Preparation and Structure of Two Highly Reactive Intermediates: \[[\text{Li(thf)}_2]\text{Cu(SiMe}_3\text{)}_2\]\n
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The large steric requirement and the good solubility of the products in organic solvents make the tris(trimethylsilyl)silyl ligand developed by Gilman and Smith\(^1\) a versatile ligand both in transition metal chemistry\(^2-4\) and main group metal chemistry.\(^5-8\) With this information and the electron-releasing properties of the Si(SiMe\(_3\))\(_2\) unit, we thought that this ligand would also be suitable for the stabilization of intermediates.

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\[^2\] This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

The importance of silyl groups in organic synthesis is unquestioned, but very little is known about the structures of the intermediates involved in lithium cuprate reactions.\(^9,10\) This and a report by Eaborn et al. in 1983 on the preparation and structure of the lithium cuprate \[[\text{Li(thf)}_2]\text{Cu(SiMe}_3\text{)}_2\]\n
This empirical formula can be rationalized as containing four additional Cu\(_3\) units. At the end of the reaction this lithium silylcuprate, similar to that described by Eaborn et al., might be the final product, although we have been unable to confirm that unequivocally. Figure 1 shows the cuprate anion. To our knowledge I is the first structurally characterized lithium silylcuprate,\(^11\) a class of compound which is used more and more in situ in organic synthesis. As yet only one other Si–Cu bond length has been determined by X-ray analysis; that found in \[[\text{Ph}_3\text{SiCu(PMe}_3\text{)}_2\]\n
The molecule has C\(_2\) symmetry. The bridged Cu(I)–Cu(II) bond (2.403(2) Å) is by far the shortest of the Cu–Cu bonds in I and 0.25 Å shorter than the next longest Cu–Cu bond (Cu(1)–Cu(2) 2.654(2); Cu(1)–Cu(3) 2.736(2); Cu(2)–Cu(2a) 2.952(3)). Although slightly shorter Cu–Cu distances are known in complexes where the Cu atoms are forced to come into close contact by chelating ligands...
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The average Si-Si-Si angle (109.96°) in [(Me₅Si)₂SiLi(thf)] is less than the Si--Al bond is much more covalent than the Si--Si bond. The Cu(1)-Cu(2) distance is 2.134(2) Å, and the Cu(1)-Al(1)-Cu(2) angle is 106.34(6)°, indicating that the bond in each case is a three-center two-electron bond. The Cu(1)-Cu(2) distance proves that the Si-Li bond is not a simple Si-Li bond but is rather a Si-Li(thf) bond.

The reaction product is the aluminate in [Li(thf)]⁺[AlCl₃(SiMe₃)]⁻. The structure of [Li(thf)]⁺[AlCl₃(SiMe₃)]⁻ is again the cation (Fig. 2). This molecule may be written as [AlCl₃(SiMe₃)]⁻[Li(thf)]⁺.

The blocks began to grow. Single crystals suitable for an X-ray structure analysis were mounted directly on the goniometer and cooled crystal (dimensions 0.5 × 0.4 × 0.2 mm) in a stream of nitrogen at room temperature. After the white precipitate that was formed had been filtered off the solution was stored at -30 °C. After 2 days, colorless crystals of 2 were obtained at -30 °C. Their spectroscopic data were identical to those reported in the literature. The absolute structure has been determined by refining the Flack parameter to 0.021 (22). The Flack parameter was refined to be 0.044 and its reliability factor R was 0.113 (all data). The absolute structure has been determined by refining the Flack parameter to 0.022 (23).

The structure of 2 in the solid state. Selected bond lengths [Å] and angles [°]: Si(1)-Al(1) 2.446(1), Si(2)-Si(3) 1.941(1), Al(1)-Cl(1) 2.16(1), Si-Si 1.89(1) Å, Cl-Al-Ci 106.34(6)°, those marked with an asterisk are average values.

In the structure of 2, the Si-Si bond length is 2.446(1) Å, which is longer than the average Si-Si bond length in [(Me₅Si)₂SiLi(thf)]. The average Si-Si angle is 109.96° in 2, which is smaller than the average Si-Si angle in [(Me₅Si)₂SiLi(thf)] (115°). The Si-Si bond is much more covalent than the Si-Li bond. The Si-Si angle in [(Me₅Si)₂SiLi(thf)] is 107.7°. The Si-Si bond in 2 is closer to the ideal Si-Si bond in the silicon crystal (111°). The Si-Si bond in 2 is more covalent than the Si-Li bond in [(Me₅Si)₂SiLi(thf)].

The Experimental Procedure

1. A solution of [(Me₅Si)₂SiLi(thf)] in modified preparation ref [12]. (1.88 g, 4.0 mmol) in pentane (5 mL) was added to CuCl (1 g, 10 mmol) in THF at -78 °C over 2 h. A dark purple solution was formed and, after removal of the pentane THF solvent, cold toluene added, and the solution was cooled to -30 °C. A brown powder of LiCl, CuCl₂, and Cu precipitated slowly. After 14 h at -30 °C, cubic, air-sensitive, and extremely thermolabile blocks, identified as LiCl, were isolated. Yield = 20%, dec. temp. > 30 °C. color: deep purple. Because of the extreme sensitivity of the compound it was not possible to obtain any spectroscopic data.

2. A solution of [(Me₅Si)₂SiLi(thf)] (modified preparation ref [12], 2.0 g, 4.3 mmol) in toluene (25 mL) was added to a suspension of AI₂C₁₃ (0.5 g, 3.8 mmol) in toluene (20 mL, 123 K, 24 h). The solution was stirred for 7 h at -78 °C, then for 10 h at 0 °C and finally for 7 h at room temperature. The white precipitate, which formed during stirring, was filtered off. A white precipitate was formed from the clear solution at -30 °C, which was redisolved by adding cold THF (3 mL). After 2 days, colorless crystals of 2 were obtained at -30 °C. Yield 70%, decomp 7%.

Received: September 3, 1992. [J 5554E] German version: Angew. Chem. 1993, 105, 90

[13] Crystal Data: C₅H₉Al₂[AlCl₃Li₄], Mᵢ = 325.41, monoclinic, space group C2, a = 26.106(6), b = 9.320(3), c = 14.758(4) Å, β = 123.97(2)°, V = 9767(6) Å³, Z = 2, g = 1.394 M·g⁻¹·cm⁻³, F(000) = 3170, λ = 0.7107 Å, F(100) = 213 mm⁻¹, data were collected on a Stoe-Siemens AED diffractometer. Intensities of a rapidly cooled crystal (dimensions 0.5 × 0.4 × 0.2 mm) in an oil drop were collected with a 2θ/ω method in the range θ = 5–26°. Of the 2095 collected reflections, 2083 were independent and corrected for absorption with a semiempirical method, largest difference maximum and minimum: 0.85 and -0.80 eÅ⁻³, R = 0.044 and wR = 0.113 (all data). The absolute structure has been determined by refining the Flack parameter to 0.022 (23).
[14] R. A. Cowley, W. E. G. Brown, J. Chem. Soc. Chem. Commun. 1976, 3525–3528. Structures of both were solved with direct methods (SHELXS-90) [24] and refined by full-matrix least-squares of F² (SHELXL-92) [25]. The hydrogen atom positions were refined with a riding model where the CH₂ groups were free to rotate around their local C-C bonds. Further details of the crystal structure investigations are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, GB-Cambridge CB2 1EW (UK), on quoting the full journal citation.