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Preliminary communication

PREPARATION AND CRYSTAL STRUCTURE OF THE TETRAHYDROFURAN ADDUCT OF LITHIUM BIS[TRIS(TRIMETHYLSILYL)METHYL]CUPRATE, $[Li(THF)_4][Cu\{C(SiMe_3)_3\}_2]$. THE FIRST STRUCTURAL CHARACTERIZATION OF A GILMAN REAGENT

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Summary

A crystal structure determination on the product of the reaction between tris(trimethylsilyl)methyllithium and copper(I) iodide has shown it to be the lithium dialkylcuprate $[Li(THF)_4][Cu\{C(SiMe_3)_3\}_2]$, which is isomorphous with the corresponding lithium ate complex $[Li(THF)_4][Li\{C(SiMe_3)_3\}_2]$.

Gilman reagents, lithium diorganocuprates, are usually assumed to be dimeric species [1], but none has previously been structurally characterized. We have now carried out a crystal structure determination on the product of the reaction of the organolithium reagent I with copper(I) iodide, which shows it to be the dialkyl cuprate II. This represents the first structural characterization of a lithium diorganocuprate*, or of any dialkylcuprate, but the structure of a copper diarylcuprate (III, dppe = 1,2-bis(diphenylphosphinoethane)) was recently reported [2].

$[Li(THF)_4][Li\{C(SiMe_3)_3\}_2]$ (I)
$[Li(THF)_4][Cu\{C(SiMe_3)_3\}_2]$ (II)
$[Cu(dppe)_2][Cu(C_6H_2Me_3\text{-}2,4,6)_2]$ (III)
$[Li(tmeda)_2][Li\{C(SiMe_3)_3\}_2]$ (IV)

A solution of I [3] (5.15 g, 6.7 mmol) in Et_2O (20 cm^3) was added dropwise to a stirred suspension of CuI (2.5 g, 13 mmol) in Et_2O (15 cm^3) at −60°C. The mixture was allowed to warm to room temperature with stirring, and stirred for

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*It is fitting that the first structurally characterized Gilman reagent should contain silicon, another element with which Professor Gilman's name is closely associated.

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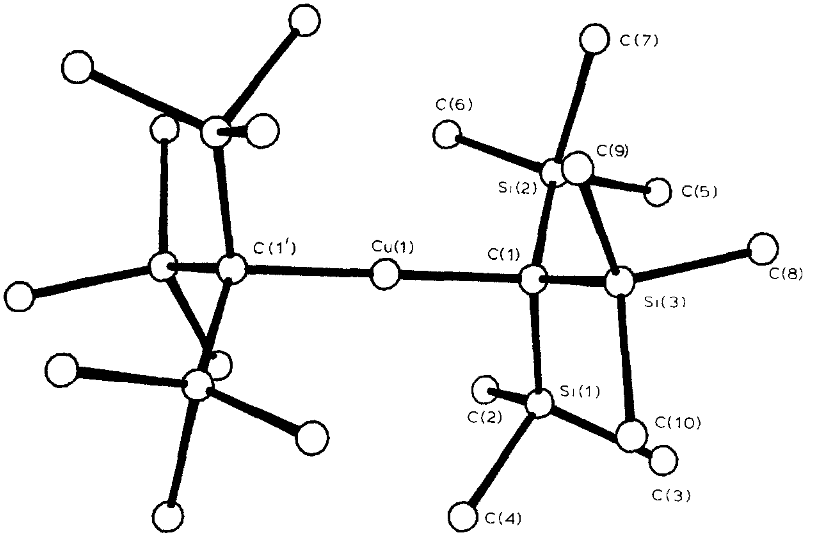

Fig. 1. The structure of one of the anions of $[Li(THF)_4][Cu\{C(SiMe_3)_3\}_2]$.

a further 12 h. The solvent was removed in vacuo and the residue was extracted with toluene. The toluene extract was filtered through Celite, then kept at −10° C, when it deposited long needles of II (1.43 g, 26%). The crystal used for the diffraction study was taken from a second crop obtained by concentrating and cooling the mother liquor*.

Crystal data: $C_{36}H_{86}CuLiO_4Si_6$, M = 822.1, triclinic, a 9.404(5), b 11.946(3), c 23.262(10) Å, α 94.37(3), β 89.98(4), γ 94.35(3)°, U 2598.1 $Å^{-3}$, Z = 2, D_c 1.05 g cm^{-3}, F_{000} = 900. Monochromated Mo-K_α radiation, λ 0.71069 Å, μ 6.0 cm^{-1}. Space group $P\bar{1}$ from successful refinement.

Intensities for unique reflections with $\theta < 18°$ were measured on a CAD 4 diffractometer using a crystal sealed in a capillary under argon, and 2500 reflections with $|F^2| > \sigma(F^2)$ were used in the refinement. The structure was found to be isomorphous with that of the lithium analogue I [3], and to contain two non-equivalent $[Cu\{C(SiMe_3)_3\}_2]^-$ anions. Successful refinement required the assumption that some iso-structural $[Li\{C(SiMe_3)_3\}_2]^-$ anions were incorporated in a random manner at the Cu(2) site centred on 0,0,0, the Cu and Li occupancies of the site being in ca. 60/40 ratio. Refinement with all atoms anisotropic then converged at R = 0.144, R' = 0.169**. Hydrogen atoms were not included.

The two cuprate anions lie across inversion centres and are therefore linear (as are those in III) with the $C(SiMe_3)_3$ groups staggered about the C—Cu—C direction (see Fig. 1). Within experimental error the two anions have the same geometry (the Cu(1)—C(1) and Cu(2)—C(11) bond lengths are 2.027(7) and

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*Compound II was the main product isolated for a wide range of reactant ratios; an excess of the copper(I) iodide was used in the reported preparation in the hope of minimizing the amount of residual I. The cuprate is very difficult to handle because of its high reactivity, and many crystals were rejected before the one used gave acceptable diffraction data.

**The atomic coordinates are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

2.070(9) Å, though because of the Cu—Li disorder the latter value is rather unreliable), but the interionic interactions must be sufficiently different to account for the fact that the lithium appears essentially at only the Cu(2) site. (We cannot rule out the possibility that a little Li is incorporated at the Cu(1) site, but the amount is unlikely to be large enough to affect the observed Cu(1)—C(1) bond length.) The lengths of the Cu—C bonds are close to those of the Li—C bonds in I (Li(1)—C(1) 2.16, Li(2)—Cu(11) 2.20 Å) [1]; they are longer than those of the Cu—C bonds in III (1.915(9)) [2], as expected from the difference in hybridization at the attached carbon centres.

It is noteworthy that the observed lengths of the Si—Me bonds (mean 1.95 Å) are larger than those of the Me_3Si—C bonds (mean 1.84 Å), as they are in I (1.95 and 1.82 Å), and in the closely related lithium ate species IV (tmeda = $Me_2NCH_2CH_2NMe_2$) (1.98 and 1.83 Å) [4], whereas for all other known structures of tris(trimethylsilyl)methyl derivatives, including the mercurial $Hg[C(SiMe_3)_2]_2$ [5], the opposite is the case (see ref. 3). For none of the complexes I, II, and IV separately are the data reliable enough to give confidence in the actuality of this apparent inversion of the usual behaviour*, but the close similarity of the results in all three cases suggests that it may be real. Calculations on the model anion $[LiMe_2]^-$ indicate that all the negative charge is shared between the two carbon atoms [6], and if this is the case in the complexes I, II, and IV, delocalization of the electronic excess into the Me_3Si groups could result in shortening of the C—$SiMe_3$ and consequent lengthening of the Si—Me bonds; the stability of the carbanion $(Me_3Si)_3C^-$ [7] and the shortness of the central C—Si bond (1.83 Å) in the 9-[(chlorobis(trimethylsilylmethyl)silyl]-fluoren-9-yl carbanion [8] may be relevant observations, although in this last case the carbionic carbon atom is sp^2-hybridized.

There is, of course, no implication that the more commonly encountered lithium dialkylcuprates have structures analogous to that of II. The monomeric structure of the latter may be favoured because the bulk of the $(Me_3Si)_3C$ group inhibits the alkyl-bridging between Li and Cu which is usually assumed to be present in simple diorganocuprates.

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*In the case of IV the *R* value, 0.093, is lower, but the reliability of the derived parameters is reduced by disorder associated with the occupancies of alternative Si sites in the anions [4].