

# Perturbation of Conjugation in Internally Solvated Allylic Lithium Compounds: Variation of Ligand Structure. NMR and X-ray Crystallography

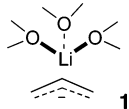
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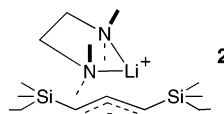
**Abstract:** Several allylic lithium compounds were prepared with different potential ligands tethered at C<sub>2</sub>. These are with CH<sub>3</sub>OCH<sub>2</sub>CH<sub>2</sub>NCH<sub>3</sub>CH<sub>2</sub>-, **5** and 1-TMS **6**, with (CH<sub>3</sub>)<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>NCH<sub>3</sub>CH<sub>2</sub>-, 1-TMS **7**, and with ((CH<sub>3</sub>)<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>NCH<sub>2</sub>-, **8** and 1-TMS **9**. In all these compounds Li is fully coordinated to the pendant ligand and is sited off the axis perpendicular to the allyl plane at one of the allyl termini as indicated by a combination of X-ray crystallography and NMR spectra. Compounds **5** and **8** are Li-bridged dimers as shown by X-ray crystallography and also dimeric in benzene solution as determined from freezing point determinations. Compounds **6**, **7**, and **9** are monomeric in THF-*d*<sub>8</sub> or diethyl ether-*d*<sub>10</sub> solution and exhibit one bond <sup>13</sup>C,<sup>6</sup>Li scalar coupling at low temperature. Taken together the crystallographic and NMR data indicate that all of these compounds incorporate partially delocalized allylic moieties. Compounds **5** and **8** undergo fast 1,3-Li-sigmatropic shifts that are proposed to take place within low concentrations of monomers in fast equilibrium with prevalent dimers. Averaging with increasing temperature of the one-bond <sup>13</sup>C,<sup>6</sup>Li coupling constant in **6**, **7**, and **13** provided the dynamics of bimolecular C–Li exchange with Δ*H*<sup>‡</sup> values of 6.7, 12, and 13 kcal·mol<sup>–1</sup>, respectively. Averaging of the diastereotopic N(CH<sub>3</sub>)<sub>2</sub> <sup>13</sup>C resonances of **7** is indicative of fast transfer of coordinated ligand between faces of the allyl plane Δ*H*<sup>‡</sup> = 5.3 kcal·mol<sup>–1</sup> combined with slower inversion at nitrogen. Compound **8** exhibits similar effects. It is concluded that variation of the ligand structure changes dynamic behavior of the compounds but has little influence of their degrees of delocalization.

Extensive chemical,<sup>1</sup> X-ray crystallographic,<sup>2</sup> NMR,<sup>3</sup> and calculational studies<sup>4</sup> establish the delocalized character of solvated allyllithium and how coordinated lithium is sited normal to the center of the allyl plane, **1**.



Barriers to rotation have been determined around the C<sub>1</sub>–C<sub>2</sub> bond of different allylic lithium compounds by use of NMR

line shape analysis.<sup>5</sup> In related studies on ion-pairing we reported how <sup>13</sup>C NMR at 150 K revealed the unsymmetrical character of **2**. With increasing temperature above 150 K, NMR line shape

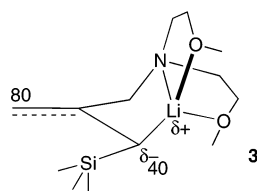


analysis of signal averaging effects in the <sup>13</sup>C NMR of **2** distinguished the dynamics of two different first-order reorganization processes. These are rotation of coordinated ligand on one side of the allyl plane and transfer of coordinated ligand between faces of the allyl plane.<sup>6</sup>

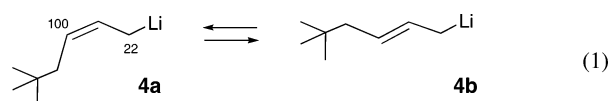
In experiments to slow these molecular reorganization processes to facilitate structure determination of ion-pairs using

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different NOE-based procedures we prepared several internally solvated allylic lithium compounds;<sup>7</sup> see, for example, **3** shown with <sup>13</sup>C shifts. As revealed by our NMR and X-ray crystal-



lographic<sup>7,8</sup> studies these structures do not incorporate the expected delocalized allylic anion; rather, the anion is partly localized as shown in **3**.<sup>8</sup> The terminal <sup>13</sup>C NMR shifts of **3** lie between those of a typical externally solvated delocalized allylic lithium compound at 55  $\delta$ , **1** and values reported for an unsolvated localized system, see the cis/trans equilibrium **4a** with **4b** in eq 1, shown with terminal allyl <sup>13</sup>C shifts of ca. 22



$\delta$  and 100  $\delta$ .<sup>9</sup> We proposed that the ligand tethers in the internally solvated compounds such as **3** are too short to place coordinated Li<sup>+</sup> normal to the center of the allyl plane as in **1** but instead places it off normal to the allyl plane at one of the allyl termini.<sup>7,8</sup> As a result, the Li<sup>+</sup> polarizes the allyl moiety to become partly localized. Thus, it appears that the site of Li<sup>+</sup> relative to allyl determines the degree of delocalization of the allyl carbanionic moiety.

In principle the degree of allylic delocalization should be influenced by the length of the ligand tether, the nature of substitution on the allyl unit, and the structure of the tethered ligand. Thus far in our studies of internal solvation effects we have mainly used the bis(2-methoxyethyl)amino ligand.<sup>7,8</sup> This article is addressed to the effect of changing the structure of the pendant ligand.

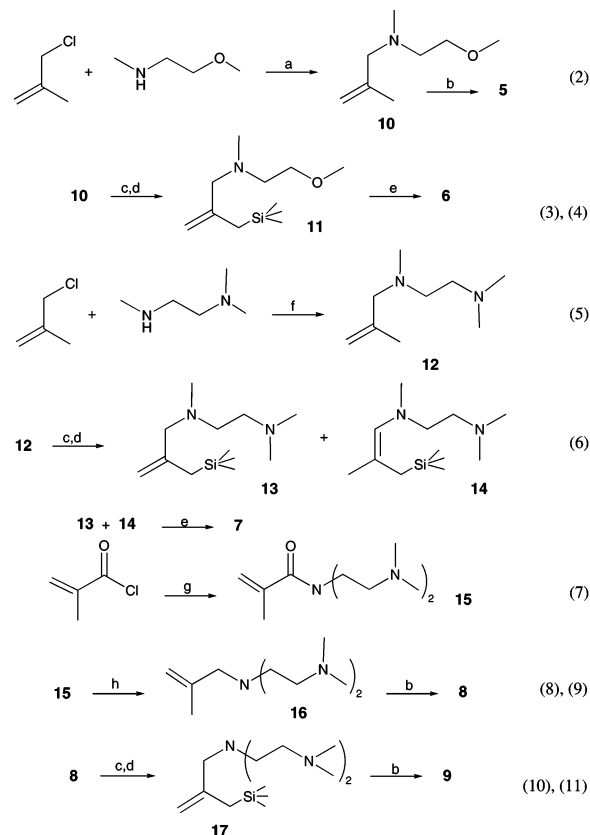
## Results and Discussion

For the convenience of readers, Table 1 lists the structures of the internally solvated organolithium compounds **5**, **6**, **7**, **8**, and **9**, which are reported in this article, together with their <sup>1</sup>H and <sup>13</sup>C chemical shifts. Preparation of these compounds is summarized in reactions 2–11 (see Scheme 1). In common, compounds **5**, **6**, **7**, **8**, and **9** were prepared by metalating, respectively, compounds, **10**, **11**, **13**, **16**, and **17** with *n*-butyllithium in a mixture of hydrocarbon with diethyl ether or THF. Note that treatment of the mixture of **13** and **14** with *n*-butyllithium yielded only **7**. Compound **14** remained unchanged.

**Table 1.** Structures of Internally Solvated Allylic Lithium Compounds Shown with <sup>13</sup>C and (Proton) Chemical Shifts,  $\delta$  Scale

Compound	<sup>13</sup> C Chemical Shifts (ppm)	(Proton) Chemical Shifts (ppm)
<b>5</b>	81.35, 38.70, 56.37 (2.450), 70.01 (3.467), 58.40, (3.330)	(2.140) 43.25, (2.5774) 58.803, 157.61
<b>6</b>	79.73, 156.00, 40.29 (0.536), 58.69 (3.425), 72.94, (3.684)	(2.340) 45.56, (2.7801) 71.331, (2.660) 57.45
<b>7</b>	77.20, 154.8, 39.28 (0.465), 44.161, 43.935 (2.2396), 56.815, 52.390	(2.2687) 43.394, 72.136, 56.815
<b>8</b>	58.125 (2.5885), 56.241 (2.0770), 157.305, 56.831, 66.831, (2.6959) 68.831	(2.3915) 52.014, (2.6959) 66.831, (2.407) 50.44
<b>9</b>	0.013 (0.0691), 40.80 (0.618), 74.918 (2.9671), 3.2795, 155.20, 43.87 (2.2885)	(2.6221) 54.943, (2.407) 50.44, (2.6959) 68.831

**Scheme 1**




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<sup>a</sup> K<sub>2</sub>CO<sub>3</sub>, CH<sub>3</sub>OH, reflux; <sup>b</sup> *n*-Bu<sup>+</sup>Li, hexanes, Et<sub>2</sub>O, -78 °C; <sup>c</sup> *n*-BuLi, THF, hexanes, 0 °C;

<sup>d</sup> TMSCl; <sup>e</sup> *n*-Bu<sup>+</sup>Li, pentane, THF, 0 °C; <sup>f</sup> Et<sub>3</sub>N; <sup>g</sup> NH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>Cl; <sup>h</sup> LiAlH<sub>4</sub>, Et<sub>2</sub>O, reflux

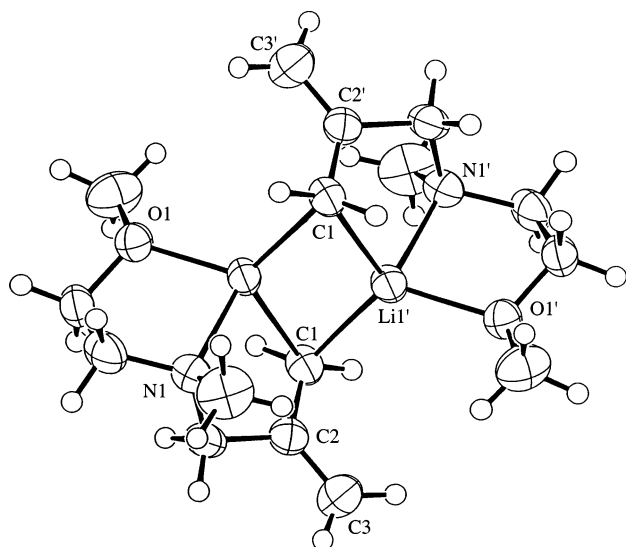
**Dimeric Internally Solvated Allylic Lithium Compounds.** Compound **5**, formed by metalation of **10** with *n*-butyllithium

**Table 2.** Internally Solvated Allylic Lithium Compounds, Solid: Allylic Bond Lengths Å, and Aggregation, Agg. Solution:  $^{13}\text{C}$  Allyl Shifts  $\delta$ , Agg. and  $^1J$  ( $^{13}\text{C}$ ,  $^6\text{Li}$  or  $^{13}\text{C}$ ,  $^7\text{Li}$ ); Numbering


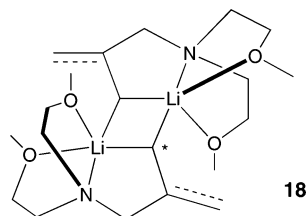
cmpd	solid			soln				ref
	C1–C2 Å	C2–C3 Å	agg.	C1 $\delta$	C3 $\delta$	agg.	$^1J(^{13}\text{C}, \text{Li})$ Hz	
<b>3</b>	1.397 (4)	1.361 (4)	poly.	41.10	76.30	mon	3.0 $^6\text{Li}$	<i>a</i>
<b>5</b>	1.442 (2)	1.347 (2)	dim	38.70	81.36	dim	<sup>c</sup>	<i>d</i>
<b>6<sup>b</sup></b>	—	—	?	40.29	74.73	mon	4.05 $^6\text{Li}$	<i>d</i>
<b>7<sup>b</sup></b>	—	—	?	39.28	77.20	mon	3.7 $^6\text{Li}$	<i>d</i>
<b>8</b>	1.4355 (12)	1.3585 (12)	dim	52.24 <sup>c</sup>	52.24 <sup>c</sup>	dim	<sup>c</sup>	<i>d</i>
<b>9<sup>b</sup></b>	—	—	?	41.80	74.92	mon	3.5 $^6\text{Li}$	<i>d</i>
<b>18</b>	1.436 (4)	1.349 (1)	dim	58.55 <sup>c</sup>	58.55 <sup>c</sup>	dim	<sup>c</sup>	<i>a</i>
<b>21</b>	1.415 (7)	1.351 (8)	mon	42.81	72.95	mon	7.0 $^6\text{Li}$	<i>a</i>
<b>22</b>	1.431 (3)	1.351 (3)	mon	54.12	78.10	mon	6.1 $^7\text{Li}$	<i>a</i>
<b>23</b>	1.426 (2)	1.366 (2)	mon	51.62 <sup>c</sup>	51.62 <sup>c</sup>	mon	<sup>c</sup>	<i>a</i>

<sup>a</sup> Reference 8. <sup>b</sup> Did not crystallize. <sup>c</sup> Averaged. <sup>d</sup> This work.

was crystallized from diethyl ether. X-ray crystallography reveals **5** to be an internally solvated lithium-bridged dimer. The ORTEP diagram is shown in Figure 1. Selected structural parameters are listed in Table 2.

**Figure 1.** ORTEP diagram of compound **5** showing 50% ellipsoids, and selected atoms have been labeled. The hydrogen atoms have been drawn with an artificial radius.

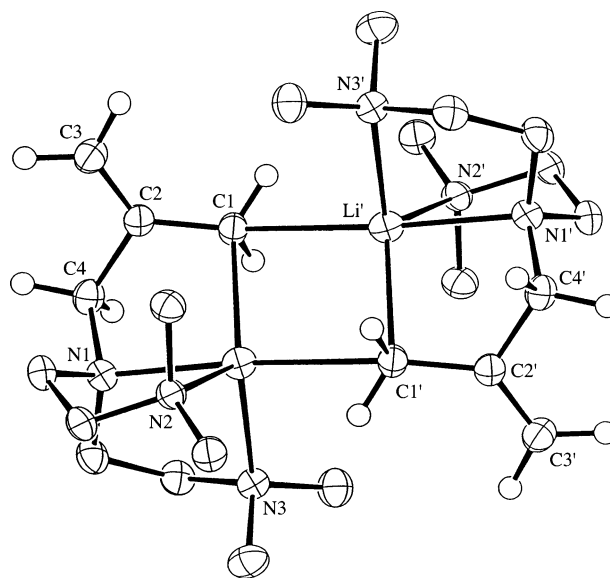
The structure of **5** has features in common with that of **18** that was reported previously.<sup>8</sup> The allyl carbon–carbon bond lengths of both compounds lie between those of the reference-limiting localized **4a** and **4b** and delocalized **1** allylic lithium compounds, respectively.



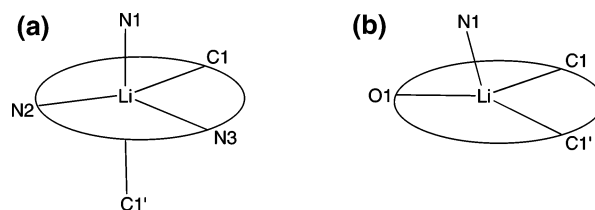
The dimeric state of **5** also prevails in benzene solution as determined by a freezing point determination. In principle, dimer **5** should consist of a mixture of meso and DL forms. This is not detected among the NMR data most likely due to a fast

1,3-lithium sigmatropic shift that accompanies a rapid dimer–monomer interconversion with the latter in low concentration.

Compound **8** is also a dimer according to X-ray crystallography, see Figure 2, in fashion similar to **5** and **18** and with allyl bond lengths similar to those of the latter two, Table 2. Clearly all three compounds display similar degrees of localization associated with their allylic moieties.

**Figure 2.** ORTEP diagram of compound **8** showing 50% ellipsoids, and selected atoms have been labeled. The hydrogen atoms that are included have been drawn with an artificial radius.

The arrangement around lithium in **8** is best described as a distorted trigonal bipyramid within which lithium is closely centered in the plane of C1, N2, and N3 and nearly collinear with the span N1...C1', see Figure 3 and Table 3. By contrast in **5**, within the distorted tetrahedron N1, O1, C1, and C1'

**Figure 3.** Stereochemistry of lithium in (a) **8** and (b) **5**.

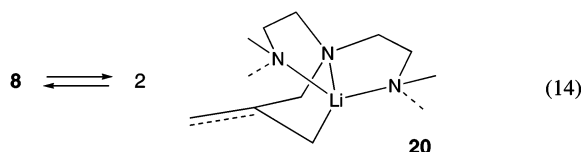
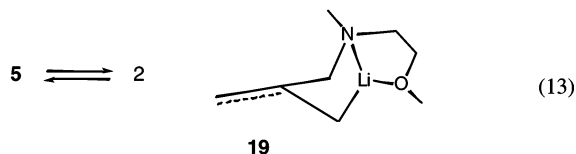
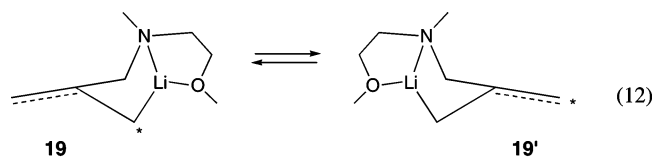
**Table 3.** Stereochemistry of Lithium in Compounds **5** and **8** (for Numbering See Figures 1 and 2)

C1	Li1	C1'	113.87 (8)	C1	Li1	C1'	102.83 (7)
C1	Li1	N1	87.55 (7)	C1	Li1	N1	83.90 (6)
C1'	Li1	N1	123.81 (9)	C1	Li1	N2	123.99 (8)
C1	Li1	O1	119.07 (9)	C1	Li1	N3	117.60 (7)
C1'	Li1	O1	120.05 (9)	C1'	Li1	N1	171.60 (8)
N1	Li1	O1	85.14 (7)	C1'	Li1	N2	91.80 (6)
				C1'	Li1	N3	100.59 (6)
				N1	Li1	N2	80.18 (6)
				N1	Li1	N3	80.33 (6)
				N2	Li1	N3	111.98 (8)

lithium is near coplanar with O1, C1, and C1', see Figure 3b and Table 3.

Carbon-13 NMR of **5** in THF does not exhibit one-bond  $^{13}\text{C},^6\text{Li}$  spin coupling. The allyl termini give rise to a single, sharp  $^{13}\text{C}$  resonance at room temperature. This line progressively broadens with decreasing temperature and resolves into two broad lines at 38.78  $\delta$  (C1) and 81.36  $\delta$  (C3) by 140 K, Figure 4. These values are similar to those for terminal allyl shifts in other internally solvated allylic lithium compounds reported previously.<sup>7,8</sup>

NMR line shape analysis of the terminal allyl  $^{13}\text{C}$  resonance of **5** gives rates for a dynamic process with  $\Delta H^\ddagger = 4.8 \pm 0.5$  kcal·mol<sup>-1</sup> and  $\Delta S^\ddagger = -10 \pm 2$  eu, Table 4. We propose that these results are most consistent with a fast 1,3-lithium sigmatropic shift (eq 12) which takes place within a low undetectable concentration of monomer, with the latter in fast equilibrium with dimer **5** (eq 13). Then fast recombination of monomers from different dimers would be responsible for averaging out the  $^{13}\text{C},^6\text{Li}$  coupling constant.



The NMR behavior of **8** parallels that of **5**. Compound **8** does not exhibit  $^{13}\text{C},^6\text{Li}$  spin coupling down to 140 K. The terminal allyl  $^{13}\text{C}$  NMR which is a single sharp line at room temperature, broadens with decreasing temperature and disappears into the baseline by 150 K and is not detected down to 140 K. Below this temperature compound **8** precipitates from solution. A fast interconversion of dimer **8** with monomer **20**, in low concentration concurrent with a fast 1,3-lithium sigmatropic shift in monomer would be consistent with the above behavior.

Two other temperature-dependent changes of the  $^{13}\text{C}$  NMR line shapes of **8** provide qualitative insight into the nature of dynamic effects. At 130 K the  $\text{N}(\text{CH}_3)_2$   $^{13}\text{C}$  resonance consists

of a broad doublet, separation 5.8 ppm (400 Hz at 75.47 MHz) centered at 56  $\delta$ . With increasing temperature above 130 K the latter doublet progressively averages to a single line by 180 K. In similar fashion, the doublet, centered at 52  $\delta$ , due to the N  $(\text{CH}_2\text{CH}_2\text{N}(\text{CH}_3)_2)_2$   $^{13}\text{C}$  resonance, separation 1.060 ppm (81 Hz at 75.47 MHz), averages to a single line by 160 K. The latter effect is most likely due to transfer of the coordinated ligand between faces of the allyl plane within monomer **20**. By contrast, two processes are most likely responsible for changes of the  $\text{N}(\text{CH}_3)_2$  resonance. These would be face transfer, described above, combined with fast reversible N–Li dissociation/recombination. During the dissociated phase, fast inversion at nitrogen accompanied by rotation around the  $(\text{CH}_3)_2\text{N}-\text{CH}_2$  bond would average the shift between the geminal *N*-methyls.

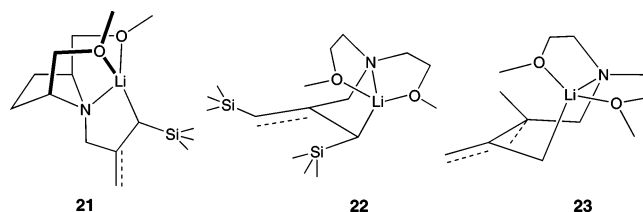
**Monomeric Internally Solvated Allylic Lithium Compounds.** Compounds **6**, **7**, and **9** are monomers as indicated by the equal triplet multiplicity of the  $^{13}\text{C}$  resonance due to one-bond  $^{13}\text{C},^6\text{Li}$  scalar coupling. The NMR data are consistent with coordination of lithium to the pendant ligand. Terminal allyl  $^{13}\text{C}$  shifts which lie between those for reference delocalized **1** and localized, **4a**  $\rightleftharpoons$  **4b**, allylic lithiums respectively, show **6**, **7**, and **9** to be partially localized, see Table 2.

Monomers **6**, **7**, and **9** also display evidence of the dynamics of interesting fast equilibrium reorganization behavior. The  $^{13}\text{C},^6\text{Li}$  coupling constants of all three compounds average with increasing temperature as a result of bimolecular C,Li exchange. Line shape analysis provides the associated activation parameters listed in Table 3.

Averaging of the shift between the  $\text{N}(\text{CH}_3)_2$  methyls of **7** with increasing temperature is indicative of a fast face transfer of coordinated lithium combined with some contribution from inversion at dimethylamino nitrogen. The activation parameters of  $\Delta H^\ddagger = 5.3 \pm 0.4$  kcal·mol<sup>-1</sup> and  $\Delta S^\ddagger = -19 \pm 5$  eu are very similar to values obtained for related internally solvated allylic lithium compounds undergoing the face transfer reorganization process alone.<sup>7,8</sup> As noted above, similar effects were ascribed as responsible for averaging of the diastereotopic  $^{13}\text{C}$  shift between the geminal  $\text{N}(\text{CH}_3)_2$  methyls of **8**. Previous results indicate that the nitrogen inversion process for both **8** and **7** would be significantly slower than that of face transfer of coordinated lithium.

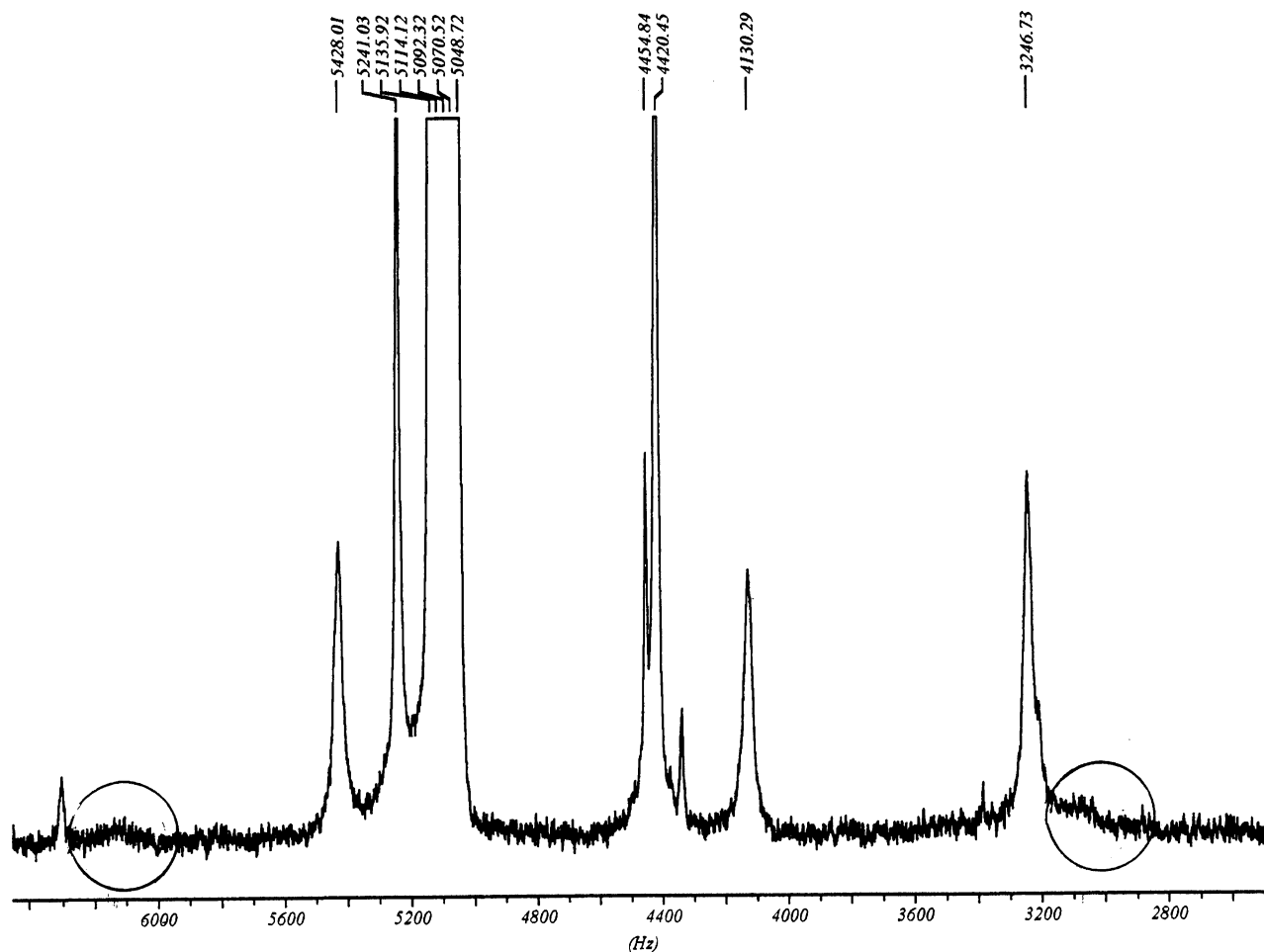
## General Remarks

The X-ray crystallographic allylic carbon–carbon bond distances of **5** and **8** are so similar to those reported previously for **18**, **21**, **22**, and **23** that one can conclude that the allylic moieties in all the above compounds are partially localized to the same extent.<sup>8</sup> This conclusion is supported by close similarities among the terminal allyl  $^{13}\text{C}$  shifts of **6**, **7**, and **9** to those, respectively, of **3**, **18**, **21**, and **22**, see Table 2. As yet



unavailable among these data are the bond distances for **6**, **7**, and **9** and the terminal allyl  $^{13}\text{C}$  shifts of **8** and **23**. The latter





**Figure 4.**  $^{13}\text{C}$  NMR compound **5**,  $\text{THF-}d_8$  solution, 140 K. Resonances for terminal allyl carbons are circled.

**Table 4.** Dynamic Behavior Internally Solvated Allylic Lithium Compounds  $\Delta H^\ddagger$  kcal·mol $^{-1}$  ( $\Delta S^\ddagger$  eu)

	$^{13}\text{C-Li}$ exchange	1,3-Li sigmatropic shift	$\text{N}(\text{CH}_3)_2$ inversion
resonance used	$^{13}\text{C}_1$	$\text{C}_1, \text{C}_3$	$\text{N}(^{13}\text{CH}_3)_2$
<b>5<sup>a</sup></b>	—	$4.8 \pm 0.5$ ( $-10 \pm 2$ )	
<b>6<sup>b</sup></b>	$6.7 \pm 0.5$ ( $-2.6$ )		
<b>7<sup>a</sup></b>	$12 \pm 0.8$ ( $-15 \pm 4$ )		$5.3 \pm 0.4$ ( $-19 \pm 5$ )
<b>9<sup>a</sup></b>	$13 \pm 0.8$ ( $-14.6 \pm 4$ )		

<sup>a</sup> THF- $d_8$ . <sup>b</sup> Diethyl ether- $d_{10}$ .

shifts remain averaged, even at low temperature due to fast 1,3-lithium sigmatropic shifts. Also note that the allylic carbon-carbon bond lengths of **3** are similar because **3** is a polymer in the solid state via a fifth coordination of Li to the terminal allyl  $\text{CH}_2$  carbon of a neighbor **3** unit.<sup>8</sup>

However, the totality of the data reflect a common partial degree of localization for all the compounds in Table 1 and most reported previously<sup>7,8</sup> which prevails despite variations in degrees of aggregation, substitution, lengths of the ligand tethers, and structures of the ligands themselves.

Within the context of results from previous studies of internally coordinated organolithium compounds<sup>11</sup> only the allylic lithium compounds display partial localization of the carbanionic entity. The degrees of partial localization are similar

for systems with ligand tethers of one to three carbons and changes in the structure of the pendant ligand as presented herein and previously.<sup>7,8</sup>

While the compounds in Table 1 have common structural features, they are differentiated by their dynamic behavior. For example in cases where  $^{13}\text{C}_6\text{Li}$  or  $^{13}\text{C}_7\text{Li}$  spin coupling has been observed, it is always averaged with increasing temperature due to fast intermolecular C,Li bond exchange. The corresponding  $\Delta H^\ddagger$  values for **7** and **9** of  $12.5 \pm 0.5$  kcal·mol $^{-1}$  are close to all such values obtained in previous studies of several internally solvated allylic lithium compounds.<sup>7,8</sup> It was suggested that the slow step for C,Li exchange involved complete decoordination of Li to the pendant ligand. The smaller  $\Delta H^\ddagger$  for C-Li exchange between monomers of **6** is similar to  $\Delta H^\ddagger$  values for face transfer of coordinated lithium. Most likely in the case of **6** both processes are due to a common mechanism. By contrast to the dynamics of C-Li exchange the dynamics of the 1,3-Li sigmatropic shift takes place at widely different rates. This process has only been detected in the case of symmetrical

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internally solvated allylic lithium compounds which are either 1,3-unsubstituted or 1,3-di-substituted. Thus at 240 K the first-order rate constant in  $\text{s}^{-1}$  for **5**, **18**<sup>8</sup> (unsubstituted), and **22**<sup>8</sup> ((1,2-bis(TMS))) are, respectively,  $1.45 \times 10^6$ ,  $8.8 \times 10^6$ , and 1.0. This effect is most likely the result of steric interactions.

### Experimental Section

**2-[(*N*-(2-Methoxyethyl)-*N*-methyl)aminomethyl]allyllithium **5**.** Under an atmosphere of argon 2-[(*N*-(2-methoxyethyl)-*N*-methyl)aminomethyl]-1-propene (**10**) (0.156 g, 1.1 mmol) in 4 mL of diethyl ether was syringed into a Schlenk tube. After cooling to  $-78^\circ\text{C}$  *n*-butyllithium (1.26 mL, 0.8 M, 1 mmol) was carefully added by syringe, and the mixture was stirred for 3 h. Solvent was removed under vacuum. The residue was crystallized in 5 mL of diethyl ether. Crystals were washed with cold pentane ( $3 \times 3$  mL) and vacuum dried. For NMR studies a solution was prepared of 30 mg of the title compound in 0.5 mL of  $\text{THF-}d_8$ .

**Freezing Point Depression of **5** in Benzene.** Compound **5** (250 mg) was dissolved in 8.8 g of benzene. This solution gave a freezing

point depression of  $0.42^\circ\text{C}$ . The expected depression value for dimer is  $0.46^\circ\text{C}$ . Hence, **5** is best described as a dimer.

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**Note Added after ASAP Publication.** After this paper was published ASAP on June 6, 2006, the captions of Figures 1 and 2 were modified to better explain the drawings. The corrected version was published on June 8, 2006.

**Supporting Information Available:** Synthetic procedures, NMR spectra, Eyring plots, and crystallographic data (CIF format). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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