Formation Study and X-ray Structures of Dinuclear β-Diketonate Copper(I) Complexes with Conjugated Ene−Yne Lewis Base. Implications for the Use of (hfac)Cu(MHY) as a Precursor for Copper CVD

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Dinuclear [(hfac)Cu]$_2$(MHY) and [(hfac)Cu]$_2$(HY) species, where hfac = hexafluoroacetylacetonate, MHY = 2-methyl-1-hexen-3-yne, and HY = hex-3-yn-1-ene), are formed during copper chemical vapor deposition experiments when a bubbler containing the corresponding mononuclear species is used. These compounds and the so far unknown (hfac)Cu(HY) have been characterized by ^{1}H and ^{13}C NMR and IR spectroscopy and the two dinuclear species by X-ray crystallography and elemental analysis. As expected, in the structure of the dinuclear species, two roughly perpendicular Cu(hfac) moieties are bound to a single ene−yne: one to the C≡C triple bond, the other to the conjuguated double bond. Weak intra- and intermolecular Cu···Cu interactions have been detected in the solid. [(hfac)Cu]$_2$(HY) is more stable and more easily formed than [(hfac)Cu]$_2$(MHY) because of the hindrance character of the additional methyl groups. The formation of the dinuclear species from the mononuclear species is reversible as it has been demonstrated by ^{1}H NMR. The mononuclear species can be recovered from the dinuclear species when free ene−yne base is added. Crystallographic data for [(hfac)Cu]$_2$(MHY): $C_{17}H_{12}O_4F_{12}Cu_2$, triclinic, $P\bar{1}$ (No. 2), $Z = 4$; at 298 K, $a = 11.112(3)$ Å, $b = 13.472(4)$ Å, $c = 15.747(3)$ Å, $\alpha = 94.95(2)°$, $\beta = 98.15(2)°$, $\gamma = 100.27(2)°$; Crystallographic data for [(hfac)Cu]$_2$(HY): $C_{16}H_{10}O_4F_{12}Cu_2$, orthorhombic, *Cc*2*a* (No. 41, *Aba*2), $Z = 8$; at 230 K, $a = 12.280(3)$ Å, $b = 13.531(3)$ Å, $c = 25.461(5)$ Å.

Introduction

Chemical vapor deposition (CVD) processes[1] are increasingly important for ULSI (ultralarge-scale integration) metallization and interconnection. The deposition of pure, conformal metal films is required for multilevel devices with ≤0.13 μm features. As previously reported, the electrical resistivity of the interconnections 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[1,4,5] has clearly demonstrated the potential of Lewis base stabilized copper(I) β-diketonate complexes as copper CVD precursors. The reactive copper(I) β-diketonate moiety may be ligated with phosphines or unsaturated organics, such as alkenes, dienes, and alkynes, to obtain an assortment of precursors with different physical-chemical properties. The deposition of pure copper films from the Cu(I) precursors results from a thermally induced disproportionation reaction, shown in eq 1. Since the Lewis base ligand is weakly bound in the

$$2(\beta\text{-diketonate})\text{Cu}^{\text{I}}(\text{L}) \rightarrow \text{Cu}^0 + \text{Cu}^{\text{II}}(\beta\text{-diketonate})_2 + 2\text{L} \quad (1)$$

complex, the thermal decomposition of these complexes occurs at low temperatures (150−250 °C) and results in the formation of copper films with near-bulk resistivity. Film resistivities between 1.8 and 2.5 $\mu\Omega\cdot$cm, as opposed to 1.67 $\mu\Omega\cdot$cm for bulk copper, have been reported.[6, 7]

In general, CVD copper processes have utilized (hfac)Cu(VTMS) (where VTMS = vinyltrimethylsilane and hfac = hexafluoroacetylacetonate, Cupra-select),[6] which is commercially available, but is a thermally labile material. (hfac)Cu(MHY) (MHY = 2-methyl-1-hexen-3-yne), which has also been reported to be a powerful precursor for Cu CVD, has been the object of patents[8] and studies by our group[9−13] and others.[14, 15]

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During CVD experiments using (hfac)Cu(MHY) precursor, a less volatile compound was formed in the bubbler that was not the same kind as those reported for (hfac)Cu(BTMSA) (BTMSA = bis(trimethylsilylacetylene) where two Cu(hfac) moieties share the same $C\equiv C$ bond in a butterfly geometry.[16] The formation of this species *did not hamper the CVD process when an injection system was used*, but we wanted to have more information about the compound and its formation conditions. It is more easily isolated when HY (hex-3-yn-1-ene) was used instead of MHY. The results and the study are reported here.

Experimental Section

All the starting materials were commercially available except hex-3-yn-1-ene (HY), which was synthesized according to Bransma.[17] Infrared spectra were obtained using a Perkin-Elmer 1600 series FT-IR spectrophotometer. The spectra were obtained neat between two NaCl plates or in Nujol. ^{1}H and ^{13}C NMR spectra were provided by a Bruker Instrument 300 MHz spectrometer. Elemental analyses were performed by the Service Central d'Analyse du CNRS (Vernaison, France).

Synthesis and Characterization of the Complexes. (hfac)Cu(MHY) is commercially available from Merck (Darmstadt, Germany).

Bis(copper(I) hexafluoroacetylacetonate) 2-Methyl-1-hexen-3-yne, [(hfac)Cu]$_2$(MHY). Liquid mononuclear (hfac)Cu(MHY) (10 g) was loaded into a CVD bubbler and heated to 50 °C under vacuum (1 Torr, oil pump) with helium (100 sccm) as carrier gas for 2 h in a process similar to the CVD procedure. A less-volatile viscous brown-yellow dinuclear complex was formed and remained in the bubbler. Yellow crystals of [(hfac)Cu]$_2$(MHY) were grown at 30 °C by sublimation; some of them were suitable for X-ray analysis. Yield: 62%. The yield dropped to 37% when 15% (w, 1.5 g) of free MHY was added to the starting (hfac)Cu(MHY). Mp > 80 °C dec. IR (neat): 3274 (w), 3140 (w), 2988 (m), 2945 (w), 2012 ($C\equiv C$, w), 1645 (s), 1558 (m), 1532 (m), 1472 (s), 1380 (m), 1350 (s), 1260 (s), 1148 (s), 1103 (m), 1001 (w), 948 (w), 919 (w), 880 (w), 803 (m), 770 (w), 746 (s), 675 (s) cm^{-1}. ^{1}H NMR (CDCl$_3$, $T = 298$ K): 6.16 (s, 1H, CH on hfac), 4.88 (s, 1H, $=CH_2$ on MHY), 4.65 (d, $J = 72.1$ Hz, 2H, $=CH_2$ on MHY), 2.78 (q, $J = 7.4$ Hz, 2H, $-CH_2-$ on MHY), 2.16 (s, 3H, $-CH_3$ on MHY), 1.39 ppm (t, $J = 7.4$ Hz, 3H, $-CH_3$ on MHY). ^{13}C {1H} NMR (CDCl$_3$, $T = 298$ K): 178.7 (q, $J_{FC} = 34.5$ Hz, $-C{=}O$), 117.7(q, $J_{FC} = 284.2$ Hz, $-CF_3$), 99.7 ($-C=$), 97.7 ($-C\equiv$), 90.6 ($-CH$ on hfac), 85.6 ($CH_2=$), 84.5 ($-C\equiv$), 24.8 ($-CH_3$), 18.4 ($-CH_2-$), 13.6 ($-CH_3$). ^{19}F NMR (CDCl$_3$, CFCl$_3$ as a standard, $T = 298$ K): −76.7 ppm. Anal. Calcd for [$C_{17}H_{12}F_{12}O_4Cu_2$]: C, 32.1; H, 1.91; F, 35.9. Found: C, 32.4; H, 2.05; F, 35.7.

Copper(I) Hexafluoroacetylacetonate Hex-3-yn-1-ene, (hfac)Cu(HY). A Schlenk flask was loaded with 5.2 g (36 mmol, Aldrich) of Cu$_2$O and 3 g (37 mmol) of hex-3-yn-1-ene and stirred in 25 mL of spectroscopic grade pentane. 1,1,1,5,5,5-Hexafluoroacetylacetone (5 mL, 35 mmol, ABCR) was added dropwise to the stirred solution and the stirring continued for an additional 30 min. The solution was purified by passage over alumina (7 g, in 7 × 2 cm column), with pentane eluant. Removal of solvent gave a bright yellow liquid, (hfac)Cu(HY). Mp = 5 °C. IR data (thin film): 2986 (w), 2944 (w), 2881 (w), 2016 ($C\equiv C$, w), 1671 (w), 1642 (s), 1604 (w), 1556 (m), 1530 (m), 1476 (m), 1260 (s), 1205 (s), 1149 (s), 1103 (w), 976 (w), 939 (w), 800 (m), 674 (m), 588 (m). ^{1}H NMR (CDCl$_3$, $T = 298$ K): 6.15 (s, 1H, CH on hfac), 6.07 (dd, $J = 16.9$ and 10.7 Hz, 1 H, $=CH-$ on HY), 5.79 (d, $J = 16.9$ Hz, 1 H, $=CH_2$ on HY), 5.49 (d, $J = 10.7$ Hz, 1 H, $=CH_2$ on HY), 2.68 (q, $J = 7.5$ Hz, 2H, $-CH_2-$ on HY), 1.33 ppm (t, $J = 7.4$ Hz, 3H, $-CH_3$ on HY). ^{13}C {^{1}H} NMR (CDCl$_3$, $T = 298$ K): 178.3 (q, $J_{FC} = 33.7$ Hz, $-C{=}O$), 121.9 ($=CH_2$), 117.8 (q, $J_{FC} = 283.8$ Hz, $-CF_3$), 112.5 ($-CH=$), 96.1 ($-C\equiv$), 89.8 ($-CH$ on hfac), 83.7($-C\equiv$), 16.1 ($-CH_2-$), 13.5 (s, $-CH_3$). No satisfactory elemental analysis was obtained.

Table 1. Crystal and Intensity Collection Data for [(hfac)Cu]$_2$(MHY) and [(hfac)Cu]$_2$(HY)

	[(hfac)Cu]$_2$(MHY)	[(hfac)Cu]$_2$(HY)
formula	$C_{17}H_{12}O_4F_{12}Cu_2$	$C_{16}H_{10}O_4F_{12}Cu_2$
fw, amu	635.35	621.32
cryst habit, color	block, yellow	block, yellow
cryst syst	triclinic	orthorhombic
space group	$P\bar{1}$	$Cc2a$
a, Å	11.112(3)	12.280(3)
b, Å	13.472(4)	13.531(3)
c, Å	15.747(3)	25.461(5)
α, deg	94.95(2)	
β, deg	98.15(2)	
γ, deg	100.27(2)	
V, Å^3	2281(1)	4230(2)
Z	4	8
D(calcd), g cm^{-3}	1.85	1.95
temp, K	298	230
λ, Å	0.71069	0.71069
R^a	0.0495	0.0478
$R_w{}^b$	0.0499	0.0485

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w = [\sum w||F_o| - |F_c||^2/\sum w|F_o|^2]^{1/2}$.

Bis(copper(I) hexafluoroacetylacetonate) Hex-3-yn-1-ene, [(hfac)Cu]$_2$(HY). Liquid mononuclear (hfac)Cu(HY) (10 g) was heated to 30 °C under vacuum (1 Torr, oil pump) until all the yellow liquid reacted to give yellow crystals that were the dinuclear complex. Some of them were suitable for X-ray analysis. Yield: 97%. Mp > 90 °C dec. IR data (Nujol): 2012 ($C\equiv C$, w), 1654 (w), 1638 (m), 1560 (w), 1534 (w), 1258 (s), 1210 (s), 1152 (s), 1102 (s), 802 (w), 722 (m), 670 (m). ^{1}H NMR (CDCl$_3$, $T = 298$ K): 6.17 (s, 2H, CH on hfac), 5.62 (dd, $J = 9.3$ and 15.5 Hz, 1H, $-CH=$ on HY), 4.92 (d, $J = 15.5$ Hz, 1 H, $=CH_2$ on HY), 4.69 (d, $J = 9.3$ Hz, 1 H, $=CH_2$ on HY), 2.73 (q, $J = 7.5$ Hz, 2H, $-CH_2-$ on HY), 1.35 ppm (t, $J = 7.5$ Hz, 3H, $-CH_3$ on HY). ^{13}C NMR (CDCl$_3$, $T = 298$ K): 178.3 (q, $J_{FC} = 34.7$ Hz, $-C{=}O$), 117.4 (q, $J_{FC} = 283.4$ Hz, $-CF_3$), 98.0 ($-C\equiv$), 90.2 ($-CH$ on hfac), 86.9 ($=CH_2$), 84.7 ($-CH=$), 81.9 ($-C\equiv$), 16.9 ($-CH_2-$), 13.2 ($-CH_3$). Anal. Calcd for [$C_{16}H_{10}O_4F_{12}Cu_2$]: C, 30.9; H, 1.62; F, 36.2. Found: C, 30.9; H, 1.42; F, 36.7.

Study of the Reversible Formation of (hfac)Cu(HY) from [(hfac)Cu]$_2$(HY) and HY. A Schlenk flask was loaded with 100 mg (0.16 mmol) of [(hfac)Cu]$_2$(HY) and 65 mg (0.8 mmol) of hex-3-yn-1-ene and stirred during 30 min in 2 mL of CDCl$_3$ (Euriso-top). Removal of solvent and excess HY under vacuum (oil pump, down to 5×10^{-2} mBar during 20 min), while maintaining the flask at 15 °C, gave a bright yellow liquid, (hfac)Cu(HY), identified by its ^{1}H NMR spectrum.

Single-Crystal X-ray Diffraction: X-ray Crystallographic Analysis for [(hfac)Cu]$_2$(MHY) and [(hfac)Cu]$_2$(HY). The crystals were picked directly in the Schlenk flask under cold nitrogen flow and glued in Araldite at the top of a glass needle. Data collections were performed on an Enraf-Nonius MACH-3 diffractometer with the crystal steeped in a cold nitrogen flow. Crystals, data collection, and refinement parameters are given in Table 1. Accurate cell dimensions and orientation matrices were obtained by least-squares refinements of 25 accurately centered reflections. No significant variations were observed in the intensities of two checked reflections during data collection. The data were corrected for Lorentz and polarization effects. Computations were performed using the PC version of CRYSTALS.[18] Scattering factors and corrections for anomalous absorption were taken from ref

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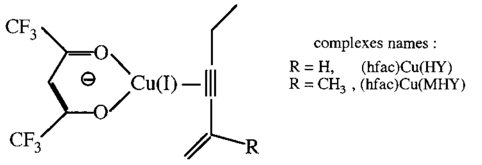
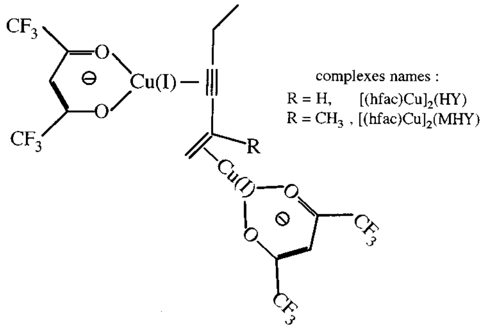
19. The structures were solved by direct methods (SHELXS[20,21]). The final refinements were carried out by full-matrix least-squares using anisotropic displacement parameters for all non-hydrogen atoms. Hydrogen atoms were introduced at calculated positions, and only one overall isotropic displacement parameter was refined.

Results and Discussion

Synthesis and Characterization of [(hfac)Cu]$_2$(MHY), (hfac)Cu(HY), and [(hfac)Cu]$_2$(HY). The new air-sensitive compounds were synthesized and then characterized by NMR and FT-IR spectroscopy. Two of them, [(hfac)Cu]$_2$(MHY) and [(hfac)Cu]$_2$(HY), were characterized by an X-ray structure and elemental analysis.





(hfac)Cu(HY) synthesis was inspired from a previously reported method.[12] The 1:1 stoichiometry was checked by ^{1}H NMR. By ^{13}C NMR, we verified that the ligand is bound to the metal center via the triple bond while the double bond remains free. When heated under vacuum, (hfac)Cu(HY) or (hfac)Cu(MHY), which are liquids at 25 °C (mp = respectively 5 and 13 °C) were slowly transformed into solids with time. No green color revealing the Cu(hfac)$_2$ formation due to the disproportionation reaction was visible. ^{1}H NMR revealed that (hfac)Cu(HY) had been transformed into a dinuclear species, [(hfac)Cu]$_2$(HY), and (hfac)Cu(MHY) into [(hfac)Cu]$_2$(MHY), following equations

$$2(\mathrm{hfac})\mathrm{Cu}(\mathrm{HY}) \rightarrow [(\mathrm{hfac})\mathrm{Cu}]_2(\mathrm{HY}) + \mathrm{HY}\uparrow \qquad (2)$$

and

$$2(\mathrm{hfac})\mathrm{Cu}(\mathrm{MHY}) \rightarrow [(\mathrm{hfac})\mathrm{Cu}]_2(\mathrm{MHY}) + \mathrm{MHY}\uparrow \qquad (3)$$

The dinuclear nature of the complexes was confirmed by the X-ray structure study given below, where it is shown that the Cu(hfac) moiety is bound to the triple bond and another to the double bond which was also demonstrated by NMR and FT-IR spectroscopy. It is not the same kind of dinuclear species that has been reported for [(hfac)Cu]$_2$(BTMSA) or [(hfac)Cu]$_2$(3-hexyne) where two Cu(hfac) share the same C≡C triple bond,[16] but it is close to what has been found for [(hfac)Cu]$_2$(COT) (with COT = cyclooctatetraene).[22] First, the integration of the ^{1}H NMR peaks confirms the 1:2 (MHY or HY:hfac) ratio. Second, the C≡C chemical shift in the ^{13}C NMR spectra is poorly affected by a second Cu(hfac) chelation whereas, in the case of (hfac)Cu(BTMSA),[16] the shift is 9.6 ppm; it is 87.8 and 95.9 ppm for (hfac)Cu(MHY) versus 84.5 and 97.7 ppm for [(hfac)Cu]$_2$(MHY) and 83.7 and 96.1 ppm for (hfac)Cu(HY) versus 81.9 and 98.0 ppm for [(hfac)Cu]$_2$(HY) while the C=C carbons are seriously shielded by the second Cu(hfac) binding: 125.5 and 120.3 ppm for (hfac)Cu(MHY) versus 99.7 and 85.6 ppm for [(hfac)Cu]$_2$(MHY), 112.5 and 121.9 ppm for (hfac)Cu(HY) versus 84.7 and 86.9 ppm for [(hfac)Cu]$_2$(HY). Third, the position of the C≡C vibration is poorly affected after a second Cu(hfac) binding: 2017 cm^{-1} for (hfac)Cu(MHY) versus 2012 cm^{-1} for [(hfac)Cu]$_2$(MHY), 2016 cm^{-1} for (hfac)Cu(HY) versus 2012 cm^{-1} for [(hfac)Cu]$_2$(HY) while, for [(hfac)Cu]$_2$(BTMSA), [16] the C≡C peak shift after the second chelation was more than 200 cm^{-1}. Nothing can be deduced from the C=C vibration peak locations because they are hidden by other molecular vibration peaks.

We observed by a ^{1}H NMR study that the oligomerization reaction is reversible (see Supporting Information). When 5 equiv of HY was added to [(hfac)Cu]$_2$(HY), followed by pumping the excess of HY under vacuum, we obtained a spectrum that can be attributed to pure (hfac)Cu(HY).

Implications for the Use of (hfac)Cu (MHY) as a Precursor for Copper CVD. (hfac)Cu(MHY) is a stable volatile molecule that has been studied and used as a precursor for Cu CVD.[8−15] But, under our experimental conditions, formation of the dinuclear species occurs. The yield of the reaction is 62%, meaning that just 38% of the mononuclear species is vaporized. In a separate experiment, we added 15% of free MHY to the starting (hfac)Cu(MHY), and dinuclear species formation then dropped to 37%, giving 63% of vaporized (hfac)Cu(MHY). This last experiment demonstrates that the formation of dinuclear species can be limited by adding free MHY but cannot be completely prevented. In the case of (hfac)Cu(HY), the yield of dinuclear molecule formation is almost quantitative. It is surprising that just a methyl group in the structure can partially block the ploynuclear species formation; we believe that it comes from steric hindrance more than from electronic effects.

To avoid dinuclear species formation completely, in the CVD process, we recommend the use of an injection system[12] instead of a bubbler. In such a system, the precursor is heated during just the vaporization time which can be very short before being introduced into the reaction chamber. In the vapor phase, inelastic collisions between precursor molecules producing the dinuclear species are extremely unlikely.

Crystal Structures of [(hfac)Cu]$_2$(MHY) and [(hfac)Cu]$_2$(HY). The X-ray crystallographic molecular structures of [(hfac)Cu]$_2$(MHY) and [(hfac)Cu]$_2$(HY) are displayed in Figures 1 and 2, respectively. The relevant bond lengths and angles are listed in Table 2. As expected, two Cu(hfac) moieties are bound to a single ene−yne: one to the C≡C triple bond, the other to the conjuguated double bond. Moreover, the asymmetric unit of [(hfac)Cu]$_2$(MHY) contains two independent molecules, A and B, connected by a weak Cu···Cu bond of 3.121(1) Å.

As for all other (hfac)Cu(alkyne) and (hfac)Cu(alkene) complexes, the C=C and the C≡C bonds to the copper cation are slightly deformed as compared to the free ligand (see Table 3). The copper−carbon bond distances of the alkyne in [(hfac)Cu]$_2$(MHY) are almost equal, being 1.966(8) and 1.943(7)

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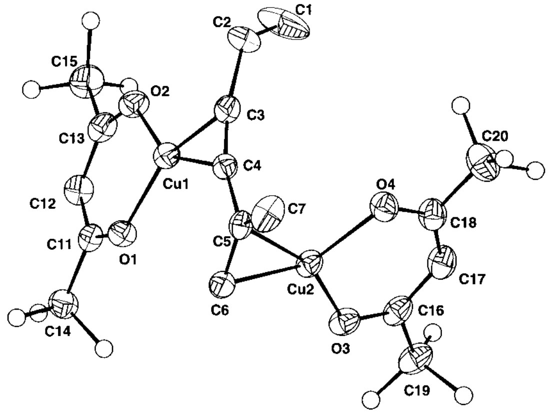

Figure 1. Representation of the X-ray crystal structure of [(hfac)Cu]$_2$-(MHY), showing 30% probability thermal ellipsoids. Hydrogen atoms have been omitted for clarity.

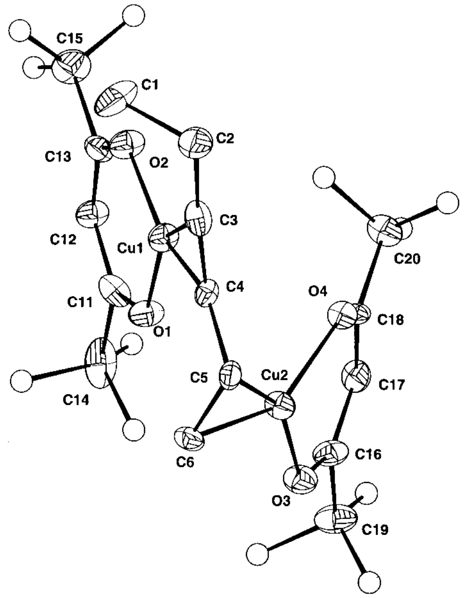

Figure 2. Representation of the X-ray crystal structure of [(hfac)Cu]$_2$-(HY), showing 30% probability thermal ellipsoids. Hydrogen atoms have been omitted for clarity.

Å for molecule A and 1.969(7) and 1.946(6) Å for molecule B. They are very close to the values obtained for (hfac)Cu(MHY) (the X-ray structure contains also two independent molecules), (pfac)Cu(MHY) (pfac = perfluoroacetylacetonate), and (tfac)Cu(MHY) (tfac = 1,1,1-trifluoroacetylacetonate), being respectively 1.94(1), and 1.97(2), 1.941(5) and 1.954(7) Å.[12] The corresponding distances of 1.93(1) and 1.94(1) Å for [(hfac)Cu]$_2$(HY) are slightly shorter. The copper−carbon bond distances of the alkene of 2.015(6) and 1.992(7) Å for A, 2.027(6) and 1.977(7) Å for B in [(hfac)Cu]$_2$(MHY) are very close to the corresponding distances found in the (hfac)Cu-(alkene) family (between 2.013(5) and 2.277(7) Å in (hfac)-Cu(COD)[23,24] (COD = 1,5-cyclooctadiene) or 2.011(3) and 2.029(3) Å in (hfac)Cu(7-*t*-BuO-NBD)[25] (7-*t*-BuO-NBD = 7-*tert*-butoxy-2,5-norbornadiene). In [(hfac)Cu]$_2$(HY) again the corresponding distances of 1.97(1) and 1.95(1) Å are slightly shorter. In both cases, these shorter Cu−(C=) bond distances may come from an electronic contribution of a remaining π nonbonding electron of the conjugated C≡C bond. The two independent C≡C distances found in [(hfac)Cu]$_2$(MHY) are 1.237(9) and 1.222(8) Å and are not appreciably elongated when compared to "free" 2-butyne (1.211 Å) [26] unlike what was previously reported for (hfac)Cu(MHY), (pfac)Cu(MHY), and (tfac)Cu(MHY).

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for [(hfac)Cu]$_2$(MHY) and [(hfac)Cu]$_2$(HY)

		[(hfac)Cu]$_2$(MHY)		
		molecule A	molecule B	[(hfac)Cu]$_2$(HY)
Cu−(C≡)	Cu(1)−C(3)	1.966(8)	1.969(7)	1.93(1)
	Cu(1)−C(4)	1.943(7)	1.946(6)	1.94(1)
Cu−(C=)	Cu(2)−C(5)	2.015(6)	2.027(6)	1.97(1)
	Cu(2)−C(6)	1.992(7)	1.977(7)	1.95(1)
C≡C	C(3)−C(4)	1.237(9)	1.222(8)	1.27(2)
C=C	C(5)−C(6)	1.373(9)	1.375(9)	1.38(2)
Cu···Cu	Cu(1)−Cu′(1)	3.121(1)		
	Cu(1)−Cu(2)	3.844(1)	3.427(1)	3.377(2)
	Cu(2)−Cu(2′)			3.404(3)
C−C≡C	C(2)−C(3)-C(4)	164.4(9)	163.6(7)	161.4(13)
C≡C−C=	C(3)−C(4)-C(5)	158.5(7)	159.4(7)	160.7(12)
C−C=C	C(4)−C(5)-C(6)	121.4(6)	120.4(6)	123.9(11)
Cu−(C≡C)	C(3)−Cu(1)-C(4)	36.9(3)	36.4(2)	38.5(5)
Cu−(C=C)	C(5)−Cu(2)-C(6)	40.1(3)	40.1(3)	41.0(5)

In [(hfac)Cu]$_2$(MHY), the two C−C≡C angles are almost identical: 164.4(9)° and 158.5(7)° for A and 163.6(7)° and 159.4(7)° for B. They are not significantly different from the corresponding angles found in (hfac)Cu(MHY)[12] (averaged at 161.0(15)°) not far from the assumed linear geometry of the "free" alkyne. The corresponding angles are 161.4(13)° and 160.7(12)° for [(hfac)Cu]$_2$(HY).

The Cu−(C=) bond distances (see Table 3) are longer for [(hfac)Cu]$_2$(MHY) than for [(hfac)Cu]$_2$(HY). The ligand MHY contains a methyl group connected to the C=C double bond which, for hindrance reason, chelates Cu(hfac) less strongly than HY. This is confirmed by ^{13}C NMR spectroscopy. When comparing the ^{13}C NMR chemical shift of the C=C bond of the free alkyne with the copper coordinated C=C bond,[27] they are smaller for [(hfac)Cu]$_2$(MHY), −18 (C5) and −35 (C6) ppm, than for [(hfac)Cu]$_2$(HY), −33 (C5) and −38 (C6) ppm, indicating that the Cu−(C=) bond is stronger in [(hfac)Cu]$_2$-(HY) than in [(hfac)Cu]$_2$(MHY). Both crystallographic and NMR data confirm what we experimentally found, i.e., that [(hfac)Cu]$_2$(HY) is more stable and more easily formed than [(hfac)Cu]$_2$(MHY).

In the two dinuclear complexes both intra- and intermolecular Cu···Cu interactions exist. The Cu···Cu distances are 3.844(1) (Cu(1)−Cu(2)), 3.121(1) (Cu(1)−Cu′(1)) (the prime symbol (′) refers to the second independent molecule present in the [(hfac)Cu]$_2$(MHY) structure), and 3.427(1) Å (Cu′(1)−Cu′(2)) for [(hfac)Cu]$_2$(MHY) and 3.377(2) (Cu(1)−Cu(2)) and 3.404(2) Å (Cu(2)−Cu(2′)) for [(hfac)Cu]$_2$(HY). These distances are longer than the Cu···Cu distance found in [(hfac)Cu]$_2$(BTMSA) (2.800(4) Å) where the C≡C bond bridges the two Cu(hfac) moieties. It should be noted that even shorter Cu···Cu bonds have been reported in the literature (down to 2.6078(3) Å in {Cu(SC(OAr)=NPh)}$_4$.[28]

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Table 3. C≡C, C=C, and Cu−C Bond Length (Å) Found in Selected (β-Diketonate)Cu(L)[a]

complexes	C≡C	C=C	Cu−C	ref
[(hfac)Cu]$_2$(MHY)	1.237(9), 1.222(8)	1.373(9), 1.375(9)	1.966(8), 1.943(7) 1.969(7), 1.946(6)	this work
[(hfac)Cu]$_2$(HY)	1.27(2)	1.38(2)	1.93(1), 1.94(1)	this work
(hfac)Cu(MHY)	1.16(2), 1.22(2)	1.28(2), 1.35(3)	1.94(1), 1.95(1) 1.97(2), 1.95(1)	12
(pfac)Cu(MHY)	1.232(9)	1.33(1)	1.954(7), 1.957(7)	12
(tfac)Cu(MHY)	1.224(8)	1.317(9)	1.941(5), 1.937(5)	12
(hfac)Cu(BTMSA)	1.17(5)		2.02(3), 1.92(3)	16
[(hfac)Cu]$_2$(BTMSA)]	1.25(3)		1.96(2), 1.97(2) 1.98(2), 1.94(2)	16
(hfac)Cu(COD)		1.356(6), 1.311(6)	2.007(9), 2.131(9)	24b
(hfac)Cu(7-*t*-BuO-NBD)		1.346(5)	2.011(3), 2.029(3)	25

[a] L = alkene, alkyne, or ene−yne, see abbreviations in the text.

Like most (hfac)Cu(alkene) and all (hfac)Cu(alkyne) families, the Cu(I) environment is approximately planar in [(hfac)Cu]$_2$(MHY) and [(hfac)Cu]$_2$(HY). Moreover, it has been demonstrated in the (hfac)Cu(MHY)[12] structure that the π C=C orbital is perpendicular to the planar (hfac)Cu(C≡C) moiety, the π electrons being delocalized between the π nonbonding C=C and C≡C orbitals. Hence, the (hfac)Cu(C=C) plane should be perpendicular to the (hfac)Cu(C≡C) plane in [(hfac)Cu]$_2$(MHY) and [(hfac)Cu]$_2$(HY). Due to the presence of Cu···Cu interactions, the environment around the Cu(I) and the dihedral angles between the (hfac)Cu(C=C) and the (hfac)Cu(C≡C) planes are deformed from the ideal values. The stronger the Cu···Cu interactions, the greater the deformation.

The Cu′(1)···Cu′(2) interaction in [(hfac)Cu]$_2$(MHY) is stronger than the Cu(1)−Cu(2) interaction and than the corresponding one existing in [(hfac)Cu]$_2$(HY). Hence, the dihedral angles between the Cu′(1)(C≡C) and Cu′(2)(C=C) in [(hfac)Cu]$_2$(MHY) (75°) and between Cu(1)(C≡C) and Cu(2)(C=C) in [(hfac)Cu]$_2$(HY) (73°) are smaller than that between Cu(1)(C≡C) and Cu(2)(C=C) in [(hfac)Cu]$_2$(MHY) (85°). In [(hfac)Cu]$_2$(MHY), the planar environment around Cu′(1) and Cu′(2) is slightly more deformed than around Cu(1) and Cu(2) ions, a deformation that can be attributed to the packing or/and to the existence of Cu···Cu interactions. On the contrary, in [(hfac)Cu]$_2$(HY) there is a short Cu(2)−O4′ distance (2.563(8) Å) that gives a very deformed structure for the Cu(2) ion with a dihedral angle of 29° between the Cu(2)(C=C) and the (hfac)Cu(2) planes.

Conclusion

The existence of dinuclear species has been demonstrated in which Cu(hfac) moieties are stabilized with ene−yne Lewis bases, each unsaturation binding a single copper ion. In the case of (hfac)Cu(MHY), the formation of dinuclear species is not easy because of the hindrance of the methyl group when compared to (hfac)Cu(HY) and can be prevented by adding a small proportion of free MHY (typically 5 wt %). Hence, the existence of the dinuclear species is not an obstacle to the use of (hfac)Cu(MHY) as a successful precursor for copper CVD. Moreover, this study demonstrates the strong capability of the double bond in (hfac)Cu(MHY) to interact with another metallic center that can also be a substrate surface atom during copper CVD film growth. Such interactions may be at the origin of the very low value found for the activation energy in the surface-reaction-limited regime for the growth of copper films from (hfac)Cu(MHY), as suggested,[12] and of the very good filling properties that have been found for (hfac)Cu(MHY) compared to other precursors.[15]

Supporting Information Available: X-ray crystallographic data for compounds [(hfac)Cu]$_2$(HY) and [(hfac)Cu]$_2$(MHY), in CIF format. ^{1}H NMR spectra of (A) (hfac)Cu(HY), (B) [(hfac)Cu]$_2$(HY), and (C) [(hfac)Cu]$_2$(HY) + HY demonstrating the reversible reaction of the mononuclear (hfac)Cu(HY) formation from [(hfac)Cu]$_2$(HY) and HY. This material is available free of charge via the Internet at http://pubs.acs.org.

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