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Dicopper(I) Oxalate Complexes Stabilized by Lewis Bases: Potential Precursors for Copper Deposition

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The synthesis, characterization, and thermal behavior of the dicopper(I) oxalate complexes $L_2Cu_2O_4C_2$ (L = $Me_3SiC{\equiv}CSiMe_3$ (**1**), $Me_3SiC{\equiv}C^nBu$ (**2**), $EtC{\equiv}CEt$ (**3**), $H_2C{=}C(H)SiMe_2{}^tBu$ (**4**), $H_2C{=}C(H)SiEt_2Me$ (**5**), norbornene (**6**)) is reported. All complexes can be prepared in a straightforward manner by the reaction of stoichiometric amounts of Cu_2O and oxalic acid with 2 equiv of the respective alkyne or alkene. The complexes are stable at room temperature, and in solid form they can be handled in air for some time. Their thermal behavior was studied by thermal gravimetric analysis (TGA). The order of thermal stability was found to be **1** > **6** > **4** > **2** ≈ **3** > **5**. Decomposition starts between 50 and 100 °C and is completed between 300 and 350 °C. All compounds fully decompose via an efficient internal redox process to give elemental copper, CO_2, and the free alkyne or alkene ligands, which makes these new complexes promising precursors for copper deposition (in the case of **4**, it is likely that $H_2C{=}C(H)SiMe_2H$ and isobutene is formed via β-hydrogen elimination from $H_2C{=}C(H)SiMe_2{}^tBu$). Distinct two- or three-step decomposition sequences for the individual complexes are revealed by the TGA analyses and are discussed. The single-crystal X-ray structures of **1** and **3** are reported, which are the first for copper(I)/oxalato compounds. Both complexes exhibit the anticipated planar dinuclear structure with the oxalate in a μ-1,2,3,4 bridging mode and the alkynes or alkenes as capping ligands.

Introduction

Copper deposition has become an important and rapidly growing area in integrated circuit manufacturing in the microelectronics industry.[1] This has stimulated a search for molecular copper(I) and copper(II) complexes that may serve as precursor compounds for, inter alia, chemical vapor deposition (CVD) and atomic layer deposition (ALD).[2] In the case of copper(II) precursor complexes, however, an additional reducing agent is usually required and the conversion to elemental copper often is inefficient, due to limited volatility and high decomposition temperatures (T > 200 °C). More suitable are copper(I) precursors, among which the Lewis base stabilized fluorine-containing copper(I) β-diketonates **A** have received the most attention.[3] These complexes are volatile and decompose at low temperatures (T > 40 °C) on a heated substrate by a clean and efficient disproportionation reaction, shown in eq 1.

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

Despite these favorable characteristics of type **A** complexes, however, the search for fluorine-free copper(I) precursors has recently attracted increasing interest as a result of adhesion problems of the copper layer deposited onto the diffusion barrier layer, TiN, when using fluorine-containing copper(I) complexes. Unfortunately, fluorine-free analogues of the Lewis base stabilized copper(I) β-diketonate complexes **A** are very sensitive to air and thermally unstable under CVD process conditions.[4] Other alternatives to fluorine-free copper(I) precursors are available, such as the earlier synthesized $(R_3P)Cu^I(\eta^5\text{-}C_5H_5)$[5] and copper(I) *tert*-butoxide tetramer,[6] but these compounds also have some drawbacks. For example, reproducibility problems appeared while scaling up the CVD process using (R_3P)-

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$Cu^I(\eta^5\text{-}C_5H_5)$ at IBM.[1b] In the case of the copper(I) *tert*-butoxide tetramer, the resulting copper films are contaminated with oxygen due to homolytic decomposition.[1b,7] Thus, new classes of fluorine-free copper(I) precursors are highly desirable. Some new types, such as Lewis base stabilized copper(I) acetoacetates[8] and pyrazolates,[9] have recently been reported. On the other hand, alternative precursor delivery methods are being developed in order to circumvent the general limitations of the conventional CVD process, such as the requirement of high volatility of the metal precursor. Current approaches in this direction include copper deposition from supercritical carbon dioxide,[10] spin coating,[11] or aerosol-assisted CVD (AACVD).[12] These latter methods utilize solutions of the precursor compounds and thus are also applicable for low-volatility precursors or even nonvolatile metal salts.

In this paper we describe the synthesis, structure, and properties of novel dicopper(I) oxalate complexes stabilized by Lewis bases, where the neutral Lewis base is an alkyne or alkene. We have investigated their thermal behavior with respect to copper deposition. In contrast to most other copper(I) precursors, the new compounds show excellent thermal behavior and air stability. TGA measurements indicate a decomposition mechanism corresponding to ligand dissociation followed by an internal redox reaction and loss of CO_2, thus ensuring a 100% yield of copper(0). The byproduct CO_2 is nontoxic, which is advantageous for a safe and environmentally friendly process, and the formed neutral uncoordinated Lewis base can potentially be reused.

Experimental Section

All operations were carried out under an inert atmosphere of argon using standard Schlenk techniques in dry, oxygen-free solvents. The NMR spectra were recorded on a Bruker DPX 250 (^1H, 250.13 MHz; $^{13}C\{^1H\}$, 62.90 MHz) or AMX 300 (^1H, 300.13 MHz; $^{13}C\{^1H\}$, 75.47 MHz) at ambient temperature. Chemical shifts are reported in ppm relative to the ^1H and ^{13}C residues of the deuterated solvents. Elemental analyses were performed on a Vario EL instrument; only moderate elemental analyses could be obtained for the complexes bearing alkene ligands, probably due to their lower stability. IR spectra were recorded on a Bruker EQUINOX 55 as KBr pellets or as a film in CH_2Cl_2. Mass spectra were collected using a Bruker Reflex III. Thermal gravimetric analysis data were obtained on a TA Instruments TGA 2050 using an open pan which was purged with N_2 at a heating rate of 5 °C/min. All starting materials were used as purchased.

Bis{[bis(trimethylsilyl)acetylene]copper(I)} Oxalate (1). A 100 mL Schlenk flask was loaded with Cu_2O (3.4 g, 23.8 mmol, Alfa Aesar), dichloromethane (60 mL, Merck), $Me_3SiC{\equiv}CSiMe_3$ (8.0 g, 46.3 mmol, ABCR), and $(COOH)_2$ (2.1 g, 23.8 mmol, Fluka). The red suspension was stirred for 4 h, and the solution became almost colorless as the reaction proceeded. The remaining Cu_2O was filtered off, and the solvent was removed under vacuum (0.01 mbar), leaving a colorless solid. Recrystallization from dichloromethane at −20 °C gave colorless crystals of **1** (11.7 g, 89%); mp 153 °C dec. ^1H NMR ($CDCl_3$): δ 0.30 (s, $SiMe_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 0.0 ($SiMe_3$), 114.2 ($C{\equiv}C$), 171.8 (COO). IR (KBr; cm^{-1}): $\nu_{C\equiv C}$ 1935 (m); ν_{CO_2} 1642 (s), 1354 (w), 1309 (m). MS (*m/z* (%)): 788 (25) $[M + Cu(Me_3SiC{\equiv}CSiMe_3)]^+$, 618 (10) $[M + Cu]^+$, 403 (68) $[M - CuO_4C_2]^+$, 233 (100) $[M - (Me_3SiC{\equiv}CSiMe_3)CuO_4C_2]^+$. Anal. Calcd for $C_{18}H_{36}Cu_2O_4Si_4$ (mol wt 555.92): C, 38.9; H, 6.5. Found: C, 38.7; H, 6.6.

Bis{[1-(trimethylsilyl)-1-hexyne]copper(I)} Oxalate (2). In analogy to the preparation of **1**, Cu_2O (1.8 g, 12.6 mmol, Alfa Aesar), dichloromethane (50 mL, Merck), $Me_3SiC{\equiv}C^nBu$ (5 mL, 25.2 mmol, ABCR), and $(COOH)_2$ (1.1 g, 12.6 mmol, Fluka) were used. Recrystallization from dichloromethane at −20 °C gave colorless crystals of **2** (4.9 g, 75%). ^1H NMR ($CDCl_3$): δ 0.29 (s, 18 H, $SiMe_3$), 0.93 (t, $^3J_{HH}$ = 7.0 Hz, 6 H, $(CH_2)_3CH_3$), 1.3−1.6 (m, 4 H, $(CH_2)_2CH_2CH_3$), 1.5−1.8 (m, 4 H, $CH_2CH_2CH_2CH_3$), 2.58 (t, $^3J_{HH}$ = 7.0 Hz, 4 H, $CH_2(CH_2)_2CH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 0.0 ($SiMe_3$), 13.4 ($(CH_2)_3CH_3$), 21.7 ($(CH_2)_2CH_2CH_3$), 22.5 ($CH_2CH_2CH_2CH_3$), 30.9 (${\equiv}CCH_2$), 85.4 (${\equiv}CCH_2$), 112.9 ($SiC{\equiv}C$), 171.4 (COO). IR (KBr; cm^{-1}): $\nu_{C\equiv C}$ 1986 (m); ν_{CO_2} 1643 (vs), 1355 (w), 1311 (m). MS (*m/z* (%)): 741 (20) $[M + Cu(Me_3SiC{\equiv}CBu)]^+$, 587 (20) $[M + Cu]^+$, 371 (93) $[M - CuO_4C_2]^+$, 217 (100) $[M - (Me_3SiC{\equiv}CBu)CuO_4C_2]^+$. Anal. Calcd for $C_{20}H_{36}Cu_2O_4Si_2$ (mol wt 523.76): C, 45.9; H, 6.9. Found: C, 45.5; H, 7.1.

Bis[(3-hexyne)copper(I)] Oxalate (3). In analogy to the preparation of **1**, Cu_2O (1.8 g, 12.6 mmol, Alfa Aesar), dichloromethane (50 mL, Merck), $EtC{\equiv}CEt$ (3 mL, 26.3 mmol, Merck), and $(COOH)_2$ (1.1 g, 12.6 mmol, Fluka) were used. Recrystallization from dichloromethane at −20 °C gave colorless needles of **3** (2.6 g, 55%). ^1H NMR ($CDCl_3$): δ 1.22 (t, 12 H, ^3J = 7.3 Hz, CH_3), 2.49 (q, 8 H, ^3J = 7.4 Hz, CH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 14.4 (CH_3), 15.5 (CH_2), 87.6 ($C{\equiv}C$), 171.4 (COO). IR (KBr; cm^{-1}): $\nu_{C\equiv C}$ 2053, 2020 (w); ν_{CO_2} 1645 (vs), 1355 (w), 1314 (m). MS (*m/z* (%)): 525 (7) $[M + Cu(EtC{\equiv}CEt)]^+$, 443 (7) $[M + Cu]^+$, 227 (100) $[M - CuO_4C_2]^+$, 145 (96) $[M - (EtC{\equiv}CEt)CuO_4C_2]^+$. Anal. Calcd for $C_{14}H_{20}Cu_2O_4$ (mol wt 379.40): C, 44.3; H, 5.3. Found: C, 44.7; H, 4.9.

Bis[(vinyl-*tert*-butyldimethylsilane)copper(I)] Oxalate (4). In analogy to the preparation of **1**, Cu_2O (1.8 g, 12.6 mmol, Alfa Aesar), dichloromethane (50 mL, Merck), $H_2C{=}C(H)Si(^tBu)Me_2$ (4.7 mL, 25.2 mmol, ABCR), and $(COOH)_2$ (1.1 g, 12.6 mmol, Fluka) were used. Recrystallization from dichloromethane at −20 °C gave colorless crystals of **4** (3.7 g, 59%). ^1H NMR ($CDCl_3$): δ 0.14 (s, 12 H, $Si(CH_3)_2$), 0.90 (s, 18 H, $C(CH_3)_3$), 4.50 (dd, J_{trans} = 18.3 Hz, J_{gem} = 2.5 Hz, 2 H, $SiCH{=}CHH$), 4.78 (dd, J_{trans} = 18.3 Hz, J_{cis} = 13.3 Hz, 2 H, $SiCH{=}CH_2$), 4.86 (dd, J_{cis} = 13.3 Hz, J_{gem} = 2.5 Hz, 2 H, $SiCH{=}CHH$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ −5.8 ($SiMe_2$), 16.8 (CMe_3), 26.2 (CMe_3), 91.0 (${=}CH_2$), 97.4 (${=}CHSi$), 171.6 (COO). IR (KBr; cm^{-1}): ν_{CO_2} 1647 (vs), 1344 (w), 1312 (m). MS (*m/z* (%)): 347 (62) $[M - CuO_4C_2]^+$, 206 (80) $[M - (H_2C{=}CHSiMe_2Bu)CuO_4C_2]^+$, 149 (63) $[M - (H_2C{=}CHSiMe_2Bu)CuO_4C_2 - \text{butene}]^+$, 127 (92) $[H_2C{=}CHSiMeBu]^+$, 115 (57) $[SiMe_2Bu]^+$, 86 (14) $[H_2C{=}CHSiMe_2H]^+$. Anal. Calcd for $C_{18}H_{36}Cu_2O_4Si_2$ (mol wt 499.74): C, 43.3; H, 7.3. Found: C, 42.7; H, 7.2.

Bis[(vinyldiethylmethylsilane)copper(I)] Oxalate (5). In analogy to the preparation of **1**, Cu_2O (1.8 g, 12.6 mmol, Alfa Aesar), dichloromethane (50 mL, Merck), $H_2C{=}C(H)Si(Me)Et_2$ (4.4 mL, 25.7 mmol, ABCR), and $(COOH)_2$ (1.1 g, 12.6 mmol, Fluka) were used. Recrystallization from dichloromethane at −20 °C gave a colorless solid of **5** (3.5 g, 59%). ^1H NMR ($CDCl_3$): δ 0.12 (s, 6 H, $SiCH_3$), 0.65 (q, 8 H, ^3J = 7.8 Hz, CH_2CH_3), 0.98 (t, 12 H, ^3J = 7.9 Hz, CH_2CH_3), 4.48 (dd, J_{trans} = 17.5 Hz, J_{gem} = 3.6 Hz, 2 H, $SiCH{=}CHH$), 4.75 (dd, J_{trans} = 17.7 Hz, J_{cis} = 13.0 Hz, 2 H, $SiCH{=}CH_2$), 4.81 (dd, J_{cis} = 13.0 Hz, J_{gem} = 3.5 Hz, 2 H, $SiCH{=}CHH$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ −5.5 ($SiCH_3$), 5.3 ($SiCH_2CH_3$), 7.3 ($SiCH_2CH_3$), 89.7 ($H_2C{=}CH$), 96.6 ($H_2C{=}CH$), 171.5 (COO). IR (KBr; cm^{-1}): $\nu_{C=C}$ 1496 (m); ν_{CO_2} 1645 (vs), 1343 (s), 1310 (s). Anal. Calcd for

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Table 1. Crystal Data and Refinement Details for 1 and 3

	1	3
formula	$C_{18}H_{36}Cu_2O_4Si_4$	$C_{14}H_{20}Cu_2O_4$
M_r	555.9	379.4
cryst syst	monoclinic	monoclinic
space group	$C2/c$	$P2_1/c$
a (Å)	15.435(3)	9.837(2)
b (Å)	9.6089(19)	5.3678(11)
c (Å)	18.519(4)	15.316(3)
β (deg)	100.02(3)	108.10(3)
V (Å^3)	2704.7(9)	768.7(3)
ρ_{calcd} (g cm^{-3})	1.365	1.639
Z	4	2
F(000) (e)	1160	388
T (K)	133	133
μ(Mo Kα) (mm^{-1})	1.769	2.774
hkl range	−18 to +18, −11 to +11, −20 to +21	−11 to +11, −6 to +6, −17 to +17
2θ range (deg)	4.5−49.6	5.6−49.7
no. of measd rflns	7764	3873
no. of unique rflns (R_{int})	2255 (0.053)	1290 (0.037)
no. of obsd rflns, $I > 2\sigma(I)$	2172	1168
no. of refined params	128	93
resid electron dens (e Å^{-3})	0.54/−0.47	0.34/−0.18
R1	0.029	0.020
wR2 (all data)	0.074	0.052
goodness of fit	1.065	1.013

$C_{16}H_{32}Cu_2O_4Si_2$ (mol wt 471.70): C, 40.7; H, 6.9. Found: C, 41.9; H, 7.2.

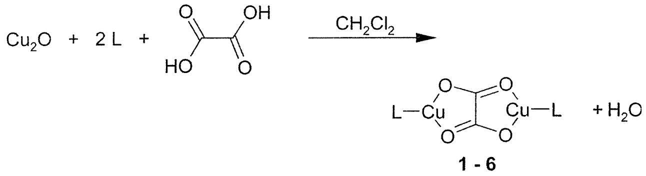
Bis[(norbornene)copper(I)] Oxalate (6). In analogy to the preparation of **1**, Cu_2O (1.8 g, 12.6 mmol, Alfa Aesar), dichloromethane (50 mL, Merck), norbornene (2.4 g, 98%, 25.2 mmol, Merck), and $(COOH)_2$ (1.1 g, 12.6 mmol, Fluka) were used. Recrystallization from dichloromethane at −20 °C gave a colorless solid of **6** (2.6 g, 52%). ^1H NMR ($CDCl_3$): δ 1.00 (d, $^2J = 7.8$ Hz, 4 H, H_{endo}), 1.03 (d, $^2J = 9.5$ Hz, 2 H, H_{anti}), 1.28 (d, $^2J = 9.6$ Hz, 2 H, H_{syn}), 1.59 (d, $^2J = 7.7$ Hz, 4 H, H_{exo}), 3.08 (s, 4 H, CH), 5.25 (s, 4 H, =CH). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 24.4 (CH_2CH_2), 42.7 ($CHCH_2$), 45.7 ($CHCH_2CH$), 109.2 (=CH), 171.4 (COO). IR (KBr; cm^{-1}): $\nu_{C=C}$ 1473 (w); ν_{CO_2} 1644 (m), 1362 (m), 1303 (vs). Anal. Calcd for $C_{16}H_{20}Cu_2O_4$ (mol wt 403.43): C, 47.6; H, 5.0. Found: C, 46.9; H, 5.2.

X-ray Structure Determination. The measurements were carried out on a Stoe IPDS II diffractometer using graphite-monochromated Mo Kα radiation. The structures were solved by direct methods (SHELXS-97) and refined with all data by full-matrix least-squares calculations based on F^2 (SHELXL-97). All non-hydrogen atoms were refined anisotropically. In general, the hydrogen atoms of C−H bonds were added in idealized positions. Table 1 compiles the data for the structure determinations.

Results and Discussion

Synthesis and Characterization. While copper(II) oxalate and its complexes are well-known and commercially available, only a few reports about copper(I) oxalate complexes have been published.[13] To the best of our knowledge, no structural data for copper(I) oxalate complexes are known. Since copper(I) oxalate bears the potential to decompose in an effective internal redox reaction to yield elemental copper and CO_2, we aimed to synthesize stable adducts of this compound as molecular precursors for copper deposition. The neutral Lewis bases chosen for stabilizing the copper(I) oxalate fragment and for preventing formation of polymeric species should be stable by themselves and volatile. The synthetic route to such complexes was inspired by previously reported methods for the preparation of various Lewis base stabilized copper(I) compounds.[3,4,14] These routes proceed either by reaction of a Lewis base stabilized copper(I) halide complex with the sodium salt of an acid (e.g. sodium acetylacetonate or sodium carboxylate) or by reaction of Cu_2O, the free acid (e.g. hexafluoroacetylacetone), and a Lewis base. In the present case, the first method using sodium oxalate did not lead to the desired products, but the latter procedure proved to be successful. Copper(I) oxalate complexes **1**−**6** could be prepared by reacting Cu_2O, oxalic acid, and 2 equiv of a neutral Lewis base (an alkene or alkyne) at room temperature in dichloromethane according to Scheme 1.

Scheme 1. Synthesis of the Complexes



1 - 6

1 L = $Me_3SiC{\equiv}CSiMe_3$
2 L = $Me_3SiC{\equiv}C^nBu$
3 L = $EtC{\equiv}CEt$
4 L = $H_2C{=}C(H)SiMe_2{}^tBu$
5 L = $H_2C{=}C(H)SiEt_2Me$
6 L = norbornene

After the reaction mixture was stirred for 2−5 h and filtered and the solvent evaporated, the crude complexes were isolated. Crystallization from dichloromethane yielded the Lewis base stabilized copper(I) oxalates **1**−**6** in a pure form, which were characterized by elemental analysis, NMR and IR spectroscopy, mass spectrometry, and thermal gravimetric analysis. All complexes are colorless solids. These solids are almost air stable and can therefore be handled in air for a short period of time. In solution the compounds are sensitive to oxygen, leading to green copper(II) species. The complexes are only moderately soluble in toluene or diethyl ether but show good solubility in more polar solvents such as dichloromethane and tetrahydrofuran. All complexes are thermally stable to 50−100 °C, which is an important criterion for their potential use in copper deposition. Sublimation tests at 10^{-1} mbar using **1** and **3** failed in the available temperature range (up to around 80 °C), indicating a rather low volatility of these complexes.

The ^1H NMR spectra of **1**−**6** in $CDCl_3$ consist of the expected sharp and well-resolved signals for each of the organic groups of the coordinated neutral Lewis base. In the ^{13}C NMR spectra of the alkyne-stabilized copper(I) oxalate complexes **1**−**3**, the resonances of the acetylenic carbon atoms are barely shifted upon η^2 coordination of the C≡C triple bond to the copper(I) center (Table 2), which is a common observation in alkyne−copper(I) chemistry.[15] In contrast, in the case of the alkene-

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Table 2. Selected ^{13}C NMR Data for Complexes 1−6

complex	δ (ppm)		
	C≡C[a]	C=C[b]	OCO
1	114.2 (113.8)		171.8
2	85.4, 112.9 (84.0, 107.5)[c]		171.4
3	87.6 (81.9)		171.4
4		91.0, 97.4 (132.3, 137.4)	171.6
5		89.7, 96.6 (131.9, 137.8)	171.5
6		109.2 (135.7)	171.4

[a] Values for the free alkynes in parentheses. [b] Values for the free alkenes in parentheses. [c] Reference 28.

Table 3. Selected IR Absorptions for Complexes 1−6

compd	$\nu_{C\equiv C}$ [a]	$\nu_{C=C}$ [b]	ν_{C-O}(asym)
1	1935 (2109)[c]		1642
2	1986 (2200)[d]		1643
3	2053/2020 (2301/2247/2231)[e]		1645
4		n.a. (1592)	1647
5		1496 (1594)	1645
6		1473 (1567)	1644

[a] Values for the free alkynes in parentheses (IR and Raman, respectively). [b] Values for the free alkenes in parentheses; na = not assignable. [c] References 29 and 30. [d] Reference 31. [e] Reference 32.

containing complexes **4**−**6** the signals for the olefinic carbon atoms are significantly shifted to lower frequency (by ∼40 ppm for the Si-substituted alkenes in **4** and **5**, 26.5 ppm for norbornene in **6**). Similar shifts have been reported previously for other olefin−copper(I) complexes and have been interpreted in terms of π-back-bonding according to the Chatt−Dewar−Duncanson model.[16] The resonance signals of the oxalato carbon atoms appear in the narrow range from 171.4 to 171.8 ppm for all complexes studied. This is at slightly higher frequency compared to the oxalato carbon signal of a dicopper(I) oxalate complex described earlier, in which the oxalato ligand was proposed to be bonded to two copper(I) centers in a μ-1,3 bridging mode (i.e. different from the μ-1,2,3,4 bridging mode in **1**−**6**).[13c]

The IR spectra of all complexes display the characteristic strong ν_{C-O}(asym) band of the oxalato ligand at around 1645 cm^{-1}, corroborating its tetradentate bridging mode (Table 3).[17−19] ν_{C-O}(sym) bands around 1340 cm^{-1} cannot be unequivocally assigned in all cases, due to additional ligand absorptions in that region. The $\nu_{C\equiv C}$ vibrations of the capping ligands in **1**−**3** are shifted by ∼200 cm^{-1} to lower energy compared to the free alkynes. Such a shift of $\nu_{C\equiv C}$ upon η^2 coordination to the copper oxalate building block in **1**−**3** is similar to what is generally observed for alkynes π-bonded to copper(I) centers, if the alkyne is acting as a two-electron donor.[15] The C≡C stretch of the 3-hexyne ligand in **3** appears as a doublet due to the well-known Fermi resonance in dialkylacetylenes.[20,32] The $\nu_{C=C}$ vibrations of the alkene ligands in **4**−**6** are shifted bathochromically by ∼100 cm^{-1} compared to the free alkenes, again indicating significant weakening of the C=C bond because of η^2 coordination of the alkene ligand to the copper(I) center.[21]

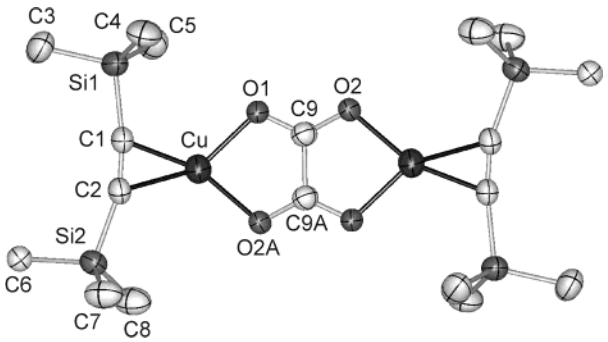

Figure 1. View of the molecular structure of **1**. In the interests of clarity, all hydrogen atoms have been omitted. Selected atom distances (Å) and bond angles (deg): Cu−O1 = 2.004(2), Cu−O2A = 1.990(2), Cu−C1 = 1.973(2), Cu−C2 = 1.984(2), O1−C9 = 1.255(3), O2−C9 = 1.252(3), C1−C2 = 1.243(3), C1−Si1 = 1.866(2), C2−Si2 = 1.862(2), C9−C9A = 1.557(4); O1−Cu−O2A = 84.75(6), C1−C2−Si2 = 163.2(2), C2−C1−Si1 = 170.5(2), O1−C9−C9A = 116.5(2), O2−C9−C9A = 117.4(2).

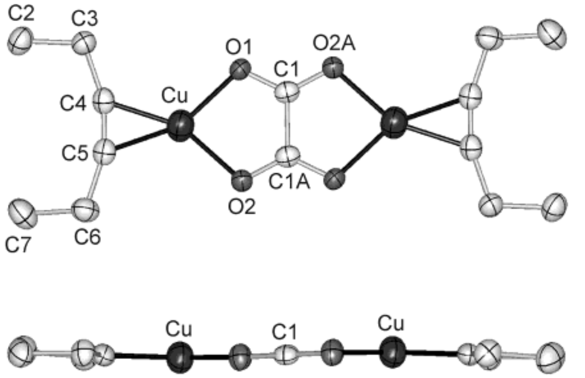

Figure 2. Top view (upper) and side view (lower) of the molecular structure of **3**. In the interests of clarity, all hydrogen atoms have been omitted. Selected atom distances (Å) and bond angles (deg): Cu−O1 = 1.992(1), Cu−O2 = 1.987(1), Cu−C4 = 1.952(2), Cu−C5 = 1.960(2), O1−C1 = 1.255(2), O2−C1A = 1.258(2), C4−C5 = 1.236(3), C5−C6 = 1.483(3), C3−C4 = 1.479(3), C1−C1A = 1.554(3); O1−Cu−O2 = 85.34(6), C3−C4−C5 = 161.0(2), C4−C5−C6 = 161.9(2), O1−C1−C1A = 117.4(2), O2−C1A−C1 = 116.6(2).

Solid-State Structures. To confirm the constitution of the new complexes as deduced from spectroscopy and to gain first insight into the structural details of copper(I) oxalate species, **1** and **3** were analyzed by X-ray crystallography. Colorless single crystals of both complexes could be obtained by cooling solutions in CH_2Cl_2 to −20 °C. Molecular structures are depicted in Figures 1 and 2, respectively.

Both **1** and **3** exhibit the anticipated planar dinuclear structure with the oxalate in a μ-1,2,3,4 bridging mode (which is the mode most frequently observed for the oxalato group)[22] and the terminal alkyne ligands side-on bound to the copper ions. While μ-1,2,3,4-oxalato dicopper(II) compounds have been extensively investi-

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gated, in particular with respect to magnetic exchange interactions,[23] **1** and **3** represent the first structurally characterized oxalato complexes of copper(I). The Cu−O bond lengths in **1** and **3** (1.987(1)−2.004(2) Å) are similar to those usually observed for μ-1,2,3,4 oxalato copper(II) compounds,[24] and they are also comparable to the Cu−O bond lengths in alkyne-stabilized copper(I) carboxylates.[15] With respect to the metric parameters of the oxalato group, complexes **1** and **3** are basically identical (Figures 1 and 2), and no significant differences could be found in comparison to the structural data of μ-1,2,3,4 oxalato bridges in copper(II) compounds described earlier.[19,23] The Cu−C$_{\text{alkyne}}$ distances are similar for **1** (1.973(2), 1.984(2) Å) and **3** (1.952(2), 1.960(2) Å) and are within the range typical for copper(I) alkyne complexes, although the Cu−C$_{\text{alkyne}}$ distances in dimeric $[(\eta^2\text{-Me}_3\text{SiC}{\equiv}\text{CSiMe}_3)\text{Cu}(\mu\text{-X})]_2$ (X = Cl, Br) are slightly longer.[25,30] In accordance with the IR spectroscopic results, alkyne binding to the metal ions results in a lengthening of the C≡C bond from 1.208(3) Å in noncoordinated $\text{Me}_3\text{SiC}{\equiv}\text{CSiMe}_3$ [26] to 1.243(3) Å in **1** (1.236(3) Å in **3**), which is characteristic for η^2 coordination to copper(I).[15] In addition, a significant bending of the initially linear arrangement of the SiC≡CSi entities in **1** as well as the CC≡CC entities in **3** is observed (**1**, C1−C2−Si2 = 163.2(2)°, C2−C1−Si1 = 170.5(2)° versus 179.1(2)° in free $\text{Me}_3\text{SiC}{\equiv}\text{CSiMe}_3$;[26] **3**, C3−C4−C5 = 161.0(2)°, C4−C5−C6 = 161.9(2)°).

With respect to the thermal decomposition behavior of the new complexes, intermolecular interactions are of interest. In the case of **1**, the closest intermolecular contacts in the crystal are those between the Cu−O unit and the SiMe$_3$ group of a neighboring molecule (*d*(Cu···C8#) = 3.493 Å; *d*(O2···C7#) = 3.336 Å), in the typical range for van der Waals distances. In the crystal structure of **3**, the closest intermolecular contacts are found between the Cu atoms of adjacent molecules (*d*(Cu···Cu#) = 3.250 Å) and to the oxalato-*O* atoms (*d*(Cu···O2#) = 3.516 Å; *d*(Cu···O1#) = 3.404 Å; *d*(O1···C6#) = 3.182 Å; *d*(O2···C3#) = 3.387 Å). The shortest O···C distances may be interpreted as very weak O···HC hydrogen bonds, while the intermolecular Cu···Cu distance in **3** is clearly longer than any closed-shell (cuprophilic) interactions.[27]

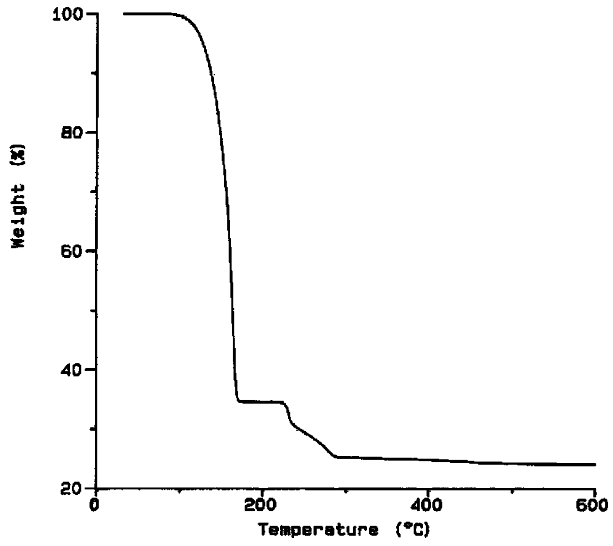
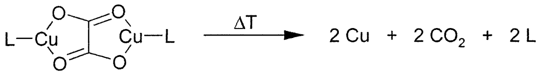


Figure 3. TGA curve for complex **1**; heating rate 5 °C/min.

Scheme 2. Thermal Decomposition of Complexes 1−3, 5, and 6



1 - 3, 5, 6

Thermal Behavior. Thermal gravimetric analysis (TGA) was employed to evaluate the thermal stability of the copper(I) oxalate complexes **1**−**6** and their decomposition behavior with increasing temperature. In general, compounds **1**−**3**, **5**, and **6** fully decompose to elemental copper, CO$_2$, and the free alkyne or alkene ligand (Scheme 2). The thermal decomposition pattern of complex **4** is slightly different with respect to the alkene ligand, which will be described below.

The order of thermal stability was found to be **1** > **6** > **4** > **2** ≈ **3** > **5**. While $[\text{H}_2\text{C}{=}\text{C(H)SiEt}_2\text{Me}]_2\text{Cu}_2\text{C}_2\text{O}_4$ (**5**) already starts to decompose at 50 °C, $(\text{Me}_3\text{SiC}{\equiv}\text{CSiMe}_3)_2\text{Cu}_2\text{C}_2\text{O}_4$ (**1**) turned out to be stable up to 100 °C. The decomposition of all complexes is completed between 300 and 350 °C. Two types of decomposition processes could be observed using a heating rate of 5 °C/min: a two-step process for compounds **1**, **2**, **5**, and **6** (Figure 3) and a three-step process for compounds **3** and **4** (Figure 4).

The two-step decomposition process corresponds to the initial loss of both neutral Lewis bases (step 1) followed by an internal redox reaction with concomitant loss of CO$_2$ (step 2) (Figure 3, Scheme 3). The difference between the final weight percentage and the theoretical value expected for elemental copper is less than 0.1% for complexes **1**, **5**, and **6** and 3.2% for complex **2**.

The TGA plot of compound **3** shows a three-step decomposition process (Figure 4, Scheme 4) with sequential loss of the two neutral Lewis bases. The first step occurs in a temperature range of 60−125 °C (loss of one hexyne ligand), followed by the second step in a temperature range of 125−150 °C (loss of the second hexyne ligand). The third step proceeds between 200 and 310 °C and corresponds to the loss of CO$_2$. The remaining weight percentage of 34.1% is in good agree-

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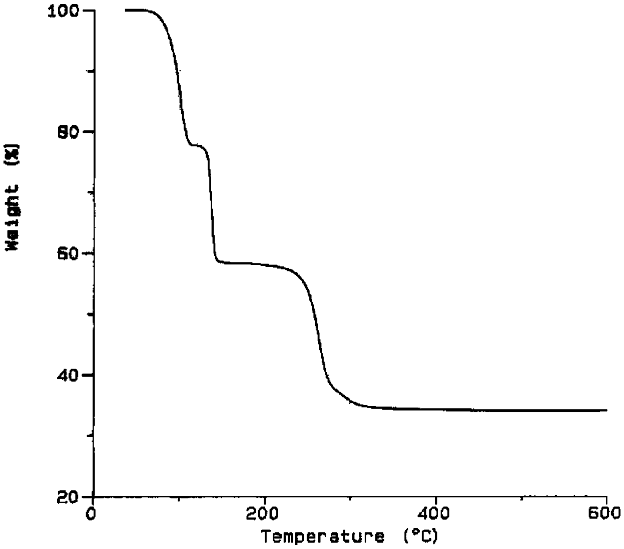
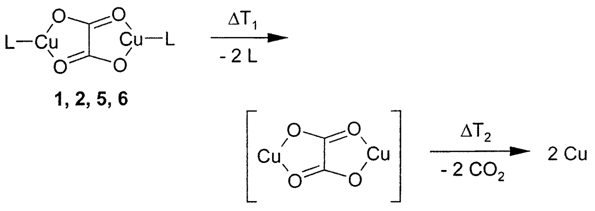
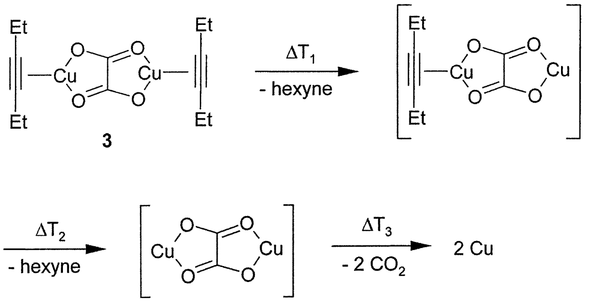


Figure 4. TGA curve for complex **3**; heating rate 5 °C/min.

Scheme 3. Proposed Decomposition Sequence for Complexes 1, 2, 5, and 6



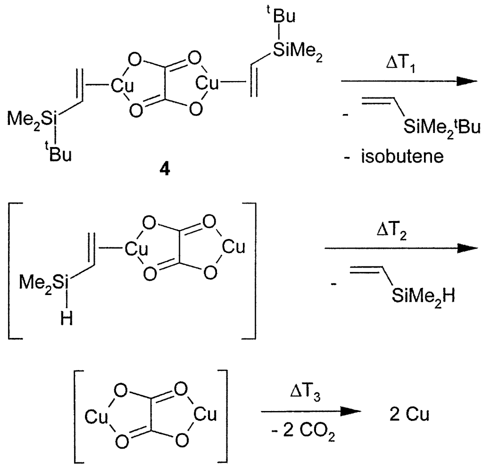
Scheme 4. Proposed Decomposition Sequence for Complex 3



ment with the calculated value of 33.6% expected for elemental copper.

Complex **4** also shows a three-step decomposition process. However, in this case the decomposition occurs in a slightly different way (Scheme 5). Compared to complex **3**, which exhibits an equal weight loss for the first and second steps (sequential loss of the 3-hexyne ligands), the TGA plot of **4** shows two unequal weight losses for steps 1 and 2 (step 1, 38.8%; step 2, 15.1%). A likely explanation for this behavior is that within the first step complex **4** loses 1 equiv of the neutral ligand $H_2C{=}C(H)SiMe_2(^tBu)$ as well as 1 equiv of isobutene (or $H_2C{=}C(H)SiMe_2(H)$ and 2 equiv of isobutene). Formation of the latter should result from *β*-hydrogen elimination in $H_2C{=}C(H)SiMe_2(^tBu)$ to yield volatile isobutene and $H_2C{=}C(H)SiMe_2(H)$, which remains coordinated to copper(I). This assumption is corroborated by the observation of prominent peaks for both $[Cu(H_2C{=}C(H)SiMe_2{}^tBu)]^+$ at *m*/*z* 206 and $[Cu(H_2C{=}C(H)SiMe_2H)]^+$ at *m*/*z* 149 in the MALDI-MS spectrum of **4**. The calculated weight loss for this scenario (39.7%) is in good agreement with the experimental value. With increasing temperature the resulting copper species then loses the remaining alkene ligand $H_2C{=}C(H)SiMe_2(H)$ formed during step 1 to give $Cu_2O_4C_2$—this corresponds to step 2 (calculated weight loss 17.3%). The third step in the TGA plot of complex **4** is similar to the third decomposition step of complex **3** (i.e. loss of CO_2 to form elemental copper). The final weight percentage of 27.6% is in relatively good agreement with the calculated value of 25.4% expected for elemental copper.

Scheme 5. Proposed Decomposition Sequence for Complex 4



In all cases, the loss of the neutral alkyne or alkene capping ligands is well separated from the internal redox process that liberates CO_2, as the latter only takes place above 200 °C. There is no indication of formation of $CuCO_3$ or CuO as the decomposition product, since in each case the final weight is consistent with elemental copper being the only residue.

Conclusion

Six new dinuclear copper(I) oxalate complexes with neutral alkyne and alkene capping ligands have been prepared and fully characterized. X-ray crystal structures of **1** and **3** bearing $Me_3SiC{\equiv}CSiMe_3$ and 3-hexyne as the neutral Lewis base, respectively, provide the first insight into the molecular details of oxalato complexes of copper(I). The characteristics of the oxalato moieties in **1** and **3** turn out to be very similar to those of the heavily studied copper(II) oxalate compounds, while the spectroscopic and structural features of the capping ligands are typical for alkynes and alkenes coordinated to copper(I).

As anticipated, the new complexes show favourable thermal behavior: although the exact pattern of the thermal decomposition is slightly different for the various capping ligands employed, the weight of the residue in each case is consistent with elemental copper being the final product. Their combined properties of straightforward accessibility, good stability at room temperature, and clean thermal conversion to elemental copper make these complexes promising precursors for copper deposition. Since their low volatility hampers their use in conventional CVD, future investigations will focus on alternative liquid delivery approaches such as spin coating and AACVD. Particular advantages of the new complexes are the 100% yield based on copper that results from the internal metal–ligand redox decomposition process, as well as the nontoxicity of the byproduct CO_2.

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Supporting Information Available: Tables of all bond lengths and angles and atomic coordinates and thermal parameters for all X-ray crystal structures reported in this paper; these data are also available as CIF files. This material is available free of charge via the Internet at http::/pubs.acs.org.

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