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An Alkyllithium Compound with a Free Planar Carbanion. The Crystal Structure of $[Li(THF)_4][C(SiMe_2C_6H_4Me\text{-}o)_3]$

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Summary: The title compound, ***1****, has been made by an improved method involving treatment of* $(o\text{-}MeC_6H_4Me_2Si)_3CH$ *with LiBu in the presence of tetramethylethylenediamine in a hexane−heptane mixture at room temperature followed by crystallization of the product from a mixture of heptane and tetrahydrofuran (THF). In contrast to solid* $Li\{C(SiMe_2Ph)_3\}(THF)$*, which has a molecular structure with a C−Li bond and a Ph−Li interaction,* ***1*** *contains a discrete planar carbanion with no such interaction.*

Introduction

Alkali metal compounds containing the very bulky ligands $(Me_3Si)_3C$, R*, or $(PhMe_2Si)_3C$, R**, show a remarkable range of crystal structures.[1] The compound LiR* can be obtained as a solvent-free dimer with a $Li(\mu\text{-}R^*)_2Li$ core and supplementary agostic Me−Li interactions[2] or as solvated ate complexes $[Li(THF)_4][LiR_2^*]$ (THF = tetrahydrofuran)[3] or $[Li(TMEDA)_2][LiR_2^*]$ (TMEDA = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine).[4] The sodium compound NaR* also forms a solvated ate complex, $[Na(TMEDA)_2(Et_2O)][NaR^*_2]$,[5] but the corresponding potassium[6] and rubidium[7] compounds crystallize even from ether solutions as solvent-free linear arrays of alternate cations and planar carbanions, but with agostic interactions between the metal atoms and some of the Me groups. The cesium analogue crystallizes from benzene with three molecules of the latter solvating the metal and a lattice consisting of discrete ion pairs.[7] The solvated species LiR**(THF) has a molecular structure in which the Li atom interacts with the *ipso* carbon of a Ph group.[1,8] The solvent-free MR** species with M = Na,[5] K,[6] Rb,[9] and Cs[9] crystallize from THF with polymeric structures involving both intra- and intermolecular metal−phenyl interactions.

$R^* = (Me_3Si)_3C \qquad R^{**} = (PhMe_2Si)_3C$

$[Li(THF)_4][C(SiMe_2C_6H_4Me\text{-}o)_3]$

1

$[Li(12\text{-}crown\text{-}4)_2][C(SiMe_3)(SiMeBu^t{}_2)(SiMe_2F)]$

2

Phenyl−metal interactions are likewise present in (a) the monophenyl species $M\{C(SiMe_3)_2(SiMe_2Ph)\}$ with M = $Li(OEt_2)$ or Na(TMEDA), both of which have monomeric molecular structures, (b) the solvent-free diphenyl species $[Li\{CH(SiMe_2Ph)_2\}]_2$, which has an electron-deficient structure like that of $(LiR^*)_2$ but with supplementary intradimer Li−Ph instead of Li−Me interactions, and (c) $Na(TMEDA)\{C(SiMe_3)(SiMe_2Ph)_2\}$.[9] We now describe the structure of the tri-*o*-tolyl derivative $[Li(THF)_4][C(SiMe_2C_6H_4Me\text{-}o)_3]$ (**1**), which is unique among the compounds in this general series in being a lithium derivative containing an independent carbanion and in being an aryl-containing species without an aryl−metal interaction. There are, however, independent carbanions in the salts $[Li(12\text{-}crown\text{-}4)_2][C(SiMe_3)(SiMeBu^t{}_2)(SiMe_2F)]$, **2**,[10] and $[Li(12\text{-}crown\text{-}4)_2][CPh_2X](THF)$ with X = Ph or H,[11] in each of which the Li^+ ion is sequestered within the crown ether molecules.

Results and Discussion

One of us previously reported the preparation of a solution of $LiC(SiMe_2C_6H_4Me\text{-}o)_3$ by a rather complex procedure involving addition of an excess of MeLi in Et_2O in portions to a solution of $(o\text{-}MeC_6H_4Me_2Si)_3CH$ in THF followed by removal of the Et_2O and refluxing after each addition, with a total reflux time of 48 h.[12] The product was not isolated but was identified in solution by derivatization with MeI, to give $(o\text{-}MeC_6H_4Me_2Si)_3CMe$. We have now found that it can be made much more satisfactorily by overnight treatment of $(o\text{-}MeC_6H_4Me_2Si)_3CH$ with LiBu in the presence of TMEDA) in a hexane−heptane mixture at room temperature and isolated as a yellow solid that was judged from its ^1H NMR spectrum in THF-d_8 to be $[Li(TMEDA)_2][C(SiMe_2C_6H_4Me\text{-}o)_3]$ containing some 12% of additional TMEDA. However, the signals from TMEDA were

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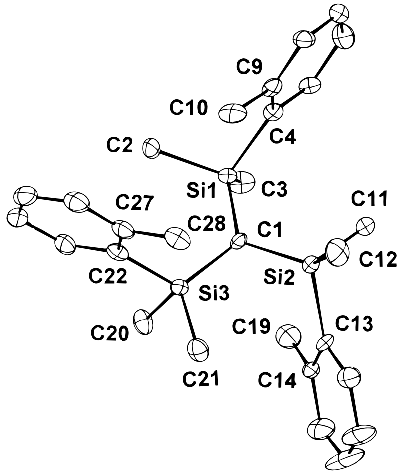

Figure 1. Molecular structure of the carbanion $[C(SiMe_2C_6H_4Me\text{-}o)_3]^-$ in **1**.

Table 1. Selected Bond Lengths (Å) and Angles (deg) in the Carbanion of 1, with ESDs in Parentheses

C1−Si1	1.807(7)	C1−Si2	1.791(8)
C1−Si3	1.803(7)	Si1−C2	1.886(8)
Si1−C3	1.901(8)	Si1−C4	1.905(8)
Si2−C11	1.877(8)	Si2−C12	1.898(8)
Si2−C13	1.909(8)	Si3−C20	1.906(8)
Si3−C21	1.869(8)	Si3−C22	1.914(8)
Si1−C1−Si2	118.0(4)	Si1−C1−Si3	120.6(4)
Si2−C1−Si3	120.7(4)	C1−Si1−C2	115.1(4)
C1−Si1−C3	114.6(4)	C1−Si1−C4	115.2(3)
C1−Si2−C11	115.0(4)	C1−Si2−C12	113.1(4)
C1−Si2−C13	115.7(4)	C1−Si3−C20	114.6(3)
C1−Si3−C21	114.4(4)	C1−Si3−C22	115.5(3)
C2−Si1−C3	101.5(4)	C2−Si1−C4	104.3(3)
C3−Si1−C4	104.6(4)	C11−Si2−C12	103.7(4)
C11−Si2−C13	103.3(4)	C12−Si2−C13	104.7(4)
C20−Si3−C21	102.6(4)	C20−Si3−C22	103.3(4)
C21−Si3−C22	104.9(3)		

solely at the positions corresponding to the free diamine, showing that the TMEDA had been displaced by the solvent, and recrystallization from THF−heptane gave yellow crystals of the THF−solvated salt **1** suitable for an X-ray diffraction study.

The structure of the carbanion of **1** is shown in Figure 1 (that of the cation is well-known), and selected bond lengths and angles are given in Table 1. The significant features are as follows: (a) the ion is planar, with mean Si−C1−Si angles of effectively 120° (mean 119.8(5)°); (b) the Me−Si−C(Me/tolyl) angles, mean 103.6(4)°, are notably narrow; (c) the Si−C1 bonds, mean 1.800(3) Å, are exceptionally short; and (d) the outer Si−C bonds mean 1.896(8) Å, are fairly long. (For simplicity the small differences between lengths of the Si−Me and Si−tolyl bonds are here ignored.) These values compare respectively with those of 114.0(1)°, 106.8(13)°, 1.895(1) Å, and 1.862(13) Å, for the corresponding bonds and angles in the neutral species $(PhMe_2Si)_3CH$,[13] and 112.6(1)°, 105.4(2)°, 1.877(3) Å, and 1.881(4) Å in, for example, the neutral organometallic derivative $Mg\{C(SiMe_3)_3\}_2$.[14] The short Si−C1 bonds in **1** are attributed[15] to delocalization of the charge on the carbanionic carbon by negative hyperconjugation (which gives them partial double-bond character) as is the planarity of the ion and the high coupling constant, ${}^1J$(Si−C1), 66 Hz.[1]

The corresponding mean Si−C bond length is a little larger in $Li(Et_2O)\{C(SiMe_3)_2(SiMe_2Ph)\}$, 1.830(5) Å, but not significantly so in $Na(TMEDA)\{C(SiMe_3)_2(SiMe_2Ph)\}$, 1.820(3) Å, in $Na(TMEDA)\{C(SiMe_3)(SiMe_2Ph)_2\}$, 1.813(5) Å, or in the solvent-free $M\{C(SiMe_2Ph)_3\}$ with M = Na, 1.812(12) Å, K, 1.84(2) Å, Rb, 1.813(2) Å, and Cs, 1.812(7) Å,[9] showing that in these essentially ionic compounds the bond length within the anion is not significantly influenced by interaction with the cation. (The interaction can, however, lead to a small but appreciable departure from planarity of the carbanion; for example, the sum of the Si−C−Si angles is 353° in both $Na(TMEDA)\{C(SiMe_3)_2(SiMe_2Ph)\}$ and $Na(TMEDA)\{C(SiMe_3)(SiMe_2Ph)_2\}$.[9])

The mean Si−C1 distance in **1** is closely similar to that in **2**, in which, however, the mean is lowered by the presence of the F atom in the $SiMe_2F$ group which reduces the $C{-}SiMe_2F$ distance to 1.779(6) Å.[10] [For $Li(THF)\{C(SiMe_2Ph)_3\}$, the poor quality of the data rule out meaningful comparison.] In general the mean Si−C1−Si angles in the lithium compounds specified above, are significantly less than 120°, e.g., 116.5(3)° in $Li(Et_2O)\{C(SiMe_3)_2(SiMe_2Ph)\}$; in **2**, the mean angle is 120.0°, but the separate angles range between 115.3(3)° and 125.0(3)°. The unusually narrow outer C−Si−C angles in **1** are also probably a consequence of the hyperconjugative delocalization; the corresponding angles are similarly narrow in, for example, the carbanions in KR*, mean 102.8(7)°,[9] RbR*, 102.9(4)°,[7] and NaR**, 103.4(6)°,[9] and the Me−Si−Me angles in **2** have a mean of 103.4(5)°.[10]

Within the carbanion of **1**, the corresponding bond lengths and angles in each $SiMe_2C_6H_4Me$-*o* group are the same within experimental uncertainty, but one *o*-tolyl group (C13) lies on one side of the CSi_3 plane and the other two lie on the opposite side in order to minimize *o*-Me and Me-Si contacts. The roughly spherical $[Li(THF)_4]^+$ cations and thick disk-like anions pack in an ionic lattice without specific interactions within ion pairs. The larger anions form a distorted but recognizable cubic close-packed array but the interpenetrating cation lattice is extremely distorted, so that it is not possible to relate the overall structure to that of any simple binary compound. Each central carbon has two Li neighbors at 7.34 Å and further such neighbors at 7.94, 8.17, 9.80, 10.75, and 10.96 Å.

There is no obvious reason why $Li\{C(SiMe_2C_6H_4Me\text{-}o)_3\}$ solvated by THF should adopt an ionic structure and $Li\{C(SiMe_2Ph)_3\}$ solvated by THF a molecular one with a Li−Ph interaction. In terms of electronic effects, $SiMe_2C_6H_4Me$-*o* groups would be expected to stabilize the carbanion center less effectively than $SiMe_2Ph$ groups, and an *o*-tolyl would be expected to interact with the metal more strongly than a Ph group, but the *o*-Me groups could have an unfavorable steric effect in respect of such an interaction. It is of interest that in spite of the fact that the carbanion in **1** is "free" the compound

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is markedly less reactive than Li{C(SiMe$_2$Ph)$_3$}(THF) toward electrophiles such as Me$_2$SiHCl and SiCl$_4$[12] (although it is possible that for the triphenyl compound the Li−Ph interaction is absent in solution). Presumably the additional unfavorable steric interactions that are likely to be present in the expected products from **1** are partly present in the transition states for the inhibited reactions.

Experimental Section

All operations were carried out under argon and in Schlenk tubes where appropriate. The frequencies (MHz) used for recording NMR spectra were ^{1}H, 300.1; ^{13}C, 125.8; ^{29}Si, 99.4; and ^{7}Li, 194.37. For the quaternary carbon the signal was enhanced by polarization transfer (INEPT).

Preparation of 1. A solution of anhydrous TMEDA (0.4 g, 3.6 mmol) and LiBu (3.6 mmol) in hexane (1.45 cm^3) was added from a syringe to a stirred solution of (o-MeC$_6$H$_4$-Me$_2$Si)$_3$CH[12] (0.50 g, 1.08 mmol) in heptane (20 cm^3). The mixture was stirred overnight, after which it consisted of a yellow solid and an orange supernatant solution. The solid was filtered off and washed with heptane (3 × 15 cm^3). The yellow air- and moisture-sensitive solid (0.59 g) thus obtained was judged from its ^{1}H NMR spectrum in THF-d_8 to be Li{C(SiMe$_2$C$_6$H$_4$Me-o)$_3$}(TMEDA)$_2$ (84%) containing ~12% of additional TMEDA. The spectrum showed only one set of signals from TMEDA, at the positions observed for the uncomplexed diamine, indicating that the latter had been displaced from the coordination shell by THF. ^{1}H NMR: δ −0.01 (18 H, s, SiMe$_2$), 2.15 (s) and 2.30 (s) (together 36 H, uncomplexed TMEDA), 2.58 (9 H, s, o-Me), 6.7−7.3 (12 H, m, C$_6$H$_4$). (When the procedure was repeated but with the (o-MeC$_6$H$_4$Me$_2$Si)$_3$CH, BuLi, and TMEDA in 1:1:1 molar ratio, the same product was obtained but in only 33% yield.)

The product was recrystallized from a mixture of THF and heptane at −30 °C to give yellow plates of Li{C(SiMe$_2$C$_6$H$_4$Me-o)$_3$}(THF)$_4$. Mp: 112.0−112.8 °C (Found: C, 69.3; H 9.3. C$_{44}$H$_{71}$O$_4$LiSi$_3$ requires C, 70.0; H 9.5); ^{1}H NMR: δ (THF-d_8) δ −0.01 (s, 18 H, SiMe$_2$), 1.78 (s, 17 H, THF), 2.58 (9 H, s, o-Me), 3.63 (s, 16 H, THF), 6.7−7.3 (12 H, m, C$_6$H$_4$). ^{13}C NMR: δ −4.75 (^1J(Si−C) 66 Hz, quat. C), 2.72 (SiMe$_2$), 23.7 (o-Me), 26.3 and 68.1 (both THF), and 123.5, 125.9, 128.9, 135.5, 144.6, 151.1 (all six from C$_6$H$_4$); δ_{Si} −16.8. ^{7}Li NMR: δ −3.16 (s).

Reaction with MeI. An excess of MeI (0.05 cm^3) was added to a stirred slurry of Li{C(SiMe$_2$C$_6$H$_4$Me-o)$_3$}(TMEDA)$_2$ (0.20 g) in light petroleum (bp 40−60 °C, 10 cm^3). The yellow solid slowly disappeared to leave a white precipitate. The solution was filtered and the solvent removed to leave (o-MeC$_6$H$_4$Me$_2$Si)$_3$CMe. ^{1}H NMR: δ (C$_6$D$_6$) 0.28 (18 H, s, SiMe$_2$), 1.90 (3 H, s, Me), 2.33 (9 H, s, o-Me), 6.8−7.5 (12 H, m, C$_6$H$_4$) (lit.,[12] in CDCl$_3$, 0.17, 1.89, 2.41, 7.0−7.5.) .

Table 2. Crystallographic Data and Details of Structure Refinement for 1

empirical formula	C$_{44}$H$_{71}$LiO$_4$Si$_3$
fw	755.2
temp (K)	173(2)
λ (Å)	0.710 73
cryst size (mm)	0.4 × 0.4 × 0.1
cryst syst	monoclinic
space group	$P2_1/n$ (nonstandard No. 14)
a (Å)	11.463(3)
b (Å)	26.780(6)
c (Å)	14.987(4)
β (deg)	100.81(2)
V (Å^3)	4519(2)
Z	4
d_c (g cm^{-3})	1.11
F(000)	1648
μ (mm^{-1})	0.14
θ range (deg)	2−22
index range	$0 \le h \le 12$, $0 \le k \le 28$, $-15 \le l \le 15$
no. of rflns collected	5846
no. of unique reflns	5525 (R_{int} = 0.08)
no. of rflns with $I > 2\sigma(I)$	2653
R1; wR2 (I > 2σ(I))	0.084, 0.174
R1; wR2 (all data)	0.187, 0.234
data/restraints/parameters	5525/0/478
GOF on F^2	0.989
max shift/error	0.002
largest diff peak/hole (e Å−^{3})	0.29 and −0.29
abs corr	not applied

Crystallography. Details are given in Table 2. All non-H atoms were refined anisotropically. The H atoms were included in riding mode with U_{iso}(H) = 1.2U_{eq}(C) except for Me groups, which were fixed at idealized geometry but with the torsion angles defining the H atom positions refined and U_{iso}(H) equal to 1.5U_{eq}(C). The high R factor is a consequence of the weak diffraction from a thin crystal.

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Supporting Information Available: An ORTEP, a packing diagram, and tables of crystallographic data, atom coordinates, bond lengths and angles, and anisotropic thermal parameters (6 pages). Ordering information is given on any current masthead page.

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