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Carbolithiations of *N,N*′-Di-*tert*-butyl-1,4-diazabuta-1,3-diene

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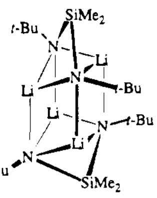
Dimeric (*E*)-4-lithio-1,4-diazabut-1-ene and *N,N*′-dilithioethylenediamine complexes [*cis*-{Li[μ-N(*t*-Bu)CH(*t*-Bu)CHN-*t*-Bu]}$_2$] (**1**) and [{Li[*rac*-N(*t*-Bu)CH(Me)CH(Me)N-*t*-Bu]Li}$_2$] (**2**) have been prepared by carbolithiations of the 1,4-diazabuta-1,3-diene precursor using *t*-BuLi in pentane or MeLi in Et$_2$O. Hydrolysis of **1** and **2** yields the substituted (*E*)-1,4-diazabut-1-ene HN(*t*-Bu)CH(*t*-Bu)CHN*t*-Bu (**3**) and the racemic 2,3-dimethylethylenediamine *rac*-HN(*t*-Bu)CH(Me)CH(Me)N(H)*t*-Bu (**4**). Crystals of **1** are monoclinic, space group *C*2/*c* (No. 15), a = 10.507(5), b = 15.419(2), and c = 20.075(9) Å, β = 92.13(2)°, V = 3250(2) Å^3, Z = 4. Crystals of **2** are orthorhombic, space group *Fddd* (No. 70), a = 9.562(6), b = 18.36(1), and c = 33.04(2) Å, V = 5799(6) Å^3, Z = 8. *Ab initio* calculations on the dimerization of the unsubstituted analogue of **1** (*E*)-4-lithio-1,4-diazabut-1-ene give relative stabilization energies of 31.91 and 31.99 kcal mol^{-1} for the amido nitrogen-bridged dimers of C_i and C_2 symmetry, respectively, relative to the monomer of C_s symmetry containing a planar five-membered chelate ring.

Introduction

Amido−lithium complexes have attracted considerable interest since the 1980s in response to their escalating use as non-nucleophilic Brønsted−Lowry bases in organic synthesis and their application as anionic transfer reagents for the preparation of other main group and transition metal amides. As a result of the research effort by the research groups of Mulvey, Snaith, Schleyer, and others devoted to the systematic structural characterization of "simple" amido−lithium complexes, the ground rules have been laid concerning the aggregation of unsolvated and Lewis base solvated simple amido−lithium species in the solid state. *Ab initio* theoretical molecular orbital calculations on the association of solvent-free and solvated LiNH$_2$ were also undertaken during this period and have made an invaluable contribution to the field. These contributions have been summarized recently in two excellent reviews.[1,2] The theories concerning autocomplexation of these species have considerable predictive utility, though exceptions are not uncommon in the literature. Semiempirical molecular orbital calculations and multinuclear NMR studies by Collum *et al.* have given unequivocal evidence for the solution structure of lithium diisopropylamide (LDA) and lithium 2,2,6,6-tetramethylpiperidide in a number of solvent systems in which these synthetically important reagents are commonly used.[3]

In comparison, relatively little synthetic effort has been focused toward the structural characterization of Lewis base functionalized lithium amides and polylithiated polyamines. Prior investigations have shown that the geometry constraints imposed by dilithiated secondary diamines,[4] **I**, and trilithiated secondary tripodal triamines,[5] **II**, can result in "stacked" dimeric species containing Li$_n$N$_n$ (n = 4, 6) cage cores, previously known for only one unsolvated aggregate of a simple amido−lithium compound,[6] [{(CH$_2$)$_6$NLi}$_6$].



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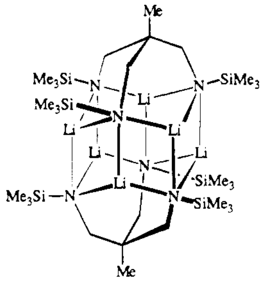

II

Herein we report the synthesis and X-ray structure determinations of the lithium amides [*cis*-{Li[μ-N(*t*-Bu)CH(*t*-Bu)CHN-*t*-Bu]}$_2$] (**1**) and [{Li[*rac*-N(*t*-Bu)CH(Me)CH(Me)N-*t*-Bu]Li}$_2$] (**2**), formed by the carbolithiation of *N,N*′-di-*tert*-butyl-1,4-diazabuta-1,3-diene. Complex **1** is best described as an intramolecularly coordinated imine adduct of an amido−lithium dimer containing a central four membered Li$_2$N$_2$ ring. The dimeric structure of **2** can be seen to arise from the "stacking" together of two dilithium-bridged dilithiated ethylenediamine units to form a central Li$_4$N$_4$ cage. We also report *ab initio* theoretical studies of the unsubstituted analogue of **1**, *viz.*, (*E*)-4-lithio-1,4-diazabut-1-ene, focusing on the energetics of association to the possible diastereoisomers arising from amido nitrogen bridging. It is noteworthy that, while there has been extensive theoretical studies on amido−lithium species, few have dealt with the aggregation of Lewis base functionalized derivatives at the *ab initio* level of theory.

Experimental Section

Syntheses. All manipulations were carried out using standard Schlenk and glovebox techniques under an atmosphere of high-purity argon or nitrogen. Solvents were dried and then freeze/thaw degassed

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[⊗] Abstract published in *Advance ACS Abstracts,* July 1, 1995.

(1) Gregory, K.; Schleyer, P. v. R.; Snaith, R. *Adv. Inorg. Chem.* **1991**, *37*, 47.

(2) Mulvey, R. E. *Chem. Soc. Rev.* **1991**, *20*, 167.

(3) See, for example: (a) Hall, P. A.; Gilchrist, J. H.; Harrison, A. T.; Fuller, D. J.; Collum, D. B. *J. Am. Chem. Soc.* **1991**, *113*, 9575. (b) Gilchrist, J. H.; Collum, D. B. *J. Am. Chem. Soc.* **1992**, *114*, 794. (c) Romesberg, F. E.; Collum, D. B. *J. Am. Chem. Soc.* **1992**, *114*, 2112. (d) 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.* **1992**, *114*, 5100.

(4) Brauer, D. J.; Bürger, H.; Liewald, G. R. *J. Organomet. Chem.* **1986**, *308*, 119.

(5) Gade, L. H.; Mahr, N. *J. Chem. Soc., Dalton Trans.* **1993**, 489.

(6) Barr, D.; Clegg, W.; Mulvey, R. E.; Reed, D.; Snaith, R. *Angew. Chem.* **1985**, *97*, 322; *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 328.

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prior to use. *N,N'*-di-*tert*-butyl-1,4-diazabuta-1,3-diene was prepared according to a literature procedure.[7] All other reagents were obtained from Aldrich. ^{1}H NMR spectra were recorded on Bruker WM-250 and Varian Gemini-200 and Unity-400 spectrometers in deuterated benzene, chloroform, or toluene and referenced to the residual ^{1}H resonances of the solvent (δ 7.15, 7.24, and 6.98, respectively). ^{7}Li NMR spectra were recorded on a Varian Unity-400 spectrometer in deuterated benzene or toluene and referenced to external $LiNO_3$ (1 M in D_2O, δ 0.00). ^{13}C NMR spectra were recorded in deuterated benzene and chloroform on Bruker WM-250 and Varian Gemini-200 spectrometers operating at 62.8 and 50 MHz, respectively, using broad band proton decoupling and were referenced to the ^{13}C resonances of the deuterated solvents (δ 128.00 and 77.00, respectively). Elemental analyses were performed by the Canadian Microanalytical Services Ltd., Vancouver, and the Chemical and Micro Analytical Services Pty. Ltd., Melbourne. Melting points were determined in sealed glass capillaries under argon and are uncorrected. IR spectra were recorded as thin films or Nujol mulls on NaCl plates, as appropriate, using a Perkin-Elmer 1725X Fourier-transformed infrared spectrometer.

Synthesis of [*cis*-{Li[μ-N(*t*-Bu)CH(*t*-Bu)CHN-*t*-Bu]}$_2$] (1). Method a. To a stirred solution of *t*-BuLi (7.0 mL, 1.7 M in pentane, 11.90 mmol) was added *N,N'*-di-*tert*-butyl-1,4-diazabuta-1,3-diene (2.00 g, 11.90 mmol) portionwise over 20 min at 0 °C. The yellow solution was allowed to warm to room temperature and was left to stir for 30 min, whereupon concentration *in vacuo* and cooling to −30 °C yielded large yellow crystals of the title compound overnight. Subsequent cropping of the crystals yielded further product (2.38 g, 86% yield): mp 154−157 °C; ^{1}H NMR (250 MHz, C_6D_6) δ 1.05, 1.10, 1.38 (3 × 18 H, s, Me), 3.43 (2 H, d, $^3J_{H-H}$ = *ca.* 2.2 Hz, CH), 8.38 (2 H, d, $^3J_{H-H}$ = *ca.* 2.2 Hz, N=CH); ^{13}C NMR (62.8 MHz, C_6D_6) δ 30.1, 30.1, 32.4 (Me), 36.4 (C−*C*Me$_3$), 55.0, 56.4 (N−*C*Me$_3$), 72.5 (N−CH), 180.0 (N=CH); ^{7}Li NMR (155.5 MHz, C_6D_6) δ 0.49; IR ν (cm^{-1}) N=C 1650 (s). Anal. Found: C, 71.64; H, 12.15; N, 11.94. Calcd: C, 72.37; H, 12.58; N, 12.06.

Method (b). To a stirred solution of **3** (1.00 g, 4.42 mmol) in hexane (10 mL) was added *n*-BuLi (2.87 mL, 1.54 M in hexane, 4.42 mmol) dropwise over 10 min at 0 °C. The pale yellow solution was allowed to warm to room temperature and left to stir for 1 h. The solution was then concentrated *in vacuo* and cooled to −30 °C, whereupon yellow crystals of the title compound deposited overnight. Subsequent cropping of the crystals yielded further product (0.93 g, 91% yield). (This product was spectroscopically identical to that of the above synthesis.)

Synthesis of [{Li[*rac*-N(*t*-Bu)CH(Me)CH(Me)N-*t*-Bu]Li}$_2$] (2). Method (a). To a stirred solution of MeLi (10.0 mL, 1.4 M in Et_2O, 14.0 mmol) was added *N,N'*-di-*tert*-butyl-1,4-diazabuta-1,3-diene (1.17 g, 6.96 mmol) portionwise over 10 min at 0 °C. The pale yellow solution was allowed to warm to room temperature and left to stir for 1 h. The solution was then concentrated *in vacuo* and cooled to −30 °C, whereupon large colorless crystals of the title compound deposited overnight. Subsequent cropping of the crystals yielded further product (1.24 g, 84% yield): mp 170 °C dec; ^{1}H NMR (250 MHz, C_6D_6) δ 1.13, 1.18 (2 × 6 H (*ca.* 3:1)), d, $^3J_{H-H}$ = 6.60 Hz, Me), 1.20, 1.22 (2 × 18 H (*ca.* 3:1), s, Me), 2.86 (2 H, q $^3J_{H-H}$ = 6.60 Hz, N−CH); ^{13}C NMR (62.8 MHz, C_6D_6) δ 27.0, 27.1 (Me (*ca.* 3:1)), 32.7, 33.1 (C*Me$_3$* (*ca.* 1:3)), 53.8, 54.0 (N−*C*Me$_3$ (*ca.* 3:1)), 56.6, 56.7 (N−CH (*ca.* 1:3)); ^{7}Li NMR (155.5 MHz, C_6D_6) δ 2.11, 2.17 (*ca.* 1:3). Anal. Found: C, 66.48; H, 12.06; N, 12.77. Calcd: C, 67.91; H, 12.35; N, 13.20.

Method (b). To a stirred solution of **4** (1.00 g, 4.99 mmol) in hexane (20 mL) was added *n*-BuLi (6.50 mL, 1.54 M in hexane, 10.01 mmol) dropwise over 10 min at 0 °C. The colorless solution was allowed to warm to room temperature and left to stir for 1 h. The solution was then concentrated *in vacuo* and cooled to −30 °C, whereupon colorless crystals of the title compound deposited overnight. Subsequent cropping of the crystals yielded further product (0.92 g, 87% yield). (This product was spectroscopically identical to that of the above synthesis.)

Synthesis of HN(*t*-Bu)CH(*t*-Bu)CHN-*t*-Bu (3). To a stirred solution of *t*-BuLi (17.5 mL, 1.7 M in pentane, 29.75 mmol) in hexane (50 mL) was added *N,N'*-di-*tert*-butyl-1,4-diazabuta-1,3-diene (5.00 g, 29.75 mmol) portionwise over 15 min at 0 °C. The yellow solution was allowed to warm to room temperature and left to stir for 30 min. Water (50 mL) was added dropwise over 10 min at 0 °C, and the mixture was left to stir for 1 h. The organic layer was extracted with hexane (3 × 50 mL), dried (Na_2SO_4), and filtered, and the solvent was removed *in vacuo*. The title compound was distilled as a colorless viscous liquid under reduced pressure (5.50 g, 85% yield). bp 58 °C (*ca.* 1 mmHg); ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.91, 1.03, 1.18 (3 × 9 H, s, Me), 1.25 (1 H, b, NH), 2.80 (1 H, d, $^3J_{H-H}$ = 6.20 Hz, CH), 7.54 (1 H, d, $^3J_{H-H}$ = 6.20 Hz, N=CH); ^{13}C NMR (62.8 MHz, $CDCl_3$) δ 26.7, 29.2, 30.2 (Me), 34.5 (C−*C*Me$_3$), 50.6, 56.4 (N−*C*Me$_3$), 64.3 (N-CH), 162.2 (N=CH); IR ν (cm^{-1}) N=C 1663 (m), N−H 3303 (w).

Table 1. Crystal Data for [*cis*-{Li[μ-N(*t*-Bu)CH(*t*-Bu)CHN-*t*-Bu]}$_2$] (**1**) and [{Li[*rac*-N(*t*-Bu)CH(Me)CH(Me)N-*t*-Bu]Li}$_2$] (**2**)

1 ($C_{28}H_{58}N_4Li_2$)	fw 464.68
$a = 10.507(5)$ Å	space group *C*2/*c* (No. 15)
$b = 15.419(2)$ Å	$T = 24$ °C
$c = 20.075(9)$ Å	$\lambda = 0.71069$ Å
$\beta = 92.13(2)°$	$\varrho_{calcd} = 0.950$ g cm^{-3}
$V = 3250(2)$ Å^3	$\mu = 0.59$ cm^{-1}
$Z = 4$	$R(F_o)^a = 0.052$
	$R_w(F_o)^b = 0.052$
2 ($C_{24}H_{52}N_4Li_4$)	fw 424.47
$a = 9.562(6)$ Å	space group *Fddd* (No. 70)
$b = 18.36(1)$ Å	$T = 24$ °C
$c = 33.04(2)$ Å	$\lambda = 0.71069$ Å
$V = 5799(6)$ Å^3	$\varrho_{calcd} = 0.972$ g cm^{-3}
$Z = 8$	$\mu = 0.59$ cm^{-1}
	$R(F_o)^a = 0.092$
	$R_w(F_o)^b = 0.092$

[a] $(R(F_o) = \sum||F_o| - |F_c||/\sum|F_o|)$. [b] $(R_w(F_o) = (\sum w||F| - |F_c||^2/\sum w|F_o|^2)^{1/2})$.

Synthesis of *rac*-HN(*t*-Bu)CH(Me)CH(Me)N(H) *t*-Bu (4). To a stirred solution of MeLi (50.0 mL, 1.4 M in Et_2O, 70.0 mmol) was added *N,N'*-di-*tert*-butyl-1,4-diazabuta-1,3-diene (5.83 g, 34.7 mmol) portionwise over 20 min at 0 °C. The pale yellow solution was allowed to warm to room temperature and left to stir for 1 h. Water (50 mL) was added dropwise over 10 min at 0 °C, and the mixture was left to stir for 1 h. The organic layer was extracted with hexane (3 × 50 mL), dried (Na_2SO_4), and filtered, and the solvent was removed *in vacuo*. The title compound was distilled as a colorless viscous liquid under reduced pressure (5.02 g, 72% yield): bp 40 °C (*ca.* 1 mmHg); ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.83 (2 H, b, NH), 0.91 (6 H, d, $^3J_{H-H}$ = 6.15 Hz, Me), 0.95 (18 H, s, Me), 2.26 (2 H, q, $^3J_{H-H}$ = 6.15 Hz, N-CH); ^{13}C NMR (62.8 MHz, $CDCl_3$) δ 20.1 (Me), 30.1 (C*Me$_3$*), 50.4 (N−*C*Me$_3$), 53.0 (N-CH) (N=CH); IR ν (cm^{-1}) N−H 3307 (w).

Structure Determinations. Crystals of **1** and **2** suitable for X-ray structure determination were grown from hexane solutions at −30 °C and were mounted in sealed capillaries under an argon atmosphere. Suitable crystals of **2** could also be obtained by sublimation (140 °C, *ca.* 1 mmHg). Unique diffractometer data sets were measured using an Enraf−Nonius CAD4 diffractometer. Reflections with $I > 2.5\sigma(I)$ were considered "observed" and were used in the full matrix least-squares refinements, minimizing $\sum w\Delta^2$ after solution of the structures by direct methods. Conventional residuals on F at convergence are quoted. No extensive, significant extinction effects were found. Neutral-atom complex scattering factors were employed.[8] Computation used the XTAL 3.0[9] and SHELXS-86[10] program systems implemented on a Sun SPARCstation 2 computer. Molecular core geometries, atom coordinates, and crystal data are given in Tables 1−5, and molecular projections showing numbering schemes are given in Figures 1 and 2. Averaged structural parameters will be used in the structural comparisons where appropriate and are distinguished by the absence of the least-squares error term from the determined quantity. Anisotropic thermal parameters were refined for all non-hydrogen atoms in both

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(7) Kliegman, J. M.; Barnes, R. K. *Tetrahedron* **1970**, *26*, 2555.

(8) *International Tables for X-ray Crystallography*; Ibers, J. A., Hamilton, W. C., Eds., Kynoch Press: Birmingham, England, 1974; Vol. 4.

(9) *XTAL User's Manual - Version 3.0*; Hall, S. R., Stewart, J. M., Eds.; The Universities of Western Australia and Maryland, 1990.

(10) SHELXS-86, Program for the Solution of Crystal Structures, University of Göttingen, Göttingen, Germany, 1986.

Table 2. Non-Hydrogen Atom Coordinates and Isotropic Thermal Parameters for [*cis*-{Li[μ-N(*t*-Bu)CH(*t*-Bu)CHN-*t*-Bu]}$_2$] (**1**)

atom	*x/a*	*y/b*	*z/c*	U,[a] Å^2
Li	0.0978(5)	0.4560(4)	0.2747(3)	0.064(2)
N(1)	0.1789(3)	0.4201(2)	0.3607(1)	0.057(1)
N(4)	−0.0781(3)	0.4626(2)	0.3234(1)	0.058(1)
C(1)	0.3148(3)	0.4121(3)	0.3821(2)	0.073(2)
C(2)	0.0919(3)	0.4004(3)	0.3992(2)	0.067(1)
C(3)	−0.0492(3)	0.4091(3)	0.3817(2)	0.063(1)
C(4)	−0.1307(4)	0.5476(3)	0.3426(2)	0.083(2)
C(11)	0.3833(4)	0.3818(4)	0.3214(2)	0.131(3)
C(12)	0.3415(4)	0.3491(4)	0.4394(2)	0.117(2)
C(13)	0.3578(4)	0.5021(4)	0.4040(3)	0.132(3)
C(31)	−0.1113(4)	0.3163(3)	0.3815(2)	0.082(2)
C(32)	−0.0797(5)	0.2681(3)	0.4471(2)	0.133(3)
C(33)	−0.0674(5)	0.2639(3)	0.3231(2)	0.125(3)
C(34)	−0.2561(5)	0.3237(4)	0.3743(3)	0.133(3)
C(41)	−0.1687(4)	0.5973(3)	0.2787(2)	0.104(2)
C(42)	−0.0341(5)	0.6022(3)	0.3846(2)	0.116(2)
C(43)	−0.2557(5)	0.5411(4)	0.3821(2)	0.137(3)

[a] Isotropic equivalent thermal parameters.

Table 3. Non-Hydrogen Atom Coordinates and Isotropic Thermal Parameters for [{Li[*rac*-N(*t*-Bu)CH(Me)CH(Me)N-*t*-Bu]Li}$_2$] (**2**)

atom	*x/a*	*y/b*	*z/c*	U,[a] Å^2
Li	0.276(3)	0.336(1)	0.4028(7)	0.09(1)
N	0.280(1)	0.4531(6)	0.4044(3)	0.110(6)
C(1)	0.158(2)	0.462(1)	0.4342(5)	0.14(1)
C(11)	0.110(3)	0.385(1)	0.4478(5)	0.20(1)
C(12)	0.034(2)	0.508(1)	0.4160(6)	0.20(1)
C(13)	0.213(3)	0.505(1)	0.4712(6)	0.24(1)
C(2)	0.323(3)	0.5271(8)	0.3901(6)	0.20(2)
C(21)	0.242(3)	0.209(1)	0.4206(7)	0.29(2)

[a] Isotropic equivalent thermal parameters.

Table 4. Selected Structural Parameters for [*cis*-{Li[μ-N(*t*-Bu)CH(*t*-Bu)CHN-*t*-Bu]}$_2$] (**1**)

Bond Distances (Å)					
Li−Li^a	2.248(7)	Li−N4^a	1.974(6)	C2−C3	1.517(5)
Li−N1	1.977(6)	N1−C1	1.481(5)	N4−C3	1.454(4)
Li−N4	2.125(6)	N1−C2	1.256(5)	N4−C4	1.481(5)

Bond Angles (deg)			
N1−Li−N4	88.0(2)	N4−C3−C2	114.2(3)
N1−Li−N4^a	155.7(3)	Li−N4−C3	100.6(2)
N4−Li−N4^a	113.3(3)	Li−N4−C4	120.1(3)
Li−N1−C1	131.0(3)	C3−N4−C4	111.2(3)
Li−N1−C2	107.8(3)	C3−N4−Li^a	141.6(3)
C1−N1−C2	121.2(3)	C4−N4−Li^a	106.2(3)
N1−C2−C3	124.3(3)	Li−N4−Li^a	66.4(2)

[a] Symmetry operator $-x, y, {}^1/_2 - z$.

structure determinations. Methine and methylene hydrogen atoms were located and positionally constrained with fixed temperature factors for **1**; all other hydrogen atoms for **1** and **2** were calculated and constrained at estimated values (C−H 1.0 Å). Temperature factors for methyl hydrogen atoms were estimated at 1.5 × U_{ii}(average) of the attached carbon atom and 1.25 × U_{ii}(average) for other hydrogen atoms. A packing disorder of the 2,3-dimethyl substituents of **2** was apparent in Fourier maps which could not be successfully modeled. Refinement was by a single conformation with large anisotropic thermal parameters. Hydrogens were not included for the disordered 2,3-dimethyl groups and the methine protons of **2**. A second data set was obtained for compound **2** on a prismatic shaped crystal crystalized from hexane, which yielded an inaccurate highly disordered structure.[11] Structural commentary will be restricted to the former structure determination; suffice to say, the molecular geometry in the latter determination approximates that of the former.

Theoretical Calculations. *Ab initio* molecular orbital calculations were carried out on [HN(Li)CH$_2$CHNH], [*cis*-{Li[μ-N(H)CH$_2$CHNH]}$_2$], and [*trans*-{Li[μ-N(H)CH$_2$CHNH]}$_2$] using Gaussian 90[12] implemented on a Sun SPARCstation 2 computer. The structures were found initially either with the minimal basis set STO-3G and then minimized with the larger basis set or adapted from the crystal structure data of compound **1** and minimized directly with the 3-21G* basis set. The structures were shown to be true energy minima by frequency analysis. The energies do not include zero point energy corrections.

Table 5. Selected Structural Parameters for [{Li[*rac*-N(*t*-Bu)CH(Me)CH(Me)N-*t*-Bu]Li}$_2$] (**2**)

Bond Distances (Å)					
Li−Li^c	2.38(3)	Li−N^c	2.00(3)	C2−C2^a	1.40(3)
Li−Li^b	2.32(3)	Li−N^b	2.02(3)	C2−C21^c	2.04(3)
Li−Li^a	2.64(4)	N−C1	1.53(2)	C2−C21	2.17(3)
Li−N	2.15(2)	N−C1	1.50(2)		

Bond Angles (deg)			
N^b−Li^b−N^a	110(1)	C2−N−Li^c	93(1)
N−Li^b−N^b	112(1)	C2−N−Li	92(1)
N−Li^b−N^a	83(1)	Li−N−C2	155(1)
Li−N−Li^b	70(1)	C1−N−C2	109(1)
Li−N−Li^c	67.6(9)	N−C2−C21^a	101(1)
Li^b−N−Li^c	82(1)	N−C2−C2	107(1)
Li−N−C1	96(1)	N−C2−C2^a	115(1)
C1−N−Li^c	140(1)	C21−C2^a−C2	75(2)
C1−N−Li^b	128(1)	C21−C2−C2^a	66(1)

[a] Symmetry operator ${}^1/_2 - x, y, {}^1/_2 - z$). [b] Symmetry operator $x, {}^1/_2 - y, {}^1/_2 - z$). [c] Symmetry operator ${}^1/_2 - x, {}^1/_2 - y, z$).

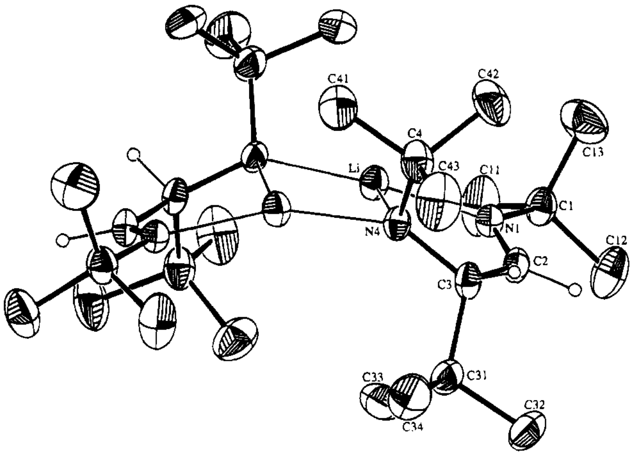

Figure 1. Molecular projection of [*cis*-{Li[μ-N(*t*-Bu)CH(*t*-Bu)CHN-*t*-Bu]}$_2$] (**1**) showing atom labeling scheme. Thermal ellipsoids are drawn at the 20% probability level. For clarity, only methine hydrogens are shown as spheres of arbitrary radii.

Discussion

Synthesis. The amido−lithium complexes **1** and **2** were prepared by 1,2-addition reactions of *t*-BuLi and MeLi to the

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(11) Complex **2** crystallizes from hexane as prismatic crystals in the orthorhombic space group *Pbnn* (No. 52) with eight dimers in the unit cell, the asymmetric unit containing two half-dimers of **2**, the other halves being generated by 2-fold rotation axes on (x, ${}^1/_2$, ${}^3/_4$) and (x, ${}^3/_4$, ${}^1/_2$): the geometry of both independent molecules of **2** is similar. A packing disorder of the 2,3-dimethyl substituents was apparent in Fourier maps which could not be successfully modeled. Low-temperature data collection failed to resolve the disorder. Refinement was as a single conformation with large anisotropic thermal parameters. Further details of this structure determination are available as supporting information. $C_{24}H_{52}N_4Li_4$, $M = 424.47$, orthorhombic, space group *Pbnn* (No. 52), $a = 8.849(3)$ Å, $b = 17.831(8)$ Å, $c = 35.61(1)$ Å, $V = 5619(4)$ Å^3, $Z = 8$, D(calcd) = 1.003 g cm^{-3}, $F(000) = 1888$ electrons, temperature 297 K, radiation Mo Kα, $\lambda = 0.71069$ Å (graphite monochromated), $\mu = 0.64$ cm^{-1}, no absorption correction applied, $2\theta_{max} = 50°$, 5562 independent reflections were measured and 993 of these were considered as "observed" ($I > 2.5\sigma(I)$) and used in the refinement, min/max final residual density = −0.8/0.7 e Å^{-3}, $R = 0.126$, $R_w = 0.126$, $s = 5.83$.

(12) Frisch, M. J.; Head-Gordon, M.; Trucks, G. W.; Foresman, J. B.; Schlegel, H. B.; Raghavachari, K.; Robb, M.; Binkley, J. S.; Gonzalez, C.; Defrees, D. J.; Fox, D. J.; Whiteside, R. A.; Seeger, R.; Melius, C. F.; Baker, J.; Martin, R. L.; Kahn, L. R.; Stewart, J. J. P.; Topiol, S.; Pople, J. A. Gaussian 90, Revision J; Gaussian, Inc.: Pittsburgh, 1990.

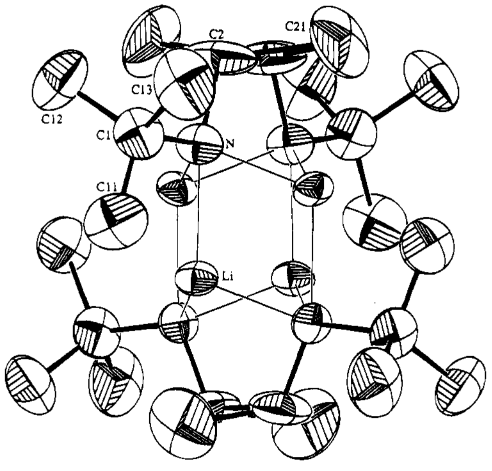
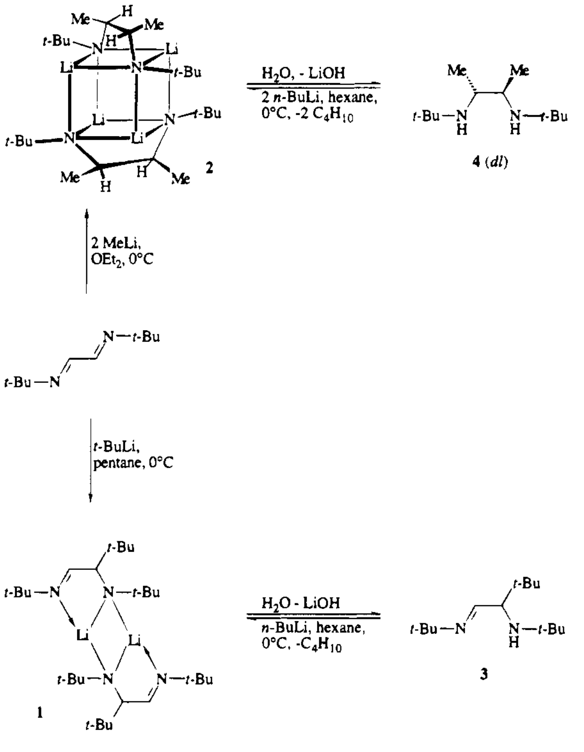


Figure 2. Molecular projection of [{Li[*rac*-N(*t*-Bu)CH(Me)CH(Me)N-*t*-Bu]Li}$_2$] (2) showing atom labeling scheme. Thermal ellipsoids are drawn at the 20% probability level.

Scheme 1



imine functionalities of *N,N'*-di-*tert*-butyl-1,4-diazabuta-1,3-diene, as outlined in Scheme 1.

The di-1,2-addition product **2** is obtained by the reaction of *N,N'*-di-*tert*-butyl-1,4-diazabuta-1,3-diene with 2 equiv of MeLi in Et$_2$O at 0 °C. In contrast, mono-1,2-addition results from the reaction of *N,N'*-di-*tert*-butyl-1,4-diazabuta-1,3-diene with an excess of *t*-BuLi in pentane at 0 °C, the product being the dimeric lithium amide **1**. Hydrolysis of the amido–lithium complexes affords the secondary amines **3** and **4** in high yield as viscous colorless liquids. The secondary amines are readily lithiated by *n*-BuLi in hexane to regenerate the amido–lithium complexes **1** and **2**. The lithium complexes can be isolated in high yield by either route as very air- and moisture-sensitive yellow and colorless crystalline solids, respectively.

Presumably, the steric hindrance associated with the carbon-centered *t*-Bu substituent in **1** protects the remaining imine functionality against addition. Furthermore, MeLi fails to add to the same imine functionality of **1** even under reflux in tetrahydrofuran (THF). Reaction of *N,N'*-di-*tert*-butyl-1,4-diazabuta-1,3-diene with 1 equiv of MeLi in Et$_2$O at low temperature, *ca.* −50 °C, gives a mixture of unreacted *N,N'*-di-*tert*-butyl-1,4-diazabuta-1,3-diene and mono- and di-addition products (by ^{1}H NMR spectroscopy of hydrolysis products), from which the lithium complex resulting from mono-addition could not be isolated.

Group transfer reactions of diorganozinc and triorganoaluminum compounds with 1,4-diazabuta-1,3-dienes and related 1,4-diheterodienes such as 2,2'-bipyridines have been the subject of extensive studies by the research groups of van Koten, tom Dieck, Kaim, Stoll and Kaupp, and others. Product distributions from alkyl transfer from dialkylzinc and trialkylaluminum species to 1,4-diazabuta-1,3-dienes are highly dependent on the metal, the alkyl group present on the metal, and the *N*-substituent of the diazabutadiene. In the case of zinc,[13] the reaction proceeds by the initial formation of a highly colored dialkylzinc σ,σ,N,N'-diazabutadiene chelate complex, R$_2$Zn(1,4-diazabuta-1,3-diene), which then undergoes regioselective thermal or light-induced alkyl transfer to give *N*- or *C*-alkylated products *via* an intramolecular single electron transfer mechanism. In the analogous reactions involving trialkylaluminum species,[14] the species formed initially is the σ,*N*-diazabutadiene complex R$_3$Al(1,4-diazabuta-1,3-diene), which rearranges to a *C*-alkylated product. In some cases, this undergoes a 1,2-hydrogen shift to give a second *C*-alkylated product, with the alkyl group originating from the trialkylaluminum being attached to the imine carbon. *N*-Alkylation is a minor product only for R = Et.

Alkyllithium and also dialkylmagnesium reactions with 1,4-diazabuta-1,3-dienes, in contrast, have been given but fleeting attention.[15,16] Mechanistic studies of the magnesium reactions are limited, and no mechanisms have been proposed with any evidence for the addition of lithium alkyls to diazabutadienes. This is perhaps because of the facile addition which occurs in the case of lithium, making EPR characterization of any intermediates difficult. Our interest here is in the structures of the lithium amide products. We note that the observed *rac* isomer for the di-addition product **2** is consistent with the simplistic view of Cram-type chelation control of the reaction; attack is from the least hindered side of the imine-functionalized lithium amide mono-addition intermediate, giving the observed *rac* isomer. The reaction of *N,N'*-di-*tert*-butyl-1,4-diazabuta-1,3-diene with MeLi and *t*-BuLi gives an intensely colored blue intermediate only when the order of reactant addition is adding the alkyllithium species to the 1,4-diazabuta-1,3-diene. The blue intermediate has a lifetime of several minutes at low temperature, and the nature of these species is under investigation. We note that the dialkylzinc σ,σ,*N,N'*-diazabutadiene chelate complexes R$_2$Zn(1,4-diazabuta-1,3-diene) initially formed in the analogous dialkylzinc reactions are also highly colored species.[13] *C*-Alkylation with *t*-BuLi is consistent with the *t*-Bu group transfer reactions in the literature for *t*-Bu$_2$Zn and *t*-Bu$_3$Al adding to *N,N'*-di-*tert*-butyl-1,4-diazabuta-1,3-diene, whereas *C*-alkylation with MeLi contrasts with the behavior seen for Me$_2$Zn. The group transfer reactions reported in the literature for alkyllithium species adding to diazabutadienes are limited to those involving EtLi and *n*-BuLi.[15] Both *N*- and *C*-alkylation products could be obtained as the major product for both

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(13) Kaupp, M.; Stoll, H.; Preuss, H.; Kaim, W.; Stahl, T.; van Koten, G.; Wissing, E.; Smeets, W. J. J.; Spek, A. L. *J. Am. Chem. Soc.* **1991**, *113*, 5606 and references therein.

(14) Wissing, E.; Jastrzebski, J. T. B. H.; Boersma, J.; van Koten, G. *J. Organomet. Chem.* **1993**, *459*, 11.

(15) Stamp, L.; tom Dieck, H. *J. Organomet. Chem.* **1984**, *277*, 297.

(16) Neumann, W. L.; Rogic, M. M.; Dunn, T. J. *Tetrahedron Lett.* **1991**, *32*, 5865.

systems, depending on the reaction conditions employed and the solvent system. In the present study, no *N*-alkylation products were isolated. Di-addition reaction products have not been reported for alkyllithium group transfer reactions of diazabutadienes but are obtained in the case of allylic Grignard reagents adding to diazabutadienes at −78 °C.[16]

There has been considerable interest in the literature in recent years concerning the diastereoselective and enantioselective synthesis of vicinal diamines.[16,17] Synthetic approaches have included multistep modifications of amino acids and the di-addition of allylmagnesium chlorides to diazabutadienes to give *rac*-2,3-disubstituted ethylenediamines; modest enantiomeric excesses (6:1) have been achieved by the use of chiral diazabutadienes.[16] The *rac*-2,3-dimethyl substituted ethylenediamine **4** is formed here almost quantitatively, with no trace of the *meso* isomer (^{1}H NMR spectroscopy). The identity of the *rac* isomer has been confirmed by the crystal structure of **2** and another derivative.[18]

^{1}H, ^{7}Li, and ^{13}C NMR and IR spectra of complex **1** are largely uninformative. The vicinal coupling constant between the C-imine proton and the methine proton of the complex of 2.2 Hz is in reasonable agreement with the H−C−C−H dihedral angle of 42.2° observed in the crystal structure of the complex, suggesting that the integrity of the chelate ring remains intact in solution. The resonance of the C-imine proton in the ^{1}H NMR spectrum of **1** at 8.38 ppm is shifted downfield some 0.84 ppm relative to that of the 1,4-diazabut-1-ene **3**. The C=N IR absorption stretch at 1650 cm^{-1} of the lithium-coordinated imine is only slightly shifted to a lower frequency relative to that of the 1,4-diazabut-1-ene, found at 1663 cm^{-1}.

In solution, compound **2** is present as a mixture of two species, as evidenced by the ^{1}H, ^{7}Li, and ^{13}C NMR spectra of the complex. The ratio of the two species in benzene and toluene solutions is *ca.* 1:3 and shows no marked temperature or concentration dependence. This is consistent with the presence of two diastereoisomers arising from the aggregation of dilithio species of the same chirality or opposite chirality. The NMR spectra of **2** are otherwise largely uninformative, having ^{1}H and ^{13}C resonances similar to those of **4**.

Extensive theoretical studies on the association of $LiNH_2$ by Schleyer[1] *et al.* have shown that laddering of amido−lithium complexes is generally preferred over vertical association, or stacking, owing to the relatively small change in geometry of the dimeric [{Li(μ-NH$_2$)}$_2$] building block on lateral association. This results in a small reorganizational energy of the [{Li(μ-NH$_2$)}$_2$] unit which takes little away from the association energy, giving a large net stabilization energy. In comparison, when two [{Li(μ-NH$_2$)}$_2$] units stack together the *N*-substituents have to move considerably, giving rise to a large reorganizational energy of the [{Li(μ-NH$_2$)}$_2$] unit. The association energy of the stacking may be comparable to the laddering of the [{Li(μ-NH$_2$)}$_2$] units, but the large reorganizational energy results in the lateral association being energetically favorable relative to vertical association, or stacking. This effect is expected to be greater when the *N*-substituents are larger.

Ab initio calculations on *N,N'*-dilithiated ethylenediamine revealed a dilithium-bridged species to be the most stable geometry in which the ethylene bridge of the dianion effectively butterflies the Li_2N_2 ring and pulls the other *N*-substituents to one side of the Li_2N_2 ring.[19] This structural motif was found for the crystal structure of the hexamethylphosphoramide (HMPA) adduct[19] [(CH$_2$NPh)$_2$Li$_2$(HMPA)$_3$]. In forming a dilithium-bridged species, the geometry of the unsolvated monomeric unit of a dilithiated ethylenediamine would have to change very little to allow for the stacking of two of these units. The result is a small reorganizational energy, taking little away from the association energy, and, hence, a relatively large net stabilization energy.[20] Previous experimental evidence of the capabilities of lithiated diamines and tripodal triamines to give rise to stacking in amido−lithium chemistry has been found in several instances. Examples of Li_4N_4 cages, as are present in **2**, are limited to one other example,[4] [{Me$_2$Si[N(Li)*t*-Bu]$_2$}$_2$], while a number of Li_6N_6 cages have been structurally authenticated,[5,21] [{H$_3$CC[CH$_2$N(Li)R]$_3$}$_2$] (R = *i*-Pr and SiMe$_3$), [{PhSi[N(Li)*t*-Bu]$_3$}$_2$], and [{RSi[N(Li)SiMe$_3$]$_3$}$_2$] (R = Me, Ph, *t*-Bu). These Li_6N_6 cages, along with the hexameric simple amido−lithium complex[6] [{(CH$_2$)$_6$NLi}$_6$], have also been alternatively classified as cyclized ladders. Molecular orbital considerations enable the prediction of any expected alternations in Li−N bond lengths in the structures of cyclized ladders, but severe crystal packing disorders/high crystallographic site symmetries in many of these molecules limit the utility of this empirical measure for classifying these complexes.

X-ray Structure Commentary. Structure of 1. Complex **1** crystallizes as prismatic crystals in the monoclinic space group *C2/c* with four dimers in the unit cell, the asymmetric unit comprising one half of the dimer of composition [*cis*-{Li[μ-N(*t*-Bu)CH(*t*-Bu)CHN-*t*-Bu]}$_2$], the other half being generated by the 2-fold rotation axis on (0, *y*, $^1/_4$) (Figure 1). The complex is best described as an intramolecularly coordinated imine adduct of an amido−lithium dimer containing a central four-membered Li_2N_2 ring core. The *N*-lithiated (*E*)-1,4-diazabut-1-ene acts as a bidentate ligand, chelating a lithium atom and bridging the other lithium atom through the amido nitrogen atom, achieving 3-fold coordination for the lithium atoms. The overall molecular symmetry is crystallographically constrained to be C_2.

Selected geometrical parameters are given in Table 4. The Li−N(amido) distances vary considerably, the Li−N distance to the nitrogen in the chelate ring of 2.125(5) Å being longer than the "cross-dimer" distance of 1.977(6) Å. The latter distance is more typical for di-bridging amido *N*-three-coordinate Li distances, while the former distance is more typical of a coordinatively saturated four-coordinate lithium atom. Theoretical calculations on the model complex *cis*-{Li[μ-N(H)CH$_2$-CHNH]}$_2$ did not reveal such large disparities between the two different Li−N(amido) distances, *vide infra*. The same Li−N distances for the related intramolecularly coordinated secondary amine functionalized amido−lithium dimer,[22] [*cis*-{Li[μ-N(*t*-Bu)CH$_2$CH$_2$N(H)*t*-Bu]}$_2$], measure 2.017(7) and 1.973(6) Å, respectively. The added steric strain in the five-membered chelate ring introduced by the unit of unsaturation in **1** results in the transannular amido nitrogen (N4') being 1.43(2) Å from the plane defined by C3−N4−C4, resulting in nonequivalent nitrogen orbital donation to both the lithium atoms (*viz.* atoms N4, Li', C3, and C4 are almost planar, Σ(Li'−N4−C3,C4;C3−N4−C4) = 359.0°). This presumably leads to the elongation of the Li−N bond in the chelate ring. In comparison, the transannular amido nitrogen in [*cis*-{Li[μ-N(*t*-Bu)CH$_2$CH$_2$N-

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[17] (a) Jones, D. S.; Srinivasan, A.; Kasina, S.; Fritzberg, A. R.; Wilkening, D. W. *J. Org. Chem.* **1989**, *54*, 1940. (b) Reetz, M. T.; Jaeger, R.; Drewlies, R.; Hübel, M. *Angew. Chem.* **1991**, *103*, 76; *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 103. (c) Denmark, S. E.; Kim, J.-H. *Synthesis* **1992**, 229. (d) Gamez, P.; Dunjic, B.; Fache, F.; Lemaire, M. *J. Chem. Soc., Chem. Commun.* **1994**, 1417.

[18] Lawrence, S. M.; Raston, C. L. Unpublished results.

[19] Armstrong, D. R.; Barr, D.; Brooker, A. T.; Clegg, W.; Gregory, K.; Hodgson, S. M.; Snaith, R.; Wright, D. S. *Angew. Chem.* **1990**, *102*, 443; *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 410.

[20] Gardiner, M. G.; Raston, C. L. Unpublished calculations.

[21] Brauer, D. J.; Bürger, H.; Liewald, G. R.; Wilke, J. *J. Organomet. Chem.* **1985**, *287*, 305.

[22] Gardiner, M. G.; Raston, C. L. Unpublished results.

(H) *t*-Bu]}$_2$] lies only 0.41(2) Å from the same C−N−C plane, the lithium atoms being more symmetrically disposed on either side of the plane.

The Li−N(imine) distance of 1.977(6) Å in **1** is quite short relative to the dative Li−N(amine) bond distance of 2.037(7) Å in [*cis*-{Li[μ-N(*t*-Bu)CH$_2$CH$_2$N(H) *t*-Bu]}$_2$], presumably to compensate for the longer Li−N(amido) distance in **1**. The Li−N(imine) bond distance is similar to that of the only other example having a three-coordinate lithium atom,[23] [*trans*-{Li[μ-N(SiMe$_3$)C(Ph)CHC(Ph)NSiMe$_3$]}$_2$] (1.95(1) Å), and is shorter than that in [Li(*N,N′*-di-*tert*-butyl-1,4-diazabuta-1,3-diene)$_2$][24] (2.14) Å, and [{LiO[4-Me-2,6-(CHN-*i*-Pr)$_2$C$_6$H$_2$]}$_3$][25] (2.12 Å), in accordance with the coordination number of the lithium atoms being four in those cases.

The C_2 symmetry of **1** results in only a slight folding, or butterflying, of the Li$_2$N$_2$ ring, the Li−N−N−Li dihedral angle measuring 169.7(5)°, comparable with the same dihedral angle of 169.4(3)° in the related C_2 symmetric dimer [*cis*-{Li[μ-N(*t*-Bu)CH$_2$CH$_2$N(H) *t*-Bu]}$_2$].[22] Typically, intramolecularly coordinated amido−lithium complexes are centrosymmetric, often having crystallographically imposed planar Li$_2$N$_2$ rings.

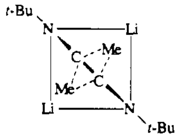
A close Li• • •Li distance is observed across the Li$_2$N$_2$ ring in **1** (2.248(7) Å), a consequence of the tendency for lithium amides to adopt highly acute Li−N−Li angles at the bridging amido nitrogen centers, 66.4(2)° in this case. The Li• • •Li distance is the closest observed in an amido−lithium complex containing a simple Li$_2$N$_2$ ring. An Li−Li distance as low as 2.20 Å has been observed in a complex Li$_8$ alkyllithium−lithium amide oligomeric structure.[26]

Two close Li−H agostic interactions are observed between the lithium atoms and the protons of the *t*-Bu substituents attached to the amido nitrogen atom with which it is not chelated by the imine nitrogen of the same ligand (*i.e.*, Li′−C41). The Li−C contact to the same methyl carbon of 2.551(8) Å corresponds to calculated Li−H distances of 2.28 and 2.37 Å, which are *ca.* 0.7 Å less than the sum of the van der Waals radii of the lithium and hydrogen atoms. Close Li−H contacts are a common structural feature of low-coordinate lithium complexes, typically being in the range 2.2−2.4 Å, and are looked on as being compensatory interactions in cases when the steric requirements of the ligand prevent further association, as in the two-coordinate lithium complex[27] [{Li[μ-2-(Me$_3$Si)$_2$CC$_5$H$_4$N]}$_2$], where the Li−H distances are 2.20, 2.23 and 2.31 Å.

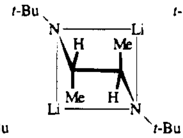
The sum of the N−Li−N angles about each lithium atom in **1** is 357.0°, indicating essentially planar coordination of the lithium atom and imposing only a small dihedral angle between the planes defined by the central Li$_2$N$_2$ ring and the chelate rings, 26.1(2)°. The C_2 symmetry of **1** results in the three edge-fused rings forming a slightly "concave" or "U-shaped" conformation. The dihedral angle between the Li$_2$N$_2$ ring and the five-membered chelate ring in the related complex[28] [*trans*-{Li[8-(μ-NSiMe$_3$)C$_9$H$_6$N]}$_2$] is much greater, this complex exhibiting a "stepped" centrosymmetric structure. The ligand bite angle in **1** measures 88.0(2)°. The lithium atom, the two carbon atoms of the chelate ring, and the imine nitrogen of **1** form a good plane, the amido nitrogen deviating some 0.38(1) Å from this plane. Other bond distances and angles within the molecule are unexceptional and do not require comment.

Structure of 2. Complex **2** crystallizes as prismatic crystals in the orthorhombic space group *Fddd* with eight dimers in the unit cell, the asymmetric unit containing one quarter of the dimer, with molecules lying on sites of D_2 symmetry (Figure 2). The dimeric structure is best described as an amido−lithium complex containing a central, distorted cubane-like Li$_4$N$_4$ cage core. The coordination sphere of the lithium atoms contains two bridging amido nitrogen atoms of the one dilithiated ethylenediamine which they bridge and is complemented by a bridging amido nitrogen atom of the other dilithiated ethylenediamine. The overall molecular symmetry of the dimer is crystallographically imposed to be D_2, but approximates to D_{2d}, with torsion in the ethylene linkage of the ligand and the 2,3-dimethyl substituents being the largest deviation from this symmetry.

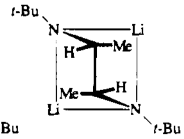
Selected geometrical parameters are given in Table 5. The disorder in the structure of **2** is limited to the four carbon atoms of the 2,3-dimethylethylene linkages of the ligand. Anisotropic refinement of these groups leads to a small C−C bond between the methine carbons, 1.40(3) Å, long C−N bond lengths, 1.50(2) Å, a small N−C−C−N torsion angle, 3(3)°, and long C−Me bond lengths, 2.11 Å, as depicted in **III**, which is a schematic projection of the molecule onto the butterfly-shaped Li$_2$N$_2$ ring of the dimer. This refined geometry is seemingly an artifact of a packing disorder of the *d* and *l* enantiomers of the *rac*-2,3-disubstituted ligand, as depicted in **IV** and **V**. Similar torsional disorder has previously been observed for the ethylene linkage in the substituted *N,N′*-dimetalated ethylenediamine complex [(CH$_2$N*t*-Bu)$_2$Ge].[29]



III



IV



V

The structure of **2** can be viewed as two dilithium-bridged monomers containing butterfly-shaped Li$_2$N$_2$ rings stacking together to form the observed Li$_4$N$_4$ cage core. Once formed, the Li$_4$N$_4$ cage core can alternatively be interpreted as containing a cyclic arrangement of four planar Li$_2$N$_2$ rings whose geometry is similar to that seen for simple amido−lithium dimers (Li• • •Li, 2.35 Å, Li−N−Li, 69°, Li−N−N−Li, 175°). The edges of this cyclic four-rung ladder define the remaining two faces of the Li$_4$N$_4$ core as butterfly-shaped Li$_2$N$_2$ rings (Li• • •Li, 2.64(4) Å, Li−N−Li, 83°, Li−N−N−Li, 123(1)°).

The Li−N bond distances in **2** are not in agreement with those predicted for a cyclic four-rung Li−N ladder core.[1,2] The Li−N(amido) distances in complex **2** are in two distinct ranges, the Li−N distances within the butterfly-shaped Li$_2$N$_2$ ring of the dimer being shorter (2.00(3)-2.02(3) Å) than the Li−N distances "across" the dimer (2.15(2) Å). These Li−N distances are in the lower and upper range, respectively, seen for Li−N(tri-bridging amido N−three-coordinate Li) distances. This observation of Li−N distances is the opposite to that found for the only other amido−lithium complex containing the Li$_4$N$_4$ cage core motif,[4] [{Me$_2$Si[N(Li)tBu]$_2$}$_2$]. In that case, the Li−N distances of the butterfly-shaped Li$_2$N$_2$ ring measured 2.087(6)−

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(23) Hitchcock, P. B.; Lappert, M. F.; Liu, D.-S. *J. Chem. Soc., Chem. Commun.* **1994**, 1699.

(24) Gardiner, M. G.; Hanson, G. R.; Henderson, M. J.; Lee, F. C.; Raston, C. L. *Inorg. Chem.* **1994**, *33*, 2456.

(25) Korobov, M. S.; Minkin, V. I.; Nivorozhkin, L. E.; Kompan, O. E.; Struchkov. Y. T. *Zh. Obshch. Khim.* **1989**, *59*, 429.

(26) Barr, D.; Clegg, W.; Hodgson, S. M.; Mulvey, R. E.; Reed, D.; Snaith, R.; Wright, D. S. *J. Chem. Soc., Chem. Commun.* **1988**, 367.

(27) Colgan, D.; Papasergio, R. I.; Raston, C. L.; White, A. H. *J. Chem. Soc., Chem. Commun.* **1984**, 1708.

(28) Engelhardt, L. M.; Jacobsen, G. E.; Junk, P. C.; Raston, C. L.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1988**, 1011.

(29) Herrmann, W. A.; Denk, M.; Behm, J.; Scherer, W.; Klingan, F.-R.; Bock, H.; Solouki, B.; Wagner, M. *Angew. Chem.* **1992**, *104*, 1489; *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1485.

2.129(6) Å, significantly longer than those seen for the "inter-dimer" bonds (2.003(6)–2.036(6) Å). Presumably, the Li–N distances in these Li_4N_4 cages are influenced more by the different organyl groups bridging the two amido nitrogen atoms, *viz.* -C(Me)HC(Me)H- versus $-SiMe_2-$, rather than the predicted influence on the Li–N distances by the nitrogen atomic orbitals in a cyclic ladder arrangement.

The coordination environment about the lithium atoms in **2** is far from planar (Σ(N–Li–N) = 305°), which leaves a large portion of the coordination sphere of the lithium atoms devoid of primary interactions. A close interaction between the lithium atoms and a carbon atom of the *t*-Bu group is observed in this region, Li–C11 2.35(3) Å, and can be looked on as a compensatory interaction which serves to protect the lithium atom. Indeed, two close agostic Li–H contacts (hydrogen positions calculated) are observed to the protons of the same carbon atom, 2.04 and 2.15 Å. The ligand bite angle in **2** measures 83(1)°. Other bond angles within the molecule are unexceptional and do not require comment.

Theoretical Structures. The formation of both centrosymmetric and C_2 symmetric dimers of the model compound (*E*)-4-lithio-1,4-diazabut-1-ene, $LiN(H)CH_2CHNH$, has been investigated by *ab initio* molecular orbital calculations at the 3-21G* level of theory. The computed structures of [$LiN(H)CH_2CHNH$], [*cis*-{Li[μ-$N(H)CH_2CHNH$]}$_2$], and [*trans*-{Li[μ-$N(H)CH_2CHNH$]}$_2$] are shown in Figure 3. All structures were fully optimized within the point groups, C_s, for the monomer, C_i, for the centrosymmetric dimer, and C_2, for the C_2-symmetric dimer.

The only minima to be found for a monomer containing a chelate ring was the planar 4-lithio-1,4-diazabut-1-ene of C_s symmetry. Removing the symmetry constraint resulted in convergence on the same structure containing the planar five-membered ring of C_s symmetry possessing an sp^2 hybridized amido nitrogen atom. The Li–N bond distances in this highly electron deficient complex are as expected, much shorter than typically observed in practice (Li–N(amido) = 1.76 Å, Li–N(imine) = 1.95 Å).

The search for dimeric species was limited to C_i and C_2 symmetric species bridged through the amido nitrogen atom. True minima were found for each of these species which contain central four-membered Li_2N_2 ring cores and maintain reasonably planar five-membered chelate rings. The Li–N bond distances in these dimers are closer to those typically found in lithium amide complexes with three coordinate lithium centers, Li–N(amido) = 1.94 and 1.96 Å, and 1.93 and 1.98 Å and Li–N(imine) = 1.99 and 2.00 Å for the C_i and C_2 symmetric dimers, respectively. The calculated structures reproduce the Li••Li distance commonly seen across the central four-membered Li_2N_2 ring in amido–lithium complexes to good accuracy, 2.29 and 2.30 Å, for the C_i and C_2 symmetric dimers, respectively. The amido nitrogen atoms in the dimers are sp^3 hybridized, which introduces stepped and concave secondary structures into the three edge-fused rings of the C_i and C_2 symmetric dimers, respectively.

The formation of the C_i and C_2 symmetric dimers gives net stabilization energies of 31.91 and 31.99 kcal mol^{-1}, respectively. This energy difference between the two isomers is well within the realms of crystal packing forces, which may be responsible for the C_2 symmetric dimer being observed in the case of **1**. Molecular models do not reveal any unrealistic nonbonding interactions for a centrosymmetric dimer of the heavily substituted complex **1**. The stabilization energies here compare with those found for the dimerization of $LiNH_2$, 31.4 (MNDO)[30] and 35.9 kcal mol^{-1} (MP2/6–31G*//3-21G*).[31]

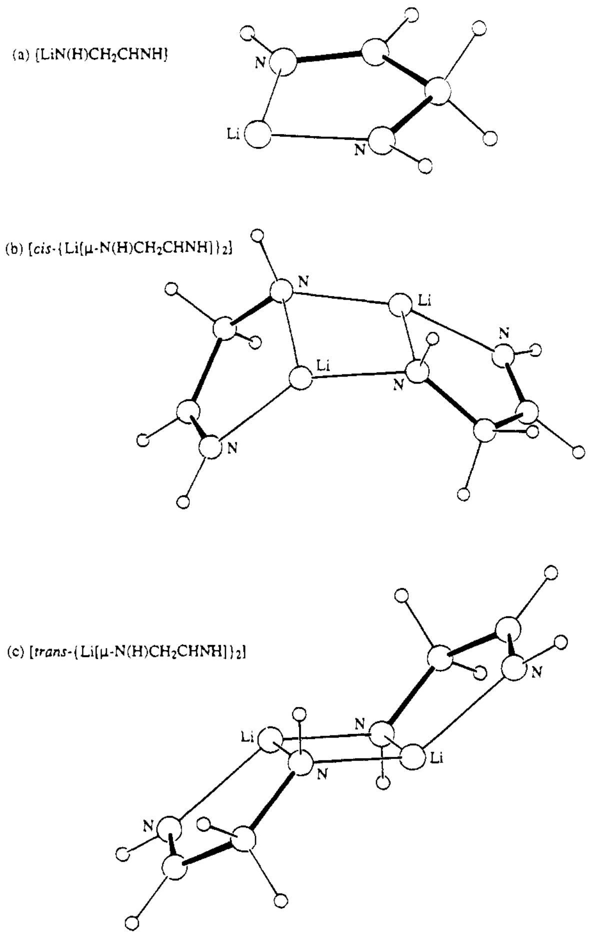

Figure 3. Optimized geometries for minima located using the 3-21G* basis set for (a) [$LiN(H)CH_2CHNH$], (b) *cis*-{Li[μ-$N(H)CH_2CHNH$]}$_2$, (c) [*trans*-{Li[μ-$N(H)CH_2CHNH$]}$_2$].

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Supporting Information Available: Tables giving full crystallographic experimental details, atomic positional parameters, nonhydrogen atom thermal parameters, hydrogen atom parameters, and bond distances and angles for compounds **1** and **2** (both modifications) and molecular projections of the second structural modification of compound of **2** (14 pages). Ordering information is given on any current masthead page.

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(30) (a) Kaneti, J.; Schleyer, P. v. R.; Clark, T.; Kos, A. J.; Spitznagel, G. W.; Andrade, J. G.; Moffat, J. B. *J. Am. Chem. Soc.* **1986**, *108*, 1481. (b) Sapse, A.-M.; Kaufmann, E.; Schleyer, P. v. R.; Gleiter, R. *Inorg. Chem.* **1984**, *23*, 1569.

(31) Kaufmann, E.; Clark, T.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1984**, *106*, 1854.