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# Dicoordinate Copper(I) Silanechalcogenolates

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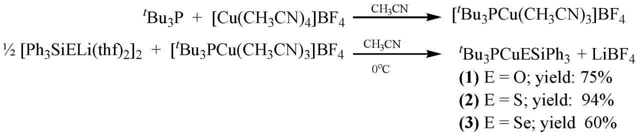
The copper silanechalcogenolates ${}^t$Bu$_3$PCuESiPh$_3$ (**1**, E = O; **2**, E = S; **3**, E = Se) were prepared from the reaction of [${}^t$Bu$_3$PCu(CH$_3$CN)$_3$]BF$_4$ with [Ph$_3$SiELi(THF)$_2$]$_2$ in acetonitrile. The compounds were obtained as colorless, crystalline, but thermally labile solids. X-ray crystallography shows that complexes **1**–**3** are monomeric in the solid state with no Cu···Cu interactions. The Cu atoms have either a linear or a near-linear coordination geometry in all three complexes. Interestingly, the O atom in complex **1** is also linear, which is in contrast to the highly bent S (**2**) and Se analogues (**3**). Density functional theory calculations suggest that both the linear geometry of **1** and an associated extremely short Cu–O distance [1.769(4) Å] are not the result of $\pi$ delocalization but are the result of a fine balance of electrostatic interaction and Pauli repulsion.

Cu$^{\mathrm{I}}$ complexes with the group 16 elements are of great interest as models for metalloprotein active sites,[1] as catalysts,[2] and for use as photovoltaic materials.[3,4] Because of the ability of the group 16 atom to adopt either terminal or bridge bonding modes, complexes of the type L$_n$CuX (L = monodentate phosphine; X = O, S, Se) display a rich coordination chemistry. Bridge bonding allows for the formation of Cu-based oligomers, cluster compounds, and polymers.[5] However, monomeric Cu$^{\mathrm{I}}$ complexes are relatively rare and generally exist either as loose bimolecular aggregates with short Cu···Cu or Cu···X contacts or as structures with a cyclic Cu$_2$X$_2$ core.[6] Nonetheless, discrete monomeric copper(I) chalcogenides may be isolated in systems in which the Cu atom is coordinatively saturated by phosphine ligands and the chalcogen is sterically protected. For instance, the solid-state structures of the copper chalcogenide complexes (R$_3$P)$_3$CuESiMe$_3$ (R = Et, ${}^n$Pr; E = S, Se, Te) show discrete monomeric units with a coordination number of 4 about the Cu atom.[7] These thermally labile complexes are prone to the removal of the silyl group via acetoxydesilylation or thermolysis, resulting in the formation of clusters with extensive chalcogen bridge bonding.[8]

**Scheme 1**



We now report the *first* series of monomeric *dicoordinate* copper(I) silanolates and silanechalcogenolate complexes, ${}^t$Bu$_3$PCuESiPh$_3$ (E = O, S, Se). The sterically demanding ${}^t$Bu$_3$P ligand in conjunction with the bulky silyl chalcogenide ligand both promotes coordinative unsaturation at the Cu center and also prevents association with other molecules. The empty orbitals on the Cu atom are, therefore, potentially available for novel $\pi$-bonding interactions with the lone pairs of the chalcogen atoms.

The compounds ${}^t$Bu$_3$PCuESiPh$_3$ (**1**, E = O; **2**, E = S; **3**, E = Se) have been synthesized in moderate to high yields from the reaction of [${}^t$Bu$_3$PCu(CH$_3$CN)$_3$]BF$_4$ with [Ph$_3$SiELi(THF)$_2$]$_2$ (E = O, S, Se) in acetonitrile (Scheme 1).

Compounds **1**−**3** were isolated as colorless crystalline, air-sensitive solids that decompose before melting (~100 °C), generating black powders. The thermal stability of **1** and **2** is significantly greater than that observed for **3**. Whereas compounds **1** and **2** can be handled briefly at room temperature, compound **3** slowly decomposes in solution even at 0 °C.[9] All compounds gave satisfactory analytical

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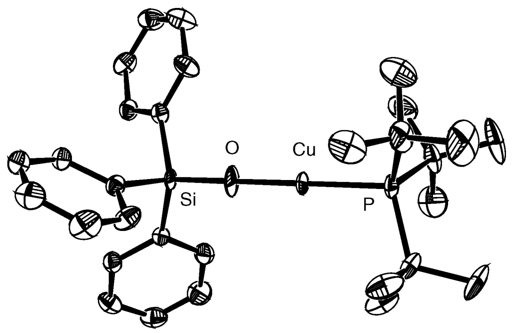

**Figure 1.** Molecular structure of **1** with atomic numbering (ORTEP, 50% probability ellipsoids; H atoms are omitted for clarity). Selected bond lengths (Å) and angles (deg) for **1**: O−Cu, 1.769(4); Cu−P, 2.1496(17); O−Si, 1.578(4); Cu−O−Si, 180.00(1); O−Cu−P, 180.00(1).

and spectroscopic data.[10] Interestingly, the $^{31}P\{^{1}H\}$ NMR spectra of all three complexes show a single broadened resonance due to quadrupolar interactions with the multiple $I > {}^{1}/_{2}$ Cu isotopes in a low-coordinate environment.[11]

X-ray-quality crystals of complexes **1**−**3** were grown from benzene/pentane (1:3) mixtures at low temperatures. The X-ray structures of **1**−**3** reveal that these compounds are monomeric in the solid state and possess a linear coordination environment about the Cu atom. The isolation of coordinatively unsaturated $Cu^{I}$ complexes is a likely result of the combined steric demand of both the phosphine and the chalcogenide moieties.

The copper siloxide (**1**) crystallizes in the $P\bar{3}$ point group; the linear P−Cu−O−Si skeleton lies exactly on a crystallographic 3-fold rotation axis (Figure 1). Two monomeric units of **1** pack in a head-to-tail fashion in the unit cell. Although there are some nonbonding interactions between the peripheral phenyl and isopropyl groups, there are no apparent $d^{10}$−$d^{10}$ Cu···Cu interactions (shortest contact, 8.077 Å).[12] This contrasts with an analogous linear gold siloxide system, $Ph_3PAuOSiPh_3$, which exists as head-to-tail monomers in the unit cell but with a Au···Au interaction distance of 3.376(2) Å.[13] The observed Cu−O bond distance of 1.769(4) Å in **1** is significantly shorter than the Cu−O distances reported for related compounds (hfac)Cu($PMe_3$) [1.990(8) and 2.034(7) Å], (dmp)Cu($PMe_3$) [1.941(5) and 2.030(5) Å], and (dmb)Cu($PMe_3$) [1.985(2) Å] (where hfac = hexafluoroacetylacetonate, dmp = dipivaloylmethanate, and dmb = dibenzoylmethanate).[14]

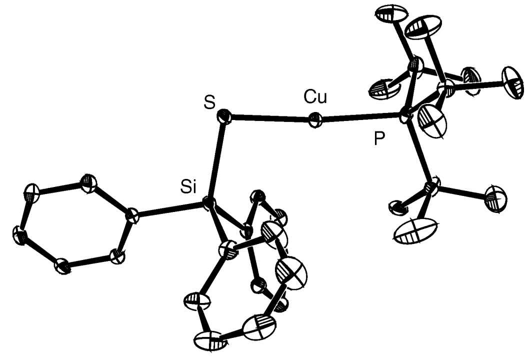

**Figure 2.** Molecular structure of **2** with atomic numbering (ORTEP, 50% probability ellipsoids; H atoms are omitted for clarity). Selected bond lengths (Å) and angles (deg) for **2**: S−Cu, 2.1578(11); Cu−P, 2.2016(10); S−Si, 2.0916(14); Cu−S−Si, 97.63(5); P−Cu−S, 174.12(4).

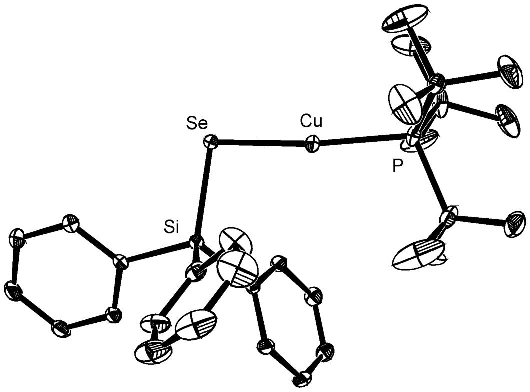

**Figure 3.** Molecular structure of **3** with atomic numbering (ORTEP, 50% probability ellipsoids; H atoms are omitted for clarity). Selected bond lengths (Å) and angles (deg) for **3**: Se−Cu, 2.2650(6); Se−Si, 2.2326(10); Cu−P, 2.2014(10); Cu−Se−Si, 95.27(3); Se−Cu−P, 173.28(3).

The molecular geometries of the S (**2**) and Se (**3**) analogues are shown in Figures 2 and 3, respectively. These isomorphic structures of **2** and **3** show a linear geometry at the Cu atom similar to the siloxide **1**; however, they strikingly differ from the linear siloxide structure by the nearly orthogonal angle at the chalcogen atom [97.63(5)° for **2** and 95.27(3)° for **3**]. Complex **3** is one of the few examples of a terminally bonded copper(I) selenolate complex.

The length of the Cu−S bond in **2** [2.1578(11) Å] is in the normal range for homoleptic copper thiolates: $[Cu(SSiMe_2Bu^t)]_4$[15] [2.1666(4) Å], $[Cu(SSiPh^tBu_2)]_4$ [2.1597(7) Å],[16] and $[Cu(SSiPh_3)]_4$[17] [2.1633(5) Å]. However, the Cu−S bond of **2** is significantly shorter than that reported for $(Et_3P)_3CuSSiMe_3$ [2.4022(5) Å] and $(^nPr_3P)_3CuSSiMe_3$ [2.3970(10) Å]. Complex **3** also shows a shorter Cu−Se bond length when compared with the Cu−Se bond lengths in the analogous complexes $(Et_3P)_3CuSeSiMe_3$ [2.5124(6) Å] and $(^nPr_3P)_3CuSeSiMe_3$ [2.5160(4) Å].[7] The shorter Cu−chalcogen bond lengths in **2** and **3** may be attributed to a combination of diminished sterics at the Cu atom (dicoor-

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[10] **Compound Characterization. 1.** $^{1}H$ NMR ($\delta$, $C_6D_6$): 0.98 (d, 27H, $^{3}J_{H-P}$ = 13 Hz), 7.32 (m, 9H), 8.16 (m, 6H). $^{13}C$ NMR ($\delta$, $C_6D_6$): 142.5 (*o*-Ph), 135.6 (*m*-Ph), 128.4 (*p*-Ph), 36.2 (d, $C(CH_3)_3$), 31.6 (d, $C(CH_3)_3$). $^{31}P$ NMR ($\delta$, $C_6D_6$): 72.17. $^{29}Si$ NMR ($\delta$, $C_6D_6$): −24.29. Elem anal. Calcd: C, 66.57; H, 7.82. Found: C, 66.65; H, 7.25. Mp: 126 °C (dec). **2.** $^{1}H$ NMR ($\delta$, $C_6D_6$): 0.90 (d, 27H, $^{3}J_{H-P}$ = 13 Hz), 7.20 (m, 9H), 8.12 (m, 6H). $^{13}C$ NMR ($\delta$, $C_6D_6$): 141.6 (*o*-Ph), 135.9 (*m*-Ph), 128.4 (*p*-Ph), 36.3 (d, $C(CH_3)_3$), 31.7 (d, $C(CH_3)_3$). $^{31}P$ NMR ($\delta$, $C_6D_6$): 62.4. Elem anal. Calcd: C, 64.65; H, 7.59. Found: C, 64.53; H, 7.07. Mp: >100 °C (dec). **3.** $^{1}H$ NMR ($\delta$, $C_6D_6$): 0.93 (d, 27H, $^{3}J_{H-P}$ = 13 Hz), 7.25 (m, 9H), 7.75 (m, 6H). $^{13}C$ NMR ($\delta$, $C_6D_6$): 140.9 (*o*-Ph), 136.2 (*m*-Ph), 128.6 (*p*-Ph), 36.5 (d, $C(CH_3)_3$), 31.8 (d, $C(CH_3)_3$). $^{31}P$ NMR ($\delta$, $C_6D_6$): 61.2. Mp: >100 °C (dec).

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dinate vs tetracoordinate) and an increase in the nominal "s" character at the Cu ("sp" vs "sp$^3$").

Trends in the Cu−E−Si bond angles for complexes **1**−**3** closely parallel those for the Si−E−Si bond angles of $(Ph_3Si)_2E$. Thus, for $(Ph_3Si)_2E$, $\theta$(Si−E−Si) varies in the series E = O (180°),[18] S [111.94(8)°],[19] Se [110.51(2)°].[20] In addition, the unique bonding in the Cu−O−Si fragment of **1** is manifested not only by its linear geometry but also in some *extremely* short Cu−O and Si−O bond distances. To our knowledge, the Cu−O bond distance of 1.769(4) Å in **1** is the shortest known for a $Cu^I$−O bond.[21] The very short Si−O bond distance of 1.578(4) Å is also notable. In contrast, Cu−E and Si−E (E = S and Se) bond distances found for **2** and **3**, respectively, are more in the expected range.

Traditionally, the siloxane linkage is believed to have considerable multiple-bond character because of dative $\pi$ bonding from the O lone pairs to low-lying acceptor orbitals on the Si, thus giving rise to shorter than expected Si−O bonds and near-linear geometries about the O atom. However, density functional theory (DFT) calculations on $H_3PCuOSiH_3$ suggest that almost no $\pi$ bonding occurs between the O and Cu atoms and that the primary interaction is electrostatic in nature.[22] The combined effects of ionic bonding and Pauli repulsion result in a very flexible bending potential at a significantly bent Cu−O−Si bond. Thus, the equilibrium bond angle $\theta$(Cu−O−Si) found for $H_3PCuOSiH_3$ is 135° but requires only 3 kJ/mol to deform to a linear geometry. In the case of **1**, it is likely that crystal packing forces would be sufficient to stabilize the observed linear geometry. In contrast, DFT calculations indicate predominately covalent interactions for $H_3PCuSSiH_3$ and $H_3PCuSeSiH_3$ with nearly orthogonal bond angles (97.1° and 93.1°, respectively) and a large difference in energy between the bent ground state and the linear transition state (67 and 85 kJ/mol, respectively).[23]

The chemistry of low-coordinate copper(I) silanechalcogenolates is currently being investigated. These coordinatively unsaturated complexes may serve as building blocks to heterobimetallic complexes or as chemical vapor deposition precursors to CuE (E = O, S, Se).

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**Supporting Information Available:** Synthetic procedures and crystallographic data (CIF) for compounds **1**−**3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(23) Details of the calculations will be published in a full paper.