Synthesis and Spectroscopic Studies of Novel *β*-Diketonate Copper(I) Compounds and Solid State Structure of Tetravinylsilane Tetrakis Copper(I) 1,1,1,5,5,5-Hexafluoroacetylacetonate (TVST[Cu]hfac)

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Reactions between tetraalkene silanes SiR_4 (R = vinyl and allyl), copper(I) oxide, and 1,1,1,5,5,5-hexafluoroacetylacetonate (hfac) gave novel multicoordinated *β*-diketonate copper(I) Lewis base ligand complexes. The synthesis and spectroscopic data of tetravinylsilane biscopper(I)hfac complex (TVSB[Cu]hfac) (**1**), tetravinylsilane tetrakiscopper(I)hfac (TVST[Cu]hfac) (**2**), and tetrallylsilane triscopper(I)hfac complex (TASTri[Cu]hfac) (**3**) are presented, and the structural characterization of tetravinylsilane tetrakiscopper(I)hfac (TVST[Cu]hfac) (**2**) is reported.

Introduction

A wide variety of Cu(I) complexes have been synthesized and characterized to date where the most recently synthesized compounds have been prepared with the intention to be used as copper precursor complexes in metal-organo chemical vapor deposition (MO-CVD).[1] The features sought from these precursors include, high volatility, stability at room temperature, clean disproportionation at low temperatures, facile synthesis, and nontoxic decomposition byproducts.[2] In the limit there is a compromise between ease of synthesis, stability, and processability, on one hand, and volatility, low disproportionation temperatures, ultraviolet stability, etc., on the other. We are trying to address this by synthesizing highly stable copper precursors that can be converted simply, prior to use, into reactive precursors. We are also looking into using novel deposition techniques, e.g., ink-jet, reel-to-reel, and gravure printing among others, as an alternative to MO-CVD.[3] These printing methods are generally low-temperature (<100 °C) techniques and require liquid or solution-based formulations. Here we present our results of reactions between tetraalkene silanes SiR_4 (R = vinyl and allyl), copper(I) oxide (Cu_2O), and 1,1,1,5,5,5,-hexafluoroacetylacetonate (hfac). We describe the synthesis and spectroscopic data of novel multicoordinated *β*-diketonate copper(I) Lewis base ligand complexes that exhibit some of the process benefits we are aiming to achieve.

Experimental Section

General Considerations. In the following examples all the chemicals used were purchased from Avocado Research Chemicals Ltd, Heysham, Lancs., U.K., Sigma-Aldrich Co Ltd, Gillingham, Dorset, U.K., or Fluorochem Ltd, Old Glossop, Derbys., U.K. All the solvents used were distilled from sodium/benzophenone under an inert nitrogen atmosphere. As well as using standard Schlenk line techniques in all the handling steps during the synthesis of the compounds, the materials were kept cool (<4 °C) and away from strong to moderate light sources. Nuclear magnetic resonance spectra were acquired using a JEOL GSX 270 instrument with JEOL Delta control software and referenced to the residual protons in C_6D_6. Electron impact (EI) and fast atom bombardment (FAB) mass spectra were obtained using JEOL DX-303, VG-7070B, VG-12253, VG ZAB-E, or VG Autospec Q instruments. Uncorrected melting points are given. UV−vis spectra were obtained using a Hewlett-Packard 8453 diode array spectrometer, using dry cyclohexane as solvent and as blank reference. A quartz cell with 1 cm path length was used. Solid-state thin film infrared spectroscopy was performed using a Mattson Satellite 3000 FTIR spectrometer and NaCl disks. Elemental analyses were performed at the Microanalysis SACS center at the University of North London. Compounds **1** and **3** were too unstable to yield meaningful elemental analysis data. A stainless steel nozzle plate with a 300 μm ejection hole was used to produce drop-on-demand jetting. The amplitude, frequency, and shape of the pressure pulse for the ink-jet were controlled using a personal computer equipped with the appropriate PCI bus and a wave generation application (WaveCad 7223pc Version 1.0; MS-Dos platform, Tabor Electronics Ltd, U.K.). The pulse was then amplified to the required amplitude using a 500V Linear Amplifier with monitoring capability (Bournlea Instruments

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Ltd. U.K.). By using a 2 mm head pressure of ink and applying a square wave (frequency 100 Hz, amplitude 4.0 V, amplitude offset 2.0 V, duty cycle 5% of entire wave) on the piezo actuator, a custom-built PZT piezoelectric ceramic unimorph research printhead operating in the bend mode, produced discreet droplets of the copper precursor. All parts of the apparatus in contact with the ink were heated to ∼70 °C.

Synthesis of Tetravinyl Silane Bis[copper(I) 1,1,1,5,5,5-hexafluoroacetylacetonate], 1. Tetravinylsilane [TVS, (0.954 g, 7.0 mmol, 1.2 mL)] was added to a stirred hexane (20 mL) solution containing copper oxide [Cu_2O (1.00 g, 7.0 mmol)]. 1,1,1,5,5,5-Hexafluoroacetylacetonate [hfac (2.91 g, 14.0 mmol, 1.98 mL)] was then added while cooling the mixture on an ice-bath. The appearance during the addition changed from pink to yellow-green, and a gray precipitate forms. The mixture was not allowed to warm above 25 °C during the addition. This mixture was then kept excluded from light and stirred at ambient temperature until the red copper oxide had mostly disappeared. This suspension was then filtered under inert atmosphere, and the solvents were removed from the filtrate under reduced pressure (1.0 mmHg) while cooling the mixture (<0 °C). Pale yellow crystals (2.5 g, 53% yield) formed during the cooling. The product was stored in cold conditions (<4 °C), under an atmosphere of nitrogen. NMR analysis indicates ∼1.8 Cu(I)hfac ligands per tetravinylsilane molecule. Mp: 42−44 °C. $C_{18}H_{14}Cu_2F_{12}0_4Si$ (M = 677.5 g/mol). ^1H NMR (C_6D_6): δ (ppm vs TMS) 4.70−5.10 (m, 12H, $-CH{=}CH_2$) and 6.17 (s, 4H, $-CO-CH-CO-$). ^{13}C NMR (C_6D_6): δ (ppm vs TMS) 90.1, 113.3, 115.8, 117.5 (q, $-CF_3$, $^1J_{CF}$ = 286 Hz) and 177.9 (q, $-CO-$, $^2J_{CF}$ = 35 Hz). MS (m/z): 676, <1%, $[(CH_2CH)_4Si(Cuhfac)_2]^{\bullet+}$, 477, 37%, $[Cu(hfac)_2]^{\bullet+}$, 406, 63%, $[(CH_2CH)_4Si(Cuhfac)]^{\bullet+}$, 339, 43%, $[(CH_2CH)_4Si(CuO_2C_2CHCF_3)]^{\bullet+}$, 201, 100%, $[Cu(O_2C_2CHCF_3)]^{\bullet+}$, 69, 72%, $[CF_3]^{\bullet+}$. UV−vis (λ_{max} in nm, abs. in arbitrary units): λ_{max1} = 312 nm, 2.5 AU, λ_{max2} = 641 nm, 10^{-3} AU, λ_{max3} = 656 nm, 10^{-3} AU, λ_{max4} = 592 nm, 10^{-4} AU, λ_{max5} = 762 nm, 10^{-4} AU. IR (NaCl disk, ν in cm^{-1}): 2923 (m), 2853 (w), 1637 (vs), 1604 (m), 1554 (m), 1528 (m), 1462 (vs), 1340 (m), 1254 (s), 1196 (s), 1145 (s), 799 (m), 736 (m), 665 (s).

Synthesis of Tetravinylsilane Tetrakis[copper(I) 1,1,1,5,5,5-hexafluoroacetylacetonate] Complex, 2. Tetravinylsilane [TVS, (0.954 g, 7.0 mmol, 1.2 mL)] was added to a stirred hexane (30 mL) solution containing copper oxide [Cu_2O (2.00 g, 14.0 mmol)]. 1,1,1,5,5,5-Hexafluoroacetylacetonate [hfac (5.82 g, 28.0 mmol, 3.96 mL)] was then added while cooling the mixture on an ice-bath. By treating the mixture in same way as in the synthesis of **1**, pale yellow crystals (5.2 g, 61% yield) were obtained. NMR analysis indicates ∼3.8 Cu(I)hfac ligands per tetravinylsilane molecule. Recrystallization from hexane yielded pale yellow microcrystals. NMR analysis indicates >3.95 Cu(I)hfac ligands per tetravinylsilane molecule. Mp: 56−58 °C. $C_{28}H_{16}Cu_4F_{24}0_8Si$ (M = 1218.7 g/mol), $C_{28}H_{16}Cu_4F_{24}0_8Si{\cdot}0.3\ C_6H_{14}$ ($C_{29.80}H_{20.20}Cu_4F_{24}0_8Si$, M = 1244.51 g/mol), found (calc): C 28.24 (28.76); H 1.01 (1.64). ^1H NMR (C_6D_6) δ ppm vs TMS: 4.25 (br.s, 12H, $-CH{=}CH_2$) and 6.17 (s, 4H, $-CO-CH-CO-$). ^{13}C NMR (C_6D_6): δ (ppm vs TMS) 90.1, 109.6, 112.2, 117.5 (q, $^1J_{CF}$ = 286 Hz), and 177.9 (q, $^2J_{CF}$ = 35 Hz). MS (m/z): 1215, ≪1%, $[(CH_2CH)_4Si(Cuhfac)_4]^{\bullet+}$, 477, 38%, $[Cu(hfac)_2]^{\bullet+}$, 406, 59%, $[(CH_2CH)_4Si(Cuhfac)]^{\bullet+}$, 339, 41%, $[(CH_2CH)_4Si(CuO_2C_2CHCF_3)]^{\bullet+}$, 201, 100%, $[Cu(O_2C_2CHCF_3)]^{\bullet+}$, 92, 72%, $[CF_3]^{\bullet+}$. UV−vis (λ_{max} in nm, abs. in arbitrary units): λ_{max1} = 314, 0.8 AU, λ_{max2} = 641, 10^{-3} AU, λ_{max3} = 487, 10^{-3} AU, λ_{max4} = 656, 10^{-3} AU, λ_{max5} = 757, 10^{-4} AU. IR (NaCl disk, ν in cm^{-1}): 2924 (m), 2853 (m), 1692 (w), 1640 (vs), 1610 (m), 1556 (m), 1529 (m), 1466 (vs), 1337 (m), 1257 (s), 1198 (s), 1148 (s), 969 (m) 803 (m), 739 (m), 673 (s), 588 (s).

Synthesis of Tetraallylsilane Tris[copper(I) 1,1,1,5,5,5-hexafluoroacetylacetonate] Complex, 3. Tetraallylsilane [TAS, (0.673 g, 3.5 mmol, 0.81 mL)] was added to a stirred hexane (30 mL) solution containing copper oxide [Cu_2O, (1.052 g, 7.35 mmol)]. 1,1,1,5,5,5-Hexafluoroacetylacetonate [hfac, (2.99 g, 14.35 mmol, 2.04 mL)] was then added while cooling the mixture on an ice-bath. The appearance during the addition changed from pink to yellow-green, and a gray precipitate formed. By treating the mixture in the same way as in previous examples, yellow crystals (1.7 g, 48% yield) were obtained. The product was stored in cold conditions (<4 °C), under an atmosphere of nitrogen. NMR analysis indicates ∼2.8 Cu(I)hfac ligands per tetraallylsilane molecule. Mp: 47−49 °C, $C_{27}H_{23}Cu_3F_{18}0_6Si$ (M = 1004.2 g/mol). ^1H NMR (C_6D_6): δ (ppm vs TMS) 1.05 (d, 8H, $Si-CH_2-$, J = 7.7 Hz)), 4.13 (d, 4H, *trans*-$CH_2{=}CH-$, J = 16.8 Hz), 4.16 (d, 4H, *cis*-$CH_2{=}CH-$, J = 7.4 Hz), 4.92 (dt, 4H, $-CH{=}CH_2$, J = 15.8 Hz and 7.4 Hz), and 6.16 (s, 4H, $-CO-CH-CO-$).

X-ray Structure of $C_{28}H_{16}Cu_4F_{24}O_8Si{\cdot}0.3\ (C_6H_{14})$. Details for the crystal data and a summary of data collection parameters are given in Table 1. Intensity data were recorded at 150 K, using a Nonius Kappa CCD area-detector diffractometer mounted at the window of a rotating anode FR591 generator with a molybdenum anode (λ = 0.71073 Å) operating at 50 kV, 90 mA. The crystal-to-detector distance was 40 mm,

Table 1. Crystal Data for $2{\cdot}0.3C_6H_{14}$

empirical formula	$C_{29.80}H_{20.20}Cu_4F_{24}O_8Si$
fw	1244.51
cryst syst	triclinic
space group	$P\bar{1}$
a [Å]	9.6308(4)
b [Å]	13.181(1)
c [Å]	17.944(2)
α [deg]	94.64(2)
β [deg]	97.13(2)
γ [deg]	109.54(1)
volume [Å^3]	2111.8(3)
Z	2
density(calcd) [Mg/m^3]	1.957
abs coeff [mm^{-1}]	2.167
crystal	yellow block
crystal size [mm^3]	0.10 × 0.10 × 0.10
θ range for data collection [deg]	2.97−25.05
index range	$-11 \leq h \leq 11$, $-15 \leq k \leq 15$, $-21 \leq l \leq 21$
no. of reflns collected	11 837
no. of ind reflns	6731 [R_{int} = 0.0424]
max. and min. transmn	0.8125 and 0.8125
no. of data/params	6731/631
goodness-of-fit on F^2	1.185
final R indices [$F^2 > 2\sigma(F^2)$]	R1 = 0.0648, wR2 = 0.1211
R indices (all data)	R1 = 0.1082, wR2 = 0.1310
largest diff peak and hole [e Å^{-3}]	1.083 and −0.979

Table 2. Selected Bond Lengths [Å] and Angles [deg] for $2{\cdot}0.3C_6H_{14}$[a]

Cu1−O2	1.945(4)	Cu3−C31	1.964(7)
Cu1−O1	1.958(4)	Cu3−C30	1.995(7)
Cu1−C11	1.982(7)	Cu4−O8	1.947(5)
Cu1−C10	1.997(6)	Cu4−O7	1.957(5)
Cu2−O4	1.938(4)	Cu4−C41	1.993(7)
Cu2−O3	1.951(5)	Cu4−C40	2.003(7)
Cu2−C21	1.978(6)	C10−C11	1.392(10)
Cu2−C20	1.994(7)	C20−C21	1.382(10)
Cu3−O5	1.927(5)	C40−C41	1.386(9)
Cu3−O6	1.931(5)	C30−C31	1.386(9)
Cu1−X1	1.864(7)	Cu3−X3	1.854(7)
Cu2−X2	1.862(7)	Cu4−X4	1.874(7)
O2−Cu1−O1	94.2(2)	O5−Cu3−O6	95.8(2)
O1−Cu1−X1	132.5(3)	O5−Cu3−X3	128.5(3)
O2−Cu1−X1	132.2(3)	O6−Cu3−X3	135.6(3)
O4−Cu2−O3	95.3(2)	O8−Cu4−O7	93.9(2)
O2−Cu2−X2	131.7(3)	O7−Cu4−X4	136.1(3)
O3−Cu2−X2	132.8(3)	O8−Cu4−X4	130.0(3)
C10−Si1−C20	106.3(3)	C10−Si1−C30	107.7(3)
C10−Si1−C40	117.1(3)	C20−Si1−C40	109.4(3)
C20−Si1−C30	109.2(3)	C40−Si1−C30	106.8(3)

[a] Xn is the bond centroid of the Cn0−Cn1 bond with n = 1, 2, 3, 4.

and φ and ω scans (2° increments, 20 s exposure time) were carried out to fill the Ewald sphere. Data collection and processing were carried out using the programs DIRAX,[4] COLLECT,[5] DENZO,[6] and MAXUS,[7] and an empirical absorption correction was applied using SORTAV.[8] The structure was solved by direct methods[9] and refined on F^2 by full-matrix least-squares refinements.[10] The F atoms in five CF_3 groups are disordered over two positions and have been refined isotropically. All other non-hydrogen atoms were refined anisotropically. The hexane molecule lies on a center of inversion and shows a partial occupancy that was refined to be 0.6. All hydrogen atoms were included in the refinement in calculated positions using a riding model.

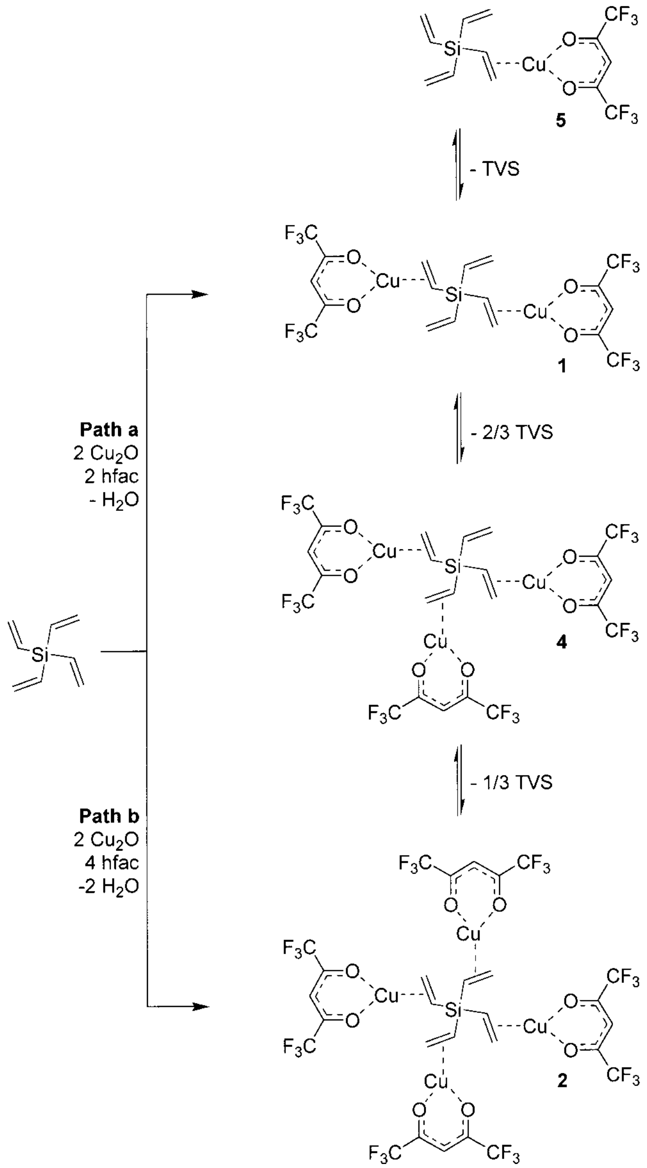
Results and Discussion

Synthesis. The copper complexes in this report were prepared using a previously described but slightly modified synthesis procedure.[11] By changing the stoichiometry of reagents we obtained complexes with different numbers of copper hfac groups bound to a tetraligand silane molecule. Using equimolar amounts of reagents, the fully occupied tetravinylsilane tetrakiscopper 1,1,1,5,5,5-hexafluoroacetylacetonate (**2**) complex was obtained (Scheme 1, path b) as pale yellow microcrystals (mp 56−58 °C).

The isolation of this complex was found to be facile due to the fact that it is a solid that exhibits relatively high thermal stability when compared to other precursors, e.g., vinyltrimethylsilane copper(I) 1,1,1,5,5,5-hexafluoroacetylacetonate (VTMSCu(I)hfac).[12] We noted that decomposition of the solid compound, as disproportionation, starts to occur at around 130 °C at normal pressure. However, if exposed to light sources when dissolved in solvents, particularly polar and oxygen-containing solvents, e.g., diethyl ether and THF, which are strong Lewis base donors, rapid decomposition (within minutes depending on the wavelength of light and intensity) is observed. This decomposition process is slower when the compound is dissolved in nonpolar solvents like benzene, toluene, hexane, or cyclohexane.

By using an excess of tetravinylsilane as reagent we believe a mixture of complexes is obtained. Mono (**5**), bis (**1**), tris (**4**), and tetrakis (**2**) Cu(hfac) containing compounds are expected to form in a statistical ratio, as shown in Scheme 1, followed by an equilibration toward the most stable isomers through intermolecular Cu(hfac) exchange. We noted that when adding small amounts of tetravinylsilane to a C_6D_6 solution of **2**, a change occurs in the ^1H NMR intensity ratio between the Cu(hfac) methine protons (at ~6.17 ppm) and the vinylic protons. The tetravinylsilane tetrakis(Cu)hfac complex (**2**) is thus equilibrating through ligand exchanges to a species of lower average coordination number. Furthermore, the ^1H δ-shift of the vinylic protons in these complexes shifts upfield the higher the average coordination number. For example, in compound **1** the vinylic protons are in the 4.70−5.20 ppm region, whereas in compound **2** complexed vinylic protons are at ~4.3 ppm. Noncomplexed tetravinylsilane vinylic protons show as multiplets between 5.78 and 6.25 ppm in C_6D_6. An analogous trend is observed for the ^{13}C shifts of the unsaturated carbons atoms. The rates for these equilibria have not yet been established, but this type of intermolecular ligand exchange is likely to be slightly slower than the intramolecular exchange observed in 1,5-cyclooctadiene (Cu)hfac (COD[Cu]h-

Scheme 1. By Changing the Stoichiometry of Reagents Different Adducts Were Obtained[a]



[a] The tetravinylsilane bisCu(I) 1,1,1,5,5,5-hexafluoroacetylacetonate complex (**1**) was obtained using tetravinylsilane (TVS) in 100% excess (path a), whereas tetravinylsilane tetrakisCu(I) 1,1,1,5,5,5-hexafluoroacetylacetonate complex (**2**) was obtained by using equimolar amounts (path b). Also represented are the dynamic equilibria of tetravinylsilane copper(I)hfac complexes **1**, **2**, **4**, and **5** in C_6D_6.

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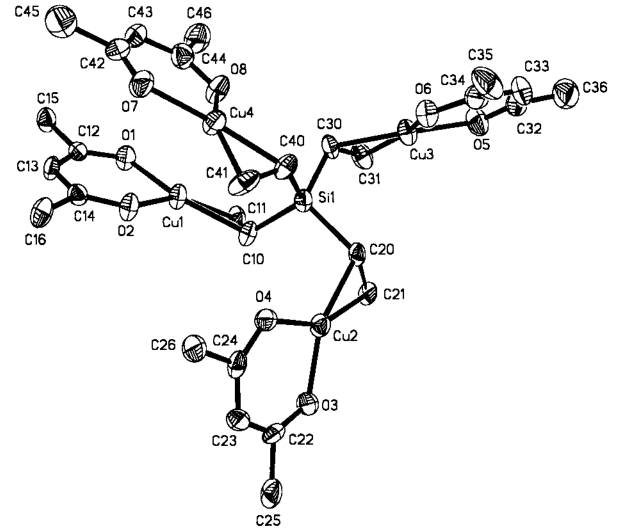

Figure 1. Molecular structure of tetravinylsilane tetrakiscopper 1,1,1,5,5,5-hexafluoroacetylacetonate (**2**) showing 50% probability displacement ellipsoids. Hydrogen and fluoride atoms are omitted for clarity.

fac).[13] Chi et al. and Kumar et al. independently observed an intermolecular exchange for 1,5-CODCu(hfac) but were, like us, unable to confirm the transition energy required for this process.[14] We are currently investigating these phenomena further.

In Figure 1 the solid-state molecular structure of tetravinylsilane tetrakiscopper(I) 1,1,1,5,5,5-hexafluoroacetylacetonate (**2**) as determined by X-ray crystallographic analysis is shown.

Each copper atom is coordinated by two hfac oxygen atoms with the Cu−O distances ranging from 1.927 to 1.958 Å, while the ligand bonds between each copper atom and the centroid X at the adjacent C=C double bond are between 1.854 and 1.874 Å. Thus, the Cu−X bonds in **2** are significantly shorter than those observed for the ligand exchanging double bonds in COD[Cu]hfac (1.95 and 2.34 Å) or the complexing bonds in 1,3,5,7-cyclooctatetraene (COT) Cu(hfac) (mean value for Cu−X = 1.91 Å).[15] The relatively small lengthening of the double bond (mean value = 1.386(10) Å) in complex **2** is an indication that the Cu−X bond should, nevertheless, be weak enough to break and re-form at room temperature. It is noteworthy that the complex-forming bonds in compound **2** are similar in length and deviation angle to the values reported for VTMSCu(I)hfac.[16] This dynamic ligand exchange process may well proceed through a η^4-type transition complex, similar to one suggested by Kumar et al. for 1,5-CODCu(I)(hfac).[17] Two separate olefins, in our case on separate molecules, would share one copper atom during the dynamic fluctuation. It is currently difficult to assess whether this type of intermediate complex is likely with the data available. However, as the nonstabilized copper(I) hfac are known to be highly reactive,[18] this would suggest that a more rapid disproportionation process should be expected if an intermediate complex did not form.

This suggests that the bond order is more reduced in complex **2** than for the other two crystallographically characterized olefin copper(I)hfac complexes, thus giving a comparatively more stable compound. The intra-ring O−Cu−O bond angles range from 93.6° to 95.8° and the O−Cu−X angles from 128.5° to 136.1°. Similar parameters have been reported for 1,3,5,7-cyclooctatetraene (COT) Cu(hfac).[15]

The configuration of the molecule **2** shows two of the four CuC_3O_2 rings being almost parallel, which is an essential prerequisite for the realized crystal packing arrangement. The recrystallization of compound **2** from hexane resulted in a 1:0.3 solvate structure of the space group $P\bar{1}$, where the hexane molecules partially occupy the corners of the unit cell. Five of the eight independent CF_3 groups show rotational disorder about the C−C bonds.

By using 100% excess of tetravinylsilane as reagent, a mixture with a high content of tetravinylsilane biscopper(I) 1,1,1,5,5,5-hexafluoracetylacetonate (**1**) was isolated as a pale yellow powder after recrystallization (Scheme 1, path a). The relatively sharp melting point (42−44 °C) suggests a comparatively monodisperse product.

The solid-state infrared data (as thin films on NaCl disks) for the tetravinyl silane complexes **1** and **2** are very similar. For example, noncomplexed tetravinylsilane exhibits four strong C−H stretching frequencies between 3050 and 2950 cm^{-1}, but both the TVSB(Cu)hfac (**1**) and TVST(Cu)hfac (**2**) complexes exhibit deformation frequencies at 2950−2850 cm^{-1}. This reduction of detected energy ($\Delta\nu = 100$ cm^{-1}) corresponds to the less vinylic nature of the C=C−H deformations in the back-bonding complex. It is more difficult to assign complexed and, in the case of **1**, noncomplexed vinylic C−H out-of-plane bending vibrations due to a large number of additional fingerprint absorptions from C−F and Si−C functionalities (see Experimental Section). The enolized 1,3-dicarbonyl stretching frequencies are 1637 cm^{-1} for complex **1** and 1639 cm^{-1} for complex **2**. This is comparable to 1637 cm^{-1} found for 1,5-COD(Cu)hfac. A weak absorption at 1610−1605 cm^{-1} corresponds to the stretching bands of the conjugated C=C bonds. The complexes have sharp C−F deformation frequencies at 1462 and 1466 cm^{-1} for complexes **1** and **2**, respectively. The UV−vis spectra (recorded in cyclohexane) of complexes **1** and **2** show again similarities with a strong absorbance between 285 and 325 nm and the rest of the visible part (400−800 nm) of the optical spectrum giving very low absorbance.

The thermal stability of the tetraallylsilane(Cu)hfac analogues were much lower than that of the tetravinylsilane complexes. This tendency is comparable to the thermal stability of vinyltrimethylsilane copper 1,1,1,5,5,5-hexafluoroacetylacetonate (VTMS(Cu)hfac) and allyltrimethylsilane copper 1,1,1,5,5,5-hexafluoroacetylacetonate (ATMS(Cu)hfac). For example, the ATMS(Cu)hfac is reported to disproportionate at ∼80

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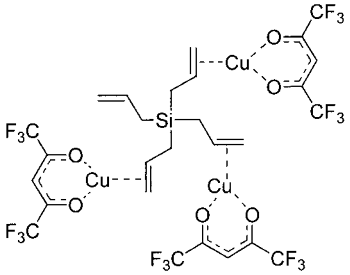

Figure 2. Structure of tetraallylsilane triscopper(I) 1,1,1,5,5,5-hexafluoroacetylacetonate (**3**).

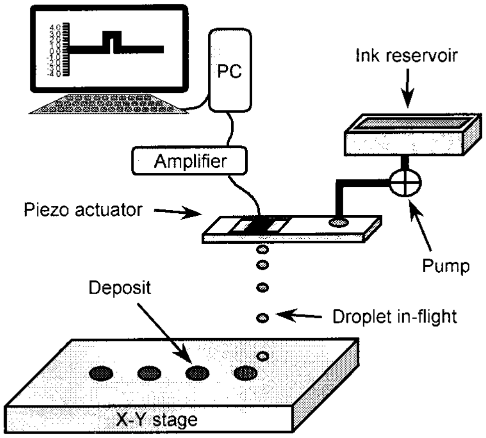

Figure 3. Schematic illustration of the ink-jet printing equipment used.

°C, whereas VTMS(Cu)hfac decomposes at ~170 °C.[19] Isolation and analysis of pure tetraallyl silane(Cu)hfac analogues was hindered, as disproportionation occurred quite readily. For example, reasonable ^{1}H NMR spectra of the tetraallyl complexes were obtained in most cases; however, ^{13}C NMR spectra, which require extended scan times, give deteriorating spectra due to the continuous formation of disproportionation products and line broadening due to the increasing amount of Cu(II) byproducts during the experiment.

Ink-Jetting Experiments. Droplets were generated using a piezo ceramic actuation as part of an experimental ink-jet setup (Figure 3). They ranged from spherical, approximately 600 μm in diameter, to more undefined sprays. The droplets traveled with a velocity of approximately 1.0 m s^{-1} at a distance of 7 mm from the ejection hole. They were then allowed to hit a thermally preactivated (200 °C) area on a microscope grade glass slide at a distance of approximately 10 mm. An instant reaction followed in both cases, giving off a plume of volatile byproducts and leaving a visible copper mirror on the substrate. The resulting features were round with a diameter of approximately 600 μm. It is interesting to note that the final deposit has the same approximate diameter as the droplet in-flight; that is, the droplet volume converted and/or evaporated before it had time to spread out on the substrate surface. X-ray emission spectroscopy (EDAX) of droplet impact regions indicates a copper-coated film with peaks at 0.9, 8.1, and 8.9 keV which are emissions originating from copper. Further investigations on these films are currently in progress.

Conclusions

We have synthesized copper precursor materials that are intended to be used as liquids but stored as solids. All the materials described in this paper have melting points lower than 70 °C. This makes them applicable to liquid processing such as ink-jet, silkscreen, reel-to-reel, and soft lithography printing. They disproportionate upon heating, giving copper films at temperatures similar to VTMSCu(I)hfac (>130 °C). As solids, they exhibit relatively low volatility, which can be attributed to the fact that they are relatively large molecules. Furthermore, the processes of intermolecular as well as intramolecular ligand exchanges increase molecular interactions, thus further lowering volatility. In the dimeric and trimeric precursors (including mixtures), a dipole momentum and molecular asymmetry are also introduced. This lowers the volatility even further. High volatility would be a distinct disadvantage for our processes, as more material would be lost through, for example, evaporation. It is also more difficult to achieve controlled patterned deposition, as more material would deposit as a plume of vapor rather than a liquid.

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Supporting Information Available: This material is available free of charge via the Internet at http://pubs.acs.org.

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