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Mono- and Dilithiation of Primary Amine/Secondary Amine Mixtures: Transamination, Solvation, and Cocomplexation

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Addition of 1 equiv of *N*,*N*,2,2-tetramethylpropanediamine (**4**) to 1 equiv of either lithium dibenzylamide (**1**) or lithium 2,2,6,6-tetramethylpiperidide (**2**) results in the exclusive formation of the primary amide $[\{Me_2NCH_2CMe_2CH_2N(H)Li\}_6]$ (**5**). Compound **5** was determined to be a prismatic hexamer in the solid state, with each lithium being tetracoordinated by binding to three amido anions and one chelating dimethylamino unit. In contrast, when 1 equiv of **4** is added to lithium hexamethyldisilazide (**3**), the sole product isolated from solution was the primary amine solvate $[\{(Me_3Si)_2NLi{\cdot}H_2NCH_2CMe_2CH_2NMe_2\}_2]$ (**6**). Similarly, reaction of 1 equiv of 1,3-diaminopropane with **3** gave the solvate $[\{(Me_3Si)_2NLi{\cdot}H_2NCH_2CH_2CH_2NH_2\}_2]$ (**12**). Crystallographic analyses of **6** and **12** revealed dimeric aggregation, with each amine η^1-bonding to a metal center through the primary amine group. Addition of 1 equiv of Bu^nLi to the amine/amide mixtures resulted in lithiation of the remaining amine to yield the mixed-anion aggregates [(**1**.**5**)$_2$] (**9**), [(**2**.**5**)$_2$] (**10**), and [(**3**.**5**)$_2$] (**11**). These compounds adopt similar solid-state structures which can be regarded as four-rung ladders formed by the association of two mixed-anion heterodimers. Each metal center of the ladders is three-coordinate, either by bridging three amido nitrogens or by coordinating to two amido nitrogens and to one chelating dimethylamino unit.

Introduction

An ever-increasing number of publications concerning the action and structure of lithium amides have appeared over recent years.[1] The representation of lithium amide bases as simple anions, $R_2N^-Li^+$, with no regard for the metal is far too simplistic, since oligomers, $[(R_2NLi)_n]$, are almost always formed.[2] Studies in solution and in the solid state reveal a multitude of possible aggregates for lithium amides, including monomers, dimers, trimers, tetramers, hexamers, and higher oligomers.[3] In addition, lithium amide bases are widely used as selective proton abstractors and convenient anion exchange reagents.[4] Their ease of use and high reactivity have led to them becoming one of the most regularly used tools of the synthetic chemist. In practice, reagents derived from lithium secondary amides, $[(R_2NLi)_n]$, have mainly been the focus of study. Bases such as lithium dibenzylamide (**1**), lithium 2,2,6,6-tetramethylpiperidide (**2**), and lithium hexamethyldisilazide (**3**) have been used. In contrast, lithium primary amides, $[\{RN(H)Li\}_n]$, have received relatively little attention as bases, although a variety of these compounds have been structurally characterized.[5] However, there has been some recent interest in the utility of

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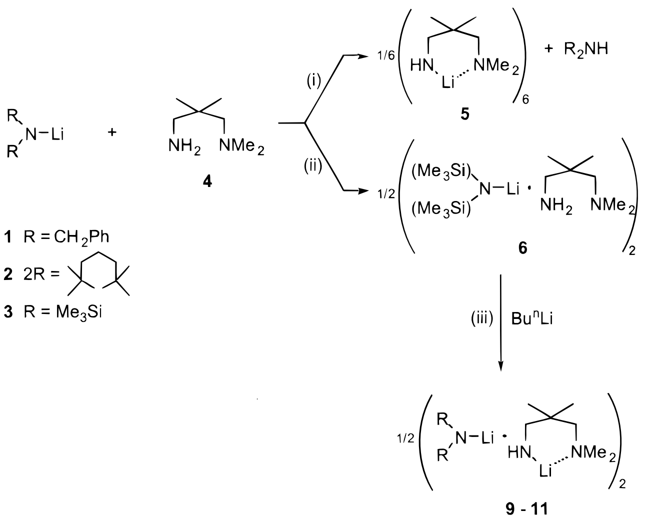
Scheme 1



lithiated primary amides in asymmetric synthesis.[6] We have also recently reported a synthetic and theoretical investigation into the structure−activity relationship of the reaction between 1 equiv of Bu^nLi and 1:1 mixtures of alkyl primary and secondary amines.[7] This study showed that lithiation of simple alkyl primary amines is favored over alkyl secondary amines as a consequence of electrostatic and steric factors. We now report on the reactivity of the difunctional amine *N*,*N*,2,2-tetramethylpropanediamine (**4**) with the lithium amide bases **1**−**3**. In addition, the effect of reacting 1 equiv of Bu^nLi with these amine/amide mixtures is detailed.

Reactivity Studies

In all instances the compounds isolated were independent of the order of addition of the reagents. For example, mixing the primary and secondary amines followed by addition of 1 equiv of Bu^nLi or preformation of one lithium amide followed by addition of the second amine resulted in the isolation of identical products. This indicates that it is the thermodynamic product of each reaction which is obtained. For simplicity and consistency the reactions will be described in terms of adding the primary amines to solutions of the preformed lithium secondary amides. All the reactions described were carried out in hexane or pentane solution, in the absence of polar donor solvents.

Addition of 1 equiv of primary amine **4** to the secondary amides **1** and **2** resulted in the exclusive precipitation of the anion exchange product $[Me_2NCH_2CMe_2CH_2N(H)Li]$ (**5**). In direct contrast, reaction of 1 equiv of **4** with the silyl amide **3** resulted in the isolation of the solvate $[(Me_3Si)_2NLi{\cdot}H_2NCH_2CMe_2CH_2NMe_2]$ (**6**). These reactions are illustrated as routes i and ii in Scheme 1. The results of the reactions of **1** and **2** with **4** are in accord with those studied previously, showing a preference for primary amine lithiation.[7] However, identification of the solvate **6** demonstrates an alternative reaction pathway: solvation of the lithium secondary amide by a primary amine. Collum has recently delineated the solution equilibria for **3** solvated by a variety of primary, secondary, and tertiary amines.[8] In all instances studied, monofunctional amines were found to solvate **3** with no evidence for transamination. In contrast, when the potentially chelating ligand *N*,*N*-dimethylethylenediamine (**7**) is added to pentane/toluene solutions of **3**, a highly complex series of aggregation equilibria is established, the position of which is dependent on the relative stoichiometries of the amine and amide present.[9] In summary, mixed-anion aggregates between **3** and the metalated primary amide $[Me_2NCH_2CH_2N(H)Li]$ (**8**) predominate when 0.5 equiv of **7** is present. When the primary amine concentration is increased to >0.75 equiv, solvates of **3** with the amine **7** are established, and these become the sole species present when higher concentrations of **7** are introduced.

The difference in reactivities of **1** and **2** compared to **3** (anion exchange and solvation, respectively) is, in part, a consequence of the large difference in basicities between the alkyl amides and the silyl amide. Acidity measurements by Fraser place the pK_a values of the amines hexamethyldisilazane and 2,2,6,6-tetramethylpiperidine at 25.8 and 37.3, respectively, as determined by the equilibrium in eq 1.[10] The unusually low

$$R_2NH + LiR \rightleftharpoons R_2NLi + RH \qquad (1)$$

reactivity of the silyl amide has also been demonstrated by the isolation and structural characterization of a stable methyl phosphane oxide as a Lewis base adduct of **3**.[11]

Addition of 1 equiv of Bu^nLi to the amine/amide reaction mixtures described above resulted in the deprotonation of the remaining amine and the formation of the mixed-anion aggregates [**1**.**5**] (**9**), [**2**.**5**] (**10**), and [**3**.**5**] (**11**), as illustrated in route iii of Scheme 1. Although mixed-anion aggregates of lithium compounds have been widely studied, no reports of structurally characterized aggregates between two different amides have appeared in the literature to date.[2]

Crystallographic Studies

The primary amide **5** crystallizes as two independent cyclic ladder hexamers in a trigonal unit cell. Figure 1 shows one of the two molecules, and the discussion of bond lengths and angles of **5** will be for averaged values

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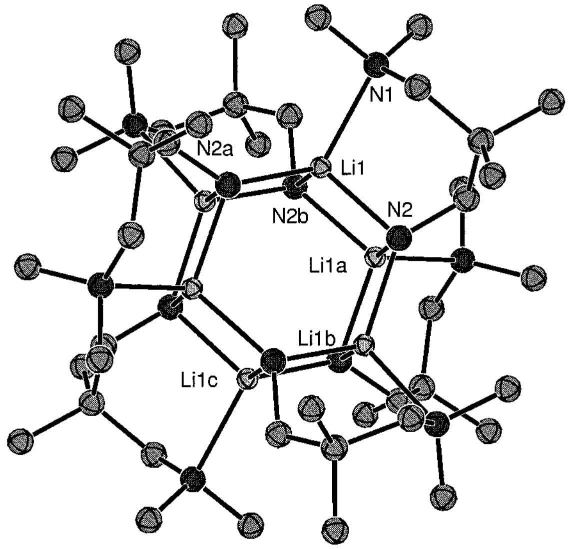

Figure 1. Crystal structure of one molecule of **5** with hydrogen atoms omitted for clarity. Key bond lengths (Å) and angles (deg): Li(1)–N(1) = 2.227(6), Li(1)–N(2) = 2.051(6), Li(1)–N(2a) = 2.098(6), Li(1)–N(2b) = 2.061(6); N(2)–Li(1)–N(2a) = 109.4(3), N(2)–Li(1)–N(2b) = 109.0(3), N(1)–Li(1)–N(2) = 98.8(2), N(1)–Li(1)–N(2a) = 112.8(3), N(1)–Li(1)–N(2b) = 119.2(3), N(2a)–Li(1)–N(2b) = 107.1(3), Li(1)–N(2)–Li(1a) = 72.4(2), Li(1)–N(2)–Li(1b) = 111.6(3), Li(1a)–N(2)–Li(1b) = 71.5(2).

over the two structures. Prismatic hexamers have been documented for lithium carbanions, alkoxides, enolates, and imides; however, **5** is a rare example of a hexameric primary amidolithium.[12] The crystal structure of **5** is in agreement with solution studies of compound **8**, which indicated the presence of a single highly symmetric aggregate.[9] Prismatic lithium amide structures closely related to **5** include the primary amides $[\{(Me_3Si)_2NN(H)Li\}_6]$,[12d] $[\{Bu^t{}_2MeSiN(H)N(H)Li\}_6]$,[12b] and $[\{Bu^tN(H)Li\}_8]$[5j] and the secondary amides $[\{EtN(H)N(Et)Li\}_6]$[12d] and $[\{(CH_2)_6NLi\}_6]$.[13] In addition, the primary amide $[\{H_2NCH_2CH_2N(H)Li\}_\infty]$ forms an extended one-dimensional ladder structure, with the terminal NH_2 groups providing chelation to the metal centers.[14] In **5** each lithium atom is four-coordinate, through bonding to three amido nitrogens and one chelating dimethylamino unit. This results in a near-tetrahedral geometry around each lithium (average being 109.4°).

Each of the six-membered rings of the hexamer has alternating long and short Li–N bonds (at 2.05 and 2.11 Å, respectively), with intermediate Li–N bond lengths connecting the two rings (at 2.06 Å). This structural motif has been observed previously in similar prismatic lithium compounds.[5j,13,15]

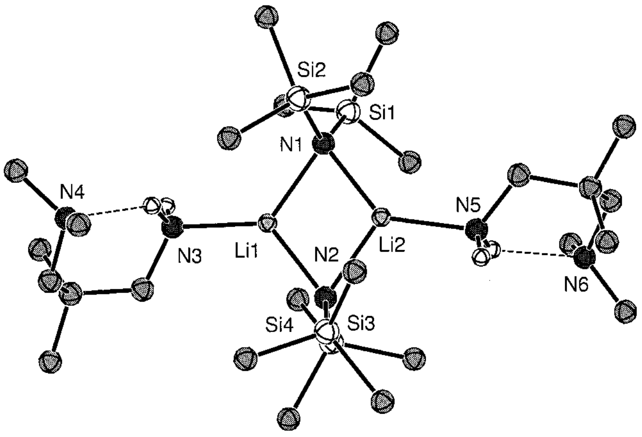

Figure 2. Crystal structure of **6** with hydrogen atoms (except those of the amine) omitted for clarity. Key bond lengths (Å) and angles (deg): Li(1)–N(1) = 2.060(9), Li(1)–N(2) = 2.029(10), Li(1)–N(3) = 2.065(8), Li(2)–N(5) = 2.048(8), Li(2)–N(1) = 2.009(10), Li(2)–N(2) = 2.051(10); N(1)–Li(1)–N(3) = 127.6(5), N(2)–Li(1)–N(3) = 127.1(5), N(1)–Li(1)–N(2) = 105.2(3), N(1)–Li(2)–N(5) = 136.5(5), N(2)–Li(2)–N(5) = 117.2(5), N(1)–Li(2)–N(2) = 106.3(3), Li(1)–N(1)–Li(2) = 74.3(4), Li(1)–N(2)–Li(2) = 74.1(4), Si(1)–N(1)–Si(2) = 123.0(3), Si(3)–N(2)–Si(4) = 121.9(3).

Solvate **6** was found to adopt a dimeric framework with the Lewis bases complexing the metals through the primary amine function (Figure 2). Only one other example of a primary amine solvated lithium secondary amide has been reported, that of a highly stabilized heterocyclic thioamide.[16] Although dimers are commonly found for solvates of **3**, it is worth noting that amine **4** only utilizes one of its two basic amino functions to bind to the metal. In contrast, *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) forms a chelated monomer with **3**.[17] Steric crowding as a consequence of complexation of a dimethylamino unit in the dimer and the chelate effect combine to favor monomeric aggregation of **3** in the presence of TMEDA.[18] By binding to the metal through the primary amine group, ligand **4** allows the retention of the two Li–N(amide) linkages in **6** without destabilizing the dimeric framework by steric congestion. This illustrates the delicate balance between sterics, solvation, and chelation which determines the relative stability of the various aggregation states possible in such systems.[9,17]

A complex related to **6** was prepared by the addition of 1 equiv of 1,3-diaminopropane to **3**. The amine-solvated complex $[(Me_3Si)_2NLi{\cdot}H_2NCH_2CH_2CH_2NH_2]$ (**12**) also adopts a disolvated dimeric arrangement in the solid state, as can be seen from Figure 3. Analysis of the structural details between **6** and **12** show little variation. Once again, only one of the two amino groups is involved in bonding to the metal centers. In both **6** and **12** relatively short Li–N(dative) bonds are present (averaged values being 2.06 and 2.07 Å, respectively), compared to the tertiary amine disolvated dimer $[\{(Me_3Si)_2NLi{\cdot}Me_2NCH_2Ph\}_2]$ (average being 2.22 Å), which

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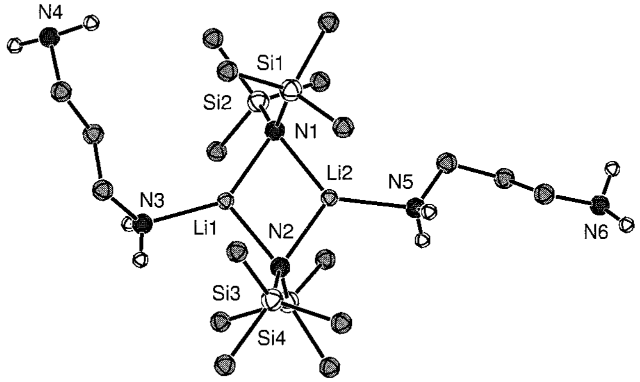

Figure 3. Crystal structure of **12** with hydrogen atoms (except those of the amine) omitted for clarity. Key bond lengths (Å) and angles (deg): Li(1)−N(1) = 2.058(11), Li(1)−N(2) = 2.048(11), Li(1)−N(3) = 2.061(11), Li(2)−N(1) = 2.073(10), Li(2)−N(2) = 2.029(12), Li(2)−N(5) = 2.078(11); N(1)−Li(1)−N(3) = 140.4(6), N(2)−Li(1)−N(3) = 114.2(5), N(1)−Li(1)−N(2) = 105.4(5), N(1)−Li(2)−N(5) = 135.7(6), N(2)−Li(2)−N(5) = 118.8(5), N(1)−Li(2)−N(2) = 105.6(5), Li(1)−N(1)−Li(2) = 73.9(4), Li(1)−N(2)−Li(2) = 75.1(4), Si(1)−N(1)−Si(2) = 121.1(3), Si(3)−N(2)−Si(4) = 123.1(3).

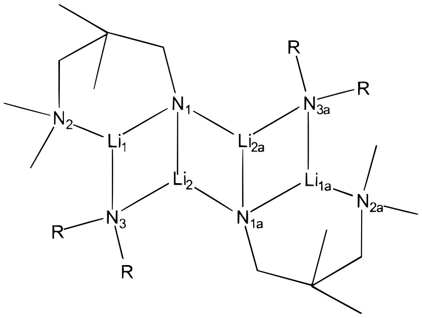

Figure 4. General labeling scheme for the mixed-anion aggregates **9**−**11**.

has dimethylamino units complexing the dimeric core. This supports the hypothesis that steric congestion in combination with the chelate effect is the driving force for destabilization of dimers of **3**. The enhanced stability of the lithiated silyl amide **3** with respect to alkyl amides **1** and **2** is highlighted by the fact that in **6** and **12** each metal is only three-coordinate, whereas tetracoordination is achieved for the metal centers in **5**; i.e., in **6** and **12** solvation is preferred despite the increase in coordination number achieved by transamination to **5**.

Another feature of interest in comparing **6** and **12** is the position adopted by the primary amine ligands. In **6** the terminal dimethylamine units twist around to interact with a hydrogen of each primary amine, with an average $H-NMe_2$ distance of 2.28 Å. No such hydrogen bonding is found in the structure of **12**, where the terminal and coordinated NH_2 groups are clearly separated.

Three complexes were crystallographically characterized as aggregates between **5** and the lithium secondary amides **1**−**3**. These studies confirmed that each compound consists of a pair of lithium primary/secondary amide heterodimers. Figure 4 outlines the general framework of the structures, and for simplicity the labeling of the atoms in the text is with respect to this figure. Each of the individual crystal structures is shown in Figures 5−7 with key bond lengths and angles also given. Compounds **10** and **11** each crystallize as two independent but almost identical molecules in their respective unit cells. Discussion of these structures will be for averaged bond lengths and angles of the two molecules.

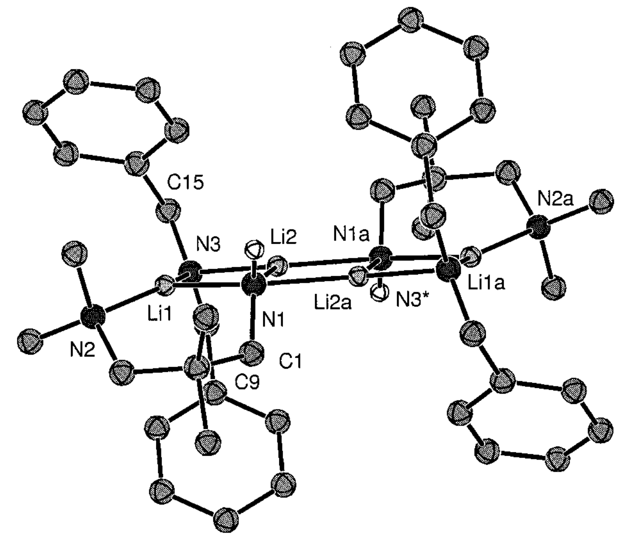

Figure 5. Crystal structure of **9** with hydrogen atoms (except those of the amide) omitted for clarity. Key bond lengths (Å) and angles (deg): Li(1)−N(1) = 2.023(5), Li(1)−N(2) = 2.048(5), Li(1)−N(3) = 1.962(5), Li(2)−N(1) = 1.994(5), Li(2)−N(3) = 2.001(6), Li(2)−N(1a) = 2.036(5); N(1)−Li(1)−N(3) = 107.4(2), N(1)−Li(1)−N(2) = 101.8(2), N(2)−Li(1)−N(3) = 149.4(3), N(1)−Li(2)−N(3) = 107.0(2), N(1)−Li(2)−N(1a) = 109.2(2), N(3)−Li(2)−N(1a) = 143.3(3), Li(1)−N(1)−Li(2a) = 142.8(2), Li(1)−N(1)−Li(2) = 72.1(2), Li(2)−N(1)−Li(2a) = 70.8(2), Li(1)−N(3)−Li(2) = 73.2(2), C(8)−N(3)−C(15) = 110.5(2).

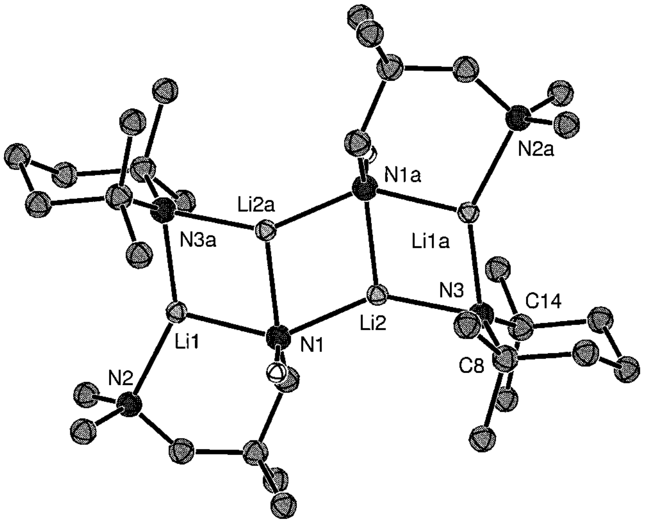

Figure 6. Crystal structure of one molecule of **10** with hydrogen atoms (except those of the amide) omitted for clarity. Key bond lengths (Å) and angles (deg): Li(1)−N(1) = 1.997(8), Li(1)−N(2) = 2.063(9), Li(1)−N(3a) = 1.962(8), Li(2)−N(1) = 2.039(8), Li(2)−N(1a) = 2.044(8), Li(2)−N(3) = 1.987(8; N(1)−Li(1)−N(3a) = 109.0(4), N(2)−Li(1)−N(3a) = 145.4(4), N(1)−Li(1)−N(2) = 105.5(4), N(1)−Li(2)−N(3) = 146.1(4), N(1)−Li(2)−N(1a) = 107.3(3), N(3)−Li(2)−N(1a) = 106.2(4), Li(1)−N(1)−Li(2) = 143.6(4), Li(1)−N(1)−Li(2a) = 71.4(3), Li(2)−N(1)−Li(2a) = 72.7(3), Li(1a)−N(3)−Li(2) = 73.3(3), C(8)−N(3)−C(14) = 115.4(3).

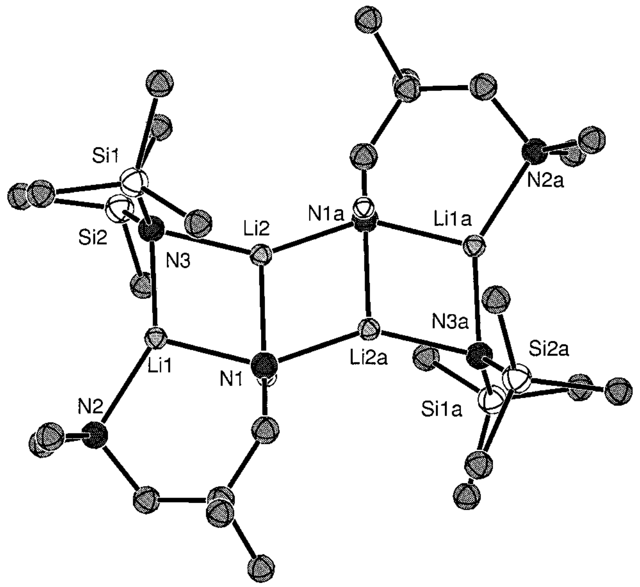

Figure 7. Crystal structure of one molecule of **11** with hydrogen atoms (except those of the amide) omitted for clarity. Key bond lengths (Å) and angles (deg): Li(1)−N(1) = 2.012(10), Li(1)−N(2) = 2.033(10), Li(1)−N(3) = 1.974(10), Li(2)−N(1) = 2.024(10), Li(2)−N(3) = 2.023(9), Li(2)−N(1a) = 2.012(10); N(1)−Li(1)−N(3) = 106.9(5), N(1)−Li(1)−N(2) = 107.8(5), N(2)−Li(1)−N(3) = 145.1(5), N(1)−Li(2)−N(3) = 104.6(4), N(1)−Li(2)−N(1a) = 108.6(4), N(3)−Li(2)−N(1a) = 146.7(5), Li(1)−N(1)−Li(2) = 73.5(4), Li(1)−N(1)−Li(2a) = 143.8(5), Li(2)−N(1)−Li(2a) = 71.4(4), Li(1)−N(3)−Li(2) = 74.3(4), Si(1)−N(3)−Si(2) = 127.5(3).

The structures of **9**−**11** can be viewed as four-rung ladders, with Li(1)−N(3), Li(2)−N(1), and their symmetry equivalents representing the rungs. This mode of aggregation was observed by Collum for solutions containing **3** and **8**.[9] Similar ladders have been documented in "flat", "curved" or "step" arrangements.[19] Each of the structures outlined here have an essentially linear, flat, ladder core. The primary amido hydrogen atoms on the two ligands lie *trans* with respect to each other, which allows the ladder core to remain almost planar. The central Li(2)N(1)Li(2a)N(1a) ring is strictly planar, with the terminal lithiums being 0.103, 0.194, and 0.251 Å out of the ladder plane for **9**−**11**, respectively. Similarly, the terminal nitrogen atoms deviate by 0.205, 0.204, and 0.533 Å for **9**−**11**, respectively, from this plane (with a dihedral angle of only 4.4° for **9**, 6.0° for **10**, and 5.7° for **11** between the central and outer rings). In each case the ladders do not have linear sides but are bent, with the angles Li(1)−N(1)−Li(2a) and N(3)−Li(2)−N(1a) being similar in the three structures, averaging 143.2 and 145.3°, respectively.

In **10** and **11** the secondary amido NR_2 planes are almost perfectly perpendicular to the plane of the ladder core (being 88.6° for **10** and 89.2° for **11**). However, in **9** a reduced angle of 76.9° is found between the $N(CH_2)_2$ plane of the dibenzyl unit and the ladder core. This may be explained in terms of the relative flexibilities of the secondary amido ligands. **10** and **11** have no significantly short carbon to lithium distances. In contrast, **9** has the relatively short contact distance of 2.71 Å between Li(2) and one of the benzylic CH_2 units, C(8). Also, the terminal lithium atom Li(1) has bond distances of 2.94 and 2.87 Å to the benzylic carbon C(15) and the *ipso* carbon C(16), respectively. A profusion of similar contacts were observed in $[\{(PhCH_2)_2NLi\}_3]$.[20] Hence, the tilting of the NR_2 plane is likely due to weak agostic Li···C(H) interactions.[21]

Preparation of the mixed-anion complexes is accomplished in the absence of polar solvent. The bulk of the secondary amide bases, coupled with the internal chelation of the tertiary dimethylamino group of **5**, leads to the complexes being highly soluble in hydrocarbon media. A six-membered ring is formed at each side of the ladder by the internally chelating NMe_2 unit. A significant structural difference among **9**−**11** is the dihedral angle between the mean planes of the ladder core and the six-membered chelate ring. These dihedral angles range from 29.9° for **9** to 15.2° for **10** and to 10.9° for **11**. The large dihedral angle quoted for **9** supports the contention that the terminal lithium atoms of the ladder interact with the aromatic π system of a phenyl ring and, thus, force the chelating sidearm further out of the ladder plane.

Each lithium center in **9**−**11** is formally three-coordinate, but two distinct types of metal environments are present. The central lithiums, Li(2) and Li(2a), are bound to two primary amido nitrogens and a single secondary nitrogen, while the terminal lithium atoms, Li(1) and Li(1a), are surrounded by nitrogens from a primary, a secondary, and a tertiary unit. All the lithium atoms lie in pseudo-trigonal-planar geometry. Also, both the central and outer $(LiN)_2$ rings of the complexes are rhombohedral, with averaged angles at the lithiums being 107.8, 107.9, and 107.0° for **9**−**11**, respectively. More acute angles are found for the internal ring nitrogens, with averaged angles of 72.0, 72.2, and 72.6° for **9**−**11**, respectively.

In summary, we have reported the reactions of (dialkylamido)-, (dibenzylamido)-, and (disilylamido)lithium compounds with a potentially chelating primary amine. Two reaction pathways have been elucidated: (i) transamination to give a primary amide and (ii) solvation of the secondary amide by primary amine. The presence of the silyl groups greatly stabilizes the lithium amide **3** and results in solvation being preferred over transamination. Addition of a second equivalent of Bu^nLi to the amine/amide mixtures results in the formation of mixed-anion aggregates. A common structural ar-

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rangement is found for each of these complexes, association of two heterodimers giving four-rung ladders.

Experimental Section

Reagents and Purification. All chemicals are commercially available from Aldrich. The amines were distilled from CaH_2 and stored over 4 Å molecular sieves prior to use. All solvents were distilled from Na/benzophenone ketyl under nitrogen and used directly from the still. Exact concentrations of Bu^nLi in pentane (~2 M) were determined by titration with 3,5-dimethoxybenzyl alcohol. ^6Li metal was purchased from Martin Marietta Energy Systems Inc., operating contractor for Oak Ridge National Laboratory. The synthesis of $[^6Li]Bu^nLi$ was carried out by literature methods.[22] Schlenk-line and inert-atmosphere techniques were used for the preparation of the air- and moisture-sensitive materials.[23] Solid samples were manipulated in an argon-filled Vacuum Atmospheres HE-43-2 drybox fitted with a VAC HE-493 recirculating system. Full analysis of compounds **6** and **12** proved problematic due to rapid decomposition on isolation. As stated in the text, the products isolated from the reactions involving more than one amine were independent of the order of addition of the reagents. For brevity the experimental procedure only details the addition of Bu^nLi to mixtures of the amines.

NMR Spectroscopic Analyses. Standard ^1H, ^{13}C, and ^6Li NMR spectra were run on a Bruker AM400 spectrometer operating at 400.14, 100.61, and 58.88 MHz, respectively. All samples were run in d_8-toluene solution (Cambridge Isotope Laboratories) with ^1H and ^{13}C spectra referenced to the solvent. ^6Li spectra were referenced externally to a 0.3 M solution of $[^6Li]LiCl$ in d_4-methanol at the temperature each sample was run. NMR spectroscopic analyses are consistent with one major species being present in solutions of the mixed-anion compounds **9**−**11**.[9] Only the key signals were assigned for each of the complexes.

X-ray Crystallography. Suitable crystals were mounted in an oil drop directly from the crystallization vessels to the diffractometer, under a stream of nitrogen gas at −60 °C. Data were collected on a Siemens P4 X-ray crystallographic system fitted with a LT-2 low-temperature device. The structures were solved by direct methods using SHELXL-90. All atoms are refined isotropically with the exception of the hydrogens (fitted in idealized positions), which were allowed to ride the atoms they were attached to. Full-matrix least-squares refinement on F^2 was completed using SHELXL-93.

Crystal data for **5**: $C_{21}H_{52}Li_3N_6$, $M_w = 408.5$, trigonal, $P\bar{3}$, $a = 20.923(4)$ Å, $b = 20.923(4)$ Å, $c = 10.806(5)$ Å, $V = 4097$ Å^3, $Z = 6$, $\rho_{calcd} = 0.993$ Mg/m^3, $T = -78$ °C, $2\theta_{max} = 50°$, 2758 reflections collected, 2738 independent reflections, 2735 reflections used in the refinement, $R1 = 0.0651$, $wR2 = 0.1915$, $GOF = 0.884$.

Crystal data for **6**: $C_{26}H_{70}Li_2N_6Si_4$, $M_w = 593.1$, monoclinic, $P2_1/c$, $a = 16.537(2)$ Å, $b = 22.085(2)$ Å, $c = 11.477(2)$ Å, $V = 4075$ Å^3, $Z = 4$, $\rho_{calcd} = 0.967$ Mg/m^3, $T = -78$ °C, $2\theta_{max} = 47°$, 3520 reflections collected, 3175 independent reflections, 3172 reflections used in the refinement, $R1 = 0.0441$, $wR2 = 0.1241$, $GOF = 0.840$.

Crystal data for **9**: $C_{21}H_{31}Li_2N_3$, $M_w = 339.4$, monoclinic, $P2_1/n$, $a = 10.0220(10)$ Å, $b = 16.296(3)$ Å, $c = 12.583(2)$ Å, $\beta = 90.45°$, $V = 2080$ Å^3, $Z = 4$, $\rho_{calcd} = 1.084$ Mg/m^3, $T = -80$ °C, $2\theta_{max} = 48°$, 4203 reflections collected, 3270 independent reflections, 3270 reflections used in the refinement, $R1 = 0.0664$, $wR2 = 0.2105$, $GOF = 1.050$.

Crystal data for **10**: $C_{32}H_{70}Li_4N_6$, $M_w = 566.7$, monoclinic, $P2_1/c$, $a = 17.944(5)$ Å, $b = 9.691(2)$ Å, $c = 22.455(4)$ Å, $\beta = 102.26(2)°$, $V = 3816$ Å^3, $Z = 4$, $\rho_{calcd} = 0.986$ Mg/m^3, $T = -80$ °C, $2\theta_{max} = 45°$, 6342 reflections collected, 4994 independent reflections, 4992 reflections used in the refinement, $R1 = 0.0848$, $wR2 = 0.2559$, $GOF = 0.907$.

Crystal data for **11**: $C_{26}H_{70}Li_4N_6Si_4$, $M_w = 607.0$, triclinic, $P\bar{1}$, $a = 9.307(2)$ Å, $b = 12.670(3)$ Å, $c = 18.075(5)$ Å, $\alpha = 98.44°$, $\beta = 103.16°$, $\gamma = 105.40°$, $V = 2106$ Å^3, $Z = 2$, $\rho_{calcd} = 0.957$ Mg/m^3, $T = -60$ °C, $2\theta_{max} = 47°$, 6601 reflections collected, 6158 independent reflections, 6156 reflections used in the refinement, $R1 = 0.0882$, $wR2 = 0.2688$, $GOF = 0.974$.

Crystal data for **12**: $C_{18}H_{56}Li_2N_6Si_4$, $M_w = 482.9$, monoclinic, Cc, $a = 10.2050(10)$ Å, $b = 38.024(4)$ Å, $c = 9.1270(10)$ Å, $\beta = 115.83°$, $V = 3188$ Å^3, $Z = 4$, $\rho_{calcd} = 1.006$ Mg/m^3, $T = -60$ °C, $2\theta_{max} = 50°$, 3311 reflections collected, 3211 independent reflections, 3210 reflections used in the refinement, $R1 = 0.0523$, $wR2 = 0.1390$, $GOF = 0.989$.

Preparation of $[\{Me_2NCH_2CMe_2CH_2N(H)Li\}_6]$ (5). This complex was originally prepared by the reaction of Bu^nLi (1 mmol in pentane) with a 0 °C chilled solution of diisopropylamine (1 mmol) in 3 mL of pentane, followed by addition of **4** (1 mmol). The mixture was stirred for 15 min and the clear colorless solution cooled to −50 °C. After 12 h, crystals of **5** were deposited. In this sequence lithium diisopropylamide is prepared first, which then reacts with the primary amine to give the anion exchange product. Direct lithiation of **4** (1 mmol) in 2 mL of pentane by Bu^nLi (1 mmol in pentane) precipitates **5**, which was used for analysis. Mp: 148−150 °C. IR (Nujol mull): 2860 s, 1591 w, 1460 s, 1377 m, 1239 s, 1184 w, 1154 w, 1040 s, 932 w, 884 m, 824 s, 761 m, 663 m. ^1H NMR: δ −1.48, t, NH; δ 0.98, s, C−CH_3; δ 2.12, s, CH_2; δ 2.27, s, N−CH_3; δ 3.13, d, CH_2. ^{13}C NMR: δ 28.19, C−CH$_3$; δ 38.04, C−CH$_3$; δ 47.89, N−CH$_3$; δ 57.75, CH$_2$; δ 69.37, CH$_2$. ^6Li NMR: +20 °C, δ 1.02; −80 °C, δ 0.81.

Preparation of $[(Me_3Si)_2NLi\cdot H_2NCH_2CMe_2CH_2NMe_2]$ (6). Bu^nLi (1 mmol in pentane) was added dropwise to a 0 °C chilled solution of hexamethyldisilazane (1 mmol) and **4** (1 mmol) in 4 mL of pentane. The solution was stirred for 2 h and then cooled to −78 °C for 24 h. After this time crystals of **6** were deposited. Only X-ray analysis proved possible, due to difficulties in isolating the sample. However, the synthesis of **6** proved reproducible by determining the unit cell parameters of several batches of crystals.

Preparation of $[\{(PhCH_2)_2NLi\}\cdot 2\{Me_2NCH_2CMe_2CH_2N(H)Li\}]$ (9). Dibenzylamine (1 mmol) and **4** (1 mmol) were mixed with 2 mL of toluene and cooled to 0 °C. Bu^nLi (2 mmol in pentane) was dripped into the reaction flask over a period of 2 min. The red, cloudy mixture was stirred for 15 min at room temperature. Gentle warming and addition of 5 mL of toluene gave complete dissolution, leaving a deep red solution. Good-quality crystals were grown over a 12 h period at 20 °C. Mp: 153−154 °C. IR (Nujol mull): 3268 w, 2913 s, 2750 m, 2674 m, 1941 w, 1868 w, 1802 m, 1596 w, 1459 s, 1377 s, 1299 m, 1184 w, 1098 m, 1028 s, 991 m, 906 m, 840 m, 802 w, 745 s, 701 s. ^1H NMR: δ −1.88, t, NH; δ 0.85, s, C−CH_3; δ 1.87, s, CH_2; δ 1.96, s, N−CH_3; δ 2.95, d, CH_2; δ 4.32, s, Ph−CH_2. ^{13}C NMR: δ 27.12, C−CH$_3$; δ 37.76, C−CH$_3$; δ 47.84, N−CH$_3$; δ 58.03, CH$_2$; δ 63.80, Ph−CH$_2$; δ 70.95, CH$_2$. ^6Li NMR: +20 °C, δ 1.77; −80 °C, δ 1.35, 1.54, 1.93, 2.13.

Preparation of $[\{Me_2C(CH_2)_3CMe_2NLi\}\cdot 2\{Me_2NCH_2CMe_2CH_2N(H)Li\}]$ (10). 2,2,6,6-Tetramethylpiperidine (1 mmol) and **4** (1 mmol) were mixed in 2 mL of pentane and cooled to 0 °C. Bu^nLi (2 mmol in pentane) was dripped into the reaction flask over a period of 2 min. The clear colorless solution was stirred for 15 min at 0 °C and then cooled to −40 °C. After 12 h crystals of **10** were formed. Mp: 166 °C. IR (Nujol mull): 2852 s, 1583 m, 1461 s, 1376 s, 1304 w, 1248 m, 1138 w, 1042 m, 1017 m, 892 w, 845 m, 723 m. ^1H NMR: δ −1.94, t, NH; δ 1.05, s, C−CH_3; δ 1.26, s, CH_3 (×4); δ 1.90, s, CH_2; δ 1.99, s, N−CH_3; δ 3.05, d, CH_2. ^{13}C NMR: δ 28.00, C−CH$_3$; δ 36.62, CH$_3$ (×4); δ 37.71, C−CH$_3$; δ 48.09, N−CH$_3$;

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δ 56.88, $C\mathrm{H}_2$; δ 69.92, $C\mathrm{H}_2$. ^{6}Li NMR: +20 °C, δ 2.28, 2.57; −80 °C, δ 2.21, 2.69.

Preparation of [$\{(\mathrm{Me_2Si})_2\mathrm{NLi}\}\cdot 2\{\mathrm{Me_2NCH_2CMe_2CH_2N(H)Li}\}$] (11). HMDS (1 mmol) and **4** (1 mmol) were mixed with 2 mL of pentane and cooled to 0 °C. Bu^{n}Li (2 mmol in pentane) was dripped into the reaction flask over a period of 2 min. The clear colorless solution was stirred for 15 min at 0 °C and then placed at −50 °C. After 12 h crystals of **11** were formed. Mp: 193−195 °C. IR (Nujol mull): 3258 m, 2921 s, 1597 w, 1459 s, 1377 s, 1248 w, 1172 w, 1152 w, 1060 s, 1020 m, 978 w, 932 w, 844 m, 772 w, 722 m. ^{1}H NMR: δ −1.88, t, $\mathrm{N}H$; δ 0.26, s, $\mathrm{Si{-}C}H_3$; δ 0.85, s, $\mathrm{C{-}C}H_3$; δ 1.87, s, $\mathrm{C}H_2$; δ 1.96, s, $\mathrm{N{-}C}H_3$; δ 2.95, d, $\mathrm{C}H_2$. ^{13}C NMR: δ 5.88, $\mathrm{Si{-}}C\mathrm{H_3}$; δ 27.51, $\mathrm{C{-}}C\mathrm{H_3}$; δ 37.86, $C\mathrm{{-}CH_3}$; δ 48.00, $\mathrm{N{-}}C\mathrm{H_3}$; δ 57.22, $C\mathrm{H_2}$; δ 70.63, $C\mathrm{H_2}$. ^{6}Li NMR: +20 °C, δ 1.98, 2.32; −80 °C, δ 1.66, 2.19.

Preparation of [$(\mathrm{Me_3Si})_2\mathrm{NLi}\cdot\mathrm{H_2NCH_2CH_2CH_2NH_2}$] (12). Bu^{n}Li (1 mmol in pentane) was added dropwise to a 0 °C chilled solution of hexamethyldisilazane (1 mmol) and 1,3-diaminopropane (1 mmol) in 4 mL of pentane. The solution was stirred for 2 h and then cooled to −78 °C for 24 h. After this time crystals of **12** were deposited. Only X-ray analysis proved possible, due to difficulties in isolating the sample. However, the synthesis of **12** proved reproducible by determining the unit cell parameters of several batches of crystals.

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Supporting Information Available: X-ray structural information on **5**−**7** and **9**−**11**. This material is available free of charge via the Internet at http://pubs.acs.org.

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