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Isolation and X-ray Crystal Structures of the Mononuclear Cuprates $[\text{CuMe}_2]^-$, $[\text{CuPh}_2]^-$, and $[\text{Cu}(\text{Br})\text{CH}(\text{SiMe}_3)_2]^-$

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Lithium diorganocuprates (Gilman reagents, LiCuR_2) have been widely used in organic synthesis.² Nevertheless, details for their reaction pathways remain unclear, partly because the structures of the solution species have not been completely defined. Earlier ^1H NMR and molecular weight investigations have suggested the presence of species such as LiCuR_2 , LiCu_2R_3 , $\text{Li}_2\text{Cu}_2\text{R}_3$, or $\text{Li}_2\text{Cu}_3\text{R}_3$ in ether solution.³ Recent work by van Koten, Noltes, and co-workers, using the chelating ligand $2\text{-Me}_2\text{NCH}_2\text{C}_6\text{H}_4^-$, has resulted in the characterization of the complex $[\text{Li}_2\text{Cu}_2(2\text{-Me}_2\text{NCH}_2\text{C}_6\text{H}_4)_4]$ in solution and solid phases.⁴ Work in this laboratory has shown that aggregates involving lithium and copper atom frameworks with simple aryl substituents, e.g., $[\text{Li}_2\text{Cu}_3\text{Ph}_6]^-$, can be isolated and structurally characterized.⁵ Parallel X-ray structural work by Bau et al. has shown that the closely related complexes $[\text{Cu}_3\text{Ph}_6]^-$ and $[\text{LiCu}_4\text{Ph}_6]^-$ can also be present in these solutions.⁶ Further information has come from the use of very large groups such as $-\text{C}_6\text{H}_2\text{Me}_3\text{-2,4,6}$ or $-\text{C}(\text{SiMe}_3)_3$ which has allowed the isolation of the first monomeric organocuprates of formula $[\text{Cu}\{\text{C}(\text{SiMe}_3)_3\}_2]^-$ ⁷ and $[\text{Cu}\{\text{C}_6\text{H}_2\text{Me}_3\text{-2,4,6}\}_2]^-$ ⁸ In these cases it is thought⁷ that, because of the very large substituent size, their structures are not representative of the more frequently encountered lithium cuprates such as "LiCuMe₂" which form polynuclear aggregates in solution. We now report a facile route to simple mononuclear cuprates crystallized as their lithium crown ether salts. These complexes, which have been characterized by

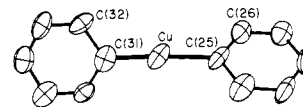
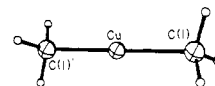


Figure 1. Computer-generated drawings of the anions in **1** and **2**. Selected bond distances (Å) and angles (deg) for $[\text{CuPh}_2]^-$ not given in text: C(25)–C(26) = 1.387 (16); C(26)–C(27) = 1.379 (14); C(27)–C(28) = 1.385 (22); C(28)–C(29) = 1.371 (18); C(29)–C(30) = 1.368 (14); C(25)CuC(31) = 178.5 (4); CuC(25)C(26) = 125.0 (11); CuC(25)C(30) = 122.0 (8); C(25)C(26)C(27) = 123.9 (14); C(26)C(27)C(28) = 120.5 (12); C(27)C(28)C(29) = 118.2 (10); C(28)C(29)C(30) = 120.3 (14); C(29)C(30)C(25) = 124.0 (12). Dihedral angle between the phenyl rings = 47.3 (9)°.

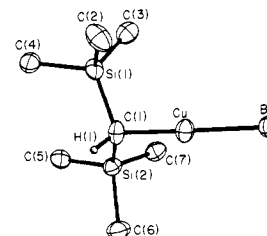


Figure 2. Computer-generated drawing of **3**. Bond distances (Å) and angles (deg) not given in text: Cu–Br = 2.267 (2); C(1)–Si(1) = 1.842 (7); C(1)–Si(2) = 1.837 (8); other Si–C distances average ca. 1.88 Å; C(1)CuBr = 178.7 (2).

X-ray diffraction, are $[\text{Li}(12\text{-crown-4})_2][\text{CuMe}_2]$ (**1**), $[\text{Li}(12\text{-crown-4})_2][\text{CuPh}_2]\cdot\text{THF}$ (**2**), and the intermediate, monosubstituted species $[\text{Li}(12\text{-crown-4})_2][\text{Cu}(\text{Br})\text{CH}(\text{SiMe}_3)_2]\cdot\text{PhMe}$ (**3**).

The compounds **1** and **2** were prepared by the addition of 1 equiv of the halide-free organolithium reagent to 1 equiv of CuI in ether at 0 °C. The slurry was stirred for 15 min and the solid isolated by filtration. Suspension in Et_2O and addition of a second equivalent of MeLi or PhLi gave a clear solution (occasionally slightly colored). Two equivalents of the crown ether were added via syringe and the solid product redissolved in a minimum volume of warm THF. Cooling to –10 °C afforded the products **1** or **2** as colorless crystals in about 50% yield. In the case of the $-\text{CH}(\text{SiMe}_3)_2$ -substituted compound the only product we were able to characterize was **3** which was isolated as colorless crystals by adding a 1:1 toluene/hexane mixture to the THF solution of **3**.

The structures of **1–3** were determined by X-ray crystallography.⁹ Their structures consist of well-separated cations, $[\text{Li}(12\text{-crown-4})_2]^+$, and anions, $[\text{CuMe}_2]^-$, $[\text{CuPh}_2]^-$, or $[\text{Cu}(\text{Br})\text{CH}(\text{SiMe}_3)_2]^-$. The anion structures are illustrated in Figures 1 and 2. In these the copper atom has the rare^{7,8,10} mononuclear, two-coordinate configuration with essentially linear geometry at copper. The Cu–C distances in all three anions are fairly uniform, with values of 1.935 (8), 1.925 (10)_{av}, and 1.920 (6) Å for **1**, **2**, and **3**, respectively. These compare well with bond lengths in other

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(9) Crystal data at 140 K with Mo K α ($\lambda = 0.71069$ Å, **1** and **3**) or Cu K α ($\lambda = 1.54178$ Å, **2**) radiation: **1**, triclinic $P\bar{1}$, $Z = 1$, $a = 7.951$ (4) Å, $b = 8.237$ (7) Å, $c = 9.517$ (6) Å, $\alpha = 88.70$ (6)°, $\beta = 86.59$ (4)°, $\gamma = 61.85$ (6)°, $R = 0.070$ at the present stage of refinement, 90 parameters, 1984 unique observed data. **2**, triclinic $P\bar{1}$, $Z = 2$, $a = 11.859$ (5) Å, $b = 12.483$ (12) Å, $c = 13.634$ (11) Å, $\alpha = 67.59$ (6)°, $\beta = 66.54$ (5)°, $\gamma = 64.61$ (6)°, $R = 0.081$, 388 parameters, 2056 unique observed data. **3**, monoclinic, $P2_1/c$, $Z = 4$, $a = 11.810$ (9) Å, $b = 23.362$ (19) Å, $c = 13.881$ (7) Å, $\beta = 98.21$ (5)°, $R = 0.054$, 395 parameters, 3445 unique observed data.

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cuprates,^{4-6,8} which suggests that the long Cu-C distance seen in $[\text{Cu}\{\text{C}(\text{SiMe}_3)_3\}_2]^-$, 2.027 (7) Å,⁷ may be due to disorder problems involving its isomorphism with $[\text{Li}\{\text{C}(\text{SiMe}_3)_3\}_2]^-$ (see ref 7 for details). The lattices of **2** and **3** also contain THF and toluene. The sandwich structures of the $[\text{Li}(12\text{-crown-4})_2]^+$ cations are very similar to those previously described by us.¹¹ In all three $[\text{Li}(12\text{-crown-4})_2]^+$ cations, the average Li-O distance is 2.37 Å, with a range of 2.21-2.56 Å. Various types of disorder are common in the crown ether rings, and two of these occur in the ring of **1** and in one of the two rings of **3**. Details for **2** and **3** are presented in the supplementary material.¹²

In summary, our results show that monomeric cuprates with commonly used organic substituents are readily obtained simply by adding crown ethers which coordinate lithium. These monomeric compounds are somewhat less soluble than their oligomeric counterparts due to their greater ionic character. Nonetheless they are sufficiently soluble in THF for mechanistic study. Investigations on these organocuprates and other lithium/transition-metal anionic complexes¹³ are continuing.

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Supplementary Material Available: Tables of fractional coordinates, thermal parameters, bond distances and angles, and hydrogen coordinates for $[\text{Li}(12\text{-crown-4})_2][\text{CuPh}_2]\cdot\text{THF}$ and $[\text{Li}(12\text{-crown-4})_2][\text{Cu}(\text{Br})\text{CH}(\text{SiMe}_3)_2]\cdot\text{PhMe}$ (14 pages). Ordering information is given on any current masthead page.

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(12) Details of the structure of **1** and the treatment of the crown ether disorder problem will be submitted for publication to *Acta Crystallographica* by Professor H. Hope.

(13) Olmstead, M. M.; Power, P. P., unpublished work.

Photoisomerization of a Highly Substituted Silene

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The successful isolation of remarkably stable solid silenes $(\text{Me}_3\text{Si})_2\text{Si}=\text{C}(\text{OSiMe}_3)\text{R}$ ($\text{R} = \text{C}_{10}\text{H}_{15} = 1\text{-adamantyl}$ or $\text{R} = \text{CET}_3$)¹ has led us to investigate the effects that the various substituents have on the stability and chemistry of silenes. In the course of this study a remarkable silene-to-silene photochemical rearrangement was observed when one of the silyl groups on silicon in the above silene was replaced by *tert*-butyl.²

Photolysis³ of $(\text{Me}_3\text{Si})_2\text{-}t\text{-BuSiCOC}_{10}\text{H}_{15}$ (**1**)^{4,5} (prepared by coupling of $(\text{Me}_3\text{Si})_2\text{-}t\text{-BuSiLi}$ ⁶ with adamantoyl chloride in 55% yield) in methanol gave two diastereomeric methanol adducts of

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(2) The silene $(\text{Me}_3\text{Si})_2\text{Si}=\text{C}(\text{OSiMe}_3)\text{C}_{10}\text{H}_{15}$ does not rearrange photochemically under similar conditions.

(3) Photolysis employed one to four 100-W Par 38 mercury flood or spot lamps, $\lambda > 360$ nm, usually for 2-24 h.

(4) All new compounds had IR, ¹H, ¹³C, and ²⁹Si NMR, and mass spectral data consistent with the assigned structure. All NMR spectra were run in C₆D₆ unless otherwise noted.

(5) Properties of **1**: mp 87-88 °C; IR 1625 cm⁻¹ (C=O); ¹H NMR 0.30 (18 H, s, Me₃Si), 1.17 (9 H, s, Me₃C), 1.5-2.1 ppm (15 H, m, C₁₀H₁₅); ¹³C NMR 2.13 (Me₃Si), 22.13 (Me₃C), 31.72 (Me₃C), 28.42 (d), 37.04 (t), 37.08 (t), 51.46 (s) (all C₁₀H₁₅ H coupled), 246.53 ppm (C=O); ²⁹Si NMR -15.48 (Me₃Si), -32.24 (Si) ppm.

(6) By cleavage of $(\text{Me}_3\text{Si})_2\text{Si-}t\text{-Bu}$ (from the reaction of *t*-BuSiCl₃, Li, and Me₃SiCl) with MeLi in THF under reflux over 22 h.

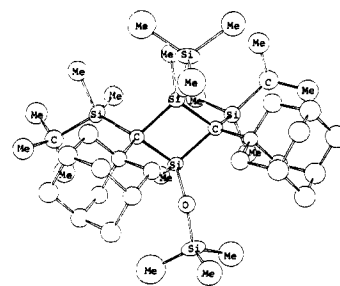
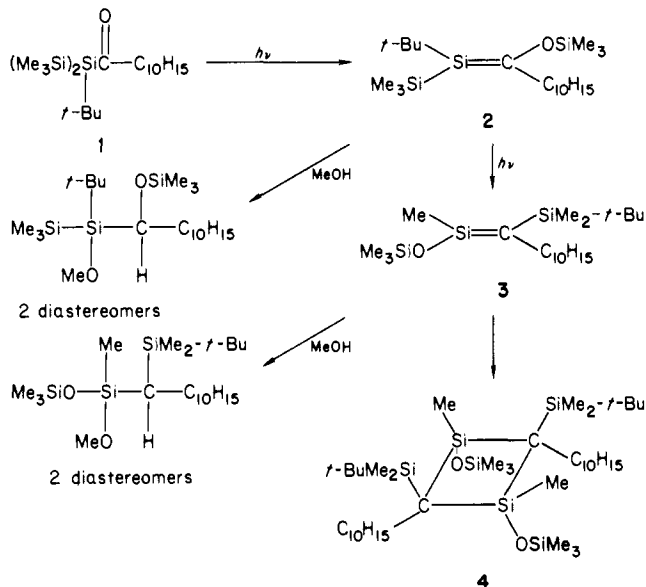


Figure 1. Crystal structure of dimer **4**.

Scheme I



the anticipated silene **2** in about 3:1 proportions. When photolyzed in C₆D₆, NMR signals attributable to the silene **2** were seen to develop⁷ as the acylsilane concentration diminished, but on further irradiation to convert all the acylsilane to silene **2** a new species **3** was formed at the expense of **2**. After prolonged photolysis (but not in the dark where no change occurred) a clean set of NMR signals resulted, attributable to a new silene **3**,⁸ whose structure appeared to have little relationship to that of its precursor **2**. In particular, the ²⁹Si and ¹³C NMR signals due to the sp² hybridized silicon and carbon of **3** were strongly shifted downfield (from 73.7 to 126.5 ppm) and upfield (from 195.6 to 118.1 ppm), respectively, relative to **2**. In addition none of the ²⁹Si NMR signals observed for **3** was upfield of Me₄Si, indicating the probable absence of silicon-silicon bonds in **3**. The new silene (which gave new adducts if treated with methanol) was relatively stable, surviving for time periods varying from a few days to a few weeks before spontaneously disappearing with the simultaneous formation of two dimers, the major one as a precipitate. The spectral properties of the major dimer⁹ were consistent with its being a head-to-tail

(7) Properties of **2**: ¹H NMR 0.33, 0.39 (each 9 H, s, Me₃Si), 1.33 (9 H, s, Me₃C), ca. 1.5-2.2 ppm (C₁₀H₁₅, overlapped); ¹³C NMR 2.13 (Me₃Si, accidental overlap with starting material), 4.47 (Me₃Si), 28.34 (Me₃C), 31.54 (Me₃C), 37.33 (t), 42.34 (t), 29.35 (d), 43.46 (s) (C₁₀H₁₅, DEPT), 195.59 ppm (C=Si); ²⁹Si NMR -13.17 (Me₃Si), 12.25 (Me₃SiO), 73.69 (Si=C) ppm.

(8) Properties of **3**: ¹H NMR 0.19 (9 H, s, Me₃SiO), 0.42 (3 H, s, MeSi), 0.61 (6 H, s, Me₂Si), 1.08 (Me₃C), 1.6-2.2 ppm (C₁₀H₁₅); ¹³C NMR 2.75 (Me₃Si), 4.77 (MeSi), 6.99 (Me₂Si), 21.13 (Me₃C), 28.45 (Me₂C), 30.47 (d), 37.19 (t), 49.03 (t), 39.65 (s), (C₁₀H₁₅, DEPT), 118.07 ppm (C=Si); ²⁹Si NMR (INEPT, H coupled) 6.33 (decet, Me₃SiO), 8.55 (sept, Me₂Si), 126.53 (q, Si=C) ppm.

(9) Properties of **4**: mp 220-222 °C; ¹H NMR (C₆H₆) 0.27 (9 H, s, SiMe₃), 0.43 (6 H, s, SiMe₂), 0.71 (3 H, s, MeSi), 1.14 (9 H, s, CMe₃), 1.54-2.51 ppm (15 H, m, C₁₀H₁₅); ¹³C NMR (CDCl₃), 2.96 (Me₃Si), 8.13 (Me₂Si), 12.57 (Me₂Si), 24.57 (Me₃C), 30.79 (Me₃C), 30.19 (d), 36.55 (t), 44.49 (t), 45.57 (s), (C₁₀H₁₅, DEPT), 50.74 ppm (C ring); ²⁹Si NMR (CDCl₃, INEPT, H coupled), 3.87 (m, Me₂Si), 4.26 (q, MeSi), 7.82 (decet (8 seen), Me₃Si) ppm; MS, *m/e* 788 (M⁺).