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Organometallic Compounds of the Alkali Metals with Phenylsilyl Substituents at the Carbanionic Center. Crystal Structures of $LiC(SiMe_3)_2(SiMe_2Ph)\cdot Et_2O$, $NaC(SiMe_3)_2(SiMe_2Ph)\cdot TMEDA$, $NaC(SiMe_3)(SiMe_2Ph)_2\cdot TMEDA$, $\{LiCH(SiMe_2Ph)_2\}_2$, $RbC(SiMe_2Ph)_3$, and $CsC(SiMe_2Ph)_3$ (TMEDA = Tetramethylethylenediamine)

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The syntheses of a number of alkali metal compounds $MC(SiMe_3)_{3-n}(SiMe_2Ph)_n$, are described ($n$ = 1, M = Li(TMEDA) (**3a**), $Li(Et_2O)$ (**3b**), or Na(TMEDA) (**3c**); n = 2, M = $Li(THF)_2$ (**6a**), Li(TMEDA) (**6b**), Na(TMEDA) (**6c**), or K (**6d**); n = 3, M = Rb (**7d**) or Cs (**7e**); THF = tetrahydrofuran, TMEDA= tetramethylethylenediamine). The compounds **3b**, **3c**, and **6c** adopt molecular structures with intramolecular metal−phenyl interactions. The lithium compound $LiCH(SiMe_2Ph)_2$, **5**, is dimeric with electron-deficient μ-Li bridges and intramolecular metal−phenyl interactions. The compounds $MC(SiMe_2Ph)_3$, M = Na (**7b**), K (**7c**), Rb (**7d**), or Cs (**7e**), form polymeric chains in the solid state with both intra- and intermolecular metal−phenyl interactions. For the lighter alkali metals the interaction is unsymmetrical and mainly with the *ipso* and *ortho* carbon atoms, but for the heavier metals there are almost equal metal−carbon distances to all six atoms of the phenyl ring. The long M−C and short Si−C bond lengths and the wide Si−C−Si angles indicate that the structures are highly ionic. The presence of ionic species in solution is revealed by multinuclear NMR data, in particular by the low frequency shifts associated with the central carbon atoms, by the high carbon−silicon coupling constants, and by the low barriers to inversion compared with those in the trisilylmethanes from which the carbanions are derived.

Introduction

The tris(trimethylsilyl)methyl derivatives of the alkali metals adopt an astonishing range of structures.[1] The lithium compound LiR, R = $C(SiMe_3)_3$, may be obtained as a solvent-free dimer[2] or as a series of ate complexes $[LiL_n][LiR_2]$, L_n = $(THF)_4$ (THF = tetrahydrofuran)[3] or $(TMEDA)_2$ (TMEDA = tetramethylethylenediamine).[4] Molecular and ionic species, $(LiR)_n$ and $[LiR_2]^-$, coexist in solution.[5] The unsolvated sodium derivative NaR has not been isolated so far, but a dialkylsodate containing the ion $[NaR_2]^-$ has been obtained.[6a] The potassium[6b] and rubidium[7] compounds KR and RbR crystallize, even from ether solution, as solids with solvent-free linear arrays of alternate cations and planar carbanions. In contrast, the cesium analogue crystallizes from benzene with a lattice consisting of solvated ion-pairs, $CsC(SiMe_3)\cdot 3C_6H_6$.[7] The following species have been described:

MR: $LiC(SiMe_3)_3$ (**1a**), $NaC(SiMe_3)_3$ (**1b**),
$KC(SiMe_3)_3$ (**1c**), $RbC(SiMe_3)_3$ (**1d**),
$CsC(SiMe_3)_3\cdot 3C_6H_6$ (**1e**), $KC(SiMe_3)_3\cdot TMEDA$ (**1f**)

$[MR_2]^-$: $[Li\{C(SiMe_3)_3\}_2]^-$ (**2a**),
$[Na\{C(SiMe_3)_3\}_2]^-$ (**2b**)

MR′: $Li\{C(SiMe_3)_2(SiMe_2Ph)\}\cdot TMEDA$ (**3a**),
$Li\{C(SiMe_3)_2(SiMe_2Ph)\}\cdot Et_2O$ (**3b**),
$Na\{C(SiMe_3)_2(SiMe_2Ph)\}\cdot TMEDA$ (**3c**)

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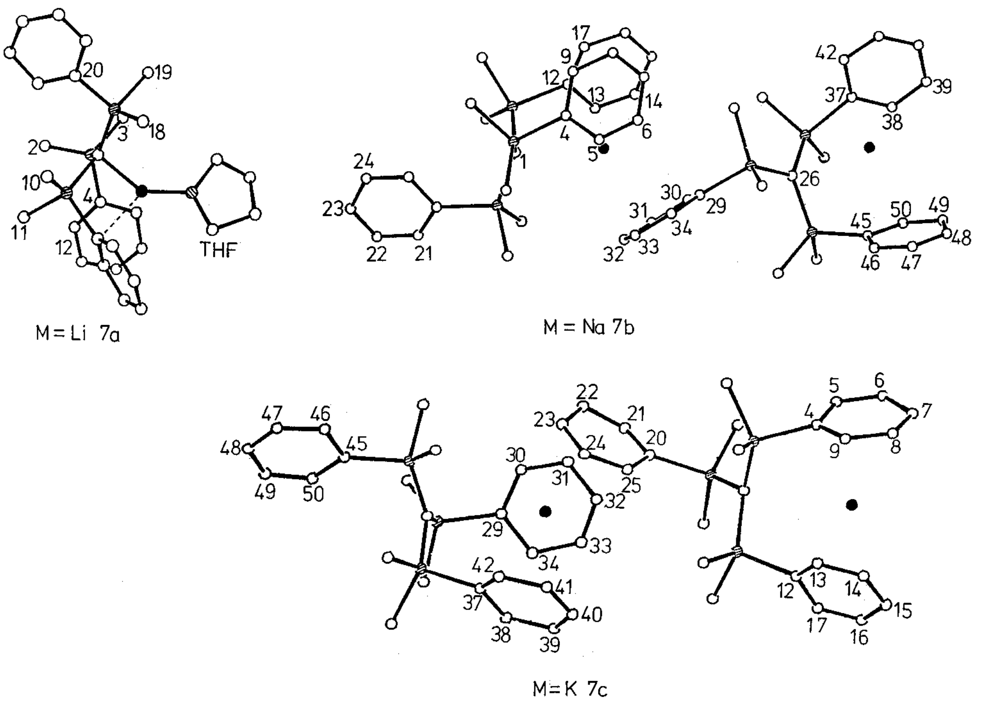

M = Li 7a M = Na 7b M = K 7c

Figure 1. Tris(dimethylphenylsilyl)methyl derivatives of lithium, sodium, and potassium.

$[MR'_2]^-$: $[K\{C(SiMe_3)_2(SiMe_2Ph)\}_2]^-$ (**4**),
$[\{LiCH(SiMe_2Ph)_2\}_2]$ (**5**)

MR″: $Li\{C(SiMe_3)(SiMe_2Ph)_2\}\cdot 2THF$ (**6a**),
$Li\{C(SiMe_3)(SiMe_2Ph)_2\}\cdot TMEDA$ (**6b**),
$Na\{C(SiMe_3)(SiMe_2Ph)_2\}\cdot TMEDA$ (**6c**),
$K\{C(SiMe_3)(SiMe_2Ph)_2\}$ (**6d**)

MR‴: $LiC(SiMe_2Ph)_3\cdot THF$ (**7a**),
$NaC(SiMe_2Ph)_3$ (**7b**), $KC(SiMe_2Ph)_3$ (**7c**),
$RbC(SiMe_2Ph)_3$ (**7d**), $CsC(SiMe_2Ph)_3$ (**7e**),
$[Li(THF)_4][C(SiMe_2C_6H_4Me\text{-}2)_3]$ (**8**)

The structures of the tris(dimethylphenylsilyl)methyl compounds MR‴ are a little less varied. The lithium compound LiR‴·THF, **7a** (Figure 1), adopts a molecular structure.[8] The solvent-free derivatives of Na,[6a] K,[6b] Rb, and Cs crystallize from solutions containing THF and have polymeric structures with both intra- and intermolecular metal–phenyl interactions. The *o*-tolyl compound, **8**, however, crystallizes from THF with an ionic structure in which there is no close Li···C interaction.[9]

In this paper, we describe the syntheses, spectroscopic data, and crystal structures of the tris(trimethylsilyl)methyl (R) derivative KR·TMEDA, **1f**, the (dimethylphenylsilyl)bis(trimethylsilyl)methyl (R′) derivatives of lithium and sodium, **3b,c** (the potassium compound, containing the anion **4**, has been described previously[7]), bis(dimethylphenylsilyl)methyllithium, **5**, bis(dimethylphenylsilyl)(trimethylsilyl)methyl(R″)sodium, **6c**, tris(dimethylphenylsilyl)methyl(R‴)rubidium and -cesium, **7d,e**, and the syntheses of several other compounds for which diffraction data were not obtained. We have combined the results from a series of preliminary communications, in addition to significant unpublished information, and discuss the structural trends for the alkali metals as a whole.

Experimental Section

Air and moisture were excluded as much as possible from all reactions by the use of Schlenk techniques and Ar as blanket gas. Solvents were dried by standard procedures and distilled immediately before use. 'Light petroleum' denotes the fraction with a bp of 40–60 °C. NMR spectra were recorded from samples in sealed tubes at 300 (^{1}H), 62.88 (^{13}C), and 99.36 MHz (^{29}Si); chemical shifts are relative to $SiMe_4$. Signals from quaternary ^{13}C nuclei were enhanced by polarization transfer (INEPT). ^{7}Li shifts (97.26 MHz) are relative to aqueous LiCl and ^{133}Cs (65.59 MHz) to CsF in H_2O/D_2O. The solvent was C_6D_6 except where indicated. All spectra were clean, indicating that new compounds were isolated in high purity. Mass spectra were obtained by EI at 70 eV; *m/z* values refer to ions containing ^{28}Si, ^{35}Cl, and ^{79}Br, and intensities (%) are relative to that of the strongest peak. Analyses for C and H were made by an established commercial company: samples of pyrophoric compounds were weighed (without a combustion aid) and manipulated in a glovebox, but values for C were persistently low presumably because of adventitious hydrolysis during sample preparation and perhaps carbide or silicide formation during combustion.

$KC(SiMe_3)_3\cdot TMEDA$ (1f). A solution of TMEDA (2.0 cm^3, 13.3 mmol) and $HC(SiMe_3)_3$ (3.7 cm^3, 13.2 mmol) in Et_2O (60 cm^3) was carefully added to solid KMe[6b] (13.9 mmol) at −10 °C, and the stirred mixture was allowed to warm to room temperature overnight. The slightly cloudy solution was filtered, and the solvent was removed from the filtrate to give a white oily solid. This was dissolved in light petroleum (15 cm^3), and after concentration, colorless needles of KR·TMEDA, **1f** , mp 80 °C (dec), separated out. Yield: 1.83 g, 34% (a further crop of crystals was obtained from the supernatant solution). The crystals were exceedingly pyrophoric, and satisfactory analytical data could not be obtained, but the structure was confirmed by an X-ray study. ^{1}H NMR: δ 0.41 (s, 18H, $SiMe_3$), 1.79 (s, 4H), 1.84 (s, 12H, TMEDA). ^{13}C NMR: δ 5.2 (J(SiC) = 53 Hz, CSi_3), 8.5 ($SiMe_3$), 45.4, 57.1 (TMEDA). ^{29}Si NMR: δ −12.7.

(Dimethylphenylsilyl)bis(trimethylsilyl)methane. The compound $Me_2PhSiCl$ (4.3 g, 25 mmol) was added slowly to a

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solution of $LiCH(SiMe_3)_2$[10] (21.5 mmol) in ether (30 cm^3) at −78 °C, and the mixture was allowed to warm up slowly overnight. The solvents were removed under vacuum, the residue was extracted with light petroleum (2 × 10 cm^3), and the solvent was removed from the extract under vacuum. The residual oil was distilled at 0.001 Torr, and the fraction boiling at 73−75 °C was recrystallized from cold (−30 °C) methanol to give $HC(SiMe_3)_2(SiMe_2Ph)$, mp *ca.* 30 °C. Yield: 5.0 g, 79%. Anal. Calcd for $C_{15}H_{30}Si_3$: C, 61.2; H, 10.2. Found: C, 60.0; H, 10.1. ^1H NMR: δ −0.39 (s, 1H, CH, ^1J(CH) = 9.8 Hz), 0.08 (s, 18H, $SiMe_3$), 0.36 (s, 6H, $SiMe_2$), 7.2−7.4 (m, 5H, Ph). ^{13}C NMR: δ 1.8 ($SiMe_3$), 3.2 (CSi_3), 6.0 ($SiMe_2$), 128.0 (*m*-C), 128.3 (*o*-C), 128.8 (*p*-C), 133.7 (*ipso*-C). ^{13}C NMR ($CDCl_3$): δ 1.6 ($SiMe_2$), 2.5 (CSi_3), 3.2 ($SiMe_3$), 127.5, 128.4, 133.4, 142.5(Ph). ^{29}Si NMR: δ −4.7 ($SiMe_2$), −0.2 ($SiMe_3$). ^{29}Si MNR ($CDCl_3$): δ −2.6 ($SiMe_2$), 2.0 ($SiMe_3$). MS/EI: *m/z* 279 (100, *M* − Me), 263 (20, *M* − Me − CH_4), 135 (30, Me_2PhSi), 129 (30, $Me_2Si{=}CHSiMe_2$), 73 (50, $SiMe_3$).

$LiC(SiMe_3)_2(SiMe_2Ph)\cdot TMEDA$ (3a). The compound $HC(SiMe_3)_2(SiMe_2Ph)$ (1.97 g, 5.0 mmol) was added to a solution of LiMe (6.5 mmol) in THF (20 cm^3) at room temperature, and the mixture was stirred overnight. The solvent was removed under vacuum, the sticky residue was extracted with heptane (20 cm^3) containing TMEDA (0.70 g, 6.0 mmol) at 60 °C, the extract was filtered, and the filtrate was concentrated and cooled to give colorless air- and moisture-sensitive crystals of $LiR'\cdot TMEDA$, **3a**, mp 125 °C. Yield: 1.12 g (54%): Anal. Calcd for $C_{21}H_{45}LiN_2Si_3$: C, 60.52; H, 10.88; N, 6.72. Found: C, 59.06; H, 10.63; N, 6.42. ^1H NMR ($C_6D_5CD_3$): δ 0.28 (s, 18H, $SiMe_3$), 0.51 (s, 6H, $SiMe_2$), 1.43 (s, 4H), 1.63 (s, 12H, TMEDA), 7.05 (m, 1H, *p*-H), 7.11 (m, 2H, *m*-H), 7.65 (d, 2H, *o*-H). ^{13}C NMR: δ 1.7 ($SiMe_2$), 3.3 ($SiMe_3$), 28.2 (CSi_3), 45.9 (TMEDA), 127.2 (*p*-C), 127.4 (*m*-C), 129.1 (*o*-C), 134.4 (*ipso*-C). ^{29}Si NMR: δ −9.7 ($SiMe_3$), −12.7 ($SiMe_2$). ^7Li NMR: δ 0.54.

$LiC(SiMe_3)_2(SiMe_2Ph)\cdot Et_2O$ (3b). This was made in a similar way to **3a**, but with Et_2O as the solvent and without the addition of TMEDA during work-up. Yield: (colorless moisture-sensitive crystals from Et_2O) 54%. ^1H NMR: δ 0.46 (s, 18H, $SiMe_3$), 0.71 (s, 6H, $SiMe_2$), 7.05 (1H, t, *p*-H), 7.25 (2H, m, *m*-H), 7.79 (2H, d, *o*-H). The structure was confirmed by an X-ray study.

$NaC(SiMe_3)_2(SiMe_2Ph)\cdot TMEDA$ (3c). Neat $HC(SiMe_3)_2(SiMe_2Ph)$ (1.97 g, 5.0 mmol) was added from a syringe to a suspension of NaMe[6a] (0.25 g, 6.6 mmol) and TMEDA (1.2 g, 10 mmol) in light petroleum (20 cm^3). The mixture was stirred overnight at room temperature and became yellow. It was then filtered, and the residue was washed with further portions (3 × 10 cm^3) of light petroleum. The washings and filtrate were concentrated to 10 cm^3 and cooled to 8 °C to give pale yellow air- and moisture-sensitive crystals of $NaR'\cdot TMEDA$, **3c**. Yield: 0.73 g (34%). Anal. Calcd for $C_{21}H_{45}N_2NaSi_3$: C, 58.2; H, 10.5; N, 6.5. Found: C, 55.0; H, 9.8; N, 4.4. ^1H NMR: δ 0.42 (s, 18H, $SiMe_3$), 0.67 (s, 6H, $SiMe_2$), 1.48 (m, 4H, TMEDA), 1.60 (s, 12H, TMEDA), 7.10 (m, 1H, *p*-H), 7.22 (m, 2H, *m*-H), 7.83 (d, 2H, *o*-H). ^{13}C NMR: δ 6.76 ($SiMe_2$), 8.56 ($SiMe_3$), 45.3, 56.6 (TMEDA), 127.1 (*p*-C), 127.9 (*m*-C), 128.3 (*o*-C), 133.8 (*ipso*-C). ^{29}Si NMR: δ −10.1 ($SiMe_3$), −13.1 ($SiMe_2$).

Bromobis(dimethylphenylsilyl)methane. A cold (−80 °C) solution of LiBu (0.20 mol) in hexane (80 cm^3) was added dropwise to a mixture of $CHBr_3$ (25.3 g, 0.10 mol), $Me_2PhSiCl$ (37 g, 0.22 mol), and THF (100 cm^3) at −84 °C, care being taken to avoid any rise in temperature. The mixture was stirred for 1 h at −84 °C, then left to warm up slowly overnight, and the solvents were removed. The residue was extracted with light petroleum (4 × 20 cm^3), and the solvent was removed from the combined extracts by rotary evaporation. The residual oil was shown to be $HCBr(SiMe_2Ph)_2$. Yield: 29.0 g, 80%. Anal. Calcd for $C_{17}H_{23}BrSi_2$: C, 56.16; H, 6.38. Found: C, 56.13; H, 6.62. ^1H NMR: δ 0.20 and 0.24 (s, 6H, Me), 2.46 (s, 1H, CH), 7.2 and 7.4 (m, 5H, Ph).^{13}C NMR: δ −2.6 and −2.1 (Me), 25.7 (CH), 127.8, 129.6, 134.3, 137.7 (Ph). ^{29}Si MNR: δ −2.6. MS(EI): *m/z* 347 (10, *M* − Me), 267 (23, *M* − Me −HBr), 208 (26, *M* − Ph_2), 135 (100, $SiPhMe_2$).

$LiCH(SiMe_2Ph)_2$ (5). A solution of LiBu (15 mmol) in hexane (6.0 cm^3) was added to a cold (−78 °C) solution of $HCBr(SiMe_2Ph)_2$ (5.00 g, 13.7 mmol) in Et_2O (20 cm^3). The mixture was kept at −78 °C for 1 h, and then the solvent was removed under vacuum at as low a temperature as possible. The residue was extracted with heptane (2 × 20 cm^3) at 0 °C to leave a white solid. The heptane extract was reduced to 10 cm^3 and stored overnight at 8 °C to give pale yellow crystals of $LiCH(SiMe_2Ph)_2$, **5**. Anal. Calcd for $C_{17}H_{23}LiSi_2$: C, 70.29; H, 7.98. Found: C, 68.50; H, 7.94. ^1H NMR ($C_6D_5CD_3$): δ −2.9 (s, 1H, CH), 0.21 (s, 12H, Me), 7.04−7.22 (m, 10H, Ph). ^{13}C NMR: δ 1.6 (CH), 2.9 (Me), 145.0 (*ipso*-C), 132.7 (*o*-C), 129.8 (*m*-C), 129.2 (*p*-C). ^7Li NMR: δ 0.58. ^{29}Si NMR: δ −7.7.

Bis(dimethylphenylsilyl)(trimethylsilyl)methane. A cold (−78 °C) solution of LiBu (60 mmol) in hexane (24 cm^3) was added slowly to $HCBr(SiMe_2Ph)_2$ (19.6 g, 60 mmol) in Et_2O (50 cm^3) at −78 °C. The mixture was kept at −78 °C for 1 h, then Me_3SiCl (7.05 g, 65 mmol) was added dropwise, and the mixture was allowed to warm up slowly overnight. The solvents were removed under vacuum, and the residue was extracted with light petroleum (4 × 20 cm^3). The solvent was removed from the combined extracts, and the residue was heated at 100 °C/0.01 Torr to remove volatile impurities and leave $HC(SiMe_3)(SiMe_2Ph)_2$ as a colorless oil. Anal. Calcd for $C_{20}H_{32}Si_3$: C, 67.32; H, 8.98. Found: C, 66.76; H, 9.29. ^1H NMR: δ −0.03 (s, 9H, $SiMe_3$), 0.08 (s, 1H, CH), 0.25 and 0.37 (s, 6H, $SiMe_2$), 7.42 and 7.18 (5H, m, Ph). ^{13}C NMR: δ 1.5 (CH), 1.7 and 1.9 ($SiMe_2$), 3.3 ($SiMe_3$), 127.9 (*m*-C), 128.7 (*p*-C), 133.7(*o*-C), 142.3 (*ipso*-C). ^{29}Si NMR: δ −4.4 ($SiMe_2$), 0.2 ($SiMe_3$). MS (EI): *m/z* 356 (3, *M*), 341 (60, *M* − Me), 263 (80, *M* − Me − PhH), 135 (100, $SiMe_2Ph$), 73 (50, $SiMe_3$).

$LiC(SiMe_3)(SiMe_2Ph)_2\cdot 2THF$ (6a). A solution of LiMe (18 mmol) in THF (12.8 cm^3) was added to a solution of $HC(SiMe_3)(SiMe_2Ph)_2$ (5.0 g, 14 mmol) in THF (20 cm^3), and the mixture was stirred overnight, during which methane was evolved slowly. The solvent was removed, and light petroleum (10 cm^3) was added to the residue. The solvent was decanted and the last traces removed in vacuum to leave a white free-flowing powder shown to be $LiR''\cdot 2THF$, **6a**. ^1H NMR (C_6D_6): δ 0.40 (s, 9H, $SiMe_3$), 0.63 and 0.70 (6H, br, $SiMe_2$), 1.25 and 3.25 (8H, br, THF), 7.10 and 7.66 (10H, m, Ph). ^{13}C NMR: 7.06 ($SiMe_2$), 9.47 ($SiMe_3$), 25.3, 68.0 (THF), 127.4 (*p*-C), 128.6 (*m*-C), 133.6 (*o*-C), 149.9 (*ipso*-C). ^7Li NMR: δ 1.80. ^{29}Si NMR: −12.6 ($SiMe_2$), −9.7 ($SiMe_3$). Crystals of **6a** were obtained from light petroleum, but they were not suitable for an X-ray study.

$LiC(SiMe_3)(SiMe_2Ph)_2\cdot TMEDA$ (6b). This was isolated as pale yellow crystals by dissolving **6a** in light petroleum, adding an excess of TMEDA, and concentrating and cooling the resulting solution. Anal. Calcd for $C_{26}H_{47}LiNSi_3$: C, 65.21; H, 9.89; N, 5.85. Found: C, 63.03; H, 9.67; N, 5.95. ^1H NMR: δ 0.36 (s, 9H, $SiMe_3$), 0.64 (s, 12H, $SiMe_2$), 1.76 (br, 16H, TMEDA), 7.25−7.85 (m, 10H, Ph). ^{13}C NMR: 7.09 (s, $SiMe_2$), 8.45 ($SiMe_3$), 45.9, 57.2 (TMEDA), 127.3 (*p*-C), 127.4 (*m*-C), 134.5 (*o*-C), 149.7 (*ipso*-C). ^7Li NMR: −1.71. ^{29}Si NMR: −12.6 ($SiMe_3$), −9.7 ($SiMe_2$).

$NaC(SiMe_3)(SiMe_2Ph)_2\cdot TMEDA$ (6c). A solution of $HC(SiMe_3)(SiMe_2Ph)_2$ (1.28 g, 3.60 mmol) and TMEDA (0.358 g, 5.0 mmol) in light petroleum (20 cm^3) was added to solid NaMe[6a] (7.9 mmol), and the mixture was stirred overnight. The solvent was removed from the pale yellow solution, and the residue was dissolved in light petroleum. The solvent was again pumped away, together with any unchanged TMEDA, and the residue was washed with heptane at 0 °C to leave a yellow powder which appeared to be $NaR''\cdot TMEDA$, **6c**. Crystals suitable for an X-ray study were obtained by concentrating the heptane extract. Anal. Calcd for $C_{26}H_{47}N_2NaSi_3$: C, 63.10; H, 9.57; N, 5.66. Found: C, 62.41; H, 9.40; N, 5.95. ^1H NMR: δ 0.39 (s, 9H, $SiMe_3$), 0.61 (br, 12H, $SiMe_2$), 1.46

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(4H, s), 1.55 (s, 12H, TMEDA), 7.15 (t, 2H, *p*-H), 7.24 (t, 4H, *m*-H), 7.87 (d, 4H, *o*-H). ^{13}C NMR: δ −0.1 (J(SiC) = 50 Hz, CSi$_3$), 6.7, 6.9 (SiMe$_2$), 8.5 (SiMe$_3$), 45.1, 56.2 (TMEDA), 127.1 (*p*-C), 127.7 (*m*-C), 133.7 (*o*-C), 151.0 (*ipso*-C). ^{29}Si NMR: −12.7 (SiMe$_3$), −10.5 (SiMe$_2$).

KC(SiMe$_3$)(SiMe$_2$Ph)$_2$ (6d). Neat HC(SiMe$_3$)(SiMe$_2$Ph)$_2$ (1.25 g, 3.51 mmol) was added from a syringe to a suspension of KMe^{6b} (0.56 g, 10.4 mmol) in Et$_2$O (20 cm^3) at −20 °C. The stirred heterogeneous mixture was allowed to warm to room temperature overnight. The solvent was removed under vacuum, and light petroleum (10 cm^3) was added to the solid residue to assist in the removal of ether under vacuum. After the solvent had been pumped away, benzene (20 cm^3) was added. The black suspension was filtered through Celite, and the solvent was removed from the filtrate. The brown residue was again washed with light petroleum (3 × 10 cm^3) to remove colored impurities and recrystallized from benzene to give white crystals of KR″, **6d,** from a dark red solution. Yield: 60%. Anal. Calcd for C$_{29}$H$_{31}$KSi$_3$: C, 60.8; H, 7.91. Found: C, 58.5; H, 7.83. ^{1}H NMR: δ 0.26 (s, 9H, SiMe$_3$), 0.70 (s, 12H, SiMe$_2$), 6.92 (d, 2H, *p*-H), 7.00 (t, 4H, *m*-H), 7.69 (d, 4H, *o*-H). ^{13}C NMR: δ 4.4(J(SiC) = 59 Hz, CSi$_3$), 6.2 (SiMe$_2$), 8.8 (SiMe$_3$), 126.6 (*p*-C), 128.2 (*m*-C), 133.4 (*o*-C), 153.2 (*ipso*-C). ^{29}Si NMR: δ 12.3 (SiMe$_3$), −13.6 (SiMe$_2$).

RbC(SiMe$_2$Ph)$_3$ (7d). A solution of LiMe (5.7 mmol) in Et$_2$O (3.4 cm^3) was added to a cold (−10 °C) solution of 2-ethylhexoxyrubidium (1.22 g, 5.68 mmol) in Et$_2$O (40 cm^3).[7,11] After 3 min, HC(SiMe$_2$Ph)$_3$ (2.37 g, 5.70 mmol) was added and the mixture was allowed to warm to room temperature overnight. The solvent was removed under vacuum, and the residue was washed with light petroleum (4 × 20 cm^3) and then Et$_2$O (20 cm^3) to remove the lithium alkoxide. The remaining solid was extracted with THF, the extract filtered, and the filtrate concentrated to give RbR‴, **7d**, as an air- and moisture-sensitive solid. Yellow crystals suitable for investigation by X-ray diffraction were obtained from hot toluene containing the minimum amount of THF necessary for complete dissolution. Yield: 2.12 g, 74%; mp 124 °C (dec). Anal. Calcd for C$_{25}$H$_{33}$RbSi$_3$: C, 59.7; H, 6.6. Found: C, 58.4; H, 6.8. ^{1}H NMR (THF-d_8): 0.00 (s, 18H, Me), 6.93 (m, 3H, *p*-H), 7.03 (m, 6H, *m*-H), 7.78 (6H, d, *o*-H). ^{13}C NMR: δ −6.0 (J(SiC) = 68 Hz, CSi$_3$), 6.9 (Me), 125.5 (*p*-C), 126.3 (*m*-C), 135.3 (*p*-C), 155.1 (*ipso*-C). ^{29}Si NMR: δ −8.3.

CsC(SiMe$_2$Ph)$_3$ (7e). A solution of LiMe (4.96 mmol) in Et$_2$O (3.5 cm^3) was added to a cold (−78 °C) solution of 2-ethylhexoxycesium (1.30 g, 4.96 mmol) and HC(SiMe$_2$Ph)$_3$ in ether (40 cm^3).[7,11] The solution was allowed to warm and then stirred at room temperature for 3 h. The solvent was removed in vacuum, and the residue was washed with light petroleum (3 × 50 cm^3) and recrystallized from hot toluene containing the minimum amount of THF to achieve complete dissolution. Bright yellow air- and moisture-sensisitive hexagonal plates of CsR‴, **7e**, were obtained. Yield: 1.80 g, 66%, mp >140 (dec). The compound was too reactive to give good analytical results, but the structure was confirmed by an X-ray study. ^{1}H NMR (THF-d_8): δ 0.03 (18H, s, Me), 6.96 (dd, 3H, *p*-H), 7.06 (m, 6H, *m*-H), 7.79 (dd, 6H, *o*-H). ^{13}C NMR: δ −7.0 (J(SiC) = 67 Hz, CSi$_3$), 5.9 (Me), 124.7 (*p*-C), 125.5 (*m*-C), 134.3 (*o*-C), 153.9 (*ipso*-C). ^{29}Si NMR: δ −14.0. ^{133}Cs NMR: δ −33.4, $\Delta\nu_{1/2}$ 450 Hz.

Crystal Data. C$_{19}$H$_{39}$LiOSi$_3$, **3b**, M_w = 374.7, monoclinic, space group $P2_1/c$, a = 14.443(10) Å, b = 12.099(4) Å, c = 13.796(10) Å, β = 100.44(6)°, U = 2371(3) Å^3, λ = 0.710 73 Å, Z = 4, D_c = 1.05 Mg m^{-3}, F(000) = 824, colorless, air- and moisture-sensitive block, 0.3 × 0.2 × 0.1 mm, μ (Mo Kα) = 0.20 mm^{-1}, T = 173(2) K.

C$_{21}$H$_{45}$N$_2$NaSi$_3$, **3c**, M_w = 432.9, monoclinic, space group $P2_1/n$, a = 9.256(3) Å, b = 20.153(5) Å, c = 14.656(4) Å, β = 92.74(2)°, U = 2730.7(13) Å^3, λ = 0.710 73 Å, Z = 4, D_c = 1.05 Mg m^{-3}, F(000) = 952, colorless air- and moisture-sensitive block, 0.40 × 0.40 × 0.40 mm, μ (Mo Kα) = 0.20 mm^{-1}, T = 173(2) K.

C$_{34}$H$_{46}$Li$_2$Si$_4$, **5**, M_w = 580.9, triclinic, space group $P\bar{1}$, a = 11.563(3) Å, b = 11.585(5) Å, c = 13.413(5) Å, α = 96.26(3)°, β = 93.95(3)°, γ = 101.57(3)°, U = 1742.1(12) Å^3, λ = 0.710 73 Å, Z = 2, D_c = 1.11 Mg m^{-3}, F(000) = 624, colorless air- and moisture-sensitive block, 0.3 × 0.2 × 0.2 mm, μ = 0.19 mm^{-1}, T = 173(2) K.

C$_{26}$H$_{47}$N$_2$NaSi$_3$, **6c**, M_w = 494.9, monoclinic, space group $P2_1/c$, a = 9.715(6) Å, b = 17.823(12) Å, c = 18.095(9) Å, β = 104.92(5)°, U = 3028(3) Å^3, λ = 0.710 73 Å, Z = 4, D_c = 1.09 Mg m^{-3}, F(000) = 1080, colorless air- and moisture-sensitive block, 0.4 × 0.3 × 0.3 mm, μ = 1.2(6) mm^{-1}, T = 173(2) K.

C$_{25}$H$_{33}$RbSi$_3$, **7d**, M_w = 503.3, orthorhombic, space group *Pbca*, a = 9.5140(7) Å, b = 16.8954(12) Å, c = 31.969(2) Å, U = 5138.7(6) Å^3, λ = 0.710 73 Å, Z = 8, D_c = 1.301 Mg m^{-3}, F(000) = 2096, yellow air- and moisture-sensitive block, 0.3 × 0.2 × 0.12 mm, μ = 2.076 mm^{-1}, T = 160(2) K.

C$_{25}$H$_{33}$CsSi$_3$, **7e**, M_w = 550.7, orthorhombic, space group $Cmc2_1$, a = 16.364(4) Å, b = 9.566(4) Å, c = 16.428(5) Å, U = 2572(1) Å^3, λ = 0.710 73 Å, Z = 4, D_c = 1.42 Mg m^{-3}, F(000) = 1120, yellow air- and moisture-sensitive block, 0.15 × 0.15 × 0.15 mm, μ = 1.57 mm^{-1}, T = 173(2) K.

Data Collection and Structure Determination. The structures of LiR′ (**3b**), NaR′ (**3c**), [{LiCH(SiMe$_2$Ph)$_2$}$_2$] (**5**), NaR″·TMEN (**6c**), and CsR‴ (**7e**), were determined at the University of Sussex, from data collected on an Enraf-Nonius CAD4 diffractometer in the $\theta/2\theta$ mode with Mo Kα radiation and 2° < θ < 25° (28° for **3c** and 30° for **7e**). Absorption corrections were not applied. The structures of **3b**, **3c**, **5**, and **6c** were solved by direct methods (SHELXS-86) and refined by full-matrix least-squares on all F^2 (SHELXL-93), with non-hydrogen atoms anisotropic. Hydrogen atoms were included in the riding mode with $U_{iso} = 1.2U_{eq}(C)$ or $1.5U_{eq}(C)$ for the Me groups. For **3b**, 4155 independent reflections were used to give $R1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o| = 0.108$ (for 2785 reflections with $I > 2\sigma(I)$) and $wR2 = \{\Sigma w[(F_o{}^2 - F_c{}^2)^2]/\Sigma w(F_o{}^2)^2\}^{1/2} = 0.299$ (all data). Similarly, for **3c**, 6583 unique reflections gave $R1$ = 0.060 (4165 reflections with $I > 2\sigma(I)$), wR2 (all data) = 0.175. For **5**, 6114 independent reflections gave $R1$ = 0.075 (3990 reflections with $I > 2\sigma(I)$) and wR2 (all data) = 0.21; hydrogen atoms on C(1) and C(18) were freely refined. For **6c**, 4195 independent reflections gave R1 = 0.068 (2752 reflections with $I > 2\sigma(I)$) and wR2 = 0.180. For **7e**, 1768 reflections out of 2106 measured were used in the structure solution by the heavy-atom method (SHELXS-86) and parameters refined on F by use of the Enraf-Nonius MOLEN programs to give $R = (\Sigma||F_o| - |F_c||)/\Sigma|F_o| = 0.036$, $R' = \{\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2\}^{1/2} = 0.039$, $S = 1.1$, where $w = 1/\sigma^2(F)$. The structure with the opposite absolute configuration gave R = 0.038, R' = 0.042, S = 1.22 (some of the crystals examined showed a different unit cell, which was orthorhombic, space group *Pbca*, with a = 32.851(11) Å, b = 9.482(2) Å, c = 16.601 Å. Data were collected from one such crystal and a set of atom positions corresponding to **7e** could be located, but as there were also peaks from a ghost molecule reflected through a mirror plane the crystals appeared to be twinned).

The structure of RbR‴, **7d,** was determined at the University of Newcastle from data collected with a Siemens SMART CCD diffractometer, Mo Kα radiation and 2.41° < θ < 28.16°; 6057 independent reflections were used for the structure solution by direct methods and full-matrix least-squares refinement on F^2. A semiempirical correction for absorption from φ-scans was applied. Values of R1 = 0.040 (4574 reflections with $I > 2\sigma(I)$) and wR2 (all data) = 0.076 were obtained.

Results and Discussion

Synthesis. Treatment of tribromomethane at low temperature with 3 equiv of butyllithium in the presence of 3 equiv of chlorodimethylphenylsilane gave HC(SiMe$_2$Ph)$_3$, HR‴. The product when 2 equiv of LiBu/Me$_2$PhSiCl was used was (Me$_2$PhSi)$_2$CHBr, and this was converted into HC(SiMe$_3$)(SiMe$_2$Ph)$_2$, HR″, by treatment

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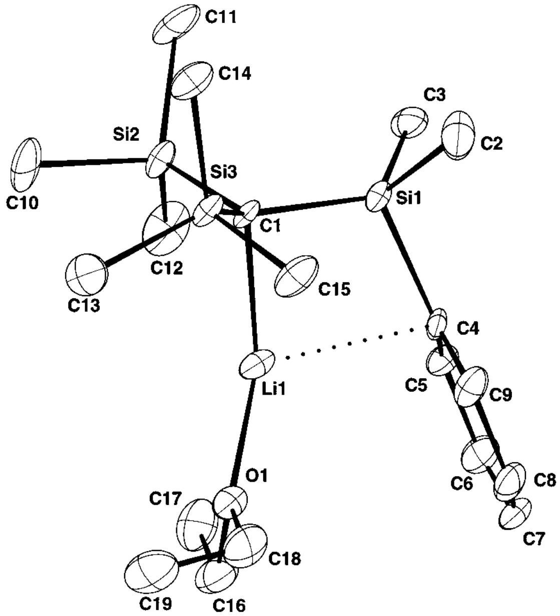

Figure 2. Molecular structure of $LiC(SiMe_3)_2(SiMe_2Ph)\cdot Et_2O$, **3b**.

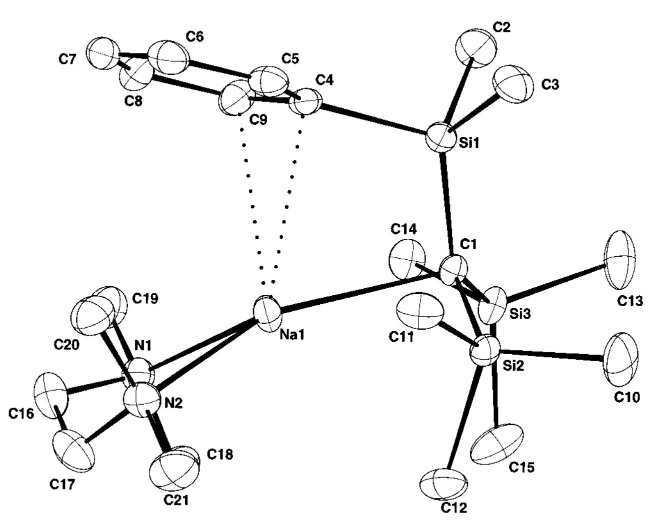

Figure 3. Molecular structure of $NaC(SiMe_3)_2(SiMe_2Ph)\cdot$TMEDA, **3c**.

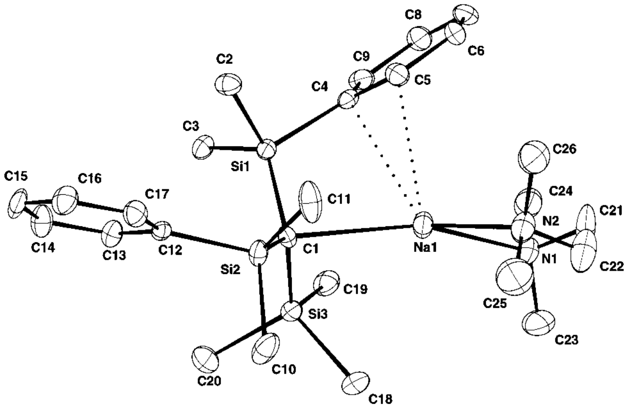

Figure 4. Molecular structure of $NaC(SiMe_3)(SiMe_2Ph)_2\cdot$TMEDA, **6c**.

with LiBu/Me_3SiCl. In the same way, $HC(SiMe_3)_2(SiMe_2Ph)$, HR′, was obtained by use of 2 equiv of LiBu/Me_3SiCl in the first step and 1 equiv of LiBu/$Me_2PhSiCl$ in the second. Good yields could be obtained at each stage, provided the temperature was rigorously controlled.

The reaction between these silicon-substituted methanes and the appropriate methyl−alkali metal derivatives gave the new air- and moisture-sensitive organometallic compounds. Methylsodium and -potassium were obtained from methyllithium and sodium or potassium tertiary butoxides, but methylrubidium and -cesium were made from Rb or Cs 2-ethylhexoxides to make it easier to wash out the lithium alkoxide product.[11] The organolithium compounds described here were fairly soluble in hydrocarbon and ether solvents. The tris(dimethylphenylsilyl)methyl derivatives of Na, K, Rb, and Cs were much less soluble in hydrocarbons and readily separated as yellow solids.

Crystal Structures. The compounds MR′ were isolated as TMEDA complexes LiR′·TMEDA, **3a**, and NaR′·TMEDA, **3c**, but in the case of **3a**, crystals suitable for an X-ray structure determination could not be isolated. It was found that the complex LiR′·Et_2O, **3b**, gave better crystals so its structure was obtained.

Molecular parameters for LiR′·Et_2O, NaR′·TMEDA, NaR″·TMEDA (Figures 2−4), and LiR‴·THF, **7a** (described previously in a preliminary communication[8]), are listed in Table 1. All four compounds are monomeric and adopt molecular structures in the solid state. There are only a few examples of monomeric compounds η^1-$RLiL_n$ (L = oxygen or nitrogen donor)[12−15] in the literature, and as far as we are aware, there is no example of an organosodium analogue. The Li−C and Na−C bond lengths in LiR′·Et_2O, NaR′·TMEDA, and NaR″·TMEDA are among the shortest reported (for reviews see references 16−18), but in view of the estimated standard deviations, the differences between the values found in the present work and those in the literature (2.136(16) Å in LiPh·PMDTA,[12] PMDTA= pentamethyldiethylenetriamine, 2.12 Å in $LiC_6H_2Bu^t_3$-2,4,6·TMPN, TMPN = *N*,*N*,*N*′,*N*′-tetramethylpropane-1,2,-diamine,[13] and 2.13(5) Å in $Li\{CH(SiMe_3)_2\}\cdot$ PMDTA[14]) may not be significant. All the C(1)−Si bond lengths are short; those in **3b, 3c**, and **6c** are not significantly different from the mean, but a range of values is found in LiR‴·THF, **7a**. The Si−Me and Si−Ph bond lengths are normal. In all four compounds there is a clear interaction between the alkali metal and the *ipso*-carbon atom of a phenyl ring. In the case of the sodium compounds **3c** and **6c** the interaction extends to the *ortho*-carbon and in **6c** the *ortho*-carbon, is the closest ring atom to the sodium. Metal−aryl interactions have been noted in the structures of $MCPh_3$, M = Li[19,20] or Na,[21] $LiPhCHSiMe_3\cdot$TMEDA,[22] $NaN\{SiH(C_6H_2Me_3\text{-}2,4,6)_2\}_2\cdot Et_2O$,[23] and $AlMe_2N(Si$-

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Table 1. Comparison of Bond Lengths (Å) and Angles (deg) in 3b, 3c, 6c, and 7a

	LiR′·Et$_2$O **3b**	NaR′·TMEDA **3c**[a]	NaR″·TMEDA **6c**	LiR‴·THF **7a**[a]
M−C	2.096(10)	2.566(3)	2.565(5)	2.12(2)
C−Si(1)	1.830(5)	1.820(3)	1.813(5)	1.954(14)
C−Si(2)	1.824(5)	1.816(3)	1.819(5)	1.819(12)
C−Si(3)	1.832(5)	1.818(3)	1.816(5)	1.786(12)
Si−Me (av)[b]	1.879(6)	1.886(4)	1.886(6)	1.853(15)
Si−Ph (av)[b]	1.919(5)	1.909(3)	1.903(5)	1.900(13)
C−C (av)[b]	1.383(10)	1.388(5)	1.381(7)	1.38(2)
M···C	2.487(11)	*4* 2.934(3) *9* 2.965(3)	*4* 3.026(5) *5* 2.885(6)	2.40(2)
M−O(N)	1.885(10)	2.468(3), 2.511(3)	2.490(5), 2.479(5)	1.85(2)
M−C−Si(1)	90.5(3)	97.3(1)	97.7(2)	99.9(8)
M−C−Si(2)	104.5(4)	92.8(1)	108.2(2)	89.7(7)
M−C−Si(3)	107.4(4)	106.0(1)	91.1(2)	105.0(7)
Si−C−Si	116.5(3) (av)	117.0(2),117.1(2), 119.2(2)	115.9(3), 119.1(3), 117.8(3)	114.9(6), 119.9(6), 119.0(7)
Me−Si−Me in SiMe$_2$	102.6(3)[b]	101.1(2)[b]	104.9(2), 103.8(3)	104.1(6), 101.4(6), 98.7(7)
Me−Si−Me in SiMe$_3$	104.1(3)[b] (av)	104.0(2)[c]	104.6(3)[d]	
C(1)−Si−Ph	108.5(2)	111.1(1)	113.2(2)	*12* 107.4(5)
C(1)−Si(1)−C(2)	118.0(3)	117.3(2)	114.7(2)	*11* 122.1(6)
C(1)−Si(1)−C(3)	116.9(3)	117.8(2)	116.0(2)	*10* 114.5(6)
C(1)−Si(2)−C(10)	115.3(3)	116.0(2)	115.3(3)	*2* 116.7(5)
C(1)−Si(2)−C(11)	117.3(3)	112.2(2)	113.8(2)	*3* 114.8(5)
C(1)−Si(2)−C(12)	111.0(3)	114.4(2)	113.9(2)	*4* (Ph) 108.4(5)
C(1)−Si(3)−C(13)	114.3(3)	113.7(2)	113.6(2)[e]	*18* 109.7(6)
C(1)−Si(3)−C(14)	114.9(3)	115.1(2)	112.4(2)[e]	*19* 121.4(6)
C(1)−Si(3)−C(15)	113.8	115.4(2)	115.8(2)[e]	*20* (Ph) 116.5(5)
Me−Si−Ph	106.5(3), 102.9(2)	105.5(2), 102.2(2)	101.2(2), 105.3(2), 105.8(3), 103.0(2)	105.0(5)[b]
C(1)−M−O(N)	156.8(6)	142.1(1), 136.4(1)	141.0(2), 139.1(2)	144(1)
C(Ph)−M−O(N)	113.7(4)	117.2(1), 124.0(1)	129.6(2), 104.9(2)	129(1)
C(1)−M−C(Ph)	82.7(4)	67.6(1), 84.3(1)	66.8(2), 85.4(2)	83.9(8)
C(5)−C(4)−C(9)	116.6(5)	116.0(3)	115.1(5),[f] 116.2(5)[g]	114(1), 115(1), 114(1)

[a] The italic numbers refer to Figures 1, 3, and 4 of this paper and the figure in ref 8. In **7a**, the *ipso* carbon atom *12* attached to Si(2) is closest to lithium. [b] No individual value is significantly different from the average. [c] Range from 102.4(2) to 106.2(2)°. [d] Range from 103.0(3) to 106.3(3)°. [e] C18−20. [f] Coordinated to the metal. [g] Not coordinated to the metal.

Ph^{t}Bu$_2$)(SiMe^{t}Bu$_2$).[24] The Si−C−Si angles are shown in Table 1. In LiR′·Et$_2$O, **3b**, and LiR‴·THF, **7a,** the individual values do not differ significantly from the mean, but in NaR′·TMEDA, **3c,** one angle is wider than the other two, and the three angles in NaR″·TMEDA, **6c,** are significantly different. The sum of the angles is 349.5° in **3b**, 353° in **3c**, 353° in **6c**, and 354° in **7a**, indicating[25] that in all three compounds the M−C bonds are strongly ionic, as would be expected from quantum mechanical calculations.[18,26] In LiR′·Et$_2$O and LiR‴·THF the smallest M−C−Si angle is that to the silicon bearing the coordinated phenyl group, but this is not so in NaR′·TMEDA or NaR″·TMEDA. In all cases, however, the coordination of the phenyl group to the metal center tilts the almost planar CSi$_3$ system to one side. The Me−Si−Me angles are markedly narrowed from the tetrahedral value, and the C−C−C angles in the phenyl groups adjacent to silicon are compressed below 120°, as is common in organometallic compounds.[13,26b] This compression is observed whether or not the phenyl group is coordinated to another metal, as is seen from the angles in the two rings in NaR″·TMEDA, **6c**. The remaining data in Table 1 require no comment.

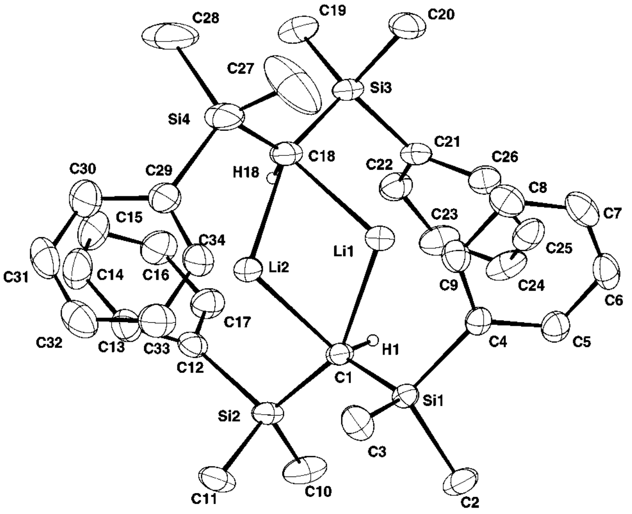

Figure 5. Molecular structure of [{LiCH(SiMe$_2$Ph)$_2$}$_2$], **5**.

The compound {LiCH(SiMe$_2$Ph)$_2$}$_2$, **5**, was isolated as solvent-free crystals from the reaction between butyllithium and (Me$_2$PhSi)$_2$CHBr in diethyl ether and was found to have an electron-deficient dimeric structure (Figure 5) like that of LiC(SiMe$_3$)$_3$, **1a**,[2] but with intradimer lithium−phenyl instead of lithium−methyl interactions. There is no crystallographically imposed symmetry. The atoms C28, C29, and Si4 have rather large anisotropic displacement parameters so derived bond lengths and angles are unreliable. If these are excluded, chemically equivalent bonds within the CH(SiMe$_2$Ph)$_2$ fragments are not significantly different; therefore, in most cases, average values are given in Table 2. The Li$_2$C$_2$ ring is almost planar (sum of angles 358.1°) and slightly unsymmetrical. The average Li−C

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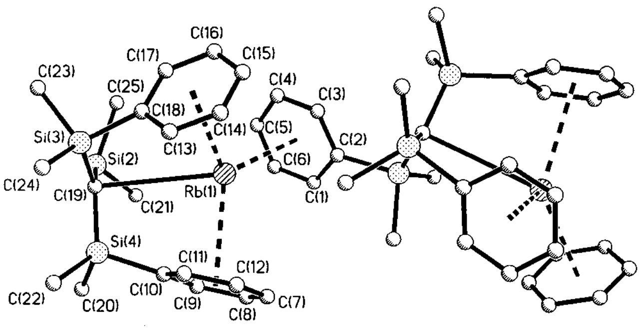

Figure 6. Molecular structure of $RbC(SiMe_2Ph)_3$, **7d**.

Table 2. Bond Lengths (Å) and Angles (deg) (with Esd's in Parentheses) for $\{LiCH(SiMe_2Ph)_2\}_2$, 5

Li1−C1	2.164(8)	Li1−C18	2.217(10)
Li1−C21	2.492(9)	Li1−C26	2.501(10)
Li1−C4	2.687(9)	Li1−C9	2.569(10)
Li2−C18	2.146(10)	Li2−C1	2.223(9)
Li2−C12	2.477(10)	Li2−C13	2.626(10)
C1,C18−Si mean	1.823(4)	Si−Me mean	1.870(5)
Si−Ph mean	1.901(5)	C−C mean	1.381(8)
C1−Li1−C18	112.6(4)	C1−Li2−C18	113.1(4)
C1,C18−Si−Me mean	114.2(3)	C1,18−Si−Ph	107.5(2)
Me−Si−Me mean	107.8	Me−Si−Ph	106.3(2)
SiC1,18−Si mean	120.3(3)	C− *ipso*C−C mean	116.0(4)
Si1−C1Li1	95.8(3)	Si2−C1−Li	143.7(3)
Si1−C1−Li2	128.1(4)	Si2−C1−Li2	86.8(3)
Li−C1−Li2	66.2(3)	Li−C−Li mean	112.9(6)

bond lengths (2.155 and 2.220 Å) are similar to those in **1a** (2.291(6) and 2.303(6) Å)[2] and in complexes such as LiC_4H_5·TMEDA, C_4H_5 = bicyclo[1.1.0]buta-1-yl (2.23(5) Å),[27a] $\{Li^tBu(OEt_2)\}_2$ (2.184(6) Å),[27b] $(LiPh·TMEDA)_2$ (2.208(6), 2.278(6)Å),[27c] $(LiCH_2SMe·TMEDA)_2$ (2.240(7) Å),[27d] and $(Li(C{\equiv}CPh)TMPA)_2$, TMPA = tetramethyl-1,3-propanediamine (2.148(7) Å).[27e] The Si−C, Si−Me, and C−C bond lengths are normal, the C1(or C18)−Si−C angles wide, and the Me−C−Me and Me−C−Ph angles compressed. The most interesting features of the structure are (a) the two-coordinate lithium, also found in $[LiC(SiMe_3)_3]_2$ and $\{LiN(SiMe_3)_2\}_2$,[28] and (b) the short distances from lithium to the *ipso*- and one *ortho*-carbon of each phenyl ring. Thus, each lithium interacts with two methine carbon atoms at 2.1−2.2 Å and four phenyl carbon atoms at 2.5−2.7 Å, and this coordination is sufficient to exclude molecules of the ether solvent (compare **7b**−**e** below).

Whereas LiR‴·THF, **7a,** has a molecular structure in the solid state, the analogues containing the heavier alkali metals crystallize with structures comprising chains of cations and planar anions (Figures 1, 6, and 7). In MR‴, **7b**−**d**, each metal atom M is linked to two phenyl groups attached to the nearest carbanionic center and to one from the adjacent carbanion. In **7e**, each Cs is linked to one phenyl group from the nearest carbanion and to two from the next carbanion. In all cases, the coordination at the central carbon is planar (sum of angles 355°, 358° for M = Na, 354° for K, 359° for Rb, and 358° for Cs). Other planar carbanions are found in MR, **1c,d**, $[Li(THF)_4][C(SiMe_2C_6H_4Me\text{-}2)_3]$, **8**, $[Li(12\text{-}crown\text{-}4)_2][C(SiMe_3)(SiMeBu^t{}_2)(SiMe_2F)]$,[29] $NaCH(SiMe_3)_2$,[30] the compounds $M'C(SiMe_2NMe_2)_3$ (M′ = Li or MgI),[31] and a number of triphenylmethyl(alkali metal) complexes with nitrogen or oxygen donors.[21,32] Despite the similarity of the crystal structures, all four compounds MR‴, **7b**−**e**, crystallize in different space groups. In **7b** the chains are formed by a *c* glide repetition of a $(NaR‴)_2$ unit and in **7c** by a 3_1 screw repetition of $(KR‴)_2$. In **7d** the chains are formed by a *b* glide repetition of $(RbR‴)_2$ parallel to the *a* axis, and in **7e** the chains are formed by a *c* glide repetition of a single CsR‴ unit. As the alkali metal ion becomes heavier and softer, there is a progressive shift from interaction with the negative charge on the central atom of the carbanion to interaction with the π-electrons of the phenyl rings. This shift is shown by the M−C(Ph) bond lengths given in Table 3, in which values greater than 3.5 Å for Na−Rb and 3.75 Å for Cs are omitted, and has also been documented in several other series of compounds, *e.g.*, sulfinimidamides $Me_3SiN{=}SRNMR$,[33] and organometallic compounds MCH_2Ph[26b] and $MC_6H_3(TRIP)_2$-2,6, TRIP = $C_6H_2Pr^i{}_3$-2,4,6,[34] and interpreted theoretically.[26b] In the lithium compound LiR‴, **7a**, the metal is probably too small and the interaction with the phenyl group too weak for polymer formation, and it is possible that a dimeric structure like that of $[\{LiCH(SiMe_2Ph)_2\}_2]$, **5**, is ruled out on steric grounds, *i.e.*, there may not be room to replace the methine hydrogen atoms (Figure 5) by $SiMe_2Ph$ groups. In MR‴, **7b**−**e**, the M−C bond lengths are similar to those in a range of organometallic compounds described elsewhere.[18,26b,33−36] The increase with the ionic radius of the alkali metal gives an effective anionic radius of 1.96−2.03 Å for the central carbon of MR‴, **7c**−**e**, slightly greater than the values (1.84−1.89 Å) found from methyl−alkali metal compounds.[11] The distance from the metal to the centroid of the phenyl ring increases from 3.00 Å in NaR‴ to 3.28 Å in CsR‴. If the ionic radii of the alkali metals are subtracted from these M−centroid distances, the residual distances decrease from 2.05 Å in NaR‴ to 1.96

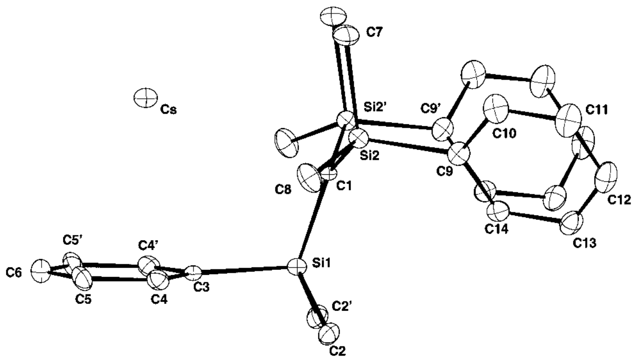

Figure 7. Molecular structure of $CsC(SiMe_2Ph)_3$, **7e**.

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Table 3. Comparison of Bond Lengths (Å) and Angles (deg) in Tris(dimethylphenylsilyl)methyl Compounds

	NaR‴ **7b**				KR‴ **7c**				RbR‴ **7d**		CsR‴ **7e**	
M−C(1)		2.754(14)				3.26(2)		3.46(3)	*19*	3.507(3)		3.655(7)
M−C(Ph)^a *i*-	*29*	3.378(13)			*20*	3.53(2)	*45*	3.31(2)	*2*	3.520(3)	*3*	3.347(7)
o-	*30*	3.373(14)	*21*	3.33(2)	*21*	3.29(2)	*46*	3.15(2)	*3*	3.349(3)	*4*	3.442(4)
m-	*31*	3.18(2)	*22*	2.90(2)	*22*	3.21(2)	*47*	3.17(2)	*4*	3.285(3)	*5*	3.630(6)
p-	*32*	2.933(13)	*23*	2.81(2)	*23*	2.99(3)	*48*	3.16(2)	5	3.347(3)	6	3.717(9)
m-	*33*	2.865(14)	*24*	3.17(2)	*24*	3.22(3)	*49*	3.30(2)	*6*	3.465(3)		
o-	*34*	3.067(13)			*25*	3.38(3)	*50*	3.36(2)				
i-	*4*	2.809(13)	*37*	2.820(13)	*29*	3.04(2)	*4*	2.97(2)	*10*	3.174(2)	*9*	3.647(5)
o-	*5*	2.915(14)	*38*	2.90(2)	*30*	3.12(2)	*5*	3.03(2)	*11*	3.299(2)	*10*	3.620(6)
m-	*6*	3.536(14)	*39*	3.41(2)	*31*	3.39(2)	*6*	3.28(2)			*11*	3.566(6)
p-					*32*	3.44(2)	*7*	3.49(2)			*12*	3.516(5)
m-					*33*	3.30(3)	*8*	3.46(3)	*8*	3.475(3)	*13*	3.520(6)
o-	*9*	3.368(14)	*42*	3.21(2)	*34*	3.15(3)	*9*	3.23(2)	*9*	3.254(2)	*14*	3.578(5)
i-	*12*	2.801(13)	*45*	2.831(14)	*37*	3.06(2)	*12*	2.96(2)	*18*	3.217(2)		
o-	*13*	2.820(15)	*46*	3.095(15)	*38*	3.19(2)	*13*	3.26(2)	*13*	3.314(2)		
m-	*14*	3.39(2)	*47*	3.48(2)	*39*	3.36(2)	*14*	3.47(2)	*14*	3.505(3)		
p-			*48*	3.60(2)	*40*	3.49(2)	*15*	3.58(2)				
m-			*49*	3.37(2)	*41*	3.39(2)	*16*	3.36(2)				
o-	*17*	3.367(13)	*50*	3.01(2)	*42*	3.18(2)	*17*	3.13(2)	*17*	3.317(3)		
Si−C (av)		1.812(12)^b				1.84(2)^b				1.813(2)^b		1.812(7)^b
Si−Me (av)		1.872(12)^b				1.89(2)^b				1.887(2)^b		1.897(6)^b
Si−Ph (av)		1.914(14)^b				1.92(2)^b				1.910(2)^b		1.913(7)^b
C−C (av)		1.38(2)^b				1.38(3)^b				1.389(4)^c		1.391(10)^b
Si−C−Si		119.6(6), 120.3(6), 115.0(6)		117.8(7), 119.8(7), 120.7(7)		118(1)^b				118.6(1), 122.2(1), 118.3(1)		119.9(2), 119.1(4)^d
C−Si−Ph		111.9(6)^b (av)				111(1)^b				111.7(1) 112.1(1), 113.5(1)		111.8(3), 115.6(3)^d
C−Si−Me		116.5(6)^e (av)				117(1)^b				116.8(1), 116.5(1), 114.7(1), 117.6(1), 116.9(1), 115.8(1)		117.1(2),^{d} 114.9(3), 116.2(3)
Me−Si−Me		102.2(6)^b (av)				103(1)^b				99.9(1), 102.6(1), 102.9(1)		103.2(2),101.8(3)
Me−Si−Ph		104.5(6)^e (av)				103.6(9)^b				105.8(1), 103.8, 103.3, 102.4, 103.6, 105.5		102.9(2),^{d} 103.2(3)103.3(3)
M−C−Si										93.0(1), 94.7(1), 91.9(1)		94.1(3), 93.0(2)

[a] Numbers in italics refer to the carbon atoms in Figures 1, 6 and 7 in this paper, Figure 2 of ref 6a, and Figure 2 of ref 6b in which phenyl groups of **7c** may be identified as *1* C4−9, *2* C12−17, *3* C20−25, *4* C29−34, *5* C37−42, *6* C45−50. [b] There are no significant deviations from the average value. [c] One value out of 12, that for C(5)−C(6), 1.361(6), is significantly lower than the average. [d] There is also a second symmetry-related bond or angle. [e] Two values out of 12 are significantly different from the mean but there is no obvious reason for this.

Å in CsR‴ as both the strength and the hapticity of the metal−phenyl interaction increases and the coordination of the phenyl group becomes more symmetrical.

The cesium atoms in $CsC(SiMe_3)_3 \cdot 3C_6H_6$, **1e**, and $CsC(SiMe_2Ph)_3$, **7e**, are in similar environments. That in **1e** is less strongly bound to the benzene rings (Cs−C 343−379 Å) than is the Cs atom in **7e** to the more negatively charged phenyl rings, but this weaker cesium−arene bonding is offset by stronger bonding to the central carbon (Cs−C 3.325(12) Å in **1e**). The $Si(SiMe_3)_3$ derivatives of the heavier alkali metals also form solvates with neutral arenes,[37] and further examples have recently been reported.[38]

From the results presented so far, it appears that the introduction of phenylsilyl substituents into the organometallic derivatives of the alkali metals stabilizes molecular forms relative to ate complexes. Thus, $LiC(SiMe_3)_3$, **1a**, crystallizes as an ate complex and $LiC(SiMe_3)_2(SiMe_2Ph)$ in molecular form, **3b**. The sodium−TMEDA derivative with R = $C(SiMe_3)_3$ crystallizes as an ate complex containing the ion **2b**, and the phenyl-substituted analogues, **3c** and **6c**, form molecular structures. For the heavier alkali metal potassium, however, the ate form containing the ion $[MR'_2]^-$ is stabilized by metal−phenyl and metal−benzene interactions.[7]

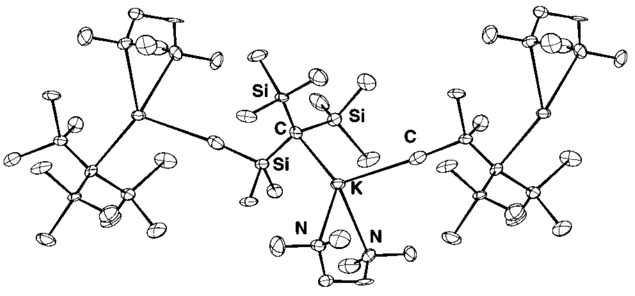

Figure 8. Molecular structure of $KC(SiMe_3)_3 \cdot$TMEDA, **1f**.

The role of phenyl coordination in determining chemical reactivity is well-illustrated by a comparison between the group of compounds NaR′·TMEDA, NaR″·TMEDA, and MR‴, **7b**−**e**, all of which, though reactive, can be handled satisfactorily by Schlenk techniques, and the compound KR·TMEDA, **1f,** which is very pyrophoric indeed. Many attempts were made before a crystal was successfully mounted for an X-ray study. The data were insufficiently precise for a detailed discussion, but the main features of the structure, shown in Figure 8, are clear. Molecules of $KC(SiMe_3)_3 \cdot$TMEDA are linked into chains by coordination of the potassium by one of the

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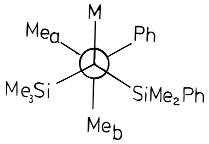

Figure 9. Newman projection about a C−Si bond in compounds **6a**−**d**.

peripheral methyl groups of the adjacent molecule. Each potassium is four-coordinate with two nitrogen atoms at 2.85(1) and 2.88(1) Å and two carbon atoms at 2.92(1) and 3.21(2) Å. The exposed positions of the potassium ion and carbanion account for the extreme sensitivity of the compound toward air and moisture. The structure determination is described in the Supporting Information.

NMR Spectra. Information about species in solution can be obtained from multinuclear NMR studies. Three lines of evidence suggest that solutions of the alkali metal derivatives, like the solid state structures, contain carbanionic species with a significant delocalization of negative charge over the almost planar CSi_3 skeletons. First, the signals for the central carbon in ^{13}C spectra are found at low frequency. Secondly, the values of the coupling constants *J*(SiC) for the short inner bonds of the organometallic compounds (50−70 Hz) are much larger than those (34−37 Hz) for the corresponding bonds in halides such as R′Cl or R′I. Thirdly, some of the ^1H NMR signals from samples at room temperature are broad, indicating that the species in solution are fluxional. In the precursors $HCBr(SiMe_2Ph)_2$ and $HC(SiMe_3)(SiMe_2Ph)_2$, the methyl groups of the $SiMe_2Ph$ group are inequivalent and give separate signals in the ^1H and ^{13}C NMR spectra, as expected from the Newman projection shown in Figure 9. However, in the 300 MHz ^1H spectra of R″Li·2THF, **6a**, the $SiMe_2$ signals were broad and two peaks were just resolved at room temperature, indicating that the two groups Me_a and Me_b in Figure 9 were exchanging rapidly on the NMR time scale, *e.g.*, by a flattening of the bonds at the central carbon.[39] The rate of exchange between the groups Me_a and Me_b was higher for the sodium compound **6c** than for the lithium compound **6a.** Variable-temperature NMR measurements on **6c** indicated that the coalescence temperature was 18 °C and the free energy of activation 58.6 kJ mol^{-1}. The signal from the methyl groups of the Me_2Si fragment in KR″, **6d**, at room temperature was sharp showing that the methyl groups were equivalent on the NMR time scale. Two signals were observed on cooling, and from the coalescence temperature of −84 °C, the free energy of activation was calculated to be 38.9 kJ mol^{-1}. The barrier to inversion, thus, decreases in the series Li > Na > K as the M−C bond becomes more ionic.

There is some evidence that the polymeric chains found in crystals of MR‴, **7b**−**e**, are broken in solutions containing donor solvents. For example, the ^1H NMR spectra of NaR‴ in the presence of TMEDA showed broad signals in the amine region, and on cooling these peaks separated to give signals assigned to free and complexed TMEDA, showing the presence of distinct complexes in solution. Further, no interaction between the phenyl protons and the cesium in solutions of **7e** was detected by ^{133}Cs HOESY spectroscopy,[40] again suggesting that the chains were broken in THF-d_8 solution. In contrast, significant Cs−*ortho*-C(Ph) interactions were found in solutions of $CsCPh_3$·TMEDA in THF.[32]

Conclusions. It is remarkable that the organometallic derivatives of the alkali metals KR and RbR, $[\{LiCH(SiMe_2Ph)_2\}_2]$, KR″, and NaR‴−CsR‴, **7b**−**e**, crystallize from solutions containing THF and in some cases TMEDA without incorporation of donor solvents. This suggests that interactions between the metal centers and the methyl or phenyl groups are sufficiently strong to exclude the oxygen and nitrogen donors from the coordination sphere. The competition between donor and arene coordination is also shown in the range of solid state structures adopted. Thus, when there is only one phenyl group in the carbanion as in LiR′·TMEDA and NaR′·TMEDA or none as in KR·TMEDA, molecular structures with good solubility in hydrocarbons result. In NaR″·TMEDA, which has two phenyl groups in the carbanion, the second phenyl group does not interact sufficently strongly with the metal to exclude the donor TMEDA. However, the weaker donor Et_2O is excluded from the lithium coordination sphere in $[\{LiCH(SiMe_2Ph)_2\}_2]$, so that the compound which separates from a hydrocarbon−ether mixture is solvent-free, with a dimeric structure in which all four phenyl groups interact with metal centers. Where there are three phenyl groups, their coordination to the metal gives chain structures, so that the resulting compounds are sparingly soluble in both aliphatic and aromatic hydrocarbons. Solvation of the metal atom by neutral arenes to form ion pairs such as those in solid $CsC(SiMe_3)_3·3C_6H_6$ is, thus, insufficient to break the polymeric chains in the solid structure. The compounds MR‴ (M = Na, K, Rb, Cs) do, however, dissolve in THF or in mixtures of benzene and TMEDA, suggesting that the donor molecules are able to break the polymer chains and give ion pairs in solution. However, whereas the complexes NaR′·TMEDA, **3c**, and NaR″·TMEDA, **6c**, can be isolated in the solid state, the THF or TMEDA complexes of MR‴cannot. The donor molecules are lost under vacuum or upon treatment with light petroleum, and on crystallization the cesium−phenyl interactions are strong enough to exclude THF or TMEDA from the solid phase.

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Supporting Information Available: Tables of the crystal structure details, atomic coordinates, bond lengths and angles, hydrogen coordinates and least squares planes for **3b**, **3c**, **5**, **6c**, **7d**, **7e**, and **1f** (24 pages). Ordering information is given on any current masthead page.

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