Structural Studies of {9-[2-(Dimethylamino)ethyl]fluorenyl}lithium Compounds

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Two lithium compounds of the substituted fluorenyl ligand 9-[2-(dimethylamino)ethyl]-fluorenyl (Fl^N) have been prepared and isolated. The X-ray crystal structures of $Fl^NLi·Et_2O$ **(2)** and $Fl^NLi·2THF$ **(3)** have been obtained. In **2** the lithium atom is coordinated η^5 to the fluorenyl anion while **3** exhibits an η^2 arrangement. Structural details have been analyzed to provide additional insights regarding the nature of the lithium-π interactions in organolithium compounds with delocalized π-systems.

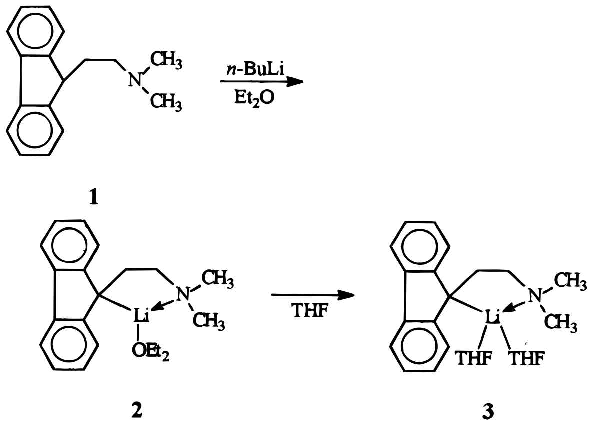
Introduction

Organolithium compounds have evolved into one of the most widely used classes of organometallic synthons.[1] The importance of organolithium reagents has led to a desire for increased understanding of their chemical behavior. This in turn has lead to considerable interest in their solid-state structures with particular emphasis on the degree of aggregation, the extent of solvation, and the nature of bonding to the carbanion.[2,3] Many organolithium compounds involve lithium atoms bonded to the carbon atoms of delocalized π-electron systems. Often, the structures of such compounds exhibit close interactions of the lithium atom with two or more carbon atoms. Previously, the geometries of these complexes have been interpreted in terms of both covalent[4] and electrostatic[5] models; however, it is now generally accepted that the nature of the lithium−carbon bond is approximately 85−90% ionic.[6] Additional structural studies of related compounds would be quite useful in helping to further define the bonding in these complexes.

In the present paper we report the preparation, isolation, characterization, and X-ray crystal structures of two derivatives of {9-[2-(dimethylamino)ethyl]fluorenyl}lithium: $Fl^NLi·Et_2O$ **(2)** and $Fl^NLi·2THF$ **(3)** [$Fl^N = C_{13}H_8CH_2CH_2NMe_2$]. These compounds are of interest because the fluorenyl ligand features a pendant $-(CH_2)_2NMe_2$ arm capable of intramolecular coordination, a concept developed over the past four decades by Klumpp, van Koten, and others.[7] The hydrocarbon parent of **2** and **3**, Fl^NH **(1)**, was first synthesized over 40 years ago in work oriented toward the search for new pharmaceuticals.[8] Twenty years later, the electronic spectra of a series of substituted fluorenyl lithium compounds, including Fl^NLi, were studied in on a qualitative basis.[9] More recently, quantitative studies of the effects of hetero-substituted pendant groups on the kinetic and thermodynamic stabilities of these fluorenyl lithium derivatives have been published.[10,11] Despite the foregoing work, no structural or other characterization data for the isolated fluorenyl lithium compounds have been reported.

Results and Discussion

The organic precursor **1** was synthesized by modification of the literature methods. Fluorenyllithium was allowed to react with 2-(dimethylamino)ethyl chloride in tetrahydrofuran to eliminate LiCl and afford **1** as a viscous pale yellow liquid. Previously fluorenyl sodium[8] or fluorenyl magnesium bromide[10] had been used instead of fluorenyl lithium as the nucleophile source. When **1** was treated with *n*-BuLi a bright yellow powder precipitated out of the diethyl ether/hexane solution (eq 1). This yellow powder is only slightly soluble in diethyl



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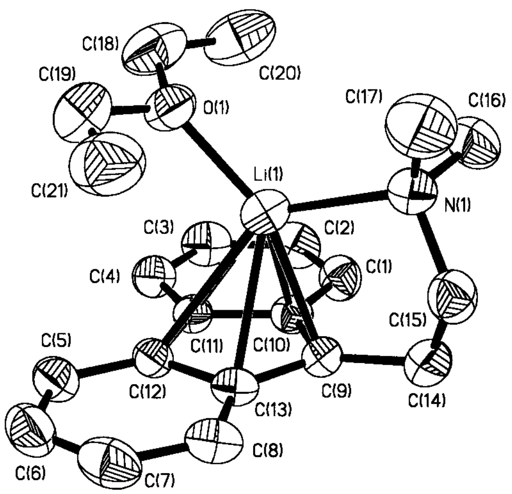

Figure 1. Molecular structure and atom-numbering scheme for $\mathrm{Fl^NLi{\cdot}Et_2O}$ **(2)** (thermal ellipsoids are shown at the 30% probability level).

ether but is quite soluble in aromatic solvents. On the basis of the proton NMR spectrum, it was established that the yellow powder is the monoetherate **2**. Dissolution of **2** in tetrahydrofuran afforded orange crystalline **3**, which, on the basis of ^{1}H NMR assay, resulted from the replacement of one diethyl ether by two tetrahydrofuran molecules of crystallization. The superior solvation of Li^+ by tetrahydrofuran *vis-à-vis* diethyl ether is not surprising, as similar observations have been made in an indenyl system.[12] As further confirmation of the structure assignments, and to investigate the molecular geometries, X-ray crystal structures were obtained for both compounds.

Compound **2** crystallizes in the monoclinic space group $P2_1/n$ with four molecules per unit cell. Figure 1 shows the molecular geometry together with the atom-numbering scheme; selected bond distances and angles are assembled in Table 1. The coordination sphere of the lithium atom is made up of the fluorene group, the nitrogen atom of the pendant arm, and one molecule of diethyl ether. The N–Li–O angle is 117.4(3)°, which corresponds closely to the ideal value of 120° for an sp^2-hybridized lithium atom with a coordination number of **3**. The Li–N bond distance of 2.079(6) Å falls within the range observed for other such distances in similar compounds.[13–15] The Li–O bond distance of 1.886(5) Å falls at the short end of the range observed for solvent stabilized lithium complexes.[16–18] The lithium atom is located 2.113(5) Å above the plane of the fluorenyl group and resides within the periphery of the five-membered ring, approximately equidistant between C(10) and C(13). A perpendicular line from the lithium atom intersects the ring plane at a point which is 0.73 Å from C(9), 1.20 Å from C(10), and 1.09 Å from C(13). This projection is depicted in Figure 2. The geometry around C(9) is also of interest. Within experimental error, the geometry at C(9) is trigonal planar (sum of angles 359.6(5)°); however, C(14) is located 0.150(5) Å out of the least squares plane of the fluorenyl five-membered ring (C(9) through C(13)) and in the direction of Li(1). In turn this implies an angle of 5.7(3)° between the least-squares plane and the C(9)–C(14) vector.

Table 1. Selected Bond Distances (Å) and Angles (deg) for $\mathrm{Fl^NLi{\cdot}Et_2O}$ (2) and $\mathrm{Fl^NLi{\cdot}THF}$ (3)

Bond Distances for Compound 2			
Li(1)–N(1)	2.079(6)	Li(1)–C(11)	2.684(6)
Li(1)–O(1)	1.886(5)	Li(1)–C(12)	2.660(6)
Li(1)–C(9)	2.235(5)	Li(1)–C(13)	2.379(6)
Li(1)–C(10)	2.431(6)	Li(1)–plane 1[a]	2.113(5)
Bond Angles for Compound 2			
O(1)–Li(1)–N(1)	117.4(3)	N(1)–Li(1)–C(9)	85.1(2)
O(1)–Li(1)–C(9)	157.5(3)	N(1)–Li(1)–C(10)	104.4(2)
O(1)–Li(1)–C(10)	130.4(3)	N(1)–Li(1)–C(13)	105.8(2)
O(1)–Li(1)–C(13)	127.5(3)		
Bond Distances for Compound 3			
Li(1)–N(1)	2.060(10)	Li(2)–N(2)	2.111(9)
Li(1)–C(9)	2.386(10)	Li(2)–C(39)	2.383(10)
Li(1)–C(10)	2.659(10)	Li(2)–C(43)	2.604(10)
Li(1)–O(1)	1.947(9)	Li(2)–O(3)	1.946(9)
Li(1)–O(2)	1.909(9)	Li(2)–O(4)	1.935(9)
Li(1)–plane 1[a]	2.386(9)	Li(2)–plane 2[b]	2.366(9)
Bond Angles for Compound 3			
O(1)–Li(1)–O(2)	99.6(4)	O(3)–Li(2)–O(4)	97.4(4)
O(1)–Li(1)–N(1)	112.8(5)	O(3)–Li(2)–N(2)	111.7(4)
O(2)–Li(1)–N(1)	108.1(4)	O(4)–Li(2)–N(2)	108.5(4)
O(1)–Li(1)–C(9)	126.9(4)	O(3)–Li(2)–C(39)	128.7(4)
O(2)–Li(1)–C(9)	123.8(4)	O(4)–Li(2)–C(39)	124.3(4)
N(1)–Li(1)–C(9)	83.6(3)	N(2)–Li(2)–C(39)	84.1(3)
O(1)–Li(1)–C(10)	96.1(4)	O(3)–Li(2)–C(43)	96.9(3)
O(2)–Li(1)–C(10)	133.2(5)	O(4)–Li(2)–C(43)	136.3(5)
N(1)–Li(1)–C(10)	105.7(4)	N(2)–Li(2)–C(43)	104.0(4)

[a] Plane 1 is the least-squares mean plane calculated for 5 atoms, C(9)–C(13). [b] Plane 2 is the least-squares mean plane calculated for 5 atoms, C(39)–C(43).

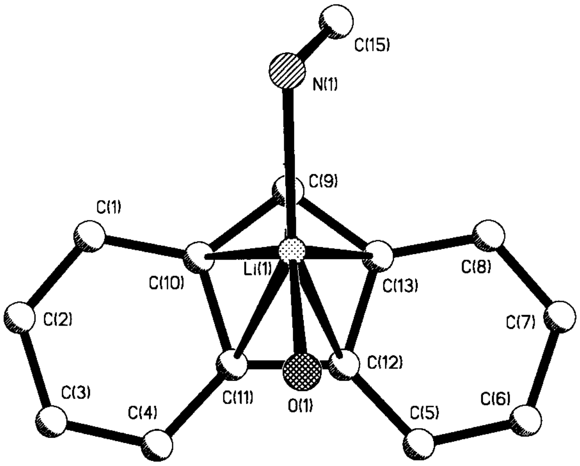

Figure 2. Diagram of **2** showing the projection of Li(1) onto the mean plane of the five-membered ring of the fluorene group. Some atoms have been omitted for clarity.

Compound **3** crystallizes in the monoclinic space group $P2_1/c$ with two independent molecules and a total of eight molecules per unit cell. Figure 3 shows the molecular geometry together with the atom-numbering scheme for both molecules. Selected bond distances and angles are assembled in Table 1. Except for a few insignificant differences, the two independent molecules are identical with regard to the pertinent structural details. The coordination sphere of the lithium atom

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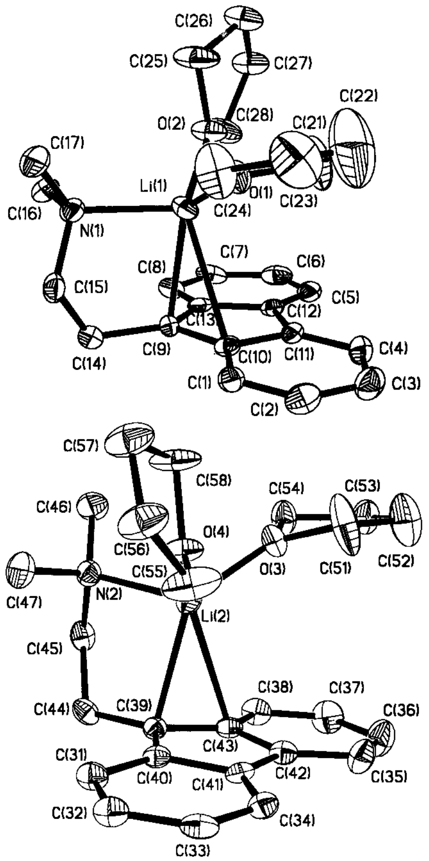

Figure 3. Molecular structure and atom-numbering scheme for the two independent molecules of Fl^{N}Li·2THF **(3)** (thermal ellipsoids are shown at the 30% probability level).

comprises the fluorene group, the nitrogen atom of the pendant arm, and two molecules of THF. The arrangement of ligands around the lithium atom is approximately tetrahedral. The values for the N−Li−O angles range from 108.1(4) to 112.8(5)° but the two THF molecules are somewhat squeezed together with O−Li−O angles of 99.6(4) and 97.4(4)° for molecules 1 and 2, respectively. The Li−N bond distances of 2.060(10) and 2.111(9) Å, as well as the Li−O bond distances which average 1.93(2) Å, fall within the ranges observed in similar compounds *(vide supra)*. The lithium atom is located 2.376(14) Å above the fluorenyl plane (average for both molecules) and is bonded in an η^2 fashion to C(9) and C(10). However, note that the C(9)−Li(1) distance is shorter than that between C(10) and Li(1). This projection onto the plane of the fluorene ring is shown in Figure 4. As in the case of the diethyl ether complex, the geometry around C(9) is planar within experimental error (sum of angles 359.3(8) and 359.7(8)° for molecules 1 and 2, respectively). Once again, there is a slight deviation of the α-carbon atom of the pendant arm from the mean plane of the fluorenyl five-membered ring. However, in this case, the α-carbon is pointed away from the lithium atom: C(14) is located 0.130(9) Å below the mean plane which translates to an angle of 5.0(3)° between this plane and the C(9)−C(14) vector while C(34) lies 0.085(9) Å (3.2(3)°) below the corresponding plane in the other molecule of **3**.

The position of the metal atom relative to the delocalized π-systems of carbanion complexes such as benzyl, fluorenyl, and triphenylmethyl has been the subject of many theoretical and experimental studies. Stucky and co-workers made many early insightful studies of such systems using a combination of molecular orbital calculations and X-ray structural data.[4] In the most common arrangement for all three of the foregoing carbanions, the lithium atom adopts an η^3 allylic geometry by interaction with the benzylic, *ipso*, and *ortho* carbon atoms. This geometry is revealed in the projection onto the aromatic plane of fluorenyllithium bisquinuclidine **(4)**[13] as depicted in Figure 5. The original explanation for these observations was based upon molecular orbital calculations. These showed that the location of the lithium atom and the orientation of the nitrogen atoms maximize the favorable overlap between the vacant p orbital on lithium and the HOMO of the aromatic ring. However, it is now generally recognized that lithium−carbon bonds are primarily ionic and Bushby and Tytko were able to show that the structures could be explained on the basis of electrostatic considerations.[19] Modern methods, in which benzyllithium was modeled as a purely ionic system, give an η^1 structure with lithium bonded exclusively to the benzylic carbon atom.[20] However, high level *ab initio* calculations on benzyllithium correctly predict the observed η^3 arrangement as the lowest energy structure.[20−22]

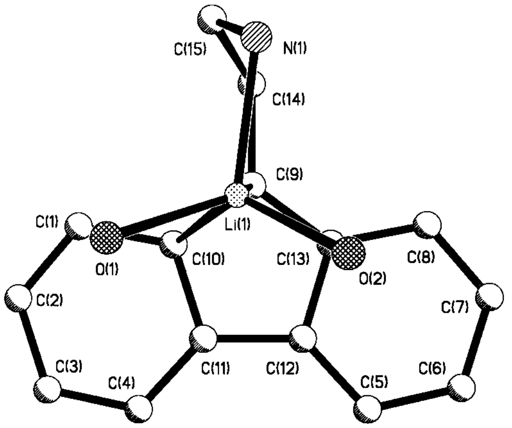

Figure 4. Diagram of **3** showing the projection of Li(1) onto the mean plane of the five-membered ring of the fluorene group. Some atoms have been omitted for clarity.

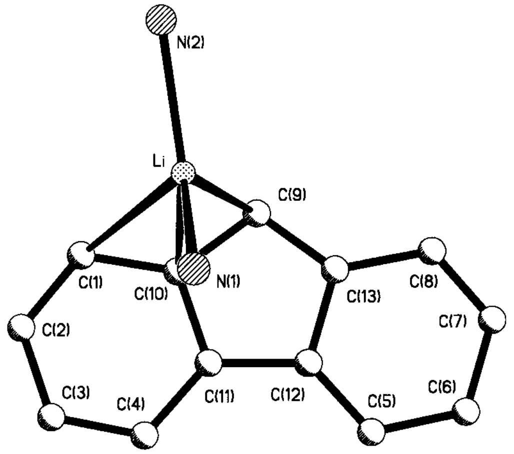

Figure 5. Diagram of fluorenyllithium bisquinuclidine **(4)**[13] showing the projection of Li onto the mean plane of the five-membered ring of the fluorene group. Some atoms have been omitted for clarity.

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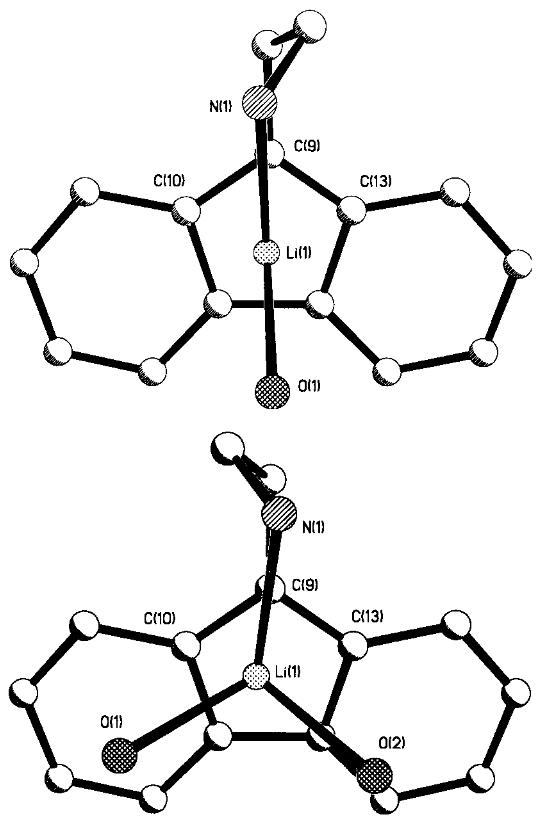

Figure 6. Projection of **2** along the bisector of the N−Li−O angle and projection of **3** along the vector V that makes all V−Li−X angles equal.

In addition to the η^3 structure, organolithium compounds with fluorenyl carbanions show a variety of other bonding arrangements. These range from "naked" fluorenyl anions in which the lithium is in direct contact with only ethylenediamine[23] or tetrahydrofuran[24] molecules to "sandwich" structures where the lithium atoms exhibit η^6 coordination to two six-membered rings and are thus similar to bis(arene)metal complexes.[25−27] Intermediate between these extremes is the structure of bifluorenylbis(lithium TMEDA), in which the lithium atoms bridge the two benzylic carbons.[28] The structures reported here exhibit two additional geometries, one in which the lithium is η^5 bonded **(2)**; in the other compound **(3)**, the lithium is η^2 bonded. In both structures, an interesting similarity is evident which should be considered when discussing organolithium compounds with delocalized π-systems. If the lithium atom in **3** were considered to be sp^3 hybridized with one sp^3 orbital interacting with the nitrogen atom and two sp^3 orbitals interacting with the oxygen atoms, a question arises regarding the orientation of the fourth sp^3 orbital. The idealized orientation of this orbital can, in fact, be calculated by constructing a vector, V, such that all V−Li−X angles are equal. When this vector is projected onto the plane of the five-membered ring, the point of intersection is extremely close (0.16 Å) to the unweighted centroid of the ring. If the same calculations are performed for the diethyl ether complex (assuming the lithium atom is sp^2 hybridized), the third sp^2 orbital is also directed toward the center of the five-membered ring. In fact, the vector that bisects the O−Li−N angle intersects the plane of the five-membered ring only 0.15 Å from the unweighted centroid of the ring. Both of these projections are depicted in Figure 6. In benzyllithium, the potential energy surface is somewhat flat, with various structures only separated by about 1 kcal/mol.[22] It is expected that this should also be true for the fluorenyl carbanions. Thus, while the carbon−lithium bonds are indeed primarily ionic, the potential energy surfaces of these molecules are sufficiently soft that the remaining covalent character is enough to influence the solid-state geometries.

Experimental Section

General Procedures. Unless otherwise noted, all reactions were carried out under a dry, oxygen-free argon atmosphere utilizing standard Schlenk manifold techniques or a Vacuum Atmospheres drybox. All solvents were distilled under nitrogen from sodium−benzophenone immediately prior to use. Unless otherwise noted, reagents were obtained from commercial suppliers and used without further purification. NMR spectra were recorded on a GE QE-300 spectrometer (^{1}H, 300.16 MHz; ^{13}C, 75.48 MHz; ^{7}Li, 116.65 MHz). ^{1}H and ^{13}C chemical shifts are referenced to the solvent and are reported relative to $Si(CH_3)_4$ ($\delta = 0.00$). ^{7}Li chemical shifts are referenced to an external standard (1 M LiCl in D_2O, $\delta = 0.00$). Melting points were obtained in capillaries sealed under argon (1 atm) and are uncorrected. Elemental analyses were performed by Atlantic Microlab, Norcross, GA.

Preparation of 1.[8] Fluorenyllithium[29] (34.4 g, 0.20 mol) was dissolved in 200 mL of THF, and the solution was cooled to −10 °C. To this flask, the 2-(dimethylamino)ethyl chloride freshly liberated[30] from 43.2 g (0.30 mol, 50% excess) of the hydrochloride salt was added over a period of 30 min. The reaction mixture was then allowed to heat at reflux overnight which resulted in the formation of a pale yellow solution and a large amount of white precipitate. The solvent was removed *in vacuo* and extracted with toluene (4 × 100 mL) and filtered through a glass frit covered with diatomaceous earth. Hydrochloric acid (4 N) was added to the filtrate until pH paper turned red. The aqueous layer was separated and the organic layer was washed with additional 1 N HCl (2 × 100 mL). Solid KOH was added to the combined aqueous layers until pH paper turned blue. The solution was extracted with diethyl ether (4 × 100 mL), dried with potassium carbonate, and filtered. The solvent was then removed via rotary evaporation to give **1** as a viscous pale yellow liquid (28.5 g, 61% yield). ^{1}H NMR (C_6D_6): δ 1.99 (s, 6H, Me), 2.00 (q, 2 H, $J = 6.0$ Hz, α CH_2), 2.11 (t, 2 H, $J = 6.0$ Hz, β CH_2), 3.94 (t, 1 H, $J = 6.0$ Hz, H-9), 7.19 (t, 2 H), 7.24 (t, 2 H), 7.38 (d, 2 H, $J = 7.2$ Hz, H-1), 7.62 (d, 2 H, $J = 6.6$ Hz, H-4). ^{13}C{^{1}H} NMR (C_6D_6): δ 31.64 (α CH_2), 45.35 (Me), 45.80 (C-9), 56.26 (β CH_2), 120.15 (C-3), 124.76 (C-1), 127.12 (C-2/4), 127.23 (C-2/4), 141.50 (C-11), 147.89 (C-12).

Preparation of 2. To a solution of **1** (14.0 g, 59 mmol) in 100 mL of diethyl ether was added n-BuLi (37 mL, 1.6 M in hexane) dropwise over a period of 1 h. After being stirred

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overnight, the reaction mixture had turned orange and large amounts of yellow precipitate were present. The solution was filtered onto a large glass frit and washed with hexane (2 × 75 mL). The filter cake was dried under vacuum to give a bright yellow powder which was identified as the monoetherate, **2** (12.13 g, 65% yield). Compound **2** is slightly soluble in diethyl ether and moderately soluble in aromatic solvents. Mp: 116−8 °C (loses Et_2O), 250 °C dec. ^1H NMR (C_6D_6): δ 0.13 (t, J = 7.0 Hz, 6 H, ether Me), 1.46 (s, 6 H, NMe_2), 2.40 (q, J = 7.0 Hz, 4 H, ether CH_2), 2.46 (t, J = 6.2 Hz, 2 H, α CH_2), 3.21 (t, J = 6.2 Hz, 2 H, β CH_2), 7.08 (t, J = 7.3 Hz, 2 H, H-3), 7.40 (t, J = 7.4 Hz, 2H, H-2), 7.57 (d, J = 8.3 Hz, 2 H, H-1), 8.35 (d, J = 7.9 Hz, 2 H, H-4). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 13.70 (ether Me), 23.40 (α CH_2), 45.07 (NMe_2), 60.29 (β CH_2), 66.00 (ether CH_2), 84.94 (C-9), 112.13 (C-3), 115.21 (C-1), 120.69 (C-2/4), 121.25 (C-11), 121.93 (C-2/4), 131.26 (C-10). ^{7}Li NMR (C_6D_6): δ −5.53 ($w_{1/2}$ = 5.0 Hz). $^{13}C\{^1H\}$ NMR (Et_2O): δ 22.92 (α CH_2), 45.26 (NMe_2), 60.39 (β CH_2), 84.14 (C-9), 111.46 (C-3), 114.61 (C-1), 119.73 (C-2/4), 120.26 (C-11), 121.15 (C-2/4), 130.32 (C-10). ^{7}Li NMR (Et_2O): δ −4.74 ($w_{1/2}$ = 3.9 Hz).

Preparation of 3. When THF is added to **2**, the color darkens instantly from yellow to orange. The THF displaces the Et_2O molecule and, upon removal of solvent, the bistetrahydrofuran adduct, **3**, is obtained as yellow-orange crystalline needles in quantitative yield. ^1H NMR (THF-d_8): δ 2.26 (s, 6 H, Me), 2.77 (t, 2 H, J = 6.8 Hz, α CH_2), 3.23 (t, 2 H, J = 6.8 Hz, β CH_2), 6.49 (t, 2 H, J = 6.9 Hz, H-3), 6.90 (t, 2 H, J = 7.4 Hz, H-2), 7.34 (d, 2 H, J = 8.1 Hz, H-1), 7.94 (d, 2 H, J = 7.8 Hz, H-4). $^{13}C\{^1H\}$ NMR (THF-d_8): δ 25.50 (α CH_2), 46.22 (NMe_2), 62.72 (β CH_2), 86.12 (C-9), 109.64 (C-3), 114.21 (C-1), 119.66 (C-2/4), 120.52 (C-2/4), 123.34 (C-11), 135.99 (C-10). ^{7}Li NMR (THF-d_8): δ −2.30 ($w_{1/2}$ = 4.4 Hz).

X-ray Crystallography. Crystals of **2** and **3** were grown from diethyl ether and tetrahydrofuran solutions respectively at −20 °C. A suitable yellow plate of **2** was cut and mounted inside a thin-walled glass capillary and sealed under argon (1 atm), and a suitable yellow-orange needle of **3** was cut, coated with mineral oil, mounted on a thin glass fiber, and placed into a cold nitrogen stream. Data for **2** were collected at 25 °C on an Enraf Nonius CAD4 diffractometer operating in the $2\theta-\theta$ scan mode ($4.2 < 2\theta < 48.0°$). Data for **3** were collected at −100 °C on a Siemens P4 diffractometer operating in the ω scan mode ($4.0 < 2\theta < 47.0°$). In both cases graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å) was utilized. The structures were solved using direct methods and refined by full-matrix least-squares on F^2 using the Siemens SHELXTL PLUS 5.0 (PC) software package.[31] All non-hydrogen atoms were refined with anisotropic thermal parameters in the later stages of refinement. All hydrogen atoms except those of the methyl groups were placed in idealized positions and refined using the riding model with general isotropic temperature factors. The methyl hydrogens were placed by using a difference electron density synthesis to set the initial torsion angle and then refined as a riding-rotating model with general isotropic temperature factors. In the case of **2** the $CH_2CH_2NMe_2$ arm is disordered and the positions for the β CH_2 and both methyl groups were refined with unrestrained anisotropic displacement parameters over two sites with occupation factors of 0.823(10) and 0.177(10). Details of the crystal data and a summary of intensity data collection parameters are given in Table 2.

Table 2. Crystal Data for Fl^{N}Li·Et_2O (2) and Fl^{N}Li·2THF (3)

	2	3
emp formula	$C_{21}H_{28}LiNO$	$C_{25}H_{34}LiNO_3$
fw	317.38	387.47
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/c$
a, Å	10.1826(10)	15.994(2)
b, Å	14.5973(14)	14.574(2)
c, Å	13.391(2)	19.654(4)
β, deg	102.970(8)	103.87(1)
V, Å^3	1939.6(3)	4447.7(12)
Z	4	8
d(calc), g cm^{-3}	1.087	1.157
μ, cm^{-1}	0.65	0.71
cryst size, nm^3	0.56 × 0.47 × 0.28	0.47 × 0.31 × 0.25
tot reflns	5557	7479
ind reflns	3046 [R(int) = 0.0409]	6264 [R(int) = 0.0515]
abs corr	none	none
params	257	536
$R1$ [$I > 2\sigma(I)$]	0.0447	0.0797
w$R2$ (all data)	0.1389	0.1569

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Supporting Information Available: Listings of bond distances, bond angles, atomic coordinates, and thermal parameters and ORTEP diagrams for **2** and **3** (21 pages). Ordering information is given on any current masthead page.

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[31] Sheldrick, G. M. *SHELXTL PC Version 5.0*; Siemens Analytical X-ray Instruments, Inc.: Madison, WI, 1994.