$[Cu_2R_2BrLi(thf)_3]$, R = $Si(SiMe_3)_3$—a Complex containing Five-coordinate Silicon in a Three-centre Two-electron Bond (thf = tetrahydrofuran)

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The title compound is obtained from the reaction of $(Me_3Si)_3SiLi(thf)_3$ with CuBr in *n*-hexane and structurally characterised by X-ray diffraction; in $[Cu_2R_2BrLi(thf)_3]$, R = $Si(SiMe_3)_3$ one silyl ligand is bridging a very short Cu–Cu bond, resulting in a three-centre two-electron bond, while the second is terminally bound to copper; the other copper atom is linked to a lithium atom *via* a Cu···Br···Li bridge.

Recently, we have reported the synthesis and structure of the lithium silyl cuprate $[Li(thf)_4][Cu_5Cl_4\{Si(SiMe_3)_3\}_2]$[1] from the reaction of $[(Me_3Si)_3SiLi(thf)_3]$[2–4] with copper(I) chloride. This was the first successful isolation of a lithium silyl cuprate. The tris(trimethylsilyl)silyl ligand is extremely good at stabilising metal complexes in low coordination numbers.[5] The growing interest in organocopper compounds, in particular the consideration of the theoretical aspects, encouraged us to react the tris(trimethylsilyl)silyl ligand with copper(I) bromide.

The different reactivity of Cu^{I}Br compared with that of Cu^{I}Cl should give rise to different unprecedented intermediates in the lithium silyl cuprate reaction. More commonly, these species have been employed as *in situ* reagents in both organic and inorganic synthesis. The use of silyl cuprates[6] and more recently even of stannyl cuprates[7] in organic synthesis was pioneered by Fleming.

We reacted Cu^{I}Br with [(Me$_3$Si)$_3$SiLi(thf)$_3$] in 1 : 1 ratio at −78 °C. Pure (Me$_3$Si)$_3$SiLi(thf)$_3$ is extremely pyrophoric and should be handled with care.[4] All manipulations should be performed under an inert atmosphere of dry argon. The reaction mixture was allowed to warm to room temp. and immediately cooled to −35 °C.†

$$2\,\mathrm{CuBr} + 2\,(\mathrm{Me_3Si})_3\mathrm{SiLi(thf)_3} \xrightarrow[-\mathrm{LiBr}]{\mathrm{thf}} [\mathrm{Cu_2\{Si(SiMe_3)_3\}_2BrLi(thf)_3}]$$

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Under these conditions the title compound **1** was isolated and structurally characterised. The complex was found to be extremely air- and moisture-sensitive. During crystal selection and mounting, the flask and the flushing argon were cooled to *ca.* −50 °C. A portion of crystals was scooped up and covered with cold inert oil from a syringe. The sample was then transferred to a microscope slide, which was cooled by a nitrogen stream. At *ca.* −50 °C a suitable single crystal was selected and transferred to the diffractometer.[8] A low-temperature X-ray crystallographic study‡ shows **1**, in contrast to [Li(thf)$_4$][Cu$_5$Cl$_4${Si(SiMe$_3$)$_3$}$_2$], to be a contact ion pair.

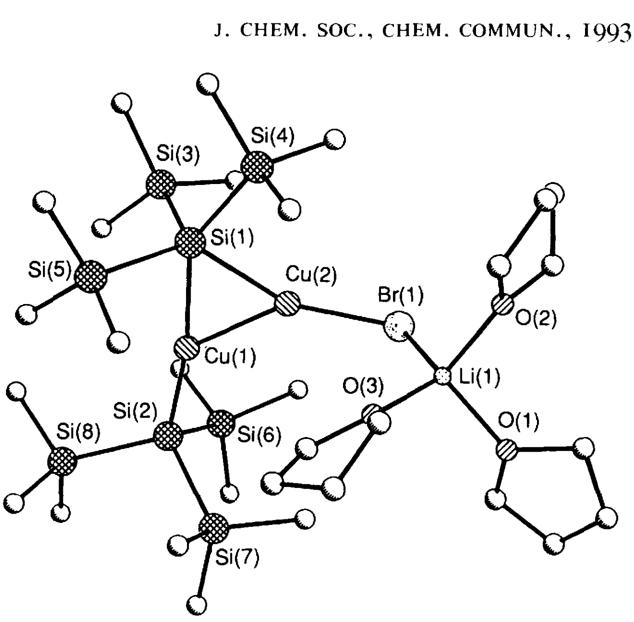

Fig. 1 Molecular structure of **1**; selected bond lengths (pm) and angles (°): Cu(1)–Cu(2) 236.9(1), Cu(1)–Si(1) 240.6(2), Cu(1)–Si(2) 226.6(2), Cu(2)–Si(1) 228.3(2), Cu(2)–Br(1) 226.0(5), Br(1)–Li(1) 250(1), mean Si(1)–Si 234.7(3), mean Si(2)–Si 232.7(3); Si(1)–Cu(1)–Si(2) 170.5(1), Br(1)–Cu(2)–Si(1) 158.5(2), Cu(2)–Br(1)–Li(1) 107.7(2), mean Si–Si(1)–Si 109.0(1), mean Si–Si(2)–Si 106.8(1).

Compound **1** is the first isolated and structurally characterized silyl cuprate containing an additional LiBr equivalent and with two differently bound (Me$_3$Si)$_3$Si groups. The tris(trimethylsilyl)silyl group around Si(1) is coordinated side on to a very short Cu(1)–Cu(2) bond, leading to a five-coordinate central Si(1) atom. The Cu(1)–Cu(2) distance is 236.9(1) pm and although some shorter Cu–Cu distances are known [234.8(1) and 236.1(1) pm],[9–11] this distance falls into the lower end of the range observed in copper clusters, especially considering that here the copper centres are not forced into close contact by chelating ligands. The three-centre two-electron bond does not form an equilateral triangle. While the Si(1)–Cu(2) bond is 228.3(2) pm long, the Si(1)–Cu(1) bond is more than 12 pm longer [240.6(2) pm]. The shortest Si–Cu bond is that of the terminally-bound tris(trimethylsilyl)silyl group around Si(2) and Cu(1) [226.6(2) pm]. In view of the two other known Cu–Si distances (in Ph$_3$SiCu(PMe$_3$)$_3$: 234.0(2)[12] and in [Li(thf)$_4$][Cu$_5$Cl$_4${Si(SiMe$_3$)$_3$}$_2$]: av. 234.1(3) pm[1]), this bond seems to be very short. Cu(2) is coordinated by a (thf)$_3$LiBr group. The Cu(2)–Br(1) distance of 226.0(5) pm is notably longer than in CuBr (217.3 pm),[13] but comparable to the published value in [CuBrCH(SiMe$_3$)$_2$]$^-$ [226.7(2) pm].[14] The Li–Br bond length is 250(1) pm and comparable to the distances found in molecular lithium bromide [250.8 pm in coordination to pmdta {pmdta = MeN(CH$_2$CH$_2$NMe$_2$)$_2$} and 251.5 and 255.1 pm, respectively, as dimeric compound with acetone].[15,16]

Therefore, the (thf)$_3$LiBr group could be considered as the leaving group of the intermediate. When reacted further Cu$_2${Si(SiMe$_3$)$_3$}$_2$ might be the product. On the other hand CuBr might leave the complex to give [Li(thf)$_4$][Cu{Si(SiMe$_3$)}$_2$], which would presumably be isostructural with [Li(thf)$_4$][Cu{C(SiMe$_3$)$_3$}$_2$].[17] Further experiments to isolate other intermediates in the reactions of copper(I) halides, as well as to elucidate the final products, are underway.

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† *Preparative details and spectroscopic data*: A suspension of 0.60 g CuBr (4.2 mmol) in 25 ml *n*-hexane was mixed dropwise with 3.95 g [(Me$_3$Si)$_3$SiLi(thf)$_3$] (8.4 mmol) in 21 ml thf, during 1 h at −78 °C. The solution was stirred for another 12 h under warming to −20 °C and then 3 h at room temp. The solvent was removed under reduced pressure and the oily residue was dispersed in 25 ml *n*-pentane and filtered after 2 h of stirring. A clear and a red-brown phase were obtained. After 3 d at −35 °C small crystals grew at the phase boundary, which were suitable for an X-ray determination. 0.91 g (23%) of colourless crystals were obtained. The compound decomposes above 124 °C. MS [*m*/*z* (%)]: EI 247 (32) Si(SiMe$_3$)$_3$ and 73 (100) SiMe$_3$; IR ν/cm^{-1}: 2051s, 1260s, 1245m, 1091m, 837vs, 689m; NMR (in C$_6$D$_6$): δ_H 0.25 [s, 27 H, Si(SiMe$_3$)$_3$], 0.36 [s, 27 H, Si(SiMe$_3$)$_3$], 1.46 [m, 12 H, OCH$_2$CH$_2$], 3.56 [m, 12 H, OCH$_2$CH$_2$]; $\delta_{^{29}Si}$ −9.49 [Si(*Si*Me$_3$)$_3$], −11.44 [Si(*Si*Me$_3$)$_3$], −115.97 [*Si*(SiMe$_3$)$_3$], −129.88 [*Si*(SiMe$_3$)$_3$].

‡ *Crystal data* for C$_{30}$H$_{78}$BrCu$_2$LiO$_3$Si$_8$ **1**: monoclinic, space group $P2_1/n$, a = 1422.6(4), b = 1637.3(4), c = 2240.9(4) pm, β = 100.68(1)°, U = 5.129 nm^3, Z = 4, D_c = 1.199 g cm^{-3}, μ = 1.820 mm^{-1}, F(000) = 1960. A crystal (0.7 × 0.6 × 0.5 mm) was mounted on a Stoe-Siemens AED four circle diffractometer. 7471 reflections were measured at −120 °C using Mo-Kα radiation (α = 71.073 pm) giving 6662 independent data, of which 6661 were employed for all calculations. An oil-coated shock-cooled crystal[8] was used. An empirical absorption correction using the program SHELXA-90[18] was employed. The structure was determined by direct methods (SHELXS-90).[19] All non-hydrogen atoms were refined anisotropically (SHELXL-93).[20] The bromine atom was disordered, both positions having the same occupancy. Cu–Br and Cu–Li distances were restrained. The thf molecules were severely disordered. 1–2 and 1–3 distance restraints were employed, and also rigid bond and similarity restraints were applied for the anisotropic displacement parameters. A riding model starting from calculated positions was employed for the hydrogen atoms, a total of 613 restraints were used and 514 parameters were refined. The structures were refined against F^2 with a weighting scheme of $w^{-1} = \sigma^2(F_o^2) + (0.0790P)^2 + 7.56P$ with $P = (F_o^2 + 2F_c^2)/3$. The $R2$ value based on F^2 for all data is defined as $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$ and the final $R1$ for $[F \geqslant 4\sigma(F)]$ is defined as $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. The final $R1$ $[F \geqslant 4\sigma(F)]$ and $R2$ values are 0.057 and 0.169, respectively. The final difference electron density map showed a maximum of 663 e nm^{-3}. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

Germany) for providing the perfluorinated polyethers used for crystal mounting.

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