A Novel Monomeric Alkyl-lithium Compound. Crystal Structure of [Li{C(SiMe$_2$Ph)$_3$}(tetrahydrofuran)]

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A crystal structure determination on the tetrahydrofuran (thf) adduct of tris(phenyldimethylsilyl)methyl-lithium has shown it to be a monomeric species [Li{C(SiMe$_2$Ph)$_3$}(thf)] in which the lithium is covalently bonded to oxygen and to the central carbon of the (Me$_2$PhSi)$_3$C group and interacts strongly with the *ipso* carbon atom of one of the phenyl groups without significantly distorting the hybridization at that atom.

We recently described the structure of the tetrahydrofuran adduct of tris(trimethylsilyl)methyl-lithium, showing it to be the first isolated lithium ate complex, [Li(thf)$_4$] [Li{C(SiMe$_3$)$_3$}$_2$].[1] We now present the results of an *X*-ray diffraction study of the thf adduct of the closely related tris(phenyldimethylsilyl)methyl-lithium, which has a very different and wholly novel structure.

A solution of tris(phenyldimethylsilyl)methane in thf was added to an equimolar amount of methyl-lithium, and the resulting solution was kept at the reflux temperature for 6 h and then at room temperature for 12 h. The thf was removed *in vacuo*, and the residue was extracted with heptane. The heptane solution was filtered, concentrated, and kept at -10 °C to give colourless prisms of [Li{C(SiMe$_2$Ph)$_3$}(thf)] (67%); ^{1}H n.m.r. (in C$_6$D$_6$ relative to external SiMe$_4$), δ 0.62 (s, 18H, SiMe$_2$), 1.0 (m, 4H, CH$_2$), 2.80 (m, 4H, CH$_2$), and 7.0—7.8 (m, 15H, C$_6$H$_5$) (the chemical shifts for the thf protons are noteworthy; the corresponding values for thf itself under similar conditions were δ 1.45 and 3.45); ^{7}Li n.m.r. (in toluene–[^{2}H$_8$]toluene relative to LiNO$_3$–D$_2$O), 2.90 p.p.m.

Crystal data: $C_{29}H_{41}LiOSi_3$, $M = 496.9$, orthorhombic, space group $Pca2_1$, $a = 18.069(3)$, $b = 9.732(2)$, $c = 17.256(3)$ Å, $U = 3034.4$ Å^3, $Z = 4$, $D_c = 1.09$ g cm^{-3}; $F(000) = 1072$. Monochromated Mo-K_α radiation, $\mu = 1.7$ cm^{-1}. $R = 0.069$, $R' = 0.081$ for 984 unique reflections with $|F^2| > \sigma(F^2)$, measured on an Enraf-Nonius CAD 4 diffractometer in the range $2 < \theta < 20°$.†

The structure is shown in Figure 1. It will be seen that there are two ordinary covalent bonds to Li, one from C(1) [length 2.12(2) Å] and one from oxygen [length 1.85(2) Å], and a weaker but still strong interaction between the lithium and the *ipso*-carbon atom, C(12) of one of the Ph groups; the Li–C(12) distance is 2.40(2) Å, which compares with the value of 2.278 Å for the longer bond between Li and the *ipso*-carbon of the bridging Ph in the dimeric species [LiPh(tmeda)]$_2$ (tmeda = Me$_2$N[CH$_2$]$_2$NMe$_2$).[2] This interaction between the π-electrons near C(12) and the Li does not significantly change the hybridization at C(12), since the attached silicon atom Si(2) lies almost exactly in the plane of the phenyl ring, and the geometry of this ring is not significantly different from that of the remote ring containing C(20). At first sight it would appear that the Li atom simply moves over towards the π-electrons around C(12) [resulting in an Li–C(1)–Si(2) angle of 89.7(7)° and an Li–C(12)–Si(2) angle of 79.0(6)°] without any responsive movement of the phenyl group towards the lithium, since the C(1)–Si(2)–C(12) angle, 107.4(5)°, is close to the tetrahedral value, but this may be deceptive, since without the interaction this angle would be expected to be markedly larger; *e.g.*, the C(1)–Si(3)–C(20) angle is 116.5(5)°, matching the C(1)–Si–Ph angle of 116.4(3)° in (Me$_3$Si)$_3$CSiMe$_2$Ph,[3] and even in the less crowded (Me$_2$PhSi)$_3$CH the C(1)–Si–Ph angles are 111.2°.[4]

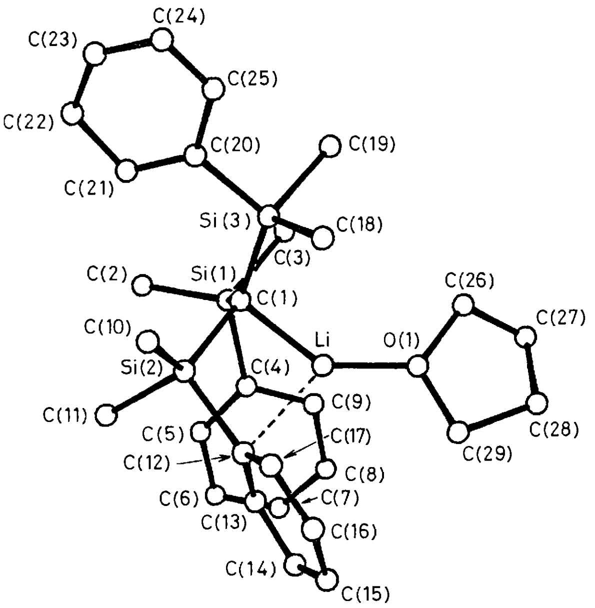

Figure 1. Molecular structure of [Li{C(SiMe$_2$Ph)$_3$}(thf)] with H atoms omitted. Selected dimensions: Li–C(1) 2.12(2), Li–C(12) 2.40(2), Li–O(1) 1.85(2), Si(1)–C(1) 1.954(14), Si(2)–C(1) 1.819(12), Si(3)–C(1) 1.786(12), Si(1)–C(4) 1.865(12), Si(2)–C(12) 1.939(13), and Si(3)–C(20) 1.897(12) Å; C(1)–Li–C(12) 83.9(8), C(1)–Li–O(1) 144(1), C(12)–Li–O(1) 129(1), C(1)–Si(1)–C(2) 116.7(5), C(1)–Si(1)–C(3) 114.8(5), C(1)–Si(1)–C(4) 108.4(6), C(1)–Si(2)–C(10) 114.5(6), C(1)–Si(2)–C(11) 122.1(6), C(1)–Si(2)–C(12) 107.4(5), C(1)–Si(3)–C(18) 109.7(6), C(1)–Si(3)–C(19) 121.4(6), C(1)–Si(3)–C(20) 116.5(5), Li–C(1)–Si(1) 99.9(8), Li–C(1)–Si(2) 89.7(7), Li–C(12)–Si(2) 79.0(6), and Li–C(1)–Si(3) 105.0(7)°.

There is substantial distortion around the other two SiMe$_2$Ph groups. Thus the Li–C(1)–Si(1) angle is only 99.9(8)° and the C(1)–Si(1)–C(4) angle only 108.4(6)°; this is not, however, the result of an interaction between the Li and C(4) [corresponding to but weaker than that to C(12)], since the Li–C(4) distance is 3.14 Å. More surprising is the distortion around the more remote SiMe$_2$Ph group; while the C(1)–Si(3)–C(20) angle, 116.5(5)°, is normal (see above) for a crowded system of this type, one of the C(1)–Si(3)–Me angles [that to C(19)] is abnormally large, *viz.* 121.4(6)°, and the other [to C(18)] is 109.7(6), resulting in a C(18)–Si(3)–C(19) angle of 98.7(7)°. As a possible explanation of this distortion we looked for an interaction between the C(18) methyl group and the lithium, but the Li–C(18) and Li–H(18C) distances of 3.23 and 2.82 Å (the H atoms being assumed to be in calculated positions) rule this out.

A noteworthy feature is that the C(1)–Si(1) bond is rather long, *viz.* 1.954(14) Å, and the C(1)–Si(2) and C(1)–Si(3) bonds are unusually short, *viz.* 1.819(12) and 1.786(12) Å, respectively.

There is a rather distorted trigonal arrangement of ligands around the lithium; the relevant angles are C(1)–Li–O 144(1),

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† The atomic co-ordinates for this work 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.

C(1)–Li–C(12) 83.9(8), and O–Li–C(12) 129(1)°, with the lithium 0.14 Å out of the plane defined by C(1), O, and C(12) (in a direction below the plane of the paper in Figure 1).‡ Presumably the steric hindrance is too great to allow attachment of a second thf molecule to give the normally favoured four-co-ordination at Li, but it is not obvious why an ate structure, such as that adopted by tris(trimethylsilyl)methyllithium, is disfavoured.

Further details of the structure and some aspects of the chemistry of the novel alkyl-lithium compound will be described elsewhere.

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‡ There is no intermolecular approach to the lithium atom of less than 4.5 Å.