offers efficient on-resonance decoupling over a large bandwidth and is well compensated for both radio-frequency inhomogeneity and flip angle errors because it is constructed with the same global symmetry as are the WALTZ, MLEV, and GARP supercycles. Although the quality of decoupling near resonance is not affected by amplitude modulation, spurious oscillations created far from resonance by traditional decoupling sequences are dramatically attenuated. Shaped decoupling can be operated at very low field strengths so as not to induce perturbations in noncoupled coherences. Shaped decoupling should virtually eliminate complications from carbonyl coupling in multidimensional spectra of labeled proteins and lend itself to other applications where selective decoupling is desirable.

Determination of Structures of Solvated Lithium Dialkylamides by Semiempirical (MNDO) Methods. Comparison of Theory and Experiment

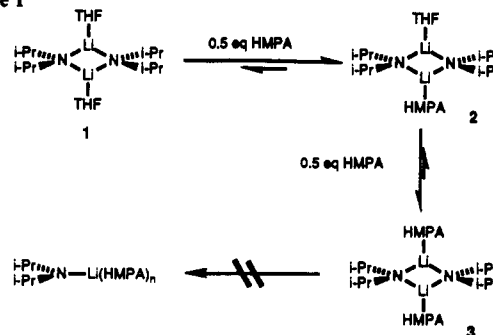**Floyd E. Romesberg and David B. Collum***

Contribution from the Department of Chemistry, Baker Laboratory, Cornell University, Ithaca, New York 14853-1301. Received August 12, 1991

Abstract: MNDO computational studies of lithium dimethylamide (Me_2NLi), lithium diisopropylamide (LDA), and lithium 2,2,6,6-tetramethylpiperidide (LiTMP) solvated by H_2O, Me_2O, THF, phosphoramide ($(NH_2)_3P=O$), and hexamethylphosphoramide (HMPA) are described. The relative stabilities of monomers, dimers, trimers, open dimers, and anionic triple ions reveal the steric and electronic factors that influence aggregation state. The calculations support previous suggestions that coordinated solvents destabilize cyclic trimers relative to cyclic dimers. The cyclic dimers appear to be most stable in the disolvated form (one solvent per lithium). The increased steric demands of *N*-alkyl moieties cause decreased stabilities of cyclic dimers relative to the monomers, open dimers, and triple ions. The optimized structures of open dimers and triple ions reveal relative rotations of the amide fragments and increased internal N–Li–N bond angles consistent with considerable relief of steric interactions. Direct comparisons between calculated structures of various HMPA and THF solvates of LDA and LiTMP with previously described solution structure studies reveal excellent correlations of theory and experiment.

Introduction

For several years we have been investigating the solution structures of lithium dialkylamides, lithiated hydrazones, and lithioimines with the long-term goal of understanding the determinants of organolithium selectivity and reactivity.[1-13] Although a combination of NMR spectroscopic and kinetic methods can deconvolute the structures[1-7] and consequences of the various aggregation states,[6,8-12] there are fundamental issues associated with solvation that remain acutely elusive. There are only a handful of instances in the vast organolithium literature in which solvation states have been determined in solution,[4,5,7,14-16] and most of these are based on relatively indirect methods.

Scheme I

(1) For leading references, see: Kim, Y.-J.; Bernstein, M. P.; Galiano-Roth, A. S.; Romesberg, F. E.; Williard, P. G.; Fuller, D. J.; Harrison, A. T.; Collum, D. B. *J. Am. Chem. Soc.* **1991**, *113*, 5053.

(2) Hall, P. L.; Gilchrist, J. H.; Harrison, A. T.; Fuller, D. J.; Collum, D. B. *J. Am. Chem. Soc.* **1991**, *113*, 9175.

(3) Kim, Y.-J.; Bernstein, M. P.; Galiano-Roth, A. S.; Romesberg, F. E.; Williard, P. G.; Fuller, D. J.; Harrison, A. T.; Collum, D. B. *J. Org. Chem.* **1991**, *56*, 4435.

(4) Kallman, N.; Collum, D. B. *J. Am. Chem. Soc.* **1987**, *109*, 7466.

(5) Depue, J. S.; Collum, D. B. *J. Am. Chem. Soc.* **1988**, *110*, 5518.

(6) Galiano-Roth, A. S.; Collum, D. B. *J. Am. Chem. Soc.* **1988**, *110*, 3546.

(7) Wanat, R. A.; Collum, D. B.; Van Duyne, G.; Clardy, J.; DePue, R. T. *J. Am. Chem. Soc.* **1986**, *108*, 3416. Jackman, L. M.; Scarmoutzos, L. M.; DeBrosse, C. W. *J. Am. Chem. Soc.* **1987**, *109*, 5355.

(8) Romesberg, F. E.; Gilchrist, J. H.; Harrison, A. T.; Fuller, D. J.; Collum, D. B. *J. Am. Chem. Soc.* **1991**, *113*, 5751.

(9) Galiano-Roth, A. S.; Collum, D. B. *J. Am. Chem. Soc.* **1989**, *111*, 6772.

(10) Depue, J. S.; Collum, D. B. *J. Am. Chem. Soc.* **1988**, *110*, 5518; 5524.

(11) Bernstein, M. P.; Romesberg, F. E.; Fuller, D. J.; Harrison, A. T.; Collum, D. B.; Liu, Q.-Y.; Williard, P. G. *J. Am. Chem. Soc.*, in press.

(12) Hall, P. L.; Gilchrist, J. H.; Collum, D. B. *J. Am. Chem. Soc.* **1991**, *113*, 9171.

(13) Gregory, K.; Schleyer, P. v. R.; Snaith, R. *Adv. Organomet. Chem.*, in press.

solvation states have been determined in solution,[4,5,7,14-16] and most of these are based on relatively indirect methods.

(14) Brown, T. L.; Gerteis, R. L.; Rafus, D. A.; Ladd, J. A. *J. Am. Chem. Soc.* **1964**, *86*, 2135. Lewis, H. L.; Brown, T. L. *J. Am. Chem. Soc.* **1970**, *92*, 4664. Quirk, R. P.; Kester, D. E. *J. Organomet. Chem.* **1977**, *127*, 111. Bartlett, P. D.; Goebel, C. V.; Weber, W. P. *J. Am. Chem. Soc.* **1969**, *91*, 7425. Cheema, Z. K.; Gibson, G. W.; Eastham, J. F. *J. Am. Chem. Soc.* **1963**, *85*, 3517. Eastham, J. F.; Gibson, G. W. *J. Am. Chem. Soc.* **1963**, *85*, 2171. Waack, R. Doran, M. A.; Stevenson, P. E. *J. Am. Chem. Soc.* **1966**, *88*, 2109. Bauer, W.; Klusener, P. A. A.; Harder, S.; Kanters, J. A.; Duisenberg, A. J. M.; Brandsma, L.; Schleyer, P. v. R. *Organometallics* **1988**, *7*, 552. Harder, S.; Boersma, J.; Brandsma, L.; Kanters, J. A.; Bauer, W.; Pi, R.; Schleyer, P. v. R.; Schölhorn, H.; Thewalt, U. *Organometallics* **1989**, *8*, 1688. Bauer, W.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1989**, *111*, 7191. Fraenkel, G.; Chow, A.; Winchester, W. R. *J. Am. Chem. Soc.* **1990**, *112*, 1382. Quirk, R. P.; McFay, D. *J. Polym. Sci., Polym. Chem. Ed.* **1981**, *19*, 1445. Wehman, E.; Jastrzebski, J. T. B. H.; Ernsting, J.-M.; Grove, J. M.; van Koten, G. *J. Organomet. Chem.* **1988**, *353*, 145.

(15) Reich, H. J.; Gree, D. P. *J. Am. Chem. Soc.* **1989**, *111*, 8729. Reich, H. J.; Green, D. P.; Phillips, N. H. *J. Am. Chem. Soc.* **1989**, *111*, 3444. Reich, H. J.; Borst, J. P. *J. Am. Chem. Soc.* **1991**, *113*, 1835.

Table I. Heats of Formation of Solvated Lithium Dialkylamides[a]

	Me$_2$NLi	(Me$_2$NLi)$_2$	(Me$_2$NLi)$_3$	LDA	(LDA)$_2$	(LDA)$_3$	LiTMP	(LiTMP)$_2$
unsolvated	−4.9	−60.4	−109.8	−22.7	−94.2	−146.7	−17.7	−64.7
H$_2$O	−83.2	−134.9		−99.8	−157.8		−94.8	−135.7
2 H$_2$O	−155.3	−208.3		−169.8	223.7		−164.5	−200.8
3 H$_2$O	−223.5	−273.0	−318.7	−231.7	−276.6	−318.0	−224.3	
4 H$_2$O		−337.0			−325.6			
6 H$_2$O		−497.2						
Me$_2$O	−71.3	−121.3		−87.8	−142.6		−82.7	−118.6
2 Me$_2$O	−129.7	−180.9		−141.8	−189.3		−135.6	−162.2
3 Me$_2$O		−226.9	−274.6					
4 Me$_2$O		−272.4						
THF	−78.9	−129.2		−95.5	−150.8		−90.5	−126.9
2 THF	−145.2	−196.6		−157.7	−206.1		−151.8	−183.6
3 THF	−203.0	−250.8	−296.4					
4 THF		−303.5						
(H$_2$N)$_3$P=O	−77.7	−126.2		−92.2	−147.9		−88.7	−123.7
2 (H$_2$N)$_3$P=O	−138.7	−188.5		−151.1	−202.0		−145.3	−177.8
3 (H$_2$N)$_3$P=O	−189.6	−236.0	−284.3	−193.8			−185.5	
4 (H$_2$N)$_3$P=O		−283.2						
HMPA	−62.7	−109.4		−78.0	−128.4		−73.2	−103.1
2 HMPA	−103.2	−154.2		−113.2	−159.9		−106.8	−134.7
3 HMPA	−126.3	−175.8	−226.1					
Me$_2$O/(H$_2$N)$_3$P=O	−135.1	−185.9		−147.4	−196.0		−141.4	−171.6
THF/HMPA	−125.2	−175.3		−136.8	−184.0		−131.0	−160.3

[a] Enthalpies are reported on a per molecule basis. *Relative* heats of formation in subsequent tables are listed on a per *lithium* basis (kcal/mol per Li). The heats of formation (kcal/mol) of the donor solvents are as follows: H$_2$O, −60.9; Me$_2$O, −51.2; THF, −59.3; (H$_3$N)$_2$P=O, −48.9; HMPA, −34.4.

Our attention has been drawn to two recent developments that hold promise to provide especially incisive views of organolithium solvation. The groups of Reich[15] and Snaith[16] documented the first examples of two-bond Li–P coupling in hexamethyl-phosphoramide (HMPA) solvates of lithium salts by NMR spectroscopy.[17] The resulting direct determination of organo-lithium solvation state provides a view of lithium ion solvation with unprecedented clarity. We recently capitalized on this technique to elucidate the detailed structures of lithium diiso-propylamide (LDA; Scheme I) and lithium 2,2,6,6-tetra-methylpiperidide (LiTMP; Scheme II) in THF–HMPA mixtures.[8] Computationally, Schleyer and co-workers have initiated an extensive program to study organolithium solvation using semi-empirical MNDO methods.[13,18] Despite the potential limitations of MNDO relative to the ab initio methods, MNDO appears to stand alone among the computational methods for studying the often large organolithium aggregates with the full complement of chemically realistic *N*-alkyl substitutents and coordinated solvents.

We describe herein MNDO computational studies of Me$_2$NLi, LDA, and LiTMP solvated by H$_2$O, Me$_2$O, THF, (NH$_2$)$_3$P=O, and HMPA. We have explored the factors that influence the relative stabilities of monomers, dimers, trimers, open dimers, and anionic triple ions.[19] The previously assigned structures of LDA/THF/HMPA and LiTMP/THF/HMPA solvates illustrated in Schemes I and II provide for a direct experimental comparison and allow us to critically evaluate the merits of the MNDO methods when applied to hindered lithium dialkylamides.

Methods

MNDO[20] calculations were performed on an IBM 3090 supercomputer using the MOPAC[21] program with lithium parameters generated by

Scheme II

(16) Barr, D.; Doyle, M. J.; Mulvey, R. E.; Raithby, P. R.; Reed, D.; Snaith, R.; Wright, D. S. *J. Chem. Soc., Chem. Commun.* **1989**, 318.

(17) See also: Denmark, S. E.; Miller, P. C.; Wilson, S. R. *J. Am. Chem. Soc.* **1991**, *113*, 1468.

(18) (a) Kaufmann, E.; Gose, J.; Schleyer, P. v. R. *Organometallics* **1989**, *8*, 2577. (b) Kaufmann, E.; Raghavachari, K.; Reed, A.; Schleyer, P. v. R. *Organometallics* **1988**, *7*, 1597. (c) Kaufmann, E.; Tidor, B.; Schleyer, P. v. R. *J. Comput. Chem.* **1986**, *7*, 334.

(19) The terms "ion triplet", "ion triple", "triple ion", and "triplet ion" have been used to describe clusters of three ions. The clusters can be either anionic, e.g. [R⁻M⁺R⁻]⁻, neutral, e.g. [R⁻M²⁺R⁻], or cationic, e.g. [M⁺R⁻M⁺]⁺. Throughout this paper we will refer only to the anionic forms and use only the "triple ion" nomenclature.

(20) Dewar, M. J. S.; Thiel, W. J. *J. Am. Chem. Soc.* **1977**, *99*, 4899, 4907.

(21) Stewart, J. J. P. *QCPE 581*.
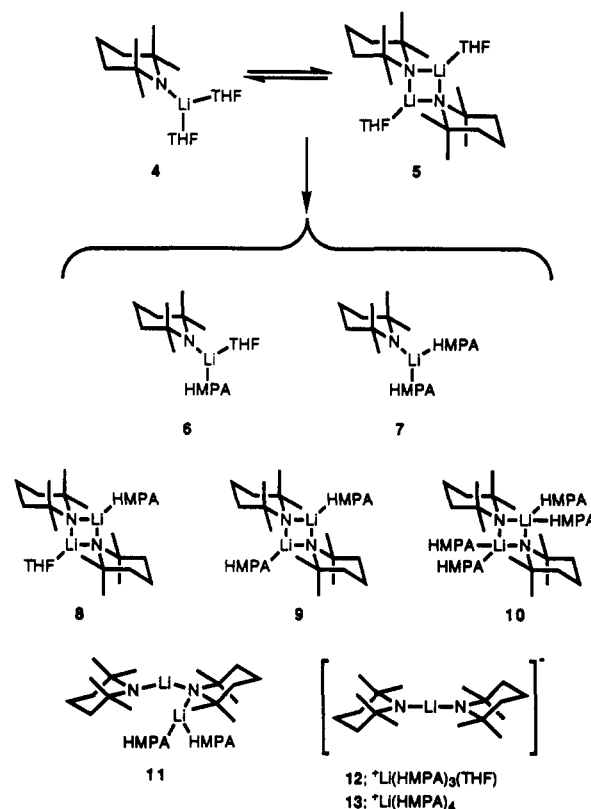
Clark and Theil.[22] Unless otherwise noted, all structures were fully optimized under the more rigorous criteria of the keyword PRECISE with no constraints. Each reported heat of formation is the result of a search for the global minimum starting from several different initial geometries. Symmetrical structures were optimized from distorted geometries to ensure that the symmetry is not a calculational artifact. For more sterically crowded systems, the keyword GEO-OK was used with caution to override the small interatomic distance check. The energies quoted do not include entropies associated with mass action effects.

It has been shown that the current MNDO lithium parameters accurately reproduce lithium interactions with nitrogen and oxygen through

(22) Thiel, W.; Clark, T. Unpublished results.

Table II. Heats of Solvation of Lithium Amide Monomers, Dimers, and Trimers[a]

$$(R_2NLi)_xS_y + S \rightleftharpoons (R_2NLi)_xS_{y+1} \qquad (1)$$

	Me$_2$NLi	(Me$_2$NLi)$_2$	(Me$_2$NLi)$_3$	LDA	(LDA)$_2$	(LDA)$_3$	LiTMP	(LiTMP)$_2$
H$_2$O	−17.4	−6.8		−16.3	−1.4		−16.2	−5.0
2 H$_2$O	−11.2	−6.2		−9.1	−2.5		−8.8	−2.4
3 H$_2$O	−7.3	−1.9	−2.9	−1.0	4.0	1.3	1.0	
4 H$_2$O		−1.6			6.0			
6 H$_2$O			0.5					
Me$_2$O	−15.2	−4.8		−13.9	1.4		−13.8	−1.3
2 Me$_2$O	−7.2	−4.2		−2.9	2.2		−1.7	3.8
3 Me$_2$O	1.3	2.6	−1.2					
4 Me$_2$O		2.8						
THF	−14.9	−4.8		−13.5	1.4		−13.5	−1.4
2 THF	−6.8	−4.0		−3.0	2.0		−2.0	+1.3
3 THF	1.5	2.6	−1.0					
4 THF		3.3						
(H$_3$N)$_2$P=O	−23.9	−8.4		−20.6	−2.4		−22.1	−5.1
2 (H$_3$N)$_2$P=O	−12.2	−6.7		−10.0	−2.6		−7.5	−2.5
3 (H$_3$N)$_2$P=O	−1.9	−0.6	−3.1	6.2			8.5	
4 (H$_3$N)$_2$P=O		−0.8						
HMPA	−23.5	−7.3		−20.9	0.0		−21.1	−2.0
2 HMPA	−6.0	−5.2		−0.8	1.4		0.8	1.3
3 HMPA	11.3	6.4	−1.5					

[a] Enthalpies are listed on a per lithium basis (kcal/mol per Li).

Table III. Heats of Dimerization of Lithium Amides[a]

$$2 R_2NLiS_2 \rightleftharpoons (R_2NLi)_2S_2 + 2 S \qquad (2)$$

	unsol-vated	H$_2$O	Me$_2$O	THF	(H$_2$N)$_3$P=O	HMPA
Me$_2$NLi	−35.1	−9.8	−12.0	−12.4	−4.4	−8.3
LDA	−24.4	−3.0	−4.0	−4.7	1.2	−1.1
LiTMP	−18.4	3.2	3.3	0.6	7.5	5.0

[a] Enthalpies are listed on a per lithium basis (kcal/mol per Li).

Table IV. Relative Stabilities of Lithium Amide Dimers and Trimers[a]

$$3 (R_2NLi)_2S_2 \rightleftharpoons 2(R_2NLi)_3S_3 \qquad (3)$$

	unsol-vated	H$_2$O	Me$_2$O	THF	(H$_2$N)$_3$P=O	HMPA
Me$_2$NLi	−6.4	−2.1	−1.1	−0.5	−0.5	1.7
LDA	−1.8	5.9				

[a] Enthalpies are listed on a per lithium basis (kcal/mol per Li).

comparisons with experimental results[23] and ab initio calculations.[24] However, the parameterization based on small molecules can lead to anomalous destabilizations in larger systems as observed in other semiempirical methods.[25] The results described below show evidence of overestimation of steric effects.

Results

The heats of formation of the solvated and aggregated forms of the three amides calculated with MNDO are shown in Table I. Heats of solvation, dimerization, and trimerization are summarized in Tables II–IV. Data on the stabilities of selected mixed solvates are found in Tables V and VI. The stabilities of open dimers and triple ions along with selected optimized bond angles and distances are listed in Table VII. Table VIII lists energies associated with the cleavage of dimers to give open dimers, ion-paired anionic triple ions, and fully ionized anionic triple ions. The results of solvation by combinations of HMPA and THF are summarized in Schemes IV–VI for referral in the Discussion.

Me$_2$NLi. Serial solvations of the Me$_2$NLi monomer with water, dimethyl ether, or THF show strong parallels with the behavior

(23) Kaufmann, E.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1984**, *106*, 1856. Sapse, A.-M.; Kaufmann, E.; Schleyer, P. v. R.; Gleiter, R. *Inorg. Chem.* **1984**, *23*, 1569.
(24) Glaser, R.; Streitwieser, A., Jr. *Theochem.* **1988**, *163*, 19. See also ref 10.
(25) Scano, P.; Thomson, C. *J. Comput. Chem.* **1991**, *12*, 172.

Table V. Heats of Ligand Exchange in Lithium Amide Disolvated Monomers[a]

$$(4)$$

	S$_1$	S$_2$	ΔH_1	ΔH_2
Me$_2$NLi	Me$_2$O	(H$_2$N)$_3$P=O	−7.7	−5.9
	THF	HMPA	−4.9	−3.0
LDA	Me$_2$O	(H$_2$N)$_3$P=O	−7.8	−6.9
	THF	HMPA	−4.1	−1.3
LiTMP	Me$_2$O	(H$_2$N)$_3$P=O	−8.1	−6.2
	THF	HMPA	−4.1	−0.7

[a] Enthalpies are listed on a per lithium basis (kcal/mol per Li).

Table VI. Heats of Ligand Exchange in Lithium Amide Disolvated Dimers

$$(5)$$

	S$_1$	S$_2$	ΔH_1/Li	ΔH_2/Li
(Me$_2$NLi)$_2$	Me$_2$O	(H$_2$N)$_3$P=O	−7.3	−4.9
	THF	HMPA	−1.8	−1.9
(LDA)$_2$	Me$_2$O	(H$_2$N)$_3$P=O	−4.5	−4.2
	THF	HMPA	−1.4	−0.4
(LiTMP)$_2$	Me$_2$O	(H$_2$N)$_3$P=O	−5.9	−4.3
	THF	HMPA	−0.8	0.3

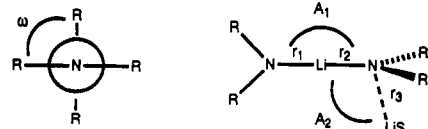[a] Enthalpies are listed on a per lithium basis (kcal/mol per Li).

Scheme III
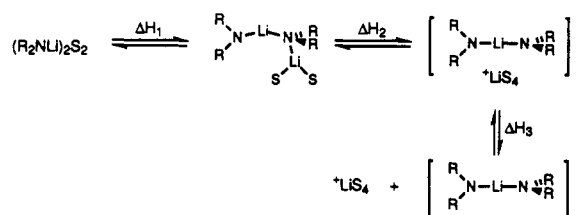
of other monomeric LiX species.[18c] The calculated energies support the conclusion of Schleyer and co-workers that substituent effects on the organolithium fragment are minimal in sterically unhindered environments.[18] The heats of solvation by H$_2$O and phosphoramide are negative for three consecutive solvation steps.

Table VII. Heats of Formation and Selected Geometric Parameters for Lithium Amide Open Dimers and Triple Ions[a]

	H_f	r_1	r_2	r_3	$r_4{}^b$	A_1	A_2	ω
				Open Dimers				
Me$_2$NLi/2THF	−180.4	1.87	2.11	2.01	2.16	167.7	121.8	76.4
LDA/2THF	−205.1	1.96	2.20	2.10	2.27	151.3	118.0	83.6
LiTMP/2THF	−188.6	1.99	2.28	2.11	2.30	165.4	123.4	88.6
Me$_2$NLi/2HMPA	−143.4	1.90	2.11	2.07	2.08	174.4	133.1	86.9
LDA/2HMPA	−162.2	1.97	2.18	2.16	2.16	156.9	133.0	77.7
LiTMP/HMPA	−111.4	1.97	2.16	2.08	2.01	165.1	131.9	89.1
				Triple Ions				
Me$_2$NLi/4THF	−272.8	1.94	1.97	6.04	2.18	172.4	104.0	74.2
LDA/4THF	−295.8	1.97	2.00	7.13	2.18	168.3	116.0	82.2
LiTMP/4THF	−286.0	2.01	2.01	7.70	2.19	176.8	76.9	85.1
Me$_2$NLi/4HMPA	−187.8	1.95	1.96	8.06	2.19	168.5	97.1	81.9
LDA/4HMPA	−212.0	1.99	1.99	9.09	2.19	162.7	102.0	85.6
LiTMP/4HMPA	−203.1	2.01	2.01	9.60	2.19	178.6	83.1	88.6

[a] Enthalpies are listed on a per lithium basis (kcal/mol per Li). Distances in angstroms; angles in degrees. [b] r_4 corresponds to the average O–Li bond length within the lithium solvent coordination sphere.

Scheme IV
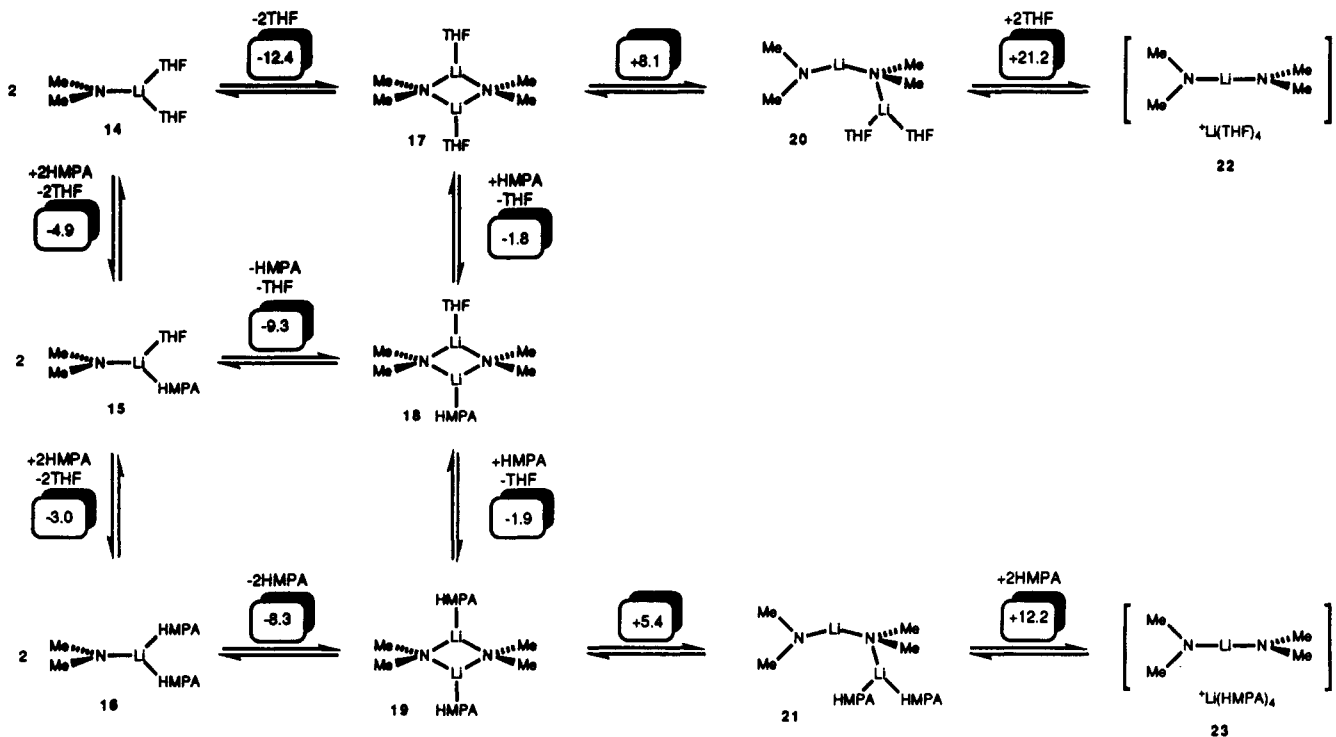
The heats of solvation by Me$_2$O, THF, and HMPA are negative for only the first two solvation steps. A comparison of phosphoramide and HMPA is of special interest in light of detailed spectroscopic studies of lithium amide–HMPA solvates (see Discussion). There are no measurable steric effects on solvation by a single phosphoryl ligand. Addition of a second ligand, however, reveals a disproportionate attenuation of the enthalpy of solvation by HMPA relative to phosphoramide. The inclusion of a third solvent on the Me$_2$NLi monomer is stabilizing by only 1.9 kcal/mol per Li for phosphoramide and is destabilizing by 11.3 kcal/mol per Li for HMPA. Heats of formation of mixed solvated monomeric LiNMe$_2$ are shown in Table I. Displacement of one ethereal ligand from Me$_2$NLi(OR$_2$)$_2$ by (H$_2$N)$_3$P=O or HMPA is stabilizing for all ethers.

The solvation enthalpies of the Me$_2$NLi dimer by H$_2$O, Me$_2$O, and THF indicate a strong preference for one ligand per lithium atom; only H$_2$O and phosphoramide afford further stabilization

Table VIII. Heats of Cleavage and Ionization of Cyclic Dimers To Give Triple Ions (Scheme III)[a,b]

| R$_2$NLi/S	ΔH_1	ΔH_2	ΔH_3
Me$_2$NLi/THF	8.1	21.2	38.6
LDA/THF	0.5	14.5	35.8
LiTMP/THF	−2.5	10.6	36.0
Me$_2$NLi/HMPA	5.4	12.2	17.8
LDA/HMPA	−1.1	9.5	15.5
LiTMP/HMPA	−5.5^c	5.2^c	16.7^c

[a] Enthalpies are listed on a per lithium basis (kcal/mol per Li). [b] The heats of formation of the free ions are as follows: $^+$Li(THF)$_4$, −135.0; $^+$Li(HMPA)$_4$, −91.8; [Me$_2$NLiNMe$_2$]$^-$, −60.5; [i-Pr$_2$NLiNiPr$_2$]$^-$, −89.2; [TMPLiTMP]$^-$, −79.0. ^{c} Correspond to heats of formation of monosolvated open dimers (see text).

at elevated solvation numbers. A comparison of phosphoramide to HMPA reveals a large destabilization attributable to the bulk

Scheme V
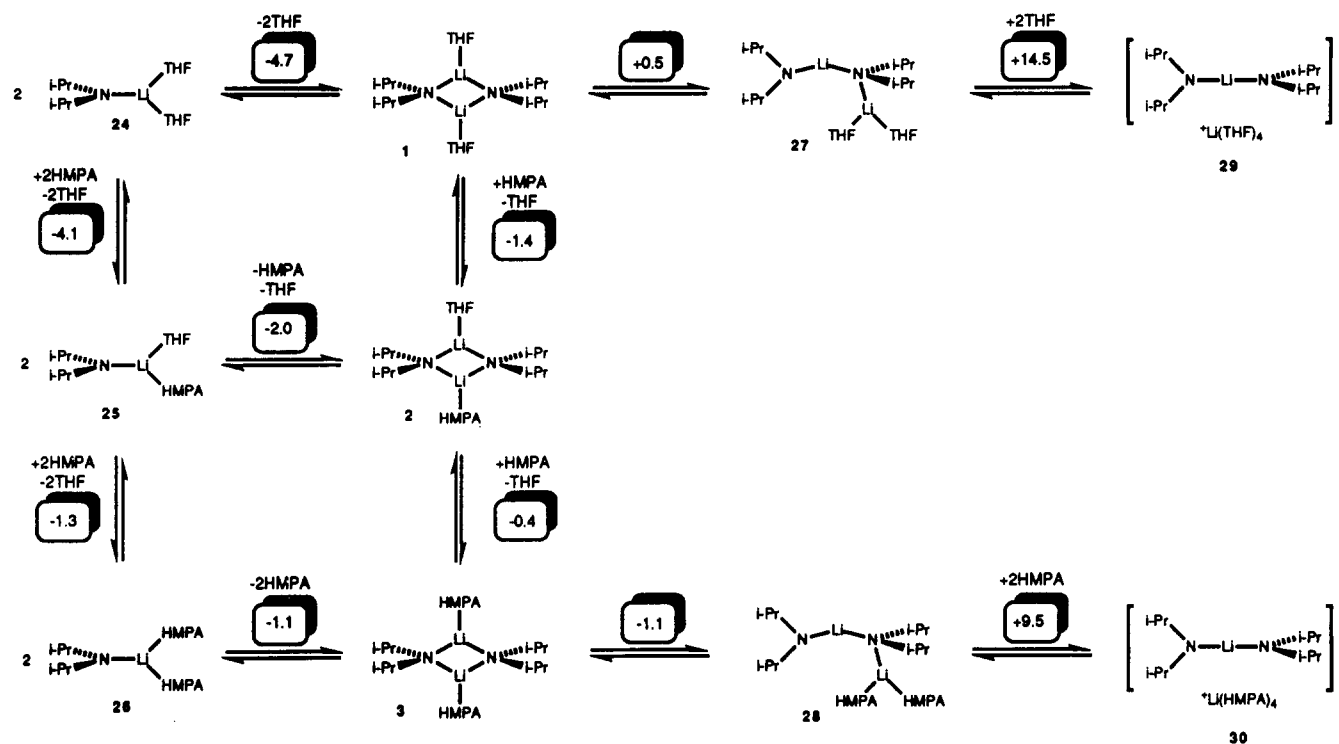
Scheme VI
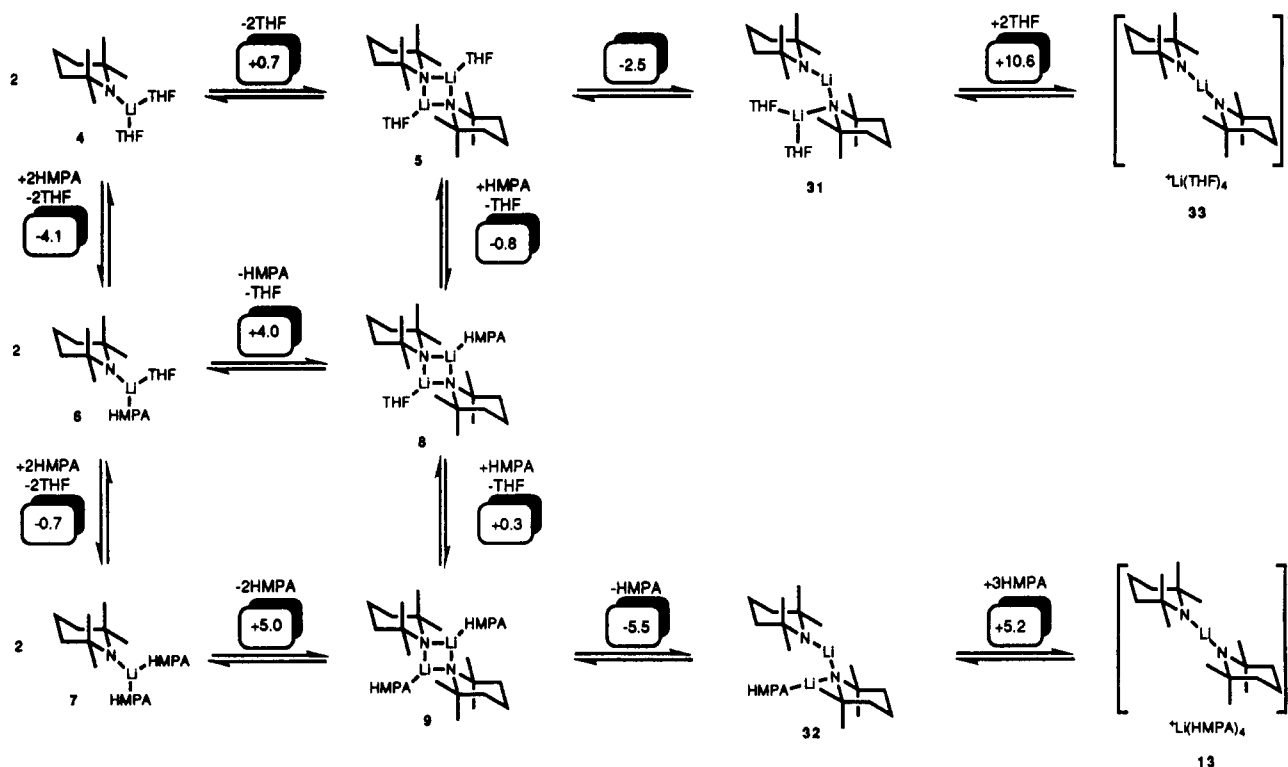
of the *N,N*-dimethylamino groups of HMPA. In fact, no minium corresponding to $(Me_2NLi)_2(HMPA)_4$ was found. Comparing H_2O to Me_2O as well as phosphoramide to HMPA, we find that an increase in the steric demand of the solvent favors dimers relative to monomers. The energies of the optimized THF/HMPA and $Me_2O/(H_2N)_3P=O$ mixed solvated dimers are listed in Tables I and V. Notably, displacements of the two THF ligands from $(Me_2NLi)_2(THF)_2$ by HMPA are exothermic. We should also add that in a number of instances we attempted to locate minima corresponding to bridged HMPA solvates of general

structure **34** to no avail; optimization reproducibly results in terminal ligation for all cases studied.[26]

Structures of Solvated Lithium Dialkylamides

J. Am. Chem. Soc., Vol. 114, No. 6, 1992 2117
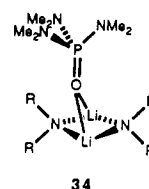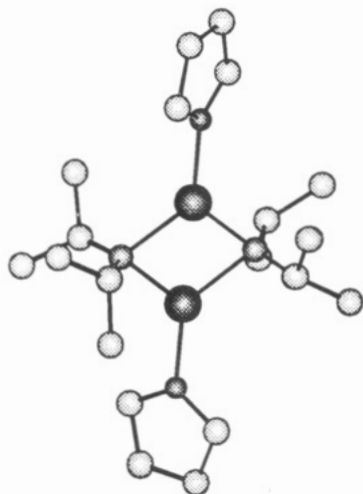
Figure 1. Optimized structure of the $(THF)_2$-solvated LDA dimer **1**. Hydrogen atoms have been omitted for clarity.

The unsolvated trimer is calculated to be more stable than the dimer. We find that solvation diminishes the stability of the trimer relative to monomers and dimers in accord with ab initio studies by Snaith and co-workers[27] (Table IV), although only the $(HMPA)_2$-solvated dimer is found to be more stable than the corresponding trimer. Calculations on the more hindered LDA reveal a dramatic relative stabilization of the dimers.

LDA. Solvation is substantially less stabilizing for LDA than for Me_2NLi. We suspect this to be, at least in part, a consequence of overestimated steric effects. The first solvation of the monomer by all solvents affords enthalpies that are similar to those of the Me_2NLi monomer discussed above. The increased bulk of the LDA monomer is apparent, however, at higher solvation states. The second Me_2O or THF ligands are substantially less stabilizing than the first. The trisolvated LDA monomer is found to be a minimum only for water and phosphoramide, and even in these instances the third ligand is only marginally stabilizing. The steric demands of HMPA are evident from the decreasing stabilization by HMPA relative to phosphoramide at each successive solvation number. Calculations of several mixed solvates (Tables I and VI) indicate that displacements of ethereal ligands by phosphoramides are exothermic.

The LDA dimer shows the lowest heats of solvation of the three lithium amides studied. Only water and phosphoramide are stabilizing up to the disolvated dimer level. Inclusion of a ligand on the second lithium center is endothermic for Me_2O, THF, and HMPA. Nevertheless, the lowest energy optimized structure found for the $(THF)_2$-solvated dimer shows an excellent correlation with the structure determined crystallographically (Figure 1).[28] Minima for tri- and tetrasolvated LDA dimer could be located only in the case of water. Furthermore, the rotations of the isopropyl groups required to locate the minima for $(i\text{-}Pr_2N)_2$-$(H_2O)_3$ and $(i\text{-}Pr_2N)_2(H_2O)_4$ result in inordinately high energies. Increasingly bulky solvents favor dimers relative to monomers in analogy to Me_2NLi. Whereas the bis(phosphoramide)-solvated LDA monomer is calculated to be slightly more stable than the corresponding disolvated dimer, the analogous comparison with HMPA shows the disolvated dimer to be more stable. Displacement of the THF ligands from $LDA_2(THF)_2$ by HMPA is only moderately exothermic.

The unsolvated LDA trimer is calculated to be slightly more stable than the dimer. However, the LDA trimer also displays

(26) Armstrong, D. R.; Barr, D.; Brooker, A. T.; Clegg, W.; Gregory, K.; Hodgson, S. M.; Snaith, R.; Wright, D. S. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 410 and references cited therein.

(27) 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. Armstrong, D. R.; Mulvey, R. E.; Walker, G. T.; Barr, D.; Snaith, R.; Clegg, W.; Reed, D. *J. Chem. Soc., Dalton Trans.* **1987**, 617.

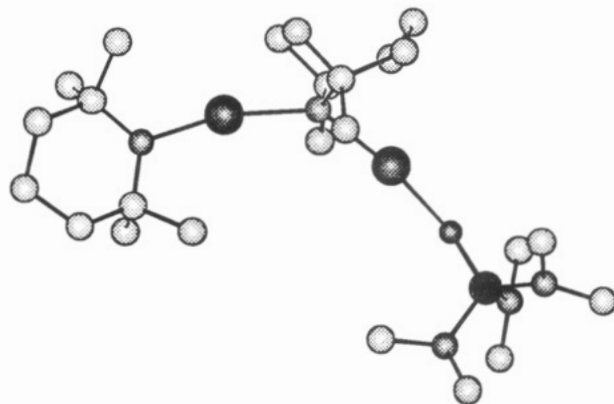(28) Williard, P. G. *Comprehensive Organic Synthesis*; Pergamon: New York, 1990; in press.

an inordinate sensitivity to solvation relative to the dimer, affording only high-energy minima with one water molecule per lithium. We failed to locate minima for all other $(i\text{-}Pr_2NLi)_3S_3$ forms. Thus, the calculations suggest that the preference for dimers over higher oligomers upon solvation may derive largely from steric effects.

LiTMP. In general, solvation energies of the LiTMP monomer show parallels with the LDA monomer, indicating similarities in the steric demands about the lithium coordination sphere. Disolvation is preferred and serial replacement of ethereal solvents by phosphoramides are found to be exothermic.

Spectroscopic studies revealed exclusively the C_{2h} conformational isomer of LiTMP dimer in THF solution.[2] Cursory investigation of several C_{2v} conformers (**35**) reproducibly afforded the corresponding C_{2h} conformers. Accordingly, all subsequent studies focused only on the C_{nh} conformers. The calculated heats

35
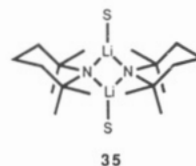
of solvation of the LiTMP dimers diverge substantially from those derived from the Me_2NLi and LDA dimers. Most notably, the $(THF)_2$-solvated dimer is calculated to be stabilized relative to the unsolvated dimer whereas the $(THF)_2$-solvated LDA dimer is destabilized. This apparent decreased steric demand of the LiTMP dimer (at least relative to the LDA dimer) is surprising in light of the results for the monomer as well as the putative high steric demands of tertiary alkyl groups. Nevertheless, experimental support for the propensity of the LiTMP dimer to attain a higher solvation number than the LDA dimer will be delineated in the Discussion. The LiTMP dimer also shows a highly magnified (negative) cooperative effect; solvation of the second lithium center is consistently and substantially less stabilizing than the first. The optimized $(LiTMP)_2S$ derivatives show an asymmetric lengthening of the solvated Li–N bonds and concomitant shortening of the unsolvated Li–N bonds not seen in the corresponding Me_2NLi and LDA dimers. This distortion could easily account for the resistance to accept a donor ligand at the transannular Li site. In fact, $(LiTMP)_2S$ derivatives show structural features that are suggestive of the open dimers described below.

Open Dimers and Triple Ions. Studies of THF- and HMPA-solvated open dimers and triple ions of general structure **36–38**
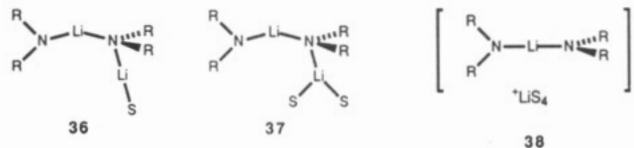
were elicited by two previous results: (1) Open dimers and triple ions have been observed for LiTMP in THF/HMPA solution[8]
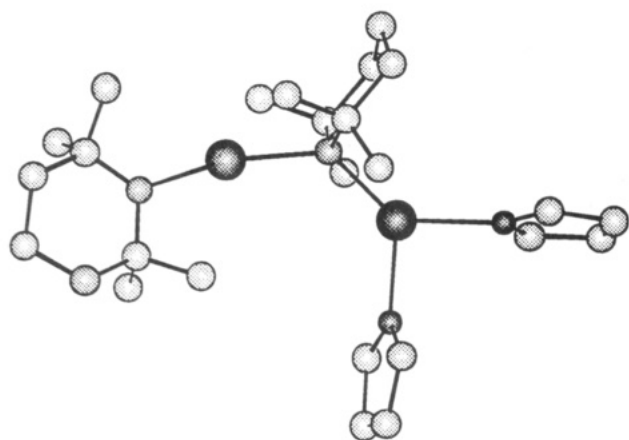
Figure 3. Optimized structure of the $(THF)_2$-solvated LiTMP open dimer **32**. Hydrogen atoms have been omitted for clarity.

(Scheme II). (2) Optimized LiTMP dimers bearing a single solvent display distortion of the Li_2N_2 rings suggestive of a partial ring fragmentation. Table VII includes the calculated enthalpies of open dimers as well as the optimized N–Li–N angles (angle A_1), Li–N–Li bond angles (angle A_2), and C–N–N–C torsion angles (angle ω). Figures 2 and 3 depict representative optimized geometries of mono- and disolvated open dimers. The mono-solvated cyclic dimers and monosolvated open dimers correspond to distinctly different minima.

While monosolvated and unsymmetrically disolvated open dimers **36** and **37** are stable minima (Tables VII and VIII), in no instance has an open dimer bearing a solvent molecule on the internal lithium been located as a minimum. Optimizations starting with the open dimers bearing solvents on both lithium nuclei (**39** or **40**) result in extrusion of the solvent from the internal lithium nucleus. The optimized structure of disolvated open dimer **11** is more akin to a solvent-deficient triple ion as evidenced most clearly by the exceedingly long (7.52 Å) N–$Li(HMPA)_2$ bond. Ironically, **11** is also the only fully characterized lithium amide open dimer reported to date.

Increases in the steric demands of the amide fragment tend to favor open dimers relative to the corresponding (isomeric) cyclic dimers. Whereas all of the (unsymmetrically) disolvated Me_2NLi open dimers are substantially destabilized relative to the isomeric disolvated cyclic dimers, the corresponding $(THF)_2$-solvated LDA open dimer **27** (Scheme V) is only slightly less stable than the $(THF)_2$-solvated cyclic dimer **1**. The $(HMPA)_2$-solvated open dimer **28** is predicted to be formed from the cyclic dimer **3** with only a slight exothermicity. Although the $(HMPA)_2$-solvated LiTMP open dimer **11** converges to a relatively destabilized triple ion-like structure, monosolvate **32** is suggested to be formed exothermically from dimer **9**.

Heats of formation and selected geometrical parameters of the calculated triple ions are listed in Table VII. Increased steric bulk in the amide fragment favors triple ion formation relative to cyclic dimers. The optimized geometries of the triple ions all show nearly 180° (linear) N–Li–N bond angles, along with amide fragments that are rotated nearly 90° about the N–Li–N axis (Figure 4). Ion pairing of the fully ionized triple ion is highly stabilizing for all three amides and is amide fragment independent (Table VIII).[29] The triple ions display the highest relative stability with the
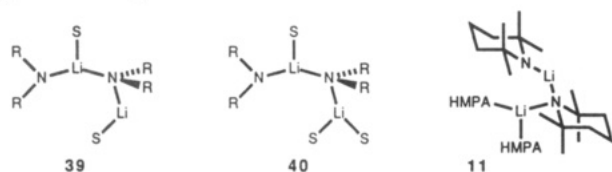

Figure 4. Optimized structure of the $(HMPA)_4$-solvated LiTMP triple ion **13**. Hydrogen atoms have been omitted for clarity.

HMPA-solvated gegenion. In fact, the HMPA-solvated LiTMP triple ion is more stable than the corresponding disolvated cyclic dimer **9**. We suspect that the driving force for formation of triple ions stems from a combination of the release of steric strain and the stabilization gained by achieving a high solvation number (net two per lithium) relatively remote from the congested amide moieties.

Discussion

Summary. By comparing calculated structures of Me_2NLi, LDA, and LiTMP solvated by H_2O, Me_2O, THF, $(H_2N)_3P{=}O$, and HMPA, we observe a number of general trends that pertain to experimental observations. The general summary described below is followed by a direct comparison of the calculated HMPA- and THF-solvated amides with experimentally observed structures.

As found in previous computational studies of organolithium solvation,[18] serial solvation of a lithium nucleus displays increasingly positive enthalpies per solvation step. This trend appears to be amplified by three related steric factors: (1) The decreasing exothermicity with increasing solvation number is heightened by increased steric demand of the solvent, as evidenced by comparisons of H_2O with Me_2O and phosphoramide with HMPA. The trend is most apparent upon proceeding from one to two solvents per Li in both the monomers and cyclic aggregates. The solvation state of neighboring lithium centers has little influence on the enthalpy of solvation in the Me_2NLi and LDA amide dimers. (2) The enthalpy of solvation becomes less negative with increasing aggregation state, producing a net trend toward deaggregation upon proceeding from unsolvated to solvated structures. (3) The steric effects described in (1) and (2) are magnified upon increasing steric demands of the N-alkyl moieties. Many of the calculated enthalpies that seem plausible for Me_2NLi become substantially (possibly unrealistically) more positive with the LDA analogues.

The steric effects deduced from comparisons of Me_2NLi and LDA solvates do not always follow for the relatively hindered LiTMP. The negative heats of solvation of the LiTMP dimer compared to the LDA dimer are strongly suggestive of a lithium coordination sphere that is less congested than that of the LDA dimer. While this could be a limitation of the calculations, we suspect it arises from distortions visible in the optimized unsolvated

---

(29) Even the most stabilized lithium ion pairs are associated in THF solution: Bhattacharyya, D. N.; Lee, C. L.; Smid, J.; Szwarc, M. *J. Phys. Chem.* **1965**, *69*, 608. Wong, M. K.; Popov, A. I. *J. Inorg. Nucl. Chem.* **1972**, *34*, 3615.
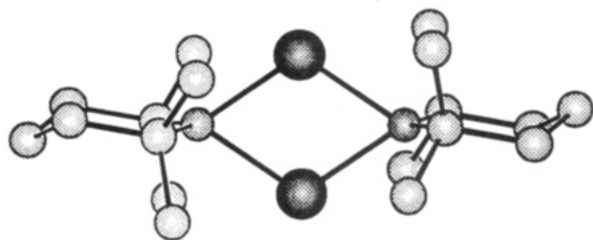
Figure 5. Optimized structure of the unsolvated LiTMP cyclic dimer showing Me–Me transannular interactions across the Li_2N_2 ring. Hydrogen atoms have been omitted for clarity.

LiTMP cyclic dimer (Figure 5). Indeed, the N–Li bond lengthening causes a net increase in the N–N distance and an apparent increase in the accessibility of the Li nuclei for solvation. We have described experimental support for the high LiTMP solvation numbers below.

Higher cyclic oligomers of lithium dialkylamides (including tetrameric LiTMP) have been observed crystallographically[30] and spectroscopically,[3,31] but only in their unsolvated forms. The corresponding solvates (including LDA·THF)[28] crystallize as cyclic dimers.[13] In addition, mounting crystallographic, spectroscopic, and kinetic evidence suggests that the only observable solvated aggregates are the corresponding dimers.[32a] A recently developed method based upon inverse-detected zero quantum NMR spectroscopy can be used to distinguish dimers from higher oligomers for symmetrically substituted lithium amides.[32b] LDA and LiTMP have now been shown to be dimeric in THF/pentane solution. Moreover, the two oligomers of unsolvated LiTMP (in C_6D_6) are higher oligomers (possibly trimer and tetramer).

As first mentioned by Snaith and co-workers in the context of ab initio calculations of $LiNH_2$,[27] destabilization of the trimer by solvation is probably a consequence of the increasing internal N–Li–N bond angle. This general view of lithium amide oligomers receives strong support from the MNDO calculations. Unsolvated Me_2NLi trimers are substantially more stable than the dimers, while the unsolvated LDA trimers and dimers are of nearly equal stability. Solvation of the Me_2NLi oligomers stabilizes the dimers, although only the $(HMPA)_2$-solvated dimer is found to be more stable than the corresponding trimer. With the sterically more demanding LDA, hydrated dimers are preferred over the corresponding hydrated trimers. Solvation of dimeric LDA with THF is found to be slightly endothermic, reflecting a contradiction to the experimental result (excluding mass action effects). However, numerous attempts to calculate LDA trimers solvated by solvents other than H_2O afforded unsolvated trimers as the optimized structures.

The relative energies of monomers and dimers are influenced by a subtle mixture of factors. Increasing the steric bulk of the solvent or *N*-alkyl moiety and increasing the solvent dipole (phosphoramides vs ethers) both facilitate deaggregation (eq 6).
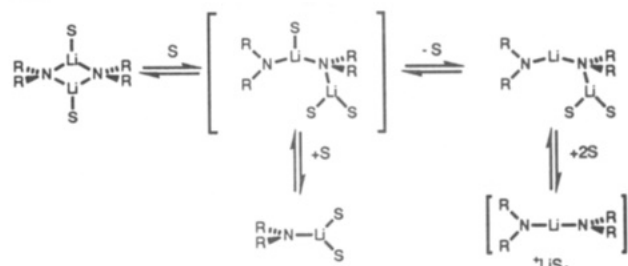
$$(R_2NLi)_2S_2 \rightleftharpoons 2 R_2NLiS \qquad (6)$$

In the case of LiTMP, the monomers are favored for all solvents except H_2O. In light of observed disolvated lithium amide monomers[8,13] as well as solvent concentration dependent monomer–dimer equilibria,[4,5] the deaggregation depicted in eq 2 and Table III is probably a more realistic depiction. Inclusion of a second ligand on the monomer is stabilizing in all cases except for $LiTMP(HMPA)_2$. More importantly, however, comparisons

Scheme VII

of H_2O with Me_2O and phosphoramide with HMPA reveal that the enthalpic gain of the second ligand on the monomer is largely attenuated by the increased steric demands of the solvent. In essence, increased steric demand by the solvent favors dimers relative to monomers. Increasing the steric demands on the amide fragment, on the other hand, destabilizes the dimers relative to monomers. Overall, the complex interplay between solvent and substrate steric effects may ultimately lead to poor correlations between perceived "solvent donicities" and aggregation states.

We have become interested in open dimers of general structure **37**. Despite the small number of open dimers reported in the crystallographic[33] and spectroscopic literature,[34] they may be key intermediates involved in deaggregation, solvent (ligand) exchange, and triple ion formation (Scheme VII). The open dimers could also provide a viable pathway for reaction of lithium amide dimers without intervening deaggregation (eq 7).[10,11,35] The partial dimer cleavage would concurrently allow for Lewis acidic activation of the substrate (electrophilic catalysis) and liberation of the lone pair on the proximate nitrogen for subsequent reaction.[36]
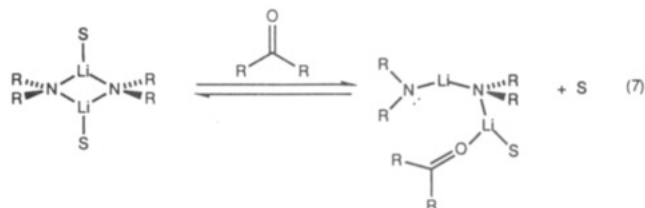
The MNDO calculations suggest that with the less bulky amides the THF-solvated open dimers are more stable than monomers, although neither should be observable due to the dominance of the disolvated dimers. HMPA dramatically stabilizes open dimers relative to cyclic dimers, presumably by virtue of the stabilization of the resulting partial charge separation. High steric demands within the cyclic dimer fragment seem to enhance open dimer formation as well. The optimized open dimer structures display considerable increases in the N–Li–N angle and a distinct relative rotation of the two amide fragments about the (approximate) N–Li–N axis (Figures 2 and 3). The internal lithium is bound to the external nitrogen with a bond length reminiscent of a monomer and to the internal nitrogen with a bond length more akin to that of a cyclic dimer.[37] The magnitudes of the $^6Li–^{15}N$ coupling constants of the LiTMP open dimer **11** are in full accord with this model.[8]

(30) (a) Rogers, R. D.; Atwood, J. L.; Grüning, R. *J. Organometallic Chem.* **1978**, *157*, 229. (b) Mootz, D.; Zinnius, A.; Böttcher, B. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 378. (c) Barr, D.; Clegg, W.; Mulvey, R. E.; Snaith, R. *J. Chem. Soc., Chem. Commun.* **1984**, 285. (d) Lappert, M. F.; Slade, M. J.; Singh, A.; Atwood, J. L.; Rogers, R. D.; Shakir, R. *J. Am. Chem. Soc.* **1983**, *105*, 302.

(31) Barr, D.; Clegg, W.; Mulvey, R. E.; Snaith, R. *J. Chem. Soc., Chem. Commun.* **1984**, 287. Snaith, R.; Barr, D.; Wright, D. S.; Clegg, W.; Hodgson, S. M.; Lamming, G. R.; Scott, A. J.; Mulvey, R. E. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1241.

(32) (a) See ref 1a for a detailed summary of the evidence supporting solvated dimers as the stable solvated amide aggregates in solution. (b) Gilchrist, J. H.; Collum, D. B. *J. Am. Chem. Soc.* **1992**, *114*, 794.

(33) Related organolithium open dimers have been characterized crystallographically: Fenton, D. E.; Truter, M. R. *J. Chem. Soc., Dalton Trans.* **1973**, 2188. Armstrong, D. R.; Barr, D.; Clegg, W.; Hodgson, S. M.; Mulvey, R. E.; Reed, D.; Snaith, R.; Wright, D. S. *J. Am. Chem. Soc.* **1989**, *111*, 4719. Brooks, P.; Craig, D. C.; Gallagher, M. J.; Rae, A. D.; Sarroff, A. *J. Organomet. Chem.* **1987**, *323*, C1.

(34) For solution structural studies of related open dimers contact ion paired triple ion, see: Paquette, L. A.; Bauer, W.; Sivik, M. R.; Bühl, M.; Feigel, M.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1990**, *112*, 8776. Jackman, L. M.; Rakiewicz, E. F. *J. Am. Chem. Soc.* **1991**, *113*, 1202.

(35) For leading references to possible lithium amide aggregation and mixed aggregation effects, see ref 2.

(36) Ab initio calculations on the degenerate exchange of LiBr with MeBr reveal a relatively low energy pathway involving direct reaction of dimer via a pathway bearing similarities to open dimers. Streitwieser, A., Jr. Unpublished observations.

(37) For comparison, the Li–N bond lengths are as follows: cyclic dimer **9**, 2.38 Å; monomer **7**, 2.01 Å; open dimer **32**, 2.16 and 1.97 Å (Table VII).

Both open dimers and monomers are favored relative to cyclic dimers by similar steric and electronic factors. The HMPA-solvated open dimers are slightly more stable than the corresponding (HMPA)$_2$-solvated monomers for most of the lithium amide–solvent combinations studied. Thus, open dimers should be observable when monomers and dimers are found to coexist. This is intuitively logical given that open dimers represent a partially deaggregated form. The notion is further supported by the spectroscopic studies of the HMPA solvates of LiTMP and LDA (see below).

In some ways the triple ions of general structure **38** are the most provocative species of all. Triple ions have been observed on a few occasions.[6,8,38,39] They typically are detected under highly ionizing conditions, presumably due to the requisite charge separation. Fraenkel and Hallden-Abberton appear to be the first to fully characterize an anionic triple ion[38a] while Jackman and co-workers were the first to clearly note that good donor solvents reputed to mediate deaggregation also promote triple ion formation.[38b,c] The importance of triple ions stems from a potential high reactivity most readily envisioned using analogy with other main-group "ate" complexes.[40] Their absence from all but a few mechanistic discussions[6,41,42] may be due to a tendency to masquerade as either simple ion pairs or cyclic oligomers.

The MNDO calculations do not predict THF- or HMPA-solvated triple ions to be the most stable species for any case studied; however, they are shown to be quite plausible in certain cases. The alleviation of steric demands in triple ions is manifested in a manner quite similar to that of the open dimers (Figures 2–4). The optimized triple ions all show an approximate 90° rotation about the axis, as defined by the linear N–Li–N linkage, and they show no tendency to maintain solvation of the internal Li nucleus. Increased steric demands promote triple ion formation relative to all other species, presumably because a high solvation number (two per lithium) can be attained by solvation events relatively distant to the sterically demanding N-alkyl substituents. The substantial stabilizations resulting from the ion pairing of the separate anionic and cationic fragments are essentially independent of the bulk of the alkyl substituents. As expected, the requisite high solvation energy is better provided by HMPA than THF. The HMPA-solvated LiTMP triple ion **13** is found to be close in energy to open dimer **32** (the most stable form) and more stable than cyclic dimer **9**.

Overall, both high steric demands on the amide fragment and high ionizing power of the solvent promote formation of monomers, open dimers, and triple ions relative to cyclic dimers, but to different extents. The influence of solvent and amide structure is more pronounced for triple ions—species that become relatively stable only when the ionizing power of the solvent and the steric bulk of the amide fragment are maximized. The monomers, on the other hand, benefit from attaining the high solvation number, but gain only limited relief of steric strain due to solvent–amide interactions.

Correlation of Theory with Experiment. An important test of any theory is whether it can reproduce available experimental results. Detailed solution structure studies of HMPA solvates to LDA and LiTMP[8] provide an excellent test. However, the complexity of the equilibria observed in LiTMP/THF/HMPA mixtures renders the omission of entropic contributions associated with mass action effects especially problematic. Although the discussion will not include further mention of entropic effects, the reader should bear in mind that the theory–experiment correlations (irrespective of their relative success) are incomplete.

The results from ^{6}Li, ^{15}N, and ^{31}P NMR spectroscopic studies of LDA in the presence of varying quantities of HMPA are illustrated in Scheme I. LDA in THF solution exists as dimer **1** to the exclusion of monomer. Addition of up to 1.0 equiv of HMPA results in serial solvation of the dimer via mixed solvate **2** and (HMPA)$_2$ solvate **3** by equilibria that are relatively hard within the detection limits of the experiment. Dimers **2** and **3** were shown to bear terminal rather than bridging HMPA ligands. Dimer **3** is the only observable structure in the limit of excess HMPA. The failure of HMPA to deaggregate LDA is notable in light of the purported ability of HMPA to deaggregate organolithiums.

Inspection of the results from the MNDO calculations of LDA solvates (Scheme V) reveals a strong correlation with experiment. The only detectable divergence of theory and experiment is the prediction that open dimer **28** is stable relative to the cyclic form **3**. The high relative stability of **28** might arise from the overestimation of steric effects discussed above. Casual perusal of the analogous predictions for Me$_2$NLi illustrated in Scheme IV reveals an excellent correspondence between the computational predictions for Me$_2$NLi and the experimental results for LDA. A similar relationship was observed in recent computational studies of Me$_2$NLi and LDA solvated by THF and TMEDA.[11] Thus, within the constraints of the present MNDO parameters, the calculated heats of formation of Me$_2$NLi structures may be better indicators of the experimental results for LDA than are the calculations of LDA.

The results of ^{6}Li, ^{15}N, and ^{31}P NMR spectroscopic studies of LiTMP in THF with added quantities of HMPA are illustrated in Scheme II. The spectroscopic studies revealed trends that were not anticipated as well as a structural complexity that is far greater than for LDA. The C_{2h} rather than C_{2v} conformational preference was also demonstrated. Both the monomer and dimer are observed to undergo serial solvation. However, in contrast to LDA, tetrasolvated cyclic dimer **10** rather than disolvated dimer **9** is the limiting LiTMP cyclic dimer in the presence of excess HMPA. As the concentration of HMPA exceeds 1.0 equiv of HMPA/Li, open dimers and triple ions emerge as prominent species. In the limit of excess HMPA, monomer **7**, dimer **10**, and triple ion **13** are the limiting structures. Quite surprisingly, the relative proportions of monomers and dimers are not significantly altered by the added HMPA despite the deep-seated structural changes.

The computational results for the THF and HMPA solvates of LiTMP are summarized in Scheme VI. The calculations reproduce a number of experimentally observed trends well. The C_{2h} conformers depicted in Scheme VI are preferred over the corresponding C_{2v} conformers (**35**). The serial solvation of the monomer to give **7** as the highest accessible solvate is adequately predicted by the calculated heats of formation of **4**, **6**, and **7**. The energies of dimers **8** and **9** resulting from serial solvation of **5** also show reasonable agreement with experiment. Although the calculations do not uncover stable tri- and tetrasolvates of the LiTMP dimer, the enthalpies of solvation are consistently higher for LiTMP dimers than for LDA dimers. Thus, it would appear that the lithium nuclei of the LiTMP dimer are more accessible

(38) (a) Fraenkel, G.; Hallden-Abberton, M. P. *J. Am. Chem. Soc.* **1981**, *103*, 5657. (b) Jackman, L. M.; Scarmoutzos, L. M.; Porter, W. *J. Am. Chem. Soc.* **1987**, *109*, 6524. (c) Jackman, L. M.; Scarmoutzos, L. M.; Smith, B. D.; Williard, P. G. *J. Am. Chem. Soc.* **1988**, *110*, 6058.

(39) Bhattacharyya, D. N.; Lee, C. L.; Smid, J.; Szwarc, M. *J. Phys. Chem.* **1965**, *69*, 612. Bhattacharyya, D. N.; Smid, J.; Szwarc, M. *J. Am. Chem. Soc.* **1964**, *86*, 5024. Vinogradova, L. V.; Zgonnik, V. N.; Nikolaev, N. I.; Tsvetanov, K. B. *Eur. Polym. J.* **1979**, *15*, 545. Arnett, E. M.; Maroldo, S. G.; Schriver, G. W.; Schilling, S. L.; Troughton, E. B. *J. Am. Chem. Soc.* **1985**, *107*, 2091. Cambillau, C.; Bram, G.; Corset, J.; Riche, C. *Nouv. J. Chim.* **1979**, *3*, 9. Cambillau, C.; Ourevitch, M. *J. Chem. Soc., Chem. Commun.* **1981**, 996. Raban, M.; Noe, E. A.; Yamamoto, G. *J. Am. Chem. Soc.* **1977**, *99*, 6527. Olmstead, W. N.; Bordwell, F. G. *J. Org. Chem.* **1980**, *45*, 3299. Teixidor, F.; Llobet, A.; Casabo, J.; Solans, X.; Font-Altaba, M.; Aguilo, M. *Inorg. Chem.* **1985**, *24*, 2315. Tsvetanov, Ch. B.; Dotcheva, D. T. *J. Polym. Sci., Part A, Polym. Chem.* **1986**, *24*, 2253. Buttrus, N. H.; Eaborn, C.; Hitchcock, P. B.; Smith, J. D.; Stamper, J. G.; Sullivan, A. C. *J. Chem. Soc., Chem. Commun.* **1986**, 969. Eaborn, C.; Hitchcock, P. B.; Smith, P. B.; Sullivan, A. C. *J. Chem. Soc., Chem. Commun.* **1983**, 827. Viteva, L.; Stefanovsky, Y.; Tsvetanov, C.; Gorrichon, L. *J. Phys. Org. Chem.* **1990**, *3*, 205. Hertkorn, N.; Köhler, F. H. *Z. Naturforsch. B* **1990**, *45*, 848. Bauer, W.; O'Doherty, G. A.; Schleyer, P. v. R.; Paquette, L. A. *J. Am. Chem. Soc.* **1991**, *113*, 7093. Arnold, J. *J. Chem. Soc., Chem. Commun.* **1990**, 976.

(40) Richey, H. G., Jr.; Farkas, J., Jr. *Organometallics* **1990**, *9*, 1778. Fabicon, R. M.; Parvez, M.; Richey, H. G., Jr. *J. Am. Chem. Soc.* **1991**, *113*, 1412. Corey, E. J.; Hannon, F. J. *Tetrahedron Lett.* **1987**, *28*, 5233. Corriu, *Pure Appl. Chem.* **1988**, *60*, 99. Pelter, A.; Smith, K. In *Comprehensive Organic Chemistry*; Barton, D. H. R., Ollis, W. D., Eds.; Pergamon Press: New York, 1979; Vol. 3, Chapter 14. Lipshutz, B. H. *Synthesis* **1987**, 325.

(41) Seebach, D. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1624.

(42) Kocienski, P.; Barber, C. *Pure Appl. Chem.* **1990**, *62*, 1933.

than those in the LDA dimer. The accessibility may stem from transannular Me–Me interactions that cause a distortion of the Li_2N_2 ring observable only in the LiTMP optimized structures (Figure 5).

The prediction that open dimers and triple ions are chemically plausible species and uniquely stabilized for LiTMP represents a notable success for MNDO. The approximate 90° twist allowed by cleaving the Li_2N_2 ring alleviates the transannular Me–Me interactions. It is also notable that the approximately equal proportions of triple ion 13 and monomer 7 observed spectroscopically are correctly predicted by MNDO. Errors resulting from the high steric effects in the dimer possibly cancel. The failure to predict the existence of cyclic dimers appears to arise more from inordinately large steric destabilization of the cyclic dimer rather than from incorrect assessments of the open dimer

and triple ion stabilities. We do not know whether the high propensity of LiTMP to exist as a diverse array of monomers, open dimers, and triple ions is characteristic of hindered lithium di-*tert*-alkylamides in general or if the conformational constraints imparted by the six-membered ring play a role.

Asymmetric Catalysis. Production of Chiral Diols by Enantioselective Catalytic Intramolecular Hydrosilation of Olefins

Steven H. Bergens, Pedro Noheda, John Whelan, and B. Bosnich*

Contribution from the Department of Chemistry, The University of Chicago, 5737 South Ellis Avenue, Chicago, Illinois 60637. Received August 22, 1991

Abstract: Rhodium(I) chiral diphosphine complexes efficiently and rapidly catalyze the intramolecular hydrosilation of silyl ethers derived from allylic alcohols. The efficiency and rates of intramolecular hydrosilations were determined for a variety of silyl and olefin substituents. The catalysts were found to tolerate a wide variety of silyl substituents, although terminal alkyl olefin substituents were found to retard catalysis. Terminal aryl olefin substituents were found to be hydrosilated efficiently and at reasonable rates. One of the chiral catalysts is highly enantioselective for terminal aryl olefin substituents. Almost quantitative ee's are obtained. Moreover, the ee's are only slightly sensitive to aryl and olefin substituents, suggesting that this enantioselective catalysis can provide a wide range of chiral species. Oxidative cleavage of the hydrosilation products gives chiral diols.

Enantioselective catalytic hydrosilation is a process which results in the addition of a silicon–hydrogen bond across a prochiral ketone or olefin. It is usually, but not always, mediated by low-valent transition metal complexes. The majority of enantioselective catalytic hydrosilations have been performed on ketones catalyzed by rhodium(I) chiral phosphine complexes. The advantages of using ketones are obvious. First, the hydrosilation is completely regioselective, giving the silyl ether. Second, the product is readily hydrolyzed to the chiral alcohol, and third, the turnover rate for ketones is generally rapid. There are now numerous cases where very high ee's have been obtained for the hydrosilation of ketones.[1,2] In general, the ee depends on the structures of all three catalytic partners, the ketone, the silane, and the catalyst, so that seemingly minor structural variations in any one of these elements can cause sharp changes in the ee.

On the other hand, asymmetric catalytic hydrosilation of prochiral olefins has received very little attention,[3] possibly for

the following reasons. Unlike ketone substrates, the reaction rates are slow; prochiral olefins do not always undergo complete regioselective addition and are subject to double bond migration prior to hydrosilation. In addition, prochiral olefins were, until recently, difficult to cleave stereospecifically at the silicon–carbon bond to give useful organic products. Like the ketone substrates, the ee's observed for prochiral olefins are dependent on the structures of the olefin, silane, and catalyst. Unlike ketones, the ee's reported for olefins have generally been modest.

One possible method of circumventing some of the complicating features of asymmetric olefin hydrosilation is by employing substrates which can undergo intramolecular hydrosilation (eq 1).[4] The advantages of this device are the following: first, the

$$X = O, CH_2$$

(1)
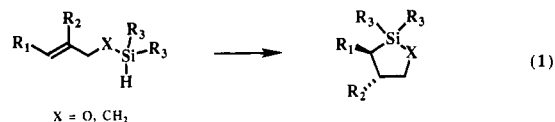
regioselectivity is generally ensured by the observation that 5-membered rings are formed; second, the silicon substituents can be systematically varied to maximize the rate and selectivity of the catalysis; third, the presumed formation of cyclic catalytic intermediates is likely to provide defined steric interactions which are more likely to lead to higher and more consistent ee's than

(1) Ojima, I.; Hirai, K. In *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic Press: New York, 1985; Vol. 5, p 103. Ojima, I.; Clos, N.; Bastos, C. *Tetrahedron* **1989**, *45*, 6901. Kagan, H. B.; Peyronel, J. F.; Yamagishi, T. In *Adv. in Chemistry Series: Inorganic Compounds with Unusual Properties-II*; King, R. B., Ed.; American Chemical Society: Washington, DC, 1979; Vol. 173, p 50.

(2) Nishiyama, H.; Sakaguchi, H.; Nakamura, T.; Horihata, M.; Kondo, M.; Itoh, K. *Organometallics* **1989**, *8*, 846.

(3) Yamamoto, K.; Hayashi, T.; Zembayashi, M.; Kumada, M. *J. Organomet. Chem.* **1976**, *118*, 161. Yamamoto, K.; Hayashi, T.; Uramoto, Y.; Ito, R.; Kumada, M. *J. Organomet. Chem.* **1976**, *118*, 331. Yamamoto, K.; Kiso, Y.; Ito, R.; Tamao, K.; Kumada, M. *J. Organomet. Chem.* **1981**, *210*, 9. Hayashi, T.; Tamao, K.; Katsuro, Y.; Nakae, I.; Kumada, M. *Tetrahedron Lett.* **1980**, *21*, 1871. Tamao, K.; Tohma, T.; Inui, N.; Nakayama, O.; Ito, Y. *Tetrahedron Lett.* **1990**, *31*, 7333.

(4) Tamao, K.; Tamaka, T.; Nakajima, T.; Sumiya, R.; Arai, H.; Ito, Y. *Tetrahedron Lett.* **1986**, *27*, 337. Tamao, K.; Nakajima, T.; Sumiya, R.; Arai, H.; Higuchi, N.; Ito, Y. *J. Am. Chem. Soc.* **1986**, *108*, 6090. Tamao, K.; Nakagawa, Y.; Arai, H.; Higuchi, N.; Ito, Y. *J. Am. Chem. Soc.* **1988**, *110*, 3712. Tamao, K.; Yamauchi, T.; Ito, Y. *Chem. Lett.* **1987**, 171.