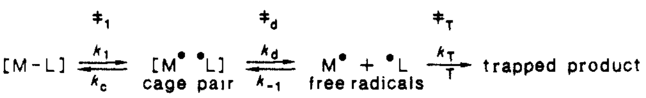
Scheme I



$$[\text{M}-\text{L}]\ \overset{\ddagger_1}{\underset{k_c}{\overset{k_1}{\rightleftharpoons}}}\ \underset{\text{cage pair}}{[\text{M}^\bullet\ {}^\bullet\text{L}]}\ \overset{\ddagger_d}{\underset{k_{-1}}{\overset{k_d}{\rightleftharpoons}}}\ \underset{\text{free radicals}}{\text{M}^\bullet + {}^\bullet\text{L}}\ \overset{\ddagger_T}{\underset{T}{\xrightarrow{k_T}}}\ \text{trapped product}$$

radical trap (T) such as DPPH,[6f] TEMPO,[1,2] or an efficient hydrogen donor.[11] Under conditions where the trap (T) is present in modest concentrations[11a] (~0.1 M) and in excess of [M–L], the observated rate constant (k_{obsd}) for the homolysis process will be given by eq 1. The term in brackets is the complement of the

$$k_{\text{obsd}} = [1 - F_c]\cdot k_1 \tag{1}$$

$$F_c = k_c/(k_c + k_d) \tag{1a}$$

fractional cage efficiency, F_c, which is defined as shown in eq 1a. Taking the first derivative of k_{obsd} (eq 1) with respect to T^{-1} yields eq 2. Here $\Delta H^\ddagger_{\text{obsd}}$ is the usual $\ln(k_{\text{obsd}}/T)/(1/T)$ slope, $\Delta H^\ddagger_1$(s)

$$\Delta H^\ddagger_{\text{obsd}} = \Delta H^\ddagger_1(\text{s}) + F_c\cdot[\Delta H^\ddagger_d - \Delta H^\ddagger_c] \tag{2}$$

is the activation enthalpy for the k_1 step *in solution*, while $\Delta H^\ddagger_d$ and $\Delta H^\ddagger_c$ are the steps in Scheme I that are unique to the solution phase where the cage intermediate pertains. Equation 2 is quite important in showing the proper connection between $\Delta H^\ddagger_{\text{obsd}}$ and $\Delta H^\ddagger_1$(s). It reveals that F_c, $\Delta H^\ddagger_d$, and $\Delta H^\ddagger_c$ but not $\Delta H^\ddagger_{-1}$ could be corrections in obtaining $\Delta H^\ddagger_1$(s) from $\Delta H^\ddagger_{\text{obsd}}$.[10b]

The relationship between the observed[10c,d] activation entropies and those for the elementary steps of Scheme I is given in eq 3. The $\Delta S^\ddagger_d - \Delta S^\ddagger_c$ term could be a substantial part of $\Delta S^\ddagger_{\text{obsd}}$ depending on F_c.

$$\Delta S^\ddagger_{\text{obsd}} \simeq \Delta S^\ddagger_1(\text{s}) + F_c\cdot[\Delta S^\ddagger_d - \Delta S^\ddagger_c] \tag{3}$$

Equations 2 and 3 make it clear that the cage efficiency factor, F_c, is a variable that must be considered. The value of F_c certainly changes with changing solvent, temperature, and M–L structure. No experimental data on even an approximate F_c value for any M–L bond homolyses, much less its variation, have been provided as yet. There is a continuum between $F_c \sim 0$ ($\Delta G^\ddagger_c$ higher than $\Delta G^\ddagger_d$) and $F_c \sim 1.0$ ($\Delta G^\ddagger_c$ lower than $\Delta G^\ddagger_d$ (Figure 1)), and it is not known, at the present time, where M–L systems fit into this spectrum.

Equation 1 teaches that measurement of both k_{obsd} and F_c at several temperatures will give k_1 and hence $\Delta H^\ddagger_1$(s) directly without the complication of $\Delta H^\ddagger_d - \Delta H^\ddagger_c$ (at least within the confines of Scheme I). Oxygen-18 scrambling studies for peresters are cases where eq 1 has been used to estimate the cage effect. In M–L homolysis, the equivalent measurement could be the rate of racemization of an M–L having a chiral carbon ligand. If either the molecular tumbling[6f,13,16–20] of the carbon radical with respect to the M· or an appropriate internal rotation[6f] in the carbon radical (at the cage pair stage) were much faster than k_c, then the rate constant for racemization would give k_1 of Scheme I directly. The cage effect would be evident in a lower value for k_{obsd} under the same conditions.[15] However, the precedents from the organic literature show that some retention of oxygen-18 label[6c] or carbon configuration[6f,16–20] are the result for cage combination, even for systems in which F_c is small. If organometallic systems do exhibit high F_c values, as has been implicitly assumed[10b] in recent work on M–L systems, then racemization rates might not count every homolytic event.[15a]

Finally, we should like to point out that a cage pair is effectively a diradical and, as Houk[21] has shown for the carbene–olefin reaction and Doubleday[22] has discussed for 1,4-diradicals, the activation enthalpy for bond formation, corresponding to k_c of Scheme I, *can be negative*. A negative value for $\Delta H^\ddagger_c$ is quite possible and simply requires that $\Delta S^\ddagger_c$ be sufficiently negative to make $\Delta G^\ddagger_c$ positive.[23] Equations 2 and 3 teach that negative values for $\Delta H^\ddagger_c$ and $\Delta S^\ddagger_c$ increase the cage effect contribution to $\Delta H^\ddagger_{\text{obsd}}$ and $\Delta S^\ddagger_{\text{obsd}}$ since they reinforce the positive values of $\Delta H^\ddagger_d$ and $\Delta S^\ddagger_d$.

In summary, we have provided an improved set of relationships for evaluating apparent activation parameters for M–L and other dissociation processes in solution. The equations make it clear that attention to the cage effect is mandatory before any final interpretation of variations in $\Delta H^\ddagger_{\text{obsd}}$ and $\Delta S^\ddagger_{\text{obsd}}$ for M–L bond homolysis is possible. The equations presented here set the stage for the evaluation of bond dissociation energies derived from solution phase kinetics. The connections between $\Delta H_1{}^\ddagger$(s) and bond dissociation energies involve an additional set of considerations which are treated elsewhere.[2f]

Acknowledgment. This work was supported in part by the National Science Foundation (CHE 8419950, Thomas Koenig) and by the NIH (DK-26214, Richard G. Finke). It is a pleasure to acknowledge the helpful comments of Professor David Tyler.

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(11) (a) Waits, H. P.; Hammond, G. S.; *J. Am. Chem. Soc.* **1964**, *86*, 1911. (b) At high (1–10 M) concentrations, the trap can be part of the cage wall with different effects[12–14] than those treated here.

(12) Skell, P. S.; Baxter III, H. N.; Tanko, J. M.; Chebolu, V. *J. Am. Chem. Soc.* **1986**, *108*, 6300. Skell, P. S.; Baxter III, H. N. *J. Am. Chem. Soc.* **1985**, *107*, 2823.

(13) Bunce, N. J.; Ingold, K. U.; Landers, J. P.; Lusztyk, J.; Sciano, J. C. *J. Am. Chem. Soc.*, **1985**, *107*, 5464–5472.

(14) Bunce, N. J.; Joy, R. B.; Landers, J. P.; Nakai, J. S. *J. Org. Chem.* **1987**, *52*, 1155.

(15) (a) Suggs, J. W.; Jun, C.-H. *J. Am. Chem. Soc.*, **1986**, *108*, 4679–4681. (b) The interpretation given in the recent report[15a] of activation parameters for racemization of a chiral Rh–C system contains the conditions of 10b *and* the implicit assumption that no racemization process can occur in the cage pair. The high implied F_c value ($F_c = 1$) could be due to a high k_c value so that rotational motions at the cage pair stage do not compete. However, a high F_c value can also arise from a low k_d, and thus the $\Delta H^\ddagger_1$(s) value for this system is not really known at present.

(16) Doering, W. von E.; Birladeanu, L. *J. Am. Chem. Soc.* **1986**, *108*, 7442–7444.

(17) Kopecky, K. R.; Gillan, T. *Can. J. Chem.* **1969**, *47*, 2371–2386.

(18) Greene, F. D., Berwick, M. A.; Stowell, J. C. *J. Am. Chem. Soc.* **1970**, *92*, 867.

(19) Lee, K.-W.; Horowitz, N.; Ware, J.; Singer, L. A. *J. Am. Chem. Soc.* **1977**, *99*, 2622.

(20) Schuh, H.-H.; Fischer, H. *Helv. Chim. Acta* **1978**, *61*, 2463–2481. Lehni, M.; Fischer, H. *Int. J. Chem. Kin.* **1983**, *15*, 733–757. Lipscher, J.; Fischer, H. *J. Phys. Chem.* **1984**, *88*, 2555–2559.

(21) Houk, K. N.; Rondan, N. G. *J. Am. Chem. Soc.* **1984**, *106*, 4293.

(22) Doubleday, C., Jr.; Camp, R. N.; King, H. F.; McIver, J. W.; Mullally, D.; Page, M. *J. Am. Chem. Soc.* **1984**, *106*, 447.

(23) The value of $\Delta H^\ddagger_c$ could be negative and substantial in associated solvents if formation of the cage pair disrupts solvent–solvent stabilization.

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^{6}Li, ^{13}C, and ^{15}N NMR Spectroscopic Studies of Lithium Dialkylamides. Solution Structure of Lithium Isopropylcyclohexylamide (LICA) in Tetrahydrofuran

Angela S. Galiano-Roth, Elias M. Michaelides, and David B. Collum*

Department of Chemistry, Baker Laboratory
Cornell University, Ithaca, New York 14853-1301

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Lithium dialkylamides have played a prominent role in the development of carbon–carbon bond-forming reactions.[1] Nevertheless, our understanding of dialkylamide solution structures relies heavily on indirect methods such as analogy with solid-state structures[2–7] or with solution structures of more-or-less related

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(1) Stowell, J. C. *Carbanions in Organic Synthesis*; Wiley: New York, 1979. Jackman, L. M.; Lange, B. C. *Tetrahedron* **1977**, *33*, 2737. d'Angelo, J. *Tetrahedron* **1976**, *32*, 2979. House, H. O. *Modern Synthetic Reactions*, 2nd ed.; Benjamin: New York, 1972.

(2) (a) Williard, P. G.; Hintze, M. J. *J. Am. Chem. Soc.* **1987**, *109*, 5539. (b) Williard, P. G.; Salvino, J. M. *J. Am. Chem. Soc.* **1988**, in press. (c) Armstrong, D. R.; Barr, D.; Clegg, W.; Mulvey, R. E.; Reed, D.; Snaith, R.; Wade, K. *J. Chem. Soc., Chem. Commun.* **1986**, 869.

(3) Reed, D.; Barr, D.; Mulvey, R. E.; Snaith, R. *J. Chem. Soc., Dalton Trans.* **1986**, 557.

(4) Barr, D.; Clegg, W.; Mulvey, R. E.; Snaith, R. *J. Chem. Soc., Chem. Commun.* **1984**, 285.

(5) Rogers, R. D.; Atwood, J. L.; Grüning, R. *J. Organomet. Chem.* **1978**, *157*, 229. Mootz, D.; Zinnius, A.; Böttcher, B. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 378. Lappert, M. F.; Slade, M. J.; Singh, A.; Atwood, J. D.; Rogers, R. D.; Shakir, R. *J. Am. Chem. Soc.* **1983**, *105*, 302.

0002-7863/88/1510-2658$01.50/0

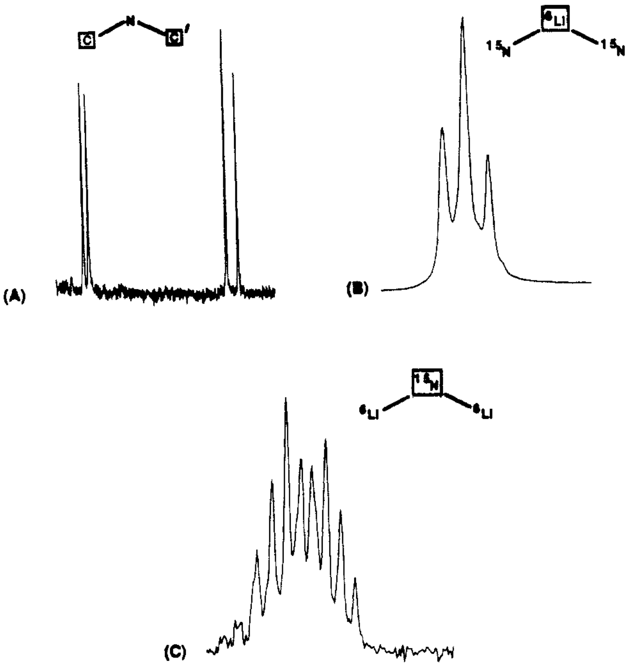
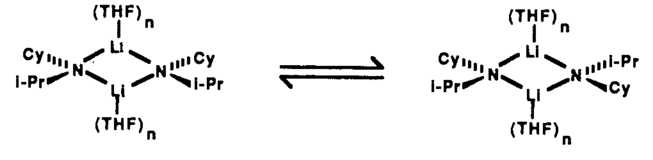


Figure 1. NMR spectra of lithium isopropylcyclohexylamide (LICA): (A) partial ^{13}C NMR spectrum of a 0.20 M solution in 0.59 M THF–toluene-d_8 at −90 °C showing the N–*C*H methine resonances (cf. ref 13); (B) ^{6}Li NMR spectrum of a 0.21 M solution of [^{6}Li,^{15}N]-LICA in 9.93 M THF/toluene-d_8 at −90 °C; (C) ^{15}N NMR spectrum of a 0.20 M solution of [^{6}Li,^{15}N]-LICA in 0.41 M THF/toluene-d_8 at −40 °C. (The small doublets appear sporatically and are believed to be trace impurities arising from the synthesis and handling of the labeled substrate.) The ^{6}Li and ^{15}N NMR spectra were calibrated to 0.30 M LiCl/MeOH (0.0 ppm) and 0.15 M [^{15}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 ^{7}Li NMR spectroscopy in conjunction with 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) $[Cy_2NLi{\cdot}HMPA]_n$ (Cy = cyclohexyl, HMPA = hexamethylphosphoramide) and unsolvated $(PhCH_2NLi)_n$ (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).



cis-1 **trans-1**

^{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.

^{6}Li NMR spectroscopy failed to resolve the two structural forms; a sharp singlet (δ 1.89 ± 0.01 ppm) was observed at all THF concentrations and temperatures. Accordingly, we turned to ^{6}Li–^{15}N double labeling studies, which, in conjunction with ^{6}Li 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 ^{6}Li and ^{15}N NMR spectra of [^{6}Li,^{15}N]-LICA are depicted in Figure 1.[16] The 1:2:1 triplet in the ^{6}Li NMR spectrum of [^{6}Li,^{15}N]-LICA (δ 1.89 ppm, $^{1}J_{\text{N-Li}}$ = 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 (δ 71.3 ppm, $^{1}J_{\text{Li-N}}$ = 4.8 Hz; δ 70.9 pm, $^{1}J_{\text{Li-N}}$ = 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 oligomers.[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 theory[18]

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(6) (a) Engelhardt, L. M.; May, A. S.; Raston, C. L.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1983**, 1671. (b) Barr, D.; Clegg, W.; Mulvey, R. E.; Snaith, R. *J. Chem. Soc., Chem. Commun.* **1984**, *285*, 287. (c) Barr, D.; Clegg, W.; Mulvey, R. E.; Snaith, R. *J. Chem. Soc., Chem. Commun.* **1984**, 700. (d) Cetinkaya, B.; Hitchcock, P. B.; Lappert, M. F.; Misra, M. C.; Thorne, A. J. *J. Chem.* Soc., *Chem. Commun.* **1984**, 148. (e) Seebach, D.; Bauer, W.; Hansen, J.; Laube, T.; Schweizer, W. B.; Dunitz, J. D. *J. Chem. Soc., Chem. Commun.* **1984**, *853*. (f) Colgan, D.; Papasergio, R. I.; Raston, C. L.; White, A. H. *J. Chem. Soc., Chem. Commun.* **1984**, 1708. (g) Dietrich, H.; Mahdi, W.; Knorr, R. *J. Am. Chem. Soc.* **1986**, *108*, 2462. (h) Barr, D.; Clegg, W.; Mulvey, R. E.; Snaith, R. *J. Chem. Soc., Chem. Commun.* **1984**, *469*.

(7) Fjeldberg, T.; Hitchcock, P. B.; Lappert, M. F.; Thorne, A. J. *J. Chem. Soc., Chem. Commun.* **1984**, 822. Bartlett, R. A.; Dias, H. V. R.; Hope, H.; Murray, B. D.; Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **1986**, *108*, 6921. Barr, B.; Clegg, W.; Mulvey, R. E.; Snaith, R. *J. Chem. Soc., Chem. Commun.* **1984**, 79. Power, P. P.; Xiaojie, X. *J. Chem. Soc., Chem. Commun.* **1984**, 358. Barr, B.; Clegg, W.; Mulvey, R. E.; Snaith, R.; Wade, K. *J. Chem. Soc., Chem. Commun.* **1986**, 295. Barr, B.; Clegg, W.; Mulvey, R. E.; Snaith, R. *J. Chem. Soc., Chem. Commun.* 1984, 226. Böche, G.; Marsch, M.; Harms, K. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 373. Brauer, D. J.; Bünger, H.; Liewald, G. R. *J. Organomet. Chem.* **1986**, *308*, 119. Haase, M.; Sheldrich, G. M. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1986**, *C42*, 1009. Reynolds, J. G.; Zalkin, A.; Templeton, D. H.; Edelstein, N. M. *Inorg. Chem.* **1977**, *16*, 1090. Hacker, R.; Kaufmann, E.; Schleyer, P. v. R.; Mahdi, W.; Dietrich, H. *Chem. Ber.* **1987**, *120*, 1533.

(8) Solution structural studies of related lithium amide derivatives: Streitwieser, A., Jr.; Padgett, W. M., II. *J. Phys. Chem.* **1964**, *68*, 2916. Kimura, B. Y.; Brown, T. L. *J. Organomet. Chem.* **1971**, *26*, 57. Wannagat, U. *Adv. Inorg. Chem. Radiochem.* **1964**, *6*, 225. Wannagat, U. *Pure Appl. Chem.* **1969**, *19*, 329.

(9) Wanat, R. A.; Collum, D. B.; Van Duyne, G.; Clardy, J.; DePue, R. T. *J. Am. Chem. Soc.* **1986**, *108*, 3416.

(10) (a) Kallman, N.; Collum, D. B. *J. Am. Chem. Soc.* **1987**, *109*, 7466. (b) DePue, J. S.; Collum, D. B., in press.

(11) Jackman, L. M.; Scarmoutzos, L. M.; Porter, W. *J. Am. Chem. Soc.* **1987**, *109*, 6524. Jackman, L. M.; Scarmoutzos, L. M. *J. Am. Chem. Soc.* **1987**, *109*, 5348. Jackman, L. M.; Scarmoutzos, L. M.; Smith, B. D.; Williard, P. G., in press.

(12) Seebach, D.; Bauer, v. W. *Helv. Chim. Acta* **1984**, *67*, 1972.

(13) Spectroscopic samples were prepared by treatment of isopropylcyclohexylamine with halide free, crystalline [^{6}Li]-ethyllithium (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 [^{6}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 (CH_2's); 28.24, 27.20 (CH_3's); 28.00; 27.85 (CH_2's).

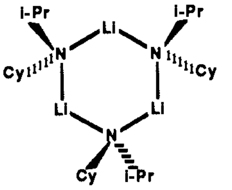
(14) Lewis, H. L.; Brown, T. L. *J. Am. Chem. Soc.* **1970**, *92*, 4664.

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

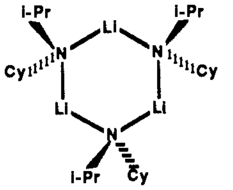
(16) [^{15}*N*]-Isopropylcyclohexylamine was prepared in 35% yield by Raney nickel reduction of [^{15}*N*]-aniline in isopropyl alcohol according to a literature procedure: Srivastava, S.; Minore, J.; Cheung, C. K.; le Noble, W. J. *J. Org. Chem.* **1985**, *50*, 394.

(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 $[(PhCH_2)_2NLi]_3$, $[(Me_3Si)_2NLi]_3$, and $[Me_2C(CH_2)_3CMe_2NLi]_4$), they are all void of coordinating solvents. In contrast, the etherates of $(PhCH_2)_2NLi$ and $(Me_3Si)_2NLi$ crystallize as disolvated cyclic dimers[4,5] (as do other related lithium amide derivatives) while an etherate of $Me_2C(CH_2)_3CMe_2NLi$ remains uncharacterized.[2,3,6] By noting the symmetry of stereoisomeric trimers i and ii, further arguments can be made supporting dimers rather than trimers (or higher oligomers) as the predominant forms of LICA in THF solution. The ^{15}N–^{6}Li coupling patterns of i and ii would exhibit as many as three ^{6}Li 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-workers[19] 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**.



i



ii

The invariance of the ^{6}Li 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.

Acknowledgment. We thank the National Science Foundation Instrumentation Program (CHE 7904825 and PCM 8018643) for support of the Cornell Nuclear Magnetic Resonance Facility. E.M.M. would like to thank the National Science Foundation REU program (CHE-8712498) for an undergraduate research fellowship and D.B.C. expresses thanks to the A. P. Sloan Foundation for unrestricted support.

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

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(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 $RMg(15\text{-}crown\text{-}5)^+$ and Magnesiate Ions[†]

Anthony D. Pajerski, Masood Parvez, and
Herman G. Richey, Jr.*

Department of Chemistry, The Pennsylvania State University
University Park, Pennsylvania 16802

Received December 24, 1987

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

$$3R_2Mg + 15\text{-}C\text{-}5 \rightleftarrows RMg(15\text{-}C\text{-}5)^+ + R_5Mg_2^- \qquad (1)$$

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 $NpMg(2,1,1\text{-}cryptand)^+Np_3Mg^-$ (Np = neopentyl) and $[EtMg(2,2,1\text{-}cryptand)^+]_2Et_6Mg_2^{2-}$ 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 analysis[6] revealed $MeMg(15\text{-}crown\text{-}5)^+$ units and $(Me_5Mg_2^-)_n$ 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 $RMg(crown)^+$ and magnesiate 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

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

(1) Richey, H. G., Jr.; King, B. A. *J. Am. Chem. Soc.* **1982**, *104*, 4672.

(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 Pennsyvania State University, unpublished observations.

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

(6) Crystal data for $MeMg(15\text{-}crown\text{-}5)^+Me_5Mg_2^-$, $C_{16}H_{38}O_5Mg_3$: a = 10.736 (2) Å, β = 18.454 (3) Å, c = 11.923 (3) Å; V = 2362 (2) Å^3, Z = 4, D_{cacd} = 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 Kα 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 analyis 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.

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