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Chelate Ring Size Controls the Formation of Mixed Complexes Involving Butyllithium and Sodium Amides

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NMR spectroscopic studies on the sodium and lithium adducts of four tridentate amines, **1**−**4**, are reported. The lithium and sodium amides of amines **1** and **2** can only form five-membered ring chelates with the alkali metals. The lithium and sodium amides of amines **3** and **4** can form both five- and six-membered chelates with the alkali metals. It is shown that addition of butyllithium (*n*-BuLi) to sodium amide dimers Na-**3** and Na-**4** in THF solution results in the formation of mixed 1:1 dimer complexes between *n*-BuLi and sodium amide. No such mixed complexes containing one lithium and one sodium are found from the amines **1** and **2**. On the basis of ^{6}Li,^{1}H HOESY experiments it is found that lithium prefers the five-membered chelate while sodium prefers the six-membered chelate in these mixed complexes.

Introduction

Chiral lithium amides have received much attention as versatile reagents for stereoselective synthesis.[1−3] Although there have been an appreciable number of studies made on the reactivity and structures of chiral lithium amides, both in solution and in the solid state, the number of studies made on chiral amides generated from the heavier alkali metals in solution are more sparse.[4]

The basic information about solvation, aggregation, and chelating effects in organolithium compounds is now at least partially understood. However, the sodium amide analogues in solution have not been studied in detail and the knowledge about the corresponding coordination chemistry is still in its infancy. The heavier alkali metals are larger than lithium (the covalent radii are 0.6 and 0.95 Å for Li and Na, respectively) and have larger coordination numbers. Sodium, for instance, can be six-coordinated compared to lithium, which is often tetracoordinated. Thus, the use of these alkali-metal reagents in asymmetric synthesis requires that reliable predictions of both the aggregation and the coordination of various ligands can be made.

There are several examples of mixed dimers of, for example, lithium amide and alkyllithium compounds found in the solid state and in solution.[5] The structure and dynamics of such complexes have been studied in some detail, mainly in ethereal solvents by NMR spectroscopy. It has also been shown that alkyllithium reagents complexed by lithium amides exhibit greater reactivity than the homoaggregated alkyllithiums.[6] Mixing the alkyllithium reagent with, for example, lithium alkoxides or heavier alkali metal organic compounds also results in increased reactivity of organolithium bases.[7] Such mixed complexes are known as superbases or LICKOR bases.[8]

In 1994 Williard and co-workers reported the first NMR and X-ray study of a mixed alkali metal cation

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amide base, the 1:1 mixture of Li−HMDS and K−HMDS in toluene.[9] To the best of our knowledge, there has not been any report of a reaction with mixed alkali metal cation amides. This is likely due to the intrinsic difficulty and the unpredictable formation of such mixed lithium/alkali metal amide dimers. Often the homo dimer analogues prevail from such mixtures. To fully explore this highly important and possibly synthetically useful class of reactive intermediates, we must be able to control the formation of the mixed complexes. Before this, we must acquire more structural and mechanistic knowledge of this class of potentially useful reagents.

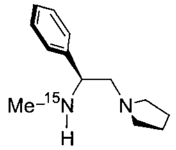
NMR spectroscopy is a powerful method to investigate the formation of mixed complexes in solution, in contrast to solid-state studies, which only reveal structures in the solid state. Lithium has two different NMR-sensitive nuclei, ^{6}Li and ^{7}Li. Sodium also has an NMR sensitive nuclei, ^{23}Na, which has the spin $I = {}^{3}/_{2}$. However, the large electric quadrupole moment of sodium (^{23}Na) results in large line widths at low temperatures, which precludes detailed NMR spectroscopic investigations of organo sodium compounds such as the complexes studied in this paper by solution NMR spectroscopy.

We recently reported a study of homo and hetero complexes of sodium and lithium amides.[10] In this study of the sodium and lithium salts of (*S*)-methyl(1-phenyl-2-pyrrolidinoethyl)[^{15}*N*]amine (**a** in Chart 1) we observe for the first time chiral sodium and mixed sodium/lithium amide dimer with internal coordination (**b** in Chart 1). The amine in DEE and in THF forms lithium and sodium amide dimers upon reaction with *n*-BuLi or *n*-BuNa. However, when the amide was prepared from a nonequal mixture of *n*-BuLi and *n*-BuNa, it formed mixed alkali metal/alkali amide dimers (**c** in Chart 1).

We herein report an NMR spectroscopic study of the aggregation of the alkali metal salts of four different tridentate amines (Chart 2). Mixed alkali metal cation complexes of the chiral amide dimers are reported.

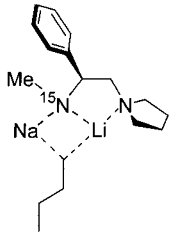
According to earlier results, the lithium amide made from amine **a** in Chart 1 forms dimers in THF. All the studied amines **1**−**4** have similar structures, but they all have a higher steric interaction around the nitrogen, and they also have greater internal coordination. It is reasonable to expect that amides formed from **1**−**4** with *n*-BuLi or/and *n*-BuNa are dimers.[11] The chemical shifts of the ^{6}Li signals are also in the same range as those of **b** and **c** in Chart 1.

Chart 1



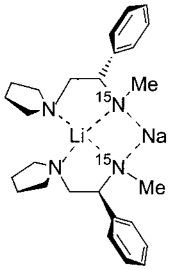
a

(*S*)-methyl(1-phenyl-2-pyrrolidinoethyl)[^{15}N]amine



b

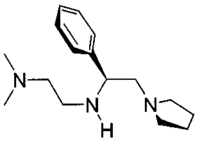
mixed BuNa/lithium amide



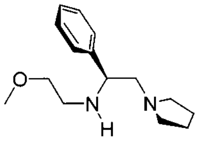
c

sodium lithium amide dimer

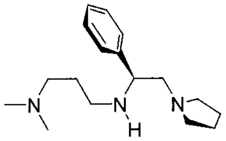
Chart 2



1



2



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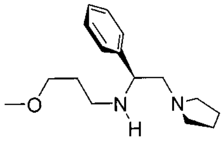

4

We have chosen to include amines that can form both five- and six-membered chelates, where amines **3** and **4** are used as six-membered-chelate analogues for amines **1** and **2**. One of the side chains of amines **3** and **4**, respectively, is extended with one extra methylene carbon, in comparison with amines **1** and **2**. Since the lithium in organolithium compounds readily forms five-membered ring chelates, we were especially interested to investigate if it was possible to control the aggregation of, for example, organosodium compounds employing a structure that could form six-membered chelates with the larger covalent radii of sodium.

Our studies of chiral lithium amides and their complexes with alkyllithium have revealed that there is a difference in mixed dimer formation when methoxy or pyrrolidine chelating groups are employed. On the basis of a limited study we have found that methoxy groups seem superior to nitrogen-based pyrrolidine for the

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Table 1. Signals from [^{6}*Li*]*n*-BuLi and *n*-BuNa Observed in ^{1}H, ^{13}C, and ^{6}Li NMR Spectra in THF-d_8 at −80 °C

	NMR (δ, ppm)		
compd	^{6}Li	^{13}C	^{1}H
[^{6}*Li*]*n*-BuLi	1.86,[a] 0.75[b]	10.71,[a] 12.81[b]	−0.97,[a] −1.25[b]
n-BuNa		10.04	−1.09

[a] Dimer. [b] Tetramer.

formation of mixed organolithium complexes.[12] But what about mixed sodium/lithium complexes? Are these dependent on the chelating groups?

Results

The NMR studies were first performed in deuterated diethyl ether, DEE-d_{10}, but since crystals were formed in DEE and not in THF when *n*-BuNa was titrated with amine **2**, all experiments were performed in deuterated tetrahydrofuran, THF-d_8, at −80 °C if not otherwise stated.

The alkali metal butyl, i.e., [^{6}*Li*]*n*-BuLi and *n*-BuNa, respectively, were dissolved in THF-d_8. The key signals observed in ^{1}H, ^{13}C, and ^{6}Li NMR spectra at −80 °C are presented in Table 1.

NMR Studies of Alkali Metal Amide Complexes of 1. Addition of Amine 1 to *n*-BuNa. When *n*-BuNa (0.23 M) in THF-d_8 was titrated with 0.33 equiv of amine **1**, the signal from the α-protons (−1.09 ppm) in the ^{1}H NMR spectra was broadened. A new signal from the quaternary carbon of the amine was observed at 153.44 ppm in the ^{13}C NMR spectrum. We propose that this signal arises from a mixed sodium amide/butylsodium dimer, **1a**. The α-carbon signal of BuNa was observed as a broad signal at 10.04 ppm in the ^{13}C NMR spectra (Figure 1).

The ^{1}H NMR only showed a single resonance from the α-protons now at −0.95 ppm when 0.67 equiv of amine **1** was added to the BuNa solution. The signal is not identical with that of BuNa itself, indicating that a mixed *n*-BuNa/sodium amide dimer complex is present, **1a** (Chart 3). The α-protons are diastereotopic, but the ^{1}H NMR signal was only observed as one unresolved broad peak. The ^{13}C NMR spectrum now showed two signals from quaternary carbons, at 153.40 and 153.94 ppm in a 4:1 intensity ratio, and a broad signal from an α-carbon at 10.68 ppm. Thus, the solution contains two dimeric complexes: one sodium amide and one mixed *n*-BuNa/sodium amide.[13] When 1 equiv of amine **1** was added, no α-proton signals were observed in either the ^{1}H or the ^{13}C NMR spectra, which indicates that no mixed *n*-BuNa/sodium amide complex is present. In the ^{13}C NMR spectra only the quaternary carbon signal at 153.96 ppm was observed. This signal arises from either of the sodium amide dimers represented as complexes **1b** and **1c**. Upon further addition of **1** also the signals from **1** appear. Thus, **1** and **1b** or **1c** are in slow chemical exchange.

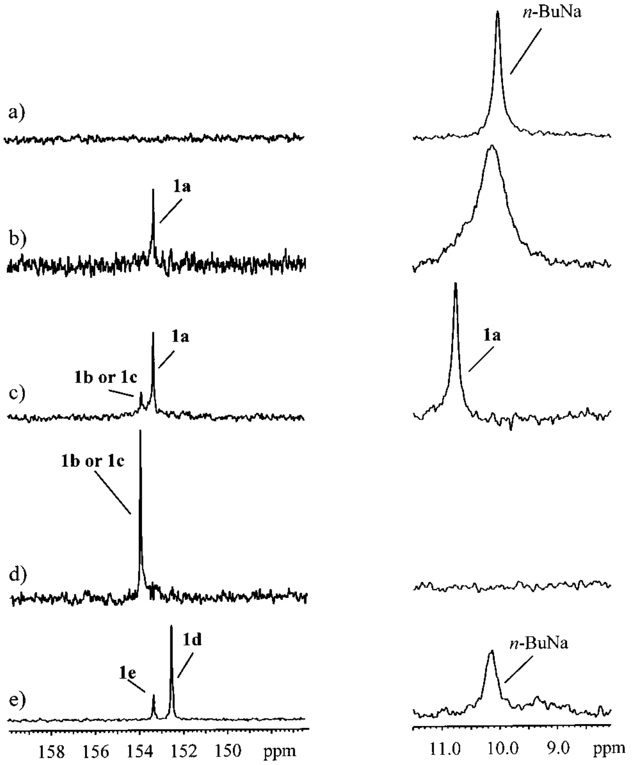
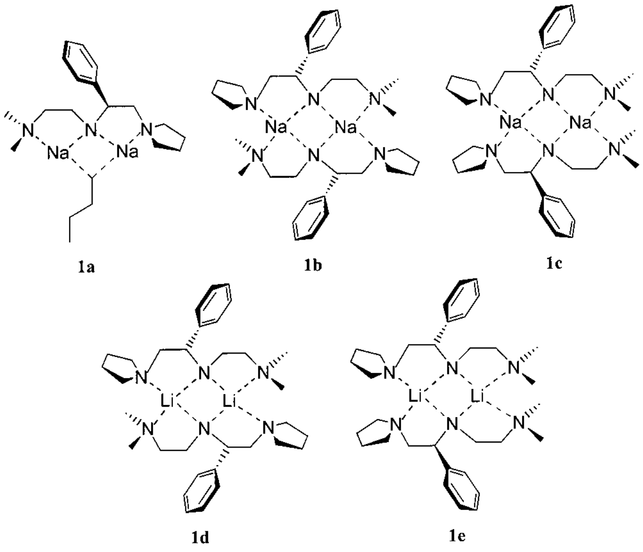


Figure 1. ^{13}C NMR spectra of the quaternary carbon and α-carbon regions of titration of *n*-BuNa with amine **1** and *n*-BuLi: (a) 0.23 M *n*-BuNa in THF-d_8 at −80 °C; (b) 0.23 M *n*-BuNa and 0.33 equiv of amine **1** in THF-d_8 at −80 °C; (c) 0.23 M *n*-BuNa and 0.67 equiv of amine **1** in THF-d_8 at −80 °C; (d) 0.23 M *n*-BuNa and 1 equiv of amine **1** in THF-d_8 at −80 °C; (e) 0.23 M *n*-BuNa, 1 equiv of amine **1**, and 0.75 equiv of *n*-BuLi in THF-d_8 at −80 °C.

Chart 3



1a **1b** **1c** **1d** **1e**

Addition of *n*-BuLi. Addition of approximately 0.75 equiv of [^{6}Li]*n*-BuLi to the solution of **1b** or **1c** gave rise to one large signal in the α-proton region at −0.95 ppm in the ^{1}H NMR spectrum. A signal from the α-protons of free *n*-BuNa was now again observed at −1.09 ppm. Thus, the addition of *n*-BuLi results in transmetalation and *n*-BuNa is formed from the sodium amide and BuLi. In the ^{6}Li NMR spectra one large signal was observed at 2.05 ppm and two small signals in a 1:1 ratio at 2.22 and 1.78 ppm. The signal at 2.05 ppm was assigned to the lithium amide dimer **1d**, and the two small signals at 2.22 and 1.78 ppm were assigned to the nonequiva-

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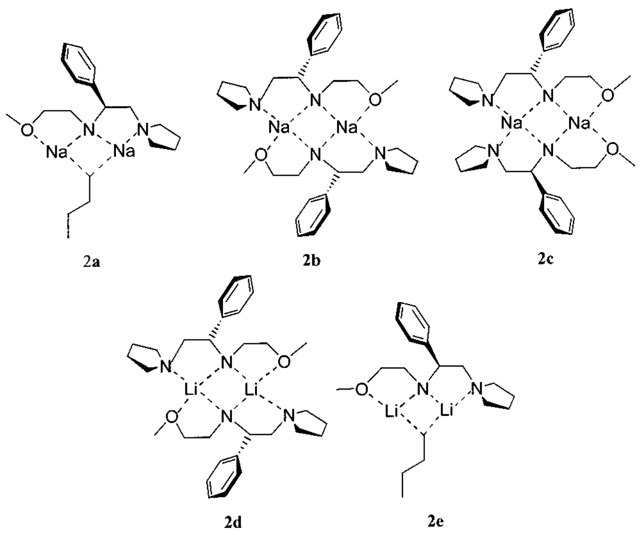
[12] Arvidsson, P. I.; Hilmersson, G.; Davidsson, Ö. *Chem. Eur J.* **1999**, *5*(8), 2348−2355.

[13] This is no proof of dimeric species, but similar amides are known to form dimers in THF solutions.

Chart 4



lent lithium atoms in **1e**, on the basis of previously published results.[14] We did not observe any signals from mixed *n*-BuNa/lithium amide dimer complexes.

NMR Studies of Alkali Metal Amide Complexes of 2. Addition of Amine 2 to *n*-BuNa. A solution of *n*-BuNa (0.24 M) in THF-d_8 was titrated with amine **2**. The ^{1}H NMR spectra recorded with 0.67 equiv of amine **2** added showed an α-proton signal at −0.95 ppm in addition to the signal at −1.09 ppm assigned to free *n*-BuNa (Table 1). The signal at −0.95 ppm was assigned to *n*-BuNa complexed with the sodium amide **2a** (Chart 4). Two quaternary carbon signals at 153.47 and 152.88 ppm were observed in the ^{13}C NMR spectra obtained with an excess of BuNa (Figure 2).

One of the signals is proposed to be from a mixed dimer complex presented as **2a**. The signal from the α-carbon was observed at 10.28 ppm. (The α-carbon in free *n*-BuNa is observed as a broad signal at 10.04 ppm.) The other quaternary carbon signal was assumed to be from the sodium amide dimer **2b** or **2c**.

Upon addition of more amine **2** the signal at 152.88 ppm was observed to increase. In the ^{1}H NMR spectra the signal at −1.09 ppm due to free *n*-BuNa had disappeared and now only the signal at −0.95 ppm from the α-protons of *n*-BuNa of the mixed dimer complex **2a** was observed. The quaternary carbon signal at 152.88 ppm in the ^{13}C NMR spectra must be from the sodium amide dimer (**2b** or **2c**) and the signal at 153.47 ppm from the mixed *n*-BuNa/sodium amide dimer complex, since this signal and the α-carbon signal from free *n*-BuNa at 10.28 ppm disappeared at equimolar amounts of amine and *n*-BuNa.

Addition of *n*-BuLi. Addition of 0.75 equiv of [^{6}*Li*]-*n*-BuLi to the above mixture resulted in the appearance of two new quaternary carbon signals at 149.58 and 152.26 ppm in the ^{13}C NMR spectra. Simultaneously, the signal at 152.88 ppm from the sodium amide dimer decreased. The signal at 152.26 ppm is from a lithium amide dimer (structure **2d**).[14] The signal at 149.58 ppm is from a mixed *n*-BuLi/lithium amide dimer, **2e**, since a quintet ($^1J_{^6\mathrm{Li}^{13}\mathrm{C}}$ = 8.2 Hz) from the α-carbon of the mixed *n*-BuLi/lithium amide dimer was observed at 12.02 ppm in the ^{13}C NMR spectra. With 1.25 equiv of [^{6}*Li*]*n*-BuLi added, the signal at 152.26 ppm disappeared and the signal at 149.58 ppm from the mixed *n*-BuLi/lithium amide dimer increased. Now the signal at 10.04 ppm from the α-carbon of free *n*-BuNa was observed with stronger intensity.

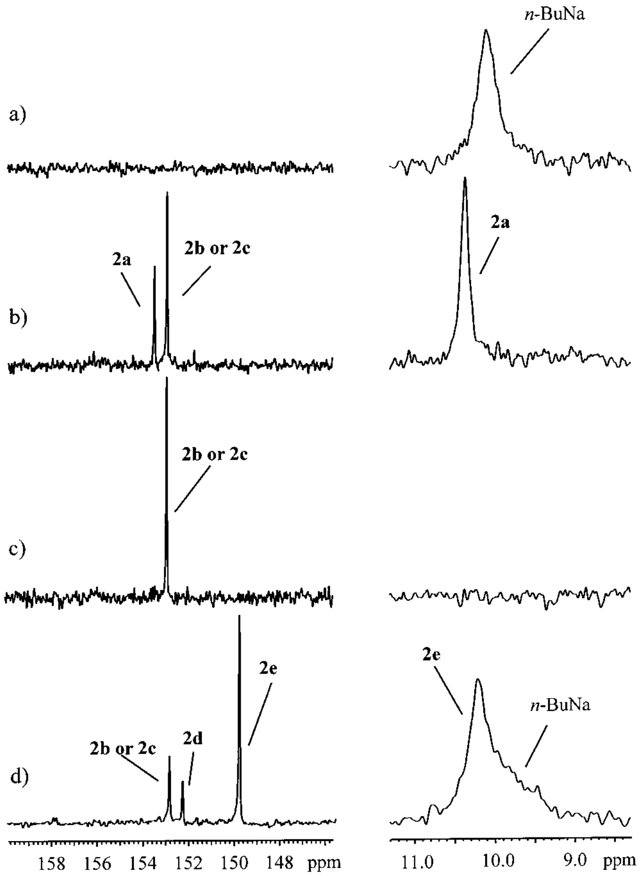


Figure 2. ^{13}C NMR spectra of the quaternary carbon and α-carbon regions of titration of *n*-BuNa with amine **2** and *n*-BuLi: (a) 0.24 M *n*-BuNa in THF-d_8 at −80 °C; (b) 0.24 M *n*-BuNa and 0.67 equiv of amine **2** in THF-d_8 at −80 °C; (c) 0.24 M *n*-BuNa and 1 equiv of amine **2** THF-d_8 at −80 °C; (d) 0.24 M *n*-BuNa, 1 equiv of amine **2**, and 0.75 equiv of *n*-BuLi in THF-d_8 at −80 °C.

In the ^{1}H NMR the signal at −1.09 ppm from *n*-BuNa increased, and next to this signal two triplets were observed at −0.97 ppm and −1.17 ppm in a 1:1 ratio. These two triplets come from the diastereotopic α-protons of *n*-BuLi in a mixed Li−N−Li−C dimer.[14]

In the ^{6}Li NMR spectra, three signals were observed at 1.65, 1.84, and 2.09 ppm. The two signals at 1.65 and 2.09 ppm were assigned to the mixed dimer complex, **e** in Chart 4, based on a ^{6}Li,^{1}H HOESY experiment. The signal at 1.84 ppm is from the lithium amide dimer **2d**, according to earlier results.[14]

NMR studies of Lithium Amide Complexes of 3. Addition of *n*-BuLi to Amine 3. The quaternary carbon of amine **3** (0.36 M) in DEE-d_{10} was observed at 144.51 ppm in the ^{13}C NMR spectra. When 0.5 equiv of [^{6}Li]*n*-*Bu*Li was added, another signal was observed at 153.17 ppm in 1:1 ratio to the signal at 144.51 ppm. The ^{6}Li NMR spectrum shows a large signal at 2.16 ppm. The signal is assigned to the lithium atoms in the **3a** dimer (Chart 5). The quaternary carbon signal at

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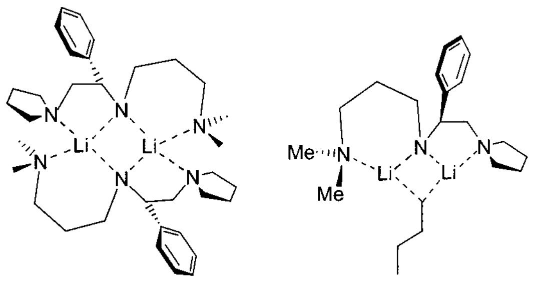
[14] Johansson, A.; Pettersson, A.; Davidsson, Ö. *J. Organomet. Chem.* **2000**, *608*, 153−163.

Chart 5



3a **3b**

153.17 ppm is also assigned to the quaternary carbon of the lithium amide dimer.

The signal at 144.51 ppm in the ^{13}C NMR spectrum decreased in intensity with further addition of [^{6}*Li*]*n*-BuLi, while the ^{13}C NMR signal at 153.17 ppm, from **3a**, increased in intensity as more lithium amide dimers were formed. At equal amounts of the amine and *n*-BuLi, the signal at 144.51 ppm from the amine disappeared. The ^{6}Li NMR spectra only showed the single resonance of the amine signal from **3a** at 2.16 ppm.

When 1.5 equiv of *n*-BuLi was added, two signals at −0.99 and −1.08 ppm from the diastereotopic α-protons of *n*-BuLi in a mixed *n*-BuLi/lithium amide dimer, **3b**, was observed in the ^{1}H NMR spectra. The ^{13}C NMR spectra showed two signals from the quaternary carbons at 153.17 and 151.00 ppm. The signal at 151.00 ppm is from a mixed *n*-BuLi/lithium amide dimer complex. The α-carbon signal from this complex was observed as a quintet at 15.60 ppm ($^1J_{^6\text{Li}^{13}\text{C}} = 7.7$ Hz). The ^{6}Li NMR spectra also showed a new signal at 2.88 ppm with low intensity.

Upon further addition of [^{6}*Li*]*n*-BuLi the signal at 2.88 ppm, from what we propose to be a mixed *n*-BuLi/lithium amide dimer, was divided into two broad signals at 2.46 and 3.12 ppm in the ^{6}Li NMR spectra in a 1:1 ratio. Lowering the temperature from −80 to −95 °C resulted in a significant sharpening of the two broad signals. Thus, there must be a fast exchange between the two lithiums in the mixed dimer.

NMR studies of Alkali Metal Amide Complexes of 3. Addition of Amine 3 to *n*-BuNa. When 0.67 equiv of amine **3** was added to an *n*-BuNa solution (0.22 M) in THF-d_8, we observed two quaternary carbon signals at 153.55 and 153.46 ppm, respectively, in the ^{13}C NMR spectra. A signal from an α-carbon was observed at 10.54 ppm.

Furthermore, in the ^{1}H NMR spectrum two signals in a 1:1 ratio were observed at −0.96 and −1.13 ppm, respectively, in addition to the signal from free *n*-BuNa at −1.09 ppm. These two signals must be from the diastereotopic α-protons in the mixed *n*-BuNa/sodium amide dimer **3c** (Chart 6). Altogether, this shows that two complexes are present in solution and that one of the complexes must be a mixed *n*-BuNa/sodium amide dimer, **3c**. The other complex is assumed to be a homoaggregated sodium amide dimer (structure **3d** or **3e**). Upon further addition of amine **3** the signal at 153.55 ppm increased. Thus, this signal is assigned to be from the sodium amide dimer. There is no uncomplexed *n*-BuNa.

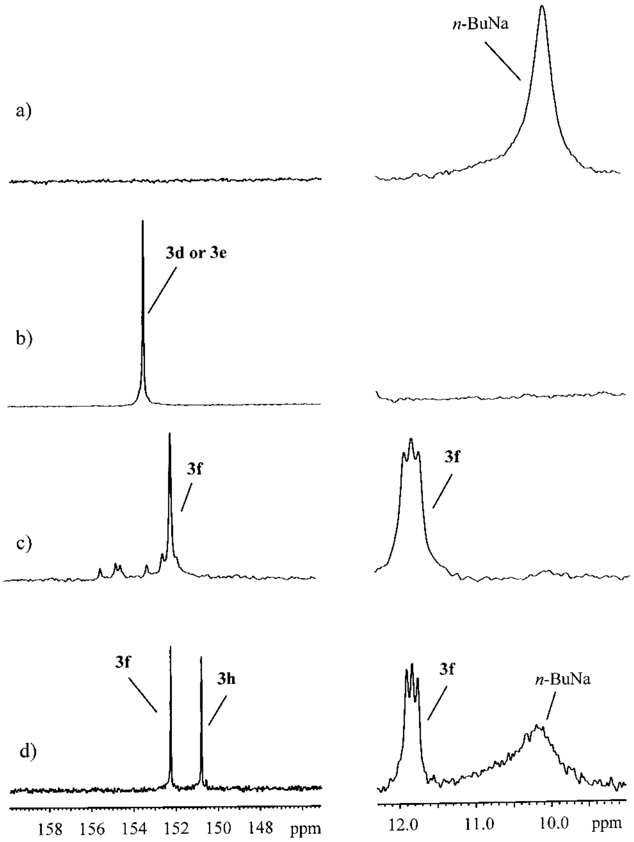
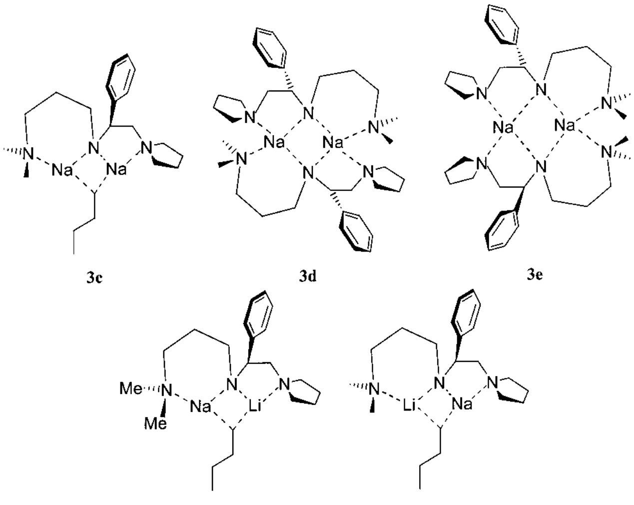


Figure 3. ^{13}C NMR spectra of the quaternary carbon and α-carbon regions of titration of *n*-BuNa with amine **3** and *n*-BuLi: (a) 0.22 M *n*-BuNa in THF-d_8 at −80 °C; (b) 0.22 M *n*-BuNa and 1 equiv of amine **3** in THF-d_8 at −80 °C; (c) 0.22 M *n*-BuNa, 1 equiv of amine **3**, and 0.35 equiv of *n*-BuLi in THF-d_8 at −80 °C; (d) 0.22 M *n*-BuNa, 1 equiv of amine **3**, and 0.75 equiv of *n*-BuLi in THF-d_8 at −80 °C.

Chart 6



3c **3d** **3e**

3f **3g**

When 1 equiv of the amine was added to *n*-BuNa, only the signal at 153.55 ppm from the sodium amide dimer was observed (**b** in Figure 3).

In the ^{1}H NMR spectra the signals at −0.96 and −1.18 ppm from the diastereotopic α-protons in the mixed sodium amide dimer had disappeared. The only complex present in the solution now is the sodium amide dimer, **3d** or **3e**.

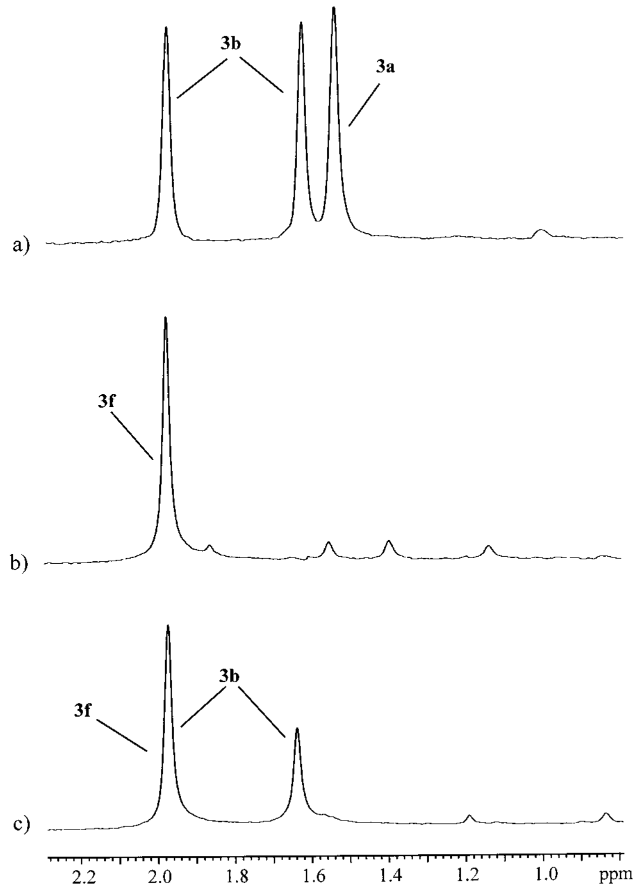


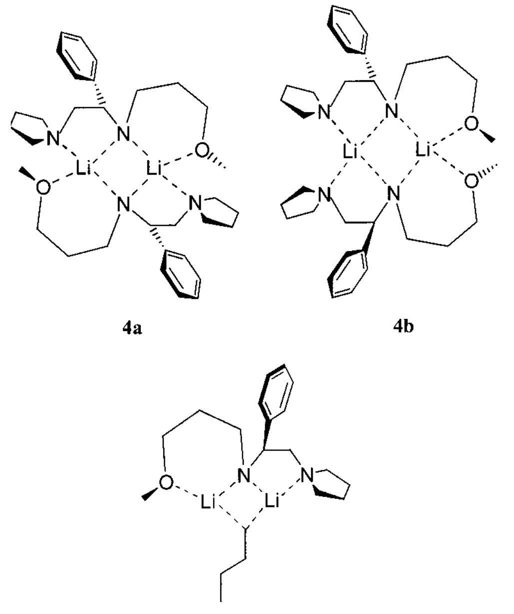
Figure 4. ^{6}Li NMR spectra of (a) amine **3** (0.36 M) in THF-d_8 at −80 °C with 1.50 equiv of *n*-BuLi added, (b) 0.22 M *n*-BuNa, 1 equiv of amine **3**, and 0.35 equiv of *n*-BuLi in THF-d_8 at −80 °C, and (c) 0.22 M *n*-BuNa, 1 equiv of amine **3**, and 0.75 equiv of *n*-BuLi in THF-d_8 at −80 °C.

Addition of *n*-BuLi. To the sodium amide dimer solution 0.35 equiv of [^{6}*Li*]*n*-BuLi was added. In the ^{13}C NMR spectra one large signal at 152.31 ppm was observed in the quaternary carbon region (**c** in Figure 3). At minor concentrations, also some unidentified complexes were observed. In the region of α-carbons, only a triplet at 11.82 ($^{1}J_{^{6}\mathrm{Li}^{13}\mathrm{C}} = 9.3$ Hz) was observed. In the ^{1}H NMR spectra a signal from α-protons at −1.02 ppm in a mixed alkali metal amide dimer complex is present. These results indicate the presence of the mixed *n*-BuNa/lithium amide dimer **3f** or **3g** in solution. In the ^{6}Li NMR spectra the only major signal observed was observed at 1.99 ppm, which comes from the lithium nucleus in the mixed *n*-BuNa/lithium amide dimer **3f** or **3g** (Figure 4).

In a ^{6}Li,^{1}H-HOESY spectrum we observed strong NOE's between the lithium signal and the signals for the pyrrolidine protons (Figure 5). This indicates that sodium prefers to be part of the six-membered chelate and that lithium prefers the five-membered chelate in **3f**.

Upon further addition to a total of 0.75 equiv of [^{6}*Li*]-*n*-BuLi, a new signal was observed at −1.09 ppm, in addition to the signal at −1.02 ppm in the ^{1}H NMR spectra. In the ^{13}C NMR spectrum two signals for quaternary carbons were observed at 150.49 and 152.31 ppm in an approximate 1:1 ratio. A quintet at 15.60 ppm ($^{1}J_{^{6}\mathrm{Li}^{13}\mathrm{C}} = 7.7$ Hz) was also observed in the region for α-carbons, in addition to the triplet from **3f**. The intensities of the quintet and the triplet were similar. This indicates that both the mixed *n*-BuNa/lithium amide dimer **3f** and the mixed *n*-BuLi/lithium amide dimer **3b** are present simultaneously in solution. The ^{6}Li NMR spectra now show two signals in a 2:1 ratio at 1.99 and 1.65 ppm. Apparently the magnetic environment is almost identical for the pyrrolidine-chelated lithiums in the two dimers. This was also supported by comparison of this ^{6}Li NMR spectra (**c** in Figure 4) with the spectra of the mixed *n*-BuLi/lithium amide dimer (**a** in Figure 4). Changing the temperature did not resolve the two lithium signals at 1.99 ppm from the two mixed complexes.

Chart 7



4a

4b

4c

In the ^{6}Li,^{1}H-HOESY spectrum (see Figure 5b) we observed strong NOE's between the lithium signal at 1.99 ppm and the signals from the pyrrolidine protons at 3.2, 3.0, and 1.8 ppm. Also, strong NOE was observed between this signal and the proton at the tertiary carbon at 3.77 ppm. In addition, strong NOE's were observed between the lithium signal at 1.65 ppm and the signals from the protons in the methyl groups but not to the pyrrolidine protons. These results are in concordance with the results obtained from a ^{6}Li,^{1}H-HOESY spectrum of **3b** as the sole complex.

NMR Studies of Lithium Amide Complexes of 4. Addition of *n*-BuLi to Amine 4. With 0.5 equiv of [^{6}*Li*]-*n*-BuLi added to amine **4** (0.38 M), no signals from α-protons of either complexed or free *n*-BuLi were observed. This clearly shows that no mixed dimer was present in solution. Two signals from quaternary carbons were observed in the ^{13}C NMR spectra at 151.26 and 152.56 ppm, in addition to the signal at 144.42 ppm from free amine. The signal at 151.26 is due to structure **4a** and is larger in intensity than the signal at 152.56 that is due to structure **4b** (Chart 7).

In the ^{6}Li NMR spectrum three signals were observed at 1.92, 1.79, and 1.23 ppm. The two lithium atoms in the dimer **4b** will result in two signals with the same intensity but at different chemical shifts. The signals

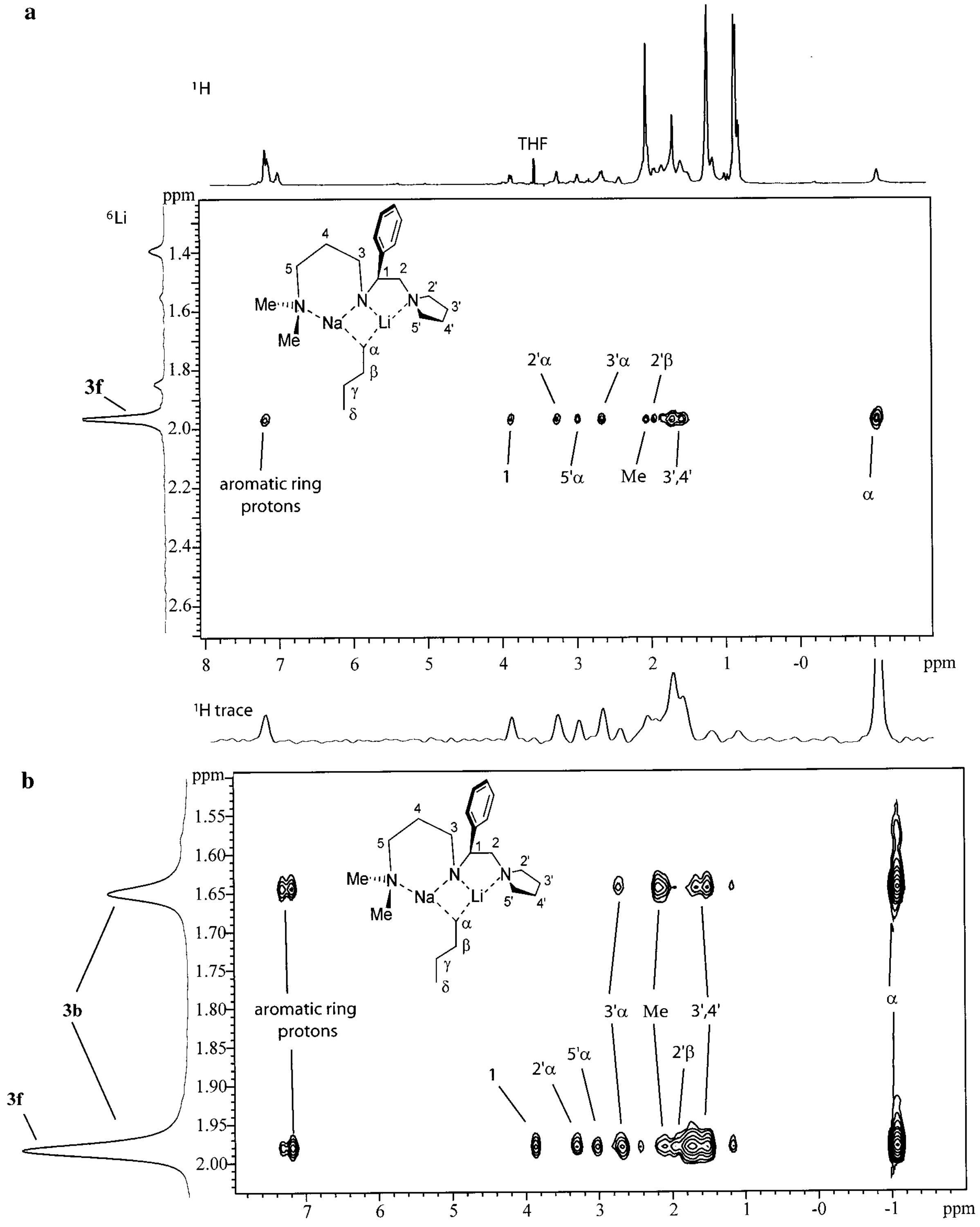


Figure 5. ^{6}Li,^{1}H-HOESY spectra of a 0.22 M solution of *n*-BuNa and 1 equiv of amine **3** in THF-d_8 at −80 °C with (a, top) 0.35 equiv of *n*-BuLi (mainly **3f**) and (b, bottom) 0.75 equiv of *n*-BuLi added (a mixture of **3b** and **3f**).

at 1.92 and 1.23 ppm were of equal intensity, and they were tentatively assigned to the **4b** dimer. The signal from the lithium nuclei in the **4a** dimer was observed at 1.79 ppm in the ^{6}Li NMR spectra. The ^{13}C NMR signal from the free amine at 144.42 ppm disappeared upon further addition of *n*-BuLi.

Two new signals, except the signal from free *n*-BuLi, were observed in the ^{6}Li NMR spectra at 2.51 and 1.97 ppm at 1.5 equiv of [^{6}*Li*]*n*-BuLi vs amine. In the ^{1}H NMR spectra a broad triplet for α-protons was observed at −0.88 ppm in addition to the signal from free *n*-BuLi. This broad signal must be from the α-protons of complexed *n*-BuLi in a mixed lithium amide dimer (structure **4c**). Structure **4c** also give rise to the two signals at 2.51 and 1.97 ppm in the ^{6}Li NMR spectra. The α-carbon signal of the mixed BuLi/lithium amide dimer complex was observed as a quintet at 10.51 ppm ($^1J_{^6\mathrm{Li}^{13}\mathrm{C}}$ = 9.8 Hz) in the ^{13}C NMR spectra.

NMR Studies of Alkali Metal Amide Complexes of 4. Addition of Amine 4 to *n*-BuNa. When 0.33

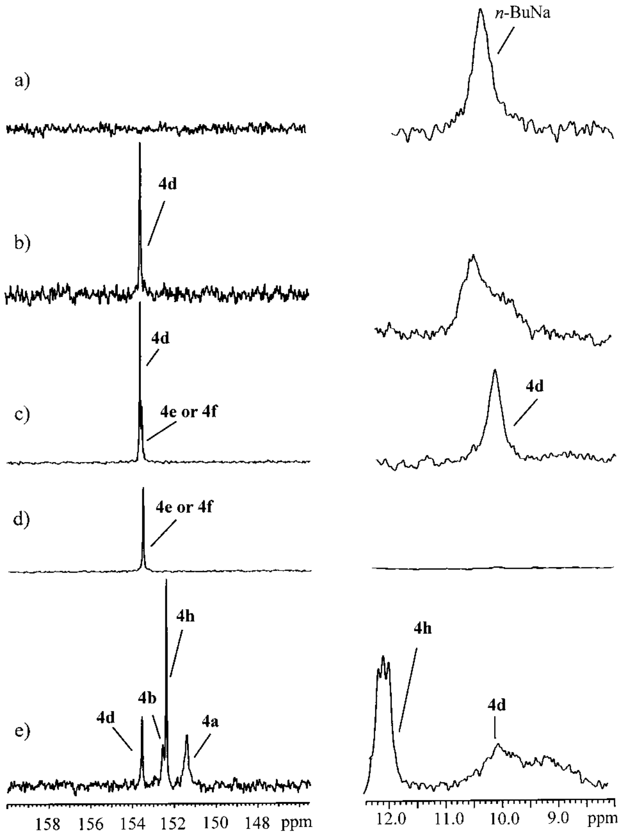


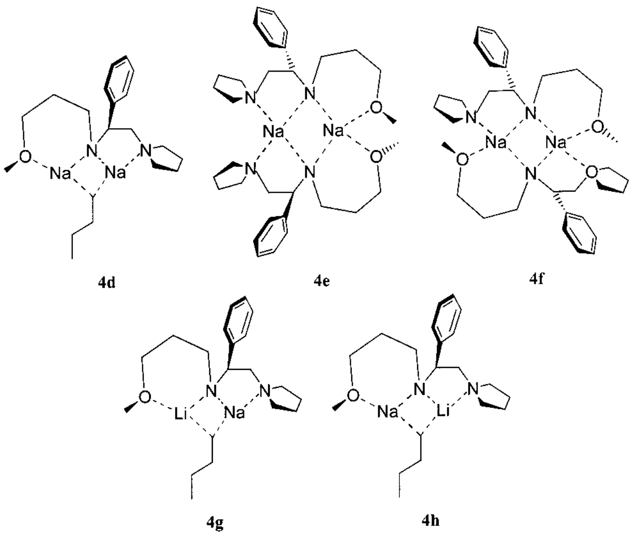
Figure 6. ^{13}C NMR spectra of the quaternary carbon and α-carbon regions of titration of *n*-BuNa with amine **4** and *n*-BuLi: (a) 0.23 M *n*-BuNa in THF-d_8 at −80 °C; (b) 0.23 M *n*-BuNa and 0.33 equiv of amine **4** in THF-d_8 at −80 °C; (c) 0.23 M *n*-BuNa and 0.67 equiv of amine **4** in THF-d_8 at −80 °C; (d) 0.23 M *n*-BuNa and 1 equiv of amine **4** in THF-d_8 at −80 °C; (e) 0.23 M *n*-BuNa, 1 equiv of amine **1**, and 0.75 equiv of *n*-BuLi in THF-d_8 at −80 °C.

equiv of amine **4** was added to the *n*-BuNa solution (0.23 M) in THF-d_8, one large quaternary carbon signal at 153.55 ppm was observed in the ^{13}C NMR spectrum (Figure 6).

Two signals from α-carbons were observed at 10.44 and 10.04 ppm, where the latter signal is from free *n*-BuNa. The signal at 10.44 ppm must be from a mixed *n*-BuNa/sodium amide dimer complex. This was verified, since in the ^{1}H NMR spectra a signal at −0.97 ppm was observed from the α-proton signals of what must be a mixed *n*-BuNa/sodium amide dimer complex, **4d** (Chart 8). The diastereotopic protons were not resolved. When 0.67 equiv of amine **4** was added, a new quaternary carbon signal was observed at 153.46 ppm in the ^{13}C NMR spectrum. Since no new α-carbon signals were observed, we conclude that this signal arise from a sodium amide dimer, **4e** or **4f**. When 1 equiv of amine **4** was added, the only quaternary carbon signal observed was the signal from the sodium amide dimer, **4e** or **4f**.

Addition of BuLi. When 0.75 equiv of [^{6}*Li*]*n*-BuLi was added to the Na-**4** solution, new α-proton signals at −1.01 and −1.12 ppm were observed. Since the signal from the α-protons in *n*-BuNa appears at −1.09 ppm and the signal from the α-protons in *n*-BuLi appears at −0.97 ppm, both of these new signals must originate from mixed alkali metal/alkali metal amide dimer complexes.

Chart 8



In the ^{13}C NMR spectra a triplet from the α-carbon in a *n*-BuNa/lithium amide dimer complex (**4g** or **4h**) was observed at 12.06 ppm ($^{1}J_{^{6}\mathrm{Li}^{13}\mathrm{C}} = 8.0$ Hz). The carbon in such a mixed complex (**4g** or **4h**) only couples to one lithium nucleus. The size of the coupling constant is in the range of those found for dimers. A broad signal, probably from a *n*-BuNa/sodium amide dimer complex, **4d**, was also observed at 10.46 ppm. In the ^{13}C NMR spectra four quaternary carbon signals were observed at 153.55, 152.56, 151.28, and 152.45 ppm. According to the results from the lithiation study of amine **4**, the signals at 152.56 and 151.28 ppm come from the lithium amide dimers (**4b** and **4a**). The large signal at 153.55 ppm comes from the mixed *n*-BuNa/sodium amide dimer, **4d**. The fourth signal must come from a mixed *n*-BuNa/lithium amide dimer complex, since the α-carbon signal is a triplet at 12.06 ppm.

In the ^{6}Li NMR spectra four signals at 1.98, 1.92, 1.79, and 1.23 ppm were observed. The larger signal at 1.79 ppm originates from the lithium amide dimer **4a**, and the smaller signals at 1.92 and 1.23 ppm in a 1:1 intensity ratio originate from the **4b** dimer. The signal at 1.98 was tentatively assigned to structure **4h**. We also performed a HOESY experiment to determine the position of the lithium in the mixed *n*-BuNa/lithium amide dimer complex. The ^{6}Li,^{1}H-HOESY experiment showed that the lithium signal at 1.98 ppm coordinates strongly to the α-protons in butyllithium (Figure 7).

The lithium signal at 1.98 ppm also shows strong NOE's to the protons of the pyrrolidine group, the aromatic ring protons, and the protons at the tertiary carbon. This shows that the sodium nucleus in the mixed *n*-BuNa/lithium amide dimer complex is preferably coordinated to the prolonged side chain with the methoxy group to form a six-membered-ring chelate. The assignment of the respective ^{1}H resonances are tentative, as a result of severe line overlap. The absence of NOE's between the lithium and the methoxy group further supports the proposed structure.

Discussion

We have found, using NMR spectroscopic techniques, that the amines **3** and **4** form mixed *n*-BuNa/lithium

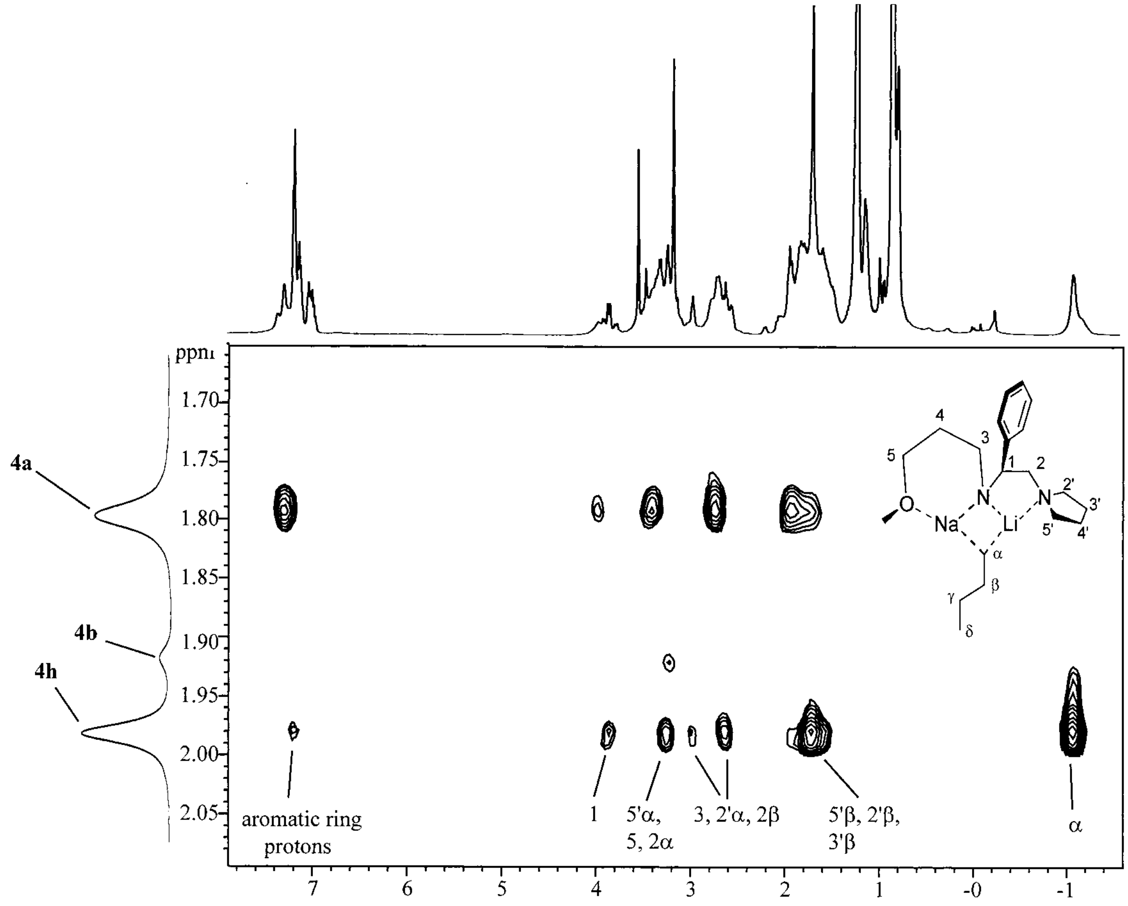


Figure 7. ^{6}Li,^{1}H-HOESY spectrum of a 0.23 M solution of *n*-BuNa, 1 equiv of amine **4**, and 0.75 equiv of *n*-BuLi in THF-d_8 at −80 °C.

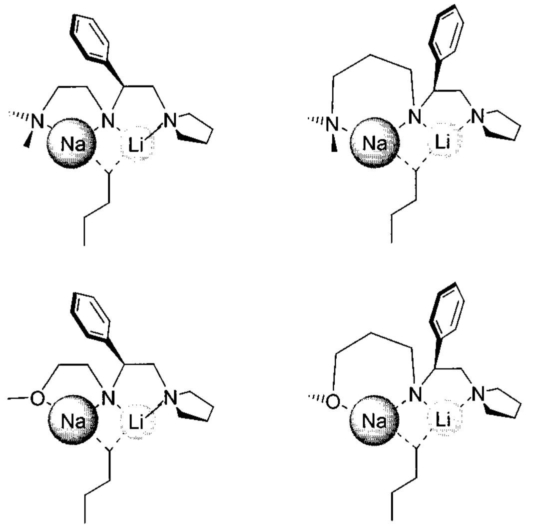
amide dimer complexes, in contrast to their analogues **1** and **2**. Mixing sodium amides Na-**1** and Na-**2** with *n*-BuLi results in the formation of their respective lithium amides and their mixed complexes with an excess of *n*-BuLi. Butylsodium homoaggrgates are consequently formed. On the basis of the results of ^{6}Li,^{1}H-HOESY experiments we conclude that amines **3** and **4** form mixed *n*-BuNa/lithium amide dimer complexes with the sodium atom preferably coordinated to the longer side chain of the amine and the lithium coordinated to the shorter side chain. It is in the competition for the five- and six-membered chelates within the dimers that sodium is found in the six-membered chelate and lithium in the five-membered chelate (Chart 9). These observations can be understood by the difference in the ionic radii of sodium (r_i(Na) = 0.95 Å) and lithium (r_i(Li) = 0.6 Å, respectively.

These findings clearly indicate that it is possible to control the formation of mixed alkali metal complexes with two different alkali metals occupying predetermined coordination sites.

These complexes are most likely dimers, since earlier studies of amides with similar structures form dimers in THF.[11] However, there is no direct proof of this statement, but the similarity in ^{6}Li NMR chemical shifts for these complexes and earlier studied amides suggests that the complexes reported herein are dimers.

Mixed *n*-BuLi/lithium amide dimers were not observed at equal amounts of *n*-BuLi and the amines **3** and **4**, in agreement with earlier results of the lithium salts of the amines **1** and **2**.

Chart 9



Amine **3**, with one extra methylene carbon at one coordinating side chain, did not form lithium amide dimer complexes with nonequivalent lithium atoms as its nitrogen analogue **1** did. The methoxy amine **4** forms lithium amide dimers with equivalent lithium atoms, in contrast to its analogue **2** with a shorter side chain.

None of the tridentate amines in this report form mixed lithium amide dimers consisting of one complexed *n*-BuLi molecule and one lithium amide at equal amounts of *n*-BuLi and the amine. Mixed alkali metal butyl/alkali metal amide complexes are favored under conditions where there is an excess of *n*-BuLi and/or *n*-BuNa.

Our results on mixed dimer formation show that the length of the side chain plays a central role in controlling the complexation of alkali metal amides. Clearly sodium, which is larger, does not fit well in five-membered chelates, while the smaller lithium does. The driving force for this selection can only be the size of the cation and the possible chelate ring size.

Experimental Section

General Considerations. Glassware and syringes were dried at 50 °C in a vacuum oven before transfer into a glovebox (Mecaplex GB 80 equipped with a gas purification system removing oxygen and moisture) containing a nitrogen atmosphere.

NMR Measurements. All NMR spectra were recorded using a Varian Unity 500 spectrometer equipped with three channels using a 5 mm ^{1}H,^{13}C,^{6}Li triple-resonance probe head custom-built by Nalorac. Measuring frequencies were 500 MHz (^{1}H) and 74 MHz (^{6}Li). The ^{1}H and ^{13}C spectra were referenced to the solvent signals: DEE-d_{10} 1.09 and 14.60 ppm ($-\mathrm{CD_2{}^1H}$), THF-d_8 1.73 and 25.37 ppm ($-\mathrm{CD^1H}$), respectively. Lithium spectra were referenced to external 0.3 M [^{6}Li]Cl in MeOH-d_4 (δ 0.0 ppm). A typical 90° ^{6}Li pulse was 20 μs. Probe temperatures were measured after more than 1 h of temperature equilibration with a calibrated standard methanol thermometer supplied by Varian instruments.

NMR Data Collection. The HOESY data were obtained, each one under identical conditions: a probe temperature of −80 °C, nonspinning 5 mm samples, and deuterium field-frequency locking. Spectral windows of 1000 Hz ($f_2 = {}^6$Li) and 8000 Hz ($f_1 = {}^1$H) were used. A total of 32 scans were collected in 96 blocks (t^2 acqusition time 1 s) using the hypercomplex method with a repetition rate of 1 scan/7 s. The value 7 s is consistent with the convention of using a recycle time on the order of 1.5T_1. The mixing time used in all HOESY experiments was 1.0 s. A homospoil pulse was used in the beginning of each relaxation delay in order to defocus remaining transversal magnetization.

All 2D spectra were acquired using nonspinning 5 mm samples with deuterium field-frequency locking. Spectra were processed in phase-sensitive mode with square sine bell weighting both in f_1 and f_2. For obtaining the ^{6}Li,^{1}H-HOESY spectrum the following parameters were used: spectral window of 1000 Hz ($f_2 = {}^6$Li) and 8000 Hz ($f_1 = {}^1$H); 128 increments and 32 scans per increment in t_1; mixing time 1.0 s. The ^{6}Li,^{1}H-HOESY sequence is described in detail.[15]

Preparation of *n*-BuLi and *n*-BuNa. [^{6}*Li*]*n*-BuLi[16] and *n*-BuNa[17] were synthesized according to literature methods.

(*R*)-(2-(Dimethylamino)ethyl)(1-phenyl-2-(pyrrolidin-1-yl)ethyl)amine (1). The synthesis of this substance and its analogues followed the method described by de Sousa et al. with some modifications:[18] (*R*)-styrene oxide (48 mmol) and pyrrolidine (100 mmol), distilled from $\mathrm{CaH_2}$, were heated to reflux in ethanol (95%) for 3 h. After evaporation of the solvent under reduced pressure, crystals were formed when put under vacuum for 1 h. The crystals were dissolved in THF (dried over sodium and benzophenone), and triethylamine (140 mmol) was added under nitrogen. The solution was cooled to 0 °C, methanesulfonyl chloride (57 mmol) was added dropwise, and the solution turned yellow. After 30 min, triethylamine (95 mmol) was added and the solution was allowed to reach room temperature. Diethylethylenediamine (1.18 mol) and water (15 mL) were added, and the solution was vigorously stirred for 3 days. The THF was evaporated, and the solution was extracted with DEE, washed with $\mathrm{NaHCO_3}$ (saturated) and $\mathrm{H_2O}$, and dried over $\mathrm{Na_2SO_4}$. The solvent was evaporated under reduced pressure. The crude product, a clear light yellow oil, was purified by distillation under high vacuum at 103 °C at 3.3×10^{-2} mbar. The yield was 62% (7.7 g, 30 mmol).[19]

(*R*)-(2-Methoxyethyl)(1-phenyl-2-(pyrrolidin-1-yl)ethyl)amine (2). The synthesis was carried out by following the procedure of **1**, with the exception that (2-methoxyethyl)amine was used instead of diethylethylenediamine. The crude product, a yellow oil, was purified by distillation to give the pure product (4 g, 39%) as a colorless oil, bp 125 °C at 1.3×10^{-1} mbar.[20]

(*R*)-*N*,*N*-Ddimethyl-*N'*-(1-phenyl-2-(pyrrolidin-1-yl)ethyl)propane-1,3-diamine (3). The synthesis was carried out by following the procedure of **1**, with the exception that 3-(dimethylamino)-1-propylamine was used instead of diethylethylenediamine. The product, a clear light yellow oil, was purified by distillation under high vacuum at 115 °C at 3.3×10^{-2} mbar for a yield of 52% (6.8 g, 25 mmol) of a clear oil.[21]

(*R*)-(3-Methoxypropyl)(1-phenyl-2-(pyrrolidin-1-yl)ethyl)amine (4). The synthesis was carried out following the procedure of **1** with the exception that (3-methoxypropyl)amine was used instead of diethylethylenediamine. The product, a

Clear light yellow oil, was purified by distillation under high vacuum at 90 °C at 2.1×10^{-2} mbar for a yield of 64% (7.9 g, 30 mmol).[22]

Preparation of NMR Samples. For the preparation of ^{6}Li-labeled lithium amides and details of the NMR sample preparations, see previously published papers.[23]

Acknowledgment. We are most grateful to the Swedish Natural Science Research Council and Carl Trygger for financial support.

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[15] For development of the ^{6}Li,^{1}H-HOESY experiment, see: Bauer, W.; Schleyer, P. v. R. *Magn. Reson. Chem.* **1988**, *26*, 827.

[16] *n*-Butyllithium was prepared according to published procedures; see: Hilmersson, G.; Davidsson, Ö. *Organometallics* **1995**, *14*(2), 912−918.

[17] *n*-Butylsodium was prepared according to published procedures; see: Schade, C.; Bauer, W.; Schleyer, P. v. R. *J. Organomet. Chem.* **1985**, 295, C25−C28.

[18] de Sousa, S. E.; O'Brien, P.; Poumellec, P. *J. Chem. Soc., Perkin Trans. 1* **1998**, 1483−1491.

[19] ^{1}H NMR data of **1** (500 MHz; [$\mathrm{D_{10}}$]DEE; 293 K; ppm): 7.36 (2H, d, *Ph*), 7.22 (2H, t, *Ph*), 7.13 (1H, t, *Ph*), 3.69 (1H, dd, $\mathrm{C}H$), 2.70 (1H, t, $\mathrm{CH}CH_2\mathrm{N}$), 2.62 (2H, m, $\mathrm{C}H_2$, pyrrolidine), 2.48 (2H, m, $\mathrm{C}H_2$, pyrrolidine), 2.42 (2H, dd, $\mathrm{NH}CH_2CH_2\mathrm{N(CH_3)_2}$), 2.23 (2H, dd, $\mathrm{NH}CH_2CH_2\mathrm{N(CH_3)_2}$), 2.16 (1H, t, $\mathrm{CH}CH_2\mathrm{N}$), 2.14 (6H, s, $\mathrm{N}(CH_3)_2$), 1.74 (4H, dd, $\mathrm{C}H_2$, pyrrolidine).

[20] ^{1}H NMR data of **2** (400 MHz; $\mathrm{CDCl_3}$; 293 K; ppm): 7.30−7.16 (5H, m, *Ph*), 3.65 (1H, dd, $\mathrm{PhC}H\mathrm{NH_2}$), 3.41−3.35 (2H, m, $\mathrm{C}H_2\mathrm{OCH_3}$), 3.26 (3H, m, $\mathrm{OC}H_3$), 2.77 (1H, t, $\mathrm{C}H_2\mathrm{N}$), 2.62−2.51 (4H, m, $\mathrm{NHC}H_2\mathrm{O}$, $\mathrm{C}H_2\mathrm{N}$), 2.60−2.54 (2H, m, $\mathrm{C}H_2\mathrm{N}$), 2.20 (1H, dd, $\mathrm{C}H_2\mathrm{N}$), 1.77−1.69 (4H, m, $\mathrm{C}H_2\mathrm{C}H_2$).

[21] ^{1}H NMR data of **3** (500 MHz; [$\mathrm{D_{10}}$]DEE; 293 K; ppm): 7.30 (2H, d, *Ph*), 7.25 (2H, t, *Ph*), 7.17 (1H, t, *Ph*), 3.63 (1H, dd, $\mathrm{C}H$), 2.68 (1H, t, $\mathrm{CH}CH_2\mathrm{N}$), 2.58 (2H, m, CH_2, pyrrolidine), 2.42 (2H, m, $\mathrm{C}H_2$, pyrrolidine), 2.25 (4H, dd, $\mathrm{NH}CH_2CH_2CH2\mathrm{N(CH_3)_2}$), 2.18 (4H, dd, $\mathrm{NH}CH_2CH_2\mathrm{N(CH_3)_2}$), 2.16 (1H, t, $\mathrm{CH}CH_2\mathrm{N}$), 2.13 (6H, s, $\mathrm{N}(CH_3)_2$), 1.58 (4H, dd, $\mathrm{C}H_2$, pyrrolidine).

[22] ^{1}H NMR data of **4** (400 MHz; $\mathrm{CDCl_3}$; 293 K; ppm): 7.26 (2H, d, *Ph*), 7.24 (2H, t, *Ph*), 7.19 (1H, t, *Ph*), 3.67 (1H, dd, $\mathrm{PhC}H\mathrm{NH2}$), 3.39−3.35 (2H, m, $\mathrm{C}H_2\mathrm{OCH_3}$), 3.20 (3H, m, $\mathrm{OC}H_3$), 2.72 (1H, t, $CH_2\mathrm{N}$), 2.59−2.51 (4H, m, $\mathrm{NHC}H_2\mathrm{O}$, $\mathrm{CH_2N}$), 2.60−2.54 (2H, m, $\mathrm{C}H_2\mathrm{N}$), 2.20 (1H, dd, $\mathrm{C}H_2\mathrm{N}$), 1.77−1.69 (6H, m, $\mathrm{C}H_2\mathrm{C}H_2\mathrm{C}H_2$).

[23] (a) Hilmersson, G.; Davidsson, Ö. *J. Organomet. Chem.* **1995**, *489*, 175. (b) Hilmersson, G.; Arvidsson, P. I.; Håkansson, M.; Davidsson, Ö. *Organometallics* **1997**, *16*, 3352. (c) Hilmersson, G.; Davidsson, Ö. *J. Org. Chem.* **1995**, *60*, 7660.