

Lithium Dialkylamide Mixed Aggregation: An NMR Spectroscopic Study of the Influence of Hexamethylphosphoramide (HMPA)

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Received February 22, 1994*

Abstract: ^6Li and ^{15}N NMR spectroscopic studies of [$^6\text{Li},^{15}\text{N}$]lithium diisopropylamide ([$^6\text{Li},^{15}\text{N}$]LDA) and [$^6\text{Li},^{15}\text{N}$]lithium-2,2,6,6-tetramethylpiperidide ([$^6\text{Li},^{15}\text{N}$]LiTMP) with [^6Li]LiCl, [^6Li]lithium cyclohexenolate (**4**), and [^6Li]lithium-2,4-dimethylpentenolate (**5**) in tetrahydrofuran–hexamethylphosphoramide (THF–HMPA) mixtures are described. LDA–LiCl mixtures show no tendency to form mixed aggregates. LiTMP–LiCl mixtures contain a 1:1 mixed cyclic dimer and a mixed aggregate assigned as an anionic open dimer. LDA–**4**, LDA–**5**, LiTMP–**4**, and LiTMP–**5** mixtures all contain 1:1 mixed cyclic dimers as the sole observable mixed aggregate forms. The influence of HMPA on mixed aggregate formation is discussed in light of previous studies of mixed aggregate formation in the absence of HMPA as well as predictions derived from semiempirical (MNDO) computational studies described in the preceding manuscript.

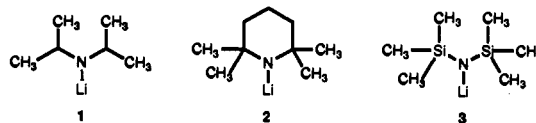
Introduction

Despite two renaissances of physicochemical studies of organolithium reagents—the first in the 1960s fueled by anionic polymerization¹ and the second in the 1980s fueled by methodological developments in natural products synthesis^{2–4}—there still exists a very limited understanding of the origins of organolithium reaction rates and selectivities. For example, seemingly systematic changes in solvents and cosolvents can afford huge variations in reaction rates, yields, and selectivities that are accompanied by a number of questions. Do solvent-dependent rate changes stem from changes in reactivity of otherwise isostructural species, or do they arise from fundamental differences in aggregation state and solvation numbers? If, for the sake of discussion, we accept the notion that the most dramatic solvent effects originate from fundamental solvent-dependent structural changes, do these changes occur at the ground state, at the transition state, or both? Do rate accelerations stem from transition state stabilization or ground state destabilization? Do mixed aggregates form during the course of the reactions? If so, are solvent-dependent rates and selectivities manifestations of solvent-dependent mixed aggregate equilibria?

This latter issue—the influence of solvent on the formation, structure, and reactivity of organolithium mixed aggregates—constitutes an essential piece of any mechanistic picture. The possible consequences of mixed aggregate formation have been known for many years¹ but were most clearly articulated in two

reviews by Seebach.³ Nevertheless, the solvent dependencies and other factors influencing mixed aggregation have received limited attention.⁵ The most detailed study is that of Jackman and Rakiewicz on mixed aggregate formation of lithium phenolates with various highly ionizable lithium salts in ethereal solvents.⁶ They reported an apparent inverse correlation of solvent donicity with the tendency to form mixed aggregates. More recently and of special relevance to this work, Reich noted that hexamethylphosphoramide (HMPA) precludes the formation MeLi–LiCl mixed aggregates that are observed in the absence of HMPA.⁷

We have carried out a two-part study of the influence of HMPA on the relative stabilities and structures of lithium dialkylamide mixed aggregates in tetrahydrofuran (THF) solution.^{8,9} In the first phase, we carried out detailed semiempirical (MNDO) calculations of lithium diisopropylamide (LDA; **1**) and lithium 2,2,6,6-tetramethylpiperidide (LiTMP; **2**) mixed aggregates of varying topologies including cyclic oligomers (dimers, trimers, and tetramers), ladders, open dimers, and triple ions.¹⁰ The



computational studies were guided by previously reported spectroscopic studies on lithium dialkylamide mixed aggregates

* Abstract published in *Advance ACS Abstracts*, August 15, 1994.

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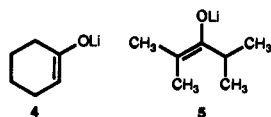
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in THF solution^{8,11-14} as well as supporting kinetic,^{15,16} structural,^{8,17,18} and computational^{9,19,20} studies of lithium dialkylamide homonuclear aggregates. They were also steered by issues pertaining to laddering^{9,21} and conformational isomerism¹² that had eluded our experimental efforts. The calculations predicted a number of effects of HMPA on the mixed aggregate equilibria. In the second phase, we have carried out ⁶Li and ¹⁵N NMR spectroscopic investigations to ascertain the influence of HMPA on the structures and stabilities of lithium dialkylamide mixed aggregates. We focused upon mixed aggregates of LDA and LiTMP with LiCl, lithium cyclohexenolate (4), and lithium 2,4-dimethylpentenolate (5). These spectroscopic studies and consequent theory-experiment correlations are described below.



Results

Preliminary investigations revealed that addition of limited quantities of HMPA (0.1–1.0 equiv/Li) to R₂NLi–LiX mixtures affords an extraordinary structural complexity, presumably due to formation of THF–HMPA mixed-solvated mixed aggregates.¹⁷ Although these mixed solvates may prove to be interesting in their own right, we excluded them from consideration in this investigation by (1) adjusting the HMPA concentration to maintain a fixed 4-fold excess over the total lithium ion concentration (referred to hereafter as "THF/HMPA solution"), (2) maintaining the lithium dialkylamide concentrations at 0.10 M, and (3) systematically varying only the LiX concentration. In the absence of added LiX salts (but otherwise under analogous conditions) LDA exists exclusively as bis(HMPA)-solvated dimer 6, while LiTMP exists as a mixture of bis(HMPA)-solvated monomer 7, tetrakis(HMPA)-solvated dimer 8, and triple ion 9.¹⁷ In the absence of lithium dialkylamides, LiCl exists as ion pair 10,⁷ while enolates 4 and 5 form HMPA solvates of unknown solvation numbers and aggregation states.^{4,22}

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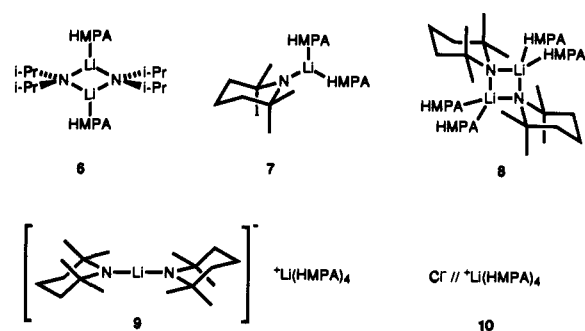
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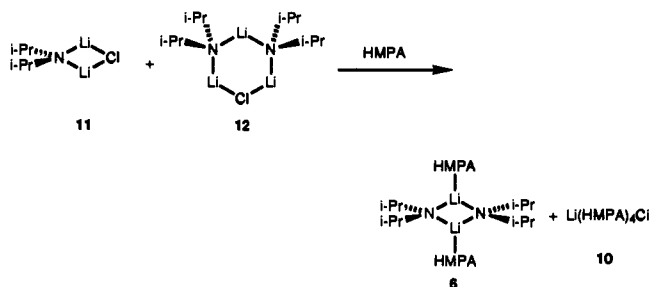
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The ⁶Li and ¹⁵N NMR spectroscopic data are summarized in Table 1. The spectra are relatively routine⁸ and are archived in the supplementary material. We generally found ³¹P NMR spectroscopy to be of marginal utility due to unresolved ⁶Li–³¹P coupling.^{22–24} Although loss of ⁶Li–³¹P coupling often obscured the details of the lithium ion coordination spheres, chemical shift differences caused by the added HMPA quite clearly document the presence of coordinated HMPA ligands. The ⁶Li resonances corresponding to the HMPA-solvated LiCl and lithium enolates were readily detected through comparisons with spectra recorded on THF/HMPA solutions of LiX salt in the absence of lithium dialkylamides. ⁶Li–¹⁵N and ⁶Li–³¹P couplings were readily distinguished through parallel spectral series using ⁶Li singly-labeled and ⁶Li–¹⁵N doubly-labeled lithium dialkylamides. The ⁶Li–¹⁵N resonance correlations affording atomic connectivities were established through a combination of single frequency irradiation methods²⁵ and ⁶Li–¹⁵N heteronuclear multiple quantum correlation (HMQC) spectroscopy.²⁶

LDA–LiX. Titration of THF/HMPA solutions of [⁶Li,¹⁵N]–LDA (dimer 6) with 0.2–2.0 equiv of [⁶Li]LiCl results in the appearance of a single new quintet centered at –0.54 ppm in the ⁶Li NMR spectrum corresponding to the +Li(HMPA)₄ counterion of LiCl (10).⁷ ¹⁵N NMR spectroscopy confirmed the absence of LDA–LiCl mixed aggregates. HMPA appears to efficiently sequester the LiCl, precluding formation of 1:1 and 2:1 mixed aggregates of general structure 11 and 12, respectively, observed in THF/pentane solutions.¹³



Spectra recorded on solutions of [⁶Li,¹⁵N]LDA in THF/HMPA with added lithium cyclohexenolate (4) display ⁶Li resonances corresponding to LDA dimer 6, the homonuclear aggregates of enolate 4, and mixed dimer 13. The three coexist

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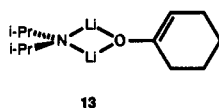
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Table 1. ^6Li and ^{15}N NMR Spectroscopic Data^a

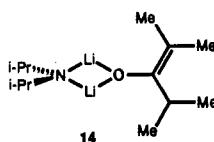
compd	<i>t</i> (°C)	^6Li δ (multiplicity, $^1J_{\text{Li-X}}$, Hz)	$^{15}\text{N}\{^1\text{H}\}$ δ (multiplicity, $^1J_{\text{Li-N}}$, Hz)
4	-115	-0.09 (s), -0.15 (s), -0.31 (s), -0.37 (s)	
5	-115	0.04 (s)	
6	-125	1.55 (q, $J_{\text{Li-N}} = 4.4$, $J_{\text{Li-P}} = 4.3$)	74.1 (quint, $J_{\text{Li-N}} = 4.5$)
7	-115	0.73 (d, $J_{\text{Li-N}} = 8.5$)	88.9 (t, $J_{\text{Li-N}} = 8.5$)
8	-115	0.80 (t, $J_{\text{Li-N}} = 3.5$)	76.8 (quint, $J_{\text{Li-N}} = 3.5$)
9	-115	2.49 (t, $J_{\text{Li-N}} = 9.9$) -0.54 (quint, $J_{\text{Li-P}} = 2.9$)	99.2 (quint, $J_{\text{Li-N}} = 10$)
10	-115	-0.54 (quint, $J_{\text{Li-P}} = 2.9$)	
13	-125	-0.79 (d, $J_{\text{Li-N}} = 5.4$)	74.3 (quint, $J_{\text{Li-N}} = 5.4$)
14	-125	0.78 (d, $J_{\text{Li-N}} = 5.0$)	76.8 (quint, $J_{\text{Li-N}} = 5.0$)
15	-125	1.24 (d, $J_{\text{Li-N}} = 4.7$) 0.32 (d, $J_{\text{Li-N}} = 5.3$ $J_{\text{Li-P}} = 2.9^b$)	76.3 (quint, $J_{\text{Li-N}} = 5.0$)
16	-125	1.56 (dd, $J_{\text{Li-N}} = 5.4$, $J_{\text{Li-N}} = 8.1$) 1.48 (d, $J_{\text{Li-N}} = 5.4$)	77.6 (quint, $J_{\text{Li-N}} = 5.4$) 87.2 (t, $J_{\text{Li-N}} = 8.1$)
18	-128	0.80 (s, no Li-N coup.) 0.45 (d, $J_{\text{Li-N}} = 5.1$)	77.3 (quint, $J_{\text{Li-N}} = 5.1$)
19	-125	0.79 (d, $J_{\text{Li-N}} = 5.1$) 0.53 (dd, $J_{\text{Li-N}} = 5.1$) $J_{\text{Li-P}} = 3.9$)	78.7 (quint, $J_{\text{Li-N}} = 5.2$)

^a Spectra were recorded on mixtures of [^6Li , ^{15}N]R₂NLi (0.1 M) and added lithium salt (0.2–2.0 equiv) in 3:1 THF/pentane containing 4.0 equiv of HMPA per total lithium ion. ^b Recorded at -128 °C.



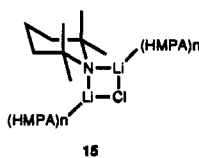
in approximately equal concentrations at 1.0 equiv of the lithium salt, indicating that mixed aggregate **13** is not formed quantitatively. We should add, however, that HMPA unequivocally promotes LDA-4 mixed dimer formation since LDA and **4** show no tendency to form mixed aggregates under similar conditions in the absence of HMPA.^{11b} It is also noteworthy that 2:1 mixed trimers (analogous to **12**) were absent at all LDA:4 proportions in the presence of HMPA.

Addition of low equivalents of extremely bulky enolate **5** to [^6Li , ^{15}N]LDA in THF/HMPA causes nearly quantitative formation of mixed dimer **14**. In this case, homonuclear enolate was



detectable only after all the LDA was consumed, revealing a measurably higher propensity for LDA to form mixed dimers with **5** than with **4**. However, the influence of HMPA relative to THF is difficult to ascertain since nearly quantitative formation of **14** occurs in THF solutions as well.²⁷

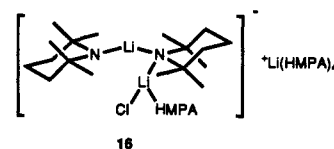
LiTMP-LiX. ^6Li and ^{15}N NMR spectra recorded on THF/HMPA solutions of [^6Li , ^{15}N]LiTMP containing varying quantities of [^6Li]LiCl reveal two mixed aggregates. The predominant mixed aggregate is readily assigned as mixed dimer **15**. Dimer



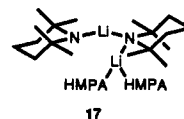
15 displays two ^6Li doublets that maintain a strict 1:1 ratio over all LiCl concentrations and were shown to be coupled to a common ^{15}N nucleus. The two resonances correspond to the chemically inequivalent axial and equatorial lithium sites characteristic of the LiTMP mixed aggregates studied previously.¹² At extremely low probe temperatures (<-125 °C), we observe weak (2.9 Hz) two-bond $^3\text{J}_{\text{P-Li}}$ coupling to the upfield lithium resonance. While we have no direct experimental support, MNDO calculations reveal a marked resistance of the equatorial lithium to attain higher solvation numbers that could be the cause of the lower solvent exchange rates.

(27) Kim, Y.-J.; Collum, D. B. Unpublished results.

We observe a second, more complex mixed aggregate assigned as anionic open dimer **16**. Dimer **16** manifests a new doublet and



a doublet-of-doublets in a [LiCl]-independent 1:1 ratio. The two upfield legs of the doublet-of-doublets are obscured by the upfield doublet but can be revealed by single frequency ^{15}N irradiations or ^6Li - ^{15}N HMQC spectroscopy (see below). In addition, a quintet characteristic of the +Li(HMPA)₄ counterion of an ion pair is observable; *this quintet is not necessarily due to the HMPA-solvated LiCl ion pair 10*. The corresponding ^{15}N NMR spectra recorded on [^6Li , ^{15}N]LiTMP in THF/HMPA solution at low LiCl concentrations reveal a quintet and a triplet. ^6Li - ^{15}N HMQC spectroscopy (Figure 1) provides the requisite resonance correlations leading to the atomic connectivities depicted in Figure 2. Although the Li-N-Li-N connectivity suggests a topology similar to that of open dimer **17**, **17** is not observable at these elevated HMPA concentrations in the absence of LiCl.¹⁷ Thus,



the assignment of **16** is founded in part on the requirement for both chloride ion and HMPA. However, we hasten to add that there are other structures involving alternative numbers and placements of chloride ions and HMPA ligands consistent with the available data. Our preference for **16** stems from an accumulation of data pertaining to open dimers described previously.^{10,17,19,21,28} Despite the +Li(HMPA)₄ ion common to **16** and LiCl solvate **10**, the disproportionate growth in the +Li(HMPA)₄ cation resonance suggests that incorporation of the LiCl into mixed aggregates is not quantitative. This contrasts with results obtained in the absence of HMPA and supports the conclusion from the LDA-LiCl series that HMPA retards mixed aggregation with LiCl. The appearance of **15** at low LiCl concentrations and **16** at higher LiCl concentrations seems

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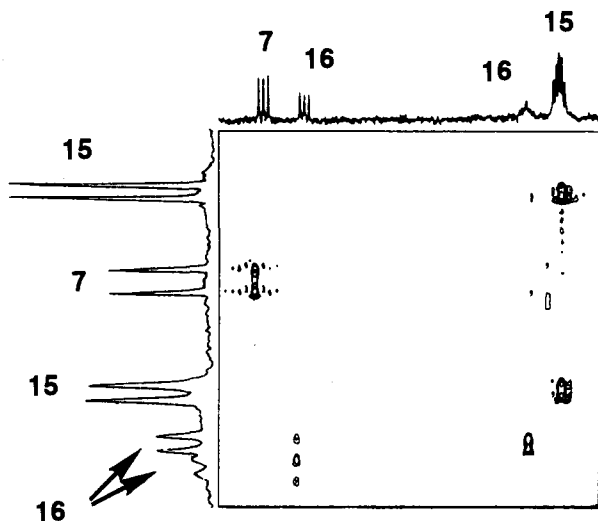


Figure 1. ${}^6\text{Li}$ - ${}^{15}\text{N}$ HMQC spectrum of 0.13 M [${}^6\text{Li}$, ${}^{15}\text{N}$]LiTMP/0.5 equiv. of added [${}^6\text{Li}$]LiCl with 4.0 HMPA relative to total [${}^6\text{Li}$] in 3:1 THF/pentane at -125°C . 256 t_1 increments were acquired with 64 transients/increment. The left-hand and upper traces are the corresponding one-dimensional ${}^6\text{Li}$ and ${}^{15}\text{N}$ NMR spectra, respectively. The spectrum was recorded on a Varian Unity 500 spectrometer equipped with a custom built 3-channel probe designed to accommodate lithium and nitrogen pulses with concurrent proton decoupling. The spectrometer operates at 73.56 MHz and 50.65 MHz for ${}^6\text{Li}$ and ${}^{15}\text{N}$, respectively. Data were processed in phase sensitive mode. Digital resolution in f_1 prior to zero filling is 2.3 Hz.

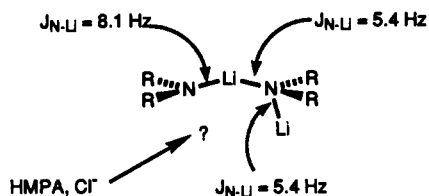
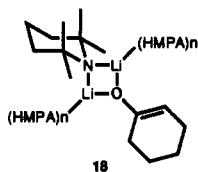


Figure 2.

inconsistent with their relative stoichiometries; however, this mass action behavior stems from the changes in HMPA concentration that accompany the change in LiCl concentration.

Spectroscopic analysis of [${}^6\text{Li}$, ${}^{15}\text{N}$]LiTMP in THF/HMPA with added lithium cyclohexenolate 4 reveals mixed dimer 18 as the only observable mixed aggregate. Resonances corresponding



to homonuclear enolate aggregates are visible even at low enolate concentrations (0.2 equiv), indicating that 18 is not formed quantitatively. The nearly equivalent propensities of LiTMP and LDA to form mixed dimers with enolate 4 and the complete absence of mixed trimers or other mixed aggregates are both notable.

Treatment of [${}^6\text{Li}$, ${}^{15}\text{N}$]LiTMP in THF/HMPA with lithium diisopropylketone enolate 5 affords mixed dimer 19. In this case,

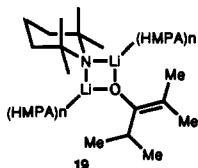


Table 2. Lithium Dialkylamide Mixed Aggregate Structures

R_2NLi	solvent, S	$\text{LiX} = \text{LiCl}$	$\text{LiX} = 4$	$\text{LiX} = 5$
LDA	THF	dimer, trimer	none	dimer
	HMPA	none	dimer	dimer
LiTMP	THF	dimer, trimer	dimer, dimer, tetramer	dimer
	HMPA	dimer, 16	dimer	dimer

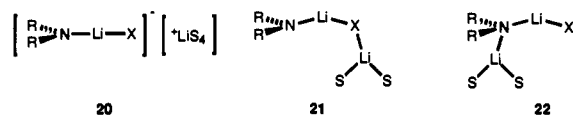
the homonuclear enolate and dialkylamide aggregates do not coexist at any LiTMP:5 proportion, indicating a quantitative formation of 19. The extent of mixed aggregation in LiTMP-5 mixtures is greater than that for either LiTMP-4 or LDA-5 mixtures. Thus, the structural factors in the R_2NLi and LiX fragments promoting mixed aggregation display a degree of cooperativity.

Lithium Hexamethyldisilazide-LiX. Previous ${}^6\text{Li}$ - ${}^{15}\text{N}$ double labeling studies¹⁸ confirmed Kimura and Brown's²⁹ conclusion that lithium hexamethyldisilazide (LiHMDS, 3) exists as a dimer-monomer mixture in THF solution and uncovered complex solution equilibria in HMPA/THF solution manifesting striking parallels with LiTMP. However, in contrast to LiTMP, LiHMDS in THF solution completely resists formation of mixed aggregates with LiCl, 4, 5, and several other lithium salts.²⁷ We note in passing that none of the three salts under study here showed any tendency whatsoever to form mixed aggregates with [${}^6\text{Li}$, ${}^{15}\text{N}$]-LiHMDS in THF/HMPA solution as well.

Discussion

It is instructive to examine the influence of HMPA on the structures and stabilities of lithium dialkylamide mixed aggregates in the context of (1) previous spectroscopic investigations of LDA-LiX and LiTMP-LiX in the absence of HMPA^{12,13} and (2) the predictions stemming from MNDO studies described in the adjoining manuscript.¹⁰ The general results are summarized in Table 2. We have included results reported previously^{12,13} for mixed aggregation in the absence of HMPA for comparison.

The MNDO studies revealed (1) exothermic substitution of THF by HMPA for most R_2NLi -LiX mixed aggregates albeit attenuated in the most congested cases; (2) an increased preference for mixed dimers relative to mixed trimers; and (3) an increased stability of mixed triple ions (20),³⁰ N-open dimers (21), and X-open dimers (22) with HMPA ligation that *might* be sufficient to make them observable species for the most sterically congested cases. Moreover, points 2 and 3 are both suggested to be more



pronounced for LiTMP than for LDA.

The prediction most strictly adhered to is that HMPA will stabilize mixed dimers relative to mixed trimers. Despite observation of 2:1 mixed cyclic trimers for LDA-LiCl, LiTMP-LiCl, and LiTMP-4 mixtures in THF solutions, in no instance are mixed cyclic trimers observable in the presence of excess HMPA.

Our protocol in the computational studies afforded only relative (rather than absolute) propensities to form mixed aggregates. It also proved difficult to ascertain the influence of HMPA on the absolute propensity to form mixed aggregates experimentally in

(29) Kimura, B. Y.; Brown, T. L. *J. Organomet. Chem.* 1971, 26, 57.

(30) For leading references to the literature of triple ions, see the companion paper (ref 10).

some cases. In several instances, mixed aggregate formation is nearly quantitative both with and without HMPA, obscuring the net influence of HMPA except to show that it does not preclude mixed aggregate formation. Similarly, the complete lack of LiHMDS-LiX mixed aggregates regardless of the choice of solvent or LiX additive demonstrates that HMPA cannot promote mixed aggregate formation in especially unfavorable cases. However, several cases provided spectroscopic support for both the promotion and the retardation of mixed aggregation by HMPA. Solutions of LDA-LiCl mixtures in THF with excess HMPA contain LDA dimer **6** and LiCl ion pair **10** to the exclusion of 1:1 mixed dimer **11** and 2:1 mixed trimer **12** observed in the absence of HMPA. It would appear that sequestering the LiCl as **10** completely inhibits LDA-LiCl mixed aggregate formation, consistent with similar observations by Reich⁷ and Jackman.⁶ Even LiTMP-LiCl mixed aggregate formation was attenuated by (although not precluded by) the HMPA. In contrast, mixtures of LDA and enolate **4** show appreciable concentrations of mixed dimer **13** only in the presence of excess HMPA. In this instance, HMPA measurably promotes mixed aggregate formation.

We were intrigued most of all by the prospects of observing mixed triple ions (**20**), *N*-open dimers (**21**), and *X*-open dimers (**22**). Although none of these three was documented in forms that we had anticipated, the LiTMP-LiCl mixed aggregate **16** embodies structural features characteristic of both *N*-open dimers and triple ions.³¹ On the one hand, **16** is simply a mixed *N*-open dimer in which chloride ion occupies a coordination site that might otherwise contain a neutral (HMPA) ligand. On the other hand, it represents a higher homolog of a mixed triple ion. Indeed, MNDO calculations carried out subsequent to the spectroscopic detection of **16** suggested an open-dimer-like geometry possessing marked stability. One should bear in mind, however, that the demonstrable requirement for HMPA and chloride ion in conjunction with the spectroscopically discernible connectivity (Figure 2) does not uniquely define the structure of **16**. Alternative placements and numbers of chloride and HMPA ligands cannot be excluded at this time.³²

Conclusion

Our interest in HMPA stems from its well-documented influence on the reactivity of the synthetically important lithium dialkylamides³³ and its general importance throughout organolithium chemistry. HMPA has also been shown to increase,²² decrease,⁷ or leave unchanged^{17,18} the aggregation states of homonuclear organolithium derivatives. It would appear that HMPA also promotes or retards lithium dialkylamide mixed aggregate formation, depending upon the structure of the lithium

dialkylamide as well as the choice of LiX additive. In general, increasing the bulk of the *N*-alkyl substituents on the amide and the steric demands of the LiX additive tends to promote mixed aggregate formation. It was especially satisfying that most of the observable trends were foreshadowed by the MNDO computational methods described in the companion paper.¹⁰ However, as we continue to try to stitch together stereochemical, spectroscopic, kinetic, crystallographic, and computational data into a coherent mechanistic picture of lithium dialkylamides, we are constantly reminded of the truism that reactivity can only be understood as a relationship between the ground state and the transition state; additional studies are in progress.

Experimental Section

Reagents and Solvents. THF and all hydrocarbons were distilled by vacuum transfer from blue or purple solutions containing sodium benzophenone ketyl. The hydrocarbon stills contained 1% tetraglyme to dissolve the ketyl. ⁶Li metal (95.5% enriched) was obtained from Oak Ridge National Laboratory. The [⁶Li]ethylolithium used to prepare the ⁶Li labeled amides was prepared and purified according to the standard literature procedure.³⁴ The isotopically labeled LDA,^{17,35} LiTMP,¹² LiCl,¹² **4**,³⁵ and **5**³⁵ were isolated as analytically pure solids as described previously. The diphenylacetic acid used to check solution titers³⁶ was recrystallized from methanol and sublimed at 120 °C under full vacuum. Air- and moisture-sensitive materials were manipulated under argon or nitrogen using standard glovebox, vacuum line, and syringe techniques.

NMR Spectroscopic Analyses. Samples for spectroscopic analyses were prepared using a sample preparation protocol described in detail elsewhere.^{12,17} Standard ⁶Li, ¹⁵N, and ³¹P NMR spectra were recorded on a Varian XL-400 spectrometer operating at 58.84, 40.52, and 161.82 MHz, respectively, and referenced to (respectively) 0.3 [⁶Li]LiCl/MeOH at -100 °C (δ 0.0 ppm), [¹⁵N]aniline at -100 °C (δ 52 ppm), and HMPA at -100 °C (δ 26.4 ppm).¹² The ⁶Li-¹⁵N HMQC spectra were recorded on a Varian Unity 500 spectrometer equipped with a custom-built 3-channel probe designed to accommodate lithium and nitrogen pulses with concurrent proton decoupling. The HMQC pulse sequence³⁷ was obtained through Varian.

Acknowledgment. We thank the National Institutes of Health for direct support of this work. We also acknowledge the National Science Foundation Instrumentation Program (CHE 7904825 and PCM 8018643), the National Institutes of Health (RR02002), and IBM for support of the Cornell Nuclear Magnetic Resonance Facility.

Supplementary Material Available: ⁶Li and ¹⁵N NMR spectra of LDA and LiTMP in the presence of LiX salts and HMPA (resonances are labeled with compound numbers from the main text) (13 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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