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Chemistry of copper(I) β-diketonate complexes

VI *. Synthesis, characterization and chemical vapor deposition of 2,2-dimethyl-6,6,7,7,8,8,8-heptafluoro-3,5-octanedione (fod), copper(I)L complexes and the solid state structure of (fod)Cu(PMe_3)

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Abstract

A series of copper(I) compounds of the general formula (fod)CuL, where fod = 2,2-dimethyl-6,6,7,7,8,8,8-heptafluoro-3,5-octanedione, and L = PMe_3, PEt_3, 1,5-cyclooctadiene (1,5-COD), vinyltrimethylsilane (VTMS), 2-butyne, bis(trimethylsilyl)acetylene (BTMSA), have been prepared by the reaction of Na[fod] with CuCl in the presence of the appropriate amount of the Lewis base, L. All the compounds were characterized by elemental analysis, ^{1}H, ^{13}C, ^{19}F, ^{31}P and IR spectroscopies. The spectroscopic data are consistent with the chelation of the β-diketonate ligand through its oxygen atoms to the copper(I) center. The analytical data are consistent with the empirical formula (fod)CuL. One compound, (fod)CuPMe_3, was characterized in the solid-state by single-crystal X-ray diffraction which confirmed the empirical formula and revealed the monomeric nature of this species in the solid state. The distorted trigonal planar coordination environment observed for this species is common to these species. The Cu–O distances are significantly different within the limits of error on the data possibly as a result of inductive effects of the different β-diketonate substituents. Crystal data: Triclinic space group $P\bar{1}$, $a = 10.052(2)$ Å, $b = 11.871(2)$ Å, $c = 16287(3)$ Å, $\alpha = 109.84(1)°$, $\beta = 92.18(2)°$, $\gamma = 90.34(2)°$, $V = 1826.5(6)$ Å^3, $Z = 4$, $R_F = 7.09\%$ and $R_{wF} = 7.28\%$. Hot- and cold-wall chemical vapor deposition experiments revealed that these species are generally not suitable as precursors for the deposition of copper due to their low thermal stability. While pure copper films could be deposited, as determined by Auger electron spectroscopy, from the compounds (fod)CuL, where L = PMe_3, 2-butyne and BTMSA, heating the precursors to increase their vapor pressures resulted in significant thermal decomposition in the source reservoir. As a result, deposition rates of only 100 Å/min were achieved. No selectivity was observed on W *versus* SiO_2 substrates under the conditions employed. The other compounds, (fod)CuL, where L = 1,5-COD, VTMS, were too thermally unstable for CVD experiments.

1. Introduction

The Chemical Vapor Deposition (CVD) of copper from compounds with general empirical formula (β-diketonate)CuL, where L = a Lewis base such as a triorganophosphine, an olefin or an alkyne, results in formation of pure copper films according to the stoichiometry of a thermally-induced disproportionation, eqn. (1) [1–14].

$$2(\beta\text{-diketonate})\text{Cu}^{\text{I}}\text{PMe}_3 \longrightarrow \text{Cu}^{0} + \text{Cu}^{\text{II}}(\beta\text{-diketonate})_2 + 2\text{PMe}_3 \quad (1)$$

A variety of compounds of this type has been synthesized to investigate the effects of various Lewis base ligands and β-diketonate substituents on deposition characteristics such as deposition rate, selectivity behavior and purity. Selective deposition refers to the preferential reaction, or a difference in reaction rate of the precursor on one surface in the presence of another. Studies of the selective deposition of copper are important for technological reasons. Variations in selective deposition of copper have been observed as a function of the β-diketonate and Lewis base ligands in

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a series of CVD experiments carried out under well-defined conditions [11]. For example, when the β-diketonate ligand is held constant and the nature of the Lewis base is varied, CVD of (hfac)CuL, where L = PMe_3 and PEt_3 resulted in selective deposition onto W substrates in the presence of SiO_2, whereas for L = 1,5-cyclooctadiene (1,5-COD), vinyltrimethylsilane (VTMS) and 2-butyne, blanket deposition was observed on both W and SiO_2 substrates under otherwise identical conditions. Based on these observations and a number of model experiments in which the temperature dependent adsorption behavior of these compounds has been investigated, we believe selective deposition is determined by competition between the adsorption strength of the copper(I) species and the strength of the copper–Lewis base bond [15]. Under different conditions, variations in selectivity can be obtained [5,9,12].

The trends in CVD of copper from (β-diketonate) CuL compounds where the β-diketonate substituents are systematically varied has only been studied for L = PMe_3 and β-diketonate = hfac (1,1,1,5,5,5-hexafluoroacetylacetonate), tfac (1,1,1-trifluoroacetylacetonate) and acac (acetylacetonate). In general, other olefin and alkyne adducts of (β-diketonate)CuL complexes, where β-diketonate is not hfac, do not exhibit sufficient stability to be suitable for CVD studies. In an attempt to provide further insight into the effects of variation of the β-diketonate ligands, we report here the synthesis and characterization of a series of compounds of empirical formula (fod)CuL, where fod = 2,2-dimethyl-6,6,7,7,8,8,8-heptafluoro-3,5-octanedione, and L = PMe_3, PEt_3, 1,5-COD, VTMS, 2-butyne and bis(trimethyl-silyl)acetylene (BTMSA). It was anticipated that CVD of copper from these precursors might provide a point of comparison to (hfac)CuL compounds for L = olefin and alkyne, provided the (fod) CuL analogs are sufficiently thermally stable.

The fod ligand was chosen for the following reasons: (i) it is analogous to the tfac ligand, having one alkyl and one fluorinated alkyl substituent and by analogy is likely to be more reactive than the corresponding hfac compounds; (ii) the higher degree of fluorination may result in higher volatility compared with tfac; (iii) the presence of the sterically demanding C_3F_7 ligand may avoid solid state intermolecular $Cu \cdots O$ interactions that have previously been observed in these species [16]; (iv) the fod ligand is asymmetric and as a result facilitates investigation of ligand exchange mechanisms in solution. These species have been prepared in reasonable yields (62–81%) from the reaction of the Lewis base adduct of copper(I) chloride ($[ClCuL]_n$) with the sodium salt of fod. One example, (fod)Cu(PMe_3), was structurally characterized in the solid state by single-crystal X-ray diffraction. The results of some qualitative CVD experiments are discussed.

2. Experimental section

2.1. General procedures

All manipulations were carried out under an atmosphere of dry (molecular sieves) dinitrogen using standard Schlenk techniques [17]. All hydrocarbon and ethereal solvents were dried and distilled from sodium benzophenone ketyl and stored over 4 Å molecular sieves. Copper(I) chloride, 1,5-cyclooctadiene (1,5-COD), vinyltrimethylsilane (VTMS), 2-butyne, bis(trimethyl-silyl)acetylene (BTMSA), and trimethylphosphine were purchased from Aldrich Chemical Co. and used without further purification. The β-diketone, fodH, was purchased from Aldrich Chemical Co., distilled under nitrogen and stored over 4 Å molecular sieves before use. The sodium salt of fodH was prepared by the reaction of the free acid with sodium hydride, analogous to that previously described for other β-diketones [16]. The compound [$ClCuPMe_3$] was prepared by the reaction of CuCl with PMe_3 [18]. The compound [ClCu(1,5-COD)] was prepared by the reaction of CuCl with 1,5-COD according to the literature procedure [19]. Elemental analyses were performed either by Oneida Research Services, New York, or by Ms R. Ju at the University of New Mexico, Department of Chemistry. NMR data were recorded on a Bruker AC-250P NMR spectrometer by using the protio impurities of the deuterated solvents as references for the ^1H NMR and the ^{13}C resonance of the solvents as reference for $^{13}C\{^1H\}$ NMR spectroscopy. Temperatures were calibrated with either ethylene glycol or methanol. $^{31}P\{^1H\}$ NMR data were recorded on the same instrument using phosphoric acid as the reference. $^{31}P\{^1H\}$ NMR chemical shifts are quoted using the high frequency = positive sign convention. $^{19}F\{^1H\}$ NMR spectra were recorded on a Bruker AC-250P instrument in C_6D_6 and were internally referenced to $CFCl_3$. The samples were prepared with similar concentrations. Chemical shifts are quoted using the high frequency = positive sign convention. The assignments, $-CF^a{}_2CF^b{}_2CF^c{}_3$, were made as described in text. Infrared data were recorded on a Perkin-Elmer Model 1620 FTIR spectrophotometer.

2.2. Syntheses

2.2.1. (fod)Cu(PMe_3)

4.04 g of CuCl(PMe_3) (23.09 mmol) and 7.81 g of Na[fod] (24.56 mmol) were mixed in 150 ml of Et_2O and the solution was stirred at −30°C for 12 h. The Et_2O was removed *in vacuo*, and 100 ml of pentane was added to dissolve the product. After filtration and removal of pentane, 7.36 g of yellow, solid (fod)Cu(PMe_3) was obtained (73% yield). The compound is thermally unstable in solution at room temperature, but stable in the solid state at room temperature.

Elemental analysis data: Calcd. for $C_{13}H_{19}O_2F_7PCu$, C 35.91, H 4.40; Found: C, 35.83, H 4.73%.

Spectroscopic data: NMR data (toluene-d_8, −30°C): ^1H δ 6.27 (s, 1H, $C\mathit{H}$ on fod), 1.16 (s, 9H, $C(C\mathit{H}_3)_3$ on fod), 0.42 (d, 9H, J(P–H) = 7.7 Hz, $P(C\mathit{H}_3)_3$) ppm. $^{13}C\{^1H\}$ δ 205.3 (s, t-Bu*C*O on fod), 171.8 (t, J(F–C) = 22 Hz, CF_2CO on fod), 121.5–107.2 (m, $\mathit{C}F_3\mathit{C}F_2\mathit{C}F_2$ on fod), 91.8 (s, $\mathit{C}H$ on fod), 42.3 (s, $\mathit{C}(CH_3)_3$ on fod), 27.8 (s, $C(\mathit{C}H_3)_3$ on fod), 14.0 (d, J(P–C) = 27 Hz, $P(\mathit{C}H_3)_3$) ppm. $^{31}P\{^1H\}$ δ −37.5 (s, $\mathit{P}Me_3$) ppm. $^{19}F\{^1H\}$: −80.5, s, br, F^c; −119.1, F^a; −126.3, F^b. IR data (KBr disc, cm^{-1}): 2977m, 1620s, 1507s, 1466s, 1345s, 1222s, 1159s, 1118s, 1019m, 954m, 908m, 834m, 794m, 738m, 693m, 631w.

2.2.2. (fod)Cu(PEt_3)

3.91 g of CuCl(PEt_3) (18.02 mmol) and 5.84 g of Na[fod] (18.36 mmol) were mixed in 150 ml of Et_2O and the solution was stirred at −30°C for 4 h. The Et_2O was removed *in vacuo*, and 100 ml of pentane was added to dissolve the product. After filtration and removal of pentane, 6.45 g of yellow, liquid (fod)Cu(PEt_3) was obtained (75% yield).

Elemental analysis data: Calcd. for $C_{16}H_{25}O_2F_7PCu$, C 40.30, H 5.28; Found: C 40.39, H 5.33%.

Spectroscopic data: NMR data (C_6D_6, 23°C): ^1H δ 6.12 (s, 1H, $C\mathit{H}$ on fod), 1.11 (s, 9H, $C(C\mathit{H}_3)_3$ on fod), 1.00 (m, 6H, $P(C\mathit{H}_2CH_3)_3$), 0.79 (m, 9H, $P(Ch_2C\mathit{H}_3)_3$) ppm. $^{13}C\{^1H\}$ δ 205.3 (s, ^{t}Bu*C*O on fod), 172.0 (t, J(F–C) = 22 Hz, CF_2CO on fod), 121.6–106.8 (m, $\mathit{C}F_3\mathit{C}F_2\mathit{C}F_2$ on fod), 91.5 (s, $\mathit{C}H$ on fod), 42.3 (s, $\mathit{C}(CH_3)_3$ on fod), 27.9 (s, $C(\mathit{C}H_3)_3$ on fod), 17.4 (d, J(P–C) = 24.5 Hz, $P(\mathit{C}H_2CH_3)_3$) 8.8 (s, $P(CH_2\mathit{C}H_3)_3$) ppm. $^{31}P\{^1H\}$ δ 2.5 (s, $\mathit{P}Et_3$) ppm. $^{19}F\{^1H\}$: d −80.6 (t, 9 Hz), F^c; −119.1 (q, 9 Hz), F^a; −126.4, F^b. IR data (KBr disc, cm^{-1}): 2969m, 1618s, 1507s, 1458s, 1346s, 1230s, 1120s, 1067m, 963m, 910m, 835m, 755m.

2.2.3. (fod)Cu(1,5-cod)

4.33 g of $[CuCl(cod)]_2$ (9.98 mmol) and 6.70 g of Na[fod] (21.07 mmol) were mixed in 150 ml of Et_2O and the solution was stirred at −30°C for 4 h. The Et_2O was removed *in vacuo*, and 100 ml of pentane was added to dissolve the product. After filtration and removal of pentane, 7.69 g of greenish-yellow, liquid (fod)Cu(COD) was obtained (81% yield).

Elemental analysis data: Calcd. for $C_{18}H_{26}O_2F_7Cu$, 46.30, H 4.75; Found: C 46.64, H 5.00%.

Spectroscopic data: NMR data (C_6D_6, 23°C): ^1H δ 6.00 (s, 1H, $C\mathit{H}$ on fod), 5.07 (s, 4H, $C\mathit{H}$ on COD), 2.02 (s, 8H, $C\mathit{H}_2$ on COD), 1.06 (s, 9H, $C(C\mathit{H}_3)_3$ on fod) ppm. $^{13}C\{^1H\}$ δ 205.8 (s, ^{t}Bu*C*O on fod), 172.5 (t, J(F–C) = 22 Hz, $CF_2\mathit{C}O$ on fod), 121.5–107.2 (m, $\mathit{C}F_3\mathit{C}F_2\mathit{C}F_2$ on fod), 112.6 (s, $\mathit{C}H$ on COD), 91.3 (s, $\mathit{C}H$ on fod), 42.3 (s, $\mathit{C}(CH_3)_3$ on fod), 28.3 (s, $\mathit{C}H_2$ on COD), 27.8 (s, $C(\mathit{C}H_3)_3$ on fod) ppm. $^{19}F\{^1H\}$: d −80.3 (t, 10 Hz), F^c; −119.2 (q, 10 Hz), F^a; −126.4, F^b. IR data (KBr disc, cm^{-1}): 2970m, 1615s, 1508s, 1464s, 1429m, 1394w, 1346s, 1229s, 1163s, 1122s, 1104m, 1068m, 964m, 939w, 912m, 835m, 791m, 756w, 740m.

2.2.4. (fod)Cu(VTMS)

2.52 g (25.14 mmol) of VTMS was added to a solution of CuCl (2.38 g, 24.04 mmol) in 50 ml of Et_2O. After 15 min of stirring, a solution of Na[fod] (8.24 g, 25.91 mmol) in 100 ml of Et_2O was transferred into the reaction flask and the solution mixture was stirred at −30°C for 4 h. Then the Et_2O was removed *in vacuo*, and 100 ml of pentane was added to dissolve the product. After filtration and removal of pentane under vacuum, 7.52 g of yellow, liquid (fod)Cu(vtms) was obtained (70% yield). This compound is thermally unstable at room temperature and was stored at −30°C.

Elemental analysis data: Calcd. for $C_{14}H_{23}O_2F_7SiCu$, C 39.26, H 4.83; Found: C 39.77, H 4.92%.

Spectroscopic data: NMR data (toluene-d_8, −30°C): ^1H δ 6.18 (s, 1H, $C\mathit{H}$ on fod), 3.97–3.75 (m, 3H, vinyl proton on VTMS), 1.05 (s, 9H, $C(C\mathit{H}_3)_3$ on fod), 0.31 (s, 9H, $Si(C\mathit{H}_3)_3$ on VTMS) ppm. $^{13}C\{^1H\}$ δ 206.5 (s, ^{t}Bu*C*O on fod), 172.3 (t, J(F–C) = 23 Hz, $CF_2\mathit{C}O$ on fod), 121.7–109.0 (m, $\mathit{C}F_3\mathit{C}F_2\mathit{C}F_2$ on fod), 93.1 (s, vinyl C on VTMS), 92.3 (s, $\mathit{C}H$ on fod), 84.1 (s, vinyl C on VTMS), 42.5 (s, $\mathit{C}(CH_3)_3$ on fod), 27.6 (s, $C(\mathit{C}H_3)_3$ on fod), −1.4 (s, $Si(\mathit{C}H_3)_3$ on VTMS) ppm. $^{19}F\{^1H\}$: d −80.5, s, br, F^c; −119.1, s, br, F^a; −126.5, F^b. IR data (KBr disc, cm^{-1}): 2967m, 1614s, 1590m, 1511s, 1458s, 1396w, 1347s, 1231s, 1125s, 1070m, 1023w, 966m, 914m, 840s, 795m, 757m, 740w, 696w.

2.2.5. (fod)Cu(BTMSA)

6.54 g of BTMSA (38.47 mmol) was added to a solution of CuCl (3.18 g, 32.12 mmol) in 50 ml of Et_2O. After stirring for 15 min, a solution of Na[fod] (10.58 g, 33.27 mmol) in 100 ml of Et_2O was transferred into the reaction flask and the mixture was stirred at −30°C for 4 h. Then the Et_2O was removed *in vacuo*, and 100 ml of pentane was added to dissolve the product. After filtration and removal of pentane under vacuum, 10.48 g of pale yellow, solid (fod)Cu(BTMSA) was obtained (62% yield).

Elemental analysis data: Calcd. for $C_{18}H_{28}O_2F_7Si_2Cu$, C 40.86, H 5.33; Found: C 40.59, H 5.59%.

Spectroscopic data: NMR data (C_6D_6, 23°C): ^{1}H δ 6.10 (s, 1H, C*H* on fod), 1.03 (s, 9H, C(C*H*$_3$)$_3$ on fod), 0.26 (s, 18H, C*H*$_3$ on BTMSA)) ppm. ^{13}C{^{1}H} δ 206.7 (s, ^{t}Bu*C*O on fod), 172.8 (t, *J*(F–C) = 23 Hz, CF$_2$*C*O on fod), 121.5–103.7 (m, *C*F$_3$*C*F$_2$*C*F$_2$ on fod), 113.9 (s, *C*SiMe$_3$ on BTMSA), 92.1 9s, *C*H on fod), 42.5 (s, *C*(CH$_3$)$_3$ on fod), 27.9 (s, C(*C*H$_3$)$_3$ on fod), −0.4 (s, *C*H$_3$ on BTMSA) ppm. ^{19}F{^{1}H}: d −80.7 (t, 9 Hz), F^c; −119.4 (q, 9 Hz), F^a; −126.5, F^b. IR data (KBr disc, cm^{-1}): 2969m, 1941m, 1616s, 1508s, 1460s, 1347s, 1252s, 1228s, 1123s, 913m, 847s, 791m, 760m.

2.2.6. *(fod)Cu(2-butyne)*

2.50 g of 2-butyne (46.30 mmol) was added to a solution of CuCl (4.32 g, 43.46 mmol) in 50 ml of Et_2O. After 15 min of stirring, a solution of Na[fod] (13.97 g, 43.93 mmol) in 100 ml of Et_2O was transferred into the reaction flask and the solution mixture was stirred at −30°C for 4 h. The Et_2O was removed *in vacuo*, and 100 ml of pentane was added to dissolve the product. After filtration and removal of pentane under vacuum, 13.56 g of pale yellow solid (fod)Cu(2-butyne) was obtained (76% yield). The compound slowly decomposes at room temperature and was stored in a refrigerator.

Elemental analysis data: Calcd. for $C_{14}H_{16}O_2F_7Cu$, C 40.73, H 3.91; Found: C 40.46, H 4.00%.

Spectroscopic data: NMR data (C_6D_6, 23°C): ^{1}H δ 6.12 (s, 1H, C*H* on fod), 1.69 (s, 6H, C*H*$_3$ on 2-butyne), 1.03 (s, 9H, C(C*H*$_3$)$_3$ on fod) ppm. ^{13}C{^{1}H} δ 206.6 (s, ^{t}Bu*C*O on fod), 172.4 (t, *J*(F–C) = 23 Hz, CF$_2$*C*O on fod), 121.5–104.2 (m, *C*F$_3$*C*F$_2$*C*F$_2$ on fod), 92.3 (s, *C*H on fod), 81.8 (s, *C*(CH$_3$) on 2-butyne), 42.4 (s, *C*(CH$_3$)$_3$ on fod), 27.6 (s, C(*C*H$_3$)$_3$ on fod), 6.2 (s, *C*H$_3$ on 2-butyne) ppm. ^{19}F{^{1}H}: d −80.5, s, br, F^c; −119.1, s, br, F^a; −126.5, F^b. IR data (KBr disc, cm^{-1}): 2974m, 1617s, 1512s, 1459m, 1347m, 1228s, 1122m, 913m, 836m, 797m, 741m, 696w.

2.3. *X-ray diffraction data*

Thin yellow plates of (fod)Cu(PMe$_3$) were grown by crystallization from n-pentane at −30°C and were mounted, under dry nitrogen, in a glass capillary. The crystal data collection and refinement parameters are summarized in Table 1. The determination of the space group was unambiguous, $P\bar{1}$, in the triclinic crystal system. A semi-empirical absorption correction was applied to the data set. The structure was solved by direct methods, which located the copper atom. The remaining non-hydrogen atoms were located through subsequent least-squares full matrix cycles and difference Fourier calculations. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were included as idealized isotropic contributions set to 1.25 U (equiv.) of the parent atom. All software and the source of scattering factors are contained in the SHELXTL program library (G. Sheldrick, Nicolet Corp., Madison, WI).

TABLE 1. Summary of crystallographic data for (fod)Cu(PMe$_3$)

Chemical Formula	$C_{13}H_{19}CuF_7O_2P$
Formula weight	434.8
a (Å)	10.052(2)
b (Å)	11.871(2)
c (Å)	16.287(3)
α (°)	109.84(1)
β (°)	92.18(2)
γ (°)	90.34(2)
V (Å^3)	1826.5(6)
Z	4
Space group	$P\bar{1}$
T (°C)	−25
λ (Å)	0.71069
ρ_{obsd} (g cm^{-3})	1.581
μ (cm^{-1})	0.1319
trans. coeff.	–
R(F)/% [a]	7.09
R_w(F)/%	7.28

[a] $R = \Sigma\, \Delta F/\Sigma F_o$; $R_w = \Sigma w^{1/2}\, \Delta F/\Sigma w^{1/2} 2F_o$

Atom coordinates are given in Table 2 and selected bond distances and angles in Tables 3 and 4 respectively. Two crystallographically independent molecules were found in the asymmetric unit. Superposition and comparison of the two molecules showed that they were chemically identical (see Supplementary materials). Structural data for both are presented in the text (see Fig. 1). Details of the metrical parameters for the other molecule are published as Supplementary materials.

3. Results and discussion

3.1. *Syntheses*

The compounds (fod)CuL where L = PMe$_3$, PEt$_3$, 1,5-COD, VTMS, 2-butyne and BTMSA were prepared according to the reactions shown in eqns. 2 and 3 below.

$$\text{ClCuL} + \text{Na[fod]} \longrightarrow \text{(fod)CuL} + \text{NaCl} \qquad (2)$$

L = PMe$_3$, PEt$_3$, 1,5-COD

$$\text{CuCl} + \text{L} + \text{Na[fod]} \longrightarrow \text{(fod)CuL} + \text{NaCl} \qquad (3)$$

L = VTMS, 2-butyne, BTMSA

Where well-defined Lewis adducts of copper(I) chloride were known, they were prepared and reacted with

Na[fod] [18,19]. In other cases (eqn. 3), copper(I) chloride was first mixed with one equivalent of the Lewis base in diethyl ether and then Na[fod] was added. Both methods resulted in good yields of the corresponding copper(I) complex. These species were generally isolated by extraction with n-pentane and evaporation of the volatile components *in vacuo* (~ 10^{-2} torr). All compounds gave satisfactory elemental analysis data and were characterized by solution NMR and IR spectroscopies. The compounds (fod)CuL, where L = PMe_3, 2-butyne and BTMSA are pale yellow solids at room temperature, while (fod)CuL, where L = PEt_3, 1,5-COD and VTMS are pale yellow liquids at room temperature. Liquid CVD precursors have the advantage over solid precursors that the liquid precursors can be evaporated more easily at a constant rate. A number of these derivatives (L = PMe_3, VTMS and 2-butyne) are thermally unstable at room temperature.

TABLE 2. Atomic coordinates

	x	y	z	U_{eq} [a]
Cu(1)	43248(11)	39952(8)	8964(6)	546(4)
P(1)	38426(21)	26600(17)	−3458(13)	448(8)
O(1)	57270(54)	46224(49)	18011(35)	592(23)
O(2)	30275(52)	52283(45)	15788(33)	531(22)
C(1)	55653(82)	54535(69)	25167(53)	499(34)
C(2)	44525(82)	61283(64)	27925(49)	512(32)
C(3)	32387(76)	59970(63)	23318(47)	422(30)
C(4)	68234(79)	57293(67)	31170(51)	490(32)
C(5)	69217(92)	50169(79)	37296(55)	624(38)
C(6)	82179(111)	51088(101)	42629(67)	750(48)
C(7)	20987(81)	68018(68)	27278(50)	508(32)
C(8)	17154(116)	65807(93)	35613(63)	914(51)
C(9)	25198(106)	81293(73)	29742(70)	875(49)
C(10)	9093(109)	65667(105)	20960(71)	1037(57)
C(11)	33519(95)	11884(66)	−3182(57)	648(37)
C(12)	51252(100)	22662(84)	−11321(56)	768(43)
C(13)	24540(95)	30086(77)	−9524(56)	710(40)
F(1)	69156(63)	68943(46)	36179(43)	1072(30)
F(2)	79128(53)	55056(63)	26554(35)	983(32)
F(3)	66337(63)	38802(46)	33013(40)	969(28)
F(4)	59766(63)	54097(71)	43308(39)	1122(36)
F(5)	91570(66)	45286(66)	37507(49)	1155(37)
F(6)	86364(70)	61782(60)	46574(44)	1164(34)
F(7)	81048(77)	45277(76)	48205(47)	1338(43)
Cu(2)	8495(11)	89735(8)	8767(6)	559(4)
P(2)	11384(22)	76485(17)	−3714(13)	461(8)
O(3)	−4692(52)	95843(47)	17558(33)	554(23)
O(4)	22173(50)	102090(43)	15958(32)	514(22)
C(14)	−2476(75)	104314(68)	24766(51)	464(33)
C(15)	8946(76)	111045(69)	27871(50)	491(32)
C(16)	21002(77)	109716(62)	23405(48)	443(31)
C(17)	−14363(81)	106986(69)	30698(53)	520(34)
C(18)	−14831(88)	100082(80)	36981(56)	604(39)
C(19)	−27100(107)	100480(90)	42090(63)	721(45)
C(20)	32770(79)	117909(68)	27665(51)	528(33)
C(21)	36651(116)	116225(97)	36256(68)	996(57)
C(22)	29194(98)	130766(74)	29422(72)	867(48)
C(23)	44195(96)	114969(98)	21749(71)	1001(54)
C(24)	24482(95)	80208(82)	−9810(57)	724(41)
C(25)	15853(99)	61884(72)	−3517(56)	699(40)
C(26)	−2436(103)	73021(89)	−11570(59)	813(46)
F(8)	−15117(61)	118564(44)	35154(42)	1007(30)
F(9)	−25785(51)	103806(60)	25685(35)	918(30)
F(10)	−11677(65)	88942(49)	33167(41)	1022(31)
F(11)	−4909(66)	105103(78)	43186(41)	1245(41)
F(12)	−36848(65)	94110(64)	36582(46)	1130(35)
F(13)	−31593(70)	111284(57)	45347(41)	1137(33)
F(14)	−25379(71)	95441(71)	47904(44)	1218(39)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

TABLE 3. Bond lengths (Å) for (fod)Cu(PMe_3)

Cu(1)–P(1)	2.140(2)	Cu(1)–O(1)	1.949(5)
Cu(1)–O(2)	2.027(5)	P(1)–C(11)	1.828(9)
P(1)–C(12)	1.802(10)	P(1)–C(13)	1.810(10)
O(1)–C(1)	1.263(8)	O(2)–C(3)	1.265(8)
C(1)–C(2)	1.378(11)	C(1)–C(4)	1.532(11)
C(3)–C(7)	1.514(11)	C(2)–C(3)	1.387(11)
C(4)–F(1)	1.347(8)	C(4)–C(5)	1.512(14)
C(5)–C(6)	1.520(14)	C(4)–F(2)	1.329(10)
C(5)–F(4)	1.358(11)	C(5)–F(3)	1.316(10)
C(6)–F(6)	1.273(12)	C(6)–F(5)	1.319(12)
C(7)–C(8)	1.530(15)	C(6)–F(7)	1.321(16)
C(7)–C(10)	1.508(13)	C(7)–C(9)	1.541(12)
Cu(2)–O(3)	1.945(5)	Cu(2)–P(2)	1.138(2)
P(2)–C(24)	1.818(10)	Cu(2)–O(4)	2.025(5)
P(2)–C(26)	1.799(10)	P(2)–C(25)	1.804(9)
O(4)–C(16)	1.254(8)	O(3)–C(14)	1.271(8)
C(14)–C(17)	1.532(11)	C(14)–C(15)	1.372(10)
C(15)–C(16)	1.419(11)	C(16)–C(20)	1.514(10)
C(17)–C(18)	1.515(15)	C(17)–F(8)	1.323(9)
C(17)–F(9)	1.357(9)	C(18)–C(19)	1.506(16)
C(18)–F(10)	1.303(10)	C(18)–F(11)	1.371(10)
C(19)–F(12)	1.342(11)	C(19)–F(13)	1.301(12)
C(19)–F(14)	1.288(15)	C(20)–C(21)	1.516(15)
C(20)–C(22)	1.503(12)	C(20)–C(23)	1.493(13)

The integrated ^1H NMR spectra and the ^{13}C NMR spectra are consistent with the empirical formula (fod)CuL. The derivatives (fod)CuL, where L = PMe_3 and PEt_3, exhibit NMR data analogous to that of the corresponding tfac derivatives. The derivative (fod)Cu(1,5-COD) exhibits ^1H and ^{13}C NMR spectra with a single type of olefinic and aliphatic 1,5-COD resonances. If the compound is stereochemically rigid in solution and the 1,5-COD ligand bidentate, then the asymmetry caused by the fod ligand is expected to result in two chemically inequivalent olefinic ^1H NMR resonances and four chemically inequivalent aliphatic ^1H NMR resonances based on a tetrahedral coordination environment about copper(I). No change in the ^1H NMR spectrum was observed on cooling to 203 K. These data are similar to those observed for (tfac)Cu(1,5-COD) [20]. Even in the presence of a symmetric β-diketonate ligand, three ^{1}H NMR resonances for a chelated 1,5-COD ligand are expected. However, ClCu(1,5-COD) and (β-diketonate)Cu(1,5-COD) where β-diketonate = hfac and acac only exhibit two ^{1}H NMR resonances for the 1,5-COD ligand, one olefinic and one aliphatic. Therefore it seems likely that the 1,5-COD adducts of these compounds undergo a dynamic rearrangement process in solution that probably has an activation barrier below ~ 7 Kcal/mol. Whether this is the result of an intra- or intermolecular dynamic exchange process has not been determined. The addition of excess 1,5-COD to toluene-d_8 solutions of (fod)Cu(1,5-COD) resulted in the observation of only a single type of 1,5-COD ligand at room temperature which implies that intermolecular ligand exchange may be possible.

TABLE 4. Bond angles (°) for (fod)Cu(PMe$_3$)

P(1)–Cu(1)–O(1)	144.4(2)	C(21)–C(20)–C(23)	110.0(8)
O(1)–Cu(1)–O(2)	91.7(2)	P(1)–Cu(1)–O(2)	123.9(2)
Cu(1)–P(1)–C(12)	117.5(3)	Cu(1)–P(1)–C(11)	115.7(3)
Cu(1)–P(1)–C(13)	115.0(3)	C(11)–P(1)–C(12)	101.3(4)
C(12)–P(1)–C(13)	103.0(4)	C(11)–P(1)–C(13)	102.2(4)
Cu(1)–O(2)–C(3)	126.5(5)	Cu(1)–O(1)–C(1)	124.0(5)
O(1)–C(1)–C(4)	112.6(7)	O(1)–C(1)–C(2)	128.7(7)
C(1)–C(2)–H(2)	117.0(4)	C(2)–C(1)–C(4)	118.7(6)
H(2)–C(2)–C(3)	117.0(4)	C(1)–C(2)–C(3)	126.0(6)
O(2)–C(3)–C(7)	117.2(6)	O(2)–C(3)–C(2)	122.9(7)
C(1)–C(4)–C(5)	114.2(7)	C(2)–C(3)–C(7)	119.9(6)
C(5)–C(4)–F(1)	106.8(7)	C(1)–F(4)–F(1)	111.8(7)
C(5)–C(4)–F(2)	106.7(7)	C(1)–C(4)–F(2)	111.0(6)
C(4)–C(5)–C(6)	117.7(8)	F(1)–C(4)–F(2)	106.0(7)
C(6)–C(5)–F(3)	109.0(8)	C(4)–C(5)–F(3)	110.2(7)
C(6)–C(5)–F(4)	104.9(7)	C(4)–C(5)–F(4)	108.1(8)
C(5)–C(6)–F(5)	109.8(8)	F(3)–C(5)–F(4)	106.2(8)
F(5)–C(6)–F(6)	108.0(9)	C(5)–C(6)–F(6)	114.0(10)
F(5)–C(6)–F(7)	103.5(10)	C(5)–C(6)–F(7)	110.4(9)
C(3)–C(7)–C(8)	109.0(8)	F(6)–C(6)–F(7)	110.5(9)
C(8)–C(7)–C(9)	108.1(7)	C(3)–C(7)–C(9)	110.6(7)
C(8)–C(7)–C(10)	109.8(8)	C(3)–C(7)–C(10)	111.2(6)
P(2)–Cu(2)–O(3)	142.6(2)	C(9)–C(7)–C(10)	108.1(8)
O(3)–Cu(2)–O(4)	91.4(2)	P(2)–Cu(2)–O(4)	126.1(2)
Cu(2)–P(2)–C(25)	115.4(3)	Cu(2)–P(2)–C(24)	114.4(3)
Cu(2)–P(2)–C(26)	117.4(3)	C(24)–P(2)–C(25)	103.5(5)
C(25)–P(2)–C(26)	102.3(4)	C(24)–P(2)–C(26)	101.8(5)
Cu(2)–O(4)–C(16)	127.9(5)	Cu(2)–O(3)–C(14)	124.2(5)
O(3)–C(14)–C(17)	113.7(6)	O(3)–C(14)–C(15)	129.0(7)
O(4)–C(16)–C(20)	118.7(7)	C(15)–C(14)–C(17)	117.2(6)
C(14)–C(17)–C(18)	115.2(7)	C(14)–C(15)–C(16)	125.3(6)
C(18)–C(17)–F(8)	109.0(7)	O(4)–C(16)–C(15)	122.1(6)
C(18)–C(17)–F(9)	105.0(7)	C(15)–C(16)–C(20)	119.2(6)
C(17)–C(18)–C(19)	119.7(8)	C(14)–C(17)–F(8)	111.6(7)
C(19)–C(18)–F(10)	108.9(8)	C(14)–C(17)–F(9)	109.1(6)
C(19)–C(18)–F(11)	104.8(7)	F(8)–C(17)–F(9)	106.6(7)
C(18)–C(19)–F(12)	108.4(7)	C(17)–C(18)–F(10)	111.0(7)
F(12)–C(19)–F(13)	105.5(9)	C(17)–C(18)–F(11)	105.1(8)
F(12)–C(19)–F(14)	105.7(9)	F(10)–C(18)–F(11)	106.3(8)
C(16)–C(20)–C(21)	109.0(8)	C(18)–C(19)–F(13)	112.1(9)
C(21)–C(20)–C(22)	108.9(7)	C(16)–C(20)–C(23)	109.6(6)
C(18)–C(19)–F(14)	112.3(9)	C(22)–C(20)–C(23)	108.8(9)
F(13)–C(19)–F(14)	112.4(8)	C(20)–C(21)–H(21B)	109.5(5)
C(16)–C(20)–C(22)	110.4(7)	C(20)–C(21)–H(21C)	109.5(5)

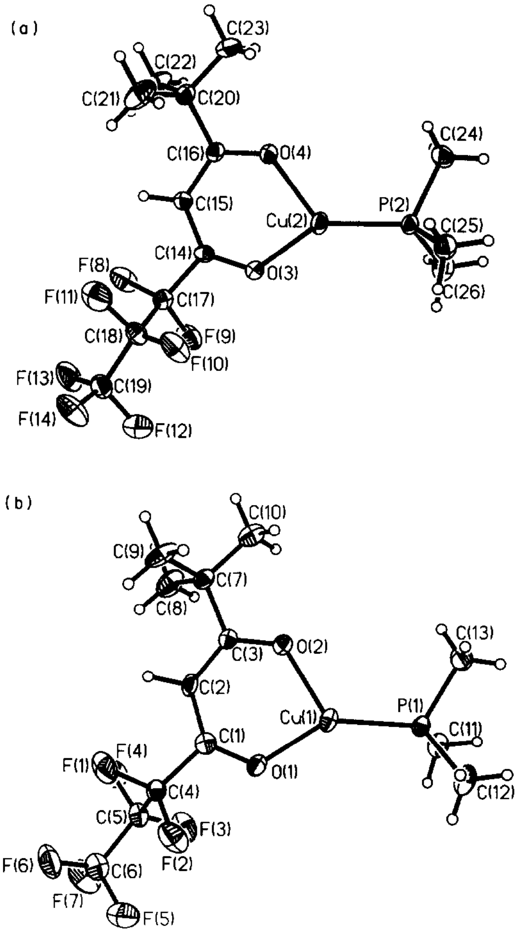

Fig. 1. ORTEP plots of the two crystallographically independent molecules found in the solid state structure of (fod)Cu(PMe$_3$) as determined by single crystal X-ray diffraction.

For (fod)Cu(2-butyne) and (fod)Cu(BTMSA), based on the asymmetry of the fod ligand, two types of alkyne substituent would be expected for in-plane orientation of the alkyne ligand, which has been observed by single crystal X-ray diffraction in the solid state. However, only a single type of alkyne substituent was observed for both compounds. This observation may result from the rapid rotation of the alkyne ligand around the copper–alkyne bond axis.

The ^{19}F{^{1}H} NMR spectra obtained for these compounds did not reveal any noteworthy subtle changes in either chemical shift or ^{19}F–^{19}F coupling constant as a function of the nature of the Lewis base adduct. The three ^{19}F resonances of the fod ligand, $-CF^a{}_2CF^b{}_2CF^c{}_3$ could be assigned through integration, and correlation of the coupling constants and chemical shifts with literature data [21–23]. Both $^3J(^{19}F-^{19}F)$ coupling constants had values close to zero with the result that F^b was observed as a slightly broadened singlet while F^c was a triplet with a coupling constant of approximately 9–10 Hz, and F^a, a quartet with the same coupling constant.

The β-diketonate ligands can exhibit a variety of coordination modes in complexes of late transition metals. The ^1H and $^{13}C\{^1H\}$ NMR data reported here (see Experimental section) are consistent with coordination to the copper(I) center through the oxygen atoms. This is corroborated by the IR data where all the compounds exhibit bands in the region 1615–1619 cm^{-1} characteristic of ν(C–O) coordinated to the metal center as previously observed [1].

3.2. Solid-state single-crystal X-ray diffraction structure

The structure of one example of these derivatives, (fod)Cu(PMe_3), was determined in the solid state by single-crystal X-ray diffraction. The crystal, collection and refinement data are summarized in Table 1, the fractional coordinates are given in Table 2 and the relevant bond lengths and angles are given in Tables 3 and 4. An ORTEP plot showing the atom labeling scheme for the two independent molecules is presented in Fig. 1. Initial attempts to collect X-ray data at room temperature were fruitless due to the thermal instability of this molecule. A yellow crystal sealed in a capillary under a nitrogen atmosphere turned blue overnight. Cooling a new sample to −25°C reduced the rate of thermal decomposition, but did not prevent decomposition and, as a result, the final *R*-value was relatively high.

The compound (fod)Cu(PMe_3) is monomeric in the solid state and adopts a structure analogous to the other structurally characterized (β-diketonate)CuL compounds with a three-coordinate approximately trigonal planar copper coordination environment [1,3,9,11,16,21]. Many of the metrical parameters of this complex are analogous to those observed for other derivatives. Considering the first crystallographically independent molecule, the Cu(1)–P(2.140(2) Å) and Cu(1)–O bond lengths (1.949(5) and 2.027(2) Å) and the angles about copper (O(1)–Cu(1)–O(2) = 91.7(2)°, O(1)–Cu(1)–P(1) = 144.4(2)° and O(2)–Cu91)–P(1) = 123.9(2)° are analogous to other derivatives. The bond lengths and angles in the β-diketonate ring and in the β-diketonate substituents are as expected. The most notable feature of this complex in the context of this work is the marked asymmetry of the Cu–O bond lengths. The Cu–O bond subtended to the carbonyl group containing the fluorinated substituent is significantly shorter compared to the Cu–O bond distance to the tertiary butyl substituted carbonyl ligand. Such a difference has not been previously observed in this system even in the case (tfac)Cu(PMe_3) [1]. It is tempting to attribute this asymmetry to the comparative inductive effects of the C_3F_7 and t-butyl substituents. However, as a result of the asymmetry in the molecule, manifest in the O–Cu–P angles it is possible that the origin of this effect may lie in intermolecular or crystal packing interactions, although no unusually short distances were observed. Similar features are true for the second independent molecule.

3.3. Chemical vapor deposition experiments

CVD experiments were carried out for (fod)CuL, L = PMe_3, 2-butyne and BTMSA compounds. The other compounds described here did not exhibit sufficient thermal stability to allow CVD experiments. The CVD experiments are not described in great detail here because these compounds are generally not as suitable as their (hfac)CuL analogs for copper CVD as a result of their limited thermal stability. Furthermore, quantitative experiments were not possible due to the thermal decomposition of the precursors in the precursor reservoir during the experiments. The experiments were carried out in both hot- and cold-wall reactors. The hot-wall reactor was operated under conditions where the precursor was heated to 40°C and the reactor was maintained at a temperature between 150 and 300°C depending on the experiment. A detailed description of the reactor and typical operating conditions has been presented previously [11]. The total pressure was approximately 10^{-2} torr, the precursor partial pressure was not measured and the experiments were conducted under dynamic vacuum. The cold-wall reactor was operated under conditions analogous to those previously described [8] for (hfac)CuL compounds where the deposition occurred in the surface-reaction-limited regime. The substrates were identical to those previously described, either tungsten-coated silicon substrates or with both W and SiO_2 features for selectivity evaluation. Substrates were cleaned according to procedures described previously [11].

In the hot-wall reactor, films deposited from (fod) CuL, L = PMe_3, 2-butyne and BTMSA compounds in the temperature range 150–300°C were generally not continuous. In addition, thermal decomposition of the precursor in the source reservoir was observed. These compounds thermally decompose at temperatures near their sublimation temperatures which results in low transport rates manifest in discontinuous films over the time of the CVD experiments. The formation of $Cu(fod)_2$ was observed on the cool walls of the reaction chamber after the furnace consistent with the disproportionation reaction of eqn. 1, previously observed for of copper(I) β-diketonate compounds. In this case, no attempt to quantify the by-product distribution was

TABLE 5. Selective deposition of copper from various (β-diketonate)CuL compounds as a function of precursor and substrate. The reader is referred to the literature cited for details of deposition conditions in each case

	Precursor	Selectivity	Temperature range (°C)	Reference
(I)	(hfac)Cu(PMe$_3$)	Pt, W, Cu *vs.* SiO$_2$	150–300	2, 11
(II)	(tfac)Cu(PMe$_3$)	Pt, W, Cu *vs.* SiO$_2$	100–150	2, 11
(III)	(acac)Cu(PMe$_3$)	Pt, W, Cu *vs.* SiO$_2$	< 80	2, 11
(IV)	(fod)Cu(PMe$_3$)	none for W *vs.* SiO$_2$	150–300	this work
(V)	(hfac)Cu(1,5-COD)	none for Pt, W, Cu *vs.* SiO$_2$	120–250	8
(VI)	(hfac)Cu(1,5-COD)	"certain degree of selectivity" for Ta, Cu, Ag, Au and Cr *vs.* SiO$_2$ and Si$_3$N$_4$	< 200	5
(VII)	(hfac)Cu(VTMS)	none for W *vs.* SiO$_2$	120–250	12, 21
(VIII)	(hfac)Cu(VTMS)	W *vs.* SiO$_2$	120–420	7
		TiN *vs.* SiO$_2$	150–180	7
		PtSi *vs.* SiO$_2$	150–200	7
(IX)	(hfac)Cu(2-butyne)	none for Pt, W, Cu *vs.* SiO$_2$	120–250	4
(X)	(hfac)Cu(2-butyne)	"under certain conditions" for Co and Mo *vs.* SiO$_2$ and polyimide	150	9
(XI)	(fod)Cu(2-butyne)	none for W *vs.* SiO$_2$	150–300	this work
(XII)	(hfac)Cu(BTMSA)	none for Pt, W, Cu *vs.* SiO$_2$	120–250	4
	(fod)Cu(2-butyne)	none for W *vs.* SiO$_2$	150–300	this work
(XIII)	(hfac)Cu(2-pentyne)	none for Pt, W, Cu *vs.* SiO$_2$	120–250	4

made due to the observed thermal decomposition in the reactor reservoir.

The most interesting observation was that copper films were deposited onto both tungsten and SiO$_2$ surfaces during these experiments over the temperature range investigated. This lack of selective deposition is consistent with the results obtained for analogous (tfac)CuL compounds, where known [11]. These data are summarized in Table 5 and compared to the other data reported in the literature. Care must be taken when interpreting these data due to the undefined influence of different substrate preparation, surface cleaning and reactor geometries on the selectivity. However, the experiments labeled (I–V), (VII), (IX), (XI–XIII) were carried out using similar substrates, the same cleaning procedures and the same reactor, and the results are therefore comparable.

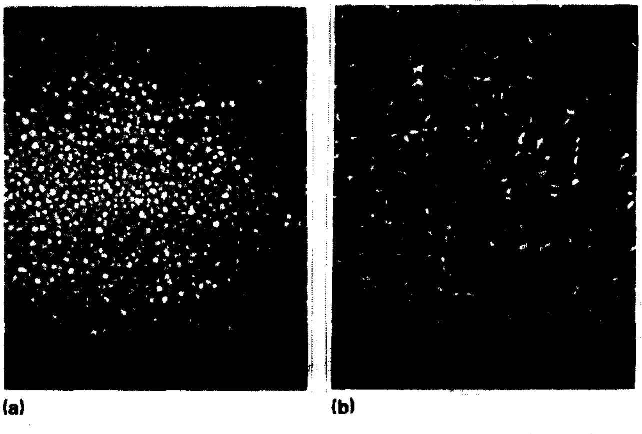

Fig. 2. Surface SEM photographs showing the morphology of two copper films deposited from (a) (fod)Cu(2-butyne) at 190°C and (b) (fod)Cu(PMe$_3$) at 170°C on W -coated Si substrates.

In the cold-wall reactor, continuous copper films were formed which had a granular morphology as determined by SEM and are shown in Fig. 2. The films did not contain any C, O or F contamination within the limits of resolution of Auger Electron Spectroscopy, with depth profiling. However, deposition rates were extremely low relative to analogous (hfac)CuL derivatives. For (fod)Cu(PMe$_3$) a deposition rate of 100 Å/min was measured with a substrate temperature of 190°C.

4. Conclusions

A series of copper(I) compounds of the general formula (fod)CuL, where fod = 2,2-dimethyl-6,6,7,7,8,8,8-heptafluoro-3,5-octanedione, and L = PMe$_3$, PEt$_3$, 1,5-COD, VTMS, 2-butyne and BTMSA, have been prepared by the reaction of Na[fod] with CuCl in the presence of the appropriate amount of the Lewis base, L. All the compounds were characterized by elemental analysis, ^{1}H, ^{13}C, ^{19}F, ^{31}P and IR spectroscopies. The spectroscopic data are consistent with the chelation of the β-diketonate ligand through its oxygen atoms to the copper(I) center. The analytical data are consistent with the empirical formula (fod)CuL. One compound, (fod)CuPMe$_3$, was characterized in the solid state by single-crystal X-ray diffraction which confirmed the empirical formula and revealed the monomeric nature of this species in the solid state. The distorted trigonal planar coordination environment observed for this example is common to these species.

Quantitative CVD experiments were not possible for any of the compounds prepared in this study due to their low thermal stability at temperatures where they exhibit suitable vapor pressures. However, pure copper films can be deposited and qualitative evidence for disproportionation was observed. Selective deposition was not observed under the CVD conditions employed, consistent with the results for (tfac)CuL compounds.

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