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Synthesis and Structures of Crystalline Lithium, Sodium, Potassium, and Magnesium Silylmethyls Derived from the Ligands $[CH(SiMe_3)\{SiMe_{3-n}(OMe)_n\}]^-$ ($n = 1, 2$), $[CH(SiMe_2OMe)_2]^-$, and $[CH(SiMe_3)(SiMe_2Ph)]^-$

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The paper deals with metal complexes of the silylmethyl ligands $[CH(SiMe_3)\{SiMe_{3-n}(OMe)_n\}]^-$ ($n = 1, 2$), $[CH(SiMe_3)(SiMe_2Ph)]^-$, and $[CH(SiMe_2OMe)_2]^-$. Treatment of the precursor alkanes with $LiBu^t$ in pentane, or of $CH_2(SiMe_3)(SiMe_2OMe)$ with $NaCH_2Ph$ in benzene, afforded the crystalline complexes $[Li\{CH(SiMe_3)(SiMe_2OMe)\}]_8$ (**2**), $[Li\{CH(SiMe_3)(SiMe(OMe)_2)\}]_\infty$ (**7**), $[Li\{CH(SiMe_2OMe)_2\}]_\infty$ (**9**), and $[Na\{CH(SiMe_3)(SiMe_2OMe)\}]_\infty$ (**3**), respectively. The yield of each, except **9**, was almost quantitative, but (under conditions which had given **2** and **7**) $CH_2(SiMe_2OMe)_2$ and $LiBu^t$ remarkably gave $[Li\{\mu\text{-}C(SiMe_2OMe)_3\}]_2$ (**10**) as the major product. The compound $[K\{CH(SiMe_3)(SiMe_2OMe)\}]_\infty$ (**4**) was obtained from **2** and $KOBu^t$ in hexane, and addition of Et_2O to **4** gave the crystalline compound $[K\{CH(SiMe_3)(SiMe_2OMe)\}(OEt_2)]_\infty$ (**5**). The crystalline compounds $[Li\{(CH(SiMe_3)(SiMe_2Ph))(TMEDA)\}]$ (**12**) and $[Mg(\mu\text{-}Br)\{CH(SiMe_3)(SiMe_2Ph)\}(OEt_2)]$ (**14**) were prepared from $CH(Br)(SiMe_3)(SiMe_2Ph)$ in Et_2O and Li followed by TMEDA or Mg, respectively. Compound **7** and $MgBr_2$ in THF yielded the crystalline cluster compound $[Li_2Mg_5(OMe)_8\{CH(SiMe_3)(SiMe(OMe)_2)\}_4]$ (**15**). The molecular structures of **2**, **3**, **5**, **7**, **9**, **12**, **14**, and **15** are described, as are the variable-temperature ^1H NMR spectra of **2** in toluene-d_8. In **2**, **3**, and **5**, the alkyl is C,O-centered and is essentially a planar chelate toward the Li, Na, or K cation, respectively. In **7**, the alkyl ligand core is planar and functions as an O,O′-centered bridge to adjacent Li cations, with rather long Li−C distances, whereas in **15** the alkyl acts as a C,O-centered bridge to peripheral Mg and Li cations. The central core of **15** is a Mg atom surrounded by a roughly hexagonal planar array of four Mg and two transoid Li cations joined by six bridging OMe anions. Crystalline **9** is a polymer, in which successive $\overline{\text{LiOSiCSiO}}$ rings are linked by Li−C bonds of unequal lengths, of ca. 2.18 and 2.50 Å. The ligand $[CH(SiMe_3)(SiMe_2Ph)]^-$ is bound to Li in **14** or Mg in **12**, in a terminal fashion.

Introduction

The trimethylsilyl-substituted methyls $[CH_{3-n}(SiMe_3)_n]^-$ ($n = 1-3$) were recognized as valuable ligands in 1969, particularly in the context of early-transition-metal chemistry.[1] These ligands often confer useful properties on their metal complexes, such as thermal stability, lipophilicity, and convenient NMR spectroscopic sensors by virtue of their bulk, absence of β-hydrogen or -alkyl substituents, and multiplicity of methyl substituents.[2] Our group has concentrated on metal bis(trimethylsilyl)methyls, i.e., complexes of the ligand $[CH(SiMe_3)_2]^-$, a topic which we reviewed about 10 years ago.[3] Organometallic complexes containing tris(trimethylsilyl)methyl, or related ligands having a C^-Si_3 or $C^-(Si)_2XC^-Si_2$ core, have received much attention, as evident from a recent comprehensive review by Eaborn and Smith.[4] Their most recent contribution to this topic is in ref 5, while our latest, on metal bis(trimethylsilyl)methyls, is given in ref 6.

The present paper is concerned with new bis(silyl)methyl ligands as lithium, sodium, potassium, and magnesium complexes. The structures of crystalline bis(trimethylsilyl)methyls of these elements are summarized as follows: $[Li\{\mu\text{-}CH(SiMe_3)_2\}]_\infty$,[7] $[Li\{CH(SiMe_3)_2\}(PMDETA)]$,[8] $[Na\{\mu\text{-}CH(SiMe_3)_2\}]_\infty$,[9]

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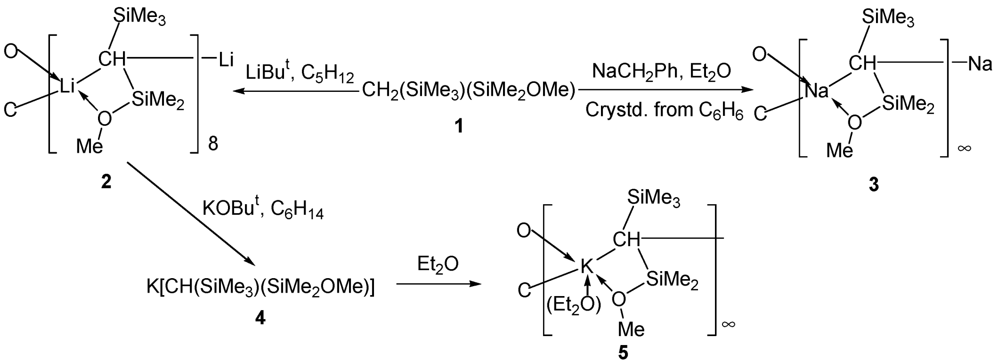
10.1021/om030041e CCC: $25.00

Scheme 1

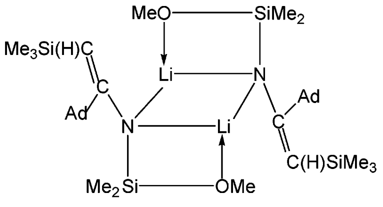


$[(PMDETA)K\{\mu\text{-}CH(SiMe_3)_2\}K\{\mu\text{-}CH(SiMe_3)_2\}_2K\{\mu\text{-}CH(SiMe_3)_2\}K(PMDETA)]$,[9] $[K\{\mu\text{-}CH(SiMe_3)_2\}(L)]_\infty$ (L = $O(Me)Bu^t$,[9] THF[6b]), $[Mg\{\mu\text{-}CH(SiMe_3)_2\}_2]_\infty$,[10] $[Mg(\mu\text{-}Br)\{CH(SiMe_3)_2\}(OEt_2)]_2$,[11] and $[Mg\{CH(SiMe_3)_2\}_2(CNC_6H_3\text{-}Me_2\text{-}2,6)_2]$. [11]

The tris(trimethylsilyl)methyl ligand has been modified by introducing one or more γ-OMe or γ-Ph groups, as in $[Li\{\mu\text{-}C(SiMe_2OMe)_3\}]_2$,[12] $[Li\{C(SiMe_2Ph)_3\}(THF)]$,[13] and $[M\{C(SiMe_3)(SiMe_2Ph)_2\}(TMEDA)]$ (M = Li, Na).[13]

Results and Discussion

The principal thrust of this research was to seek new variants of the bis(trimethylsilyl)methyl ligand by introducing one or more γ-substituents thereto. The initial target ligands were of formula $[CH(SiMe_3)\{SiMe_{3-n}(OMe)_n\}]^-$ ($n = 1, 2$) and $[CH(SiMe_3)(SiMe_2Ph)]^-$. These C_1-symmetric ligands have a number of useful features: (i) they are chiral, (ii) the relative migratory aptitude of $SiMe_3$ versus $SiMe_nX_{3-n}$ ($n = 1, 2$) in potential C−Si cleavage reactions needs to be established, and (iii) the chosen γ-substituents OMe and Ph are potential donor sites. The results now presented relate primarily to the desired lithium alkyls but also include data on selected sodium, potassium, and magnesium alkyls. Because the structures of the metal alkyls based on the ligands $[CH(SiMe_3)\{SiMe_{3-n}(OMe)_n\}]^-$ ($n = 1, 2$) revealed close methoxy−metal contacts (vide infra), it was deemed to be opportune to extend the ligand base to the C_2-symmetric $[CH(SiMe_2OMe)_2]^-$. A further objective, which will be addressed in future publications, is to use some or all of the metal alkyls **1**−**15** here presented (for **10** see ref 12) as (a) ligand transfer reagents in order to gain access to a wider range of metal alkyls and (b) substrates for reactions with various organic compounds. As for (b), we have already shown that the lithium alkyl **2**, prepared in situ from $CH_2(SiMe_3)(SiMe_2OMe)$ (**1**),[14] with 1-adamantyl cyanide (AdCN) yielded regioselectively the crystalline lithium enamide **A**, showing that in this process the migratory aptitude is $SiMe_2OMe > SiMe_3$.[15]



A

Synthesis. The colorless lithium (**2**), sodium (**3**), and potassium (**4** and **5**) alkyls based on the ligand $[CH(SiMe_3)(SiMe_2OMe)]^-$ were prepared from (methoxydimethylsilyl)(trimethylsilyl)methane (**1**),[14] as shown in Scheme 1. The crystalline complexes **2** and **3** were obtained at or below ambient temperature using *tert*-butyllithium in pentane and benzylsodium in diethyl ether as reagents, respectively. A metathetical exchange reaction between the lithium alkyl **2** and potassium *tert*-butoxide in hexane yielded the potassium alkyl as an insoluble powder, **4**, which with diethyl ether gave the crystalline complex **5**. These reactions were essentially quantitative, but the yields of X-ray-quality crystals (82%, **2**; 42%, **3**; 97%, **5**) were not optimized.

Treatment of (dimethoxymethylsilyl)(trimethylsilyl)methane (**6**)[16] with *tert*-butyllithium in pentane yielded the colorless, crystalline lithium alkyl **7** (80%) (Scheme 2); the reaction conditions were similar to those which gave **2** from **1**. However, when $CH_2(SiMe_2OMe)_2$ (**8**) was likewise treated with $LiBu^t$, the major product was the known crystalline compound $[Li\{\mu\text{-}C(SiMe_2OMe)_3\}]_2$[12] (**10**; 64%), with the colorless, crystalline compound $[Li\{\mu\text{-}CH(SiMe_2OMe)_2\}]_\infty$ (**9**) as coproduct (Scheme 3). Although **8** was a known compound,[16] its new preparation (64%) employed the readily available reagents Me_3SiOMe, $LiBu^t$, and $SiCl(Me)_2OMe$. Under different reaction conditions, **9** was obtained in acceptable (48%) yield.

(Phenyldimethylsilyl)(trimethylsilyl)bromomethane (**11**), previously prepared from $SiBr_2(SiMe_3)(SiMe_2Ph)$ and LiBu,[17] was obtained from (trimethylsilyl)dibromo-

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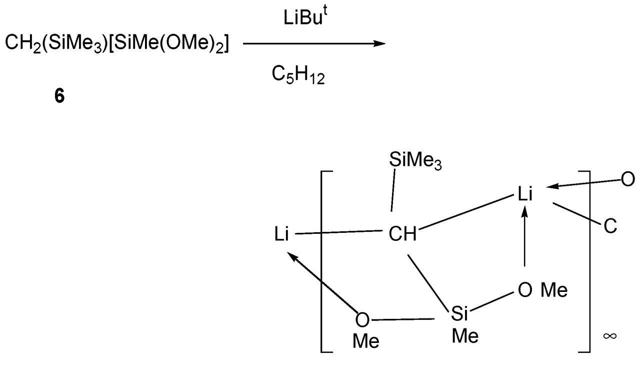
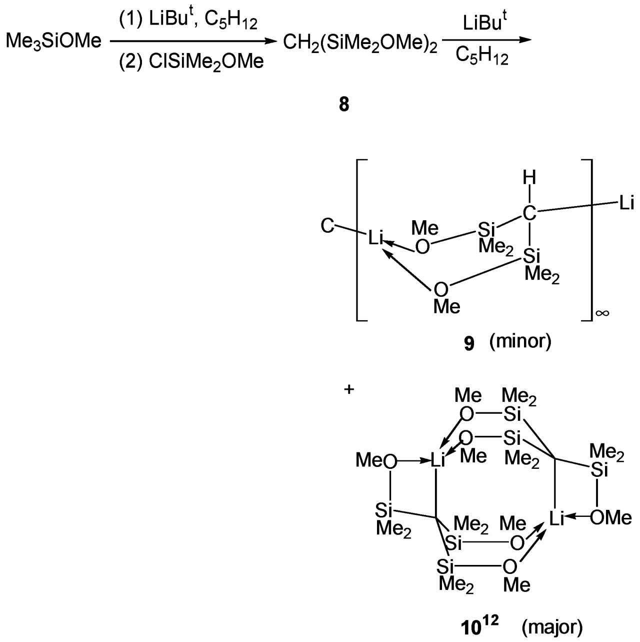
Scheme 2



Scheme 3



methane and successive low-temperature lithiation and quenching with phenyldimethylchlorosilane. Compound **11** underwent the Grignard reaction to give the dinuclear, crystalline, colorless alkylmagnesium bromide **12** (87% yield); with lithium metal in diethyl ether **11** afforded the lithium alkyl **13** (90% yield) as a diethyl ether solvate, which with TMEDA gave the mononuclear, crystalline, colorless lithium alkyl **14** (Scheme 4).

Treatment of the lithium alkyl **7** with magnesium bromide in THF gave the Li–Mg colorless, crystalline cluster compound $[Li_2Mg_5(OMe)_8\{CH(SiMe_3)(SiMe(OMe)_2)\}_4]$ (**15**) in modest (27%) yield (Scheme 5).

The essentially quantitative and regiospecific metalations under mild conditions of $CH_2(SiMe_3)(SiMe_2OMe)$ (**1**) or $CH_2(SiMe_3)[SiMe_2(OMe)_2]$ (**6**) with $LiBu^t$, yielding **2** (cf. ref 14) or **7**, respectively, and of **1** with $NaCH_2Ph$ to give **3** are noteworthy. The facile conversion of **2** into **5**, using $KOBu^t$, is an example of the Lochmann–Schlosser LiR/MOR′ procedure,[18] as is the similar transformation of $[Li\{CH(SiMe_3)_2\}]_\infty$ into $[K\{\mu\text{-}CH(SiMe_3)_2\}(L)]_\infty$ ($L = O(Me)Bu^t$,[9] THF[6b]). The reactions of Scheme 4 are unexceptional, being, for example, paralleled by those leading to $[Li\{CH(SiMe_3)_2\}(PMDETA)]$[8] and $[Mg(\mu\text{-}Br)\{CH(SiMe_3)_2\}(OEt_2)]_2$.[11] The outcomes of the procedures of Schemes 3 and 5, however, were totally unexpected.

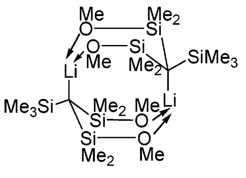
It had been envisaged that $CH_2(SiMe_2OMe)_2$ (**8**) with $LiBu^t$ in pentane, under conditions identical with those which had cleanly converted **1** into **2** (Scheme 1) and **6** into **7** (Scheme 2), would likewise have provided the lithio derivative **9** in high yield. The fact that the major product (Scheme 3) was the known compound **10**[12] represents an unprecedented skeletal redistribution. A possible rationalization is that $[Li\{\mu\text{-}CH(SiMe_2OMe)_2\}]_\infty$ (**9**) was initially formed, which in large part then underwent the redistribution reaction

$$3\,\mathbf{9} \rightarrow 2\,\mathbf{10} + \mathrm{LiMe}$$

The evidence at this time is only tenuous: (i) using even milder conditions and a slight deficiency of $LiBu^t$, crystalline **9** was a significant product and (ii) in a ^1H NMR spectroscopic experiment there was some indication that heating **9** in toluene-d_8 afforded a mixture containing **10**. Further investigations into these systems are in progress. One aspect to be examined will be to establish whether $LiBu^t$ catalyzes the transformation of **9** into **10**. Thus, it was found that addition of a trace of $LiBu^t$ to **9** in hexane/Et_2O resulted in almost complete removal of **9** to give a mixture, which included **10**.

The formation, albeit in low yield, of the cluster compound **15** from **7** and $MgBr_2$ in THF under mild conditions may stoichiometrically be attributed to the mass balance of Scheme 6. This system will be further investigated, to identify the coproducts and a possible reaction pathway.

Crystal Structures. The molecular structures of the crystalline lithium alkyls $[Li\{CH(SiMe_3)(SiMe_2OMe)\}]_8$ (**2**), $[Li\{CH(SiMe_3)(SiMe(OMe)_2)\}]_\infty$ (**7**), $[Li\{CH(SiMe_2OMe)_2\}]_\infty$ (**9**), and $[Li\{CH(SiMe_3)(SiMe_2Ph)\}(TMEDA)]$ (**14**) are shown in Figures 1–4, respectively, and selected geometrical parameters are listed in Tables 1 (**2**, **7**, **9**, and **14**), 2 (**2** and **7**), and 3 (**9**). For comparison, some data for $[Li\{\mu\text{-}CH(SiMe_3)_2\}]_\infty$,[7] (Table 1), **10**[12] (Table 2), and **10**[12] and $[Li\{C(SiMe_3)(SiMe_2OMe)_2\}]_2$ (**B**)[13] (Table 3) are also cited.



B

Crystalline **2** is an octamer of close to S_8 point group symmetry, having an approximately planar arrangement of the lithium atoms (Figure 5a), with the ligands alternately pointing above and below the plane (Figure 5b). Each monomeric unit has a $\overline{\mathrm{LiCSiO}}$ trapezoidal core ($\Sigma_{\mathrm{trapezoid}} = 359.7°$). The torsion angle between the four core atoms varies from 0.8 to 12.4°. The $SiMe_3$ group attached to the pentacoordinate carbon atom is oriented in successive units in a syndiotactic manner to diminish steric constraints.

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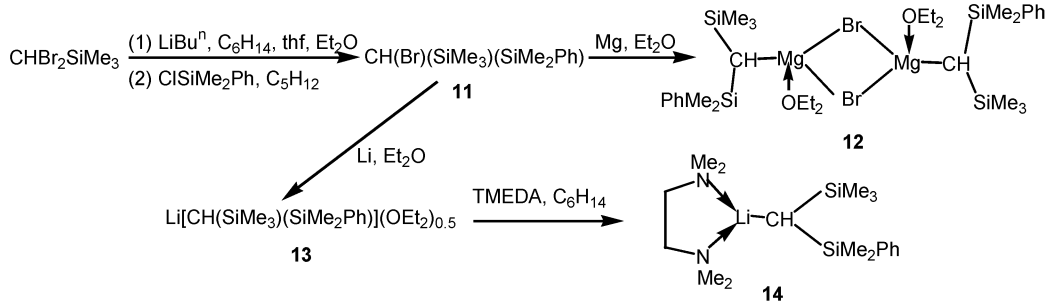
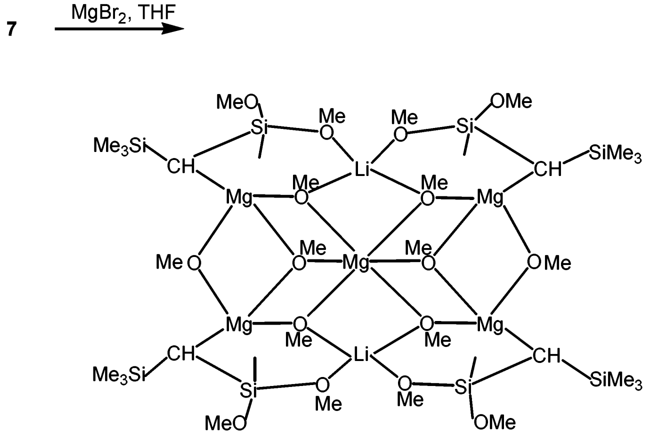
(18) Cf.: Schlosser, M. J. In *Organometallics in Synthesis: A Manual*; Schlosser, M. J., Ed.; Wiley: New York, 1994.

Scheme 4



Scheme 5



$[Li_2Mg_5(OMe)_8\{CH(SiMe_3)SiMe(OMe)_2\}_4]$

15

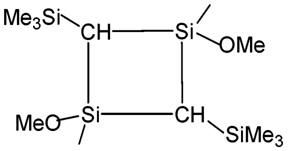
Scheme 6

$12\ Li\{CH(SiMe_3)(SiMe(OMe)_2)\} + 5MgBr_2 \longrightarrow$

$[Li_2Mg_5(OMe)_8\{CH(SiMe_3)(SiMe(OMe)_2)\}_4]$

15

$+\ 10\ LiBr\ +\ 4$



The backbone of both compound **2** and $[Li\{\mu\text{-}CH(SiMe_3)_2\}]_\infty$[7] comprises an alternating chain of Li^+ and $[CH(SiMe_3)(SiMe_2X)]^-$ (X = OMe, Me) ion pairs. Although the average Li–C bond distances in **2** and $[Li\{\mu\text{-}CH(SiMe_3)_2\}]_\infty$[7] are closely similar, the range in **2** is somewhat smaller. The Si1–C1–Si2 bond angles are likewise virtually identical and are substantially wider than the sp^2 value, attributed to the presence of the small hydrogen atom at C1. In **2** the angles subtended at each α-carbon atom are wider than in $[Li\{\mu\text{-}CH(SiMe_3)_2\}]_\infty$,[7] whereas the reverse is the case for C–Li–C′ (Table 1).

The lithium atom is in a three-coordinate (**2**) or two-coordinate ($[Li\{\mu\text{-}CH(SiMe_3)_2\}]_\infty$[7]) environment, although in the latter there are additional Li···C_γ agostic interactions.[7] The Li–O distances in **2** are much shorter than in the four-membered rings of **7** and **10**,[12] but the Si–O bond lengths and the various endocyclic bond angles in the three compounds are closely similar (Table 2).

Crystalline **7** is a polymer, in which successive units of two monomers in the chain are related by the 2_1 screw axis along *c*. The core C(H){SiMe(OMe)$_2$} moieties are planar and almost equidistant from the two adjacent lithium cations (e.g., Li1–C1 = 2.322(11) Å and Li2–C1 = 2.313(10) Å). Most bond lengths and angles are unexceptional (Tables 1 and 2), although Li···C distances are rather long (Table 1).

Crystalline **9** is a polymer, in which successive units of three monomers are related by the unit cell axis *c*. Unlike the other oligo- or polynuclear lithium alkyls $[Li\{\mu\text{-}CH(SiMe_3)_2\}]_\infty$,[7] **2**, and **7**, the lithium cations are not equidistant from the adjacent carbanion centers: e.g., Li···C1 = 2.497(6) Å and Li1–C8 = 2.180(6) Å. The two methoxy groups of each ligand are chelating to a single lithium cation, rather than bridging two cations as in **7**. The central carbon atoms of **9** (C1, C8, and C15) are slightly distorted from planarity. Most of the other geometric parameters are unexceptional (Tables 1 and 3).

The molecular structure of $[Na\{\mu\text{-}CH(SiMe_3)(SiMe_2OMe)\}]_\infty$ (**3**) is shown in Figure 6, and selected geometrical parameters are listed in Table 4, together with some data on $[Na\{\mu\text{-}CH(SiMe_3)_2\}]_\infty$.[9] Successive monomeric units in the polymer chain are related by the 2_1 screw axis parallel to *b*. The core {CH(SiMe$_3$)(SiMe$_2$OMe)} moieties are planar and roughly equidistant from adjacent sodium cations; the distance to the Na coordinated by the pendant OMe group (Na–C1) is slightly longer than the other (Na–C2) (Table 4). There may be very long contacts to the benzene solvate. The Si–C_α bonds (average 1.800 Å) are shorter than the Si–CH_3 bonds (average 1.874 Å). The X-ray structure of $[Na\{C(SiMe_3)Ph_2\}(PMDETA)]$ shows η^3-carbanion-to-Na^+ bonding.[19]

The molecular structure of the crystalline potassium alkyl $[K\{\mu\text{-}CH(SiMe_3)(SiMe_2OMe)\}(OEt_2)]_\infty$ (**5**) is shown in Figure 7, and selected geometrical parameters together with some for $[K\{\mu\text{-}CH(SiMe_3)_2\}(L)]_\infty$ (L = THF,[6b] O(Me)Bu^t [9]) are listed in Table 5. Successive monomeric units in the chain are related by a glide plane perpendicular to *b*. Each {CH(SiMe$_3$)(SiMe$_2$OMe)} core is planar and essentially equidistant from the adjacent potassium ions (cf., K–C1 and K–C1′, Table 5). The K–OMe (K–O1′) bond is shorter than the K–OEt$_2$ bond (K–O2). Allowing for the difference in Na^+ and K^+ radii, the structures of **3** and **5** are similar (Tables 4 and 5).

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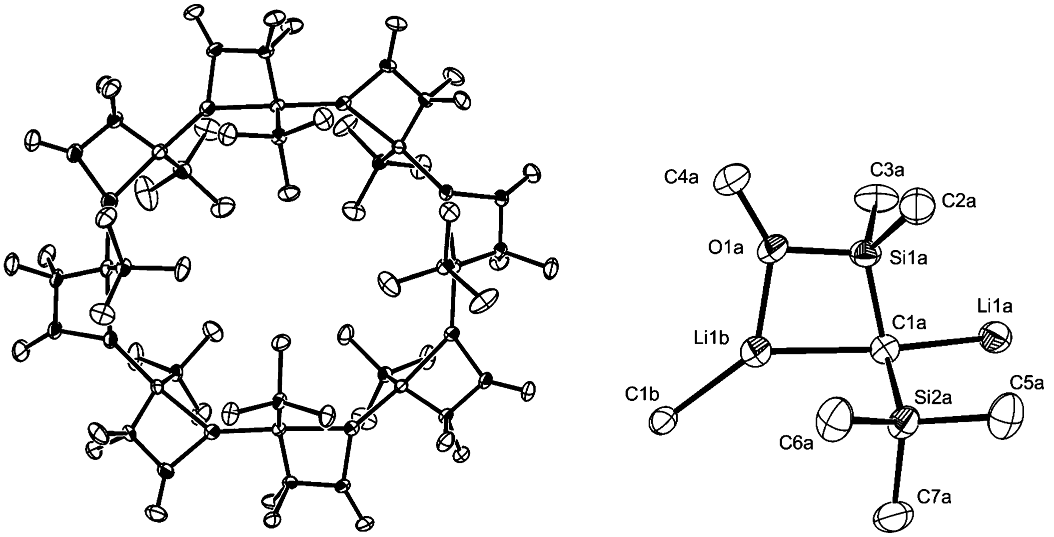

Figure 1. Molecular structure of [Li{CH(SiMe$_3$)(SiMe$_2$OMe)}]$_8$ (**2**) and a single unit of the cyclo octamer (hydrogen atoms omitted for clarity) with a selected atom-labeling scheme and thermal ellipsoids at the 30% probability level.

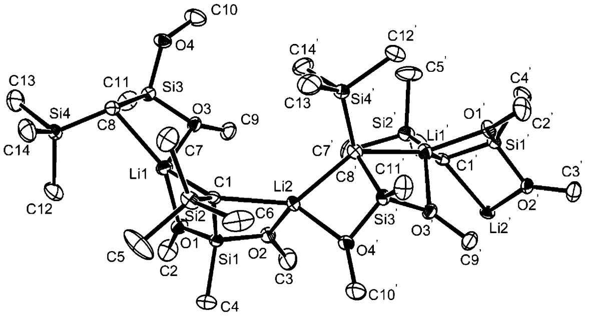

Figure 2. Molecular structure of [Li{CH(SiMe$_3$)(SiMe(OMe)$_2$)}]$_\infty$ (**7**) with a selected atom-labeling scheme (hydrogen atoms are omitted for clarity) and thermal ellipsoids at the 30% probability level.

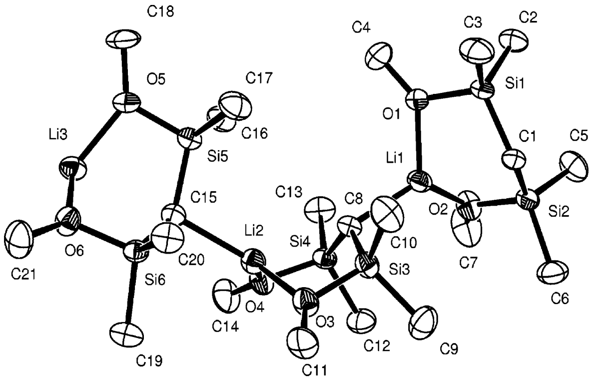

Figure 3. Molecular structure of [LiCH(SiMe$_2$OMe)$_2$]$_\infty$ (**9**) with a selected atom-labeling scheme (hydrogen atoms are omitted for clarity) and thermal ellipsoids at the 30% probability level.

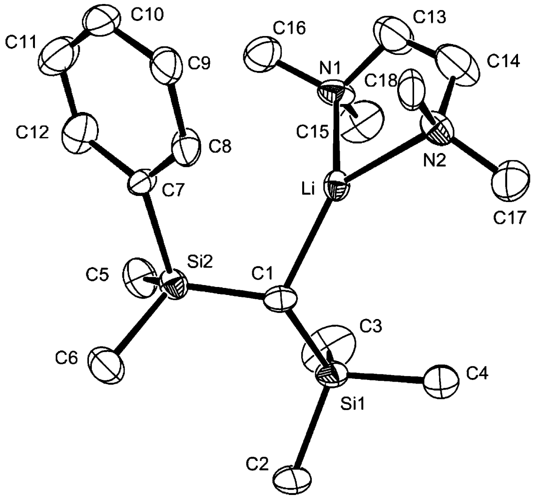

Figure 4. Molecular structure of [Li{CH (SiMe$_3$)(SiMe$_2$Ph)}(TMEDA)] (**14**) with a selected atom-labeling scheme (hydrogen atoms are omitted for clarity) and thermal ellipsoids at the 30% probability level.

Crystalline **14** is a monomer (Figure 4) with a structure closely similar to that of [Li{CH(SiMe$_3$)$_2$}(PMDETA)],[8] except that the coordination environment of the lithium atom is distorted trigonal planar in **14** but tetrahedral in [Li{CH(SiMe$_3$)$_2$}(PMDETA)]. The Li–C bond length of 2.13(5) Å and Li–C–Si (112(2), 117(2)°) and Si–C–Si′ (124(2)°) bond angles in [Li{CH(SiMe$_3$)$_2$}(PMDETA)][8] are available for comparison with corresponding data for **14** (Table 1). The C1–SiMe$_3$ bond length (1.800(9) Å; cf. 1.78(3) Å in [Li{CH(SiMe$_3$)$_2$}(PMDETA)][8]) in **14** is closely similar to the C1–SiMe$_2$Ph bond length (1.780(10) Å), and the Li–C1–SiMe$_3$ bond angle (114.3(6)°) is significantly wider than the Li–C1–SiMe$_2$Ph angle (108.5(6)°). The Si–C$_6$H$_5$ bond length of 1.901(9) Å is very slightly longer than the mean of the Si–CH$_3$ bond lengths (1.880 Å). The Li–N bond lengths of 2.061(16) and 2.101(15) Å and the N1–Li1–N2 bond angle of 88.5(6)° are unexceptional.

Crystalline **12** is a centrosymmetric dimer (Figure 8), with a central, virtually square $\overline{\text{MgBrMg}'\text{Br}'}$ core and a distorted-tetrahedral environment about each magnesium atom. The structure is very similar to that of [Mg(μ-Br){CH(SiMe$_3$)$_2$}(OEt$_2$)]$_2$[11] (Table 6). While the Si–CMe$_3$ and Si–CMe$_2$Ph bond lengths are essentially identical (Si2–C1 = 1.832(6) Å), the Mg–C1–SiMe$_3$ bond angle (120.1(3)°) is substantially wider than Mg–C1–SiMe$_2$Ph (109.3(3)°).

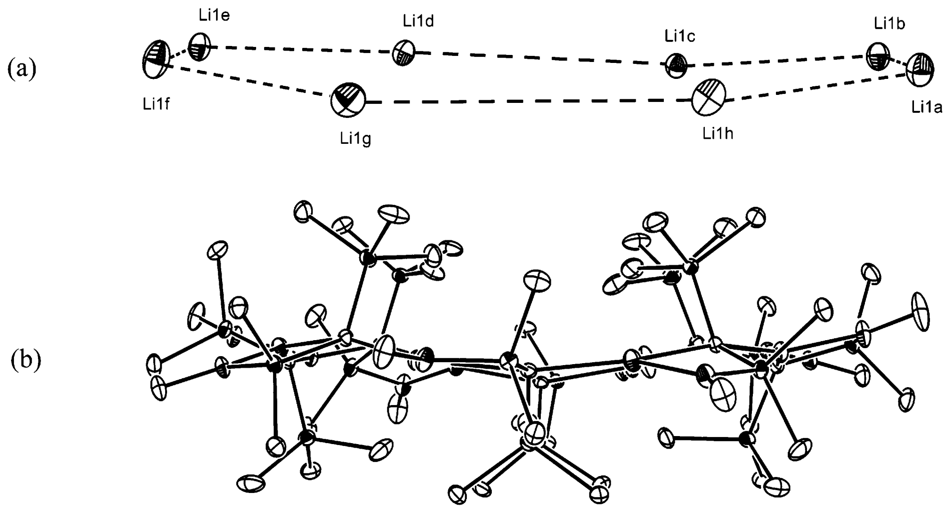

Figure 5. Arrangement of the lithium atoms (a) and of the ligands alternately pointing above and below the Li8 plane (b) of **2**.

Table 1. Li−C Bond Lengths (Å) and C−Li−C′, Li−C−Li′, and Si−C−Si′ Angles (deg) for [Li{μ-CH(SiMe$_3$)$_2$}]$_\infty$, 2, 7, 9, and 14

[Li{μ-CH(SiMe$_3$)$_2$}]$_\infty$[7]		**2**		**7**		**9**		**14**	
Li1−C1	2.14(3)	Li−C (av)	2.170	Li−C (av)	2.318	Li−C (av)	2.187	Li−C1	2.088(17)
Li2−C1	2.22(3)	range	2.152(7)−2.193(8)	range	2.313(10)−2.322(11)	range	2.180(6)−2.189(6)[a]		
C1−Li2−C2	152(1)	C−Li−C′ (av)	139.3	C1−Li1−C8	132.9(5)	C1−Li1−C8	131.2(3)		
		range	136.7(3)−140.9(3)	C1−Li2−C8′	135.2(4)	C8−Li2−C15	132.5(3)		
Li1−C1−Li2	153(1)	Li−C−Li′ (av)	162.7	Li1−C1−Li2	123.9(4)	Li1−C8−Li2	167.6(2)		
		range	156.6(3)−168.9(3)	Li1−C8−Li2″	135.3(4)	Li2−C15−Li3	170.2(2)		
Si1−C1−Si2	127.7(6)	Si−C−Si′ (av)	127.3	Si1−C1−Si2	130.7(4)	Si−C1−Si2	124.23(18)	Si1−C1−Si2	124.1(5)
		range	126.2(2)−128.2(2)	Si3−C8−Si4	131.3(3)				

[a] Transannular Li···C contacts are long: average 2.551 Å.

Table 2. Endocyclic $\overline{\text{Li−O−Si−C}}$ Bond Lengths (Å) and Angles (deg) for 2, 7, and 10

2		**7**		**10**[12]	
Li−O (av)	1.907	Li−O (av)	1.990	Li−O	1.983(9)
range	1.855(6)−1.950(7)	range	1.966(10)−2.030(11)		
Si−O (av)	1.696	Si−O (av)	1.659	Si−O	1.655(4)
range	1.682(3)−1.706(3)	range	1.656(4)−1.661(4)		
Li−C (av)	2.170	Li−C (av)	2.318	Li−C	2.401(9)
LiC−SiO (av)	1.786	LiC−SiO	1.759(6)	C−Si	1.816(4)
range	1.780(3)−1.792(4)		1.760(6)		
Li−O(Me)−SiMe$_2$ (av)	94.7	Li−O−Si (av)	92.5	Li−O−Si	98.7(3)
range	94.0(2)−95.6(2)	range	91.7(3)−93.1(3)		
Li−C−SiMe$_2$ (av)	79.1	Li−C−SiMe (av)	79.6	Li−C−Si	80.8(2)
range	77.5(2)−79.8(2)	range	78.9(3)−80.1(3)		
MeO−Si(Me)$_2$−C (av)	105.1	MeO−Si−CSiMe$_3$ (av)	106.9	O−Si−C	103.9(2)
range	104.72(16)−105.70(14)	range	105.4(2)−108.1(3)		

The molecular structure of the crystalline heterobimetallic Li$_2$Mg$_5$ cluster compound **15** is shown in Figure 9, and selected geometrical parameters are given in Table 7. The central core of the molecule is a magnesium atom (Mg1) surrounded by a roughly hexagonal planar array of four magnesium cations and the transoid lithium cation, joined to one another by six triply bridging methoxide anions, which are alternately above and below the plane of the metals (Figure 10). Around the periphery there are two further methoxide anions bridging adjacent pairs of Mg cations and four [CH(SiMe$_3$)(SiMe$_2$OMe)]$^-$ anions bridging adjacent Mg/Li pairs. The 12-membered $\overline{\text{LiOMgOMgOLiOMgOMgO}}$ macrocycle may be regarded as a hexametalla hexaoxo crown ether with respect to the central magnesium atom Mg1. The average Mg1−O bond length (2.126 Å) is longer than the endo-macrocyclic Mg−O bonds (average 1.998 Å (Mg−OLi) or 2.034 Å (Mg−OMg)) or the remaining Mg−O bonds (average 1.947 Å). The macrocyclic Li−O bonds (average 1.948 Å) are shorter than the remainder (average 1.979 Å). The *cis*-O−Mg1−O′ bond angles are in two pairs: average 98.9 and 81.1°. The macrocyclic O−Li−O′ bond angle (90.8(3)°) is wider than the corresponding O−Mg(2, 3)−O′ angle (average 86.6°), while the macrocyclic Li−O−Mg(2) bond angle of 106.0(2)° is wider than the Li−O−Mg1 angle of 99.6(1)°. The Mg−O and Li−O bond lengths may be compared with those in [Mg$_4$(μ$_3$-OMe)$_4$(OMe)$_4$(MeOH)$_8$] (2.05−2.12 Å for the bridging methoxides)[20] and [Li(OMe)]$_\infty$ (1.95 Å).[21]

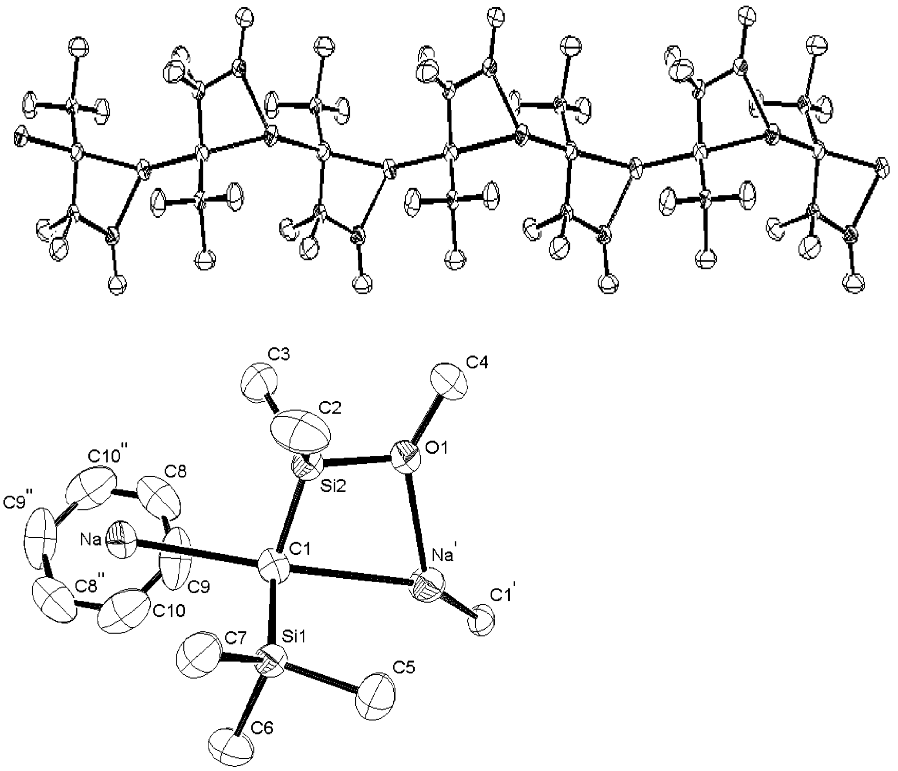

Figure 6. Molecular structure of $[Na\{\mu\text{-}CH(SiMe_3)(SiMe_2OMe)\}]_\infty$ (**3**) and a single unit of the infinite chain **3** (hydrogen atoms are omitted for clarity), with thermal ellipsoids at the 30% probability level.

Table 3. Endocyclic Li−O−Si−C−Si−O Bond Lengths (Å) and Angles (deg) for 9, 10, and $[Li\{C(SiMe_3)(SiMe_2OMe)_2\}]_2$

	9	**10**[12]	$[Li\{C(SiMe_3)(SiMe_2OMe)_2\}]_2$[13]
Li−O	1.957 (av; range 1.929(6)−1.993(6))	1.925(6)	1.912(6)
Li−C	2.186 (av; range 2.180(6)−2.189(6)[a])		2.256(9)
Si−O	1.697 (av; range 1.693(2)−1.711(2))	1.682(2)	1.683(3)
Si−C	1.789 (av; range 1.785(3)−1.792(3))	1.799(2)	1.808(3)
O−Li−O	115.9 (av; range 115.1(3)−116.9(3))	98.5(4)	101.2(4)
Li−O−Si	99.3 (av; range 97.26(19)−101.8(2))	115.5(3)	110.6(3)
O−Si−C	106.4 (av; range 105.88(13)−106.71(13))	106.0(2)	105.4(2)
Si−C−Si′	124.5 (av; range 124.22(17)−124.96(17))	117.2(2)	115.6(3)

[a] These exclude transannular Li···C contacts but refer to the exocyclic Li−C bonds.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for 3 and $[Na\{\mu\text{-}CH(SiMe_3)_2\}]_\infty$

3		$[Na\{\mu\text{-}CH(SiMe_3)_2\}]_\infty$[9]	
Na−C1	2.6064(18)	Na−C	2.549(5)
Na−C1′	2.7692(18)	Na−C′	2.551(4)
Na−O1′	2.2861(13)		
Si2−O1	1.6998(13)		
Si2−C1	1.7879(17)		
Na−C1−Na′	159.48(8)	Na−C−Na′	151.8(2)
C1−Na−C1′	134.65(3)	C−Na−C′	143.3(2)
O1′−Na−C1′	67.61(5)		
Na′−C1−Si2	82.50(6)		
C1−Si2−O1	109.07(7)		

Table 5. Selected Bond Lengths (Å) and Angles (deg) for 5 and $[K\{\mu\text{-}CH(SiMe_3)_2\}(L)]_\infty$

5		$[K\{\mu\text{-}CH(SiMe_3)_2\}(L)]_\infty$		
			L = O(Me)Bu^t[9]	L = THF[6b]
K−C1	3.050(5)	K−C1	2.998(8)	2.956(4)
K−C1′	3.094(5)	K−C1′	3.012(8)	3.012(4)
K−O1′	2.664(4)			
K−O2	2.716(6)	K−O	2.676(9)	2.645(3)
Si2−O1	1.686(4)			
Si2−C1	1.758(5)			
K−C1−K″	162.0(2)	K−C−K″	155.6(3)	153.18(15)
C1−K−C1′	123.12(5)	C−K−C1′	137.02(9)	122.18(5)
O1′−K−C1′	58.57(12)			
K″−C1−Si2	86.66(19)			
C1−Si2−O1	111.2(2)			

Solution Structure of $[Li\{CH(SiMe_3)(SiMe_2OMe)\}]_8$ (2). This was investigated by ^1H NMR spectroscopy. The ^1H NMR spectrum in toluene-d_8 at 323 K showed one set of signals, which on cooling gave rise to an additional set. At 283 K an approximately 1:1 mixture of two sets was observed, and at 213 K the first set disappeared. This is illustrated for $\delta(CH)$ in the range 203−323 K (Figure 11a). We conclude there are two species, indicated as LT and HT, preponderant at low and high temperature, respectively; their relative ratios at various temperatures are shown in Figure 11b.

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(20) Starikova, Z. A.; Yanovsky, A. I.; Turevskaya, E. P.; Turova, N. Ya. *Polyhedron* **1997**, *16*, 967.

(21) Wheatley, P. J. *Nature* **1960**, *185*, 681.

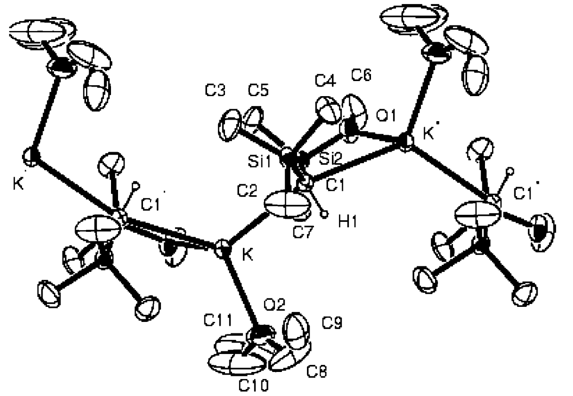


Figure 7. Molecular structure of [K{μ-CH(SiMe$_3$)(SiMe$_2$-OMe)}(OEt$_2$)]$_\infty$ (**5**) with a selected atom-labeling scheme (all hydrogen atoms, except for methine hydrogen H1, are omitted for clarity) and thermal ellipsoids at the 30% probability level.

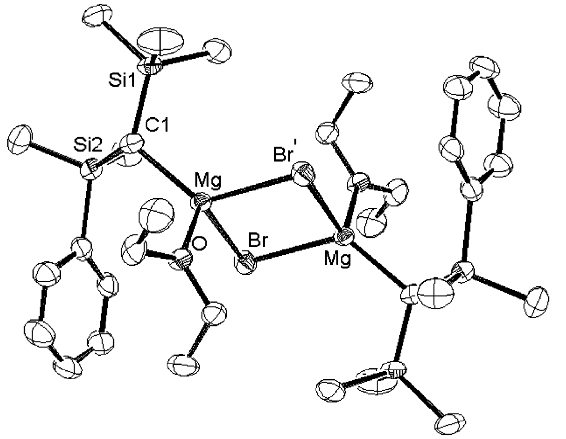


Figure 8. Molecular structure of [Mg(μ-Br){CH(SiMe$_2$Ph)-(SiMe$_3$)}(OEt$_2$)]$_2$ (**12**) with a selected atom-labeling scheme (hydrogen atoms are omitted for clarity) and thermal ellipsoids at the 30% probability level.

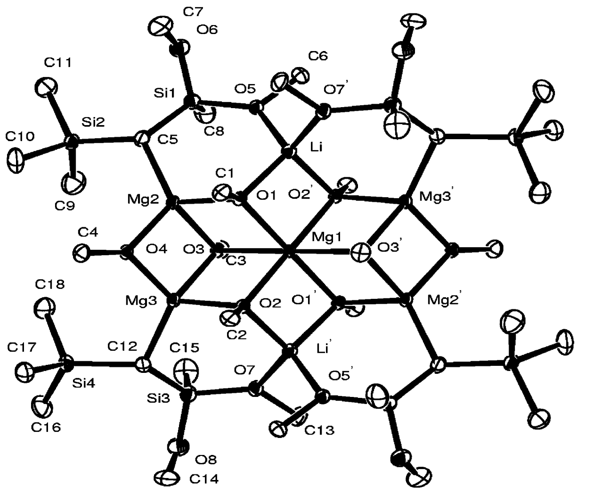


Figure 9. Molecular structure of [Li$_2$Mg$_5$(OMe)$_8${CH-(SiMe$_3$)(SiMe(OMe)$_2$)$_4$}] (**15**) with a selected atom-labeling scheme (hydrogen atoms are omitted for clarity) and thermal ellipsoids at the 30% probability level.

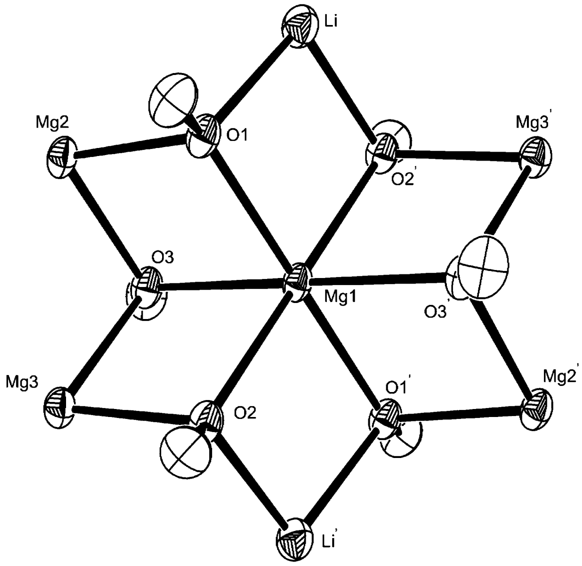


Figure 10. Central core of **15**.

Table 6. Selected Bond Lengths (Å) and Angles (deg) for 12 and [Mg(μ-Br){CH(SiMe$_3$)$_2$}(OEt$_2$)]$_2$

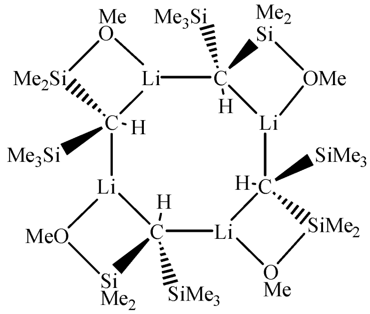
12		[Mg(μ-Br){CH(SiMe$_3$)$_2$}(OEt$_2$)]$_2$[11]	
Mg−C1	2.142(6)	Mg−C	2.114(7), 2.125(6)
Si1−C1	1.838(5)	Si−C	1.840 (av; range 1.837(7)−1.846(7))
Si1−C2	1.866(6)		
Mg−O	2.010(4)	Mg−O	2.024(5), 2.020(5)
Mg−Br	2.579(3)	av. Mg−Br	2.582 (av; range 2.579(2)−2.587(2))
Br−Mg−Br′	88.72(8)	Br−Mg−Br′	90.11(7), 90.24(7)
Mg−Br−Mg′	91.28(8)	Mg−Br−Mg′	89.69(7), 89.79(7)
C1−Mg−Br	125.49(17)	C−Mg−Br	124.1 (av; range 122.9(2)−125.3(2))
O−Mg−Br	106.10(13)		
O−Mg−Br′	97.85(14)	O−Mg−Br′	102.4 (av; range 100.8(2)−103.8(2))

Table 7. Selected Bond Lengths (Å) and Angles (deg) for 15

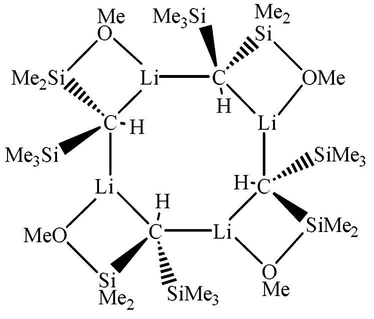
Mg1−O2	2.093(2)	Mg1−O1	2.120(2)
Mg1−O3	2.165(2)	Mg2−O4	1.948(3)
Mg2−O1	1.992(3)	Mg2−O3	2.027(3)
Mg2−C5	2.145(4)	Mg3−O4	1.945(3)
Mg3−O2	1.983(3)	Mg3−O3	2.041(3)
Mg3−C12	2.142(4)	Li−O1	1.940(7)
Li−O2′	1.955(7)	Li−O5	1.963(7)
Li−O7′	1.994(7)		
O2−Mg1−O2′	180	O2−Mg1−O1′	82.35(9)
O2−Mg1−O1	97.65(9)	O1′−Mg1−O1	180
O4−Mg2−O1	104.51(12)	O4−Mg2−O3	86.21(11)
O1−Mg2−O3	86.99(11)	O4−Mg3−O2	107.82(12)
O1−Mg2−C5	114.43(16)	O3−Mg2−C5	129.82(16)
O2−Mg3−O3	86.14(11)	O4−Mg3−O3	85.89(11)
O2−Mg1−O3	80.42(9)	O1−Mg1−O3	80.43(9)
O2′−Mg1−O3	99.58(9)	O1′−Mg1−O3	99.57(9)
O4−Mg2−C5	126.10(14)	O4−Mg3−C12	125.24(14)
O2−Mg3−C12	111.68(15)	O3−Mg3−C12	132.26(16)
O1−Li−O2′	90.8(3)	O1−Li−O5	119.0(3)
O2′−Li−O5	111.5(3)	O1−Li−O7′	113.2(3)
O2′−Li−O7′	120.7(3)	O5−Li−O7′	102.5(3)
Li−O1−Mg2	106.0(2)	Li−O1−Mg1	93.2(2)
Mg2−O1−Mg1	97.45(11)	Li′−O2−Mg1	93.5(2)
Mg3−O2−Mg1	98.45(11)	Mg2−O3−Mg3	90.78(11)
Mg2−O3−Mg1	95.00(11)	Mg3−O4−Mg2	96.14(11)
Mg3−O3−Mg1	94.43(10)		

At 203 K only one C^1H signal was recorded; we suggest that it is derived from the cyclooctamer of Figure 1. As each α-carbon atom is chiral, several stereoisomers are possible, but they are likely to interchange rapidly on the NMR time scale even at low temperature. At 233 K, there were three C^1H signals: at δ −1.03 attributed to the cyclooctamer and two of

roughly equal intensity at δ −1.94 and −2.17, possibly from the cyclotetramers **2′** and **2″**. The last two signals coalesced at 265 K ($\Delta\nu = 30$ Hz) corresponding to $\Delta G_{265\,\mathrm{K}} = 13.2$ kcal mol^{-1}; this low barrier may be due to a readily accessible transition state in which the Li←O bonds are dissociated.



2′



2″

Conclusions

The synthesis and X-ray structures of crystalline Li, Na, K, and Mg silylmethyls, derived from the ligands $[\mathrm{CH(SiMe_3)(SiMe_2OMe)}]^-$, $[\mathrm{CH(SiMe_3)\{SiMe(OMe)_2\}}]^-$, $[\mathrm{CH(SiMe_3)(SiMe_2Ph)}]^-$, and $[\mathrm{CH(SiMe_2OMe)_2}]^-$, are reported: $[\mathrm{Li\{CH(SiMe_3)(SiMe_2OMe)\}}]_8$ (**2**), $[\mathrm{Na\{CH(SiMe_3)(SiMe_2OMe)\}}]_\infty$ (**3**), $[\mathrm{K\{CH(SiMe_3)(SiMe_2OMe)\}(OEt_2)}]_\infty$ (**5**), $[\mathrm{Li\{CH(SiMe_3)(SiMe(OMe)_2)\}}]_\infty$ (**7**), $[\mathrm{Li\{CH(SiMe_2OMe)_2\}}]_\infty$ (**9**), $[\mathrm{Li\{CH(SiMe_3)(SiMe_2Ph)\}(TMEDA)}]$ (**14**), $[\mathrm{Mg(\mu\text{-}Br)\{CH(SiMe_3)(SiMe_2Ph)\}(OEt_2)}]_2$ (**12**), and $[\mathrm{Li_2Mg_5(OMe)_8\{CH(SiMe_3)(SiMe(OMe)_2)\}_4}]$ (**15**). Four of these (**2**, **3**, **7**, and **9**) were prepared under mild conditions by the regiospecific metalation of the appropriate precursor alkane, using LiBu^t in pentane or (for **3**) $\mathrm{NaCH_2Ph}$ in $\mathrm{C_6H_6}$. Compound **5** was obtained from **2** and KOBu^t in hexane at ambient temperature. Except for **9**, the yields were close to quantitative. In the reaction of $\mathrm{CH_2(SiMe_2OMe)_2}$ (**8**) and LiBu^t (under conditions identical with those which had given **2** and **7**, respectively), **9** was only obtained in low yield and, remarkably, $[\mathrm{Li\{\mu\text{-}C(SiMe_2OMe)_3\}}]_2$ (**10**) was the major product. The formation of the cluster compound **15**, from $[\mathrm{Li\{CH(SiMe_3)(SiMe(OMe)_2)\}}]_\infty$ and $\mathrm{MgBr_2}$ in THF at ambient temperature, is another unexpected result. The molecular structures of the crystalline compounds are discussed, partly in the context of analogues containing the ligands $[\mathrm{CH(SiMe_3)_2}]^-$ and $[\mathrm{C\{SiMe_{3-n}(OMe)_n\}}]^-$. Variable-temperature ^{1}H NMR spectra of **2** revealed both dissociative and fluxional processes.

Experimental Section

General Comments. All manipulations were carried out under vacuum or argon using standard Schlenk and vacuum line techniques. Pentane, hexane, TMEDA, $\mathrm{Et_2O}$, MeOBu^t, benzene, benzene-d_6, and toluene-d_8 were dried and distilled over sodium−potassium alloy and degassed prior to use. Tetrahydrofuran was distilled twice from sodium−benzophenone. LiBu^t (Acros) was a 1.5 M solution in pentane; LiBu^n (Aldrich) was a 1.6 M solution in hexane. Melting points were determined in sealed capillaries under argon on a electrothermal apparatus and are uncorrected. The NMR spectra were recorded using a WM-300 Bruker instrument at 300.13 (^{1}H), 75.42 (^{13}C), and 116.64 MHz (^{7}Li) or an AMX-500 Bruker spectrometer at 500.1 (^{1}H), 125.72 (^{13}C), 194.32 (^{7}Li), and 99.36 MHz (^{29}Si) at 293 K but 338 K for **4** (because of its low solubility; at this temperature, the ^{13}C NMR spectrum of **4** revealed significant decomposition after ca. 30 min) in benzene-d_6 or toluene-d_8 (**2**, **3**, **4, 9**), referenced internally to residual solvent resonances (^{1}H, ^{13}C) or externally (^{7}Li, ^{29}Si), and, except for ^{1}H, were proton-decoupled. Electron impact mass spectra were taken on a Kratos MS 80 RF instrument. Elemental analyses (calculated data are for empirical formulas) were carried out by Medac Ltd.; in most cases the data for carbon content were unsatisfactory, which is attributed to incomplete combustion of silicon-containing samples. The compounds $\mathrm{CH_2(SiMe_3)(SiMe_2OMe)}$ (**1**)^{14} and $\mathrm{CH_2(SiMe_3)[SiMe(OMe)_2]}$ (**6**)^{16} were prepared by literature procedures.

Synthesis of $[\mathbf{Li\{CH(SiMe_3)(SiMe_2OMe)\}}]_8$ (2). LiBu^t (40 mL, 60.00 mmol) was added dropwise to a cooled (−78 °C) and stirred solution of $\mathrm{CH_2(SiMe_3)(SiMe_2OMe)}$ (**1**; 10.6 g, 60.22 mmol) in pentane (ca. 80 mL) over a period of 30 min. The reaction mixture was slowly warmed to ca. 25 °C and stirred for 6 h. The volatiles were removed in vacuo. The residual solid was “stripped” twice with pentane and dried for 60 min at 45 °C/10^{-2} Torr and crystallized from diethyl ether solution, yielding compound **2** (9.06 g, 82%) as colorless crystals, mp 205 °C dec. ^{1}H NMR ($\mathrm{C_6D_5CD_3}$): at 303 K, δ −1.92, −1.12 1 H, (2 s, CHLi), 0.17, (s, 9 H, $\mathrm{SiMe_3}$), 0.28, 0.32 (2 s, 6 H, $\mathrm{SiMe_2}$), 3.08 (s, 3 H, MeO); at 318 K, δ −1.91 (s, 1 H, CHLi), 0.16 (s, 15 H, $\mathrm{SiMe_2}$ and $\mathrm{SiMe_3}$), 3.09, 3.11, 3.13 (3 s, 3 H, MeO); at 348 K, δ −1.90 (s, 1 H, CHLi), 0.13 (s, 9 H, $\mathrm{SiMe_3}$), 0.15 (s, 6 H, $\mathrm{SiMe_2}$), 3.13 (s, 3 H, MeO). ^{13}C NMR ($\mathrm{C_6D_5CD_3}$; at 333 K): δ 1.21 (CHLi), 3.25 ($\mathrm{SiMe_3}$), 4.45 ($\mathrm{SiMe_2}$), 49.74 (MeO). ^{29}Si NMR ($\mathrm{C_6D_5CD_3}$; 333 K): δ −7.41, 23.78. ^{7}Li NMR ($\mathrm{C_6D_5CD_3}$; 333 K): δ −0.44. Anal. Calcd for $\mathrm{C_{56}H_{152}Li_8O_8Si_{16}}$: C, 46.1; H, 10.50. Found: C, 46.2; H, 10.51.

Synthesis of $[\mathbf{Na\{\mu\text{-}CH(SiMe_3)(SiMe_2OMe)\}}]_\infty$ (3). NaBn (0.29 g, 2.54 mmol) was added in small portions to a cooled (−50 °C) and stirred solution of $\mathrm{CH_2(SiMe_3)(SiMe_2OMe)}$ (**1**; 0.58 g, 3.29 mmol) in diethyl ether (45 mL). The mixture was warmed to room temperature and was stirred for 12 h. The volatiles were removed in vacuo, and the residual solid was extracted into benzene (15 mL). The extract was filtered, and the filtrate was concentrated and stored at 15 °C for 2 days, yielding compound **3** (0.33 g, 42%) as colorless crystals, mp 46−48 °C. ^{1}H NMR ($\mathrm{C_6D_5CD_3}$): δ −1.33 (s, 1 H, CHNa), 2.23 (s, 15 H, $\mathrm{SiMe_3}$ and $\mathrm{SiMe_2}$), 3.26 (s, 3 H, MeO). ^{13}C NMR ($\mathrm{C_6D_5CD_3}$): δ 1.12 (CHNa), 4.29 ($\mathrm{SiMe_3}$), 6.53 ($\mathrm{SiMe_2}$), 50.56 (MeO). ^{29}Si NMR ($\mathrm{C_6D_5CD_3}$): δ −11.53, 10.79. MS (M denotes the monomeric unit **3**; *m/z* (% and assignment)): 221 (10), 198 (4, [M]$^+$), 161 (100), 131 (53), 115 (7).

$\mathbf{K[CH(SiMe_3)(SiMe_2OMe)]}$ (4). KOBu^t (0.30 g, 2.52 mmol) was added in small portions to a solution of **2** (0.46 g, 2.52 mmol) in hexane (40 mL) at ca. 25 °C. The resulting milky mixture was stirred for 12 h. This suspension was filtered, and the precipitate was washed with hexane (10 mL × 4). The

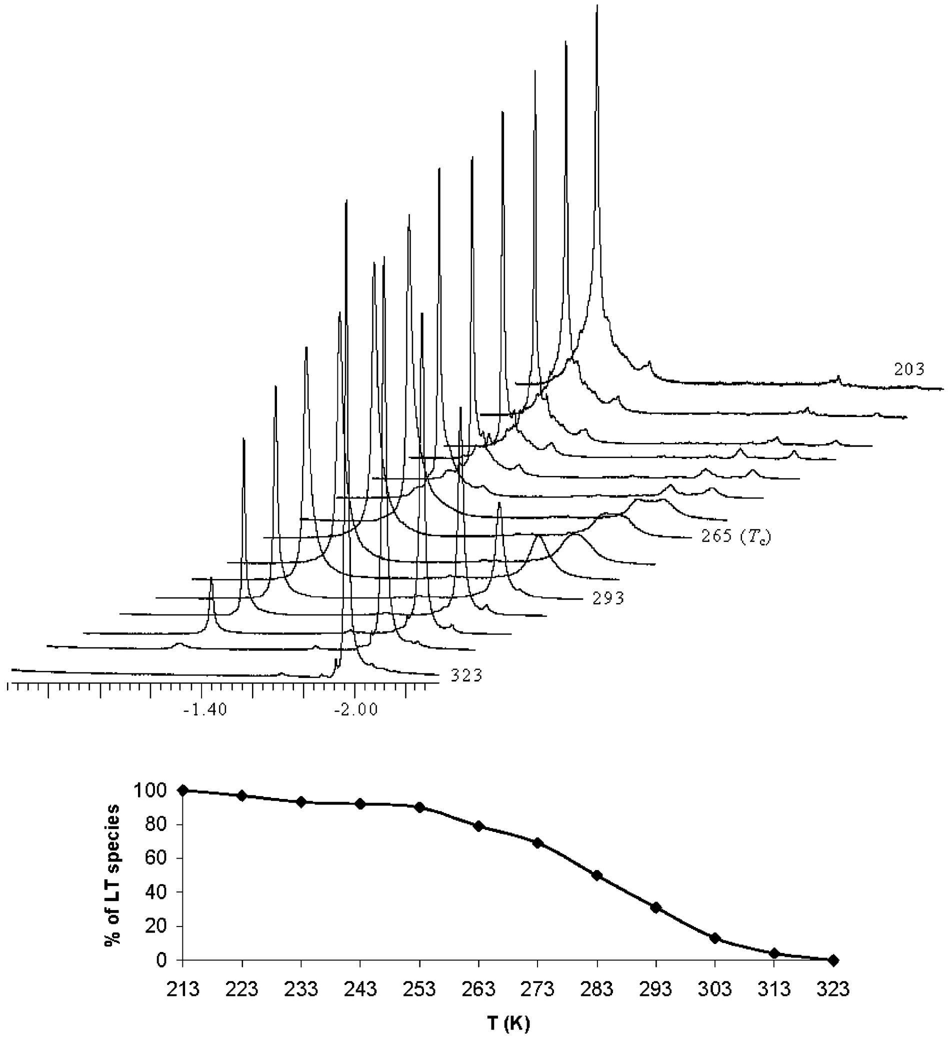


Figure 11. (a, top) VT ^{1}H NMR spectra (CH signals) of **2** illustrating the appearance and disappearance of the species throughout the temperature range 203−323 K. (b, bottom) Plot of the temperature (K) (on the abscissa) vs the percentage of the species (LT), which is preponderant at low temperature (on the ordinate).

residual solid was dried for 30 min at 45 °C/10^{-2} Torr to afford compound **4** (0.53 g, 95%) as a cream-white powder, mp 135−138 °C. ^{1}H NMR ($C_6D_5CD_3$; 318 K): δ −1.99 (s, 1 H, CHK), 0.00 (s, 9 H, $SiMe_3$), 0.04 (s, 6 H, $SiMe_2$), 3.15 (s, 3 H, MeO). ^{13}C NMR ($C_6D_5CD_3$): δ −1.00 (CHK), 1.53 ($SiMe_3$), 6.70 (and $SiMe_2$), 49.72 (MeO). MS (*m*/*z* (% and assignment): 503 (8), 429 (14), 355 (18), 281 (45), 207 (90), 147 (87), 131 (65), 73 (100, $[SiMe_3]^+$), 59 (18, $[HSiMe_2]^+$).

Synthesis of [K{*μ*-CH(SiMe$_3$)(SiMe$_2$OMe) }(OEt$_2$)]$_\infty$ (5). KOBu^t (1.51 g, 13.48 mmol) was added in small portions to a solution of **2** (2.46 g, 13.52 mmol) in hexane (40 mL) at ca. 25 °C. The resulting milky mixture was stirred for 12 h. This suspension was filtered, and the precipitate was washed with hexane (10 mL × 4). The residual solid was dried for 30 min at 45 °C/10^{-2} Torr and crystallized from diethyl ether solution, yielding compound **5** (2.77 g, 96%) as colorless crystals, mp 145−146 °C. The crystals were stored in vacuo, whereafter the NMR spectral characteristics proved to be identical with those recorded for **4**.

Synthesis of [Li{CH(SiMe$_3$)(SiMe(OMe)$_2$)}]$_\infty$ (7). LiBu^t (42 mL, 63.0 mmol) was added dropwise to a cooled (−100 °C) and stirred solution of $CH_2(SiMe_3)[(SiMe(OMe)_2]$ (**6**; 12.2 g, 63.5 mmol) in pentane (80 mL) over a period of 30 min. The reaction mixture was slowly warmed to room temperature and stirred for 12 h. The white precipitate that formed was filtered off and washed with hexane (15 mL × 3). The residual solid was dried for 30 min at 45 °C/10^{-2} Torr and crystallized from diethyl ether solution, yielding compound **7** (9.98 g, 80%) as colorless crystals, mp 135−137 °C. ^{1}H NMR: δ −1.21 (s, 1 H, CH), 0.23 (s, 3 H, SiMe), 0.28 (s, 9 H, $SiMe_3$), 3.48 (s, 6 H, OMe). ^{13}C NMR (C_6D_6): δ −2.31 (CHLi), −0.92 (Me_3Si), 1.48 (MeSi), 49.68 (MeO). MS (M denotes the monomeric unit; *m*/*z* (% and assignment)): 191 (6, $[M - Li]^+$), 177 (100, $[M - Li - Me]^+$), 147 (54), 73(26, $[SiMe_3]^+$), 43 (8, $[SiMe]^+$). Anal. Calcd for $C_7H_{19}LiO_2Si_2$: C, 42.4; H, 9.66. Found: C, 41.1; H, 9.67.

Synthesis of CH$_2$(SiMe$_2$OMe)$_2$ (8). To a solution of methoxytrimethylsilane (9.45 g, 90.86 mmol) in pentane (50 mL) at −78 °C was added LiBu^t (60.57 mL, 90.86 mmol). After it was stirred for 2 h at −78 °C, the reaction mixture was warmed to ca. 25 °C and stirred for an additional 2 h. The reaction mixture was cooled to −78 °C before methoxydimethylchlorosilane (10.0 g, 96.15 mmol) was added. Diethyl ether (20 mL) was then added dropwise. The reaction mixture was warmed to ca. 25 °C and stirred for 2 h. The precipitate was filtered off. The solvent was removed from the filtrate under reduced pressure. The residue was distilled through a glass-bead-packed fractionating column, yielding the colorless oil **8** (12.9 g, 74%), bp 88−90 °C/80 Torr. ^{1}H NMR ($CDCl_3$): δ −0.07 (s, 2 H, CH_2), 0.04 (s, 12 H, $SiMe_2$), 3.10 (s, 6 H, OMe). ^{13}C NMR ($CDCl_3$): δ 0.01 (CH_2), 4.23 ($SiMe_2$), 50.21 (OMe).

Reaction of CH$_2$(SiMe$_2$OMe)$_2$ (8) with LiBu^t. (a) LiBu^t (15.3 mL, 22.95 mmol), was added dropwise to a cooled (−78 °C) and stirred solution of $CH_2(SiMe_2OMe)_2$ (**8**; 4.2 g, 21.76 mmol) in pentane (40 mL) over a period of 30 min. The reaction mixture was slowly warmed to ca. 25 °C and stirred

Table 8. Experimental Data for the Crystal Structure Determination of the Compounds 2, 3, 5, and 7

	2	3	5	7
formula	$C_{56}H_{152}Li_8O_8Si_{16}\cdot C_6H_6$	$C_{17}H_{19}NaOSi_2\cdot 0.5C_6H_6$	$C_{11}H_{29}KO_2Si_2$	$C_7H_{19}LiO_2Si_2$
M_r	1536.84	237.45	288.62	198.34
cryst syst	monoclinic	monoclinic	orthorhombic	orthorhombic
space group	$P2_1/a$ (No. 14)	$P2_1/n$ (No. 14)	$Pbca$ (No. 61)	$Pna2_1$ (No. 33)
a (Å)	19.0679(3)	9.2006(3)	10.6877(4)	19.697(2)
b (Å)	16.3240(3)	9.7759(2)	32.0086(12)	10.2628(11)
c (Å)	35.0591(6)	16.2617(5)	11.0494(4)	12.8381(16)
α (deg)	90	90	90	90
β (deg)	102.440(1)	95.948(2)	90	90
γ (deg)	90	90	90	90
V (Å^3)	10 656.4(3)	1454.77(7)	3780.0(2)	2595.2(4)
Z	4	4	8	8
abs coeff (mm^{-1})	0.23	0.25	0.40	0.24
θ_{max} for data collecn (deg)	25.04	27.88	23.0	21.95
no. of indep rflns	18575	3445	2464	3035
R_{int}	0.111	0.046	0.123	0.098
no. of rflns with $I > 2\sigma(I)$	12 086	2748	1944	2440
no. of data/restraints/params	18 575/0/879	3445/0/131	2464/2/151	3035/1/225
R1 ($I > 2\sigma(I)$)	0.063	0.041	0.082	0.052
wR2 (all data)	0.183	0.111	0.259	0.115
largest diff peak, hole (e Å^{-3})	0.39, −0.35	0.37, −0.26	0.32, −0.40	0.16, −0.24

for 12 h. The white precipitate was filtered off and washed with pentane (10 mL × 3). The residual solid was dried in vacuo and recrystallized from diethyl ether solution, yielding compound **10** (2.67 g, 64%) as the first crop of colorless crystals; its NMR spectra and X-ray data were identical with those reported in the literature.[12] The filtrate was concentrated to ca. 1.5 mL and kept at −27 °C; after several days, the colorless crystalline compound **9** (0.17 g, 3.9%) was obtained, mp 210 °C dec. ^{1}H NMR ($C_6D_5CD_3$): δ −1.28 (s, 1 H, CH), 0.18 (s, 12 H, $SiMe_2$), 3.10 (s, 6 H, MeO), 3.22, (s, 3 H, MeO). ^{13}C NMR: δ −0.16 (CH), 1.40 ($SiMe_2$), 49.78 (MeO). ^{7}Li NMR: δ −1.10. MS (m/z (% and assignment)): 198 (26, $[M]^+$), 177 (100, $[M - Li - Me]^+$), 147 (63, $[M - Li - 3Me]^+$), 89 (17, $[SiMe_2OMe]^+$). Anal. Calcd for $C_7H_{19}LiO_2Si_2$: C, 42.4; H, 9.66. Found: C, 40.1; H, 9.70.

(b) $LiBu^t$ (20.5 mL, 30.75 mmol) was added dropwise to a cooled (−78 °C) and stirred solution of $CH_2(SiMe_2OMe)_2$ (6.2 g, 32.29 mmol) in pentane (40 mL) over a period of 30 min. The reaction mixture was stirred for 2 h at −78 °C and then warmed slowly to ca. 25 °C and stirred for another 2 h. The white precipitate was filtered off and washed with pentane (15 mL × 3). The residual solid was dried in vacuo and recrystallized from diethyl ether solution to give compound **9** (2.92 g, 48%).

Synthesis of $CH(Br)(SiMe_3)(SiMe_2Ph)$ (11). A cooled (−78 °C) solution of $LiBu^n$ (25.4 mL, 4.07 mmol) was added dropwise to a cooled (−110 °C) mixture of solvents (THF/pentane/diethyl ether 3/1/1 (90 mL)), simultaneously with the addition of a solution of $CHBr_2SiMe_3$ (10 g, 4.07 mmol) in the same solvent mixture (25 mL) over a period of 30 min. The reaction mixture was maintained at −110 °C for 3 h. A solution of $ClSiMe_2Ph$ (6.83 mL, 4.07 mmol) in pentane (20 mL) was added dropwise at −110 °C and maintained at that temperature for 1 h. The reaction mixture was warmed to ca. 25 °C and stirred for 12 h. The volatiles were removed at ca. 25 °C/10^{-2} Torr. The residue was filtered through Celite. The filtrate was distilled, yielding compound **11** (4.69 g, 38%), bp 80−86 °C/10^{-2} Torr. ^{1}H NMR: δ −0.45 (s, 9 H, $SiMe_3$), 0.39, 0.40 (s, 6 H, $SiMe_2Ph$), 2.22 (s, 1 H, CH), 7.16 (m, 2 H, Ph), 7.41 (m, 3 H, Ph). ^{13}C NMR: δ −0.74 ($SiMe_3$), −2.85, −2.45 ($SiMe_2Ph$), 26.61 (CHBr), 129.67, 134.23, 137.84 (Ph). MS (m/z (% and assignment)): 287 (15, $[M - Me]^+$), 205 (7, $[M - Me - Br]^+$), 135 (100, $[SiMe_2Ph]^+$).

Synthesis of $[Mg(\mu\text{-}Br)\{CH(SiMe_3)(SiMe_2Ph)\}(OEt_2)]_2$ (12). A solution of **11** (1.22 g, 4.05 mmol) in diethyl ether (20 mL) was added to Mg turnings (0.12 g, 4.93 mmol) in diethyl ether and refluxed for 6 h. The reaction mixture was filtered. The filtrate was concentrated and stored at −25 °C for 2 days, affording compound **12** (1.41 g, 87%) as white crystals, mp 98−100 °C. ^{1}H NMR: δ −1.25 (s, 1 H, CHMg), 0.35 (s, 9 H, $SiMe_3$), 0.61, 0.62 (s, 6 H, SiMe_2Ph), 0.80 (t, 6 H, Et_2O), 3.32 (q, 4 H, Et_2O), 7.18 (d, 1 H, $^3J_{HH}$ = 7.46, p-Ph), 7.25 (m, 2 H, $^3J_{HH}$ = 6.06, Ph), 7.78 (d, 2 H, $^3J_{HH}$ = 6.60 Hz, Ph). ^{13}C NMR: δ 0.08 (CHMg), 3.56 ($SiMe_3$), 4.05, 5.41 ($SiMe_2Ph$), 13.78 (CH_3, Et_2O), 65.21 (CH_2, Et_2O), 128.01, 128.33, 133.91 (Ph). ^{29}Si NMR: δ −6.03, −2.61. Anal. Calcd for $C_{32}H_{62}Br_2Mg_2O_2Si_4$: C, 48.0; H, 7.72; Found: C, 46.1; H, 7.60.

Synthesis of $Li[CH(SiMe_3)(SiMe_2Ph)](OEt_2)_{0.25}$ (13). In an apparatus fitted with a condenser, a solution of **11** (13.00 g, 43.19 mmol) in diethyl ether (30 mL) was added dropwise to a suspension of Li metal (1.2 g, 172.8 mmol) in refluxing diethyl ether (150 mL). The reaction was slightly exothermic. The mixture was stirred for 3.5 h and then cooled to ca. 25 °C, and the unreacted lithium was filtered off. The volatiles were removed from the filtrate at ca. 25 °C/10^{-2} Torr. The residue was filtered twice, and the precipitate was extracted into pentane. The extract was concentrated and stored at −25 °C for 7 days. The reaction mixture remained clear; hence, the volatiles were removed at 40 °C/10^{-2} Torr for 1 h, to obtain the oil **13** (established from the ^{1}H NMR spectrum) (9.57 g, 90%). ^{1}H NMR: δ −2.50 (s, 4 H, CHLi), 0.02 (s, 36 H, $SiMe_3$), 0.35 (s, 24 H, $SiMe_2Ph$), 0.76 (t, 6 H, OEt_2), 3.01 (q, 4 H, OEt_2), 7.89 (m, 12 H, Ph), 8.17 (d, 8 H, $^3J_{HH}$ = 5.60 Hz, o-Ph). ^{7}Li NMR: δ 0.12.

Synthesis of $[Li\{CH(SiMe_3)(SiMe_2Ph)\}(TMEDA)]$ (14). TMEDA (2.27 mL, 15.07 mmol) was added to a solution of compound **13** (3.14 g, 13.7 mmol) in hexane (80 mL). The mixture was stirred for 4 h and then filtered, and the filtrate was concentrated and stored at −25 °C for 4 days to yield a few crystals of compound **14**. ^{1}H NMR: δ −1.60 (s, 1 H, CHLi), 0.32 (s, 9 H, $SiMe_3$), 0.33, 0.53 (s, 6 H, $SiMe_2Ph$), 1.26 (s broad, 4 H, CH_2, TMEDA), 1.47 (s, 12 H, TMEDA), 7.19 (m, 3 H, Ph), 7.73 (d, 2 H, $^3J_{HH}$ = 5.61 Hz). ^{13}C NMR ($C_6D_5CD_3$): δ −0.07 (CHLi), 6.79 ($SiMe_2Ph$ and $SiMe_3$), 44.90 (Me, TMEDA), 55.94 (CH_2, TMEDA), 127.50, 127.61, 133.49 (Ph), 150.96 ($ipso$-C, Ph). ^{7}Li NMR: δ 0.15. ^{29}Si NMR ($C_6D_5CD_3$): δ −10.29 ($^1J_{SiH}$ = 46.8 and 55.1), −7.85 ($^1J_{SiH}$ = 47.7 and 56.1 Hz).

Synthesis of $[Li_2Mg_5(OMe)_8\{CH(SiMe_3)(SiMe(OMe)_2)\}_4]$ (15). $MgBr_2$ (0.17 g, 0.93 mmol) was added in small portions to a solution of **7** (0.46 g, 2.32 mmol) in THF (40 cm^3) at ca. −78 °C. The resulting mixture was warmed to ca. 25 °C and stirred for 24 h. The volatiles were removed in vacuo, and the residue was extracted with hexane and filtered. The filtrate was concentrated and stored for several days at −25 °C, yielding colorless crystals of compound **15** (0.18 g, 27%), mp 210 °C dec. ^{1}H NMR: δ −1.34 (s, 4 H, CH), 0.43 (s, 12 H, SiMe), 0.49 (s, 36 H, $SiMe_3$), 3.10 (s, 12 H, MeO), 3.26 (s, 12 H, MeO), 3.44 (s, 24 H, MeO). ^{13}C NMR: δ −3.11 (CH), 0.00 ($SiMe_3$),

Table 9. Experimental Data for the Crystal Structure Determination of the Compounds 9, 12, 14, and 15

	9	**12**	**14**	**15**
formula	$C_7H_{19}LiO_2Si_2$	$C_{32}H_{62}Br_2Mg_2O_2Si_4$	$C_{18}H_{37}LiN_2Si_2$	$C_{36}H_{100}Li_2Mg_5O_{16}Si_8$
M_r	198.34	799.62	344.6	1149.31
cryst syst	monoclinic	triclinic	monoclinic	monoclinic
space group	$P2_1$ (No. 4)	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)
a (Å)	9.4107(2)	9.080(8)	10.250(4)	12.7393(3)
b (Å)	16.7565(4)	9.952(6)	15.779(6)	13.2377(4)
c (Å)	12.3536(3)	13.132(4)	28.780(6)	20.0492(7)
α (deg)	90	94.64(4)	90	90
β (deg)	103.682(1)	109.08(6)	94.23(3)	98.466(1)
γ (deg)	90	104.22(6)	90	90
V (Å^3)	1892.77(8)	1070(1)	4642(3)	3344.2(2)
Z	6	1	8	2
abs coeff (mm^{-1})	0.25	2.06	0.15	0.26
θ_{max} for data collecn (deg)	25.03	24.98	22.97	25.04
no. of indep rflns	6302	3747	6436	5681
R_{int}	0.063		0.102	0.124
no. of rflns with $I > 2\sigma(I)$	5970	2901	2476	4133
no. of data/restraints/params	6302/1/337	3747/0/190	6436/30/448	5681/0/304
R1 ($I > 2\sigma(I)$)	0.044	0.065	0.094	0.068
wR2 (all data)	0.120	0.173	0.254	0.187
largest diff peak, hole (e Å^{-3})	0.20, −0.24	1.38, −1.51	0.26, −0.34	0.80, −0.38

5.48 (SiMe), 50.26, 51.29, 52.15 (MeO). ^{7}Li NMR: δ −2.59. Anal. Calcd for $C_{36}H_{100}Li_2Mg_5O_{16}Si_8$: C, 37.6; H, 8.70. Found: C, 35.2; H, 8.67.

X-ray Structure Determinations of Compounds 2, 3, 5, 7, 9, 12, 14, and 15. Unique data sets were collected with an Enraf-Nonius CAD4 (**12** and **14**) or Kappa CCD diffractometer, using a crystal coated with a layer of hydrocarbon oil, attached to a glass fiber, and cooled to 173(2) K. Refinement was on F^2 for all reflections using SHELXL-97.[22] All non-H atoms were anisotropic. The H atoms on C1A to C1H of **2** were located on a difference map and refined; other H atoms were in riding mode. The H atom on C(1) of **3** was refined. The diffraction for **5** was very weak; the Et_2O ligand was very poorly defined and was refined with bond length constraints (SADI), and the H atom on C1 was freely refined. For **14**, the diffraction was weak at higher angles; the H atoms bonded to C1 and C1A were refined, and the methyl groups attached to Si1A were disordered equally over two orientations. All other H atoms for each compound were included in the riding mode. Parameters are listed in Tables 8 and 9.

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Supporting Information Available: Full listings of X-ray crystallographic data, atomic coordinates, thermal parameters, bond distances and bond angles, and hydrogen parameters for **2**, **3**, **5**, **7**, **9**, **12**, **14**, and **15** and figures giving NMR spectra for **4** (^{1}H at 338 K and ^{1}H and ^{13}C at 338 K in $C_6D_5CD_3$ after ca. 30 min), **7** (^{1}H NMR in C_6D_6 at 293 K), **9** (^{1}H, ^{13}C, and ^{7}Li at 293 K in $C_6D_5CD_3$), and **15** (^{1}H, ^{13}C, and ^{7}Li at 293 K in C_6D_6). This material is available free of charge via the Internet at http://pubs.acs.org.

OM030041E

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[22] Sheldrick, G. M. SHELXL-97: Program for Crystal Structure Refinement; University of Göttingen, Göttingen, Germany, 1997.