

Figure 1. NMR spectra of lithium isopropylcyclohexylamide (LICA): (A) partial ^{13}C NMR spectrum of a 0.20 M solution in 0.59 M THF-toluene- d_8 at -90°C showing the N-CH methine resonances (cf. ref 13); (B) ^6Li NMR spectrum of a 0.21 M solution of $[\text{}^6\text{Li}, \text{}^{15}\text{N}]$ -LICA in 9.93 M THF/toluene- d_8 at -90°C ; (C) ^{15}N NMR spectrum of a 0.20 M solution of $[\text{}^6\text{Li}, \text{}^{15}\text{N}]$ -LICA in 0.41 M THF/toluene- d_8 at -40°C . (The small doublets appear sporadically and are believed to be trace impurities arising from the synthesis and handling of the labeled substrate.) The ^6Li and ^{15}N NMR spectra were calibrated to 0.30 M LiCl/MeOH (0.0 ppm) and 0.15 M $[\text{}^{15}\text{N}]$ -aniline/THF (50 ppm) as described previously (ref 10a).

N-lithiated species.^{3,8-11} We are aware of only three direct spectroscopic determinations of lithium dialkylamide solution structures. With ^7Li NMR spectroscopy in conjunction with

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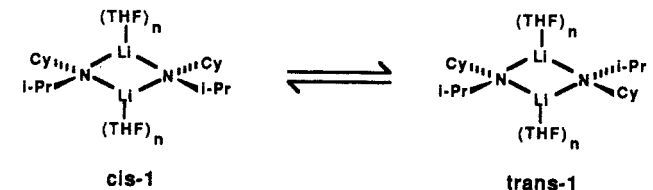
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cryoscopic measurements, Snaith and co-workers demonstrated that (1) the complex ladder structure of lithium pyrrolidide solvated by PMDETA (PMDETA = pentamethyldiethylenetriamine) observed crystallographically appeared to coexist with a variety of other uncharacterized structural forms in hydrocarbon solutions^{2c} and (2) $[\text{Cy}_2\text{NLi}\cdot\text{HMPA}]_n$ (Cy = cyclohexyl, HMPA = hexamethylphosphoramide) and unsolvated $(\text{PhCH}_2\text{NLi})_n$ (Ph = phenyl) exist in hydrocarbon solutions as concentration-dependent dimer-monomer and trimer-monomer mixtures, respectively.^{3,4} On the basis of cryoscopic measurements, Seebach reported that lithium diisopropylamide (LDA) exists as a 5:1 monomer/dimer mixture in tetrahydrofuran at -108°C .¹²

We describe herein several simple NMR spectroscopic experiments which demonstrate that lithium isopropylcyclohexylamide (LICA) exists as a 1:1 mixture of stereoisomeric dimers *cis*-1 and *trans*-1 in tetrahydrofuran (THF).



^{13}C NMR spectroscopic analysis of LICA in THF/toluene- d_8 mixtures at -89°C showed resonance duplication indicative of a 1:1 mixture of two structural forms (Figure 1A).¹³ A complete independence of the peak ratios on amide concentration over a 10-fold range (0.06–0.55 M) and THF concentration over a 60-fold range (0.20–12.0 M) showed the two species to be equivalently aggregated and equivalently solvated.

^6Li NMR spectroscopy failed to resolve the two structural forms; a sharp singlet ($\delta 1.89 \pm 0.01$ ppm) was observed at all THF concentrations and temperatures. Accordingly, we turned to ^6Li - ^{15}N double labeling studies, which, in conjunction with ^6Li and ^{15}N NMR spectroscopy, have recently been shown to provide a powerful tool for determining nitrogen-lithium connectivities of lithium anilides and lithiated imines.^{10,11,15}

The ^6Li and ^{15}N NMR spectra of $[\text{}^6\text{Li}, \text{}^{15}\text{N}]$ -LICA are depicted in Figure 1.¹⁶ The 1:2:1 triplet in the ^6Li NMR spectrum of $[\text{}^6\text{Li}, \text{}^{15}\text{N}]$ -LICA ($\delta 1.89$ ppm, $^1J_{\text{N-Li}} = 5.1$ Hz) is indicative of an N-Li-N connectivity. The partially overlapping pair of 1:2:3:2:1 pentuplets observed in the ^{15}N NMR spectrum ($\delta 71.3$ ppm, $^1J_{\text{Li-N}} = 4.8$ Hz; $\delta 70.9$ ppm, $^1J_{\text{Li-N}} = 5.3$ Hz) shows a Li-N-Li connectivity and confirms the presence of two structural forms. The combined Li-N-Li and N-Li-N connectivities indicate that LICA exists as some form of cyclic oligomer. The approximate 5-Hz N-Li coupling is notably large relative to the 3–4-Hz coupling of the corresponding N-phenyl-substituted cyclic oligomer.^{10,11}

The organolithium and THF concentration-independent resonance doublings are suggestive of stereoisomeric dimers *cis*- and *trans*-1.¹⁷ Although higher cyclic oligomers predicted by theory¹⁸

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(13) Spectroscopic samples were prepared by treatment of isopropylcyclohexylamine with halide free, crystalline $[\text{}^6\text{Li}]$ -ethylolithium (ref 14) at -78°C . Representative ^{13}C chemical shift data recorded at 100.55 MHz (-90°C) on a 0.20 M solution of $[\text{}^6\text{Li}]$ -LICA in 4.8% (0.59 M) THF/toluene- d_8 are (listed in pairs) as follows: δ 62.50, 62.23 (CH's); 53.10, 52.33 (CH's); 39.28, 39.16 (CH₂'s); 28.24, 27.20 (CH₃'s); 28.00; 27.85 (CH₂'s).

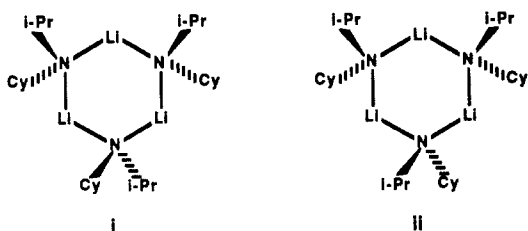
(14) Lewis, H. L.; Brown, T. L. *J. Am. Chem. Soc.* **1970**, *92*, 4664.

(15) The nuclear spins of ^6Li and ^{15}N are 1 and $-1/2$, respectively: *NMR of Newly Accessible Nuclei*; Laszlo, P., Ed.; Academic Press: New York, 1983.

(16) $[\text{}^{15}\text{N}]$ -Isopropylcyclohexylamine was prepared in 35% yield by Raney nickel reduction of $[\text{}^{15}\text{N}]$ -aniline in isopropyl alcohol according to a literature procedure: Srivastava, S.; Minore, J.; Cheung, C. K.; le Noble, W. J. *J. Org. Chem.* **1985**, *50*, 394.

(17) Similar stereoisomeric mixtures have been observed for lithiated imines (ref 9 and 10) and lithium anilides (ref 11), as well as for several group 13 amide derivatives. Lappert, M. F.; Power, P. P.; Sanger, A. R.; Srivastava, R. C. *Metal and Metalloid Amides*; Wiley: New York, 1980; Chapter 4. Amirkhalili, S.; Hitchcock, P. B.; Jenkins, A. D.; Nyathi, J. Z.; Smith, J. D. *J. Chem. Soc., Dalton Trans.* **1981**, 377. Beachley, O. T., Jr.; Bueno, C.; Churchill, M. R.; Hallock, R. B.; Simmons, R. G. *Inorg. Chem.* **1981**, *20*, 2423.

have been isolated and crystallographically characterized on three occasions (viz $[(\text{PhCH}_2)_2\text{NLi}]_3$, $[(\text{Me}_3\text{Si})_2\text{NLi}]_3$, and $[\text{Me}_2\text{C}(\text{CH}_2)_3\text{CMe}_2\text{NLi}]_4$), they are all void of coordinating solvents. In contrast, the etherates of $(\text{PhCH}_2)_2\text{NLi}$ and $(\text{Me}_3\text{Si})_2\text{NLi}$ crystallize as disolvated cyclic dimers^{4,5} (as do other related lithium amide derivatives) while an etherate of $\text{Me}_2\text{C}(\text{CH}_2)_3\text{CMe}_2\text{NLi}$ remains uncharacterized.^{2,3,6} By noting the symmetry of stereoisomeric trimers i and ii, further arguments can be made sup-



porting dimers rather than trimers (or higher oligomers) as the predominant forms of LICA in THF solution. The ^{15}N - ^6Li coupling patterns of i and ii would exhibit as many as three ^6Li resonances, three ^{15}N resonances, and three separate resonances for each carbon atom in the skeleton. Such spectral complexities were not detected by three quite different forms of NMR spectroscopy. Thus, we concur with Snaith and co-workers¹⁹ that the higher order cyclic oligomers are probably restricted to ligand-free lithium amides and, in turn, assign the observed aggregates of LICA as *cis*- and *trans*-1.

The invariance of the ^6Li shift of LICA over THF concentrations spanning 0.2–12.0 M, taken in conjunction with crystallographic studies of N-lithiated species solvated by simple monodentate donors, is consistent with a single coordinated THF per lithium in dimers *cis*- and *trans*-1. However, Seebach and co-workers have crystallographically characterized an unsymmetrical trisolvated dimer of a related N-lithiated species.^{6c} In addition, solution structural studies of lithium diphenylamide dimer and the corresponding lithium diphenylamide–lithium bromide mixed dimer in THF/hydrocarbon solutions uncovered evidence of higher degrees of solvation.^{10b} Thus, the solution solvation states of *cis*-1 and *trans*-1 are not evident at this time.

As evidence of the relative importance of aggregated, mixed aggregated, and monomeric forms of lithium dialkylamides in determining reactivity and selectivity begins to accumulate,²⁰ detailed solution structural information will become an increasingly important component of predictive models.

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Registry No. LICA, 32400-20-7; THF, 109-99-9; toluene, 108-88-3.

(18) Sapse, A.-M.; Raghavachari, K.; Schleyer, P. v. R.; Kaufmann, E. *J. Amer. Chem. Soc.* **1985**, *107*, 6483. Raghavari, K.; Sapse, A.-M.; Jain, D. C. *Inorg. Chem.* **1987**, *26*, 2585.

(19) Armstrong, D. R.; Barr, D.; Snaith, R.; Clegg, W.; Mulvey, R. E.; Wade, K.; Reed, D. *J. Chem. Soc., Dalton Trans.* **1987**, 1071. Barr, D.; Snaith, R.; Clegg, W.; Mulvey, R. E.; Wade, K. *J. Chem. Soc., Dalton Trans.* **1987**, 2141.

(20) For example, aggregate reactivity has been addressed theoretically (McKee, M. L. *J. Am. Chem. Soc.* **1985**, *107*, 7284). Residual lithium amides (or the secondary amine byproducts) appear to alter the outcome of a number of reactions utilizing lithium amide derivatives as bases (see references cited in ref 10). Williard and co-workers have successfully characterized a number of lithium diisopropylamide–enolate complexes crystallographically (ref 2a and unpublished results). We have recently observed and studied the direct N-alkylation of lithium diphenylamide dimer and lithium diphenylamide–lithium bromide mixed dimer with *n*-butyl bromide (ref 10b). The general principles of mixed aggregation effects on reaction outcomes has been discussed previously (Seebach, D. In *Proceedings of the Robert A. Welch Foundation Conferences on Chemistry and Biochemistry*; Wiley: New York, 1984; p 93).

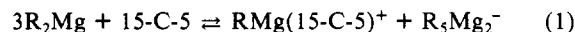
Interactions of Dialkylmagnesium Compounds with 15-Crown-5: Formation in Solutions and Solids of $\text{RMg}(15\text{-crown-5})^+$ and Magnesiato Ions[†]

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Magnesiato ions, formed by equilibria such as that in eq 1 but in amounts too small to detect by NMR spectroscopy, were



suggested as being the species responsible for the striking chemical behavior of solutions resulting from addition of 15-crown-5 to EtOEt or THF solutions of dialkylmagnesium compounds.¹ Subsequent studies showed that appropriate cryptands, far more effective than crown ethers as coordinating agents for Mg, form substantial amounts of such ions. Structures of solid $\text{NpMg}(2,1,1\text{-cryptand})^+\text{Np}_3\text{Mg}^-$ (Np = neopentyl) and $[\text{EtMg}(2,2,1\text{-cryptand})^+]_2\text{Et}_6\text{Mg}_2^{2-}$ were determined,² and ^1H NMR spectra of solutions prepared from several diorganomagnesium compounds showed absorptions attributed to similar species.²⁻⁵ This communication now reports *direct observations* of the species in eq 1.

Crystals (mp 129 °C) suitable for X-ray analysis slowly formed when an EtOEt solution of Me_2Mg (2 mL, 1.5 M) was layered over a benzene solution of 15-crown-5 (2 mL, 0.5 M). X-ray analysis⁶ revealed $\text{MeMg}(15\text{-crown-5})^+$ units and $(\text{Me}_5\text{Mg}_2^-)_n$ chains, presumably having the indicated charges. As shown in Figure 1, the Mg of the cation is bonded in an equatorial fashion to all crown ether oxygens and lies just 0.42 Å out of their mean plane. This Mg also is bonded to an apical methyl group (Mg–C 2.140 (7) Å). The other apical position is occupied by one methyl group of the anionic polymer chain, though at a Mg–C distance of 3.28 Å.⁷ Within the four-membered ring, bond angles are similar to and bond lengths slightly longer than those in the Me_2Mg structure, which has adjoining Mg's linked by two bridging methyl groups.⁸

Solutions now have been prepared, many of which are stable for days or weeks at room temperature, whose ^1H NMR spectra indicate the presence of significant amounts of $\text{RMg}(\text{crown})^+$ and magnesiato ions. The spectrum in Figure 2, of a benzene solution containing approximately 5.2 Np groups per 15-crown-5 residue, is a convenient example to consider. This spectrum shows two crown ether absorptions (A, δ 2.99; C, δ 3.31) and two sets of Np absorptions (A, δ –0.40 for the CH_2 and δ 1.22 for the CH_3 's; B, δ 0.34 for the CH_2 and δ 1.54 for the CH_3 's). For several

[†] Dedicated to Professor Paul D. Bartlett on the occasion of his 80th birthday.

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(2) Squiller, E. P.; Whittle, R. R.; Richey, H. G., Jr. *J. Am. Chem. Soc.* **1985**, *107*, 432.

(3) Richey, H. G. Jr.; Kushlan, D. M. *J. Am. Chem. Soc.* **1987**, *109*, 2510.
(4) Squiller, E. P. The Pennsylvania State University, unpublished observations.

(5) Kushlan, D. M. The Pennsylvania State University, unpublished observations.

(6) Crystal data for $\text{MeMg}(15\text{-crown-5})^+\text{Me}_5\text{Mg}_2^-$, $\text{C}_{16}\text{H}_{38}\text{O}_5\text{Mg}_2$: $a = 10.736$ (2) Å, $b = 18.454$ (3) Å, $c = 11.923$ (3) Å; $V = 2362$ (2) Å³, $Z = 4$, $D_{\text{calc}} = 1.078$ g cm⁻³; space group $Pna2_1$, $R = 0.077$ for 1470 reflections with $I > 3\sigma(I)$ measured on an Enraf-Nonius CAD-4 diffractometer by using graphite-monochromatized Mo $K\alpha$ radiation, the $\omega/2\theta$ scan method, and variable scan speed. The structure was solved by direct methods and refined by full-matrix least-squares calculations.

(7) The positions of the H's are not revealed by the analysis so it is not evident if this can be regarded as a particularly feeble Me–C bond or if H's of the methyl group lie between the C and the Mg.

(8) Weiss, E. *J. Organomet. Chem.* **1964**, *2*, 314. In polymeric Me_2Mg , C–Mg–C is 105 (2)°, Mg–C–Mg is 75 (2)°, Mg–C is 2.24 (3) Å, and Mg–Mg is 2.72 (2) Å.