

# NMR Studies of Structure and Reorganization Dynamics of an $^6\text{Li}$ -Allylic Lithium Compound Complexed to $^{14}\text{N}$ , $^{15}\text{N}$ - $N,N,N',N'$ -Tetramethylethylenediamine: Inversion and Ligand Lithium Exchange

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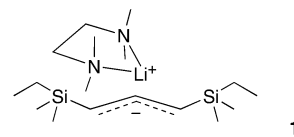
**Abstract:** Proton,  $^{13}\text{C}$ ,  $^6\text{Li}$ , and  $^{15}\text{N}$  NMR line-shape studies of *exo,exo*-1-trimethylsilyl-3-(dimethylethylsilyl)-allyllithium- $^6\text{Li}$  complexed to  $^{14}\text{N}$ ,  $^{15}\text{N}$ - $N,N,N',N'$ -tetramethylethylenediamine (TMEDA) **2** as a function of temperature and of added diamine reveal the dynamics of three fast equilibrium reorganization processes. These are (with  $\Delta H^\ddagger$  values in kilocalories per mole and  $\Delta S^\ddagger$  values in entropic units): mutual exchange of lithium between two **2** molecules (6.3,  $-21$ ), exchange of TMEDA between its free and complexed states (5.0 and  $-22$ ), and first-order transfer of complexed ligand between the allyl faces (7.0 and  $-20$ ). Intermediates that are dimeric in TMEDA are proposed for the first two of these reorganization processes.

## Introduction

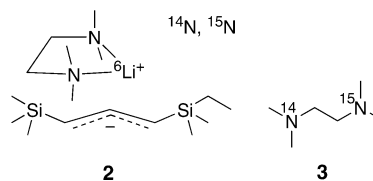
Salts in nonpolar media assemble into a variety of ion-paired species, which differ in their degrees of aggregation and solvation.<sup>1</sup> Hitherto, structure of ion pairs has been a neglected subject, let alone the dynamics of their reorganization processes. However, within the last 10 years some structures of ion pairs have been identified by use of different NMR techniques.<sup>2–4</sup>

Recently by means of dynamic NMR we have shown that ion-paired salts reorganize rapidly at equilibrium via a variety of mechanisms.<sup>5</sup> For example,  $^{13}\text{C}$  NMR studies of **1** resolved the dynamics of transfer of coordinated  $N,N,N',N'$ -tetramethylethylenediamine (TMEDA) between faces of the allyl plane, rotation of coordinated TMEDA on one face of the allyl plane, and fast reversible first-order Li–N dissociation accompanied by inversion at nitrogen and rotation around the  $(\text{CH}_3)_2\text{N}-\text{CH}_2$

bond.<sup>5g</sup> In principle, ion pairs such as **1** could also reorganize via intermolecular processes such as N–Li exchange. In this



article we report the results of the first investigation of such a process, the bimolecular N–Li exchange of the TMEDA-complexed organolithium compound **2**. We have utilized the well-known NMR spin coupling between  $^{15}\text{N}$  and directly bonded  $^6\text{Li}$ . Such coupling constants have been reported for several organolithium compounds complexed to tertiary amines<sup>6</sup> and for many lithium amides.<sup>7</sup> The results have provided important structural information on these organolithium species.



Herein we show how we have made use of the averaging of the  $^{15}\text{N}-^6\text{Li}$  coupling constants in **2** to investigate the dynamics

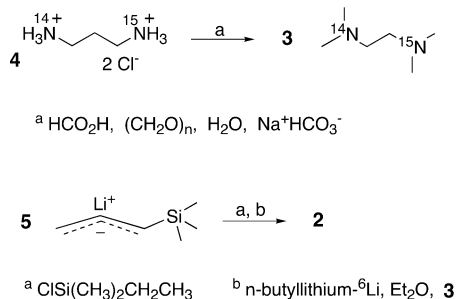
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of bimolecular N–Li exchange. Use of <sup>15</sup>N and <sup>6</sup>Li ensured that quadrupole-induced perturbation of the <sup>15</sup>N and <sup>6</sup>Li NMR spectra of **2** would be minimized. Indeed, they were not even detected.

**Results and Discussions**

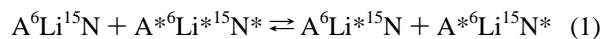
Eschweiler Clark chemistry was used to prepare [<sup>14</sup>N, <sup>15</sup>N]-*N,N,N',N'*-tetramethylethylenediamine **3** from the corresponding primary diamine dihydrochloride **4**.<sup>6a,8,9</sup> Then **2** was synthesized by sequential silylation and metalation from **5**<sup>5g</sup> and subsequently crystallized.



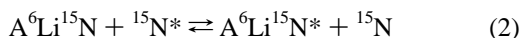
A sample of **2**, 0.4 M in diethyl ether-*d*<sub>10</sub>, showed vicinal proton proton coupling within the allyl moiety of 15.7 Hz, which indicates that both silyl substituents in **2** are *exo* as drawn. Nitrogen-15 NMR of this sample at 190 K consists of an equally spaced 1:1:1 triplet with separation 3.5 Hz (Figure 1). Since under the same conditions the <sup>6</sup>Li NMR consists solely of an equal doublet, separated by 3.5 Hz (see Figure 2), these results show that Li<sup>+</sup> is bidentately coordinated to TMEDA and that the one-bond <sup>15</sup>N–<sup>6</sup>Li coupling constant is 3.5 Hz. Just one lithium-containing species has been detected among these results.

With increasing temperature above 180 K the <sup>6</sup>Li and <sup>15</sup>N NMR multiplets of the above sample progressively average to single lines at their respective centers by 270 K; see Figures 1 and 2.

These results are necessarily diagnostic of processes that transfer lithium between two TMEDA molecules.<sup>10</sup> Most likely this can take place either by mutual exchange of lithiums between two TMEDA-complexed organolithiums

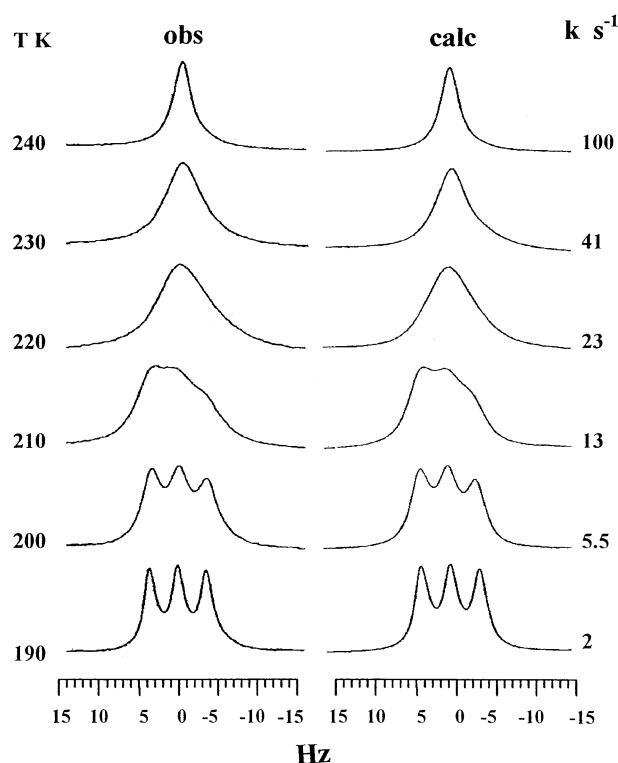


and/or by the exchange of free with complexed TMEDA

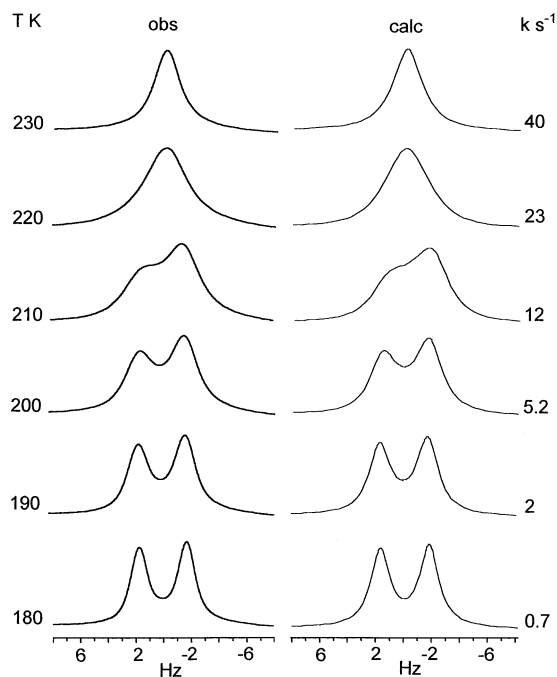


Note that a local first-order reversible dissociation of a <sup>15</sup>N–<sup>6</sup>Li coordination does not average the <sup>15</sup>N–<sup>6</sup>Li spin coupling

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**Figure 1.** <sup>15</sup>N NMR of **2**, 0.4 M, in diethyl ether-*d*<sub>10</sub>. (Left) Observed NMR, different temperatures; (right) calculated line shapes with pseudo-first-order rate constants for mutual N–Li exchange, as in eq 3.



**Figure 2.** <sup>6</sup>Li NMR of **2**, 0.4 M, in diethyl ether-*d*<sub>10</sub>. (Left) Observed NMR, different temperatures; (right) calculated line shapes with pseudo-first-order rate constants for mutual exchange (eq 3).

because the spin state of the <sup>6</sup>Li does not change during the course of the dissociation–recombination process. This is known as the “sudden approximation” originally due to Solomon and Bloembergen,<sup>10a</sup> who applied it to the NMR behavior of HF.

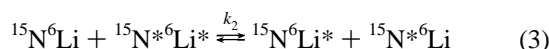
Since the above sample of **2** was recrystallized and free TMEDA was not detected in any of our NMR spectra (<sup>1</sup>H, <sup>15</sup>N, and <sup>13</sup>C) of this preparation, process 1 will be considered first.

**Table 1.** Dynamic Parameters for Intermolecular N–Li Exchange and Inversion of Compound **2** in Diethyl Ether-*d*<sub>10</sub>

process	resonance	$\Delta H^\ddagger$ <sup>a</sup> (kcal mol <sup>-1</sup> )	$\Delta S^\ddagger$ <sup>b</sup> (eu)
NLi + NLi (3)	<sup>15</sup> N	6.3	-21
NLi + NLi (3)	<sup>6</sup> Li	6.3	-21
NLi + N (5)	<sup>13</sup> CH <sub>2</sub> N	5.0	-22
inversion	<sup>13</sup> CH <sub>3</sub> Si <sup>c</sup>	7.0	-20

<sup>a</sup> ±0.5 kcal mol<sup>-1</sup>. <sup>b</sup> ±2 eu. <sup>c</sup> (CH<sub>3</sub>)<sub>2</sub>SiCH<sub>2</sub>CH<sub>3</sub>.

To calculate the <sup>15</sup>N and <sup>6</sup>Li NMR line shapes of **2** subject to mutual exchange of lithiums (eq 1 above), it is only necessary to deal with pseudospecies <sup>15</sup>N<sup>6</sup>Li. The calculation parallels our treatment of NMR for <sup>13</sup>C spin-coupled to one directly bonded <sup>6</sup>Li undergoing bimolecular C–Li exchange.<sup>11</sup> Thus <sup>15</sup>N and <sup>6</sup>Li NMR line shapes were calculated for pseudospecies “<sup>15</sup>N–<sup>6</sup>Li”, taking account of the overall <sup>15</sup>N–<sup>6</sup>Li exchange process as given in



The line shapes were calculated as a function of the pseudo-first-order rate constant for the exchange process as defined in

$$k_1 = k_2(^{15}\text{N}^6\text{Li}) \quad (4)$$

As expected, doubling the concentration of **2** doubles  $k_1$ . Comparison of observed and calculated NMR line shapes gave the experimental rate constants (see Figures 1 and 2). The resulting activation parameters are listed in Table 1.

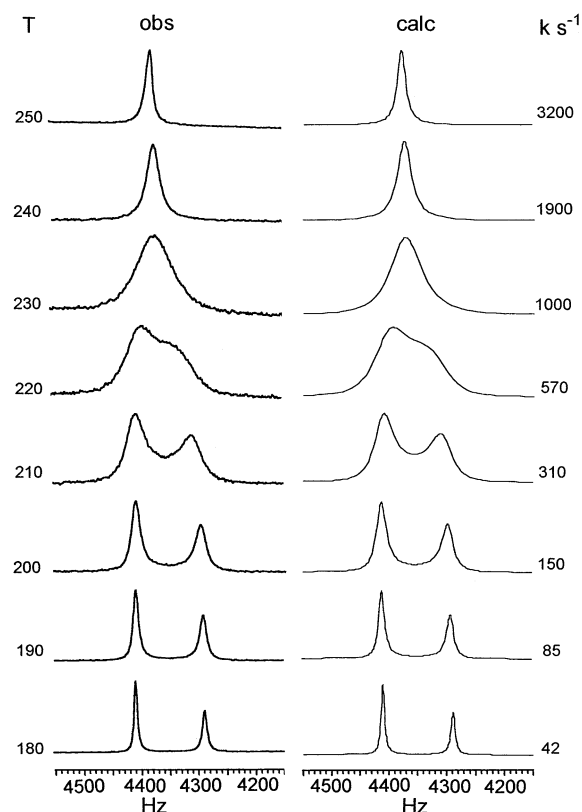
Although free TMEDA was not detected in any of the NMR spectra of the above-described sample of **2**, it is still possible that undetectable concentrations of TMEDA also contribute to the averaging of the <sup>15</sup>N–<sup>6</sup>Li coupling constant by exchange of TMEDA between its free state in solution and complex **2** as modeled by



Dynamics of this possible process were investigated by monitoring <sup>13</sup>C NMR of TMEDA methylenes in mixtures of **2** with free TMEDA. In these experiments we used TMEDA-<sup>14</sup>N<sub>1</sub>,<sup>14</sup>N<sub>2</sub>,<sup>7</sup>Li with <sup>13</sup>C in natural abundance. Thus at low temperature, 190 K, the <sup>13</sup>CH<sub>2</sub> resonances due to free and complexed TMEDA consist of a well-resolved unequal doublet (see Figure 3). With increasing temperature this doublet progressively broadened and averaged into a single sharp line by 250 K. The effects of varying the ratio of free to complexed TMEDA (in **2**) are shown in Figure 4. These results are clearly due to the overall transfer of TMEDA between its free and complexed states. The <sup>13</sup>C CH<sub>2</sub> line shapes were analyzed as resulting from an unequally populated two-site-uncoupled half-spin-exchanging system. Comparison of the observed and calculated line shapes (Figure 3) provided the pseudo-first-order rate constants  $k_{\text{NL}}^1$  and  $k_{\text{N}}^1$ . In addition, upon varying the amine concentration we find that  $k_{\text{NL}}^1$  is linear with [N] (Figure 5). Then use of the Grunwald–Loewenstein relationship<sup>12</sup>

$$k_{\text{NL}}^1 = \frac{\text{rate law}}{[\text{NL}]} \quad (6)$$

confirms the overall rate law as proposed in eq 5 as  $k_2[\text{NL}][\text{N}]$ . Activation parameters are listed in Table 1. By use of these



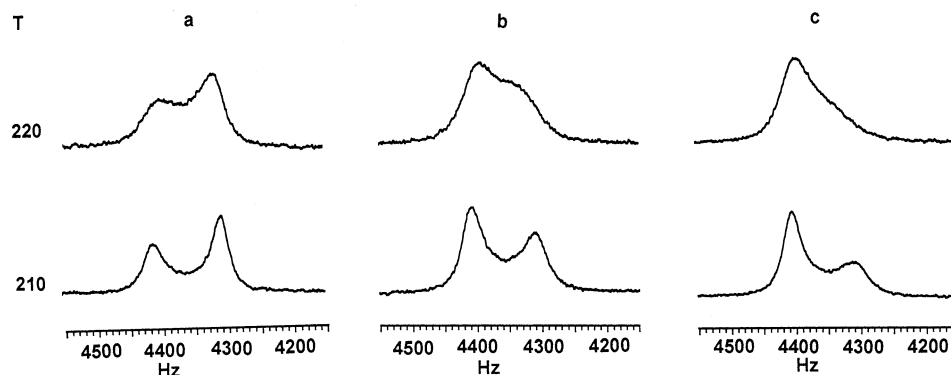
**Figure 3.** <sup>13</sup>C NMR of CH<sub>2</sub> of TMEDA in a mixture of free TMEDA, 0.44 M, with **2**, 0.4 M, in diethyl ether-*d*<sub>10</sub>; TMEDA-<sup>14</sup>N<sub>1</sub>,<sup>14</sup>N<sub>2</sub> was used. (Left) Observed NMR, different temperatures; left-hand peak is due to free TMEDA; (right) calculated for exchange process modeled as in eq 5.

results we can estimate the maximum contribution exchange via process 5 makes to the total N–Li exchange in diethyl ether-*d*<sub>10</sub> solutions of recrystallized **2**. Free diamine could not be detected by proton, <sup>6</sup>Li, <sup>15</sup>N, or <sup>13</sup>C NMR of these samples. We assume a detection limit of 1% for free to complexed TMEDA. This places the contribution of process 5 at 200 K to N–Li exchange in the latter solution at 11% or less of the total exchange rate via overall steps 3 and 5. The rate ratio for steps 5:3 should decrease with increasing temperature since  $\Delta H^\ddagger$  for process 5 is lower than that of 3 by ca. 1 kcal mol<sup>-1</sup>.

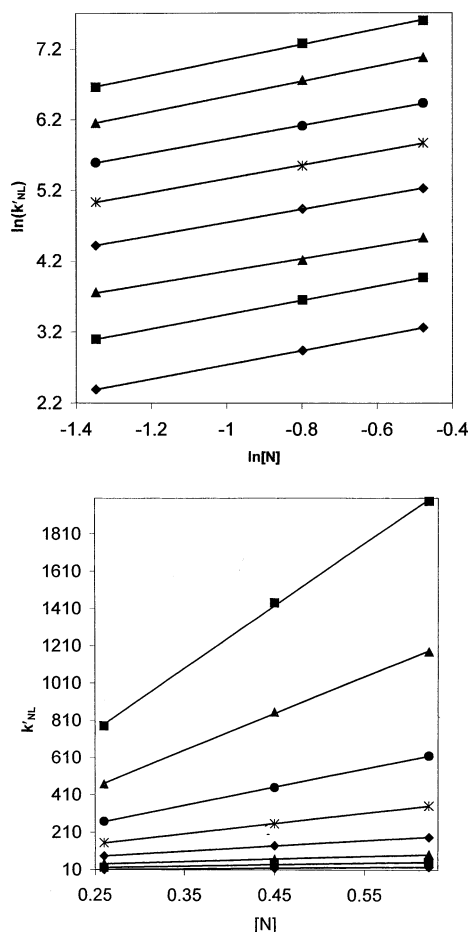
The chiral character of the proposed structure **2** should render the geminal silyl methyls diastereotopic. In fact, at 200 K <sup>13</sup>C NMR of these methyls gives rise to an equal doublet. With increasing temperature above 200 K the latter progressively averages to a single line by 270 K (see Figure 6). This behavior must be due to the inversion of **2** by transfer of coordinated lithium between its faces. The process is first-order in **2** and is independent of the concentration of added TMEDA. Comparison of experimental and calculated line shapes (see Figure 6) provides the rate constants and resulting activation parameters (see Table 1).

A discussion of mechanisms by which ion pair **2** reorganizes must be speculative since studies of ion-pair reorganization have only been initiated recently. The results reported herein are the

- (11) (a) Fraenkel, G.; Martin, K. V. *J. Am. Chem. Soc.* **1995**, *117*, 10341. (b) Kaplan, J. I.; Fraenkel, G. *NMR of Chemically Exchanging Systems*; Academic Press: New York, 1980; p 89. (c) Gutowsky, H. S.; Soaka, A. *J. Chem. Phys.* **1953**, *21*, 1688.  
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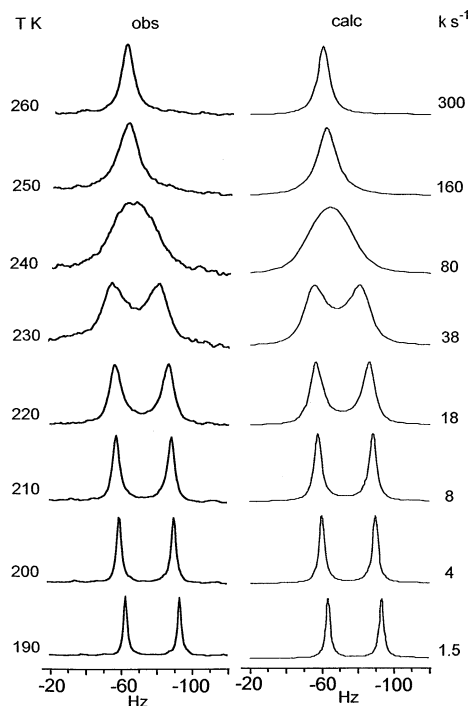
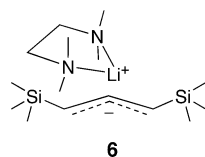
**Figure 4.** Same as described for Figure 3 but with different ratios of (TMEDA)/(2): (a) 0.26/0.4; (b) 0.45/0.4; (c) 0.62/0.4; experimental line shapes, two temperatures.



**Figure 5.** (a, top panel) Plots of  $\ln k^1_{NL}$  (process 5) versus  $\ln(N)$  ( $N$  is TMEDA,  $NL$  is **2**): temperatures, in kelvins, decreasing from top in the order 250, 240, 230, 220, 210, 200, 190, and 180. (b, bottom panel) As in panel a, plots of  $k^1_{NL}$  versus  $(N)$ ; same temperatures decreasing from top as in panel a.

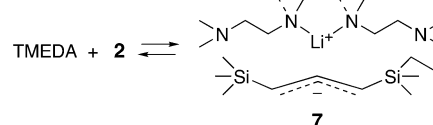
first on reorganization dynamics of an ion pair involving intermolecular N–Li exchange.

Compound **2** is most likely a monomer, as drawn by analogy to **6**, which was shown to be a monomer by X-ray crystallography.<sup>13</sup> Solution NMR data for **1**,<sup>5a</sup> **2**,<sup>3g</sup> and **6**<sup>14</sup> are all consistent with monomeric structures, as drawn.



**Figure 6.** Comparison of experimental and calculated line shapes for <sup>13</sup>C NMR of **2**.

The averaging of the <sup>15</sup>N–<sup>6</sup>Li coupling constant observed in studies of **2** requires transition structures that incorporate two TMEDA molecules, most likely preceded by intermediates of similar structure. One possible intermediate that is consistent with our kinetics for the TMEDA transfer reaction (eq 5) is **7**.

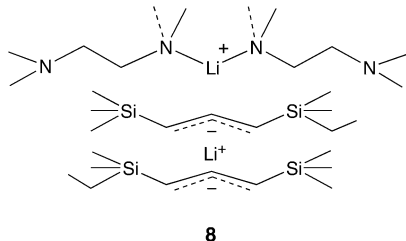


The transition structure and most likely the intermediate that precedes it for mutual exchange of lithiums between two molecules of **2** must be dimeric in **2**. Structure **8** is one of several such possible intermediates that are consistent with our results. Some aggregated allylic lithium compounds are already known

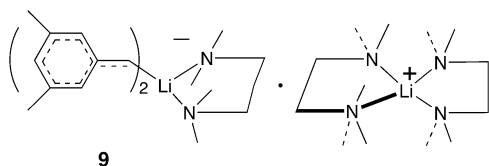
- (13) Boche, G.; Fraenkel, G.; Cabral, J.; Harms, K.; Van Eikoma Hommes, N. J. P.; Lohrenz, J.; Marsch, M.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1992**, *114*, 1562 and references therein.  
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to form sandwich structures.<sup>14</sup> Both NMR<sup>15</sup> and X-ray<sup>13</sup> crystallography place solvated lithium normal to the center of the allyl plane.<sup>13</sup> NMR studies showed that at low temperature, 170 K, transfer of coordinated lithium between faces of a monomeric allylic lithium compound is slow relative to the NMR time scale.<sup>15</sup> In dimeric **8** such a transfer process would be even slower. Structure **8** is similar to some ion-paired dimers that incorporate triple ions. They were first recognized from

**8**

NMR studies of a cyclohexadienylic lithium compound<sup>2a</sup> and later a substituted Cp<sup>-</sup>Li<sup>+</sup> compound.<sup>2b</sup> Several dimers of lithium amides assume the form (R<sub>2</sub>NLiNR<sub>2</sub>)<sup>-</sup>-Li(ligand<sup>+</sup>)<sub>n</sub>.<sup>3</sup> Similar to these species is the crystallographic structure of the product of metalation of mesitylene by *n*-butyllithium in the presence of TMEDA, reported by Mueller, **9**.<sup>16</sup>

**9**

A comment is now appropriate on the closely similar large negative entropies of activation for exchange and inversion reported herein. A  $\Delta S^\ddagger$  of  $-20$  eu is consistent with the bimolecular exchange observed in the present work. Similar values have also been reported for several other contact ion-paired allylic lithium compounds that undergo first-order inversion.

It was proposed that prior to transfer of lithium between faces of the allyl anion, the lithium allyl distance would have to increase. Thus the transition state would be more solvated than the ground state, resulting in a large negative  $\Delta S^\ddagger$  value.

## Conclusions

NMR line-shape studies of an ion-paired allylic lithium-<sup>6</sup>Li compound bidentately coordinated to TMEDA-<sup>14</sup>N,<sup>15</sup>N reveals

- (15) (a) Fraenkel, G.; Chow, A.; Winchester, W. R. *J. Am. Chem. Soc.* **1990**, *112*, 1382–1386. (b) Fraenkel, G.; Cabral, J.; Lanter, C.; Wang, J. *J. Am. Chem. Soc.* **1942**, *64*, 1302. (c) Fraenkel, G.; Winchester, W. R.; Chow, A. *J. Am. Chem. Soc.* **1990**, *112*, 2582.  
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the dynamics of three fast reorganization processes: (a) mutual exchange of lithiums between two TMEDA complexed allylic lithiums, (b) exchange of free with complexed TMEDA, and (c) first-order transfer of coordinated lithium between two faces of the allylic lithium compound.

## Experimental Section

**Equipment.** NMR data were obtained on Bruker AM 250 or Avance 300 spectrometers.

**[<sup>14</sup>N,<sup>15</sup>N]-*N,N,N',N'*-Tetramethylethylenediamine, **3**.** To a solution of sodium bicarbonate (4.6 g, 55 mmol) in 18 mL of 95% formic acid was added [<sup>14</sup>N,<sup>15</sup>N]-*N,N,N',N'*-ethylenediamine dihydrochloride (3 g, 16 mmol) and 10 mL of formalin. This mixture was refluxed for 2 h. The resulting clear orange solution was cooled to room temperature and sufficient concentrated HCl was added to bring the pH to ca. 2.0. The solution was rotary-evaporated under vacuum with warming and the remaining solid was dried on the vacuum line. Sufficient water (5 mL) was added to dissolve all solids. Solid potassium hydroxide was added and the resulting oil was distilled out. The combined distillate was extracted with saturated aqueous KOH. The oil was separated and dried over solid KOH. Distillation gave 2.5 g of the title product in 95% yield; bp 120–122 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 250 MHz)  $\delta$  2.04 (d, 4H), 1.89 (d, 6H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 62.9 MHz)  $\delta$  57.82.

**[<sup>6</sup>Li]-*exo,exo*-1-(Trimethylsilyl)-3-(dimethylethylsilyl)allyllithium-<sup>14</sup>N,<sup>15</sup>N]-*N,N,N',N'*-tetramethylethylenediamine, **2**.** *N*-Butyllithium-<sup>6</sup>Li (1 mL, 1.02 M, 1 mmol) in pentane was added slowly by syringe to a solution of **3** (0.130 g, 1.12 mmol) and a mixture of the isomeric propenes, *cis*- and *trans*-1-(trimethylsilyl)-3-(dimethylethylsilyl)-1-propene and *cis*- and *trans*-1-(dimethylethylsilyl)-3-(trimethylsilyl)-1-propene (0.223 g, 1.12 mmol), in 2 mL of diethyl ether at 0 °C. The mixture was warmed to room temperature over 3 h. Solvent was removed under vacuum and then 4 mL of dry pentane was added. This solution was cooled to  $-78$  °C. After crystals developed they were transferred to the drybox wherein 65 mg of the title compound was dissolved in 0.5 mL of dry oxygen-free diethyl ether-*d*<sub>10</sub>, forming a 0.4 M solution. <sup>1</sup>H NMR (diethyl ether-*d*<sub>10</sub>) 290 K  $\delta$  6.571 (t, *J* = 15.7 Hz, 1H), 2.494 (d, *J* = 15.7 Hz, 1H), 2.446 (d, *J* = 15.7 Hz, 1H), 2.361 (s, 4H), 2.223 (s, 12H), 0.811 (t, *J* = 7.9 Hz, 3H), 0.309 (q, *J* = 7.9 Hz, 2H), 0.1948 (s, 6H), 0.170 (s, 9H).

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**Supporting Information Available:** NMR line shape calculations, NMR spectra, kinetic data, and Eyring plots. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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