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Lithiation of Diphenyl(triorganosilyl)methanes

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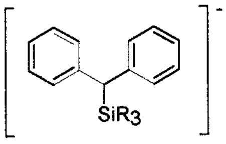
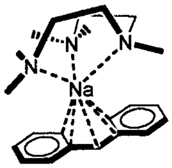
The lithiation of several triorganosilyl-substituted diphenylmethanes, $(R_3Si)Ph_2CH$, in THF has been studied. The structures of two of these compounds have been determined by X-ray diffraction studies and shown to consist of solvent-separated ion pairs $[Li(THF)_4][Li\{C(SiR_3)Ph_2\}_2]$ (**4**, $R_3 = Me_3$; **5**, $R_3 = Me_2Ph$), in which the anions are lithates, each containing lithium bound to two η^2-coordinated, silylated diphenylmethyl subunits. Despite contact with lithium the organic residues are almost planar (sum of angles around C(1) for both structures, 356.7°), indicating a high degree of anionic charge delocalization. This is further reflected by the collated multinuclear NMR data. Reaction of $[Li(THF)_4][Li\{C(SiMe_3)Ph_2\}_2]$ with TMEDA in hexane was shown by an X-ray diffraction study to have resulted in complete removal of lithium from the anion coordination sphere to give $[Li(TMEDA)_2][(Me_3Si)Ph_2C]$. This consists of discrete planar $[(Me_3Si)Ph_2C]^-$ carbanions and $[Li(TMEDA)_2]^+$ countercations. The behavior of the lithiated diphenylmethanes was rationalized to be a result of both electronic (by extensive charge delocalization) and kinetic (by the bulky R_3Si substituent) stabilization.

Introduction

The use of bulky triorganosilyl-substituted methyl ligands, $(R_3Si)_{3-n}H_nC$ ($n = 0$, 1 or 2), gives a wide range of kinetically stabilized σ-alkyl organometallic derivatives.[1] In such compounds, the geometry and coordination number at the metal are determined largely by the size and shape of the substituents bound to the methyl carbon. For example, the metal is forced to be two-coordinate in $Yb[C(SiMe_3)_3]_2$ and three-coordinate in $La[CH(SiMe_3)_2]_3$.[2,3] Low-coordinate systems of this type, although more commonly based on N- or O-centered ligands, have attracted great attention due to their ability to undergo facile oxidation by small molecule substrates.[4]



I



II

We now report ligands of the general type **I**, which can be "sterically tuned" at the carbanionic center by variation of the R_3Si substituents or substituents in the phenyl rings. Additional stabilization of electron-deficient metals may be provided by polyhapto interactions with the extended π-systems of the phenyl substituents. This is common for the widely used benzyl group, $PhCH_2$, which can coordinate as an η^1, η^2, η^3, η^5, or even η^7 ligand depending on the degree of unsaturation at the metal center.[5] In comparison to the great volume of literature relating to the synthesis and use of organometallic benzyl derivatives, reports of metalated diphenylmethanes are surprisingly scarce.[6] Structurally characterized examples of true diphenylmethyls are restricted to the planar free carbanion $[Li(12\text{-crown-}4)_2][CHPh_2]$[7] and the contact ion pairs $[Na(CHPh_2)$-

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(TMEDA)]$_4$ and [Na(CHPh$_2$)(PMDETA)], **II** (TMEDA = *N*,*N*,*N*′,*N*′-tetramethylethane-1,2-diamine; PMDETA = *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine).[8] Although the syntheses of several neutral triorganosilyl diphenylmethanes have been described and the stabilization of organometallic derivatives by the (Me$_3$Si)-Ph$_2$C ligand has been cited,[9,10] no fully characterized products have been reported previously.[11]

In the present study we have examined the lithiation of several triorganosilyl-substituted diphenylmethanes. This structural information allows an initial evaluation of the manner in which ligating behavior is affected by the mode of charge delocalization and the steric demands of the triorganosilyl substituents.

Results and Discussion

Synthesis. Treatment of diphenylmethyllithium with the appropriate chlorotriorganosilane gave the ligand precursors **1**−**3** in good yield (eq 1).[9]

$$\mathrm{Ph_2HCLi} + \mathrm{R_3SiCl} \xrightarrow{\mathrm{THF,\ RT}} \mathrm{(R_3Si)Ph_2CH} + \mathrm{LiCl} \tag{1}$$

$$\begin{aligned} \mathrm{R_3Si} &= \mathrm{Me_3Si},\ \mathbf{1} \\ &= \mathrm{Me_2PhSi},\ \mathbf{2} \\ &= {}^{t}\mathrm{BuMe_2Si},\ \mathbf{3} \end{aligned}$$

Single crystals of **1** and **3** suitable for X-ray study were obtained by slow evaporation of hexane solutions (see Supporting Information).

$$\mathrm{(R_3Si)Ph_2CH} + \mathrm{nBuLi} \xrightarrow{\mathrm{THF,\ RT}} \mathrm{(R_3Si)Ph_2CLi(THF)_2} + \mathrm{BuH} \tag{2}$$

$$\begin{aligned} \mathrm{R_3Si} &= \mathrm{Me_3Si},\ \mathbf{4} \\ &= \mathrm{Me_2PhSi},\ \mathbf{5} \\ &= {}^{t}\mathrm{BuMe_2Si},\ \mathbf{6} \end{aligned}$$

Compounds **1** and **2** were readily deprotonated by ^{n}BuLi in THF at room temperature with the concomitant formation of deep orange solutions characteristic of polyphenylated carbanions (eq 2).[12] Attempted lithiation of **3**, employing similar reagents and solvents, resulted in only partial deprotonation (ca. 60%, even under reflux conditions) possibly due to a combination of steric and inductive effects. Although a pure bulk sample of **6** could not be obtained due to consistent contamination with unreacted **3**, its identity was established by comparison of NMR chemical shift data with those of pure **4** and **5**. Attempts to synthesize solvent- or donor-free derivatives in hydrocarbon solvents were unsuccessful.

The air- and moisture-sensitive orange-yellow organolithium derivatives **4** and **5** could be crystallized at low temperature from hydrocarbon solvents (hexane or toluene) to provide samples suitable for X-ray diffraction analysis.

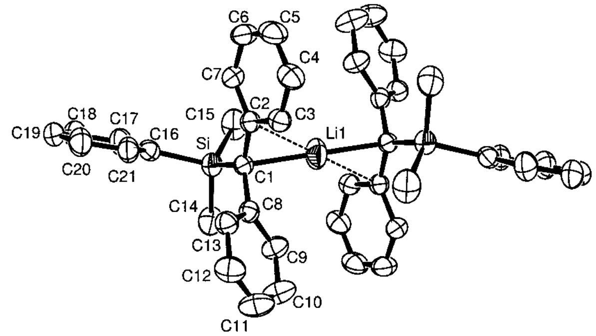

Figure 1. ORTEP drawing of the anion of **5** in the crystal and the crystallographic numbering scheme used (50% probability ellipsoids). H atoms omitted for clarity.

Table 1. Selected Bond Lengths (Å) for 1, 3, 4, 5, and 7

	1	**3**	**4**	**5**	**7**
Li(1)−C(1)			2.141(4)	2.124(3)	
Li(1)−C(2)			2.414(4)	2.356(3)	
Li(1)···C(8)			2.667(4)	2.659(3)	
Li(1)···C(3)			2.775(5)	2.697(3)	
Si−C(1)	1.918(2)	1.915(4)	1.833(5)	1.823(3)	1.828(4)
C(1)−C(2)	1.526(3)	1.518(5)	1.453(6)	1.467(4)	1.474(5)
C(1)−C(8)	1.522(3)	1.520(5)	1.494(6)	1.490(4)	1.436(5)
C(2)−C(3)	1.390(3)	1.386(5)	1.420(6)	1.417(4)	1.400(5)
C(2)−C(7)	1.398(3)	1.399(6)	1.422(6)	1.419(4)	1.407(5)
C(3)−C(4)	1.388(3)	1.385(6)	1.379(7)	1.389(4)	1.385(5)
C(4)−C(5)	1.373(3)	1.378(6)	1.376(7)	1.380(5)	1.380(6)
C(5)−C(6)	1.387(3)	1.369(6)	1.384(7)	1.374(5)	1.379(5)
C(6)−C(7)	1.383(3)	1.384(6)	1.375(6)	1.383(4)	1.376(5)
C(8)−C(13)	1.396(3)	1.393(6)	1.392(6)	1.407(4)	1.423(5)
C(8)−C(9)	1.396(3)	1.388(6)	1.405(7)	1.398(4)	1.431(5)
C(9)−C(10)	1.379(3)	1.390(6)	1.371(7)	1.381(4)	1.377(5)
C(10)−C(11)	1.388(3)	1.377(6)	1.374(9)	1.375(5)	1.378(5)
C(11)−C(12)	1.370(4)	1.373(7)	1.363(9)	1.382(5)	1.385(5)
C(12)−C(13)	1.387(4)	1.388(6)	1.387(7)	1.375(4)	1.387(5)

X-ray Structures of 4 and 5. The solid-state structures of **4** and **5** consist of solvent-separated ion pairs, [Li(THF)$_4$][Li{C(SiR$_3$)Ph$_2$}$_2$], in which the anion is a lithate containing lithium bound to two η^2-coordinated, silylated diphenylmethyl subunits. The anion of **5** is shown in Figure 1. In both structures the lithate anion lies on an inversion center and the [Li(THF)$_4$]$^+$ countercation on a 2-fold rotation axis. In **4** some disorder in the Li-bound THF ligands is responsible for the somewhat high final *R* factor (see Table 3). However the structural parameters relating to the lithate anion are entirely reliable, as shown by the esd's for individual measurements (Tables 1 and 2).

Although first proposed by Wittig more than 40 years ago,[13] few diorganolithate anions have been characterized in the solid state. Examples are restricted to several tris(triorganosilyl)methyl derivatives, in which the lithium atom is two-coordinate due to the extremely hindered nature of the carbanionic centers,[14] and the recently reported dibenzyllithate [Li(TMEDA)$_2$] [(TMEDA)-Li(CH$_2$C$_6$H$_3$-3,5,-Me$_2$)$_2$].[15] In **4** and **5** the lithium center Li(1) is asymmetrically coordinated by both the central carbon, C(1) [for **4**, 2.141(4); **5**, 2.124(3) Å], and a longer contact to the *ipso*-carbon of the C(2) phenyl

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Table 2. Selected Bond Angles (deg) for 1, 3, 4, 5, and 7

	1	3	4	5	7
C(1)′−Li(1)−C(1)			180.0	180.0	
C(1)′−Li(1)−C(2)′			36.58(16)	37.80(9)	
C(1)−Li(1)−C(2)′			143.42(16)	142.21(9)	
C(2)−C(1)−Li(1)			82.0(3)	79.71(15)	
C(8)−C(1)−Li(1)			92.6(3)	94.93(17)	
Si−C(1)−Li(1)			113.0(2)	112.89(13)	
C(3)−C(2)−Li(1)			88.8(3)	85.80(17)	
C(7)−C(2)−Li(1)			118.2(3)	119.46(18)	
C(1)−C(2)−Li(1)			61.4(2)	62.50(14)	
C(2)−C(1)−C(8)	112.71(17)	115.8(3)	117.0(4)	117.4(2)	119.4(3)
C(2)−C(1)−Si	116.60(13)	110.6(2)	122.5(3)	122.0(2)	120.0(2)
C(8)−C(1)−Si	110.39(14)	115.3(3)	117.2(3)	117.31(19)	120.5(3)
C(3)−C(2)−C(7)	117.63(19)	116.4(4)	113.4(4)	114.4(3)	114.6(3)
C(3)−C(2)−C(1)	122.78(18)	120.0(4)	122.5(4)	122.1(2)	122.7(3)
C(7)−C(2)−C(1)	119.53(18)	123.5(3)	123.9(4)	123.2(3)	122.6(3)
C(4)−C(5)−C(6)	119.5(2)	119.0(4)	117.6(5)	118.5(3)	118.3(4)
C(7)−C(6)−C(5)	120.1(2)	120.9(4)	121.8(5)	121.9(3)	121.2(4)
C(6)−C(7)−C(2)	121.2(2)	121.4(4)	122.6(5)	121.9(3)	122.4(4)
C(13)−C(8)−C(9)	117.2(2)	117.2(4)	115.8(4)	116.0(3)	113.2(3)
C(13)−C(8)−C(1)	120.73(19)	119.2(4)	122.2(4)	122.3(2)	124.1(3)
C(9)−C(8)−C(1)	122.12(19)	123.6(3)	122.0(4)	121.7(3)	122.6(3)
C(10)−C(9)−C(8)	121.4(2)	121.2(4)	122.3(5)	121.5(3)	122.8(4)
C(9)−C(10)−C(11)	120.4(2)	120.5(4)	120.2(6)	121.1(3)	122.1(4)
C(12)−C(11)−C(10)	119.3(2)	119.1(4)	119.4(5)	118.9(3)	117.5(4)
C(11)−C(12)−C(13)	120.5(2)	120.4(4)	120.6(6)	120.2(3)	121.3(4)
C(12)−C(13)−C(8)	121.3(2)	121.4(4)	121.7(5)	122.4(3)	123.1(4)

Table 3. Selected Crystallographic and Data Collection Parameters for Compounds 1, 3, 4, 5, and 7

	1	3	4	5	7
chemical formula	$C_{16}H_{20}Si$	$C_{19}H_{26}Si$	$C_{48}H_{70}Li_2O_4Si_2$	$C_{58}H_{74}Li_2O_4Si_2$	$C_{28}H_{51}LiN_4Si$
fw	240.41	282.49	781.10	905.23	478.76
T (K)	173(2)	173(2)	173(2)	173(2)	173(2)
cryst size (mm)	0.2 × 0.2 × 0.1	0.4 × 0.2 × 0.1	0.3 × 0.3 × 0.2	0.4 × 0.4 × 0.3	0.2 × 0.2 × 0.1
cryst syst	orthorhombic	monoclinic	monoclinic	monoclinic	orthorhombic
space group	$P2_12_12_1$ (No. 19)	$P2_1/c$ (No. 14)	$P2/c$ (No. 13)	$C2/c$ (No. 15)	$Pcca$ (No. 54)
a (Å)	7.7618(7)	16.8398(6)	11.7682(12)	16.5808(7)	36.4787(16)
b (Å)	13.3450(17)	6.5738(3)	10.3345(10)	13.4857(7)	9.5179(4)
c (Å)	13.4768(17)	15.6140(8)	19.558(2)	24.7299(11)	17.9464(7)
β (deg)	90	95.970(3)	95.941(5)	98.167(3)	90
Z	4	4	2	4	8
V (Å^3)	1395.9(3)	1719.1(1)	2365.9(4)	5473.6(4)	6231.0(4)
d_c (Mg m^{-3})	1.14	1.09	1.10	1.10	1.02
μ (mm^{-1})	0.15	0.13	0.11	0.11	0.10
θ range (deg)	4.03 to 24.92	3.76 to 21.97	3.87 to 21.99	3.71 to 25.02	3.84 to 21.94
R1; wR2, $I > 2\sigma(I)$	0.036, 0.083	0.059, 0.153	0.085, 0.173	0.066, 0.166	0.068, 0.138
R1; wR2, all data	0.041, 0.086	0.075, 0.160	0.102, 0.181	0.107, 0.189	0.110, 0.157
no. of measd/indep rflns/R(int)	5137/2398/0.048	7322/2069/0.074	10675/2868/0.073	13637/4764/0.065	11842/3731/0.076
rflns with $I > 2\sigma(I)$	2200	1665	2347	3150	2504

ring [for **4**, 2.414(4); **5**, 2.356(3) Å]. Preferential η^2-coordination to lithium via the C_α and *ipso*-C atoms of benzyl anions has been demonstrated by several theoretical and structural studies which indicate hyperconjugative delocalization onto the phenyl substituent and the placement of the alkali metal adjacent to the point of maximum electron density.[16,17] Steric interactions between the bulky triorganosilyl substituents of both **4** and **5** are minimized by the adoption of a *trans* configuration about the linear C(1)−Li(1)−C(1)′ axis. The planarity of the $CSiC_2$ carbanionic core is only slightly perturbed by contact to lithium (sum of angles around C(1) for both **4** and **5**, 356.7°). This minor disruption to the anionic delocalization indicates that the dialkyllithate is best regarded as a Li^+ cation sandwiched between two essentially free carbanions, consistent with the view that the C−Li bonding in organolithium compounds is largely (80−90%) electrostatic.[18] The C(1)−Li bond lengths are typical of Li contacts to more pyramidal carbon, for example those in [Li(THF)C-$(SiMe_3)_2\{SiMe_2CHLi(THF)_2PPh_2\}$] [2.148(8) and 2.151(9) Å],[19] in agreement with further calculations that estab-

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lish that the overall Li−C bond order is largely unaffected by the s-character of the central carbon.[20]

Recent quantum mechanical calculations demonstrate that $[Me_2Li]^-$ anions are very stable to dissociation of Me^- despite the large positive charge that resides on lithium (0.88).[21] From the results presented here and the limited literature precedents, it can be inferred that "ate complex" formation in the solid state is favored when the central carbanionic carbon bears bulky substituents which allow a measure of charge delocalization (and thus stabilization) and prevent the formation of oligomers. The high degree of delocalization observed in the structures of **4** and **5** is reminiscent of that in the lithocene anions, $[Cp_2Li]^-$ and $[(isodiCp)_2Li]^-$ (isodiCp = isodicyclopentadienyl).[22a−c] Similar electronic effects have also been cited to explain the stability of lithate anions observed in HMPA/RLi mixtures (HMPA = hexamethylphosphosphoric triamide).[23]

Steric constraints imposed by the bulky trialkylsilyl substituents prevent the CPh_2 systems in **4** and **5** from being coplanar as they are in $[Li(12\text{-crown-}4)_2][(CHPh_2)]$ and **II**.[7,8] The dihedral angles of the C(2) and C(8) phenyl rings to the respective C(1)C(2)C(8)Si(1) least squares planes are 7.5° and 64.2° in **4** and 11.3° and 57.9° in **5**. Orbital overlap in π-systems is a function of $\cos^2 \theta$ (where θ = dihedral angle between π-planes);[24] for example, the C(2) twist angle of 7.5° in **4** corresponds to 98% overlap and the 64.2° twist of the C(8) ring to 19%. Hence, the observed C(1)−C(2) [for **4**, 1.456(6); **5**, 1.467(4) Å] bonds are shorter by ca. 0.07 Å, and the C(1)−C(8) [**4**, 1.494(6); **5**, 1.490(4) Å] bonds by ca. 0.03 Å, than the corresponding bonds in the neutral precursors **1** and **3**.

The Si−C(1) bond lengths [**4**, 1.833(5); **5**, 1.823(3) Å] are also shortened through delocalization of the anionic charge onto the R_3Si substituents. Similar effects, ascribed to negative hyperconjugation,[25] have been observed in a number of silyl-substituted methyl carbanions.[26] The structures of **4** and **5** also display significant deformations of the phenyl rings, a common feature of anionic benzyl derivatives (Tables 1 and 2).[25c,27]

NMR Spectra of 4−6. A combination of solution and solid-state multinuclear NMR studies has shown that the highly crowded lithate anions, $[Li\{C(SiMe_3)_3\}_2]^-$, are present in solutions of tris(trimethylsilyl)methyllithium at reduced temperature.[14c] The ionic structure of $[Li(TMEDA)_2][(TMEDA)Li(CH_2C_6H_3\text{-}3,5,\text{-}Me_2)_2]$ is also reported to persist in solution and to display two signals in its ^{7}Li NMR spectrum.[15] It is not yet possible however to assign the solution-state structures of **4**−**6** unambiguously. The room-temperature ^{7}Li spectra consist of a single sharp peak at ca. − 0.1 ppm, and the respective ^{1}H and ^{13}C spectra do not display the phenyl-group asymmetry expected if the solid-state structures were retained in solution. Also no additional signals in the ^{1}H, ^{13}C, or ^{7}Li NMR spectra or appreciable alterations to spectral line widths were observed when a toluene-d_8 solution of **4** was cooled to 183 K. Taken in isolation, these data suggest that the lithate anions are not retained in solution. However, it has been noted previously that the signal due to the ^{7}Li nucleus of the anionic fragment in $[Li(THF)_4][Li\{C(SiMe_3)_3\}_2]$ is broad and difficult to observe due to quadrupolar relaxation.[14c] Moreover, lithate anion formation has been deduced from detailed analysis of ^{6}Li solution NMR spectra of ^{6}Li-enriched phenyllithium/HMPA mixtures and postulated as a general feature in organolithium solutions containing strong donors to lithium.[23] Similar persistence in solution of the negatively charged $[LiR_2]^-$ aggregates observed in the solid-state structures of **4** and **5** cannot therefore be discounted.

Alternatively the solution-state spectra of **4** − **6** may be a result of rapid exchange of lithium between the $[Li(THF)_4]^+$ cations and the dialkyllithate anions. A similar complex equilibrium involving molecular solvated species, higher molecularity aggregates, and free carbanions was proposed to explain the behavior of $[Li(THF)_4][Li\{C(SiMe_3)_3\}_2]$ solutions above room temperature.[14c] Intermolecular C−Li bond exchange and methyl group inversion in silyl-substituted benzyls has been shown to involve only small activation barriers ($\Delta H^‡ < 5$ kcal mol^{-1}).[28] It would be unsurprising therefore if the behavior of **4**−**6** contrasts with that of the much bulkier tris(trialkylsilyl)methyl derivatives, where considerable and increased structural reorganization is required.

Despite these ambiguities, the room-temperature NMR spectra do indicate significant delocalization over the $(R_3Si)Ph_2C$ skeletons. The signals for the C(1) carbons in the ^{13}C spectra appear at low frequency (ca. 63 ppm), and the high $^{1}J_{SiC}$ values for **4** and **5** (73 and 78 Hz, respectively) are much larger than those in **1**−**3** (ca. 45 Hz), reflecting a higher percentage of s-character in the Si−C bonds of the carbanions. Similar $^{1}J_{SiC}$

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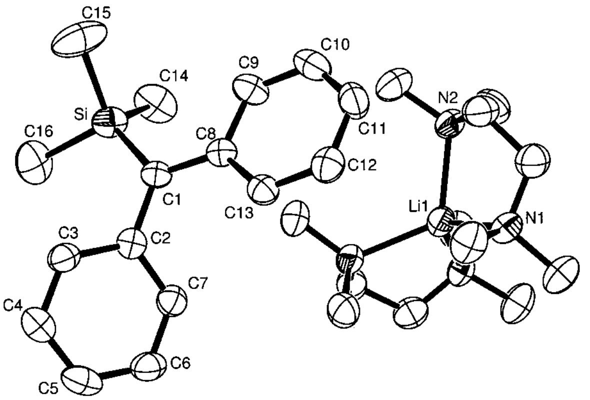

Figure 2. ORTEP drawing of the ion pair of **7** in the crystal and the crystallographic numbering scheme used (50% probability ellipsoids). H atoms omitted for clarity.

values are found in highly ionic silyl-substituted methyls such as [$(Me_3Si)_2PhCK$] (69.9 Hz),[25c] [$CsC(SiMe_3)_3$] (67 Hz),[27b] and the free planar carbanion [$Li(THF)_4$][$C(SiMe_2C_6H_4Me$-*o*$)_3$] (66 Hz).[29]

Synthesis and Structure of the TMEDA Derivative, 7. Reaction of **4** with TMEDA resulted in the formation of bright orange, highly pyrophoric crystals (eq 3). These were shown by an X-ray structure determination (Table 3) to be **7**, a rare example of a structure consisting of discrete planar [$(Me_3Si)Ph_2C$]$^-$ carbanions and [$Li(TMEDA)_2$]$^+$ countercations.[30]

$$\mathbf{4} + \text{TMEDA} \xrightarrow{\text{hexane, RT}} \underset{\mathbf{7}}{[\text{Li(TMEDA)}_2]^+[(\text{Me}_3\text{Si})\text{Ph}_2\text{C}]^-} \quad (3)$$

The structure of **7** is illustrated in Figure 2, and selected bond lengths and angles are given in Tables 1 and 2. Removal of lithium from the anion coordination sphere results in complete planarization at C(1) (sum of angles around C(1), 359.9°). The dihedral angles between the phenyl groups and the C(1)C(2)C(8)Si(1) least squares planes are 5.3° and 51.2°, only slightly smaller than those in **4** and **5**, confirming that the steric demands of the R_3Si substituent are responsible for the overall noncoplanarity of the phenyl rings. The smaller dihedral angles result in further contraction of the C(1)−C(2) [1.474(5) Å] and C(1)−C(8) [1.436(5) Å] bond lengths. These are however still not as short as those observed in the completely coplanar anion of [Li(12-crown-4)$_2$][$CHPh_2$] [1.453(6), 1.404(6) Å].[7] Despite removal of the anion from contact with lithium, the C(1)−Si bond length of **7** [1.828(4) Å] is similar to those in **4** and **5**.

In contrast to the formation of **7**, the integrity of the anions of both [$Li(TMEDA)_4$][$Li\{C(SiMe_3)_3\}_2$] and [Li(TMEDA)][(TMEDA)$Li(CH_2C_6H_3$-3,5,$Me_2)_2$] is unaffected by crystallization in the presence of an excess of TMEDA.[14c,15] The formation of the free carbanion in **7** reflects therefore both the greater basicity toward Li of the amine than of THF and the enhanced stability of the carbanion by intersubstituent delocalization.

Conclusion

Triorganosilyl-substituted diphenylmethanes may be deprotonated with ^{n}BuLi in THF to give crystalline organolithium derivatives which are characterized as the unusual diorganolithates, [$Li(THF)_4$][$Li\{C(SiR_3)Ph_2\}_2$], in the solid state.

Future work will be directed toward the use of the compounds described here for the synthesis of derivatives of other metals. The extensive charge delocalization observed in the structures of **4**, **5**, and **7** indicates that the C-centered ligands should be able to engage in polyhapto coordination to unsaturated metal centers. Although we have observed η^3-coordination to sodium via a single phenyl substituent of deprotonated **1**,[31] η^5-bonding involving both phenyl rings, as in the structure of **II**, is apparently inaccessible due to the noncoplanarity induced by the bulky triorganosilyl substituent.

Experimental Section

All reactions were conducted under an atmosphere of dry Ar and manipulated either on a double manifold vacuum line or in an N_2-filled drybox operating at less than 1 ppm of O_2. Solvents were purified by distillation from an appropriate drying agent (toluene and THF from potassium, hexane from Na/K alloy). NMR spectra were recorded at 300.13 (^{1}H), 125.8 (^{13}C), 99.4 (^{29}Si), and 194.5 MHz (^{7}Li) in C_6D_6 unless otherwise stated; intensities of the quaternary and ^{29}Si signals were enhanced by polarization transfer. Chemical shifts of the ^{1}H, ^{13}C, and ^{29}Si NMR spectra are relative to $SiMe_4$. ^{7}Li spectra are quoted relative to aqueous LiCl. Mass spectra were obtained at 70 eV; in assignments *m*/*z* values are given for ions containing ^{28}Si.

[$(Me_3Si)Ph_2CH$], 1. This compound was synthesized by a procedure similar to that reported previously.[9a] Crystals suitable for an X-ray structural analysis were grown at room temperature by evaporation of a concentrated hexane solution. ^{1}H NMR: δ 0.04 (9H, s, $SiMe_3$), 3.45 (1H, s, CH), 7.03−7.25 (10H, m, *o*, *m*, *p*-C_6H_5). ^{13}C{^{1}H} NMR: δ −1.7 ($^1J_{SiC}$ = 52.1 Hz, $SiMe_3$), 45.9 ($^1J_{SiC}$ = 46.0 Hz, CH), 125.4 (*p*-C_6H_5), 128.7 (*o*-C_6H_5), 129.1 (*m*-C_6H_5), 143.2 (*i*-C_6H_5). ^{29}Si NMR: δ 2.9.

[$(Me_2PhSi)Ph_2CH$], 2.[9] A solution of ^{n}BuLi in hexanes (23.9 mL of a 2.5 M solution) was added to a stirred solution of diphenylmethane (10.0 g, 59.5 mmol) in THF (50 mL) at room temperature, causing vigorous gas evolution and the formation of a deep orange solution. The mixture was stirred for 1 h at room temperature, then a solution of chlorodimethylphenylsilane (10.15 g, 59.5 mmol) in THF (20 mL) was added at 0 °C to give a pale yellow solution, which was stirred for a further 30 min before the addition of water (20 mL) and ether (20 mL). The organic phase was separated and dried ($MgSO_4$) before removal of solvent to give **2** as a viscous pale yellow oil, which was used without any further purification. (16.9 g, 94%). Anal. Calcd for $C_{21}H_{22}Si$: C, 83.37; H, 7.34. Found: C, 83.60; H, 7.37. ^{1}H NMR: δ 0.28 (6H, s, $SiMe_2$), 3.74 (1H, s, CH), 7.03−7.20 (ca. 13H, m, *o*, *m*, *p*-C_6H_5 and *m*, *p*-C_6H_5Si), 7.33 (2H, d, *o*-C_6H_5Si). ^{13}C{^{1}H} NMR: δ −3.0 ($SiMe_2$), 45.9 (CH), 125.5 (*p*-C_6H_5), 127.9 (*m*-C_6H_5Si), 128.5 (*o*-C_6H_5), 129.3 (*m*-C_6H_5), 129.4 (*p*-C_6H_5Si), 134.7 (*o*-C_6H_5Si), 137.8 (*i*-C_6H_5Si), 142.6 (*i*-C_6H_5). ^{29}Si NMR: δ −3.0. MS: *m*/*z* 302 (20, M^+), 287 (10, $M^+ - Me$), 165 (60), 135 (100, $SiMe_2Ph$), 105 (25, SiPh), 43 (30, SiMe).

[$(Me_2{}^tBuSi)Ph_2CH$], 3. This compound was synthesized by the same general method as above, utilizing equimolar quantities of diphenylmethane and *tert*-butylchlorodimethylsilane (47.6 mmol). Crystallization from hexane at room temperature yielded **3** as colorless blocks suitable for an X-ray structural

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determination (10.8 g, 80%). Anal. Calcd for $C_{19}H_{26}Si$: C, 80.76; H, 9.29. Found: C, 80.82; H, 9.23. ^{1}H NMR: δ 0.05 (6H, s, $SiMe_2$), 0.79 (9H, s, $(CH_3)_3C$), 3.59 (1H, s, CH), 6.98−7.06 (4H, m, *m*-C_6H_5), 7.09−7.17 (2H, m, *p*-C_6H_5), 7.29 (4H, d, *o*-C_6H_5Si). $^{13}C\{^{1}H\}$ NMR: δ −5.6 ($^{1}J_{SiC}$ = 51.3 Hz, $SiMe_2$), 18.0 ($^{1}J_{SiC}$ = 61.9 Hz, $SiC(CH_3)_3$), 27.1 ($C(CH_3)_3$), 44.3 ($^{1}J_{SiC}$ = 44.5 Hz, CH), 125.5 (*p*-C_6H_5), 128.6 (*o*-C_6H_5), 129.3 (*m*-C_6H_5), 143.7 (*i*-C_6H_5). ^{29}Si NMR: δ 8.1. MS: *m*/*z* 282 (10, M^+), 225 (6, $M^+ - C(CH_3)_3$), 166 (100, Ph_2CH), 152 (15), 115 (25, $SiMe_2{}^{t}Bu$), 91 (10), 73 (40).

[$(Me_3Si)Ph_2CLi(THF)_2$], 4. ^{n}BuLi (3.9 mL of a 2.5 M solution in hexane) was added at room temperature to a stirred solution of **1** (2.33 g, 9.7 mmol) in THF (25 mL) causing an exothermic reaction and gas evolution. The resultant orange-red solution was stirred for 14 h, then volatiles were removed in vacuo to leave an orange glass. Addition of hexane resulted in the formation of pale orange crystalline **4** in essentially quantitative yield. Crystals suitable for a single-crystal X-ray diffraction study were grown from a concentrated hexane solution at 5 °C. Anal. Calcd for $C_{24}H_{35}LiO_2Si$: C, 73.79; H, 9.05. Found: C, 73.87; H, 9.05. ^{1}H NMR: δ 0.35 (9H, s, $SiMe_3$), 1.19 (8H, m, THF), 3.06 (8H, m, THF), 6.48−6.52 (2H, m, *p*-C_6H_5), 6.96−7.02 (4H, m, *m*-C_6H_5), 7.21 (4H, d, *o*-C_6H_5). $^{13}C\{^{1}H\}$ NMR: δ 3.0 ($SiMe_3$), 25.3 (THF), 63.4 ($^{1}J_{SiC}$ = 73 Hz, $CSiPh_2$), 68.3 (THF), 115.4 (*p*-C_6H_5), 124.9 (*o*-C_6H_5), 129.1 (*m*-C_6H_5), 152.3 (*i*-C_6H_5). ^{29}Si NMR: $\delta - 13.6$. ^{7}Li NMR: $\delta - 0.11$.

[$(Me_2PhSi)Ph_2CLi(THF)_2$], 5. This compound was synthesized by the same general method as outlined for **4** above, utilizing equimolar quantities of **2** and ^{n}BuLi in hexane (8.50 mmol). Similar workup and crystallization from a concentrated hexane/toluene (ca 5:1) solution at 5 °C yielded **5** as dark yellow blocks suitable for a single-crystal X-ray diffraction study (2.50 g, 65%). Anal. Calcd for $C_{29}H_{37}LiO_2Si$: C, 76.94; H, 8.26. Found: C, 76.84; H, 8.12. ^{1}H NMR: δ 0.67 (6H, s, $SiMe_2$), 1.20 (8H, m, THF), 3.08 (8H, m, THF), 6.25−6.67 (2H, m, *p*-C_6H_5), 7.05−7.45 (ca. 11H, m, *o*, *m*-C_6H_5 and *m*, *p*-C_6H_5Si), 8.00 (2H, d, *o*-C_6H_5Si). $^{13}C\{^{1}H\}$ NMR: δ 2.0 ($SiMe_2$), 25.3 (THF), 62.2 ($^{1}J_{SiC}$ = 78 Hz, $CSiPh_2$), 68.1 (THF), 115.7 (*p*-C_6H_5), 125.0 (*o*-C_6H_5), 127.9 (*m*-C_6H_5Si), 129.1 (*m*-C_6H_5), 129.3 (*p*-C_6H_5Si), 134.7 (*o*-C_6H_5Si), 146.8 (*i*-C_6H_5Si), 152.5 (*i*-C_6H_5). ^{29}Si NMR: δ −16.6. ^{7}Li NMR: δ −0.09.

[$(Me_2{}^{t}BuSi)Ph_2CLi(THF)_2$], 6. The same general method as outlined for **4** above, utilizing equimolar quantities of **3** and ^{n}BuLi (6.50 mmol) in hexane, gave an orange solution. The reaction, even after 3 h reflux, was shown by ^{1}H NMR to be only 60% completed. Workup similar to that above gave a sample of **6** contaminated with **4**, precluding the acquisition of microanalytical data. ^{1}H NMR: δ 0.07 (6H, s, $SiMe_2$), 0.73 (9H, s, $(CH_3)_3C$), 1.68 (8H, m, THF), 3.15 (8H, m, THF), 6.48−6.78 (2H, m, *p*-C_6H_5), 6.88−7.33 (ca. 8H, m, *o*, *m*-C_6H_5). $^{13}C\{^{1}H\}$ NMR: δ −3.6 ($SiMe_2$), 18.4 ($C(CH_3)_3$), 26.3 ($C(CH_3)_3$), 67.4 (THF), 68.2 ($CSiPh_2$), 107.2 (*p*-C_6H_5), 125.9 (*o*-C_6H_5), 128.9 (*m*-C_6H_5), 151.9 (*i*-C_6H_5). ^{29}Si NMR: δ −15.8. ^{7}Li NMR: δ −0.23.

[$(Me_3Si)Ph_2CLi(TMEDA)_2$], 7. An excess of TMEDA (0.5 mL) was added to a stirred solution of **4** (0.81 g, 2.07 mmol) in hexane (30 mL). The solution was concentrated to incipient crystallization (ca. 15 mL) and clarified by gentle warming before being allowed to cool slowly to room temperature. This procedure yielded **7** as exceedingly pyrophoric orange plates which were too sensitive for satisfactory analytical data to be obtained (0.61 g, 62%). The structure was confirmed however by an X-ray study on a sample recrystallized from a concentrated toluene solution at −30 °C. ^{1}H NMR: δ 0.43 (9H, s, $SiMe_3$), 1.58 (24H, br s, NMe_2), 1.99 (8H, br s, CH_2), 6.52 (2H, m, *p*-C_6H_5), 6.98−7.05 (4H, m, *m*-C_6H_5), 7.23 (4H, d, *o*-C_6H_5). $^{13}C\{^{1}H\}$ NMR: δ 3.1 ($SiMe_3$), 46.5 (NCH_3), 57.6 (NCH_2) 66.0 ($^{1}J_{SiC}$ = 73 Hz, $CSiPh_2$), 115.0 (*p*-C_6H_5), 124.7 (*o*-C_6H_5), 129.3 (*m*-C_6H_5), 152.0 (*i*-C_6H_5). ^{29}Si NMR: $\delta - 13.5$. ^{7}Li NMR: $\delta - 0.11$.

Crystal Structure Determinations. Data were collected at 173 K on a Kappa CCD area detector, λ(Mo Kα) = 0.71073 Å; details are given in Table 3. The structures were solved by direct methods (SHELXS-97)[32] and refined by full matrix least squares (SHELXL-97)[33] with non-H atoms anisotropic and H atoms included in riding mode. In **1**, **3**, **5**, and **7** an absorption correction was not applied, and in **4** the data were corrected for absorption effects using MULTISCAN.

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Supporting Information Available: Details of crystal data and structure refinement for **1**, **3**, **4**, **5**, and **7** including thermal ellipsoid plots of **1**, **3**, and **4**, atom coordinates, equivalent isotropic displacement factors, bond lengths and angles, and hydrogen coordinates. This material is available free of charge via the Internet at http://pubs.acs.org.

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