaction 1 for the butadiene complex; see discussion above.) However, we believe this is unlikely, for two reasons. First, no metal deposition occurs at these relatively low substrate temperatures in the absence of H_2. And second, we observe no green materials (indicative of $Cu^{II}(hfac)_2$) depositing beyond the heated zone of the reactor. (Attempts to trap volatile copper(II) products by cooling the exhaust gases in a liquid nitrogen bath also failed; these yielded only COD and hfacH, along with smaller quantities of cyclooctene and cyclooctane.) Disproportionation of the Cu^I complex, followed by H_2-dependent deposition from $Cu^{II}(hfac)_2$, could also lead to essentially complete conversion of the starting material to Cu metal, without forming large quantities of $Cu^{II}(hfac)_2$. However, this is also unlikely: our method also produces Cu films cleanly on Si substrates, whereas $Cu^{II}(hfac)_2$ does not deposit Cu on Si at a measurable rate at these substrate temperatures (ca. 200 °C). Thus, we believe that our deposition reaction occurs by direct reduction of Cu^I to the metal.

Conclusions. We find that (hfac)Cu^I(COD) is well suited for efficient deposition of high-purity Cu in the presence of H_2 at low substrate temperatures. This reaction appears to occur by a mechanism different from that observed by other groups in the absence of H_2. A crystallographic study of (hfac)Cu^I(COD) suggests that it may exist in the solid state as a mixture of isomers in which the COD molecule is either η^2 or η^4 coordinated. We are now evaluating these and other Cu complexes as precursors for CVD under lower carrier gas pressures, in order to provide data under conditions intermediate between those of the present study (ca. 1 atm) and those of other groups (<1 Torr). We are also performing deposition experiments on metallized and patterned substrates, and using other spectroscopic methods to study the coordination of (hfac)Cu^I(COD).

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Registry No. Cu, 7440-50-8; (hfac)Cu(COD), 86233-74-1; [(hfac)Cu]$_2(\mu$-COT), 95345-14-5; $CpCu^I(PCCH_2CH_3)_3)$, 12261-30-2; $CpCu^I(P(OCH_3)_3)$, 31741-59-0; $CpCu^I(P(OCH_2CH_3)_3)$, 139704-30-6.

Supplementary Material Available: Packing diagram, data collection and refinement parameters, calculated atomic coordinates, and anisotropic displacement parameters (4 pages); observed and calculated structure factors for (hfac)Cu^I(COD) (5 pages). Ordering information is given on any current masthead page.