(s, C_5H_5). $^{31}P\{^1H\}$ NMR (ppm, CD_2Cl_2) 19.1 (s). Anal. Calcd for $C_{23}H_{22}BF_4NO_2PRe$: C, 42.60; H, 3.42; N, 2.16. Found: C, 42.79; H, 3.54; N, 2.11.

Isolation of $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(OH_2)]^+PF_6^-$ ($4^+PF_6^-$). A Schlenk tube was charged with $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H)$ (**15**, 0.106 g, 0.195 mmol),[19] CH_2Cl_2 (5 mL), and a stir bar, and cooled to −80 °C. Then $Ph_3C^+PF_6^-$ (0.076 g, 0.196 mmol) was added with stirring. After 15 min, distilled, degassed water (100 μL, 5.56 mmol) was added. The solution was allowed to slowly warm to −20 °C and then transferred via cannula to a Schlenk flask that contained stirring hexane (40 mL). A brown powder precipitated, which was collected by filtration, washed with hexane (10 mL), and dried under vacuum to give $4^+PF_6^-$ (0.125 g, 0.177 mmol, 91%), mp 123–127 °C dec. IR (cm^{-1}, KBr): ν_{NO} 1681 s, ν_{PF} 841 s. ^1H NMR (δ, CD_2Cl_2): 7.74–7.17 (m, 3 C_6H_5), 5.41 (br s, H_2O), 5.37 (s, C_5H_5). $^{31}P\{^1H\}$ NMR (ppm, CD_2Cl_2, −80 °C): 19.8 (s, PPh_3), −144.5 (sept, J_{PF} = 713 Hz, PF_6).

Generation of $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(OH_2)]^+X^-$ (4^+X^-). A. A Schlenk tube was charged with **5** (0.314 g, 0.562 mmol), CH_2Cl_2 (20 mL), and a stir bar and cooled to 0 °C. Then aqueous HF (0.500 mL, 13.9 mmol) was added dropwise with stirring. After 1 h, the cold bath was removed. After an additional hour, solvents were removed under vacuum. The residue was washed with hexane and dissolved in CH_2Cl_2 (ca. 10 mL). Hexane was rapidly added, and the resulting precipitate was collected by filtration and dried under vacuum to give 4^+X^- (0.270 g, ca. 0.45 mmol, 81%). IR (cm^{-1}, KBr): ν_{NO} 1683 s. $^{31}P\{^1H\}$ NMR (ppm, CH_2Cl_2): 20.4 (s).

B. A 5-mm NMR tube was charged with **5** (0.036 g, 0.064 mmol) and CH_2Cl_2 (0.5 mL) and capped with a septum. The tube was cooled to 0 °C and aqueous HF (0.005 mL, 0.14 mmol) was added. The sample was kept at 0 °C for 5 min and then allowed to warm to room temperature. $^{31}P\{^1H\}$ NMR (ppm, CH_2Cl_2): 19.6 (s).

Reaction of $4^+BF_4^-$ and CH_3CN. A 5-mm NMR tube was charged with $4^+BF_4^-$ (0.0157 g, 0.0241 mmol) and Ph_3SiCH_3 (0.0115 g, 0.0419 mmol) and capped with a septum. The tube was cooled to −80 °C, and CD_2Cl_2 (0.8 mL) and CH_3CN (0.0040 mL, 0.078 mmol) were sequentially added via syringe. The tube was warmed to 25 °C as ^1H and ^{31}P NMR spectra were periodically recorded. After 6 h at room temperature, complete conversion to $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(NCCH_3)]^+BF_4^-$ (**14**, >99%)[6a,c] and water (>99%) had occurred, as assayed by integration of their ^1H NMR resonances (δ 5.55 and 1.59) relative to the standard (δ 0.84).

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Chemistry of Copper(I) β-Diketonate Complexes. 2.[1] Synthesis, Characterization, and Physical Properties of (β-Diketonato)copper(I) Trimethylphosphine and Bis(trimethylphosphine) Complexes

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The volatile copper(I) complexes (β-diketonate)$Cu(PMe_3)_n$ where β-diketonate = hexafluoroacetylacetonate (hfac), trifluoroacetylacetonate (tfac), and acetylacetonate (acac) for $n = 1$ and 2 and β-diketonate = dipivaloylmethanate (dpm) and dibenzoylmethanate (dbm) for $n = 1$ have been prepared in high yield. These species have been characterized by spectroscopy and by elemental analysis. A number of derivatives have been characterized by single-crystal X-ray diffraction. The compound (hfac)$Cu(PMe_3)$ crystallizes in the space group $P\bar{1}$ with $a = 10.801$ (2) Å, $b = 12.676$ (3) Å, $c = 14.946$ (3) Å, $\alpha = 91.10$ (3)°, $\beta = 100.65$ (3)°, $\gamma = 94.06$ (3)°, $Z = 6$, $R = 6.71\%$, and $R_w = 7.26\%$ for 3751 reflections. The compound (dpm)$Cu(PMe_3)$ crystallizes in the space group $P\bar{1}$ with $a = 10.193$ (3) Å, $b = 12.059$ (3) Å, $c = 14.547$ (3) Å, $\alpha = 96.40$ (2)°, $\beta = 91.54$ (2)°, $\gamma = 90.65$ (2)°, $Z = 4$, $R = 5.34\%$, and $R_w = 5.57\%$ for 5261 reflections. The compound (dbm)$Cu(PMe_3)$ crystallizes in the space group $Cmc2_1$ with $a = 18.776$ (6) Å, $b = 7.995$ (3) Å, $c = 11.872$ (4) Å, $Z = 4$, $R = 2.72\%$, and $R_w = 2.83\%$ for 1620 reflections. While (acac)$Cu(PMe_3)$ and (tfac)$Cu(PMe_3)$ have only limited thermal stability, (hfac)$Cu(PMe_3)$ is thermally stable for at least 4 days at its melting point (67 °C). The vapor pressure of (hfac)$Cu(PMe_3)$ has been measured as a function of temperature, revealing reasonable volatility (100 mTorr at 60 °C). From the plot of log (vapor pressure) versus reciprocal temperature, an enthalpy of vaporization (ΔH_{vap}) of approximately 10 kcal/mol was obtained.

Introduction

The chemical vapor deposition (CVD) of metals from metal–organic molecules is the subject of much interest as a result of potential applications in the microelectronics industry.[2] The use of molecular metal–organic compounds as the source of the metal in CVD experiments, as distinct from the use of the metals themselves in physical vapor deposition (PVD) experiments, provides the potential advantages of conformal film coverage and selective deposition. However, until fairly recently, relatively little effort has been directed toward the design of metal–organic compounds specifically as precursors for CVD of metal films, especially with respect to selective deposition.

When metal–organic compounds are designed specifically for CVD of metals, the following criteria should be met. (i) The precursor should have a high vapor pressure to allow high deposition rates and controlled introduction of the precursor into the reactor. (ii) The precursor should be a liquid at the vaporization temperature used. This circumvents variable vaporization rates due to surface area changes during evaporation associated with solid precursors. (iii) A suitable (thermal) decomposition mechanism should be in place to allow clean removal of the supporting ligands and produce pure films with low resistivity values close to those of the bulk metal. (iv) Selective deposition onto a specific material in the presence of several others is desirable over a wide temperature range.

The CVD of copper films has traditionally been carried out by using copper(II) β-diketonate compounds.[3-9] While these

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compounds have reasonably high vapor pressure (for example, Cu(hexafluoroacetylacetonate)$_2$ exhibits an equilibrium vapor pressure of 250 mTorr at 60 °C[10]), pure copper films can only be deposited over a small, relatively high temperature range (340–370 °C)[11] or under conditions where hydrogen gas is present in the deposition system.[12] A number of alternatives to these species have recently been described, including Cu("nona-F")$_2$,[13] [Cu(O-*t*-Bu)]$_4$,[14] and (cyclopentadienyl)copper(I) phosphine compounds.[15,16] While each of these species has its own particular advantages and disadvantages as a precursor, none are low-melting solids or liquids at room temperature. In addition, they provide limited possibilities for systematic substitution to enable subtle tailoring of their physical and chemical properties which would allow detailed investigation of fundamental aspects of copper CVD. Further, from the data available to date, it appears that CVD using these species produces copper films via thermal decomposition of the supporting ligands. This process often leads to impurity incorporation. In contrast, we have recently demonstrated that the series of compounds (β-diketonato)copper(I) trimethylphosphine are suitable precursors for the selective CVD of high-purity copper[17–19] and undergo thermally induced disproportionation, according to eq 1. In principle, it should be possible

$$2(\beta\text{-diketonate})\mathrm{Cu^I(PMe_3)} \rightarrow \mathrm{Cu^0} + \mathrm{Cu^{II}}(\beta\text{-diketonate})_2 + 2\mathrm{PMe_3} \quad (1)$$

to vary, systematically, the physical and chemical properties of this series of compounds by variation of β-diketonate substituents or the donor ligand (phosphine in this case). Pure copper films (as determined by Auger electron spectroscopy and sputtered neutrals mass spectroscopy) have been deposited from these compounds by hot-wall CVD over a temperature range of 100–400 °C with observed resistivities (1.8 μΩ cm) close to that of bulk copper (1.673 μΩ cm at 20 °C), high deposition rates (>3000 Å/min), and deposition selectivity that can be tailored as a function of the nature of the substrate, the temperature of the substrate, and the choice of β-diketonate ligand. Other examples of disproportionation of similar copper(I) compounds have been reported. The disproportionation of (hfac)Cu(NH$_3$)$_{2.5}$ has been quantified,[20] the disproportionation of (hfac)CuCO has been observed,[21] and the original claim that copper(I) aryloxides[22] disproportionate has recently been disputed.[23]

As part of our studies in this area, we report here the synthesis, the characterization, and the chemical and physical properties of this series of molecules. A preliminary report of the synthesis of some of the title compounds has previously appeared.[1]

Experimental Section

(i) General Procedures. All manipulations were carried out under an atmosphere of dry (molecular sieves) dinitrogen using standard Schlenk techniques.[24] All hydrocarbon and ethereal solvents were dried and distilled from sodium benzophenone ketyl and stored over 4-Å molecular sieves. Copper(I) chloride, thallous cyclopentadienide, and trimethylphosphine were purchased from Aldrich Chemical Co. and used without further purification. The β-diketone starting materials were purchased from Aldrich Chemical Co. and were distilled under nitrogen and stored over 4-Å molecular sieves before use. Sodium salts of β-diketones were prepared by the reaction of the free acid with sodium hydride, as described below. The compounds [ClCu(PMe$_3$)] and (η^5-C$_5$H$_5$)Cu(PMe$_3$) were prepared by methods previously described in the literature.[16,25] The starting material "ClCu(PMe$_3$)$_2$", which exists as the halocuprate salt [CuCl$_2$]$^-$[Cu(PMe$_3$)$_4$]$^+$ in the solid state, was prepared by addition of PMe$_3$ to [ClCu(PMe$_3$)] and will be discussed elsewhere.[26] Elemental analyses were performed either by Oneida Research Services, New York, or by Ms. R. Ju at the Department of Chemistry, University of New Mexico. NMR data were recorded on a Bruker AC-250P NMR spectrometer by using the protio impurities of the deuterated solvents as references for ^{1}H NMR spectroscopy and the ^{13}C resonances of the solvents as references for ^{13}C NMR spectroscopy. Temperatures were calibrated with either ethylene glycol or methanol. ^{31}P NMR data were recorded on the same instrument using phosphoric acid as reference. ^{31}P NMR chemical shifts are quoted using the high frequency = positive sign convention. Infrared data were recorded on a Perkin-Elmer Model 1620 FTIR spectrophotometer. Mass spectra were recorded on a Finnegan GC-mass spectrometer, and molecular weights were measured cryoscopically by the freezing point depression of benzene.[27] Vapor pressures were measured by using the apparatus described below.

(ii) Syntheses. The compounds of general formula (β-diketonate)-Cu(PMe$_3$) were all prepared by two methods: a salt elimination reaction and a metalation reaction. The procedure for the synthesis of the different compounds was essentially the same except that, for (dbm)Cu(PMe$_3$), toluene was used as the solvent. Two examples are described in detail here after the synthesis of sodium β-diketonate.

All the sodium salts of the β-diketonate ligands were prepared in a similar fashion. One representative example is described here in detail.

Dry NaH (2.96 g, 123.5 mmol) powder was placed in a 250-mL Schlenk flask, and 100 mL of dry Et$_2$O was added. The suspension was cooled to 0 °C, and an excess of hexafluoroacetylacetone (1.85 mL, 130.7 mmol) was added under stirring. The solution turned white as hfacH was added. The addition rate of hexafluoroacetylacetone was adjusted to allow for steady evolution of hydrogen gas from the reaction. The solution was allowed to warm to room temperature after the addition and stirred for 2 h more. The volatile components were removed in vacuo to give a white powder, Na(hfac) (26.29 g, a yield of 93%).

a. Synthesis of (hfac)Cu(PMe$_3$) by Metalation. The compound (η^5-C$_5$H$_5$)Cu(PMe$_3$) (5.00 g, 24.4 mmol) was placed in a 100-mL Schlenk flask together with 10 mL of dry *n*-pentane. This suspension was cooled to 0 °C by placing the Schlenk flask into an ice bath. Hexafluoroacetylacetone (hfacH) (5.2 mL, 36.5 mmol) was added slowly to the cooled, rapidly stirred suspension by syringe. As hfacH was added, (η^5-C$_5$H$_5$)Cu(PMe$_3$) started to dissolve and the solution turned orange. After all the β-diketone had been added, a clear orange solution was obtained. It was stirred for an additional 0.5 h to ensure completion of the reaction. The volatile components were then removed in vacuo at room temperature to give 8.34 g of crude orange powder, a yield of 98.5%. This powder quantitatively sublimed at 30 °C and 6 × 10^{-2} Torr over a period of approximately 4 h to give an orange crystalline solid that analyzed correctly as (hfac)Cu(PMe$_3$).

b. Synthesis of (hfac)Cu(PMe$_3$) by Salt Elimination. The solids [ClCu(PMe$_3$)] (6.00 g, 34.3 mmol) and Na(hfac) (10.30 g, 44.8 mmol) were placed in a 250-mL Schlenk flask, and 100 mL of dry *n*-pentane was added at room temperature. This mixture was stirred for 3 h at room temperature, during which time the solution turned orange. The stirrer was stopped, and the white solid was allowed to settle. The solution was then filtered and the solid washed with three 10-mL portions of *n*-pentane. The orange filtrates were combined, and the volatile components were removed in vacuo to give 10.60 g of an orange powder, which sublimed at 30 °C and 10^{-2} Torr, quantitatively, to give a crystalline orange solid that analyzed correctly as (hfac)Cu(PMe$_3$): a yield of 89.2%.

c. Spectroscopic and Analytical Data for (β-diketonate)Cu(PMe$_3$). The NMR data presented here were obtained in benzene-d_6 at 23 °C at resonance frequencies of 250.13 MHz (^{1}H), 62.5 MHz (^{13}C), or 101.3

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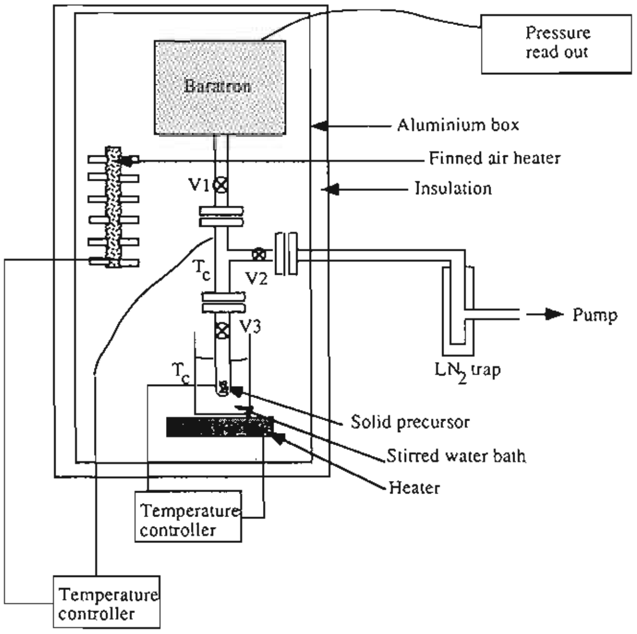

Figure 1. Schematic drawing of the vapor pressure measurement apparatus.

MHz (^{31}P). IR spectra were recorded in the solid state in KBr pellets and in the gas phase in a 10-cm cell with KBr windows. One representative example is presented here, the remaining data are available as supplementary material.

Data for (hfac)Cu(PMe_3) follow. ^1H NMR: 6.33 (s, 1 H), 0.38 ppm (d, 8.0 Hz, 9 H, P*Me*$_3$). ^{13}C NMR: 177.2 (q, 33 Hz, *C*O), 118.5 (q, 289 Hz, *C*F$_3$), 89.2 (s, *C*H), 14.0 ppm (d, 28 Hz, P*Me*$_3$). ^{31}P NMR: −42.7 ppm (s, br). IR (KBr disk, cm^{-1}): 2983 (m), 2915 (m), 1672 (s), 1646 (s), 1548 (s), 1525 (s), 1490 (s), 1327 (m), 1255 (s), 1200 (s), 1138 (s), 965 (s), 946 (s), 848 (w), 785 (s), 761 (m), 737 (m), 669 (s), 662 (s), 583 (m), 526 (w). IR (gas phase, cm^{-1}): 2978 (w), 2906 (w), 1672 (s), 1642 (m), 1524 (s), 1485 (m), 1310 (w), 1252 (s), 1202 (s), 1141 (s), 960 (m), 794 (m), 737 (m), 661 (s), 576 (w). MS (70 eV, *m/e*): 487, 19%, $[(hfac)Cu_2(PMe_3)_2]^{\bullet+}$; 346, 38%, $[(hfac)Cu(PMe_3)]^{\bullet+}$; 277, 12% $[Cu_2(PMe_3)_2]^{\bullet+}$; 215, 95%, $[Cu(PMe_3)_2]^{\bullet+}$; 201, 4%, $[Cu(O_2C_2CHCF_3)]^{\bullet+}$; 139, 100%, $[Cu(PMe_3)]^{\bullet+}$; 124, 4%, $[Cu(PMe_2)]^{\bullet+}$; 109, 2%, $[Cu(PMe)]^{\bullet+}$; 76, 30%, $[PMe_3]^{\bullet+}$; 69, 6%, $[CF_3]^{\bullet+}$; 61, 14%, $[PMe_2]^{\bullet+}$; 45, 7%, $[PMe]^{\bullet+}$. Anal. Calcd for $C_8H_{10}O_2F_6PCu$: C, 27.72, H, 2.91. Found: C, 28.28, H, 2.80. Cryoscopic mol wt (C_6H_6): calculated for (hfac)Cu(PMe_3) 347 Da; measured 340 ± 14 (0.040 M), 338 ± 7 Da (0.078 M). Mp: 67 °C.

d. Synthesis of (β-diketonate)Cu(PMe_3)$_2$. These species were prepared by two different methods. One example of each procedure is presented here in detail.

Synthesis of (hfac)Cu(PMe_3)$_2$ from (hfac)Cu(PMe_3) + PMe_3. Solid (hfac)Cu(PMe_3) (0.47 g, 1.4 mmol) was placed in a 100-mL Schlenk flask and dissolved in 4 mL of dry pentane. To this solution was added dropwise with rapid stirring 0.14 mL (1.4 mmol) of PMe_3. The orange solution was stirred for 1 h at room temperature, and then the volatile components were removed in vacuo. A pale orange powder (0.48 g, 1.3 mmol) was recovered and analyzed correctly as (hfac)Cu(PMe_3)$_2$: a yield of 93%.

Synthesis of (tfac)Cu(PMe_3)$_2$ by Metathesis. The halocuprate salt $[Cu(PMe_3)_4]^+[Cl_2Cu]^-$ (5.09 g, 5.06 mmol) was placed in a 250-mL Schlenk flask together with 150 mL of diethyl ether. To this suspension was added an excess of Na(tfac) (3.96 g, 22.49 mmol), immediately giving a yellow solution. The mixture was stirred for 3 h, after which the volatile components were removed in vacuo. The product was extracted from the yellow residue with 100 mL of *n*-pentane; the mixture was filtered and the solvent removed in vacuo to give 2.01 g (5.5 mmol) of pale yellow solid which sublimed at 50 °C and 10 Torr.

Spectroscopic and analytical data for (β-diketonate)Cu(PMe_3)$_2$ are available as supplementary material.

(iii) Vapor Pressure Measurements. Vapor pressures were measured in the apparatus shown in Figure 1. The vapor pressure measurement apparatus consists of a high-temperature MKS 221A capacitive transducer connected to a "tee" via valve V_1. The "tee" was connected to a precursor chamber via a copper-gasketed flange and valve V_3 and to a vacuum pump via valve V_2. The whole apparatus was contained within a thermally insulated box which was heated independently of the precursor by finned air heaters. The precursor was heated by an oil bath at the bottom of the insulated box. Temperatures were controlled by thermocouples connected to temperature controllers. The accuracy of the temperature controllers was better than ±1 °C. During vapor pressure measurement, the temperature of the box was maintained 1 or 2 °C higher than that of the precursor bath to prevent condensation of the precursor in the pressure transducer or other parts of the apparatus. The whole apparatus was constructed of high-vacuum, copper-sealed stainless steel parts except the sample chamber, which was glass.

Table I. Summary of the Crystallographic Data for (hfac)Cu(PMe_3), (dpm)Cu(PMe_3), and (dbm)Cu(PMe_3)

	(hfac)Cu(PMe_3)	(dpm)Cu(PMe_3)	(dbm)Cu(PMe_3)
chem formula	$C_8H_{10}O_2F_6PCu$	$C_{14}H_{28}CuO_2P$	$C_{18}H_{20}CuO_2P$
fw	346.7	322.9	362.9
a/Å	10.801 (2)	10.193 (3)	18.776 (6)
b/Å	12.676 (3)	12.059 (3)	7.995 (3)
c/Å	114.946 (3)	13.547 (3)	11.872 (4)
α/deg	91.10 (3)	96.40 (2)	
β/deg	100.65 (3)	91.54 (2)	
γ/deg	94.06 (3)	90.65 (2)	
V/Å^3	2004.9 (7)	1776.02 (1)	1782.19
Z	6	4	4
space group	$P\bar{1}$	$P\bar{1}$	$Cmc2_1$
T/°C	20	20	20
λ/Å	0.71069	0.71069	0.71069
ρ_{obsd}/g cm^{-3}	1.723	1.208	1.352
μ/cm^{-1}	0.1815	0.1315	0.1319
transm coeff	0.4430–0.5873	0.7222–0.7849	0.8039–0.8835
$R(F)$/%[a]	6.71	5.34	2.72
$R_w(F)$/%[b]	7.26	5.57	2.83

[a] $R = \sum \Delta F / \sum F_0$. [b] $R_w = \sum w^{1/2} \Delta F / \sum w^{1/2}(2F)$.

(iv) Thermal Stability Experiments. Preliminary vapor pressure measurements showed that, for some compounds, the vapor pressure did not reach an equilibrium value. The reasons for this appeared to be either contamination with solvent (even after sublimation) or long-term thermal instability of the compounds. To investigate the long-term thermal stability of the compounds before measurements, the precursors were kept at elevated temperatures for 4 days under vacuum in an apparatus consisting of a glass bulb fitted with a Teflon tap and thereafter cooled to room temperature. Decomposition products were observable on the wall of the sample container after several hours in the case of (acac)Cu(PMe_3) and (tfac)Cu(PMe_3); however, (hfac)Cu(PMe_3) was stable during these experiments on the basis of NMR spectra. The thermal decomposition products of (acac)Cu(PMe_3) were separated and analyzed by NMR spectroscopy, mass spectroscopy, and elemental analysis as described below.

A 50-mL flask fitted with a Teflon tap was charged with 0.28 g of (acac)Cu(PMe_3) and evacuated to 10^{-4} Torr. The flask was then completely immersed in an oil bath at 60 °C for 12 h. During this time, formation of a copper-colored film was observed, together with a dark solid and a white solid. The contents of the flask that were volatile at 23 °C and 10^{-4} Torr were transferred to a 5-mm NMR tube. ^1H NMR spectroscopy revealed that no proton-containing products were evolved (i.e. no PMe_3). The white product was extracted with acetone to give 0.09 g (0.29 mmol) of a species that analyzed correctly by NMR and mass spectroscopy as $[acac]^-[Cu(PMe_3)_4]^+$, compared to an authentic sample prepared independently.[26] Extraction of the remaining residue with ethanol and subsequent removal of the solvent in vacuo gave 0.16 g (0.44 mmol) of Cu(acac)$_2$·2EtOH, which was characterized by mass spectroscopy and compared with an authentic sample. The masses of products obtained are close to the values expected for the reaction of eq 2. To check whether or not the copper gasket in the vapor pressure measurement apparatus could catalyze decomposition, a piece of copper was placed in the sample flask containing (hfac)Cu(PMe_3), and the above experiment was repeated. No decomposition products were detected by NMR spectroscopy for (hfac)Cu(PMe_3) under the same conditions.

$$\begin{array}{ccccccc} 8(acac)Cu(PMe_3) & \longrightarrow & 3Cu & + & 3Cu(acac)_2 & + & 2[acac]^-[Cu(PMe_3)_4]^+ \quad (2) \\ & & & \text{calcd mmol (ratio)} & & & \\ 1.17\ (8) & & 0.44\ (3) & & 0.44\ (3) & & 0.29\ (2) \\ & & & \text{obsd mmol (ratio)} & & & \\ 1.17\ (8) & & \text{not measd} & & 0.44\ (3) & & 0.29\ (2) \end{array}$$

(v) Single-Crystal X-ray Diffraction Structural Characterization. Four examples of the compounds with molecular formula (β-diketonate)Cu(PMe_3) have been structurally characterized in the solid state by single-crystal X-ray diffraction. The structural characterization of (tfac)Cu(PMe_3) has previously been communicated, and data for the other

Table II. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$) for (hfac)Cu(PMe_3)

	x	*y*	*z*	*U*(eq)[a]
Cu(1)	4240 (1)	−77 (1)	3222 (1)	91 (1)
P(1)	4242 (4)	1043 (2)	2167 (2)	101 (2)
O(1)	3135 (7)	−636 (6)	4059 (5)	85 (3)
O(2)	5626 (6)	−994 (5)	3795 (5)	84 (3)
C(1)	3433 (11)	−1259 (9)	4678 (7)	73 (5)
C(2)	4553 (13)	−1726 (8)	4906 (7)	76 (5)
C(3)	5550 (11)	−1571 (8)	4439 (7)	68 (5)
C(4)	2366 (21)	−1510 (15)	5159 (10)	155 (10)
F(1)	2119 (18)	−818 (10)	5608 (15)	286 (12)
F(2)	1509 (10)	−2084 (11)	4820 (7)	212 (6)
F(3)	2719 (10)	−2113 (16)	5874 (10)	313 (11)
C(5)	6708 (15)	−2185 (14)	4715 (11)	113 (8)
F(4)	7717 (9)	−1612 (7)	4965 (7)	179 (5)
F(5)	6912 (8)	−2794 (7)	4075 (7)	163 (5)
F(6)	6651 (10)	−2801 (9)	5414 (8)	239 (7)
C(6)	3245 (12)	711 (9)	1100 (7)	120 (6)
C(7)	5749 (15)	1308 (14)	1805 (10)	211 (11)
C(8)	3867 (22)	2359 (9)	2468 (9)	260 (15)
Cu(2)	120 (1)	−4503 (1)	1719 (1)	90 (1)
P(2)	−802 (3)	−5080 (2)	2783 (2)	85 (1)
O(3)	236 (7)	−3355 (5)	835 (5)	76 (3)
O(4)	1496 (6)	−5267 (5)	1233 (4)	77 (3)
C(9)	915 (10)	−3347 (7)	259 (6)	60 (4)
C(10)	1756 (9)	−4050 (8)	97 (6)	63 (4)
C(11)	2000 (9)	−4934 (8)	592 (7)	65 (4)
C(12)	786 (15)	−2376 (9)	−346 (9)	86 (6)
F(7)	1485 (10)	−2363 (6)	−964 (6)	185 (6)
F(8)	−307 (9)	−2292 (7)	−776 (6)	177 (5)
F(9)	1158 (9)	−1508 (6)	114 (5)	165 (5)
C(13)	3006 (14)	−5617 (10)	380 (9)	89 (6)
F(10)	4019 (7)	−5542 (6)	1010 (6)	132 (4)
F(11)	2680 (7)	−6617 (6)	290 (6)	143 (4)
F(12)	3420 (9)	−5368 (7)	−384 (6)	179 (5)
C(14)	−482 (13)	−4293 (9)	3823 (7)	126 (7)
C(15)	−2511 (11)	−5268 (13)	2524 (8)	159 (8)
C(16)	−342 (14)	−6374 (9)	3198 (9)	141 (7)
Cu(3)	1636 (1)	−1869 (1)	2426 (1)	85 (1)
P(3)	48 (3)	−937 (2)	2399 (2)	78 (1)
O(5)	3164 (7)	−1816 (5)	1824 (5)	78 (3)
O(6)	2214 (7)	−3201 (5)	3068 (5)	82 (3)
C(17)	3958 (10)	−2489 (9)	1919 (7)	70 (5)
C(18)	4069 (10)	−3357 (8)	2482 (7)	73 (5)
C(19)	3183 (11)	−3624 (8)	3014 (7)	70 (5)
C(20)	4943 (14)	−2321 (12)	1343 (11)	103 (7)
F(13)	5479 (10)	−1358 (8)	1422 (8)	207 (7)
F(14)	4570 (9)	−2498 (13)	519 (6)	265 (9)
F(15)	5956 (10)	−2814 (9)	1546 (7)	195 (6)
C(21)	3429 (15)	−4553 (12)	3607 (11)	108 (7)
F(16)	2643 (10)	−5341 (6)	3367 (7)	187 (5)
F(17)	3357 (14)	−4384 (7)	4434 (6)	227 (8)
F(18)	4498 (10)	−4931 (8)	3647 (9)	228 (7)
C(22)	357 (15)	345 (13)	2908 (14)	259 (13)
C(23)	1157 (14)	−1436 (14)	2975 (12)	212 (12)
C(24)	−870 (14)	−687 (13)	1287 (9)	181 (10)

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

three compounds are presented here.[1]

(a) (hfac)Cu(PMe_3). Orange crystals of (hfac)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 collected in Table I. The determination of the space group was unambiguous, $P\bar{1}$, in the triclinic crystal system. A semiempirical 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 with varying group isotropic *U*'s. This model gave standard deviations on bond lengths and angles slightly better than a model in which all non-hydrogen atoms were anisotropic except C and O in the β-diketonate ring with isotropic *U* values of hydrogens fixed. All software and the source of scattering factors are contained in the SHELXTL program library (G. Sheldrick, Nicolet Corp., Madison, WI).

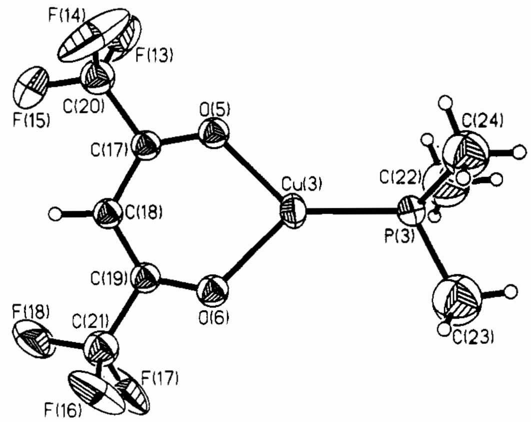

Figure 2. ORTEP plot (50% probability ellipsoids) showing the molecular structure of (hfac)Cu(PMe_3) with the atom-numbering scheme.

Table III. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$) for (dpm)Cu(PMe_3)

	x	*y*	*z*	*U*(eq)[a]
Cu(1)	655 (1)	3437 (1)	9008 (1)	67 (1)
O(1)	−573 (4)	3418 (4)	7963 (3)	66 (2)
C(1)	−307 (7)	3753 (5)	7185 (4)	54 (3)
C(2)	866 (7)	4236 (6)	6978 (4)	56 (3)
C(3)	1978 (7)	4453 (5)	7541 (4)	54 (3)
O(2)	2081 (4)	4221 (4)	8364 (3)	65 (2)
C(4)	−1418 (7)	3572 (6)	6444 (5)	61 (3)
C(5)	−954 (12)	3042 (13)	5553 (8)	202 (9)
C(6)	−1985 (12)	4660 (10)	6304 (9)	176 (7)
C(7)	−2449 (13)	2842 (14)	6723 (9)	256 (11)
C(8)	3162 (7)	5030 (6)	7165 (5)	62 (3)
C(9)	3612 (10)	4386 (10)	6303 (7)	126 (5)
C(10)	2774 (9)	6189 (7)	6945 (8)	120 (5)
C(11)	4282 (8)	5185 (10)	7888 (6)	121 (5)
P(1)	1097 (2)	2994 (2)	10363 (1)	56 (1)
C(12)	1574 (9)	1568 (6)	10418 (6)	92 (4)
C(13)	2498 (9)	3766 (8)	10918 (6)	116 (5)
C(14)	−109 (9)	3201 (9)	11262 (6)	107 (4)
Cu(2)	4228 (1)	8443 (1)	8976 (1)	68 (1)
O(3)	5380 (4)	8417 (4)	7937 (3)	65 (2)
C(15)	5089 (7)	8741 (5)	7148 (4)	53 (3)
C(16)	3906 (7)	9242 (6)	6935 (5)	58 (3)
C(17)	2844 (7)	9476 (5)	7506 (5)	53 (2)
O(4)	2786 (5)	9230 (4)	8331 (3)	67 (2)
C(18)	6134 (7)	8559 (6)	6411 (4)	57 (3)
C(19)	6748 (10)	9669 (9)	6290 (8)	134 (6)
C(20)	5526 (10)	8136 (11)	5484 (7)	148 (6)
C(21)	7125 (12)	7763 (11)	6665 (8)	184 (8)
C(22)	1666 (7)	10056 (6)	7135 (5)	63 (3)
C(23)	644 (10)	10276 (10)	7836 (7)	138 (6)
C(24)	2084 (10)	11191 (9)	6850 (9)	150 (7)
C(25)	1106 (10)	9422 (11)	6271 (7)	167 (7)
P(2)	3898 (2)	8008 (2)	10337 (1)	57 (1)
C(26)	5213 (9)	8191 (8)	11210 (6)	104 (4)
C(27)	3393 (9)	6567 (6)	10390 (5)	86 (4)
C(28)	2561 (9)	8777 (8)	10894 (6)	110 (4)

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

Atom coordinates are given in Table II, and selected bond distances and angles, in Tables V and VI, respectively. Three crystallographically different molecules were found in the unit cell. Structural data for only one are presented here in the text (see Figure 2). Details of the metrical parameters for the other two are published as supplementary material.

(b) (dpm)Cu(PMe_3). Very pale yellow prisms of (dpm)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 are collected in Table I. The space group was determined to be $P\bar{1}$ in the triclinic crystal system. A semiempirical absorption correction was applied to the data set, and the structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were included as idealized (riding model) contributions with $d(CH) = 0.960$ Å and with $U = 1.1 \times U$ of attached atoms. In the final difference map, the highest amplitude was 0.42 e/$Å^3$ and the lowest was −0.30 e/$Å^3$. Atom coordinates are given in Table III, and selected bond lengths and

Table IV. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$) for (dbm)Cu(PMe$_3$)

	x	*y*	*z*	*U*(eq)[a]
Cu	0	2131 (1)	0	51 (1)
O	768 (1)	3512 (3)	674 (2)	52 (1)
C(1)	664 (2)	4645 (3)	1404 (2)	42 (1)
C(2)	0	5170 (5)	1792 (3)	46 (1)
C(3)	1318 (2)	5514 (3)	1852 (2)	44 (1)
C(4)	1343 (2)	6134 (3)	2936 (2)	56 (1)
C(5)	1948 (2)	6910 (4)	3333 (3)	69 (1)
C(6)	2526 (3)	7108 (5)	2641 (3)	75 (2)
C(7)	2512 (2)	6472 (5)	1555 (3)	73 (1)
C(8)	1911 (2)	5664 (4)	1168 (2)	56 (1)
P	0	−146 (1)	−938 (1)	58 (1)
C(9)	−729 (3)	−1526 (6)	−612 (5)	133 (3)
C(10)	0	−6 (13)	−2455 (7)	190 (5)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

angles, in Tables V and VI, respectively. Two crystallographically different molecules were found in the unit cell. Structural data for one of them are presented here (see Figure 3). The remaining data are presented as supplementary material.

(c) (dbm)Cu(PMe$_3$). Transparent golden crystals of (dbm)Cu(PMe$_3$) were grown by crystallization from toluene at −30 °C and were mounted in a capillary under dry nitrogen. The crystal data are presented in Table I. The compound (dbm)Cu(PMe$_3$) crystallized in the orthorhombic crystal system with space group *Cmc*2$_1$. Data were collected in the nonstandard space group *Ccm*2$_1$ and transformed by the matrix (010), ($\bar{1}$00), (001) to conform with the standard setting form *Cmcm* or *Cmc*2$_1$. Preliminary solutions in the centric *Cmcm* group showed that the molecule must show *mm* symmetry and be disordered. A satisfactory solution in the noncentric space group confirmed the choice of *Cmc*2$_1$. The structure was solved by direct methods with all non-hydrogen atoms anisotropic and hydrogens included as idealized (riding model) contributions with *d*(CH) = 0.960 Å and *U* = 1.2 × *U* of attached atom. The position of H(2a) was allowed to vary. In the final difference map, the highest amplitude was 0.47 e/Å^3 and the lowest was −0.34 e/Å^3. Atom coordinates are given in Table IV, and selected bond lengths and angles, in Tables V and VI, respectively. The remaining data are available as supplementary material. The atom-labeling scheme is shown in Figure 4.

Results and Discussion

(i) Synthesis and Characterization. The compounds (β-diketonate)Cu(PMe$_3$), where β-diketonate = hfac, tfac, acac, dpm, and dbm, as defined in the Experimental Section, were prepared by both the metalation reaction and the metathesis reaction shown in eqs 3 and 4, respectively. Both reactions resulted in the for-

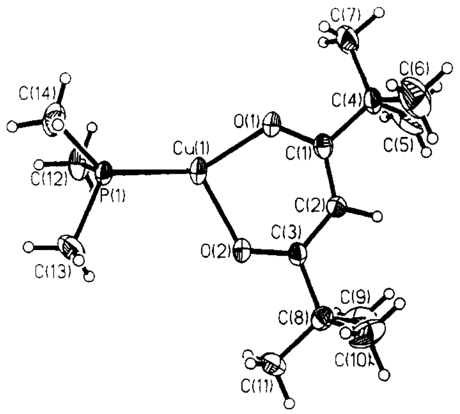

Figure 3. ORTEP plot (50% probability ellipsoids) showing the molecular structure of (dpm)Cu(PMe$_3$) with the atom-numbering scheme.

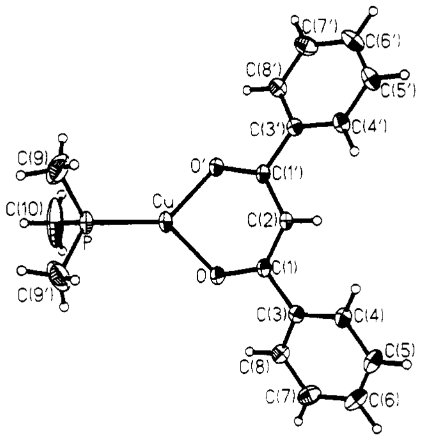

Figure 4. ORTEP plot (50% probability ellipsoids) showing the molecular structure of (dbm)Cu(PMe$_3$) with the atom-numbering scheme.

$$(\eta^5\text{-}C_5H_5)Cu(PMe_3) + \beta\text{-diketonate} \rightarrow (\beta\text{-diketonate})Cu(PMe_3) + C_5H_6 \quad (3)$$

$$Na(\beta\text{-diketonate}) + [ClCu(PMe_3)] \rightarrow (\beta\text{-diketonate})Cu(PMe_3) + NaCl \quad (4)$$

Table V. Selected Bond Lengths (Å) for (hfac)Cu(PMe$_3$), (dpm)Cu(PMe$_3$), and (dbm)Cu(PMe$_3$)

(hfac)Cu(PMe$_3$)	(dpm)Cu(PMe$_3$)	(dbm)Cu(PMe$_3$)
Cu(1)–O(1) = 1.990 (8)	Cu(1)–O(1) = 1.941 (5)	Cu–O = 1.985 (2)
Cu(1)–O(2) = 2.034 (7)	Cu(1)–O(2) = 2.030 (5)	
Cu(1)–P(1) = 2.142 (3)	Cu(1)–P(1) = 22.137 (2)	Cu–P = 2.134 (1)
P(1)–C(6) = 1.787 (1)	P(1)–C(12) = 1.803 (8)	P–C(9) = 1.801 (6)
P(1)–C(7) = 1.82 (2)	P(1)–C(13) = 1.816 (9)	P–C(10) = 1.804 (8)
P(1)–C(8) = 1.81 (2)	P(1)–C(13) = 1.818 (9)	
O(1)–C(1) = 1.24 (1)	O(1)–C(1) = 1.279 (8)	O–C(1) = 1.269 (3)
C(1)–C(2) = 1.37 (2)	C(1)–C(2) = 1.38 (1)	C(1)–C(2) = 1.394 (3)
C(2)–C(3) = 1.39 (2)	C(2)–C(3) = 1.386 (9)	
C(3)–O(2) = 1.23 (1)	C(3)–O(2) = 1.262 (8)	
C(1)–C(4) = 1.49 (3)	C(1)–C(4) = 1.54 (1)	C(1)–C(3) = 1.507 (4)
C(3)–C(5) = 1.52 (2)	C(3)–C(8) = 1.53 (1)	

Table VI. Selected Bond Angles (deg) for (hfac)Cu(PMe$_3$), (dpm)Cu(PMe$_3$), and (dbm)Cu(PMe$_3$)

(hfac)Cu(PMe$_3$)	(dpm)Cu(PMe$_3$)	(dbm)Cu(PMe$_3$)
O(1)–Cu(1)–O(2) = 90.5 (3)	O(1)–Cu(1)–O(2) = 93.2 (2)	O–Cu–O′ = 93.2 (1)
C(1)–O(1)–Cu(1) = 125.8 (8)	C(1)–O(1)–Cu(1) = 124.8 (4)	Cu–O–C(1) = 124.2 (2)
C(2)–C(1)–O(1) = 128 (1)	C(2)–C(1)–O(1) = 125.3 (6)	O–C(1)–C(2) = 125.3 (3)
C(3)–C(2)–C(1) = 124 (1)	C(3)–C(2)–C(1) = 128.4 (6)	C(1)–C(2)–C(1′) = 126.9
O(2)–C(3)–C(2) = 128 (1)	O(2)–C(3)–C(2) = 124.1 (6)	
C(3)–O(2)–Cu(1) = 124.0 (7)	Cu(1)–O(2)–C(3) = 123.9 (4)	
P(1)–Cu(1)–O(2) = 129.5 (2)	P(1)–Cu(1)–O(2) = 117.8 (1)	P–Cu–O = 133.2 (1)
P(1)–Cu(1)–O(1) = 140.2 (2)	P(1)–Cu(1)–O(1) = 149.0 (2)	
Cu(1)–P(1)–C(8) = 114.7 (5)	Cu(1)–P(1)–C(12) = 115.6 (3)	Cu–P–C(10) = 117.9 (3)
Cu(1)–P(1)–C(6) = 117.4 (2)	Cu(1)–P(1)–C(13) = 112.7 (3)	Cu–P–C(9) = 114.2 (2)
Cu(1)–P(1)–C(7) = 115.4 (5)	Cu(1)–P(1)–C(14) = 120.2 (3)	

mation of the desired product in high yield. No complications associated with difficulty in separation of sodium chloride from the final product were encountered. These complications are often the case with a metathesis reaction such as that shown in eq 2. Separation of the salt is further aided by the high volatility of these species and their essentially quantitative sublimation in all cases except (acac)Cu(PMe_3) and (dbm)Cu(PMe_3) (see later). These species all gave satisfactory analytical data, and they were characterized spectroscopically in the solid state, liquid phase, and gas phase.

A number of analogous (β-diketonato)copper(I) compounds have been prepared previously, but with different numbers or types of Lewis base substituents. Addition of acetylacetone to $CH_3Cu(PPh_3)_2$ resulted in the evolution of methane and formation of (acac)Cu(PPh_3)$_2$.[28] Doyle et al.[21] have prepared a number of (β-diketonato)copper(I) olefin and carbonyl complexes but reported that displacement of the carbonyl ligand with L = phosphines, amines, or isonitriles gave derivatives of the type (β-diketonate)CuL_2. A number of derivatives of the type (β-diketonate)CuL_2 have been reported, but we have found no examples of (β-diketonate)CuL where L = a monodentate phosphine ligand.[29–37] A large number of other Lewis base adducts of copper(I) compounds exist, and the subject has been reviewed.[23]

β-Diketonate ligands can bind to metals in a variety of coordination modes.[38] The NMR and infrared spectroscopic data are consistent with binding through the oxygen atoms rather than the carbon atom in the title compounds. This was confirmed in the solid state for (hfac)Cu(PMe_3), (tfac)Cu(PMe_3), (dpm)Cu(PMe_3), and (dbm)Cu(PMe_3) by single-crystal X-ray diffraction and is therefore probably a general feature of these complexes, regardless of the electronic and steric nature of the β-diketonate substituents.

Cryoscopic molecular weight determinations from the freezing point depression of benzene for (hfac)Cu(PMe_3) and (tfac)Cu(PMe_3) reveal that both compounds are monomeric in this solvent. These data are consistent with the solid-state X-ray diffraction data that also reveal the monomeric nature of these compounds, but they appear to be inconsistent with the mass spectroscopic data. In the positive-ion mass spectrum of all these derivatives, fragments of mass higher than that of the monomeric parent ion were observed. In a number of cases, ions of low relative abundance, consistent with the presence of dimeric species, were observed, but ions corresponding to $[(\beta\text{-diketonate})Cu_2(PMe_3)_2]^{\bullet+}$ were more abundant. These ions exhibited the characteristic three-peak pattern associated with the two naturally occurring isotopes of copper (^{63}Cu, 69.1% natural abundance; ^{65}Cu, 30.9% natural abundance)[39] in the approximate ratio 4.5:5:1. Lowering the ionization voltage did not significantly change the relative ratio of these higher mass ions to that attributed to monomeric species. Since bimolecular reactions in the gas phase at these pressures are unlikely, it seemed possible that clusters might evaporate into the gas phase from the solid state. Evidence consistent with this postulate was observed in the solid-state X-ray structural data (see later). Other ions observed by mass spectroscopy were derived from fragmentation of the molecular ion.

We had hoped to correlate various spectroscopic parameters, such as ν(C–O) and ^{1}H, ^{13}C, or ^{31}P NMR chemical shifts, with thermodynamic properties of the molecules. The trends observed, however, are not always consistent or are difficult to interpret. To shed further light, single-crystal X-ray diffraction studies of a number of these derivatives were carried out and are described in section iii.

(ii) Oxidative and Thermal Stability. All the mono(phosphine) compounds, except (dbm)Cu(PMe_3), are oxygen sensitive and, upon exposure to air, rapidly turn deep green or blue, the characteristic color of the corresponding copper(II) β-diketonate complexes. The compound (dbm)Cu(PMe_3) is air stable for several days without a detectable color change. Some complexes appear to be thermally unstable when stored in solution. For example, *n*-pentane solutions of (acac)Cu(PMe_3) showed signs of significant decomposition involving precipitation of copper metal and an intensely colored solid after 1 h at room temperature. This observation is consistent with the thermal decomposition of (acac)Cu(PMe_3) upon sublimation to form a dark, involatile solid together with (acac)Cu(PMe_3)$_2$ isolated on the cold-finger.

In a separate experiment, (acac)CuPMe_3 was heated to 60 °C at 10^{-4} Torr in a closed system. The products were separated according to their solubility in acetone and ethanol and characterized by NMR spectroscopy, mass spectroscopy, and elemental analysis. The species Cu(acac)$_2$ and $[acac]^-[Cu(PMe_3)_4]^+$ were identified.[26] No uncoordinated PMe_3 was observed at the end of the experiment. A mass balance of these products was consistent with the thermally induced disportionation reaction previously observed under CVD conditions:[19]

$$8(acac)Cu(PMe_3) \rightarrow 3Cu + 3Cu(acac)_2 + 2[acac]^-[Cu(PMe_3)_4]^+ \quad (5)$$

The compound $[acac]^-[Cu(PMe_3)_4]^+$ has previously been independently prepared from the reaction of (acac)Cu(PMe_3) with excess PMe_3.[26] In this thermolysis experiment, $[acac]^-[Cu(PMe_3)_4]^+$ could also be formed from the reaction of liberated PMe_3 with the starting material, (acac)Cu(PMe_3).

Solutions of (tfac)Cu(PMe_3) darken slightly when stored at room temperature over longer periods, and solutions of (hfac)Cu(PMe_3) show no signs of thermal decomposition in solution at room temperature. As expected, in the solid phase, these species are significantly more stable, and (hfac)Cu(PMe_3) has been heated to 67 °C in vacuo for 4 days without detectable decomposition, as determined by ^{1}H NMR spectroscopy.

(iii) Single-Crystal X-ray Diffraction. In this work, the single-crystal X-ray diffraction structures of (hfac)Cu(PMe_3), (dpm)Cu(PMe_3), and (dbm)Cu(PMe_3) are reported. The solid-state structure of (tfac)Cu(PMe_3) has previously been communicated,[1] and repeated attempts to structurally characterize (acac)Cu(PMe_3) were unsuccessful. A summary of the crystallographic data for (hfac)Cu(PMe_3), (dpm)Cu(PMe_3), and (dbm)Cu(PMe_3) is presented in Table I, atomic coordinates are given in Tables II–IV, respectively, and comparisons of selected bond lengths and bond angles are presented in Tables V and VI, respectively. While the crystallographic data obtained confirm the elemental composition of this series of compounds and their monomeric nature in the solid state, many of the metrical parameters of all the compounds are not significantly different.

All three compounds (and (tfac)Cu(PMe_3)) are monomeric in the solid state and contain copper(I) in a three-coordinate planar ligand environment of two oxygen atoms from the β-diketonate ligands and one phosphorus atom from PMe_3. The compounds (hfac)Cu(PMe_3) and (dpm)Cu(PMe_3) possess no molecular symmetry, while (dbm)Cu(PMe_3) possesses a molecular mirror plane that passes through P, Cu, and C(2). The single crystals of (hfac)Cu(PMe_3) characterized contained three independent molecules in the unit cell. Molecule 1 is shown in Figure 2; the other two are presented as supplementary material. Most of the bond lengths and bond angles within the three independent molecules are within three standard deviations of each other, with the notable exception of the O–Cu–P angles. While the "bite" angles of the β-diketonate ligands are approximately the same

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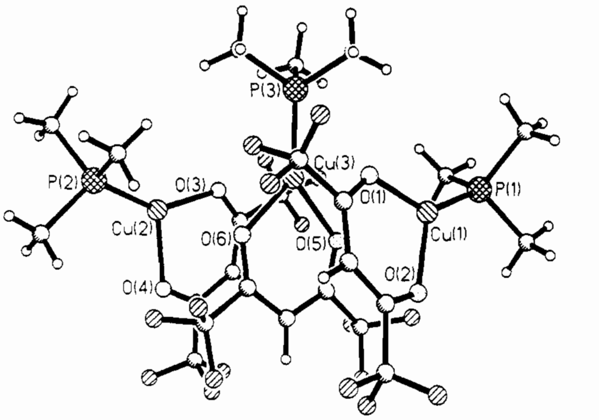

Figure 5. Ball and stick drawing of the crystal structure of (hfac)Cu(PMe_3) emphasizing the relative orientation of the three independent molecules.

for all three molecules (90.5 (3)° for molecule 1, 90.5 (3)° for molecule 2, and 89.6 (3)° for molecule 3), the O–Cu–P angles are quite different. Molecule 3 has the most symmetrical trigonal-planar coordination environment for Cu (P–Cu–O = 135.7 (2) and 134.7°), but the other two molecules are significantly distorted, particularly molecule 2 (145.5 (2) and 124.0 (2)°).

The single crystals of (dpm)Cu(PMe_3) examined contained two independent molecules in the unit cell, both of which have similar metrical parameters within the limits of error on the data and exhibit a similar distortion of the trigonal-planar coordination environment about copper as (hfac)Cu(PMe_3). Relevant data for molecule 2 are O–Cu–O = 93.3 (2)° and P–Cu–O = 148.3 (2) and 118.4 (1)°.

The compound (dbm)Cu(PMe_3) exhibits a structure in which the copper atom is symmetrically coordinated by the β-diketonate ligand with a "bite" angle of 93.2 (1)° and with P–Cu–O angles of 133.2 (1)°. The bond lengths and angles within the β-diketonate ligand of this molecule may be used to obtain standard parameters for a symmetrically coordinated ligand.

In all three species, the Cu–P and Cu–O bond lengths are the same within the error on the data. The Cu–P bond length is similar to that recently observed[15] for (η^5-C_5H_5)Cu(PMe_3) of 2.113 (1) Å. The magnitude of C–O and C–C bond lengths of the coordinated β-diketonate ligands are in the region expected for a delocalized symmetrical bonding of the β-diketonate ligand. The C–O bond distances are longer than expected for a coordinated carbonyl β-diketonate ligand (~1.21 Å), and the C–C bond is shorter than expected for the keto form of the coordinated β-diketonate ligand (~1.50 Å) but slightly longer than expected for a C–C double bond (1.33 Å). These data are analogous to those observed for (tfac)Cu(PMe_3). The angles and distances within the β-diketonate substituents are normal.

The origin of the distortions in coordination of the β-diketonate ligands to the copper centers may be the result of weak intermolecular interactions. A ball and stick drawing of the relative orientations of the three independent molecules in the unit cell of the crystal structure of (hfac)Cu(PMe_3) is shown in Figure 5. All three molecules are oriented such that the oxygen atoms of the β-diketonate ligands in one molecule occupy axial positions in the periphery of the copper coordination sphere of an adjacent molecule. The intermolecular copper–oxygen distances are all in the region of 3.0 Å. While this is clearly too long to be a bonding interaction (~2.0 Å) or even a Lewis acid–Lewis base interaction, this distance is significantly shorter than the sum of the Van der Waals radii of oxygen and copper, ~3.4 Å.[39] These interactions may also account for the P–Cu–O angle asymmetry (P(1)–Cu(1)–O(1) = 140.2 (2)°, P(1)–Cu(1)–O(2) = 129.5 (2)°) where intermolecular steric interactions may be important. These intermolecular Cu⋯O interactions may contribute to the observation of ions of molecular mass higher than that of the monomeric parent ion observed in the mass spectrum of (hfac)Cu(PMe_3). A knowledge of the gas-phase structure of these species is clearly important for an understanding of the mechanism of copper deposition from these compounds. However, it should be noted that a similar distortion of the copper coordination sphere is observed for (dpm)Cu(PMe_3), but no short intermolecular Cu⋯O distances were found. This species also exhibits mass spectral data similar to those of (hfac)Cu(PMe_3). In contrast, there is no evidence for intermolecular interaction in the solid-state structure of (dbm)Cu(PMe_3), and ions of the type (β-diketonate)Cu_2(PMe_3) are not observed in the mass spectrum of this compound.

The coordination number of 3 for copper(I) is relatively uncommon, with 4-coordination generally being preferred. Since lower coordination numbers are generally observed in the presence of sterically demanding ligands, it seems likely that the (β-diketonate)Cu(PMe_3) compounds will coordinate a third ligand to complete the tetrahedral coordination environment very easily. This appears to be the case, as evidenced by the reaction with PMe_3 to form (β-diketonate)Cu$(PMe_3)_2$.

The species (β-diketonate)Cu$(PMe_3)_2$ were prepared either by quantitative addition of 1 equiv of PMe_3 to the mono(phosphine) derivative (β-diketonate)Cu(PMe_3) or by the reaction of the sodium salts of the β-diketonate with $[CuCl_2]^-[Cu(PMe_3)_4]^+$ according to eq 6. The method of preparation and the characterization of $[CuCl_2]^-[Cu(PMe_3)_4]^+$ have been described elsewhere.[26] The (β-diketonate)Cu$(PMe_3)_2$ compounds formed by this method gave satisfactory elemental analysis and exist as volatile solids at room temperature. The spectroscopic data for these species are consistent with the presence of monomeric species with a tetrahedral copper coordination environment in solution. The absence of virtual coupling between the methyl protons (or the methyl carbons) of the coordinated PMe_3 ligands and the ^{31}P nucleus of the adjacent PMe_3 ligand is noteworthy and may be consistent with an intermolecular exchange process that occurs rapidly on the ^1H and ^{13}C NMR time scales at room temperature. No change is observed in the spectra of these derivatives upon cooling to −80 °C in toluene-d_8 solution. Investigations of the possibility of exchange processes are the subject of current further work and will be reported shortly.[26] It is interesting to note that the mass spectral data for these species are similar to those of the mono(phosphine) analogues.

$$2Na(\beta\text{-diketonate}) + [CuCl_2]^-[Cu(PMe_3)_4]^+ \rightarrow 2(\beta\text{-diketonate})Cu(PMe_3)_2 + 2NaCl \quad (6)$$

(iv) Vapor Pressure Measurements. The vapor pressure of (hfac)CuPMe_3 was measured in the vapor pressure apparatus shown in Figure 1. The apparatus was first calibrated by measuring the vapor pressure of a number of known compounds. The measured vapor pressure of naphthalene[40] was 750 mTorr at 50 °C and compares favorably with the literature value within the limits of error of the apparatus (the accuracy of the temperature measurement). It is noteworthy that this value remained constant over 24 h at 50 °C. As an additional control experiment, the vapor pressure of Cu$(hfac)_2$ was measured over the temperature range 25–80 °C. Although Cu$(hfac)_2$ was sublimed twice and subjected to freeze–pump–thaw cycles to remove traces of adventitious donor ligands such as water or ethanol, the attainment of a constant vapor pressure at any given temperature was not possible. For example, after thermal equilibrium had been established in the vapor pressure apparatus at 80 °C, the pressure rose from ~400 to ~550 mTorr over a period of 300 min. However, the values obtained at different temperatures about 150 min after attainment of thermal equilibrium agreed quite well (within 10%) with the published data for this compound,[10] although the lack of attainment of a constant equilibrium vapor pressure was not satisfactory. Unfortunately, few experimental details are available from literature data to compare the time allowed to establish equilibrium vapor pressures for Cu^{II}(β-diketonate)$_2$ compounds.

The vapor pressure of (hfac)Cu(PMe_3) was measured as a function of temperature, and the results are displayed in Figure 6. Consistent, reproducible results were obtained only after

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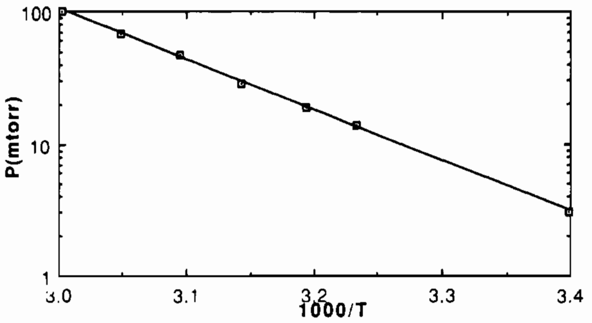

Figure 6. Plot of log (vapor pressure, P) versus $1/T$ for (hfac)Cu(PMe_3).

repeated sublimation and freeze–pump–thaw cycles. Above 60 °C, the change in measured pressure with time was large and may result from thermal instability of this compound perhaps via the dissociation of PMe_3. The enthalpy of vaporization, ΔH_{vap}, of (hfac)Cu(PMe_3) was calculated to be approximately 10 kcal/mol from the plot of log (vapor pressure) versus $1/T$ shown in Figure 6. This value is comparable to that observed for Cu(hfac)$_2$.[10]

Attempts to measure the vapor pressures of (acac)Cu(PMe_3) and (tfac)Cu(PMe_3) were unsuccessful due to the inability to obtain constant vapor pressures at a given temperature. This may be due to the poor thermal stability of those species over extended time periods.

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Supplementary Material Available: For (hfac)Cu(PMe_3), Tables S1–S3 (structure determination summary), Tables S4 and S5 (bond lengths and angles), Tables S6 and S7 (anisotropic displacement coefficients, H atom coordinates, and isotropic displacement coefficients), Figures S1–S3 (atom-numbering schemes for molecules 1–3) and Figure S4 (unit cell diagram), for (dpm)Cu(PMe_3), Tables S8–S10 (structure determination summary), Tables S11 and S12 (bond lengths and angles), Tables S13 and S14 (anisotropic displacement coefficients, H atom coordinates, and isotropic displacement coefficients), Figure S5 (atom-numbering scheme for molecule 2), and Figure S6 (unit cell diagram), and for (dbm)Cu(PMe_3), Tables S15–S17 (structure determination summary), Tables S18 and S19 (bond lengths and angles), Tables S20 and S21 (anisotropic displacement coefficients, H atom coordinates, and isotropic displacement coefficients), and Figure S7 (unit cell diagram), for naphthalene, Cu(hfac)$_2$, and (hfac)Cu(PMe_3), Figures S8–S10 (vapor pressure vs time), and textual presentations of the experimental procedure for the (hfa)Cu(PMe_3) vapor pressure measurement and spectroscopic characterization data for (tfac)Cu(PMe_3), (acac)Cu(PMe_3), (dpm)Cu(PMe_3), (dbm)Cu(PMe_3), (tfac)Cu(PMe_3)$_2$, and (acac)Cu(PMe_3)$_2$ (43 pages); Tables S22–S24 (observed and calculated structure factors for (hfac)Cu(PMe_3), (dpm)Cu(PMe_3), and (dbm)Cu(PMe_3)) (39 pages). Ordering information is given on any current masthead page.

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Hydrothermal Polychalcogenide Chemistry. Stabilization of $[Mo_9Se_{40}]^{8-}$, a Cluster of Clusters, and $[Mo_3Se_{18}]_n^{2n-}$, a Polymeric Polyselenide. Novel Phases Based on Trinuclear $[Mo_3Se_7]^{4+}$ Building Blocks

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A polymeric Mo polyselenide, $K_2Mo_3Se_{18}$, and a large molecular cluster Mo polyselenide, $K_8Mo_9Se_{40}\cdot 4H_2O$, were synthesized by the hydrothermal method. The reaction of Mo, K_2Se_4, and H_2O in a 1:1.5:22.2 ratio in a vacuum-sealed Pyrex tube at 135 °C for 3 days yielded black platelike crystals of $K_2Mo_3Se_{18}$ (I). The reaction of MoO_3, K_2Se_2, and H_2O in a 1:2:22.2 ratio under the same conditions as above yielded black chunky crystals of $K_8Mo_9Se_{40}\cdot 4H_2O$ (II). Both compounds were obtained in ~20% yield. The structures were determined by single-crystal X-ray diffraction techniques. Crystal data for $K_2Mo_3Se_{18}$: monoclinic $P2_1$, $Z = 2$, $a = 10.277$ (6) Å, $b = 12.66$ (1) Å, $c = 10.624$ (8) Å, $\beta = 116.82$ (5)°, $V = 1233$ (2) Å^3; $2\theta_{max}$(Mo Kα) = 45°; number of data measured 1824, number of unique data 1608, number of data having $F_o^2 > 3\sigma(F_o^2)$ 1382, number of variables 207, number of atoms 23; $\mu = 267$ cm^{-1}; final $R = 0.052$ and $R_w = 0.086$. Crystal data for $K_8Mo_9Se_{40}\cdot 4H_2O$: triclinic $P\bar{1}$, $Z = 2$, $a = 10.312$ (8) Å, $b = 18.55$ (3) Å, $c = 18.57$ (2) Å, $\alpha = 87.6$ (1)°, $\beta = 87.57$ (7)°, $\gamma = 84.0$ (1)°, $V = 3523$ (8) Å^3; $2\theta_{max}$(Mo Kα) = 45°; number of data measured 9888, number of unique data 8638, number of data having $F_o^2 > 4\sigma(F_o^2)$ 3592, number of variables 546, number of atoms 65; $\mu = 224$ cm^{-1}; final $R = 0.092$ and $R_w = 0.108$. I and II have rather complicated structures. I contains the $[Mo_3(Se)(Se_2)_3(Se_3)(Se_4)_2]_n^{2n-}$ polymeric anion which contains $[Mo_3Se_7]^{4+}$ clusters as building blocks. It has a zigzag chain structure which is formed by two parallel sets of face-to-face $[Mo_3Se_7]^{4+}$ clusters cross-linked by Se_4^{2-} ligands. The zigzag chains are then arranged side by side and interact through weak Se···Se contacts generated by a Se atom of a Se_3^{2-} ligand of one chain and the triangular face of Se atoms from the three bridging Se_2^{2-} ligands of a $[Mo_3Se_7]^{4+}$ cluster in another chain. $[Mo_9Se_{40}]^{8-}$ contains three trinuclear $[Mo_3Se_7]^{4+}$ subclusters which are "glued" together by the two monoselenide ions. One monoselenide ion belongs to a $[Mo_3Se_7]^{4+}$ core being coordinated to three Mo atoms and at the same time interacting with the triangular face of three Se atoms of Se_2^{2-} bridging ligands of another $[Mo_3Se_7]^{4+}$ subcluster. The other monoselenide ion interacts with six Se atoms of Se_2^{2-} bridging ligands of two $[Mo_3Se_7]^{4+}$ subclusters. Two separate $[Mo_9Se_{40}]^{8-}$ clusters come in close contact (2.98 Å) in the solid state through two terminal Se_2^{2-} ligands related by an inversion center.

Introduction

Metal polychalcogenides are of longstanding interest in the field of coordination and solid-state chemistry.[1] Conventionally, syntheses of molecular metal polychalcogenides are carried out in solution at ambient temperature.[2,3] Recently, molten salts have

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