radical trap (T) such as DPPH, TEMPO, or an efficient hydrogen donor. Under conditions where the trap (T) is present in modest concentrations (~0.1 M) and in excess of [M-L], the observed rate constant \( k_{\text{obs}} \) for the homolysis process will be given by eq 1. The term in brackets is the complement of the fractional cage efficiency, \( F_c \), which is defined as shown in eq 1a. The first derivative of \( k_{\text{obs}} \) with respect to \( T^{-1} \) yields eq 2 where \( \Delta H^\circ \) and \( \Delta S^\circ \) 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 the cage pair stage where the cage intermediate pertains. Equation 1a is the usual ln(\( k_{\text{obs}} \)/\( T \)) \( / \) (1/\( T \)) slope, whereas \( \Delta H^\circ \) and \( \Delta S^\circ \) directly and both \( \Delta H^\circ \) and \( \Delta S^\circ \) 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 the cage pair stage where the cage intermediate pertains.

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**Li, *C*, and *N* NMR Spectroscopic Studies of Lithium Dialkylamides. Solution Structure of Lithium Isopropylcarboxyhexylamide (LICA) in Tetracyanofuran**

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Lithium dialkylamides have played a prominent role in the development of carbon–carbon bond-forming reactions. Nevertheless, our understanding of dialkylamide solution structures relies heavily on indirect methods such as analogy with solid-state structures or with solution structures of more-or-less related systems in which \( F_c \) is small. If organometallic systems do exhibit high \( F_c \) values, as has been implicitly assumed in recent work on metal–lithium systems, then racemization rates might not count every homolytic event. Finally, we should like to point out that a cage pair is effectively a diradical and, as Houk has shown for the carbene–olefin reaction and Doubleday has discussed for 1,4-diradicals, the activation enthalpy for bond formation, corresponding to \( k_0 \) of Scheme I, can be negative. A negative value for \( \Delta H^\circ \) is quite possible and simply requires that \( \Delta S^\circ \) be sufficiently negative to make \( \Delta G^\circ \) positive. Equations 2 and 3 teach that negative values for \( \Delta H^\circ \) and \( \Delta S^\circ \) increase the cage effect contribution to \( \Delta H^\circ \) and \( \Delta S^\circ \) since they reinforce the positive values of \( \Delta H^\circ \) and \( \Delta S^\circ \).

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 \( \Delta H^\circ \) and \( \Delta S^\circ \) 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 \( \Delta H^\circ \) and bond dissociation energies involve an additional set of considerations that are treated elsewhere.


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

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N-lithiated species.\textsuperscript{8,11} We are aware of only three direct spectroscopic determinations of lithium dialkylamide solution structures. With \textsuperscript{6}Li NMR spectroscopy in conjunction with cryoscopic measurements, Snaithe and co-workers demonstrated that (1) the complex ladder structure of lithium pyridolide solvated by PMDETA (PMDETA = pentamethyldiethylenetriamine) observed crystallographically appeared to coexist with a variety of other uncharacterized structural forms in hydrocarbon solutions\textsuperscript{22} and (2) \([\mathrm{Cy}_3\text{N-Li} \cdot \text{HMPA}]_n\) (Cy = cyclohexyl, HMPA = hexamethylphosphoramide) and unsolvated (PhCH\textsubscript{2}NLi), (Ph = phenyl) exist in hydrocarbon solutions as concentration-dependent dimer–monomer and trimer–monomer mixtures, respectively.\textsuperscript{3,4}

On the basis of cryoscopic measurements, Seебeck reported that lithium disopropylamide (LDA) exists as a 5:1 monomer/dimer mixture in tetrahydrofuran at \(-108^\circ\text{C}\).\textsuperscript{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).

\[\text{cis-1} \quad \text{trans-1}\]

\textsuperscript{13}C NMR spectroscopic analysis of LICA in THF/toluene-d\textsubscript{8} mixtures at \(-89^\circ\text{C}\) showed resonance duplication indicative of a 1:1 mixture of two structural isomers. A concentration 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.

\textsuperscript{6}Li 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 \textsuperscript{15}N double labeling studies, which, in conjunction with \textsuperscript{6}Li and \textsuperscript{15}N NMR spectroscopy, have recently been shown to provide a powerful tool for determining nitrogen–lithium connectivities of lithium amides and lithiated imines.\textsuperscript{10,11,15}

The \textsuperscript{6}Li and \textsuperscript{15}N NMR spectra of \([\text{Li}_2,\text{N}_2] \cdot \text{LICA}\) are depicted in Figure 1. The 1:2:1 triplet in the \textsuperscript{6}Li NMR spectrum of \([	ext{Li},\text{N}] \cdot \text{LICA}\) (\(\delta = 1.89\) ppm, \(J_{\text{Li}-\text{N}} = 5.1\) Hz) is indicative of an \(\text{N} \equiv \text{Li}\)–N connectivity. The partially overlapping pair of 1:2:3:2:1 pentuplets observed in the \textsuperscript{15}N NMR spectrum (\(\delta = 7.3\) ppm, \(J_{\text{Li}-\text{N}} = 4.8\) Hz; \(\delta = 7.9\) ppm, \(J_{\text{Li}-\text{N}} = 5.3\) Hz) shows a \(\text{Li} \equiv \text{N}\)–Li connectivity and confirms the presence of two structural forms. The combination 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.\textsuperscript{16}

The organolithium and THF concentration-independent "so-nance doublets are suggestive of stereoisomeric dimers cis- and trans-1.\textsuperscript{17} Although higher cyclic oligomers predicted by theory\textsuperscript{17}


(13) Spectroscopic samples were prepared by treatment of isopropylcyclohexylamine with triethyl lithium (ref 14) at \(-78^\circ\text{C}\). Representative \(\text{13}^\text{C}\) chemical shift data recorded at 100.25 ppm (\(-90^\circ\text{C}\)) on a 0.20 M solution of \([\text{Li},\text{N}] \cdot \text{LICA}\) in 4:8 (0.59 M) THF/toluene-d\textsubscript{8} are (listed in pairs) as follows: \(\delta = 62.30, 62.23\) (CH\textsubscript{3}) and 53.23, 53.24 (CH\textsubscript{2}) of \(\text{Li} \equiv \text{N}\)–Li connectivity of 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.\textsuperscript{16}

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porting dimers rather than trimers (or higher oligomers) as the predominant forms of LICA in THF solution. The $^{13}$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$^{33}$ that the higher order cyclic oligomers are probably restricted to ligand-free lithium amides and, in turn, further arguments can be made sup-

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Interactions of Dialkylmagnesium Compounds with 15-Crown-5: Formation in Solutions and Solids of RMg(15-crown-5)$^+*$ and Magnesiate Ions$^1$

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

$$3RMg + 15-C-5 = RMg(15-C-5)^+ + 2R^+$$

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 dialkylimagnesium 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-cryptand)$^+$Np$^-$ and [EtMg(2,2,1-cryptand)]$^+\text{EtMe}_2Mg^-$$^2$ were determined, and$^1$H NMR spectra of solutions prepared from several diorganomagnesium compounds showed absorptions attributed to similar species.$^3$ 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$_2$Mg (2 mL, 1.5 M) was layered over a benzene solution of 15-crown-5 (2 mL, 0.5 M). X-ray analysis$^*$$^7$ revealed MeMg(15-crown-5)$^+$ units (and Me$_2$Mg)$^7$ 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 (Me-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.$^5$ Within the four-membered ring, bond angles are similar to and bond lengths slightly longer than those in the Me$_2$Mg structure, which has adjoining Mg's linked by two bridging methyl groups.$^5$

Solutions now have been prepared, many of which are stable for days or weeks at room temperature, whose $^1$H 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, $\delta$ 2.99; C, $\delta$ 3.31) and two sets of Np absorptions (A, $\delta$ -0.40 for the CH$_2$ and $\delta$ 1.22 for the CH$_3$; B, $\delta$ 0.34 for the CH$_3$ and $\delta$ 1.54 for the CH$_2$'s). For several

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


(6) Crystal data for MeMg(15-crown-5)$^+$Me$_2$Mg$:\text{C}_8\text{H}_{23}\text{O}_4\text{Mg}_2: a = 10.736 (2) Å, \beta = 18.454 (3) Å, \gamma = 11.923 (3) Å, V = 2362 (2) Å$^3$, Z = 4, $D_{\text{calc}} = 1.078$ g cm$^{-3}$; space group Pnma, \text{R} = 0.077 for 1470 reflections with $\theta > 3\theta$ measured on an Enraf-Nonius CAD-4 diffractometer by using graphite-monochromated 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 could 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$_2$Mg, C-Mg-C is 105 (2)$^\circ$, Mg-C-Mg is 75 (2)$^\circ$, Mg-C is 2.24 (3) Å, and Mg-Mg is 2.72 (2) Å.

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

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References


(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 dioxopropylamide-ololate complexes crystallographically (ref 2a and unpublished results). We have recently observed and studied the direct N-alkylation of lithium diethylamide dimer and lithium dipropylamide-lithium bromide mixed dimer with n-butyl bromide (ref 10b). The general principles of mixed aggregate effects on reaction outcomes have been discussed previously (Schoch, D. In Proceedings of the Robert A. Welch Foundation Conferences on Chemistry and Biochemistry; Wiley: New York, 1984; p 93).