NMR Spectroscopic Studies of Lithium Diethylamide: Insights into Ring Laddering

Jennifer L. Rutherford and David B. Collum*

Contribution from the Department of Chemistry and Chemical Biology, Baker Laboratory, Cornell University, Ithaca, New York 14853-1301

Received June 24, 1999. Revised Manuscript Received August 11, 1999

Abstract: 6Li and 15N NMR spectroscopic studies of lithium diethylamide (Et2NLi) solvated by oxetane, THF, and Et2O are described. Four-, five-, and six-rung ladders, as well as cyclic dimers and trimers, are identified. In addition, dynamic processes within the trimers and ladders are detected. The symmetries of the aggregates facilitated the determination of relatively complex solution structures and equilibria.

Introduction

Over the last two decades a consortium of European chemists have carried out detailed investigations of N-lithiated species including lithium imides (R2C≡NLi, 1) and lithium amides (R2NLi, 2) using a range of crystallographic, spectroscopic, and computational methods. From their distinctly inorganic perspective and in large part due to their crystallographic investigations of the lithium imides, they have developed the general principles underlying “ring stacking” and “ring laddering”. Lithium imides often crystallize from hydrocarbons as prismatic blocks are again (LiN)n rings, but in contrast to the lithium imides, the R groups on the lithium amide nitrogen are orthogonal to the (LiN)n planes. As a consequence, lithium dialkylamides generally crystallize and exist in solution as cyclic oligomers (primarily cyclic dimers, 4). Lithium dialkylamide ladders (5) and cyclic ladders (prisms) have been documented rarely and only in the least hindered cases.

Our group’s distinctly organic perspective has led us to focus upon lithium dialkylamides that are commonly employed in organic synthesis and emphasize the relationship between solution structures and reactivities. While we have observed R2NLi/LiX mixed trimers and tetramers displaying spectral data consistent with laddering, we have not detected ladders of homonuclear lithium dialkylamides to date.

We describe herein 6Li and 15N NMR spectroscopic studies of lithium diethylamide (Et2NLi) solvated by Et2O, THF, and the strongly coordinating7 oxetane. Et2NLi was chosen due to its role in organic synthesis8 and to provide a benchmark for the more sterically hindered analogues such as lithium diisopropylamide (LDA), lithium hexamethyldisilazide (LiHMDS), and lithium 2,2,6,6-tetramethylpiperidide (LiTMP). We will consider lithium monoalkylamides (RNHLi)3 which have been observed. Barnett, N. D. R.; Mulvey, R. E.; Clegg, W.; O’Neil, P. A. J. Am. Chem. Soc. 1991, 113, 8187.

Lithium dialkylamides (2) also show a strong tendency to form oligomers, but are more sterically congested than the corresponding lithium imides (1). The basic structural building blocks are again (LiN)n rings, but in contrast to the lithium imides, the R groups on the lithium amide nitrogen are orthogonal to the (LiN)n planes. As a consequence, lithium dialkylamides generally crystallize and exist in solution as cyclic oligomers (primarily cyclic dimers, 4). Lithium dialkylamide ladders (5) and cyclic ladders (prisms) have been documented rarely and only in the least hindered cases.

Our group’s distinctly organic perspective has led us to focus upon lithium dialkylamides that are commonly employed in organic synthesis and emphasize the relationship between solution structures and reactivities. While we have observed R2NLi/LiX mixed trimers and tetramers displaying spectral data consistent with laddering, we have not detected ladders of homonuclear lithium dialkylamides to date.

We describe herein 6Li and 15N NMR spectroscopic studies of lithium diethylamide (Et2NLi) solvated by Et2O, THF, and the strongly coordinating7 oxetane. Et2NLi was chosen due to its role in organic synthesis8 and to provide a benchmark for the more sterically hindered analogues such as lithium diisopropylamide (LDA), lithium hexamethyldisilazide (LiHMDS), and lithium 2,2,6,6-tetramethylpiperidide (LiTMP). We will consider lithium monoalkylamides (RNHLi)3 which have been observed. Barnett, N. D. R.; Mulvey, R. E.; Clegg, W.; O’Neil, P. A. J. Am. Chem. Soc. 1991, 113, 8187.

Lithium dialkylamides (2) also show a strong tendency to form oligomers, but are more sterically congested than the corresponding lithium imides (1). The basic structural building blocks are again (LiN)n rings, but in contrast to the lithium imides, the R groups on the lithium amide nitrogen are orthogonal to the (LiN)n planes. As a consequence, lithium dialkylamides generally crystallize and exist in solution as cyclic oligomers (primarily cyclic dimers, 4). Lithium dialkylamide ladders (5) and cyclic ladders (prisms) have been documented rarely and only in the least hindered cases.

Our group’s distinctly organic perspective has led us to focus upon lithium dialkylamides that are commonly employed in organic synthesis and emphasize the relationship between solution structures and reactivities. While we have observed R2NLi/LiX mixed trimers and tetramers displaying spectral data consistent with laddering, we have not detected ladders of homonuclear lithium dialkylamides to date.

We describe herein 6Li and 15N NMR spectroscopic studies of lithium diethylamide (Et2NLi) solvated by Et2O, THF, and the strongly coordinating7 oxetane. Et2NLi was chosen due to its role in organic synthesis8 and to provide a benchmark for the more sterically hindered analogues such as lithium diisopropylamide (LDA), lithium hexamethyldisilazide (LiHMDS), and lithium 2,2,6,6-tetramethylpiperidide (LiTMP). We will consider lithium monoalkylamides (RNHLi)3 which have been observed. Barnett, N. D. R.; Mulvey, R. E.; Clegg, W.; O’Neil, P. A. J. Am. Chem. Soc. 1991, 113, 8187.

Lithium dialkylamides (2) also show a strong tendency to form oligomers, but are more sterically congested than the corresponding lithium imides (1). The basic structural building blocks are again (LiN)n rings, but in contrast to the lithium imides, the R groups on the lithium amide nitrogen are orthogonal to the (LiN)n planes. As a consequence, lithium dialkylamides generally crystallize and exist in solution as cyclic oligomers (primarily cyclic dimers, 4). Lithium dialkylamide ladders (5) and cyclic ladders (prisms) have been documented rarely and only in the least hindered cases.

Our group’s distinctly organic perspective has led us to focus upon lithium dialkylamides that are commonly employed in organic synthesis and emphasize the relationship between solution structures and reactivities. While we have observed R2NLi/LiX mixed trimers and tetramers displaying spectral data consistent with laddering, we have not detected ladders of homonuclear lithium dialkylamides to date.

We describe herein 6Li and 15N NMR spectroscopic studies of lithium diethylamide (Et2NLi) solvated by Et2O, THF, and the strongly coordinating7 oxetane. Et2NLi was chosen due to its role in organic synthesis8 and to provide a benchmark for the more sterically hindered analogues such as lithium diisopropylamide (LDA), lithium hexamethyldisilazide (LiHMDS), and lithium 2,2,6,6-tetramethylpiperidide (LiTMP). We will consider lithium monoalkylamides (RNHLi)3 which have been observed. Barnett, N. D. R.; Mulvey, R. E.; Clegg, W.; O’Neil, P. A. J. Am. Chem. Soc. 1991, 113, 8187.

Lithium dialkylamides (2) also show a strong tendency to form oligomers, but are more sterically congested than the corresponding lithium imides (1). The basic structural building blocks are again (LiN)n rings, but in contrast to the lithium imides, the R groups on the lithium amide nitrogen are orthogonal to the (LiN)n planes. As a consequence, lithium dialkylamides generally crystallize and exist in solution as cyclic oligomers (primarily cyclic dimers, 4). Lithium dialkylamide ladders (5) and cyclic ladders (prisms) have been documented rarely and only in the least hindered cases.

Our group’s distinctly organic perspective has led us to focus upon lithium dialkylamides that are commonly employed in organic synthesis and emphasize the relationship between solution structures and reactivities. While we have observed R2NLi/LiX mixed trimers and tetramers displaying spectral data consistent with laddering, we have not detected ladders of homonuclear lithium dialkylamides to date.

We describe herein 6Li and 15N NMR spectroscopic studies of lithium diethylamide (Et2NLi) solvated by Et2O, THF, and the strongly coordinating7 oxetane. Et2NLi was chosen due to its role in organic synthesis8 and to provide a benchmark for the more sterically hindered analogues such as lithium diisopropylamide (LDA), lithium hexamethyldisilazide (LiHMDS), and lithium 2,2,6,6-tetramethylpiperidide (LiTMP). We will consider lithium monoalkylamides (RNHLi)3 which have been observed. Barnett, N. D. R.; Mulvey, R. E.; Clegg, W.; O’Neil, P. A. J. Am. Chem. Soc. 1991, 113, 8187.
show that Et₂NLi tends to form a mixture of structures including a number of ladders (Chart 1).

Results

Lithiation of [¹⁵N]Et₂NH using recrystallized [⁶Li]n-BuLi affords [⁶Li,¹⁵N]Et₂NLi as a hydrocarbon-insoluble white solid. Recrystallization from hexane/diethyl ether and evacuation affords solvent-free [⁶Li,¹⁵N]Et₂NLi. ⁶Li and ¹⁵N NMR spectra were recorded using methods described previously. A combination of single-frequency decoupling, broad-band decoupling, and ⁶Li,¹⁵N-heteronuclear multiple quantum correlation (HMQC) spectroscopy provided the ⁶Li-¹⁵N resonance correlations critical to the structural assignments. In some cases, analyses at several temperatures to exploit the highly temperature-dependent chemical shifts were necessary to deconvolute the complex spectra. The spectral data are summarized in Table 1, and the spectra are given in the Supporting Information. The discussion of individual resonances refers to the partial structures depicted in Chart 2.

Oxetane. Although oxetane affords the most complex equilibria involving five distinct species, it also offers optimal solubility and the clearest structural assignments. Spectra recorded on [⁶Li,¹⁵N]Et₂NLi (0.1 M) in neat oxetane (15.4 M) show exclusively cyclic dimer containing an indeterminate number of coordinated oxetane ligands. As the oxetane concentration is decreased using pentane/toluene mixtures as cosolvent, cyclic trimer appears, becomes the major species at <9.0 equiv of oxetane per lithium, and remains dominant even at <1.0 equiv of oxetane per lithium (Figure 1). Dimer appears as a ⁶Li triplet and ¹⁵N quintet characteristic of all cyclic oligomers. ⁶Li-detected ¹⁵N zero-quantum NMR spectroscopy confirmed 6a to be a dimer rather than a higher cyclic oligomer.

Table 1. ⁶Li and ¹⁵N NMR Spectral Data

<table>
<thead>
<tr>
<th>structure</th>
<th>⁶Li, δ (mult, J_{LiN})</th>
<th>¹⁵N, δ (mult, J_{LiN})</th>
</tr>
</thead>
<tbody>
<tr>
<td>6a</td>
<td>-110 0.75 (t, 4.7) 47.7 (qt, 4.7)</td>
<td>44.8 (st, 3.3)</td>
</tr>
<tr>
<td>7a</td>
<td>-105 1.27 (q, 3.5) 44.9 (qt, 5.1)</td>
<td>46.5 (m) 33.9 (m)</td>
</tr>
<tr>
<td>7a</td>
<td>-125 1.21 (t, 5.2) 44.9 (qt, 5.1)</td>
<td>45.7 (m) 34.7 (m)</td>
</tr>
<tr>
<td>8a</td>
<td>-105 1.15 (t, 4.6) 46.5 (m)</td>
<td>32.7 (m)</td>
</tr>
<tr>
<td>8a</td>
<td>-125 0.63 (m) 1.85 (m) 46.5 (m)</td>
<td>33.5 (m) 33.9 (m)</td>
</tr>
<tr>
<td>9a</td>
<td>-105 0.83 (dd, 2.7,5.4) 1.60 (m) 1.95 (m) 44.9 (m) 34.4 (m) 32.7 (m)</td>
<td>44.7 (m) 33.5 (m) 33.9 (m)</td>
</tr>
<tr>
<td>10a</td>
<td>-105 0.93 (m) 1.56 (m) 1.86 (m) 46.5 (m) 33.6 (m)</td>
<td>43.1 (st, 3.4)</td>
</tr>
<tr>
<td>6b</td>
<td>-115 1.51 (t, 5.1) 46.5 (q, 4.9)</td>
<td>43.1 (st, 3.4)</td>
</tr>
<tr>
<td>7b</td>
<td>-115 1.78 (q, 3.5) 43.1 (st, 3.4)</td>
<td>36.3 (m)</td>
</tr>
<tr>
<td>8b</td>
<td>-87 1.99 (t, 4.8) 1.83 (m) 46.5 (m) 33.6 (m)</td>
<td>43.8 (q, 5.3)</td>
</tr>
<tr>
<td>6c</td>
<td>-100 2.51 (t, 5.1) 46.5 (qt, 4.9)</td>
<td>36.3 (m)</td>
</tr>
</tbody>
</table>

Spectra were recorded on samples containing 0.1–0.15 M total lithium concentration (normality). Coupling constants were measured after resolution enhancement. Multiplicities are denoted as follows: d = doublet, dd = doublet of doublets, t = triplet, q = quartet, qt = quintet, st = septet, m = multiplet. The chemical shifts are reported relative to 0.3 M LiCl/MeOH at −90 °C (0.0 ppm) and neat Me₂NEt at −90 °C (25.7 ppm). All J values are reported in hertz.

Chart 2
oligomer. At intermediate temperatures (−105 °C) trimer 7a exhibits a 6Li quartet and an 15N septet initially attributed to a cubic tetramer (11). However, at reduced probe temperature (−125 °C), the 6Li quartet simplifies to a 6Li triplet (Figure 2A,B) while the 15N septet simplifies to an 15N quintet.13 This spectroscopic behavior is consistent with a rapid intra-aggregate exchange14 in which all 6Li and 15N nuclei exchange slowly on the NMR time scale only at the lowest temperatures. The preference for 7a at low oxetane concentrations indicates a lower per-lithium solvation number compared to dimer 6a.

A number of additional resonances begin to appear at <3.0 equiv of oxetane per lithium (Figure 1). 15N broad-band irradiation of [6Li,15N]Et2NLi (0.15 M) containing 0.75 equiv of oxetane affords a 6Li NMR spectrum containing eight resonances in addition to those attributed to 7a (Figure 2).

Figure 1. 6Li NMR spectra of 0.1 M [6Li,15N]Et2NLi in 3:2 pentane—toluene at −115 °C with (A) 20 equiv of oxetane, (B) 3 equiv of oxetane, (C) 1.25 equiv of oxetane, and (D) 0.75 equiv of oxetane.

Figure 2. 6Li NMR spectra of 0.15 M [6Li,15N]Et2NLi in 3:2 pentane—toluene with 0.75 equiv of oxetane: (A) 6Li NMR spectrum at −125 °C; (B) 6Li NMR spectrum at −105 °C; and (C) 6Li(15N) NMR spectrum at −105 °C.

(13) At >6.0 equiv of oxetane (per lithium), the 6Li quartet and 15N septets become broad mounds while two minor 15N resonances appear. We suspect that different solvation states of the static lithium trimer or a static three-rung ladder are forming.

Despite the problems presented by the complex mixtures and complex structures, the symmetries of ladders 8a–10a allowed for compelling assignments.

Oligomer 8a exhibits two $^6\text{Li}$ resonances (1:1) and two $^{15}\text{N}$ resonances (1:1) showing coupling consistent with the ladder topology. Single-frequency irradiation of the resonance corresponding to $N_a$ (−125 °C) causes the anticipated collapse of $L_{ia}$ to a doublet and $L_{ib}$ to a triplet (Chart 2). Similarly, irradiation of $N_b$ causes the collapse of $L_{ia}$ and $L_{ib}$ to doublets. A $^6\text{Li},^{15}\text{N}$-HMQC spectrum$^{11}$ recorded at −125 °C on $[^6\text{Li},^{15}\text{N}]\text{Et}_2\text{NLi}$ (0.1 M, 0.88 equiv oxetane) confirmed the assignment as ladder 8a. Once again, however, an unanticipated dynamic process proved confusing at the outset. Single-frequency irradiation of either $N_a$ or $N_b$ of 8a at a higher temperature (−105 °C) causes both $L_{ia}$ and $L_{ib}$ to collapse to singlets. In addition, the complex multiplets corresponding to $L_{ia}$ and $L_{ib}$ observed at lower temperature (−125 °C) become notably sharper and simplify at −105 °C (especially the multiplet corresponding to $L_{ib}$). We attribute this behavior to an intra-aggregate exchange within ladder 8a that is slow enough at −105 °C to afford discrete $^6\text{Li}$ and $^{15}\text{N}$ resonances, yet sufficiently fast to allow essentially a spin-saturation transfer. Both one- and two-dimensional $^6\text{Li}$−$^6\text{Li}$ exchange (EXSY)$^{15}$ spectra recorded at −105 °C confirmed the $L_{ia}$−$L_{ib}$ exchange within the 4-rung ladder 8a.

The remaining six $^6\text{Li}$ resonances observable in the samples containing 0.75 equiv of oxetane are assigned to five- and six-rung ladders 9a and 10a by exploiting their highly characteristic symmetries. The five-rung ladder 9a displays three resonances in 2:2:1 ratios, while the six-rung ladder 10a displays three resonances in 1:1:1 (2:2:2) ratios. Ladders 9a and 10a (as well as 8a) display $^{15}\text{N}$ resonances clustered in two distinct regions of the $^{15}\text{N}$ spectrum characteristic of the external ($N_b$ and $N_c$) sites. Although totally selective decouplings were not possible, regional decoupling afforded connectivities fully consistent with the assignments. A $^6\text{Li},^{15}\text{N}$-HMQC spectrum$^{11}$ provided further support (Figure 3). In contrast to the 4-rung ladder, no unusual exchange processes were detected in 9a or 10a.

THF. Spectra recorded on $[^6\text{Li},^{15}\text{N}]\text{Et}_2\text{NLi}$ (0.1 M) in neat THF reveal a $^6\text{Li}$ triplet and an $^{15}\text{N}$ quintet. A $^6\text{Li}$-detected $^{15}\text{N}$ zero-quantum NMR spectrum$^{12}$ confirms this species as the cyclic dimer 6b. Dimer 6b persists at all THF concentrations; however, at low THF concentrations (2–10 equiv) a minor $^6\text{Li}$ quartet and an $^{15}\text{N}$ septet are readily observable. Although cooling the probe to −130 °C fails to simplify the $^6\text{Li}$ quartet to a triplet expected for trimer 7b, drawing analogy to the oxetane-solvated trimer 7a strongly implicates 7b rather than tetramer 11.

![Diagram of 11 and 12](image)

Figure 3. $^6\text{Li},^{15}\text{N}$-heteronuclear multiple quantum correlation (HMQC) spectrum of 0.1 M $[^6\text{Li},^{15}\text{N}]\text{Et}_2\text{NLi}$ in 3:2 pentane–toluene with 0.75 equiv of oxetane at −105 °C.

Spectra recorded on samples containing 1.0 equiv of THF display an ensemble of overlapping $^6\text{Li}$ multiplets shown by broad-band $^{15}\text{N}$ irradiation to be comprised of four discrete $^6\text{Li}$ resonances. The chemical shifts are highly temperature dependent, making assignments possible by varying the probe temperature. A $^6\text{Li},^{15}\text{N}$-HMQC experiment$^{11}$ at −87 °C offers the clearest structural assignment, showing the two major peaks (1:1) to derive from four-rung ladder 8b and the two minor peaks deriving from dimer 6b and trimer 7b. Ladder 8b is present in higher proportions at higher temperatures. Higher-order ladders 9b and 10b are not observed within the solubility limits of $\text{Et}_2\text{NLi}$.

Diethyl Ether. $[^6\text{Li},^{15}\text{N}]\text{Et}_2\text{NLi}$ dissolves only with $\pm 5$ equiv of $\text{Et}_2\text{O}$, affording a single species displaying a $^6\text{Li}$ triplet and an $^{15}\text{N}$ quintet characteristic of a cyclic oligomer. A $^6\text{Li}$-detected $^{15}\text{N}$ zero-quantum NMR experiment$^{15}$ confirms that this species is the cyclic dimer 6c.

Discussion

Ring laddering of $N$-lithiated species is well documented by crystallographic methods, with additional support provided by computational and NMR spectroscopic studies.$^1$ The investigations of $[^6\text{Li},^{15}\text{N}]\text{Et}_2\text{NLi}$ described herein provide an unusually clear view of lithium dialkylamide ladders in solution (Chart 1). The most striking examples come from $\text{Et}_2\text{NLi}$/oxetane mixtures in which low oxetane concentrations afford 4-, 5-, and 6-rung ladders 8a–10a and cyclic trimer 7a. The analogous 3-rung ladder 12 is conspicuously absent. These higher oligomers give way to exclusively cyclic dimer 6a at high oxetane concentrations. When THF is used in place of the strongly coordinating oxetane, a slight drop in solubility is accompanied by measurably different solution behaviors. Dimer 6b is the sole observable form at the highest concentrations of THF. The four-rung ladder 8b, cyclic trimer 7b, and cyclic dimer 6b are present at the lowest THF concentrations. Last, the poor solubility of $\text{Et}_2\text{NLi}$ in $\text{Et}_2\text{O}$ coincides with the formation of only cyclic dimer 6c.

We have taken the liberty of depicting solvation numbers on oligomers 6−10 (Chart 1) in the absence of definitive assignments. What we can say is that the shifting oligomer distribu-
tions, with changes in solvent concentrations, reveal that the per-lithium solvation numbers follow the orders (1) 6a > 7a > 8a > 9a > 10a and (2) 6b > 7b > 8b. Crystallographic and computational studies are fully consistent with the ladders being capped by solvents only on the ends. The preference for cyclic trimer 7a over 3-rung ladder 12 possibly implicates an advantage of forfeiting a transannular linkage in 12 for an additional oxetane–Li interaction in 7a. Although substantial evidence suggests that the cyclic trimers are not strongly solvated for hindered lithium dialkylamides, a trisolvated trimer for such a sterically unhindered amide seems reasonable. Moreover, the persistence of trimer 7a even at relatively high oxetane concentrations is in accord with the assignment. If 7a is indeed a trisolvate, then cyclic dimer 6a would, by inference, be assigned as either a tri- or tetrasolvated dimer. Although this is not consistent with spectroscopic investigations of more sterically hindered lithium dialkylamides,7 once again it seems quite reasonable for such an unhindered lithium amide. Even so, it is less clear whether similar conclusions can be drawn for the THF- and Et2O-solvated cyclic dimers and trimers.

Several interesting and initially confusing dynamic processes surfaced during the structural studies. For example, cyclic trimer 7a undergoes an intra-aggregate exchange. The consequent coupling of all three 6Li nuclei with all three 15N nuclei afford a 6Li quartet and 15N septet in the fast exchange limit. This could be incorrectly attributed to a prismatic structure such as cubic tetramer 11 if the slow exchange limit showing a cyclic oligomer connectivity had not been attained. The mechanism of this intra-aggregate exchange is not at all obvious. Four-rung ladder 8a also displays an intra-aggregate exchange of the external and internal lithium sites (Li4 and Li3). Although the exchange is sufficiently slow to afford two distinct resonances, it was detected by single-frequency decoupling experiments and confirmed by one- and two-dimensional 6Li–6Li EXSY spectroscopy.

In summary, the structures elucidated in this study provide compelling evidence that lithium dialkylamides can form ladders in solution and contribute to the “laddering principle” developed by Snaith and co-workers.1 The synthetic importance of laddering in organolithium solution chemistry is not immediately clear at this time. However, we are only now beginning to understand how lithium amide structure influences reactivity. Our investigations of lithium amide reactivities often reveal the importance of structural features only after the fact. The study also highlights how 6Li and 15N NMR spectroscopies complement the crystallographic methods and underscores the importance of aggregate symmetries in determining solution structures.

Experimental Section

Reagents and Solvents. All solvents and ligands were distilled from blue or purple solutions containing sodium benzenophene ketyl. The hydrocarbon stills contained 1% tetraglyme to dissolve the ketyl. 6Li metal (95.5% enriched) was obtained from Oak Ridge National Laboratory. The [6Li]n-butyllithium used to prepare the [6Li,15N]-Et2NLi was prepared and purified as described previously.9 The synthesis of [15N]Et2NH and general protocols are described in the Supporting Information.

NMR Spectroscopic Analyses. Samples for spectroscopic analyses were prepared as described in detail elsewhere.9 Standard 6Li and 15N NMR spectra were recorded on a Varian XL–400 spectrometer operating at 58.8 and 40.5 MHz (respectively) or on a Varian Unity 500 spectrometer operating at 73.6 and 58.8 MHz, respectively. The 6Li and 15N resonances are referenced to 0.3 M [6Li]LiCl/MeOH at −90 °C (0.0 ppm) and neat Me2NEt at −90 °C (25.7 ppm), respectively. The 6Li,15N-HMQC spectra11 were recorded on the Varian Unity 500 spectrometer equipped with a custom-built 3-channel probe designed to accommodate 6Li and 15N pulses with concurrent proton decoupling. The 6Li-detected 15N zero-quantum NMR spectra12 were recorded using the same spectrometer configuration as for the 6Li,15N-HMQC experiments with a pulse sequence described previously.11 The 6Li-15Li exchange (EXSY) experiments were also recorded on the Varian Unity 500 spectrometer and the custom-built 3-channel probe using known protocols.15

Acknowledgment. We acknowledge the National Science Foundation Instrumentation Program (CHE 7904825 and PCM 8018643), the National Institutes of Health (RR02002), and IBM for support of the Cornell Nuclear Magnetic Resonance Facility. We thank the National Institutes of Health for direct support of this work.

Supporting Information Available: 6Li and 15N NMR spectra and syntheses of labeled compounds (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA992169M