

Cuprous Tris(*tert*-butoxy)siloxy Complexes and Their Thermolytic Conversion to Copper–Silica and Copper Oxide–Silica Nanocomposites[†]

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The (*tert*-butoxy)siloxy complex $[\text{CuOSi}(\text{O}^t\text{Bu})_3]_4$ (**1**) was prepared by silanolysis of $[\text{CuO}^t\text{Bu}]_4$ with $(^t\text{BuO})_3\text{SiOH}$ and examined as a single-source precursor to Cu/SiO_2 and $\text{Cu}_n\text{O}/\text{SiO}_2$ ($n = 1, 2$) materials. The related complex $\{\text{Cu}[\mu\text{-OSiPh}(\text{O}^t\text{Bu})_2]\}_4$ (**4**), obtained similarly, was characterized by X-ray crystallography as having a planar Cu_4O_4 core with oxygen-bridged Cu atoms. The highly associated, sublimable $\{\text{NaCu}[\text{OSi}(\text{O}^t\text{Bu})_3]_2\}_6$ (**3**) was obtained by the addition of $\text{NaOSi}(\text{O}^t\text{Bu})_3$ to **1** or by reaction of 2 equiv of $\text{NaOSi}(\text{O}^t\text{Bu})_3$ with CuCl . Thermogravimetric analysis (TGA) of **1** under both oxygen and argon reveals rather sharp, low-temperature conversions to the final ceramic compositions (onset temperatures: ca. 100 °C under oxygen; ca. 150 °C under argon). Under argon, the resulting material consists of Cu^0 and Cu_2O nanoparticles dispersed in silica, whereas an oxygen atmosphere leads to CuO nanoparticles in silica. These materials are carbon- and hydrogen-free and are produced by elimination of isobutene, *tert*-butyl alcohol, water, and silanol. The pyrolytic conversion of compound **4** occurs at higher temperature and more gradually but gives relatively clean conversion to a CuO/SiO_2 composite under an oxygen atmosphere. The volatility of **1** allows its use in CVD preparations of thin films. Amorphous thin films with a Cu/Si ratio of 1:0.85 (microprobe analysis) and thicknesses ranging from 200 nm to 6 μm have been obtained.

Introduction

Silica-supported metal particles constitute a large class of important heterogeneous catalysts.¹ Since the activities and selectivities of these catalysts are highly dependent on the size and shape of the metal particles and on the nature of the particle–support interactions,² considerable attention has been given to development of synthetic strategies for producing tailored metal–silica composite materials.³ Low-temperature sol–gel type syntheses have proven to be particularly useful in controlling the size of the metal particles.^{3b–d} We have been exploring a single-source precursor approach to metal silicate materials based on tris(alkoxy)siloxy complexes of the type $\text{M}[\text{OSi}(\text{O}^t\text{Bu})_3]_n$.⁴ This approach provides molecular-level control over stoichiometry and low-temperature pathways to homogeneous materials.

For example, $\text{M}[\text{OSi}(\text{O}^t\text{Bu})_3]_4$ ($\text{M} = \text{Zr}, \text{Hf}$) complexes undergo clean conversions at 100–150 °C to homogeneous $\text{MSi}_4\text{O}_{10}$ compositions, with loss of isobutene and water.^{4a} Similarly, related aluminum complexes are readily and cleanly converted to aluminosilicates.^{4b} In these cases, the facile elimination of isobutene may be attributed to catalysis by the Lewis acidic metal centers (e.g., Zr or Al).⁵ We are interested in testing the generality of this method by examining the behavior of related precursors containing electron-rich metal centers. Here we report that tris(alkoxy)siloxy complexes of copper also undergo rather clean pyrolytic eliminations to metal silicate materials. This system was explored mainly in order to determine (1) if convenient and/or novel routes to copper–silica materials could be developed using precursors analogous to those explored earlier for more electrophilic metals and (2) if the pyrolytic chemistry of a late metal (alkoxy)siloxy precursor would be the same as that previously observed for analogous complexes based on electropositive metals (e.g., Zr, Hf, Al).

The relatively few copper siloxide derivatives that are known have been prepared by a variety of synthetic methods.^{6–10} Schmidbauer et al. obtained tetrameric

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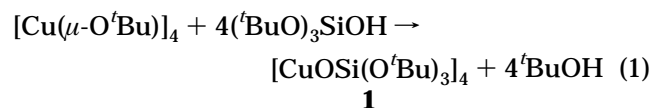
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[CuOSiMe₃]₄, which was thought to possess a cubelike structure, by the reaction of CuCl with NaOSiMe₃.⁶ Later crystallographic studies on [Cu(*μ*-O'Bu)]₄¹¹ and [Cu(*μ*-OSiPh₃)]₄⁷ suggest that tetramers of this type generally possess a structure with a planar Cu₄O₄ eight-membered ring. We have previously reported the monomeric Cu(II) siloxide Cu[OSi(O'Bu)₃]₂(py)₂, which has a distorted tetrahedral geometry, but the relatively low yield of this compound discouraged us from examining it as a precursor to copper–silica materials.⁸ Here we report high-yield routes to Cu(I) alkoxy(siloxy) complexes which undergo facile eliminations at 100–200 °C to give Cu–SiO₂, Cu₂O–SiO₂, and CuO–SiO₂ materials, depending on the conditions of the thermolysis. Interest in such materials stems primarily from their use as catalysts.¹² In addition, silica glasses containing dispersed copper particles have attracted attention as nonlinear optical materials, components in optoelectronic devices, and high-voltage switching devices.¹³

Results

Synthesis of (*tert*-Butoxy)siloxy Complexes of Copper(I). Reaction of $[\text{Cu}(\mu\text{-O}^t\text{Bu})_4]^{14}$ with 4 equiv of $(^t\text{BuO})_3\text{SiOH}^{15}$ in benzene for 0.5 h produced the cuprous siloxide $\{\text{Cu}[\mu\text{-OSi}(\text{O}^t\text{Bu})_3]_4\}$ (**1**) as colorless crystals from pentane in 58% yield (eq 1). Crystals of **1** turn



opaque and amorphous after isolation, and this has so far delayed structural analysis of the compound by X-ray crystallography. Attempts to determine the solution molecular weight of **1** in benzene using the Signer method¹⁶ gave inconsistent results due to slow decomposition (over days) in solution. However, we presume that **1** has a structure analogous to that of {Cu[μ-O-SiPh-(O*t*Bu)₂]₄ (**4**), described below. The mass spectrum of **1** (EI) contained an intense envelope of peaks centered at *m/e* 1307, corresponding to [CuOSi(O*t*Bu)₃]₄. Like other tetrameric copper(I) alkoxides and siloxides,^{7,17} **1** is readily cleaved upon addition of triphenylphosphine to give a dimeric structure with terminal phosphines, {Ph₃PCu[μ-O-Si(O*t*Bu)₃]₂ (**2**). Compound **2** is insoluble in pentane, and in the ¹H NMR spectrum (benzene-*d*₆) the *tert*-butoxy groups appear as a singlet at δ 1.65. A preliminary X-ray crystal structure determination has

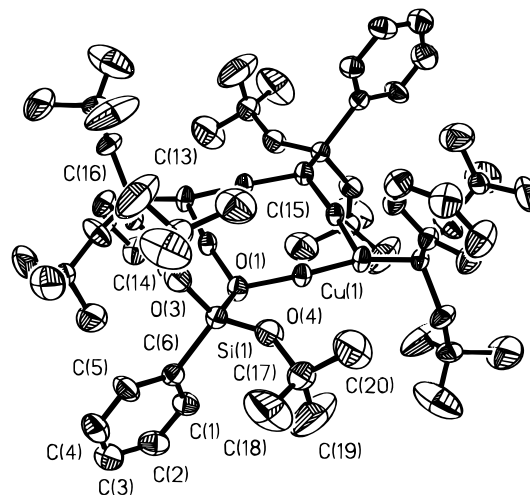
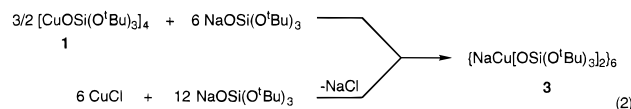


Figure 1. ORTEP view of the molecular structure of $\{\text{Cu}[\mu\text{-OSiPh}(\text{O}^t\text{Bu})_2]\}_4$ (**4**).

revealed that **2** is a centrosymmetric dimer with a planar Cu₂O₂ four-membered ring.¹⁸

Reaction of **1** with $\text{NaOSi}(\text{O}^t\text{Bu})_3$ ⁸ in diethyl ether produces the sublimable “ate” complex $\{\text{NaCu}[\text{OSi}(\text{O}^t\text{Bu})_3]_2\}_6$ (**3**), obtained as colorless crystals from pentane. This complex is also available more directly from reaction of cuprous chloride with 2 equiv of $\text{NaOSi}(\text{O}^t\text{Bu})_3$ (eq 2). Solution molecular weight measure-



ments indicate that the degree of association for **3** is concentration dependent. At a formula unit concentration of 0.014 M, **3** exists as a hexamer in pentane solution. At higher concentrations, greater degrees of association are observed, but the results were not consistent with the presence of a single species in solution.

The related copper(I) siloxide, $\{\text{Cu}[\mu\text{-OSiPh}(\text{O}^t\text{Bu})_2]\}_4$ (**4**), was prepared by the method of eq 1 with $(^t\text{BuO})_2\text{PhSiOH}$ as the silanol reagent. Compound **4** crystallizes from pentane as slightly yellow prisms. In contrast to **1**, complex **4** does not combine with $\text{NaO-SiPh}(\text{O}^t\text{Bu})_2$ in diethyl ether to produce an “ate” complex.

Crystal Structure of $\{\text{Cu}[\mu\text{-OSiPh}(\text{O}^t\text{Bu})_2]\}_4$ (4**).** Crystals of **4** suitable for X-ray crystallography were obtained by numerous recrystallizations from pentane at -31°C . An ORTEP diagram of the compound is shown in Figure 1, and important bond distances and angles are listed in Table 2. The centrosymmetric tetramers crystallize in space group $P\bar{1}$ with two crystallographically equivalent $\{\text{Cu}[\mu\text{-OSiPh}(\text{O}^t\text{Bu})_2]\}_2$ asymmetric units per unit cell. Overall, **4** resembles $[\text{Cu}(\mu\text{-O}^t\text{Bu})_4]^{11}$ and $[\text{Cu}(\mu\text{-OSiPh}_3)]_4^{18}$ in possessing a planar Cu_4O_4 core with noninteracting, oxygen-bridged Cu centers. The Cu–O distances in **4**, which range from 1.827 (5) to 1.844 (4) Å, and the Cu–O–Cu angles of 93.7 (2) and 97.7 (2) are indistinguishable from comparable parameters in the latter two compounds. As expected, the Si–O(bridging) distances in **4** (1.603 (5))

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Table 1. Crystallographic Data for $\{\text{Cu}[\mu\text{-OSiPh}(\text{O}^t\text{Bu})_2]\}_4$ (4)

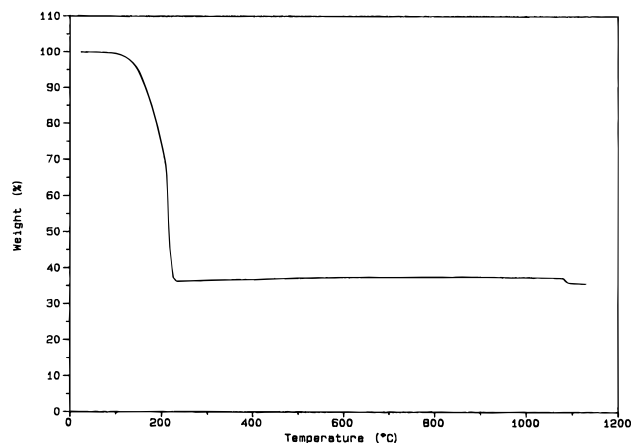
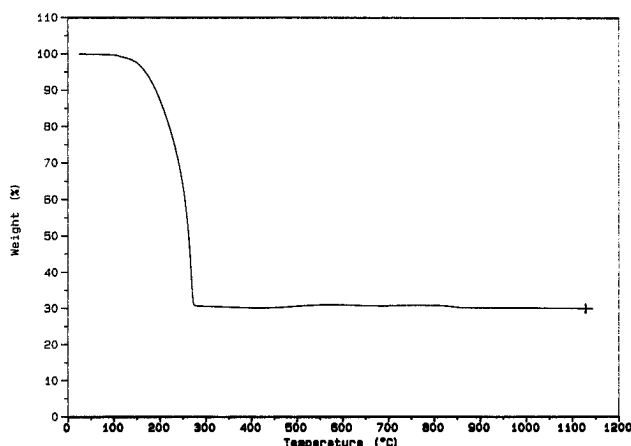
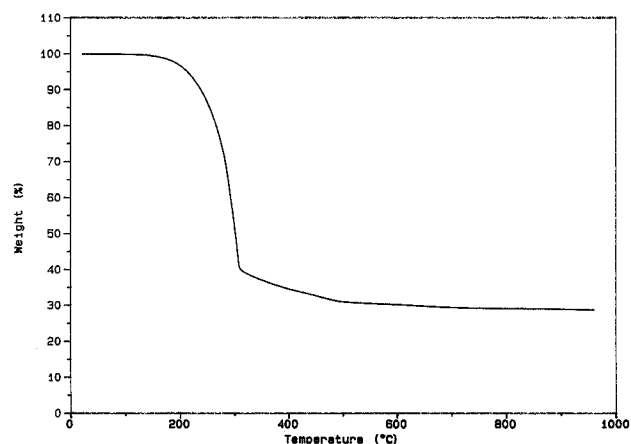
chem formula.	space group $P\bar{1}$
$\text{C}_{56}\text{H}_{92}\text{Cu}_4\text{O}_{12}\text{Si}_4$	
fw 1324	$T = 298 \text{ K}$
$a = 10.076 (2) \text{ \AA}$	$\lambda = 0.71073 \text{ \AA (Mo K}\alpha\text{)}$
$\beta = 14.328 (4) \text{ \AA}$	$\rho_{\text{calcd}} = 1.245 \text{ g cm}^{-3}$
$c = 14.571 (4) \text{ \AA}$	$\mu = 1.306 \text{ mm}^{-1}$
$\alpha = 62.41 (2)^\circ$	data/param = 12.0
$\beta = 71.45 (2)^\circ$	weighting scheme: $w^{-1} = \sigma^2(F) + 0.0007F^2$
$\gamma = 83.57 (2)^\circ$	scan type: Wyckoff
$V = 1765.9 (8) \text{ \AA}^3$	scan speed = $10.19^\circ \text{ min}^{-1}$ (constant)
$Z = 2$	
$R_F = 5.28\%$	
$R_{wF} = 6.68\%$	
GOF = 1.81	

Table 2. Selected Bond Distances (\AA) and Angles ($^\circ$) for $\{\text{Cu}[\mu\text{-OSiPh}(\text{O}^t\text{Bu})_2]\}_4$ (4)

(a) Bond Distances			
Cu(1)–Cu(2)	2.675 (1)	Si(1)–O(4)	1.569 (5)
Cu(1)–Cu(2A)	2.764 (1)	Si(2)–O(2)	1.612 (4)
Cu(2)–Cu(1A)	2.764 (1)	Si(2)–O(5)	1.581 (6)
Cu(1)–O(1)	1.827 (5)	Si(2)–O(6)	1.611 (7)
Cu(1)–O(2)	1.828 (5)	Si(1)–C(6)	1.846 (7)
Cu(2)–O(1)	1.842 (4)	Si(1)–C(12)	1.841 (8)
Cu(2)–O(2A)	1.844 (4)	O(3)–C(13)	1.398 (17)
Cu(2A)–O(2)	1.844 (4)	O(4)–C(17)	1.388 (11)
Si(1)–O(1)	1.603 (5)	O(5)–C(25)	1.386 (9)
Si(1)–O(3)	1.592 (9)	O(6)–C(21)	1.401 (15)
Bond Angles			
Cu(2)–Cu(1)–O(1)	43.4 (1)	Cu(2)–Cu(1)–O(2)	130.9 (1)
O(1)–Cu(1)–O(2)	174.1 (2)	Cu(2)–Cu(1)–Cu(2A)	89.6 (10)
O(1)–Cu(1)–Cu(2A)	132.9 (1)	O(2)–Cu(1)–Cu(2A)	41.4 (1)
Cu(1)–Cu(2)–O(1)	43.0 (1)	Cu(1)–Cu(2)–Cu(1A)	90.4 (1)
O(1)–Cu(2)–Cu(1A)	133.4 (1)	Cu(1)–Cu(2)–O(2A)	131.4 (1)
O(1)–Cu(2)–O(2A)	174.3 (2)	Cu(1A)–Cu(2)–Cu(2A)	40.9 (1)
Cu(1)–O(1)–Cu(2)	93.7 (2)	Cu(1)–O(1)–Si(1)	131.9 (2)
Cu(2)–O(1)–Si(1)	132.1 (3)	Cu(1)–O(2)–Si(2)	131.5 (3)
Cu(1)–O(2)–Cu(2A)	97.7 (2)	Si(2)–O(2)–Cu(2A)	124.6 (3)
Si(1)–O(3)–C(13)	140.8 (6)	Si(1)–O(4)–C(17)	149.3 (7)
Si(2)–O(5)–C(25)	145.2 (7)	Si(2)–O(6)–C(21)	137.9 (5)
C(6)–Si(1)–O(1)	109.5 (3)	C(6)–Si(1)–O(3)	104.5 (3)
O(1)–Si(1)–O(3)	112.1 (3)	C(6)–Si(1)–O(4)	114.7 (3)
O(1)–Si(1)–O(4)	105.8 (3)	O(3)–Si(1)–O(4)	110.4 (4)
C(12)–Si(2)–O(2)	110.5 (3)	C(12)–Si(2)–O(5)	114.9 (4)
O(2)–Si(2)–O(5)	105.9 (3)	C(12)–Si(2)–O(6)	104.7 (3)
O(2)–Si(2)–O(6)	111.2 (3)	O(5)–Si(2)–O(6)	109.7 (4)

and 1.612 (4) \AA) are slightly shorter than the comparable Si–O distances in $[\text{Cu}(\mu\text{-OSiPh}_3)]_4$ (average 1.633 \AA). Adjacent pairs of crystallographically unique siloxy groups are bent slightly out of the Cu_4O_4 plane in the same direction (–0.31 and –0.53 \AA , respectively, for Si(1) and Si(2)). In $[\text{Cu}(\mu\text{-OSiPh}_3)]_4$, the siloxy groups are ruffled about the Cu_4O_4 core such that opposite silicon atoms lie roughly in the square plane, while the other two lie above and below this plane by $\pm 1.04 \text{ \AA}$.⁸

Thermal Analysis of 1, 3, and 4. Thermolyses of the copper(I) (*tert*-butoxy)siloxy complexes were initially examined by thermogravimetric analysis (TGA). The TGA curve for **1** in a flowing oxygen atmosphere is shown in Figure 2. The decomposition, with an onset temperature of just over 100 $^\circ\text{C}$, is relatively abrupt and results in a ceramic yield of 36%. The TGA curve for **1** in flowing argon (Figure 3) shows a dramatic weight loss beginning around 150 $^\circ\text{C}$. This decomposition is complete by 270 $^\circ\text{C}$, resulting in a ceramic yield of 30%. For comparison, the theoretical ceramic yields for $\text{CuO}\cdot\text{SiO}_2$ and $\text{Cu}\cdot\text{SiO}_2$ are 42.7 and 37.8%, respectively. Analysis of compound **1** by differential scanning calorimetry (DSC) revealed the presence of a broad exotherm associated with decomposition, along with three sharp

**Figure 2.** TGA of **1** in O_2 .**Figure 3.** TGA of **1** in Ar.**Figure 4.** TGA of **4** in Ar.

endotherms (at 100.0, 125.8, and 154.0 $^\circ\text{C}$; under both Ar and O_2). The phase transitions and/or chemical changes associated with these endotherms have not been characterized, but we know that none are associated with melting, and one of them (at 100 $^\circ\text{C}$) is irreversible.

As might be expected, the presence of the Si–Ph group in **4** results in greater stability for the precursor and a more gradual conversion to the final ceramic. This is evident in the TGA curve for **4** under argon (Figure 4), which shows that the onset temperature for decomposition is just below 200 $^\circ\text{C}$. Under oxygen, the onset temperature is considerably lower, at ca. 100 $^\circ\text{C}$. Interestingly, the ceramic yield in oxygen (41%) is close to the theoretical yield for $\text{CuO}\cdot\text{SiO}_2$ (42.2%). The DSC

Table 3. Decomposition Products of Compound 1 under Argon, As Determined by Powder X-ray Diffraction^a

temp (°C)	heating time (h)	crystallites	ave size (nm)
300	0.5	<i>b</i>	
600	1.0	Cu ⁰	120
800	1.0	Cu ⁰	191
		Cu ₂ O	<i>c</i>
1000	1.0	Cu ⁰	199
		Cu ₂ O	122

^a Average crystallite sizes were determined from the Scherrer equation.¹⁹ The heating rate between temperatures was 30 °C min⁻¹. ^b No crystalline phase observed. ^c Peaks for these phases were too weak to allow for a reasonable estimate of the average particle diameter.

curve for **4** revealed only the occurrence of melting (at ca. 133 °C) before decomposition.

In oxygen, compound **3** displays an onset temperature of 90 °C and a relatively abrupt weight loss of 60%, which is complete by ca. 200 °C. Minor weight loss occurs thereafter, and the resulting ceramic yield at 1000 °C is 24%. Under argon compound **3** is stable to a much higher temperature, such that decomposition does not begin until around 270 °C. The ceramic yield is 27% at 1000 °C.

Chemistry of the Thermolyses. To characterize the chemistry of thermolysis for **1**, the compound was heated at 250 °C under vacuum in a closed vessel, and the volatile decomposition products were then vacuum-transferred to an NMR tube. Analysis of these products by ¹H NMR spectroscopy revealed the presence of (tBuO)₃SiOH, tBuOH, isobutene, and traces of water (isobutene/*tert*-butyl alcohol ratio = 5:1). The decomposition of compound **3** was carried out by gently heating the compound with a flame in an evacuated, Teflon-valved NMR tube. The NMR tube was then cooled to -196 °C, and benzene-*d*₆ solvent was added by vacuum transfer. The soluble products of the decomposition (after 94% conversion) were determined to be (tBuO)₃SiOH, tBuOH, and isobutene (in a 1:2:2 ratio), and traces of water. The mass spectrum of **1** reveals loss of isobutene as the primary fragmentation pattern.

Pyrolysis of **4** by the same procedure (to 25% conversion) gave isobutene and tBuOH (3:1 ratio) as the main products, and small amounts of (tBuO)₂PhSiOH and water were also formed. In addition, trace amounts of unidentified aromatic species were present among the volatile decomposition products. Neither (tBuO)₃SiOH nor (tBuO)₂PhSiOH decompose under the conditions of the above thermolyses, as determined by prolonged heating of each silanol with the materials produced by thermolysis (under vacuum) of **1** and **4**, respectively, at 300 °C.

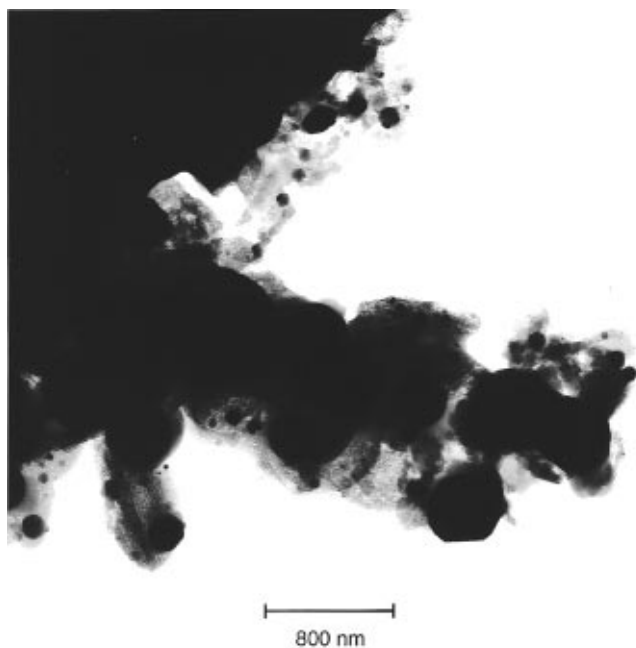
Characterization of the Copper-Silica and Copper Oxide-Silica Materials. The solid-state decomposition products from bulk thermolyses of **1** (Tables 3 and 4) were characterized by X-ray powder diffraction (XRD), transmission electron microscopy (TEM), electron microprobe analysis, and combustion analysis.

A sample of **1** was heated under flowing argon at a rate of 30 °C min⁻¹ to 300 °C, and this temperature was maintained for an additional 30 min. This procedure resulted in sublimation of the (tBuO)₃SiOH decomposition product onto the cold part of the furnace tube. The remaining olive green powder was amorphous by XRD. Further heating of this powder to 600 °C for 1 h under argon resulted in a brown material that contained

Table 4. Decomposition Products of Compound 1 under Oxygen, As Determined by Powder X-ray Diffraction^a

temp (°C)	heating time (h)	crystallites	ave size (nm)
300	0.5	Cu ⁰	12
		Cu ₂ O	<i>b</i>
		CuO	<i>b</i>
600	1.0	Cu ⁰	22
		Cu ₂ O	<i>b</i>
		CuO	15
800	1.0	CuO	15
1000	1.0	CuO	27

^a Average crystallite sizes were determined from the Scherrer equation.¹⁹ The heating rate between temperatures was 40 °C min⁻¹. ^b Peaks for these phases were too weak to allow for a reasonable estimate of the average particle diameter.

**Figure 5.** TEM photograph of Cu particles obtained by heating **1** in argon to 1000 °C.

elemental copper (by XRD). The average particle diameter, estimated by the Scherrer equation,¹⁹ was approximately 120 nm. After 1 h at 1000 °C, the Cu crystallites increased in size (average 199 nm), and a small amount of Cu₂O was also present. A TEM photograph of the material heated to 1000 °C (Figure 5) is consistent with the presence of spherulike, partially faceted particles embedded in an amorphous matrix, and a wide range in particle size. Trace elemental analysis of this material revealed the presence of negligible amounts of carbon (0.04%) and hydrogen (<0.01%).

Thermolysis of **1** in flowing oxygen by heating at 40 °C min⁻¹ to 300 °C and further heating at that temperature for 0.5 h resulted in a black material containing Cu⁰ crystallites of ca. 12 nm average diameter and minor amounts of Cu₂O and CuO (by XRD; Table 4). Further heating at 600 °C for 1 h produced larger crystallites of copper (ca. 22 nm) and CuO particles of ca. 15 nm diameter. Minor amounts of Cu₂O were also

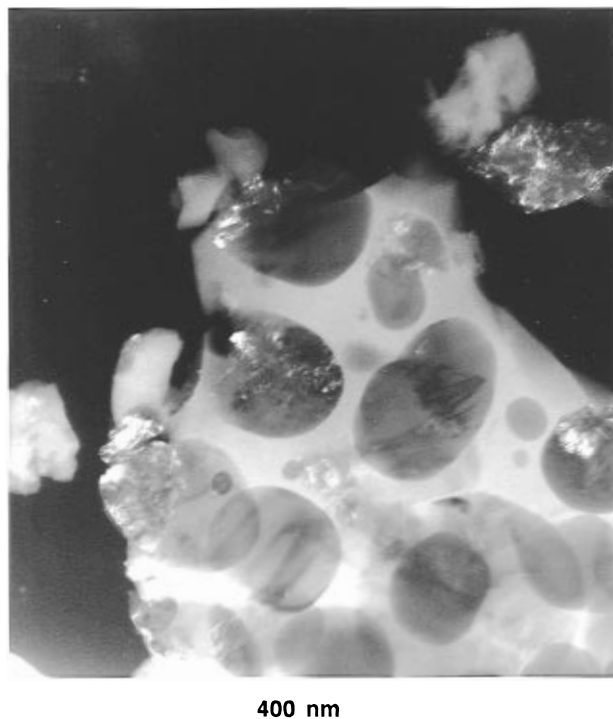


Figure 6. TEM photograph of CuO particles in a silica matrix, obtained by heating **1** under oxygen.

present. Heating to 800 °C oxidized all the copper to CuO particles, which increased in average size on further heating at 1000 °C for 1 h (to ca. 27 nm, by XRD). A TEM photograph of this material (Figure 6) clearly showed the presence of CuO particles dispersed in an amorphous matrix, and some particles with diameters as large as several hundred nm. Elemental analysis of the final sample revealed a stoichiometry of $\text{CuO} \cdot 0.5\text{SiO}_2$ (C, 0.07%; H, <0.01%).

Thermolysis of **3** under flowing argon produced copper metal as the only crystalline phase (by XRD). The average particle size for the copper crystallites was ca. 100 nm after heating the material to 1000 °C. Observation of the material under an optical microscope revealed that the sample was inhomogeneous, and consisted of colorless particles (perhaps a sodium silicate) covered with smaller, brown particles (presumably copper metal). Electron microprobe analysis of this mixture established the presence of copper, silicon, and sodium; however a quantitative analysis was not possible due to inhomogeneity of the material.

Thermolysis of **4** under flowing argon produced copper metal as the only crystalline phase. Heating this precursor to 500 °C for 1 h gave a black material which contained crystalline copper grains (average diameter ca. 18 nm, by XRD). Further heating of the sample to 1000 °C resulted in a material which had the appearance of copper metal shavings and contained Cu crystallites (ave diameter 20 nm, by XRD) and (presumably) amorphous silica. Electron microprobe analysis characterized the stoichiometry of this material as $\text{Cu} \cdot 0.8\text{SiO}_2$, which is consistent with the observed loss of $(\text{tBuO})_2\text{PhSiOH}$ during the initial phase of the thermolysis.

For a sample of **4** heated to 1000 °C under argon, a measurable amount of residual hydrocarbon was detected by combustion analysis (C, 4.20%; H, 0.45%). However, heating the compound to 1000 °C under

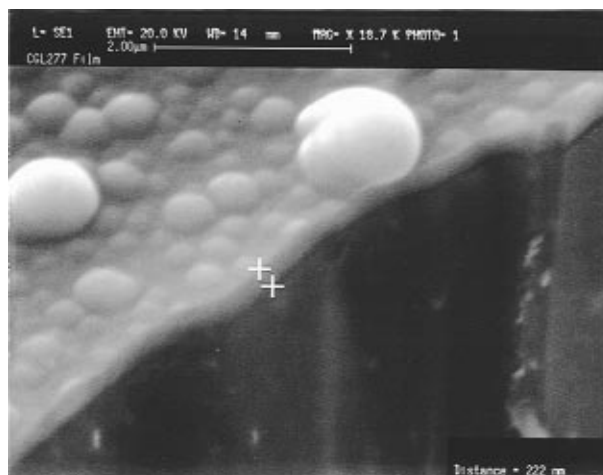


Figure 7. SEM photograph of the thin film grown by chemical vapor deposition of **1** onto a hot (450 °C) borosilicate glass slide.

oxygen produced hydrocarbon-free material (C, 0.03%; H, <0.01%). By XRD, this material contained CuO as the only crystalline phase.

MOCVD Route to Copper-Silica Thin Films.

Unlike many other metal- $\text{OSi}(\text{O}^t\text{Bu})_3$ derivatives,^{4,8} compound **1** is sublimable (120–140 °C and 0.001 mmHg). Vapor transport of this precursor in the synthesis of copper-silica thin films was accomplished by subliming the complex under vacuum onto a borosilicate glass slide heated to 450 °C. After 30 min, the glass slide was covered with a smooth, copper-colored film. This film was amorphous by XRD, but a microprobe analysis revealed a Cu/Si ratio of about 1:0.85. SEM photographs (Figure 7) revealed a somewhat lumpy surface topography for the film. By varying the chemical vapor deposition time, film thicknesses ranging from 200 nm to 6 μm were obtained.

Rapid heating of a sample of **1** to 300 °C under vacuum caused complete decomposition rather than sublimation. Further heating of this material to 600 °C produced a solid containing both Cu metal and Cu_2O (by XRD). On the basis of this observation, we suggest that the thin film described above probably also contains copper in the 0 and +1 oxidation states.

Discussion

We report here silanolysis reactions of $[\text{Cu}(\mu\text{-O}^t\text{Bu})_4]$ which produce the oxygen-rich copper(I) siloxide complexes $\{\text{Cu}[\mu\text{-OSi}(\text{O}^t\text{Bu})_3]\}_4$ (**1**) and $\{\text{Cu}[\mu\text{-OSiPh}(\text{O}^t\text{Bu})_2]\}_4$ (**4**). A second type of siloxide complex with a 1:2 ratio of Cu to Si, $\{\text{NaCu}[\text{OSi}(\text{O}^t\text{Bu})_3]\}_2$ (**3**), is readily obtained by association of $\text{NaOSi}(\text{O}^t\text{Bu})_3$ and $\text{CuOSi}(\text{O}^t\text{Bu})_3$ units in solution. The latter compound appears to be a cluster of high nuclearity, but attempts to obtain X-ray quality crystals for structure analysis have so far proven futile. Copper alkoxides and siloxides are well-known to combine with other metal alkoxides to form bimetallic complexes,²⁰ and previously reported derivatives closely related to **3** are the potassium-sequestered

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complexes [K(18-crown-6)][Cu(OSiPh₃)₂] and [K(18-crown-6)][Cu(OSiMe₂^tBu)₂].⁷

The siloxides reported here undergo rather clean pyrolytic conversions to copper- or copper oxide-silica materials at low temperatures. The ceramic yields associated with these transformations are in general quite high. Compound **1** exhibits a ceramic yield at 300 °C which is within 0.5% of the ceramic yield at 1100 °C (30%). This indicates that the *tert*-butoxy groups decompose efficiently to give a carbon-free material. Small reductions in the ceramic yields clearly result from loss of silanol from the precursor compounds during thermolysis. The facility with which these pyrolytic eliminations occur seems to be at least partially related to the preexisting oxygen coordination environments for the Cu and Si atoms. This is suggested by comparison of the TGA traces for **1** and **4**, which show that the presence of a phenyl group on the silicon atom increases the thermal stability of the compound. Caulton has previously reported TGA data for trialkyl- and (triarylsiloxy)copper complexes such as [Cu(μ -OSiPh₃)₄] and [Cu(μ -OSiMe₂^tBu)₄], which show that such complexes generally undergo more episodic weight losses over a wider temperature range.⁷

The incorporation of carbon is a common problem encountered in the organometallic precursor approach to materials. As shown by elemental analyses, the oxygen environments for silicon and copper in the precursor compound **1** result in clean conversion to carbon-free material. The presence of even one Si-C bond per silicon center (as in **4**) leads to material with a significant amount of carbon, however a thermolysis routine employing an oxygen atmosphere efficiently removes the residual carbon.

The transformations reported here give rise to Cu⁰, Cu₂O, and/or CuO particles, depending on the atmosphere present during thermolysis and the particular heat treatment employed (see Tables 3 and 4). Under oxygen, compound **1** decomposes initially to copper metal, but with further heating under oxygen a complete transformation to CuO particles takes place. Pyrolysis under argon produces both Cu and Cu₂O particles, even when the heat treatment is carried to 1000 °C (Table 3).

At this point, it is difficult to speculate insightfully about the mechanism by which **1** undergoes pyrolytic eliminations to copper-containing materials. This process is clearly distinct from those responsible for the clean conversions of Zr-OSi(O^tBu)₃^{4a} and Al-OSi(O^tBu)₃^{4b} complexes to metal silicates via isobutene elimination. This is indicated by the fact that silanol is formed as a byproduct in the pyrolysis of the cuprous tris(*tert*-butoxy)siloxy complexes described here but not in conversions based on electropositive metals such as zirconium and aluminum. The appearance of both copper metal and silanol early in the reaction indicates that Cu-O homolysis may be involved. This mechanistic step was also suggested by Caulton and co-workers in their studies on the thermal decompositions of [Cu(OSiR₃)₄] complexes to copper metal.⁷ Presumably, the siloxy radicals produced by homolysis react with adventitious sources of hydrogen to give the observed silanols. Other processes appear to be responsible for the formation of silica, since control experiments showed that silanol is not decomposed under the

thermolytic conditions which produce condensed phases at 300 °C.

It is of interest to also compare studies on chemical vapor depositions with [Cu(μ -O^tBu)]₄, which give pure Cu₂O at 510 K and relatively pure copper metal at 670 K.²¹ Thus in this case the initially formed, copper-containing crystalline phase is Cu₂O rather than copper metal. It was shown that copper metal formed at the higher temperature arises via thermal loss of oxygen from copper(I) oxide. For conversion of the alkoxide to Cu₂O, comparable amounts of isobutene and *tert*-butyl alcohol were produced. To explain these observations, a mechanism involving β -hydrogen elimination of isobutene from *tert*-butoxy groups, followed by proton-transfers that produce *tert*-butyl alcohol and water, was proposed. Currently, then, the available data suggest that cuprous siloxide complexes thermally decompose by a chemical process that is distinct from that which operates in the decomposition of [Cu(μ -O^tBu)]₄. Clearly there is much to be learned concerning the mechanism of pyrolytic eliminations from alkoxide and siloxide complexes that produce solid-state materials.²²

Experimental Section

Manipulations were performed under an atmosphere of argon or nitrogen using standard Schlenk techniques and/or a Vacuum Atmospheres drybox. Dry, oxygen-free solvents were used throughout. NMR spectra were recorded on a GE QE-300 spectrometer at 300 (¹H) or 75.5 (¹³C) MHz. Infrared spectra were obtained with a Perkin-Elmer 1330 spectrometer. Large-scale thermolyses were performed with a Lindberg 1200 °C three-zone tube furnace in flowing oxygen or argon, with a heating rate of 40 °C min⁻¹. Thermal analyses were obtained with a Du Pont Model 2000 thermal analysis system. Microscopy was performed using a Phillips CM30 transmission electron microscope or a Cambridge 360 scanning electron microscope. X-ray powder diffraction patterns were obtained with a Phillips PW1720 diffractometer. The electron microprobe analyses were performed on an ARL SEMQ spectrometer. Elemental analyses were determined at Desert Analytics or Mikroanalytisches Labor Pascher. Cuprous chloride was purchased from Aldrich and dried under vacuum before use. The compounds [CuO^tBu]₄,¹⁴ (O^tBu)₃SiOH,¹⁵ and NaOSi(O^tBu)₃⁸ were prepared as described in the literature.

[CuOSi(O^tBu)₃]₄ (1). To a toluene solution (25 mL) of [CuO^tBu]₄ (0.50 g, 0.92 mmol) was added a 30 mL benzene solution of (O^tBu)₃SiOH (0.97 g, 3.66 mmol). The resulting mixture was stirred for 35 min. The volatiles were removed under dynamic vacuum and the powder was extracted into pentane (40 mL). Concentration and cooling to -30 °C gave colorless, transparent crystals of **1** which turned opaque under vacuum (yield 0.77 g, 58%). Anal. Calcd for C₁₂H₂₇CuO₄Si: C, 44.07; H, 8.32. Found: C, 44.29; H, 8.24. MS (EI, 70 eV) [*m/e* (%)] 1307 (100) [M⁺], 1027 (18) [M⁺ - 5 CH₂=CMe₂]. ¹H NMR (benzene-*d*₆, 22 °C) δ 1.55 (s, 27 H). ¹³C{¹H} NMR (benzene-*d*₆, 22 °C) δ 32.18 (s, CMe₃), 72.57 (s, CMe₃). IR (Nujol, CsI, cm⁻¹) 1360 s, 1218 m, 1212 vw sh, 1190 s, 1068 s sh, 1050 vs, 1021 s, 955 s, 829 m, 720 vw sh, 759 m, 690 vw sh, 640 vw, 570 vw, 510 w, 479 vw.

{(Ph₃P)Cu[μ -OSi(O^tBu)₃]}₂ (2). Pentane (50 mL) was added to a solid mixture of **1** (0.40 g, 1.21 mmol) and PPh₃ (0.32 g, 1.21 mmol). After 0.5 h of stirring, the reaction

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mixture contained a white precipitate. The volatiles were removed under dynamic vacuum, and the resulting white solid was extracted into benzene (20 mL). The volume of the solution was reduced in vacuo to the point of saturation. This solution was then layered with 1.0 mL of benzene and then 50 mL of pentane. After 1 week of diffusion at room temperature, 0.35 g (49%) of **2** was isolated as colorless crystals by filtration. Anal. Calcd for $C_{30}H_{45}CuO_4PSi$: C, 60.84; H, 7.66. Found: C, 61.17; H, 7.27. 1H NMR (benzene- d_6 , 22 °C) δ 1.65 (s, 54 H) 6.94, 6.96 (Ph_3P , multiplet, 3 H) 7.24 to 7.31 (Ph_3P , multiplet, 2 H). IR (Nujol, CsI, cm^{-1}) 3044 w, 1478 m sh, 1435 s, 1385 m, 1360 m, 1310 vw, 1239 m sh, 1230 m, 1190 m, 1046 m sh, 1035 s, 1010 s, 970 s, 905 vw sh, 850 vw, 820 m, 748 s, 720 vw sh, 703 m sh, 696 s, 616 vw, 510 m, 490 m, 475 m sh, 430 w, 381 w.

{NaCu[OSi(O'Bu) $_3$] $_2$] $_6$ (3**).** Method a: To a solid mixture of NaOSi(O'Bu) $_3$ (0.32 g, 1.10 mmol) and **1** (0.36 g, 1.10 mmol) was added 50 mL of ether. The reaction was stirred for 24 h. The volatiles were then removed under dynamic vacuum and the resulting off-white residue was extracted into pentane (15 mL). Concentration and cooling of the solution to -78 °C yielded 0.39 g (57%) of **3** as a white crystalline solid. Method b: To a solid mixture of CuCl (0.22 g, 2.23 mmol) and NaOSi(O'Bu) $_3$ (1.28 g, 4.46 mmol) was added 50 mL of THF. The reaction mixture was stirred for 19 h, and then the volatiles were removed under dynamic vacuum. The resulting off-white residue was extracted with pentane (50 mL). Filtration, concentration, and cooling of the pentane extract to -78 °C yielded 0.70 g (51%) of **3** as a crystalline solid. Anal. Calcd for $C_{24}H_{54}CuNaO_8Si_2$: C, 46.99; H, 8.87. Found: C, 46.34; H, 8.47. MS (FAB) [m/e (%)] 1227 (80) [$\{NaCu[OSi(O'Bu)_3]_2\}^+$], 963 (17) [$\{NaCu[OSi(O'Bu)_3]_2^+ - OSi(O'Bu)_3\}$], 636 (66) [$Na_2Cu[OSi(O'Bu)_3]_2^+$]. 1H NMR (benzene- d_6 , 22 °C) δ 1.53 (s, 54 H). $^{13}C\{^1H\}$ NMR (benzene- d_6 , 22 °C) δ 32.04 (s, $CMes_3$), 71.94 (s, $CMes_3$). IR (Nujol, CsI, cm^{-1}) 1384 m, 1361 s, 1238 m, 1210 w sh, 1058 s sh, 1048 s, 1022 s, 996 s, 908 vw, 820 m, 632 vw, 510 m, 478 w sh, 416 w.

(BuO) $_2$ PhSiCl. To a cold (-78 °C) solution of PhSiCl $_3$ (21.4 mL, 0.128 mol) in THF (300 mL) was added dropwise a solution of NaO'Bu (24.6 g, 0.256 mol) in THF (150 mL). The -78 °C bath was removed, and the reaction was warmed to room temperature and stirred for ca. 8 h. The sodium chloride precipitate was removed by filtration and then washed with pentane (100 mL). The THF and pentane solutions were combined, and the solvents were removed under dynamic vacuum. The remaining colorless oil was distilled at 58 °C, 0.001 Torr to yield 36.5 g (99%) of the compound. 1H NMR (300 MHz, dichloromethane- d_2 , 22 °C) δ 1.43 (s, 18 H, (BuO) $_2$ PhSiCl), 7.40–7.48 (multiplet, 6 H, (BuO) $_2$ PhSiCl), 7.76–7.79 (multiplet, 5 H, (BuO) $_2$ PhSiCl).

(BuO) $_2$ PhSiOH. To a vigorously stirred solution of (BuO) $_2$ PhSiCl (35 mL, 0.127 mol) and pyridine (15 mL) in THF (250 mL) at 0 °C was added deionized water (2.3 mL, 0.127 mol) by syringe. The solution was slowly warmed to room temperature and then stirred for 6 h. The volatiles were removed in vacuo and the remaining white residue was dried under dynamic vacuum until it solidified. This white solid was extracted with pentane (100 mL), and the resulting solution was concentrated and cooled (-78 °C) to yield "oily" white crystals of the product. Further purification by sublimation at 40–50 °C under dynamic vacuum was needed to separate (BuO) $_2$ PhSiOH from a colorless oil. Pure (BuO) $_2$ PhSiOH (21.1 g, 62% yield) was thereby obtained as colorless crystals. Anal. Calcd for $C_{14}H_{24}O_3Si$: C, 62.64; H, 9.01. Found: C, 62.63; H, 9.03. 1H NMR (300 MHz, dichloromethane- d_2 , 22 °C) δ 1.32 (s, 18 H, (BuO) $_2$ PhSiOH), 2.59 (s, 1 H, (BuO) $_2$ PhSiOH), 7.31 to 7.39 (multiplet, 6 H, (BuO) $_2$ PhSiOH), 7.66–7.69 (multiplet, 5 H, (BuO) $_2$ PhSiOH). 1H NMR (300 MHz, benzene- d_6 , 22 °C) δ 1.32 (s, 18 H, (BuO) $_2$ PhSiOH), 1.97 (s, 1 H, (BuO) $_2$ PhSiOH), 7.20–7.23 (multiplet, 6 H, (BuO) $_2$ PhSiOH), 7.82–7.85 (multiplet, 4 H, (BuO) $_2$ PhSiOH). IR (Nujol, CsI, cm^{-1}) 3680 w,

3410 m br, 3020 w, 3010 w, 1580 w, 1419 m, 1365 m sh, 1355 s, 1291 vw, 1230 s, 1190 s sh, 1175 s, 1112 s, 1050 vs br, 1116 s sh, 1000 m sh, 879 m, 835 m, 812 m, 774 m, 630 m, 700 s sh, 689 s sh, 620 w, 500 m, 455 m sh, 425 w sh.

{Cu[μ -OSiPh(O'Bu) $_2$] $_4$ (4**).** Toluene (100 mL) was added to a solid mixture of [CuO'Bu] $_4$ (3.91 g, 7.16 mmol) and (BuO) $_2$ PhSiOH (7.69 g, 28.6 mmol). The resulting solution was stirred for 30 min, and then the volatiles were removed under vacuum. The resulting yellow powder was extracted into pentane (60 mL). Concentration and cooling to -30 °C gave yellow crystals (mp 132–133 °C) of **4** (7.21 g, 76%). Anal. Calcd for $C_{56}H_{92}Cu_4O_{12}Si_4$: C, 50.81; H, 7.00. Found: C, 50.74; H, 7.10. 1H NMR (benzene- d_6 , 22 °C) δ 1.36 (s, 18 H) 7.20–7.22 (Ph , multiplet, 3 H) 7.29 to 7.96 (Ph , multiplet, 2 H). IR (Nujol, CsI, cm^{-1}) 3060 vw sh, 1590 vw, 1428 m sh, 1388 m sh, 1362 m, 1300 vw br, 1238 m, 1200 m sh, 1985 m sh, 1120 m, 1050 s, 1024 m sh, 996 vw sh, 935 s, 825 w, 808 w, 740 w, 712 m, 700 m, 639 w br, 570 w br, 515 m br, 425 vw sh.

X-ray Crystallography of **4.** A slightly yellow prism of approximate dimensions $0.6 \times 0.2 \times 0.2$ mm was mounted in a glass capillary in an inert atmosphere glovebox and flame sealed. Centering on 34 reflections (15 from the rotation photograph and 19 selected at random in the 2θ range $8^\circ \leq 2\theta \leq 34^\circ$) provided a triclinic unit cell. Data were collected in the 2θ range $3^\circ \leq 2\theta \leq 45^\circ$. Of 4936 reflections collected, 4617 were independent and 3413 were observed with $F > 4\sigma(F)$. Solution of the structure in $P\bar{1}$ was achieved by direct methods, and the structure was refined using full-matrix least-squares methods. All non-hydrogen atoms were refined anisotropically except for the phenyl group carbons, which were refined isotropically. All hydrogen atoms were added in idealized positions.

Bulk Thermolyses. Thermolyses employed a heating rate of 30 or 40 °C min^{-1} . At the temperatures indicated in Tables 3 and 4, the temperature was held at that value for the time indicated, and then the sample was removed from the oven and analyzed. Anal. Calcd for Cu^0SiO_2 : Cu, 51.4; Si, 22.7. Found: Cu, 69.6; Si, 15.5; C, 0.04; H, <0.01 (compound 1 heated to 1000 °C under argon). Anal. Calcd for $CuOSiO_2$: Cu, 45.5; Si, 20.1. Found: Cu, 55.2; Si, 15.7; C, 0.07; H, <0.01 (compound 1 heated to 1000 °C under oxygen). For compound **4**, heated to 1000 °C under argon. Anal. Found: C, 4.20; H, 0.45. For compound **4**, heated to 1000 °C under oxygen. Anal. Found: C, 0.03; H, <0.01.

Thin-Film Growth by CVD of **1.** Compound **1** was placed at the sealed end of a 36 in. Pyrex tube. A glass slide was placed inside the tube 8 in. away from the precursor. The tube was placed under a dynamic vacuum of 0.001 mmHg. The section of tube where the glass slide was located was heated to 450 °C. The section of tube containing the precursor was heated to 130 °C. After 30 min the glass slide was covered with a copper-colored film. The film was amorphous by XRD. SEM pictures revealed a lumpy surface topology of the film whose thickness varied between 0.2 and 6 μm . Microprobe analysis of the thin film shows a Cu-to-Si ratio of about 1:0.85.

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Supporting Information Available: Tables of crystal, data collection, and refinement parameters, listing of atomic coordinates, anisotropic thermal parameters, bond distances and angles, and hydrogen atom coordinates (8 pages); listing of observed and calculated structure factors (17 pages). Ordering information is given on any current masthead page.

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