Synthesis and Characterization of (β -Diketonate)(7-*tert*-butoxynorbornadiene)copper(I) Compounds, a Series of New Copper CVD Precursors

Kai-Ming Chi,* Hung-Chang Hou, and Pao-Ts'un Hung

Department of Chemistry, National Chung Cheng University, Ming-Hsiung, Chia-Yi, Taiwan, Republic of China

Shie-Ming Peng* and Gene-Hsiang Lee

Department of Chemistry, National Taiwan University, Taipei, Taiwan, Republic of China

Received November 21, 1994[®]

Organocopper compounds of the general formula (β -diketonate)Cu(7-*t*-BuO-NBD) where 7-*t*-BuO-NBD = 7-*tert*-butoxynorbornadiene and β -diketonate = 1,1,1,5,5,5-hexafluoro-2,4-pentanedionate (1), 1,1,1-trifluoro-2,4-pentanedionate (2), 2,4-pentanedionate (3), 4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedionate (4), 4,4,4-trifluoro-1-phenyl-1,3-butanedionate (5), and 2,2-dimethyl-6,6,7,7,8,8,8-heptafluoro-3,5-octanedionate (6) were prepared by reaction of CuCl with Na(β -diketonate) in the presence of 7-*t*-BuO-NBD. All compounds were characterized by elemental analyses and ¹H, ¹³C, and ¹⁹F NMR, IR, and mass spectra. Single-crystal structures of compounds 1, 4, and 5 were determined by X-ray diffraction analyses that showed mononuclear copper species with coordination of a chelating β -diketonate ligand through two oxygen atoms and the 7-*t*-BuO-NBD through one C=C double bond and an oxygen atom in the solid state. Variable-temperature ¹H NMR spectral data of compound 2 in the solution are consistent with this structural nature. Hot-wall chemical vapor deposition experiments revealed that compound 1 is suitable as a precursor to deposit copper films in the temperature range 200–260 °C. Crystallographic data for compounds 1, 4, and 5: (hfac)Cu(7-*t*-BuO-NBD) (1) crystallizes in monoclinic system, space group *P*2₁/*c*, *a* = 8.923(1) Å, *b* = 19.558(4) Å, *c* = 10.495(3) Å, β = 90.45(2)°, *V* = 1831.3(7) Å³, *Z* = 4. (Ttfac)-Cu(7-*t*-BuO-NBD) (4) crystallizes in monoclinic system, space group *P*2₁/*n*, *a* = 10.689(6) Å, *b* = 9.712(4) Å, *c* = 19.323(4) Å, β = 97.22(3)°, *V* = 1990.2(15) Å³, *Z* = 4. (Btfac)Cu(7-*t*-BuO-NBD) (5) crystallizes in triclinic system, space group *P*1̄, *a* = 9.617(1) Å, *b* = 9.894(4) Å, *c* = 11.322(2) Å, α = 104.57(2)°, β = 95.50(1)°, γ = 104.76(3)°, *V* = 993.4(5) Å³, *Z* = 2.

Introduction

Metal–organic chemical vapor deposition (MOCVD) of metals has a large number of important applications in the electronics and coatings industries.¹ For instance, CVD of aluminum² and tungsten³ thin films are commonly used to deposit interconnect layers in microelectronic devices. The use of copper(I) compounds as precursors of chemical vapor deposition of copper attracts much research interest as the result of potential applications in the microelectronic industry.^{4–8} Lewis base-stabilized (β -diketonate)copper(I) complexes receive the most attention because they deposit highly

pure copper films via the disproportionation reaction of eq 1. Although such complexes have been known for

about 30 years,⁹ relatively little structural information is available.^{8b,10–12} Therefore, it is valuable to systematically investigate the structural properties of these compounds to provide insight into their volatility,

* Author to whom correspondence should be addressed.

[®] Abstract published in *Advance ACS Abstracts*, April 15, 1995.

(1) (a) Sherman, A. *Chemical Vapor Deposition for Microelectronics: Principles, Technology, and Applications*; Noyes Publications: Park Ridge, NJ, 1987. (b) Hess, D. W.; Jensen, K. F. *Microelectronics Processing, Chemical Engineering Aspects*; American Chemical Society: Washington, D. C., 1989.

(2) (a) Broadbent, E. K.; Ramiller, C. L. *J. Electrochem. Soc.* **1984**, *131*, 1427. (b) Green, M. L.; Levy, R. A. *J. Electrochem. Soc.* **1985**, *132*, 1243.

(3) (a) Levy, R. A.; Green, M. L.; Gallagher, R. K. *J. Electrochem. Soc.* **1984**, *131*, 2175. (b) Bent, B. E.; Nuzzo, R. G.; Dubois, L. H. *J. Am. Chem. Soc.* **1989**, *111*, 1634. (c) Beach, D. B.; Blum, S. E.; LeGroues, F. K. *J. Vac. Sci. Technol.* **1989**, *A7*, 3117. (d) Gross, M. E.; Dubois, L. H.; Nuzzo, R. G.; Cheung, K. P. *Mat. Res. Soc. Symp. Proc.* **1991**, *204*, 383. (e) Dubois, L. H.; Zegarski, B. R.; Gross, M. E.; Nuzzo, R. G. *Surface Sci.* **1991**, *244*, 89.

(4) ($\eta^5\text{-C}_5\text{H}_5$)Cu(PR₃) as MOCVD precursors: (a) Dupuy, C. G.; Beach, D. B.; Hurst, J. E. Jr.; Jasinski, J. M. *Chem. Mater.* **1989**, *1*, 16. (b) Beach, D. B.; LeGroues, F. A.; Hu, C.-K. *Chem. Mater.* **1990**, *2*, 216. (c) Hampden-Smith, M. J.; Kodas, T. T.; Paffett, M.; Farr, J. D.; Shin, H. K. *Chem. Mater.* **1990**, *2*, 636.

(5) (*t*-BuOCu)₄ as MOCVD precursor: (a) Jeffries, P. M.; Girolami, G. S. *Chem. Mater.* **1989**, *1*, 8. (b) Jeffries, P. M.; Dubois, L. H.; Girolami, G. S. *Chem. Mater.* **1992**, *4*, 1169.

(6) (β -diketonate)Cu(PR₃) as MOCVD precursors: (a) Shin, H.-K.; Chi, K.-M.; Hampden-Smith, M. J.; Kodas, T. T.; Farr, J. D.; Paffett, M. *Adv. Mater.* **1991**, *3*, 246. (b) Shin, H. K.; Chi, K.-M.; Hampden-Smith, M. J.; Kodas, T. T.; Farr, J. D.; Paffett, M. *Chem. Mater.* **1992**, *4*, 788.

(7) (β -diketonate)Cu(alkene) as MOCVD precursors: (a) Reynolds, S. K.; Smart, C. J.; Baran, E. F.; Baum, T. H.; Larson, C. E.; Brock, P. *J. Appl. Phys. Lett.* **1991**, *59*, 2332. (b) Jain, A.; Chi, K.-M.; Hampden-Smith, M. J.; Kodas, T. T.; Paffett, M.; Farr, J. D. *J. Mater. Res.* **1992**, *7*, 261. (c) Norman, J. A. T.; Muratore, B. A.; Dyer, P. N.; Robert, D. A.; Hochberg, A. K. *J. Phys. (Paris)* **1991**, *IV*, C2/271. (d) Jain, A.; Chi, K.-M.; Hampden-Smith, M. J.; Kodas, T. T. *J. Electrochem. Soc.* **1993**, *140*, 1434.

stability, and reactivity, especially in relation with CVD. Here, we report the syntheses and characterizations of a series of new (β -diketonate)Cu(alkene) complexes with coordination number 4, in which alkene = 7-*tert*-butoxynorbornadiene (7-*t*-BuO-NBD) and β -diketonate = 1,1,1,5,5,5-hexafluoro-2,4-pentanedionate (hfac) (1), 1,1,1-trifluoro-2,4-pentanedionate (tfac) (2), 2,4-pentanedionate (acac) (3), 4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedionate (Ttfac) (4), 4,4,4-trifluoro-1-phenyl-1,3-butanedionate (Btfac) (5), and 2,2-dimethyl-6,6,7,7,8,8-heptafluoro-3,5-octanedionate (fod) (6), variable-temperature ^1H NMR spectroscopic studies of the title compounds, single-crystal structures of compounds 1, 4, and 5, and the results of hot-wall CVD experiments with compound 1 as a precursor.

Experimental Section

General Procedures and Starting Materials. All operations were performed under an atmosphere of nitrogen purified by passage through columns of activated BASF catalyst and molecular sieves and using standard Schlenk techniques¹³ in conjunction with a double manifold vacuum line. All hydrocarbon and ethereal solvents were dried and distilled from sodium benzophenone ketyl at atmospheric pressure before use. Copper(I) chloride, sodium hydride, 1,1,1,5,5,5-hexafluoro-2,4-pentanedione, 1,1,1-trifluoro-2,4-pentanedione, 2,4-pentanedione, 4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione, 4,4,4-trifluoro-1-phenyl-1,3-butanedione, and 2,2-dimethyl-6,6,7,7,8,8-heptafluoro-3,5-octanedione (Aldrich Chemical Co.) were used without further purification. The sodium salts of the β -diketonates^{10b} and the diene 7-*tert*-butoxynorbornadiene¹⁴ were prepared by the methods previously described in the literature. Elemental analyses and mass spectral analyses were made at National Science Council Southern Instrument Center (Department of Chemistry, National Cheng Kung University). NMR data were recorded on a Varian Gemini-200 NMR spectrometer by using the protio impurities of deuterated solvents as references for the ^1H NMR and the ^{13}C signals of the solvents as references for ^{13}C NMR spectroscopies. ^{19}F NMR spectra were externally referred to CFCl_3 . Infrared data were recorded on a Perkin-Elmer Model 16 PC FTIR spectrophotometer. Melting points were measured in sealed capillaries on a Thomas-Hoover Unimelt instrument without calibration.

Synthesis and Characterization of (β -Diketonate)Cu(7-*t*-BuO-NBD). **a. (hfac)Cu(7-*t*-BuO-NBD) (1).** Addition of 7-*t*-BuO-NBD (6.2 mL, 32.3 mmol) to a 250-mL Schlenk flask containing a solution of CuCl (3.21 g, 32.3 mmol) in diethyl ether (50 mL) gave a white slurry solution. A solution of Na(hfac) (7.52 g, 32.7 mmol) in Et_2O (50 mL) was transferred into the reaction flask with stirring, and the reaction mixture turned yellow immediately. The mixture was stirred for 4 h

at room temperature. The volatile components were removed *in vacuo* (0.1 Torr), and hexane (80 mL) was added to dissolve the product. After filtration and removal of hexane, a yellow powder was obtained. Recrystallization of the compound from hexane (10 mL) at 0 °C afforded yellow, crystalline (hfac)Cu(7-*t*-BuO-NBD) (10.2 g, 73% yield).

Anal. Calcd for $\text{C}_{16}\text{H}_{17}\text{O}_3\text{F}_6\text{Cu}$: C, 44.19; H, 3.94. Found: C, 44.31; H, 3.93.

NMR data (C_6D_6 , 18 °C): ^1H δ 6.27 (s, 1H, CH on hfac), 6.04 (m, 2H, noncoordinated CH=CH on 7-*t*-BuO-NBD), 5.02 (br, s, 2H, coordinated CH=CH on 7-*t*-BuO-NBD), 3.31 (br, s, 1H, bridge H on 7-*t*-BuO-NBD), 2.93 (br, s, 2H, bridgehead H on 7-*t*-BuO-NBD), 0.85 (s, 9H, $\text{C}(\text{CH}_3)_3$ on 7-*t*-BuO-NBD) ppm; $^{13}\text{C}\{^1\text{H}\}$ δ 178.3 (q, $J_{\text{FC}} = 33.7$ Hz, CF_3CO on hfac), 139.6 (s, noncoordinated CH=CH on 7-*t*-BuO-NBD), 119.3 (q, $J_{\text{FC}} = 284.5$ Hz, CF_3 on hfac), 101.9 (s, coordinated CH=CH on 7-*t*-BuO-NBD), 92.7 (s, bridge C on 7-*t*-BuO-NBD), 90.1 (s, CH on hfac), 76.8 (s, $(\text{CH}_3)_3\text{C}$ on 7-*t*-BuO-NBD), 56.0 (s, bridgehead C on 7-*t*-BuO-NBD), 28.2 (s, $(\text{CH}_3)_3\text{C}$ on 7-*t*-BuO-NBD) ppm; $^{19}\text{F}\{^1\text{H}\}$ δ -76.3 (s) ppm.

IR data (KBr disk): 3764 (w), 2986 (w), 1644 (s), 1574 (m), 1540 (m), 1488 (s), 1387 (m), 1262 (s), 1194 (s), 1144 (s), 1084 (s), 898 (w), 800 (m), 676 (m), 586 (w) cm^{-1} .

Mass spectral data (FAB⁺, m/z): 434, 34.5 [Cu(hfac)(7-*t*-BuO-NBD)]⁺; 378, 81.8 [Cu(hfac)(7-HO-NBD)]⁺; 227, 39.4 [Cu(7-*t*-BuO-NBD)]⁺; 171, 23.8 [Cu(7-HO-NBD)]⁺; 139, 100 [CF₃C(O)CHC(O)H]⁺; 107, 50.2 [(7-O-NBD)]⁺; 91, 62.7 [C₇H₇]⁺; 77, 47.5 [C₆H₅]⁺; 63, 17.9 [Cu]⁺; 57, 50.3 [C₄H₉]⁺.

Mp: 105 °C, sublimation temperature: 75 °C/0.1 Torr.

b. (tfac)Cu(7-*t*-BuO-NBD) (2). Pale yellow, crystalline (tfac)Cu(7-*t*-BuO-NBD) was prepared in 60% yield with a procedure analogous to that of synthesis of compound 1.

Anal. Calcd for $\text{C}_{16}\text{H}_{20}\text{O}_3\text{F}_3\text{Cu}$: C, 50.46; H, 5.29. Found: C, 50.16; H, 5.28.

NMR data (C_6D_6 , 18 °C): ^1H δ 6.09 (m, 2H, noncoordinated CH=CH on 7-*t*-BuO-NBD), 5.77 (s, 1H, CH on tfac), 4.96 (br, s, 2H, coordinated CH=CH on 7-*t*-BuO-NBD), 3.40 (br, s, 1H, bridge H on 7-*t*-BuO-NBD), 3.05 (br, s, 2H, bridgehead H on 7-*t*-BuO-NBD), 1.75 (s, 3H, CH₃ on tfac), 0.99 (s, 9H, $\text{C}(\text{CH}_3)_3$ on 7-*t*-BuO-NBD) ppm; $^{13}\text{C}\{^1\text{H}\}$ δ 197.9 (s, CH_3CO on tfac), 171.4 (q, $J_{\text{FC}} = 31.0$ Hz, CF_3CO on tfac), 139.8 (s, noncoordinated CH=CH on 7-*t*-BuO-NBD), 120.8 (q, $J_{\text{FC}} = 284.1$ Hz, CF_3 on tfac), 97.4 (s, coordinated CH=CH on 7-*t*-BuO-NBD), 95.3 (s, CH on tfac), 92.2 (s, bridge C on 7-*t*-BuO-NBD), 76.5 (s, $(\text{CH}_3)_3\text{C}$ on 7-*t*-BuO-NBD), 55.9 (s, bridgehead C on 7-*t*-BuO-NBD), 29.6 (s, CH₃ on tfac), 28.5 (s, $(\text{CH}_3)_3\text{C}$ on 7-*t*-BuO-NBD) ppm; $^{19}\text{F}\{^1\text{H}\}$ δ -75.4 (s) ppm.

IR data (KBr disc): 3764 (w), 2980 (w), 1628 (s), 1518 (s), 1497 (m), 1360 (w), 1298 (s), 1233 (m), 1182 (s), 1136 (s), 1084 (s), 886 (w), 774 (w), 700 (w), 582 (w) cm^{-1} .

Mass spectral data (FAB⁺, m/z): 380, 51.2 [Cu(tfac)(7-*t*-BuO-NBD)]⁺; 324, 83.8 [Cu(tfac)(7-HO-NBD)]⁺; 227, 83.6 [Cu(7-*t*-BuO-NBD)]⁺; 216, 12.1 [Cu(tfac)]⁺; 171, 50.5 [Cu(7-HO-NBD)]⁺; 141, 23.0 [Cu(C₆H₅)]⁺; 107, 22.0 [(7-O-NBD)]⁺; 92, 39.3 [NBD]⁺; 91, 100 [C₇H₇]⁺; 79, 10.7 [C₆H₇]⁺; 63, 15.2 [Cu]⁺; 57, 51.2 [C₄H₉]⁺.

Mp: 110 °C dec, sublimation temperature: 75 °C/0.1 Torr.

c. (acac)Cu(7-*t*-BuO-NBD) (3). White, crystalline (acac)Cu(7-*t*-BuO-NBD) was prepared in 47% yield following a procedure similar to that of synthesis of compound 1 except that THF was used as the solvent for reaction.

Anal. Calcd for $\text{C}_{16}\text{H}_{23}\text{O}_3\text{Cu}$: C, 58.79; H, 7.09. Found: C, 58.40; H, 7.14.

NMR data (C_6D_6 , 18 °C): ^1H δ 6.14 (br, s, 2H, noncoordinated CH=CH on 7-*t*-BuO-NBD), 5.36 (s, 1H, CH on acac), 4.88 (br, s, 2H, coordinated CH=CH on 7-*t*-BuO-NBD), 3.47 (br, s, 1H, bridge H on 7-*t*-BuO-NBD), 3.16 (br, s, 2H, bridgehead H on 7-*t*-BuO-NBD), 1.94 (s, 6H, CH₃ on acac), 1.09 (s, 9H, $\text{C}(\text{CH}_3)_3$ on 7-*t*-BuO-NBD) ppm; $^{13}\text{C}\{^1\text{H}\}$ δ 190.3 (s, CO on acac), 139.9 (s, noncoordinated CH=CH on 7-*t*-BuO-NBD), 100.0 (s, CH on acac), 93.3 (s, coordinated CH=CH on 7-*t*-BuO-NBD), 91.6 (s, bridge C on 7-*t*-BuO-NBD), 76.1 (s, $(\text{CH}_3)_3\text{C}$ on

(8) (β -diketonate)Cu(alkyne) as MOCVD precursors: (a) Jain, A.; Chi, K.-M.; Kodas, T. T.; Hampden-Smith, M. J.; Farr, J. D.; Paffett, M. *Chem. Mater.* **1991**, *3*, 995. (b) Baum, T. H.; Larson, C. E. *Chem. Mater.* **1992**, *4*, 365.

(9) Nast, R.; Lepel, W.-H. *Chem. Ber.* **1969**, *102*, 3224.

(10) (a) Anderson, W. A.; Carty, A. J.; Palenik, G. J.; Schreiber, G. *Can. J. Chem.* **1971**, *49*, 761. (b) Shin, H.-K.; Chi, K. M.; Farkas, J.; Hampden-Smith, M. J.; Kodas, T. T.; Duesler, E. N. *Inorg. Chem.* **1992**, *31*, 424. (c) Chi, K. M.; Corbitt, T. S.; Hampden-Smith, M. J.; Kodas, T. T.; Duesler, E. N. *J. Organomet. Chem.* **1993**, *449*, 181.

(11) (a) Doyle, G.; Eriksen, K. A.; Van Engen, D. *Organometallics* **1985**, *4*, 830. (b) Chi, K. M.; Shin, H.-K.; Hampden-Smith, M. J.; Kodas, T. T.; Duesler, E. N. *Polyhedron* **1991**, *10*, 2293. (c) Kumar, R.; Fronczek, F. R.; Mavreick, A. W.; Lai, W. G.; Griffin, G. F. *Chem. Mater.* **1992**, *4*, 577.

(12) Chi, K. M.; Shin, H.-K.; Hampden-Smith, M. J.; Kodas, T. T.; Duesler, E. N. *Inorg. Chem.* **1991**, *30*, 424.

(13) Shriver, D. F.; Drezden, M. A. *The Manipulation of Air-Sensitive Compounds*, 2nd ed.; Wiley: New York, 1986.

(14) Story, P. R.; Fahrenholtz, S. R. *Organic Syntheses*; Wiley: New York, 1973; Collect. Vol. V, p 151.

7-*t*-BuO-NBD), 55.8 (s, bridgehead *C* on 7-*t*-BuO-NBD), 28.9 (s, CH₃ on acac), 28.7 (s, (CH₃)₃C on 7-*t*-BuO-NBD) ppm.

IR data (KBr disk): 3083 (w), 2976 (w), 1596 (s), 1514 (s), 1462 (m), 1406 (s), 1363 (m), 1320 (w), 1272 (w), 1232 (m), 1188 (m), 1090 (s), 1016 (m), 936 (w), 890 (w), 672 (m), 702 (m), 572 (w) cm⁻¹.

Mass spectral data (EI⁺, *m/z*): 326, 10.7 [Cu(acac)(7-*t*-BuO-NBD)]⁺; 270, 7.4 [Cu(acac)(7-HO-NBD)]⁺; 261, 10.3 [Cu(acac)₂]⁺; 163, 13.0 [HCu(acac)]⁺; 147, 9.1 [Cu(C₄H₄O₂)]⁺; 108, 31.1 [(7-HO-NBD)]⁺; 107, 18.8 [(7-O-NBD)]⁺; 91, 79.0 [C₇H₇]⁺; 85, 15.9 [(C₄H₄O₂)]⁺; 79, 50.9 [C₆H₇]⁺; 78, 19.6 [C₆H₆]⁺; 63, 6.3 [Cu]⁺; 57, 100 [C₄H₉]⁺.

Mp: 115 °C dec, sublimation temperature: 90 °C/0.1 Torr.

d. (Ttfac)Cu(7-*t*-BuO-NBD) (4). Yellow, crystalline (Ttfac)Cu(7-*t*-BuO-NBD) was prepared in 66% yield by using a procedure analogous to that of the synthesis of compound 1.

Anal. Calcd for C₁₉H₂₀O₃F₃CuS: C, 50.83; H, 4.49. Found: C, 50.62; H, 4.47.

NMR data (C₆D₆, 18 °C): ¹H δ 7.26 (d, 1H, *J* = 3.2 Hz, thienyl *H* on Ttfac), 6.85 (d, 1H, *J* = 4.8 Hz, thienyl *H* on Ttfac), 6.53 (m, 1H, thienyl *H* on Ttfac), 6.51 (s, 1H, methine CH on Ttfac), 6.09 (br, s, 2H, noncoordinated CH=CH on 7-*t*-BuO-NBD), 4.99 (br, s, 2H, coordinated CH=CH on 7-*t*-BuO-NBD), 3.39 (br, s, 1H, bridge *H* on 7-*t*-BuO-NBD), 3.06 (br, s, 2H, bridgehead *H* on 7-*t*-BuO-NBD), 0.97 (s, 9H, C(CH₃)₃ on 7-*t*-BuO-NBD) ppm. ¹³C{¹H} δ 183.0 (s, CO on Ttfac), 172.5 (q, *J*_{FC} = 32 Hz, CF₃CO on Ttfac), 146.8 (s, thienyl *C* on Ttfac), 139.6 (s, noncoordinated CH=CH on 7-*t*-BuO-NBD), 132.7 (s, thienyl *C* on Ttfac), 130.5 (s, thienyl *C* on Ttfac), 120.8 (q, *J*_{FC} = 284 Hz, CF₃ on Ttfac), 98.2 (s, coordinated CH=CH on 7-*t*-BuO-NBD), 92.3 (s, bridge *C* on 7-*t*-BuO-NBD), 91.5 (s, methine CH on Ttfac), 76.5 (s, (CH₃)₃C on 7-*t*-BuO-NBD), 55.9 (s, bridgehead *C* on 7-*t*-BuO-NBD), 28.5 (s, (CH₃)₃C on 7-*t*-BuO-NBD) ppm; ¹⁹F{¹H} δ -75.3 (s) ppm.

IR data (KBr disk): 3752 (w), 2976 (w), 1602 (s), 1536 (s), 1516 (m), 1464 (m), 1412 (m), 1354 (m), 1304 (s), 1232 (m), 1172 (s), 1144 (s), 1080 (s), 1036 (w), 930 (w), 888 (w), 782 (m), 728 (w), 688 (m), 668 (w), 584 (w) cm⁻¹.

Mass spectral data (FAB⁺, *m/z*): 568, 12.2 [Cu₂(Ttfac)₂]⁺; 448, 34.1 [Cu(Ttfac)(7-*t*-BuO-NBD)]⁺; 392, 85.2 [Cu(Ttfac)(7-HO-NBD)]⁺; 285, 24.5 [HCu(Ttfac)]⁺; 227, 67.3 [Cu(7-*t*-BuO-NBD)]⁺; 171, 39.2 [Cu(7-HO-NBD)]⁺; 141, 18.0 [Cu(C₆H₆)]⁺; 111, 21.8 [C₅H₅OS]⁺; 107, 18.8 [(7-O-NBD)]⁺; 92, 26.2 [NBD]⁺; 91, 100 [C₇H₇]⁺; 63, 7.0 [Cu]⁺; 57, 24.8 [C₄H₉]⁺.

Mp: 115 °C dec, sublimation temperature: 90 °C/0.1 Torr.

e. (Btfac)Cu(7-*t*-BuO-NBD) (5). Yellow, crystalline (Btfac)Cu(7-*t*-BuO-NBD) was prepared in 63% yield by using a procedure analogous to that of synthesis of compound 1.

Anal. Calcd for C₂₁H₂₂O₃F₃Cu: C, 56.94; H, 5.01. Found: C, 56.94; H, 5.02.

NMR data (C₆D₆, 18 °C): ¹H δ 7.86 (m, 2H, phenyl *H* on Btfac), 7.07 (m, 3H, phenyl *H* on Btfac), 6.59 (s, 1H, methine CH on Btfac), 6.16 (br, s, 2H, noncoordinated CH=CH on 7-*t*-BuO-NBD), 5.03 (br, s, 2H, coordinated CH=CH on 7-*t*-BuO-NBD), 3.43 (br, s, 1H, bridge *H* on 7-*t*-BuO-NBD), 3.12 (br, s, 2H, bridgehead *H* on 7-*t*-BuO-NBD), 0.96 (s, 9H, C(CH₃)₃ on 7-*t*-BuO-NBD) ppm; ¹³C{¹H} δ 189.9 (s, C₆H₅CO on Btfac), 173.0 (q, *J*_{FC} = 32.0 Hz, CF₃CO on Btfac), 140.4 (s, phenyl *C* on Btfac), 139.8 (s, noncoordinated CH=CH on 7-*t*-BuO-NBD), 132.6 (s, phenyl *C* on Btfac), 121.3 (q, *J*_{FC} = 284.3 Hz, CF₃ on Btfac), 97.9 (s, coordinated CH=CH on 7-*t*-BuO-NBD), 92.3 (s, methine CH on Btfac), 92.0 (s, bridge *C* on 7-*t*-BuO-NBD), 76.6 (s, (CH₃)₃C on 7-*t*-BuO-NBD), 56.0 (s, bridgehead *C* on 7-*t*-BuO-NBD), 28.5 (s, (CH₃)₃C on 7-*t*-BuO-NBD) ppm; ¹⁹F{¹H} δ -75.2 (s) ppm.

IR data (KBr disk): 3752 (w), 2982 (w), 1612 (s), 1587 (m), 1540 (m), 1482 (m), 1377 (w), 1292 (s), 1257 (m), 1178 (s), 1152 (s), 1088 (m), 898 (w), 764 (w), 686 (w), 658 (w), 596 (w) cm⁻¹.

Mass spectral data (FAB⁺, *m/z*): 720, 12.4 [Cu₂(Btfac)₂(7-*t*-BuO-NBD)]⁺; 442, 59.6 [Cu(Btfac)(7-*t*-BuO-NBD)]⁺; 386, 100 [Cu(Btfac)(7-HO-NBD)]⁺; 279, 51.4 [HCu(Btfac)]⁺; 227, 87.2 [Cu(7-*t*-BuO-NBD)]⁺; 216, 12.5 [HBtfac]⁺; 171, 41.1 [Cu(7-

HO-NBD)]⁺; 141, 15.2 [Cu(C₆H₆)]⁺; 107, 15.5 [(7-O-NBD)]⁺; 92, 12.9 [NBD]⁺; 91, 83.3 [C₇H₇]⁺; 77, 9.5 [C₆H₅]⁺; 63, 4.6 [Cu]⁺; 57, 17.6 [C₄H₉]⁺.

Mp: 116 °C, sublimation temperature: 90 °C/0.12 Torr.

f. (fod)Cu(7-*t*-BuO-NBD) (6). Yellow, crystalline (fod)Cu(7-*t*-BuO-NBD) was prepared in 53% with a procedure analogous to that for compound 1.

Anal. Calcd for C₂₁H₂₆O₃F₇Cu: C, 48.23; H, 5.01. Found: C, 48.10; H, 5.04.

NMR data (C₆D₆, 18 °C): ¹H δ 6.15 (s, 1H, CH on fod), 6.10 (br, s, 2H, noncoordinated CH=CH on 7-*t*-BuO-NBD), 4.93 (br, s, 2H, coordinated CH=CH on 7-*t*-BuO-NBD), 3.39 (br, s, 1H, bridge *H* on 7-*t*-BuO-NBD), 3.03 (br, s, 2H, bridgehead *H* on 7-*t*-BuO-NBD), 1.10 (s, 9H, C(CH₃)₃ on fod), 0.97 (s, 9H, C(CH₃)₃ on 7-*t*-BuO-NBD) ppm; ¹³C{¹H} δ 206.1 (s, (CH₃)₃CCO on fod), 172.9 (t, *J*_{FC} = 22.6 Hz, CF₂CO on fod), 139.8 (s, noncoordinated CH=CH on 7-*t*-BuO-NBD), 123.0–104.9 (m, CF₂CF₂CF₃ on fod), 97.5 (s, coordinated CH=CH on 7-*t*-BuO-NBD), 92.4 (s, CH on fod), 92.1 (s, bridge *C* on 7-*t*-BuO-NBD), 76.4 (s, (CH₃)₃C on 7-*t*-BuO-NBD), 55.9 (s, bridgehead *C* on 7-*t*-BuO-NBD), 43.0 (s, C(CH₃)₃ on fod), 28.6 (s, C(CH₃)₃ on fod), 28.5 (s, C(CH₃)₃ on 7-*t*-BuO-NBD) ppm; ¹⁹F{¹H} δ -80.5 (s), -119.0 (s), -126.2 (s) ppm.

IR data (KBr disk): 2986 (m), 1627 (s), 1581 (m), 1511 (m), 1480 (s), 1401 (w), 1355 (m), 1231 (s), 1198 (s), 1125 (m), 1083 (s), 1028 (w), 918 (w), 793 (w), 697 (m), cm⁻¹.

Mass spectral data (EI⁺, *m/z*): 522, 2.3 [Cu(fod)(7-*t*-BuO-NBD)]⁺; 466, 3.1 [Cu(fod)(7-HO-NBD)]⁺; 359, 4.9 [HCu(fod)]⁺; 301, 15.7 [Cu(C₃F₇C(O)CH-C(O))]⁺; 239, 13.7 [C₃F₇C(O)CHC(O)]⁺; 227, 10.0 [Cu(7-*t*-BuO-NBD)]⁺; 171, 7.4 [Cu(7-HO-NBD)]⁺; 149, 7.6 [(7-(CH₃)₂CO-NBD)]⁺; 141, 5.4 [Cu(C₆H₆)]⁺; 108, 37.1 [(7-HO-NBD)]⁺; 107, 27.6 [(7-O-NBD)]⁺; 92, 11.6 [NBD]⁺; 91, 97.0 [C₇H₇]⁺; 79, 63.8 [C₆H₇]⁺; 78, 21.0 [C₆H₆]⁺; 77, 27.1 [C₆H₅]⁺; 69, 24.4 [CF₃]⁺; 63, 11.3 [Cu]⁺; 57, 100 [C₄H₉]⁺.

Mp: 115 °C dec, sublimation temperature: 85 °C/0.1 Torr.

X-ray Single-Crystal Structural Determination. Three examples of the title compounds were characterized structurally in the solid state by single-crystal X-ray diffraction. All diffraction data were collected on an Enraf-Nonius CAD-4 diffractometer with monochromated Mo Kα radiation (λ = 0.709 30 Å) using Θ/2Θ scan mode. Crystal, collection, and refinement data are summarized in Table 1.

a. (hfac)Cu(7-*t*-BuO-NBD) (1). Bright yellow crystals of (hfac)Cu(7-*t*-BuO-NBD) were grown by crystallization from hexane solution at -20 °C, and a single crystal of dimensions 0.40 × 0.50 × 0.50 mm³ was selected for X-ray analysis. Cell parameters were determined from a fit of 25 reflections (23.40 < 2Θ < 27.60 °). All data were corrected for Lorentz and polarization effects and for effects of absorption. A total of 3228 reflections was collected, but only 2586 unique reflections with *I* > 2σ(*I*) were used for structural solution and refinement. The structure was solved by the heavy-atom method and refined by full-matrix least-squares methods based on *F* values. All non-hydrogen atoms were refined with anisotropic thermal parameters. The atomic scattering factors were taken from *International Tables for X-ray Crystallography*.¹⁵ The final agreement factors are *R*_F = 0.042, *R*_w = 0.042 with *w* = 1/σ²(*F*).

b. (Ttfac)Cu(7-*t*-BuO-NBD) (4). Light yellow crystals of (Ttfac)Cu(7-*t*-BuO-NBD) were grown by crystallization from hexane solution at -20 °C and a single crystal of dimensions 0.50 × 0.50 × 0.70 mm³ was selected for X-ray analysis. Cell parameters were determined from a fit of 25 reflections (19.42 < 2Θ < 25.38 °). All data were corrected for Lorentz and polarization effects and for effects of absorption. A total of 3495 reflections was collected, but only 2481 unique reflections with *I* > 2σ(*I*) were used for structural solution and refinement. The structure was solved by the heavy-atom method and

(15) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. IV.

Table 1. Summary of Crystallographic Data for Compounds 1, 4, and 5

compd	1	4	5
emp form.	C ₁₆ H ₁₆ O ₃ CuF ₆	C ₁₉ H ₂₀ O ₃ CuF ₃ S	C ₂₁ H ₂₂ O ₃ CuF ₃
form. wt	434.84	448.96	442.94
cryst size (mm ³)	0.40 × 0.50 × 0.50	0.50 × 0.50 × 0.70	0.35 × 0.50 × 0.65
space grp	monoclinic; <i>P</i> 2 ₁ / <i>c</i>	monoclinic; <i>P</i> 2 ₁ / <i>n</i>	triclinic <i>P</i> 1̄
<i>a</i> (Å)	8.9227(12)	10.689(6)	9.6174(13)
<i>b</i> (Å)	19.558(4)	9.712(4)	9.894(4)
<i>c</i> (Å)	10.495(3)	19.323(4)	11.3223(19)
α (°)			104.574(24)
β (°)	90.450(17)	97.22(3)	95.501(12)
γ (°)			104.76(3)
<i>V</i> (Å ³)	1831.3(7)	1990.2(15)	993.4(5)
<i>Z</i>	4	4	2
<i>d</i> (calcd) (g/cm ³)	1.577	1.498	1.481
λ (Å)		0.70930	
<i>T</i> (K)		298.00	
<i>F</i> (000)	880	922	457
2θ range (deg)	23.40–27.60	19.42–25.38	18.92–30.48
scan type		θ/2θ	
scan speed (deg/min)		2.06–8.24	
scan width		2(0.70 + 0.35 tan θ)	
2θ _{max}		50	
μ (cm ⁻¹)	12.623	12.412	11.446
transmission	0.864; 1.000	0.882; 1.000	0.892; 1.000
index ranges	−10 < <i>h</i> < 10 0 < <i>k</i> < 23 0 < <i>l</i> < 12	−12 < <i>h</i> < 12 0 < <i>k</i> < 11 0 < <i>l</i> < 22	−11 < <i>h</i> < 10 0 < <i>k</i> < 11 −13 < <i>l</i> < 13
<i>R</i> _F ; <i>R</i> _w ^a	0.042; 0.042	0.051; 0.052	0.035; 0.035
goodness-of-fit ^b	3.47	2.47	2.25
weights scheme		1/σ ² (<i>F</i> _o)	
refine. prog.		NRCVAX	
no. of atoms	43	47	50
no. of params refined	268	245	254
largest Δ/σ	0.0299	0.0255	0.0216

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

Figure 1. Schematic plot of hot-wall CVD reactor.

refined by full-matrix least-squares methods based on *F* values. All non-hydrogen atoms were refined with anisotropic thermal parameters. The atomic scattering factors were taken from *International Tables for X-ray Crystallography*.¹⁵ The final agreement factors are $R_F = 0.051$, $R_w = 0.052$ with $w = 1/\sigma^2(F)$.

c. (Btfac)Cu(7-*t*-BuO-NBD) (5). Yellow crystals of (Btfac)Cu(7-*t*-BuO-NBD) were grown by crystallization from hexane solution at -20°C , and a single crystal of dimensions $0.35 \times 0.50 \times 0.65 \text{ mm}^3$ was selected for X-ray analysis. Cell parameters were determined from a fit of 25 reflections ($18.92 < 2\theta < 30.48^\circ$). All data were corrected for Lorentz and polarization effects and for effects of absorption. A total of 3499 reflections was collected, but only 2940 unique reflections with $I > 2\sigma(I)$ were used for structural solution and refinement. The structure was solved by the heavy-atom method and refined by full-matrix least-squares based on *F* values. All non-hydrogen atoms were refined by full-matrix least-squares based on *F* values. All non-hydrogen atoms were refined with anisotropic thermal parameters. The atomic scattering factors were taken from *International Tables for X-ray Crystallography*.¹⁵ The final agreement factors are $R_F = 0.035$, $R_w = 0.035$ with $w = 1/\sigma^2(F)$.

Chemical Vapor Deposition of Copper Films from Compound 1. CVD experiments were conducted in the hot-

wall reactor shown in Figure 1. Substrates of two types, Si (100) wafers coated with 1000 Å of Pt and with 2000 Å of thermally grown SiO₂, were used. The substrates, typically $1.5 \text{ cm} \times 1.5 \text{ cm}^2$, were cleaned with deionized water, acetone, and 1,1,1-trichloroethane and then heated to 100°C for 20 min before use. The CVD reactor was charged with (hfac)Cu(7-*t*-BuO-NBD) (approximately 0.5 g) and a substrate in a glovebox with nitrogen atmosphere for each experiment. The assembled reactor was attached to a U-trap that was cooled with liquid N₂ and connected to a vacuum line. While the system was evacuated (0.1 Torr), the deposition zone was preheated with a furnace for 1 h to attain the deposition temperature and the precursor remained at room temperature. The precursor was then warmed to 80°C with a heating tape to transfer into the deposition zone and deposition was continued until all precursor had evaporated. Deposition was undertaken over a temperature range $140\text{--}260^\circ\text{C}$ at 30°C intervals. No carrier gas was used in these experiments. Film resistivities were measured with a four-point probe.

Results and Discussion

1. Synthesis of (β-Diketonate)Cu(7-*t*-BuO-NBD) Complexes. The title compounds were prepared from reactions of CuCl with the corresponding β-diketonate

Figure 2. ORTEP drawing of (hfac)Cu(7-*t*-BuO-NBD) (1). **Figure 3.** ORTEP drawing of (Ttfac)Cu(7-*t*-BuO-NBD) (4).

salts of sodium in the presence of 7-*t*-BuO-NBD according to eq 2. The reactions were carried out in ethereal

solutions at room temperature, and products were isolated on extraction with hexane and removal of volatile species *in vacuo*. A similar method was used to prepare analogous complexes of 1,5-cyclooctadiene (1,5-COD).^{11b} These compounds are yellow to white solids that can be sublimed at temperatures above 75 °C under a reduced pressure (about 0.1 Torr). They are thermally robust and moderately sensitive to air and moisture. All compounds gave satisfactory elemental analyses and were characterized by solution ¹H, ¹³C, and ¹⁹F NMR, IR, and mass spectroscopic methods.

2. Single-Crystal Structural Determination of Compounds 1, 4, and 5. The molecular structures of (hfac)Cu(7-*t*-BuO-NBD) (1), (Ttfac)Cu(7-*t*-BuO-NBD) (4), and (Btfac)Cu(7-*t*-BuO-NBD) (5) were determined in the solid state by single-crystal X-ray diffraction analyses. ORTEP diagrams showing the atomic labeling scheme of these molecules are presented in Figures 2–4. The crystal, collection, and refinement data are summarized in Table 1; selected bond lengths and bond angles are given in Tables 2 and 3. Unlike the dinuclear norbornadiene derivative, [(hfac)Cu]₂(norbornadiene),^{11a} these compounds are mononuclear and the central copper atom is coordinated by the chelating β-diketonate ligand through two oxygen atoms and the 7-*t*-BuO-NBD through one C=C double bond and an oxygen atom. The same coordination mode for the 7-*t*-BuO-NBD ligand is

Figure 4. ORTEP drawing of (Btfac)Cu(7-*t*-BuO-NBD) (5).**Table 2.** Selected Bond Lengths (Å) for Compounds 1, 4, and 5

compd	1	4	5
Cu–O(1)	2.249(2)	2.344(3)	2.365(2)
Cu–O(2)	1.976(2)	1.943(3)	1.953(2)
Cu–O(3)	1.988(2)	1.962(3)	1.966(2)
Cu–C(1)	2.011(3)	1.991(5)	1.987(3)
Cu–C(2)	2.029(3)	2.014(4)	2.033(3)
C(1)–C(2)	1.346(5)	1.359(8)	1.354(4)
C(4)–C(5)	1.294(6)	1.299(8)	1.311(6)

Table 3. Selected Bond Angles (deg) for Compounds 1, 4, and 5

compd	1	4	5
O(1)–Cu–O(2)	105.4(1)	104.2(1)	101.8(1)
O(1)–Cu–O(3)	109.2(1)	99.7(1)	104.4(1)
O(1)–Cu–C(1)	81.6(1)	81.8(2)	80.5(1)
O(1)–Cu–C(2)	81.2(1)	79.8(2)	81.3(1)
O(2)–Cu–O(3)	93.3(1)	95.2(1)	94.0(1)
O(2)–Cu–C(1)	152.7(1)	153.6(2)	159.3(1)
O(2)–Cu–C(2)	115.0(1)	115.2(2)	120.2(1)
O(3)–Cu–C(1)	109.5(1)	109.4(2)	105.4(1)
O(3)–Cu–C(2)	146.6(1)	149.0(2)	143.8(1)
C(1)–Cu–C(2)	38.9(2)	39.7(2)	39.3(1)
Cu–O(1)–C(7)	99.6(2)	97.1(2)	96.3(1)
Cu–C(1)–C(2)	71.3(2)	71.1(3)	72.2(2)
Cu–C(2)–C(1)	69.8(2)	69.3(3)	68.5(2)

reported in the structure of (7-*t*-BuO-NBD)₂Mo(CO)₂.¹⁶ The bond distances and angles within the β-diketonate ligand are similar to those of other β-diketonate copper(I) complexes according to previous reports.^{10–12} The coordination geometry about copper is best described as a highly distorted tetrahedron that resembles that of (hfac)Cu(1,5-COD).^{11b} The atoms O(2), O(3), C(1), and C(2) are mutually coplanar, and the copper atom lies slightly (for example, 0.091 Å for compound 1) above the plane. The O(1) atom occupies the fourth coordination site with a relatively weak interaction to copper atom (Cu–O(1) distance = 2.249(2), 2.344(3), and 2.365(2) Å for compounds 1, 4, and 5, respectively) compared with bonding between copper and oxygens of β-diketonate ligands in the same molecule (Cu–O(2), Cu–O(3) bond distances are 1.94–1.99 Å for compounds 1, 4, and 5), and with Cu–O bonding in the molecule (*t*-BuOCu)₄ (average bond length is 1.85 Å).¹⁷ Thus, the structures are best described as “3 + 1” coordination of the copper center also observed in the molecular struc-

(16) Chow, T. J.; Chao, Y.-S.; Liu, L.-K. *J. Am. Chem. Soc.* **1987**, *109*, 797.

(17) Greiser, T.; Weiss, E. *Chem. Ber.* **1976**, *109*, 3142.

Table 4. Chemical Shifts^a of Olefinic ¹H and ¹³C NMR Resonances for 7-*t*-BuO-NBD and Compounds 1–6

compd	δ ($\Delta\delta^b$) (ppm)			
	¹ H		¹³ C	
7- <i>t</i> -BuO-NBD	6.54	6.56	137.9	140.6
1	5.02 (−1.52)	6.04 (−0.52)	101.9 (−36.0)	139.6 (−1.0)
2	4.96 (−1.58)	6.09 (−0.47)	97.4 (−40.5)	139.8 (−0.8)
3	4.88 (−1.66)	6.14 (−0.42)	93.3 (−44.6)	139.9 (−0.7)
4	4.99 (−1.55)	6.09 (−0.47)	98.2 (−39.7)	139.6 (−1.0)
5	5.03 (−1.51)	6.16 (−0.40)	97.9 (−40.0)	139.8 (−0.8)
6	4.93 (−1.61)	6.10 (−0.46)	97.5 (−40.4)	139.8 (−0.8)

^a In C₆D₆. ^b $\Delta\delta = \delta_{\beta\text{-diketonate compd}} - \delta_{7\text{-}t\text{-BuO-NBD}}$.

ture of (hfac)Cu(1,5-COD).^{11b} Because hfac ligand possesses two electron-withdrawing CF₃ substituents, bond distances between copper and oxygen atoms of β -diketonate in compound 1 are longer than those in compounds 4 and 5. To compensate for the electron deficiency on the copper center, donation of more electron density from O(1) to Cu, which resulted in a shorter (approximately 0.1 Å) Cu–O(1) bond in compound 1 than in compounds 4 and 5, was observed. The longer bonds of the coordinated olefins (C(1)–C(2) = 1.346(5), 1.359(8), and 1.354(4) Å for compounds 1, 4, and 5, respectively) than those of the noncoordinated olefins (C(4)–C(5) = 1.294(6), 1.299(8), and 1.311(6) Å for compounds 1, 4, and 5, respectively) indicate the existence of π -backbonding between alkene and copper centers in these compounds (see below). No other distances and angles within the 7-*t*-BuO-NBD are exceptional.

3. NMR Spectroscopic Studies of (β -Diketonate)Cu(7-*t*-BuO-NBD) Complexes. The integrated ¹H and ¹³C NMR spectra of the title compounds are consistent with the empirical formula (β -diketonate)-Cu(7-*t*-BuO-NBD) and exhibit olefinic resonances of the two types presented in Table 4. Both resonances have smaller chemical shifts than those of free 7-*t*-BuO-NBD. The signal at higher field is associated with the coor-

dated olefinic ¹H or ¹³C and the other is attributed to the noncoordinated olefin. Comparisons of ¹H and ¹³C chemical shifts for the free alkene and the alkene coordinating to the Cu(I) center were used to evaluate the relative contributions of π and σ bonding in the complexes.^{18,19} Variations of chemical shifts ($\Delta\delta$) of olefinic protons and carbons for compounds 1–6 are listed in Table 4 and are much larger than those for other (β -diketonate)(alkene)Cu(I) compounds that were found to be between +0.02 and −0.74 ppm and between −8.14 and −29.04 ppm for ¹H and ¹³C signals, respectively.¹⁸ This feature implies the existence of relatively stronger π -backbonding between alkene and copper center in the title compounds. Shieldings of both coordinated olefinic ¹H and ¹³C nuclei of these compounds follow the increasing order of 3 > 2 > 1 in agreement with electron donor capabilities of β -diketonate ligands.

On the basis of the solid-state structures of compounds 4 and 5, those containing an asymmetrically substituted β -diketonate ligand (R $\neq$ R', see Scheme 1) are expected to exhibit bridgehead [H(3), H(6)], coordinated olefinic [H(1), H(2)], and noncoordinated olefinic [H(4), H(5)] proton NMR signals of two types. This structural feature is consistent with the variable-temperature ¹H NMR spectra of compound 2 in CD₂Cl₂ solution are shown in Figure 5. The room-temperature NMR spectrum exhibits single bridgehead, coordinated olefinic, and noncoordinated olefinic proton signals at δ 3.37, 5.21, and 6.52 ppm, respectively, probably resulting from rapid dynamic rearrangement of the molecule in solution. Upon cooling, bridgehead and coordinated olefinic proton resonances decoalesced each into two signals of equal intensity. The activation barrier $\Delta G^\ddagger$ of dynamic rearrangement was estimated to be 11.7 ± 0.5 kcal·mol^{−1} from the coalescence temperature (about 241 K, $\Delta\nu = 16.3$ Hz) of bridgehead protons. However, only one broad noncoordinated olefinic proton resonance was observed in these spectra even at a temperature of 203 K. Similar variable-

Scheme 1

Figure 5. Variable-temperature ^1H NMR spectra of $(\text{tfac})\text{Cu}(7\text{-}t\text{-BuO-NBD})$ (*, CD_2Cl_2 ; †, methine H on tfac; and ‡, bridge H on 7-*t*-BuO-NBD).

temperature NMR measurements (down to 203 K) of compounds 4–6 were made, but the low-temperature limiting spectra were not attained. Two plausible routes to undergo the dynamic rearrangement are proposed in Scheme 1: (i) rotation of the $\text{Cu}(\beta\text{-diketonate})$ moiety about the Cu –olefin bond and (ii) rotation of the $\text{Cu}(7\text{-}t\text{-BuO-NBD})$ moiety about the bond between Cu and one O atom of the β -diketonate ligand. Both routes involve cleavage of the Cu –O bond. On the basis of the structures of compounds 1, 4, and 5 in the solid state, the bonds between Cu and O of 7-*t*-BuO-NBD are more labile than those between Cu and O of the β -diketonate in the title compounds. Exchange between the free β -diketonate anion with the coordinated β -diketonate of compound 2 has also been examined. Addition of $\text{Na}(\text{tfac})$ to a CD_2Cl_2 solution of $(\text{tfac})\text{Cu}(7\text{-}t\text{-BuO-NBD})$ resulted in no exchange with coordinated tfac ligand on the ^1H NMR time scale at 303 K. Thus, it appears that molecules of compound 2 can undergo rearrangement via the rotation of $\text{Cu}(\beta\text{-diketonate})$ moiety about the Cu –olefin bond.

4. Chemical Vapor Deposition of Copper from $(\text{hfac})\text{Cu}(7\text{-}t\text{-BuO-NBD})$. Chemical vapor deposition experiments in the hot-wall system were carried out with $(\text{hfac})\text{Cu}(7\text{-}t\text{-BuO-NBD})$ as precursor over the deposition temperature range 140–260 $^\circ\text{C}$. The precursor was sublimed at 80 $^\circ\text{C}$ under reduced pressure (0.1 Torr) and was transferred through the deposition zone. Durations of deposition were 60–90 min, and the film thicknesses were 1.5–3.5 μm . Continuous copper films with a metallic color and resistivities less than 6 $\mu\Omega\text{-cm}$ were deposited on both SiO_2 - and Pt-coated substrates at deposition temperatures above 200 $^\circ\text{C}$. Hence, the

(a) 230 $^\circ\text{C}$

(b) 140 $^\circ\text{C}$

Figure 6. Scanning electron micrographs of copper films deposited from $(\text{hfac})\text{Cu}(7\text{-}t\text{-BuO-NBD})$ at (a) 230 $^\circ\text{C}$ and (b) 140 $^\circ\text{C}$.

$\text{Cu}(\text{I})$ precursor may undergo disproportionation to form Cu metal and greenish-blue $\text{Cu}(\text{hfac})_2$ which was observed on the cool end of the CVD reactor. The same mechanism was proposed for the CVD reactions with other β -diketonate complexes of copper(I) as precursors by Hampden-Smith.^{6–8} All copper films had good adhesion according to the Scotch tape test. The surface morphology of the films was determined with SEM; a typical example deposited on a Pt-coated Si substrate at 230 $^\circ\text{C}$ appears in Figure 6a. The films deposited at temperatures above 200 $^\circ\text{C}$ consist of continuous grains similar to those in previous reports.^{6–8,10c} The grain size increases with increasing deposition temperature. X-ray diffraction analyses of these films show the existence of crystalline material. A diffraction pattern of a film deposited on a SiO_2 -coated substrate at 200 $^\circ\text{C}$ (Figure 7) corresponds to cubic copper.

Films deposited at the temperatures below 170 $^\circ\text{C}$ have a dark red color that is distinct from that of films deposited at temperatures >200 $^\circ\text{C}$. It is possible that these films contain significant amount of impurities that result in larger resistivities (>1000 $\mu\Omega\text{-cm}$). These films have a morphology (Figure 6b) apparently distinct from those deposited at higher temperatures, which indicates

(18) Baum, T. H.; Larson, C. E.; May, G. J. *Organomet. Chem.* **1993**, 425, 189.

(19) (a) Salomon, R. G.; Kochi, J. K. *J. Am. Chem. Soc.* **1973**, 95, 1889. (b) Salomon, R. G.; Kochi, J. K. *J. Organomet. Chem.* **1974**, 64, 135.

Figure 7. XRD pattern of a film deposited on a SiO₂-coated substrate at 200 °C.

a different composition. Although all title compounds are volatile, compounds **2–6** exhibited insufficient thermal stability at sublimation temperatures to allow CVD experiments.

In conclusion, we prepared new copper(I) complexes of the general formula (β -diketonate)Cu(7-*t*-BuO-NBD). All compounds were characterized by analytical and spectral methods. Structural properties of three compounds were determined by single-crystal X-ray diffraction analyses. ¹H NMR spectra of all compounds in solution at varied temperatures indicated rapid rearrangements of these flexible molecules. CVD experiments using (hfac)Cu(7-*t*-BuO-NBD) as precursor demonstrated deposition of pure copper films at temperatures above 200 °C.

Acknowledgment. We thank Professor S. P. Wang of Department of Chemistry, National Cheng Kung University, for discussion of the NMR data, Dr. S.-G. Shyu of Institute of Chemistry, Academia Sinica, for obtaining SEM data, and the National Science Council of the Republic of China (NSC 82-0208-M-194-025) for support of this work.

Supplementary Material Available: Crystallographic data for compounds **1**, **4**, and **5**, including tables of crystal data, atomic coordinates, bond distances and angles, anisotropic thermal parameters (30 pages). Ordering information is given on any current masthead page.

OM940886D