

Partially Delocalized Allylic Lithium Compounds: Dynamics of Inversion, 1,3 Li Shift, and C–Li Bond, Exchange Influence of the Stereochemistry of Solvation

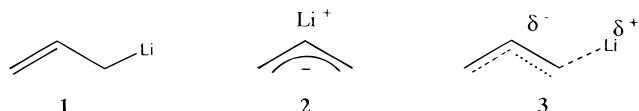
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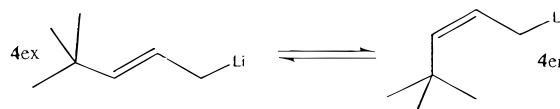
Abstract: While *exo-exo*-[1,3-bis(trimethylsilyl)allyl]lithium (**15**) and [1-(trimethylsilyl)allyl]lithium (**16**) were previously shown to be contact ion pairs containing delocalized carbanions, the corresponding species with a pendant ligand at the 2-position, [2-[[bis(2-methoxyethyl)amino]methyl]-1,3-bis(trimethylsilyl)allyl]lithium (**14**) and [2-[[bis(2-methoxyethyl)amino]methyl]-1-(trimethylsilyl)allyl]lithium (**12**), respectively, appear from their ¹³C NMR shifts and the first observation of ¹³C lithium spin coupling in an allylic lithium to be partially delocalized with detectable C–Li covalence. In proposed structures **12** and **14**, lithium is tridentately complexed. N and Li lie within the allyl carbon plane with the two oxygens normal to it on opposite sides. NMR line shape analysis and ¹³C₁ of signal averaging of the ¹³C–⁶Li coupling of **12** provides dynamics of intermolecular C–Li bond exchange with ΔH_e^\ddagger and ΔS^\ddagger of 11.6 kcal/mol and –11.5 eu, respectively. Inversion at the lithium-bound carbon of **12** averages nonequivalent ligand shifts. Line shape analysis gives ΔH_i^\ddagger and ΔS_i^\ddagger of 8 kcal/mol and –10 eu, respectively. Line shape changes observed for the methylsilyl (¹³C and ¹H) resonances as well as of the terminal ¹³C's of **14** due to a 1,3 Li sigmatropic shift yield activation parameters ΔH_s^\ddagger and ΔS_s^\ddagger of 18 kcal/mol and +15 eu. These results show that electronic structure of nominally conjugated organolithium compounds can be significantly altered by changing the stereochemistry of solvation, by use of pendant ligands, producing structures previously described in other systems as transition states for allylic rotation.

Allyllithium, the simplest of potentially conjugated organolithium compounds,¹ has been variously described, neglecting aggregation and solvation, as covalent, **1**, delocalized, **2**, and structures in between, **3**. NMR, ordinarily, does not distinguish



between **1** undergoing a fast 1,3 lithium shift and symmetrical **2**. A Saunders deuterium perturbation² of equilibrium experiment² shows allyllithium³ to be a conjugated species⁴ in THF-d₈. In general, with few exceptions, the results of spectroscopic,^{5,6} X-ray crystallographic,⁷ and calculational^{8,9} studies

support the delocalized structures. Among a few cases studied of unsolvated alkane-soluble allylic lithium compounds, for example, (3-neopentylallyl)lithium^{10a-c} (**4**), the NMR data are



consistent with the localized structure. The *cis* and *trans* forms show slightly different shifts. Carbon-13 NMR shifts of **4** in cyclopentane for C₁, C₂, and C₃ are δ 22, 145, and 100, respectively. On addition of lithium ligands such as ethers or tertiary amines to **4** in increasing concentrations, the ¹³C shifts

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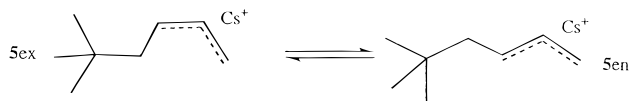
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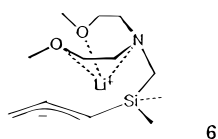
of C₁ and C₃ approach each other monotonically while that for C₂ remains essentially unchanged, limiting values for **4** complexed to 1,2-di-*N*-piperidinoethane being δ 39 and 72 for C₁ and C₃, respectively.^{10a} These approach the C₁ (51.4 δ) and C₃ (69 δ) shifts of (3-neopentylallyl)cesium (**5**).^{10e} The latter



is generally believed to be a contact ion pair.^{10e} Each of the samples of **4** with different ligands at different concentrations displayed only two spectra, one each for the exo and endo isomers.^{10a} On the basis of these results, it was proposed that in these different samples **4** consisted of rapidly interconverting covalent and delocalized ionic forms with rotation between exo and endo being slow under all conditions investigated. Aside from the better defined limiting covalent and delocalized forms, these data do not provide information on the number of these species, the nature of their structures, and the role of possible variable C–Li covalence, **3**, therein.

Prior to inception of the present work, there has been no report of spin coupling between ¹³C and ⁶Li or with ⁷Li in an allylic lithium compound.¹¹ Its absence in the case of ⁷Li could be due to fast ⁷Li nuclear electric quadrupole relaxation,¹² not so for ⁶Li, whose quadrupole moment is lower than ⁷Li's by a factor of 91.3.¹³ In addition, bimolecular C–Li bond exchange could be fast enough to also average out carbon-13–lithium coupling, even at very low temperatures. Such a bond exchange could be accompanied by interconversion of different (3-neopentylallyl)lithium species.

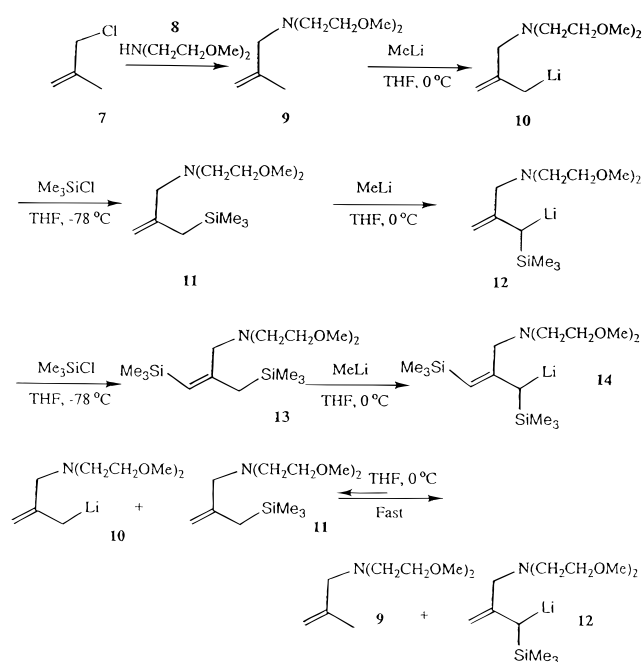
Exchange of ions among ion pairs is generally fast enough to average the very NMR parameters which would be informative of ion-pair structure.¹⁴ By constructing an allylic lithium compound internally solvated by a pendant ligand, see proposed **6**, we were able to slow the exchange of ions, investigate



structure, and uncover the dynamics of *reorientation* of coordinated lithium with respect to the allylic moiety.¹⁵ These results confirmed identification of ion reorientation effects in externally solvated allylic lithium compounds.^{4,16,17} In this paper we report examples of how small modifications of the site of the pendant ligand induce major changes in the structure of the allylic lithium and its dynamic behavior.

Results and Discussion

The sequence of transformations **7**–**14** summarizes the chemistry we have used to prepare allylic lithium compounds **12** and **14**. The latter have been drawn in the covalent form, as explained below. Amination of 3-chloro-2-methylpropene by bis(2-methoxyethyl)amine (**8**) furnishes the propene with a



pendant ligand, **9**. Sequential metalation/silylation of **9** provides the starting materials and the required substituted allylic lithium compounds **12** and **14**.

Ordinarily, allylic metalation of propene by butyllithium requires the presence of a tertiary vicinal diamine,¹⁸ such as TMEDA, and is still a slow reaction. That compounds **11** and **13** undergo deprotonation using even methyllithium implies that activation for the reaction is provided by prior complexation of the organolithium reagent with a pendant ligand.

The silylation of **10** must be carried out at low temperature to avoid concomitant formation of **13**, which takes place at higher temperature (see the Experimental Section). Evidently, during silylation of **10** at the higher temperature, unreacted **10** must metalate monosilyl product **11**, ultimately producing the disilyl product **13**. This scheme requires recovery of **9** and **13** to be equimolar, close to that found.

The two organolithium compounds **12** and **14** display NMR parameters different from those reported for all allylic lithium compounds studied to date.^{5,6} At low temperature, ¹³C lithium coupling is observed, all ligand carbons are magnetically nonequivalent by ¹³C NMR, and the allyl ¹³C NMR shifts reflect partially delocalized species (see below). Both compounds exhibit one-bond ¹³C–Li spin coupling at low temperature; for monosilyl **12** in THF at 250 K ¹J(¹³C,⁶Li) is 3 Hz; in the case of disilyl **14** in diethyl ether-*d*₁₀ at 240 K the value of ¹J(¹³C,⁷Li) is 6.1 Hz. Observation of the latter coupling implies small electric field gradients around ⁷Li in **14** compared to many [⁷Li]organolithium compounds wherein the gradients are large enough to average out ¹³C–⁷Li coupling via ⁷Li nuclear electric quadrupole relaxation.¹² The corresponding coupling in [⁶Li]-**14** would be 2.3 Hz, easily missed at low temperature due to viscosity broadening.

These results imply that there is a low detectable degree of carbon lithium covalence associated with some “s” character in **12** and **14**.¹⁹ This stands in contrast to the results of studies of most solvated allylic lithium compounds which are regarded as conjugated species, from their ¹³C NMR shifts;^{5,6} they do not exhibit ¹³C–Li coupling, even at low temperature, with either lithium isotope. However, most simple solvated mono-

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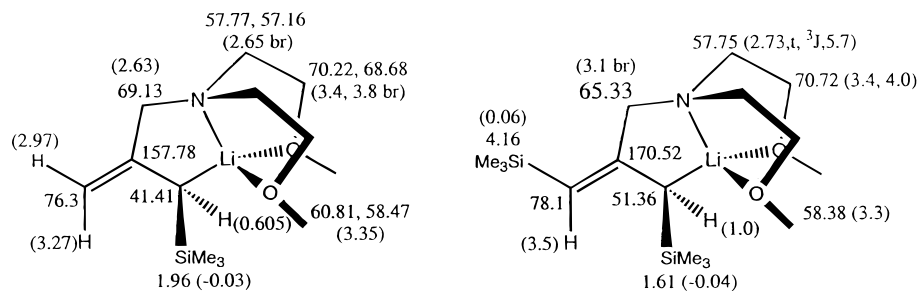


Figure 1. Proposed structures of compounds **12** and **14** with ^{13}C and ^1H shifts, δ units.

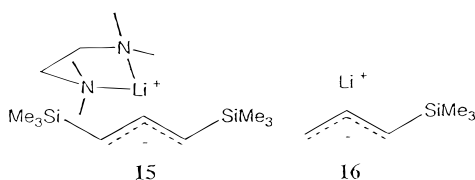
Table 1. Allyl ^{13}C NMR Shifts

compd	C ₁	C ₂	C ₃	solvent
10	39.7	158.4	77.63	Et ₃ O- <i>d</i> ₁₀
10	41.41	158.7	76.4	THF- <i>d</i> ₈
12	51.36	170.5	78.10	THF- <i>d</i> ₈
13	67.75	153.2	67.25	Et ₂ O- <i>d</i> ₁₀
14	56.00	156.1	60.00	THF- <i>d</i> ₈
allyl Li	51.2	147.2	51.20	Et ₂ O- <i>d</i> ₁₀

meric RLi species (R = alkyl, aryl, vinyl, alkynyl) exhibit one-bond ^{13}C - ^6Li coupling of *ca.* 16 Hz.^{20,21} Neglecting for the moment the explanation for this unexpected uniformity,²² see below, one can say that the C-Li covalent character in **12** and **14** must lie somewhere between those for the RLi species, above, with a common value for $^1J(^{13}\text{C},^6\text{Li})$ and the many solvated lithium compounds with potentially conjugated organic moieties which have been described as ion pairs containing delocalized carbanions.^{5,6,23}

Partial detectable C-Li covalence in **12** and **14** necessarily implies that the allyl moiety is only partly delocalized. This is clearly seen in the ^{13}C shifts (see Figure 1).

A combination of X-ray crystallography and a Saunders deuterium perturbation of equilibrium NMR^{3,7a,d} experiment establishes allyllithium and *exo-exo*-[1,3-bis(trimethylsilyl)allyl]lithium^{4,7e} (**15**) to be a delocalized species. Their shielded C₁ and C₃ ^{13}C shifts, with respect to C₂, are consistent with the expected alternation of charges in such a delocalized carbanionic species (see Table 1).²⁴ A similar conclusion applies to [1-(trimethylsilyl)allyl]lithium¹⁶ (**16**). Unsolvated (3-neopen-



tylallyl)lithium (**4**) with ^{13}C shifts of δ 23, 148, and 110, respectively, for C₁, C₂, and C₃ is a suitable reference compound for a localized allylic lithium. By comparing the allyl ^{13}C shifts of **12** and **14** to those for the delocalized, **15** and **16**, and localized, **4**, reference compounds, it is clear that **12** and **14** are indeed partly delocalized. Quantitation of these intermediate

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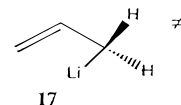
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bonding parameters must await the results of semiempirical calculations.²⁵

Evidence concerning the nature and structure of lithium complexation comes from ^{13}C shifts of the pendant ligand on **12**. All these carbons are magnetically nonequivalent (see Figure 1), implying that at least two and most likely all three donors are complexed to lithium. Construction of models and preliminary results of semiempirical calculations²⁵ indicate that tridentate coordination to lithium requires that nitrogen and lithium lie within the allyl plane, thus favoring some C-Li covalency with associated "s" character, as proposed above from the shifts, with the O-N-O plane being perpendicular to and bisected by the allyl-N-Li plane (see Figure 1). Thus the unusual structures implicated by the data for **12** and **14** must be due to the stereochemistry of solvation of lithium. In contrast, in the majority of externally solvated delocalized allylic lithium compounds, lithium is sited normal to the allyl plane.

That ^{13}C lithium coupling is observed at all for **12** and **14** is best attributed to the encapsulated sites of lithium which render intermolecular C-Li bond exchange energetically less accessible due to steric interactions. Ordinarily this process is fast enough to average out the ^{13}C - ^6Li or ^{13}C - ^7Li spin coupling even at low temperatures.

The structures **12** and **14** resemble those proposed for transition states to rotation for ground state delocalized allylic lithium compounds based on both NMR line shape measurements^{5,6} and calculations⁹ of the barriers. That the measured barriers depended significantly on the nature of the lithium ligand present implied development of some Li-C covalency in the transition state concomitant with a loosening of lithium ligand coordination²⁶ (**17**). Interestingly, while the rate of



rotation about C₂-C₃ in [1-(trimethylsilyl)allyl]lithium·TMEDA is quite fast at 300 K, 219 s⁻¹, the corresponding rate for the C₂-C₃ bond in **12** is too slow to measure at 320 K. Evidently being encapsulated at C₁ lithium cannot easily coordinate to C₃ in a transition state for bond rotation.

Above 250 K with increasing temperature, the ^{13}C - ^6Li coupling in **12**, THF solution, is progressively averaged out due to increasingly faster intermolecular C-Li bond exchange (see Figure 2). Since **12** contains ^{13}C in natural abundance, the faster of the exchange processes is the mutual exchange of ^6Li 's between a $^{13}\text{C}_1$ and a $^{12}\text{C}_1$. For purposes of calculating the $^{13}\text{C}_1$

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(26) While the published calculated (*ab initio*) transition state for allyllithium rotation shows Li at C₁ endo in the allyl plane (ref 9), a SCRF procedure yields two transition states of similar energies, with Li at C₁ in the allyl plane, one *exo* and the other *endo* (A. S. Chow and G. Fraenkel, The Ohio State University, 1996).

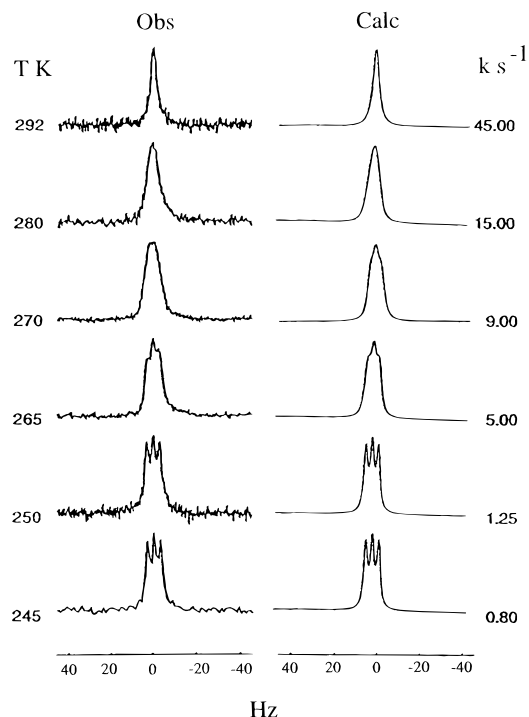
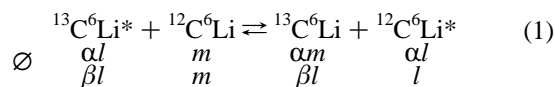


Figure 2. ^{13}C NMR of **12** (0.3 M) in $\text{THF-}d_8$, C_1 portion: (left) observed at different temperatures and (right) calculated.

Table 2. Symbols Used in the NMR Line Shape Analysis

α, β	^{13}C states	i	-1
m, l	^6Li states	Δv	$v - v_r$
ρ	density matrix	v	frequency point
$\dot{\rho}$	$d\rho/dt$	J	coupling constant
\mathcal{H}	spin Hamiltonian	C	arbitrary constant
E	exchange operator	k	pseudo-first-order rate constant
$1/T$	intrinsic line width		

NMR line shape,^{27,28} we simulate the exchange process as shown in (1) together with the spin product states \emptyset of different species present,



where α and β are states of ^{13}C and l and m are states of ^6Li . One takes all elements of the density matrix eq 2

$$\langle \beta l | i[\rho^{\text{CLi}}, \mathcal{H}] - (\rho^{\text{CLi}}/T) + E\rho | \alpha l \rangle = 0 \quad (2)$$

for pseudospecies “ $^{13}\text{C}^6\text{Li}$ ”, diagonal in ^6Li with ^{13}C states connected by a $\Delta m_z = +1$ transition, which generates the three coupled first-order inhomogeneous equations in the required three elements of the density matrix $\langle \beta l | \rho^{\text{CLi}} | \alpha l \rangle$, l 's being the three states of ^6Li ($l = 1$). All terms used in this treatment are conveniently listed and defined in Table 2. Elements of $E\rho^{\text{CLi}}$ which takes account of the exchange mechanism in the density matrix equations are evaluated as in (3).

$$[E\rho^{\text{CLi}}]_{\beta l, \alpha l} = \frac{1}{3}k \sum_{\substack{m \\ m \neq l}} (\rho_{\beta m, \alpha m}^{\text{CLi}} - 2\rho_{\beta l, \alpha l}^{\text{CLi}}) \quad (3)$$

The resulting coupled density matrix equations are shown in matrix form in (4). For brevity the $\rho_{\beta l, \alpha l}^{\text{CLi}}$ elements have been

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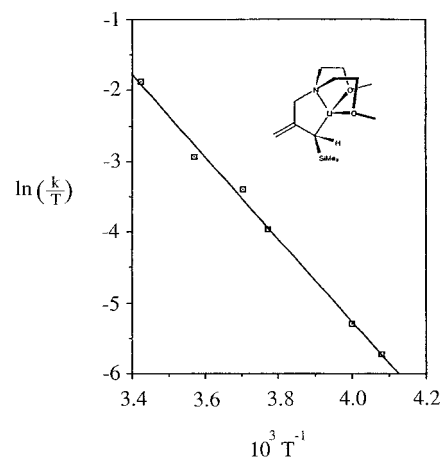


Figure 3. Eyring plot for C–Li exchange for **12** in $\text{THF-}d_8$.

redefined as ρ_i ($i = 1, 2, 3$). Equation 4 is solved and the ρ_i elements summed (5)

$$\begin{bmatrix} i2\pi(\Delta v - J) & 1/3k & 1/3k \\ -T^{-1} - 2/3k & & \\ 1/3k & i2\pi\Delta v & 1/3k \\ & -T^{-1} - 2/3k & \\ 1/3k & 1/3k & i2\pi(\Delta v + J) \\ & & -T^{-1} - 2/3k \end{bmatrix} \times \begin{bmatrix} \rho_1 \\ \rho_2 \\ \rho_3 \end{bmatrix} = iC \begin{bmatrix} 1 \\ 1 \\ 1 \end{bmatrix} \quad (4)$$

$$\text{Abs}(v) = -\ln(\rho_1 + \rho_2 + \rho_3) \quad (5)$$

to give the $^{13}\text{C}_1$ NMR absorption. Comparison of observed and calculated line shapes (Figure 2) gives the rate constants and resulting in ΔH^\ddagger and ΔS^\ddagger values of 11.6 kcal/mol and -11.5 eu, respectively; Figure 3 is the associated Eyring plot (see Table 3).

As noted, in ether- d_{10} solution at low temperature, all carbons on the pendant ligand in **12** are magnetically nonequivalent by ^{13}C NMR. Above 180 K with increasing temperature there is signal averaging of the equal ^{13}C doublets due to OCH_3 , NCH_2C , and OCH_2 , each pair collapsing to single lines at their respective centers (see Figures 4a–c). Line shape analysis of these resonances reveals that each set gives rise to closely similar rates and essentially the same activation parameters ΔH^\ddagger and ΔS^\ddagger , averaging to 8 kcal/mol and -10 eu, respectively, implying that a common mechanism is responsible for all these effects (see Figure 5a–c for the Eyring plots). Phenomenologically that must involve overall inversion at the lithium-bound carbon and/or, less likely, inversion at nitrogen. The process is clearly first order in **12** and is considerably faster than bimolecular C–Li bond exchange which leads to the averaging of the ^{13}C – ^6Li coupling (Table 3). It is also much faster than rotation around the C_3 – C_2 bond. The latter process is slow, too slow to measure by 320 K because, as proposed above, lithium is encapsulated by the pendant ligand, rendering a lithium-driven bond rotation energetically inaccessible.

The groups of Reich²⁹ and Hoffmann³⁰ have also investigated the dynamics of carbanionic inversion in a variety of α -hetero

(29) (a) Reich, H. J.; Kulicke, K. *J. Am. Chem. Soc.* **1995**, *117*, 6621–6622. (b) Reich, H. J.; Kulicke, K. *J. Am. Chem. Soc.* **1996**, *118*, 273–274. (c) Reich, H. J.; Dykstra, R. R. *J. Am. Chem. Soc.* **1993**, *115*, 7041–7042. (d) Reich, H. J.; Dykstra, R. R. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1649–1650.

Table 3. Eyring Parameters Inversion Exchange and Rearrangement

compd	concn, M	solvent	dynamics (resonance)	ΔH^\ddagger , kcal/mol	ΔS^\ddagger , eu
12	0.34	diethyl ether- <i>d</i> ₁₀	C ₁ inversion (−OCH ₂)	7.9	−10
			C ₁ inversion (−NCH ₂ C)	7.9	−10
			C ₁ inversion (−OCH ₃)	8.0	−9
12	0.3	THF- <i>d</i> ₈	C ₁ −Li exchange (C ₁)	11.6	−11.5
14	0.23	THF- <i>d</i> ₈	1,3 Li transfer (SiCH ₃)	18.2	15
			1,3 Li transfer (SiCH ₃)	18.3	15

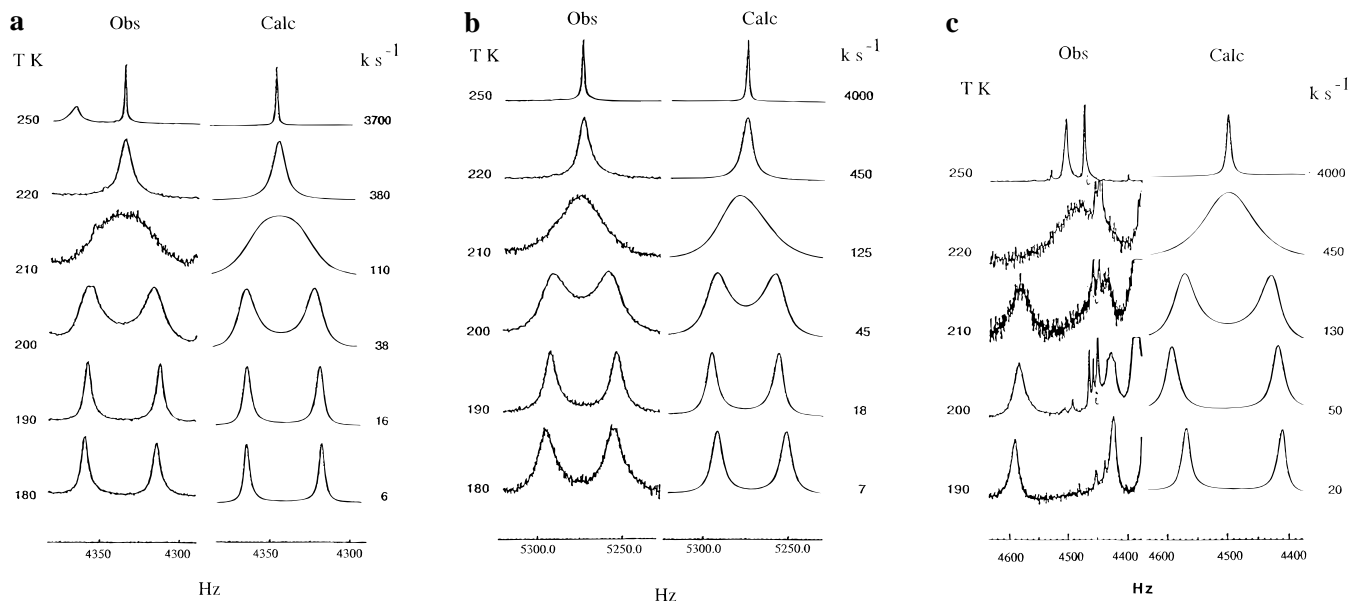


Figure 4. (a) ¹³C NMR of **12** (0.34 M) in diethyl ether-*d*₁₀ of the NCH₂C part: (left) observed at different temperatures and (right) calculated to fit with the rate constants. (b) ¹³C NMR of **12**, as in Figure 4a, of the OCH₂ portion: (left) observed at different temperatures and (right) calculated to fit. (c) ¹³C NMR of **12**, as in Figure 4a, of the OCH₃ part: (left) observed at different temperatures and (right) calculated to fit.

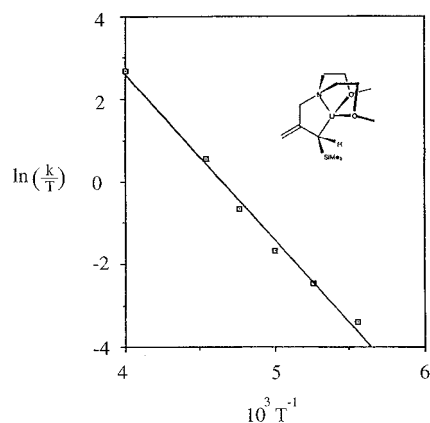
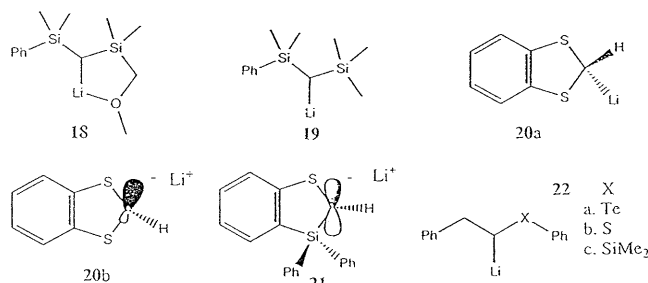


Figure 5. Eyring plot for inversion in **12** using (0.3 M) in diethyl ether-*d*₁₀ using the NCH₂, OCH₂, and OCH₃ ¹³C NMR line shapes, respectively.

and α,α^1 -dihetero organolithium compounds, where hetero = Te, Si, S, Se, see for example, **18** to **22a–c**, both internally and externally solvated. In addition, by use of HMPT as external ligand(s),²⁹ organolithium species RLi(HMPT)_{*n*} (*n* = 0–4) with different degrees of C–Li bond ionic character were generated and studied. Where ¹J(¹³C,⁷Li) was observed, this parameter had values of between 8 and 21 Hz, respectively. These are considerably less than coupling of 43 Hz (or ¹J(¹³C,⁶-Li) of 16 Hz) observed for many common solvated organolithium compounds.^{20,21} Thus the C–Li bonds in these α -hetero RLi species may be regarded as more ionic than in the “common pattern” compounds described above. In every case wherein



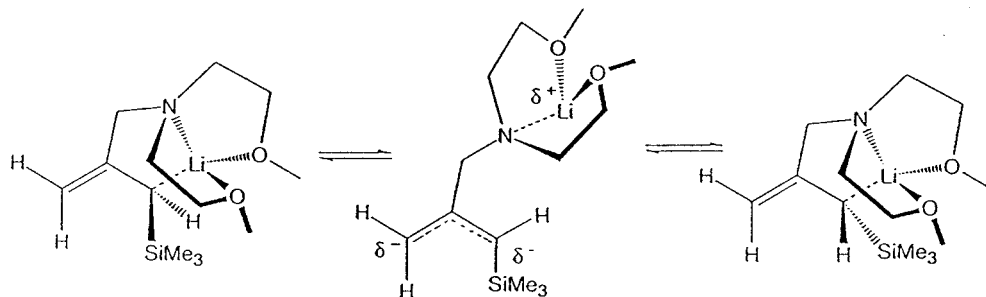
¹³C–⁷Li coupling was observed, bimolecular C–Li bond exchange was considerably slower than inversion.^{29a,d} Hence inversion in these compounds is a first-order process. Most of these published activation parameters lie in the ΔH^\ddagger range of 8–11 kcal/mol with ΔS^\ddagger neutral, i.e. small in magnitude. Exceptions involved systems subject to steric interactions.^{30a,c}

Several mechanisms have been proposed which are consistent with a first-order inversion process;^{29,30} all require some increase in symmetry on approaching the transition state, some involving a change in the ionic character of the C–Li bond. Our results regarding the dynamics of inversion of **12** parallel the previously published examples referred to above. A mechanism most consistent with the proposed structure and the above results would involve loosening of the C–Li bond with concomitant planarization of the bonding arrangement around C₁. Such a transition state could pyramidalize on either side of the three-carbon allyl plane, reforming the more covalent bond, C₁ to lithium (see Scheme 1). Our data provide no information regarding possible changes in the coordination of lithium to pendant ligand during the inversion process. Less plausible mechanisms include inversion at nitrogen accompanying some ligand lithium dissociation.

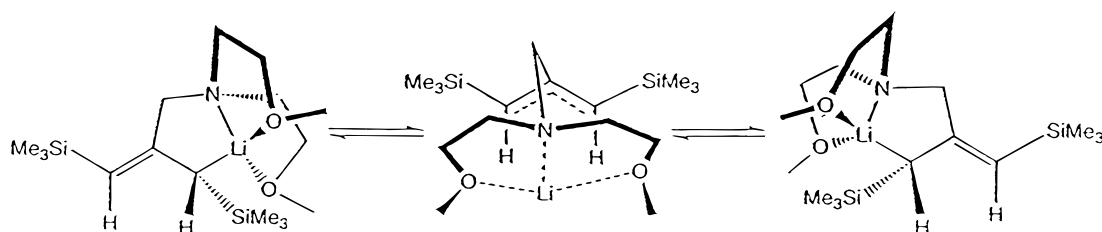
Compound **14** was also shown to assume the internally

(30) (a) Hoffmann, R. W.; Dress, R. K.; Ruhland, T.; Wenzel, A. *Chem. Ber.* **1995**, *128*, 861–870. (b) Dress, R. K.; Rölle, T.; Hoffmann, R. W. *Chem. Ber.* **1995**, *128*, 673–677. (c) Ruhland, T.; Dress, R.; Hoffmann, R. W. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1467–1468.

Scheme 1



Scheme 2



solvated, partially delocalized allylic structure with small $^{13}\text{C}_1$ – ^7Li coupling (Figure 1). At low temperature the silyl methyls are clearly nonequivalent in ^{13}C and ^1H NMR as are C_1 and C_3 . With increasing temperature above 260 K, the ^{13}C and ^1H doublets due to the silyl methyls of **14** progressively average to single lines at their respective centers (see Figure 6a,b). Meanwhile the C_1 and C_3 ^{13}C resonances broaden and disappear into the baseline. NMR line shape analysis of the two sets of methylsilyl resonances results in the same dynamic parameters (see Table 3) of $\Delta H^\ddagger = 18$ kcal/mol with $\Delta S^\ddagger = +15$ eu. Eyring plots are shown in Figure 7a,b. The process responsible for all these changes must be the degenerate 1,3 lithium sigmatropic shift. Its rate constant at 310 K is 1650 s^{-1} , still too small to average the C_1, C_3 ^{13}C shift of 2017 Hz to a single observable peak. The magnitude of ΔH^\ddagger suggests that passage through the transition state is accompanied by major changes in bonding. We would like to propose that these involve an increase in delocalization of the allyl moiety, compared to the ground state (Scheme 2). These changes in bonding character bear an inverse relationship to those proposed to accompany rotation in allylic lithium compounds—a delocalized ground state to a more localized transition state (see **17**).²⁶ The latter barriers have reported values of 13–19 kcal/mol, respectively. The interchange of energies of these states must be ascribed to stereochemistry of solvation. Further information regarding changes in lithium ligand coordination accompanying the 1,3 shift is not available from our current results. The lithium sigmatropic shift requires also that overall the two TMS groups move in opposite directions, though not necessarily concertedly.

Organolithium compounds are variously described as “carb-anions”, “ion pairs”, or “covalent”. Some comments on the nature and nomenclature of C–Li bonds as determined from NMR data are now in order. We assume that ^{13}C –Li spin coupling is Fermi³¹ contact in origin. Following the treatment of Karplus, Grant, and Lichtman,¹⁹ taking account of normalization and assuming a common excitation energy, the coupling between two isotopes, *s* and *t*, becomes proportional to $\alpha^2 Z^3$, α^2 the “*s*” character and *Z* the Slater effective nuclear charge, which is proportional to the *s*–*t* covalency. For C–H bonds in neutral molecules, the covalency is constant among many molecules, hence the proportionality of $^1J(^{13}\text{C}, ^1\text{H})$ with “*s*” character.¹⁹ In polar species *Z* varies; for example, in cyclopentadienyl anion, $^1J(^{13}\text{C}, ^1\text{H})$ is 135 Hz instead of the sp^2 value

of 167 Hz because the charge on carbon reduces *Z*. Electronegative substituents on carbon increase *Z* and also the ^{13}C – ^1H coupling constant.²⁰ Regarding the many monomeric organolithium compounds in which $^1J(^{13}\text{C}, ^6\text{Li})$ is *ca.* 15–16 Hz, independent of the organic moiety,^{20,21} and assuming that the $\alpha^2 Z^3$ dependence still holds, it is the inescapable conclusion that “*s*” character is inversely proportional to covalency or bond order.²² While assigning the relative contributions of α^2 and Z^3 to $^1J(^{13}\text{C}, ^6\text{Li})$ requires a theoretical model and detailed calculations, one can still make qualitative assessments by combining coupling constants and chemical shift data. For example, in the cases of the allylic lithium species presented above and benzyllithium compounds reported previously,³² showing $^1J(^{13}\text{C}, ^6\text{Li})$ values of 2–4 Hz, much lower than the “common pattern” values of 15 Hz, one can say that the C–Li bonding is more ionic for the first two cases than the latter. This is supported on comparing ^{13}C shift data. For allyllithium and [1-(trimethylsilyl)allyl]lithium, the C_1 and C_3 ^{13}C shifts (Table 1) are consistent with a delocalized anion with charges of *ca.* –0.5 at the terminal carbons, assuming the well-known ^{13}C shift/charge relationship of –160 ppm/e applies.²⁴ Comparing ^{13}C shifts in **12** and **14** with values for model delocalized system [1-(trimethylsilyl)allyl]lithium and localized **4**, shifts for **12** and **14** lie between those for the two reference compounds, hence these compounds, **12** and **14**, are described as partially delocalized with the C–Li bonds detectably covalent, less than among the “common pattern” RLi species. Noting that the C_1 and C_3 shifts in **6**, originally described as an ion pair, are similar to those for **12**, then C–Li bonding in **6** must resemble that for **12**, even though ^{13}C – ^6Li coupling was not seen in **6**. In sum we recommend that if C–Li coupling is detected then the bonding should be described as largely ionic (often the case) but partially covalent. It should not be described as an ion pair. The absence of ^{13}C – ^6Li coupling, alone, provides no information on the character of the C–Li bond, if there is a bond in the traditional sense.

Benzylic lithium compounds only exhibited ^{13}C – ^6Li spin coupling under conditions of slow intermolecular C–Li bond exchange, at low temperature.³² This was accomplished by use of internal coordination with a pendant ligand or by observing NMR of a dilute solution of the compound enriched with ^{13}C at C_α (Li). A variety of these benzylic lithium compounds both

(31) Ramsey, N. F. *Phys. Per.* **1953**, *91*, 303.(32) Fraenkel, G.; Martin, K. *J. Am. Chem. Soc.* **1995**, *117*, 10336–10344.

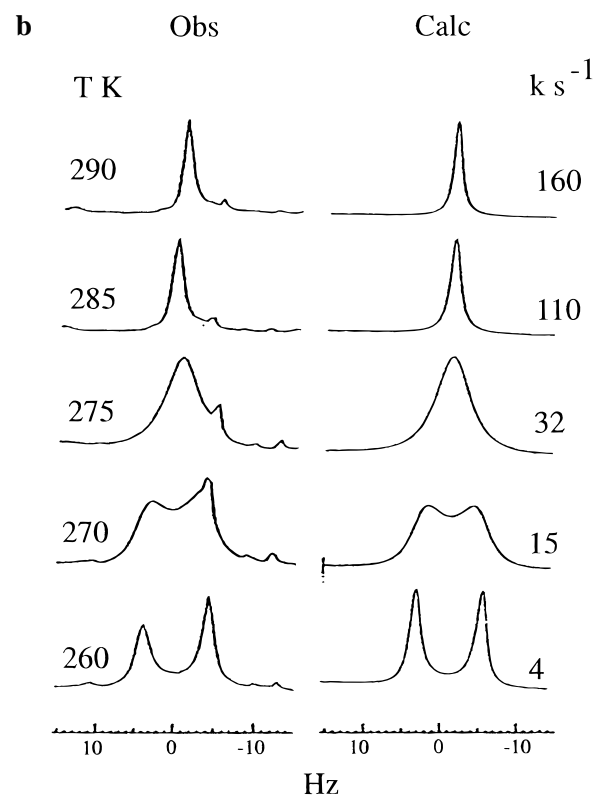
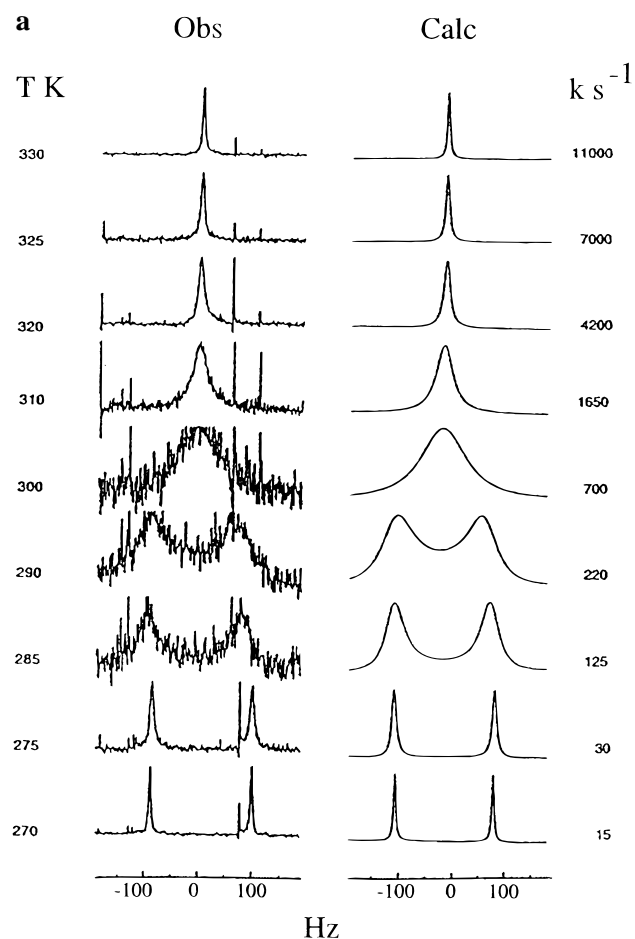


Figure 6. (a) ^{13}C NMR of **14** (0.23 M) in diethyl ether- d_{10} for the methylsilyl part: (left) experimental at different temperatures and (right) calculated to fit with the rate constants. (b) ^1H NMR of **14** (0.23 M) in diethyl ether- d_{10} for the methylsilyl part: (left) observed at different temperatures and (right) calculated to fit with the rate constants.

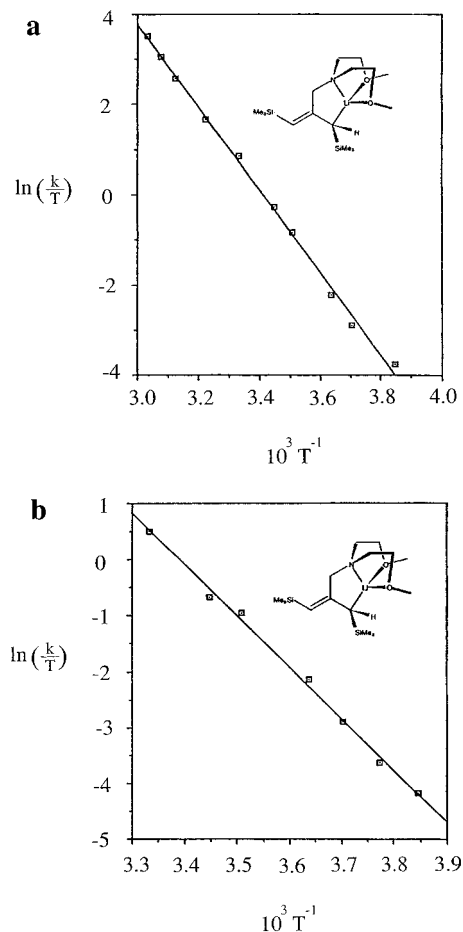


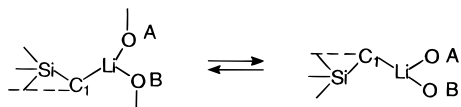
Figure 7. (a) Eyring plot for the 1,3 lithium shift in **14**, using the ^{13}C methylsilyl resonance. (b) Eyring plot for 1,3 lithium shift in **14** (0.23 M) in diethyl ether- d_{10} , using methylsilyl proton NMR.

internally and externally solvated had the same ring shifts, whether or not ^{13}C – ^6Li coupling could be observed, and hence were concluded to all have very similar electronic structures, including small detectable C_α –Li covalence.

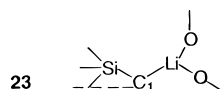
It is well-known that solvation plays a prominent role in determining molecular structure especially of organometallic compounds. Thus addition of THF to unsolvated (3-neopentylallyl)lithium turns it into a delocalized anion within a solvated ion pair.^{10a} In a similar fashion, externally complexed [1-(trimethylsilyl)allyl]lithium (**16**) and *exo-exo*-[1,3-bis(trimethylsilyl)allyl]lithium (**15**) appear to incorporate delocalized carbanions. In contrast **12** and **14**, their internally complexed derivatives, respectively, appear to be significantly more localized with detectable C–Li covalency. These species resemble structures of transition states proposed to account for barriers to rotation of delocalized allylic lithium compounds. The reversal in ground state energies must be due to the stereochemistry of solvation. It is not a forgone conclusion that lithium complexation reduces covalency.

It is now appropriate to clarify the significance of the salient features of allyllithium structure and behavior uncovered in this work. Our results show no evidence for more than one species of compounds **12** and **14** throughout the entire temperature range studied. The observation of small ^{13}C – ^6Li and ^{13}C – ^7Li spin coupling constants argues for a small detectable degree of carbon–lithium covalence. This is consistent with a partially delocalized allyl moiety as evidenced by ^{13}C shifts which lie between values for solvated delocalized ion pairs and localized unsolvated species, **2** and **4**, respectively. Nonequivalences among the pendant ligand ^{13}C shifts, the shift values themselves, and the results of our preliminary NOE experiments, all together,

Scheme 3



show that Li is tridentately coordinated to ligand; such an arrangement energetically precludes siting lithium normal to the allyl carbon plane. Instead, the system accommodates with lithium shifted toward the allyl plane with sideways coordination to the ligand. Structure **12** represents the limiting manifestation of this interaction with lithium in the allyl plane and ligand bisecting this plane. A more general representation is indicated in **23**, which shows the $\text{Me}_3\text{SiC}_1\text{Li}(\text{OMe})_2$ arrangement perpendicular to the allyl plane, the latter indicated by the dashed line.



Thus it would appear that the origin of the unusual partial delocalization and small C–Li covalence lies in the stereochemistry of coordination of lithium. Recalling that without solvation delocalization is minimized. With constraints to stereochemistry of solvation delocalization is just partial.

Compounds **12** and **14** display NMR line shape changes indicative of three different dynamic processes, C–Li bond exchange, inversion at lithium-bound carbon, and a 1,3 lithium sigmatropic shift.

Averaging of the ^{13}C – ^6Li coupling could result from fast nuclear spin relaxation and/or bimolecular C–Li exchange. The former is highly unlikely in the present cases since ^{13}C and ^6Li relaxation tends to be quite slow. We assume that the ^{13}C and ^6Li spin states do not change during a preexchange lifetime. In a mutual exchange of lithiums between two RLi species, the replacing lithium has a $1/3$ probability of having the same spin state as the original one, hence the origin of averaging of the coupling constant. Our results qualitatively confirm the second-order character of such a process, despite the small magnitude of the coupling being averaged. Were Li to dissociate out and return the coupling would not average to zero. If lithium rearranged to another site on the molecule one would observe a coupling being the weighted average of those in the two species. Further, there is no evidence that **12** or **14** exists in the form of more than one species each.

Phenomenologically, signal averaging observed among the ligand resonances in **12** must be ascribed to inversion at the lithium-bound carbon. The process is first order in **12**. While the available data do not provide definitive information in the mechanism, we propose the overall interconversion shown in Scheme 3. Finally, there is the slowest of the dynamic processes, the 1,3 lithium shift in **14**, discussed above.

Hitherto allylic lithium compounds have been reported to assume only two limiting structures—ion-paired solvated **3** and some substituted unsolvated covalent species (see **4**) with none taking the in-between arrangement **3**. We have now presented the first two examples **12** and **14** of compounds which take the missing link structures, with partial π delocalization and small detectable C–Li covalence, an effect ascribed to the unusual stereochemistry of solvation. Needless to say X-ray crystallographic studies will be needed to fully confirm these proposals. Finally, due to their unusual structures, compounds **12** and **14** exhibit three kinds of dynamic behavior—1,3 lithium sigmatropic shift, intermolecular C–Li bond exchange, and the inversion at the lithium-bound carbon, listed in order of increasing rates.

Experimental Section

Handling of Organolithium Compounds. Organolithium compounds are extremely sensitive to moisture and oxygen. The glassware used in the preparation or reaction of organolithium reagents was cleaned in a base bath, flamed before assembling, flame-dried under vacuum (1~0.1 Torr), and flushed with high-purity argon at least twice. Syringes were dried in an oven (120 °C) overnight and flushed immediately with high-purity argon three times before use. They were allowed to cool before use.

Preparation of NMR Samples. NMR sample tubes were connected to a 14/20 joint with a short section of hard glass, with an outside diameter of 5 mm. The tubes were dried in the oven (120 °C) overnight, and a stopcock adapter was attached to the tube immediately before use. The assembly was flame-dried under vacuum and flushed three times with high-purity argon, then closed with a syringe septum. Within the drybox the sample was syringed into the NMR tube, and the solvent was evaporated under vacuum (1~0.1 Torr) while cooling with a dry ice–acetone bath. When all of the solvent was removed, the tube was flushed with argon again and then transferred to a high-vacuum line (1~10 μm) trapped with liquid nitrogen. After pumping for 2~4 h, deuterated solvent, pre-dried with benzophenone ketyl sodium salt, was vacuum transferred into the NMR tube using a liquid nitrogen cooling bath. The resulting solution was degassed using the usual freeze, pump, and thaw cycle. While frozen with liquid nitrogen, the NMR sample tube was sealed off under vacuum (~10 μm) using a hot pinpoint flame at the hard glass part.

Halide-Free [^6Li]Methylolithium. A 250 mL Schlenk flask with an attached addition funnel and containing a glass stir bar was flame-dried under vacuum. The apparatus was transferred to a drybox while still hot. Lithium-6 was cut into small shavings (0.84 g, 0.14 gram atoms) in the drybox under an argon atmosphere and was transferred into the dry flask. The apparatus was then transferred into the hood and connected to a slightly positive pressure of argon. Freshly distilled dry diethyl ether (40 mL) was syringed into the flask. Into the addition funnel was introduced via syringe dimethylmercury (6.5 g, 0.028 mol) and diethyl ether (15 mL). With stirring, the dimethylmercury solution was added dropwise to the flask at room temperature over a period of 20 min. Stirring was maintained for 2 h after the addition. The mixture was refluxed for 30 min before allowing the resulting particles to settle overnight. The clear supernatant solution was transferred using a cannula into two separate centrifuge tubes previously flame-dried under vacuum and flushed with argon. After centrifugation, the clear solution was cannulated into a flame-dried Schlenk tube under argon for storage. The solution thus prepared was shown after filtration to have a concentration of ca. 1.0 M.

Titration of Organolithium Compounds. Organolithium reagents were titrated for both total base and the effective carbanion content. Total base was determined by adding a 1 mL sample of organolithium solution to a solution of methanol and water (3:1 v/v, 8–10 mL). The base was then titrated with a 0.100 M solution of benzoic acid in toluene with methylene blue as the indicator. A second titration was carried out by first reacting the organolithium sample with 1.1 equiv of dry allylbromide in THF (10 mL) for 30 min, assuming quantitative conversion of the organolithium compound during this period of time, followed by a similar titration. The amount of the effective carbanion content was determined by the difference between the results of the two titrations.

NMR Parameters. NMR spectroscopy was carried out on a Bruker MSL-300. Relevant parameters for ^{13}C and NMR proton are as follows:

parameters	^{13}C	^1H
frequency, MHz	75	300
transform, K	64	32
spectral width, Hz	15 151	3000
resolution Hz/point	0.46	0.46
acquisition time, s	2.18	2.18
transients	1600–9600	1600–9600

2-Methyl-3-[bis(2-methoxyethyl)amino]propene (9). Under an argon atmosphere, bis(2-methoxyethyl)amine (26.6 g, 200 mmol), potassium carbonate (27.6 g, 200 mmol), 2-methyl-3-chloropropene (20 g, 221 mmol), and anhydrous methanol (50 mL) were introduced into a 250 mL, flame-dried, round-bottomed flask equipped with a

magnetic stir bar and a reflux condenser. The mixture was refluxed for 24 h and monitored with thin layer chromatography. After being cooled to room temperature, the mixture was diluted with water (100 mL) and extracted with ether (50 mL \times 3). The combined organic layers were washed with saturated aqueous sodium chloride solution and dried over magnesium sulfate. After gravity filtration, the solvent was removed by rotary evaporation and the residue was fractionated on a 12-in. Vigreux column to give 28.1 g of the title compound as a clear colorless liquid, bp 64 °C (2 Torr) in 84% yield based on recovered bis(2-methoxyethyl)amine. ^1H NMR (CDCl_3 , $\delta = 7.26$ ppm): 4.81 (s, br, 1 H), 4.74 (s, br, 1 H), 3.38 (t, $J = 6.3$ Hz, 4 H), 3.26 (s, 6 H), 2.97 (s, 2 H), 2.60 (t, $J = 6.3$ Hz, 4 H), 1.66 (d, $J = \text{Hz}$, 3 H). ^{13}C NMR (CDCl_3 , $\delta = 77.00$ ppm): 143.80, 112.28, 71.10, 62.29, 58.52, 53.55, 20.44.

2-[[Bis(2-methoxyethyl)amino]methyl]-3-(trimethylsilyl)propene (11). A 100 mL, three-necked round-bottomed flask equipped with a magnetic stir bar, an argon inlet tube, a stopcock stopper, and the third neck with a glass stopper was flame-dried under vacuum and, after cooling to room temperature, was flushed twice with prepurified argon. Into the flask was introduced 2-[[bis(2-methoxyethyl)amino]methyl]propene (3.0 g, 16 mmol) and dry THF (30 mL) freshly distilled from sodium-benzophenone ketyl under argon. The mixture was cooled with an ice-water bath, and butyllithium (1.7 M, 10 mL, 1.7 mmol) was added dropwise via syringe. After 30 min at this temperature, the mixture was chilled with a dry ice-acetone bath to bring the internal temperature to about -78 °C. Chlorotrimethylsilane (2.0 g, 19 mmol) was added dropwise via syringe at such a rate that the internal temperature never exceeded -65 °C. After the addition, the mixture was warmed to ca. 0 °C over 1 h and cooled again with dry ice-acetone bath for 5 min before it was quenched with saturated sodium bicarbonate solution (10 mL). The resulting mixture was warmed to room temperature and then transferred to a round-bottomed flask to remove the THF. The residue was diluted with ether (50 mL) and washed with saturated sodium bicarbonate solution (20 mL). After being dried over magnesium sulfate, the solvent was removed on a rotary evaporator and the residue distilled under vacuum to afford 3.8 g of the desired title compound in 91% yield, bp 67–69 °C (1 Torr).

^1H NMR (CDCl_3 , $\delta = 7.26$ ppm): 4.79 (s, br, 1 H), 4.59 (s, br, 1 H), 3.42 (t, $J = 6.3$ Hz, 4 H), 3.33 (s, 6 H), 2.94 (s, 2 H), 2.66 (t, $J = 6.3$ Hz, 4 H), 1.56 (s, 2 H), 0.00 (s, 9 H). ^{13}C NMR (CDCl_3 , $\delta = 77.00$ ppm): 145.27, 109.56, 71.25, 62.67, 58.65, 53.75, 23.70, -1.36 . M^+/e : calcd for $\text{C}_{13}\text{H}_{29}\text{NO}_2\text{Si}$, 259.196 791 6; obsd, 259.196 792 6. Base peak: $\text{M}^+ - \text{C}_2\text{H}_5\text{O}$, 214.162 338 3.

2-[[Bis(2-methoxyethyl)amino]methyl]-1,3-bis(trimethylsilyl)propene (13). A 250 mL, three-necked, round-bottomed flask was equipped with a magnetic stir bar, an argon inlet tube, a stopcock stopper, and the third neck with a glass stopper. The flask was flame-dried under vacuum and, after cooling to room temperature, was flushed twice with prepurified argon. Into the flask was introduced 2-[[bis(2-methoxyethyl)amino]methyl]-3-(trimethylsilyl)propene (8.33 g, 32.1 mmol) and dry THF (80 mL) freshly distilled from sodium-benzophenone ketyl under argon. The mixture was cooled with an ice-water bath, and methyllithium (25 mL, 1.4 M, 35 mmol) was added dropwise via syringe. After 30 min, the mixture was chilled with a dry ice-acetone bath to bring the internal temperature to about -78 °C and then chlorotrimethylsilane (4.0 g, 38 mmol) was added dropwise via syringe at such a rate that the internal temperature never exceeded -65 °C. After the addition the mixture was warmed to ca. 0 °C in a period of 1 h and cooled again with the dry ice-acetone bath for 5 min before it was quenched with saturated sodium bicarbonate solution (15 mL). The resulting mixture was warmed to room temperature and then transferred to a round-bottomed flask to remove the THF. The residue was diluted with ether (100 mL) and washed with saturated sodium bicarbonate solution (40 mL). After drying over magnesium sulfate, the solvent was removed by rotary evaporation and the residue distilled under vacuum to afford 9.5 g of the desired title compound in

89% yield, bp 90 °C (1 Torr). ^1H NMR (CDCl_3 , $\delta = 7.26$ ppm): 5.28 and 5.08 (s, br, 1 H), 3.42 (t, $J = \text{H}_2$, 4H), 3.20 (s, 6H), 2.97 (s, 2H), 2.66 (t, $J = \text{H}_2$, 4H), 1.75 (s, 2H), 0.07 (s, 9H), 0.02 (s, 9H). ^{13}C NMR 154.50, 121.34, 71.23, 66.12, 58.68, 53.96, 24.90, 0.45, -0.54 . M^+/e : calcd for $\text{C}_{16}\text{H}_{37}\text{NO}_2\text{Si}_2$, 331.236 342 4; obsd, 331.236 343 4. Base peak: $\text{C}_3\text{H}_9\text{Si}^+$, 73.047 546 4.

[2-[[Bis(2-methoxyethyl)amino]methyl]-1-(trimethylsilyl)allyl]lithium (12). A 50 mL, flame-dried, three-necked, round-bottomed flask equipped with a glass-coated magnetic stir bar and a thermometer was flushed with argon. Freshly distilled dry THF (10 mL) and 3-(trimethylsilyl)-2-[[bis(2-methoxyethyl)amino]methyl]propene (0.468 g, 1.81 mmol) were introduced into the flask. After the solution was chilled to 0 °C with an ice-acetone bath under argon, a solution of methyllithium in diethyl ether (1.4 M, 1.30 mL, 1.82 mmol) was added slowly via syringe. The reaction mixture was maintained at this temperature for 0.5 h.

An NMR tube with a ground joint connected to an adapter with a glass stopper was flame-dried under vacuum and flushed with argon. An aliquot of 2 mL of the above prepared solution was syringed into the NMR tube. The solvent was removed under vacuum, and the NMR tube was flushed with argon before it was transferred to a high-vacuum line (10^{-6} Torr) trapped with liquid nitrogen to remove all volatile impurities. After about 3 h, THF- d_8 (0.8–1.0 mL) was vacuum transferred to the NMR tube. The contents were frozen with liquid nitrogen. Then the NMR tube was sealed off with pumping. The sample thus prepared had a concentration of 0.3 M and was stored in dry ice before the low-temperature NMR studies.

Another sample was also prepared using diethyl ether- d_{10} as solvent. This sample had a concentration of 0.34 M and was stored in the freezer prior to the NMR studies. ^1H NMR (THF- d_8 , $\delta = 1.73$ ppm): 3.60 (t, $J = 6.3$ Hz, 4 H), 3.35 (s, 6 H), 3.27 (s, 1 H), 2.98 (s, 1 H), 2.78 (s, 2 H), 2.71 (t, $J = 6.3$ Hz, 4 H), 0.63 (d, $J = 0.7$ Hz, 1 H), -0.05 (s, 9 H). ^{13}C NMR (THF- d_8 , $\delta = 25.30$ ppm): 157.70, 76.33, 70.83, 69.19, 58.39, 56.92, 41.52, 1.98.

[2-[[Bis(2-methoxyethyl)amino]methyl]-1,3-bis(trimethylsilyl)allyl]lithium (14). A 50 mL, flame-dried, three-necked, round-bottomed flask equipped with a glass-coated magnetic stir bar and a thermometer was flushed with argon. Freshly distilled dry THF (15 mL) and 1,3-bis(trimethylsilyl)-2-[[bis(2-methoxyethyl)amino]methyl]propene (0.423 g, 1.28 mmol) were introduced into the flask. The solution was chilled to 0 °C with an ice-acetone bath under argon. Methyllithium in diethyl ether (1.4 M, 0.91 mL, 1.28 mmol) was added via syringe. The reaction mixture was maintained at 0 °C for 0.5 h.

An NMR tube with a ground joint connected to an adapter with a glass stopper was flame-dried under vacuum and flushed with argon. An aliquot of 3 mL of the above prepared solution was syringed into the NMR tube. The solvent was removed under vacuum, and the NMR tube was flushed with argon before it was transferred to a high-vacuum line (10^{-6} Torr) trapped with liquid nitrogen to remove all volatile impurities. After about 3 h, THF- d_8 (0.8 to 1.0 mL) was vacuum transferred into the NMR tube. While frozen with liquid nitrogen and under high vacuum, the NMR tube was sealed with a torch. The sample thus prepared has a concentration of 0.23 M and was stored in dry ice until needed for NMR studies. ^1H NMR (THF- d_8 , $\delta = 1.73$ ppm): 3.62 (t, $J = 5\text{H}_2$, 4H), 3.36 (s, 6H), 3.02 (s, 2H), 2.74 (t, $J = 5\text{H}_2$, 4H), -0.04 (s, 9H). ^{13}C NMR (THF- d_8 , $\delta = 25.300$ ppm): 168.97, 71.05, 66.21, 58.58, 57.46, 3.0 (br).

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