6924 *J. Am. Chem. Soc.* **1996,** *118,* 6924−6933

Toward Planar Tetracoordinate Carbon in the Puckered Ladder Structures of Chelated Cyclopropenyllithium Aggregates

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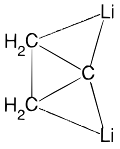
Received February 1, 1996[⊗]

Abstract: Computational predictions of planar tetracoordinate carbon $R^1R^2C_\alpha Li_2$ arrangements in the cyclopropenyllithium dimer have now been realized experimentally in derivatives with additional chelating ligands. The dimer structures of two substituted cyclopropenyllithiums bearing lithium alkoxide and lithium amide side arms, C_α and O dilithiated 1-(di-*tert*-butylhydroxymethyl)-3,3-dimethylcyclopropene (**8**) as well as C_α and N dilithiated 1-(*tert*-butylaminodimethylsilyl)-3,3-dimethylcyclopropene (**9**), were characterized by single-crystal X-ray diffraction. The complexes of **8** with tetramethylethylenediamine (TMEDA), (**8**·TMEDA)$_2$, and with THF, (**8**·2THF)$_2$, show ladder-type dimeric aggregation. The tetracoordinate $R^1R^2C_\alpha Li_2$ carbon environments in both crystal structures have a high degree of planarization (with 35−39° twist angles), partly due to chelation of one of the lithiums by the O^- moiety. Compound **9** crystallizes as a dimeric THF solvate, (**9**·2THF)$_2$, with a puckered ladder structure. Chelation of one of the lithiums by the N^- moiety in the individual (**9**·2THF)$_2$ units results in $R^1R^2C_\alpha Li_2$ environments which aproach planarity even more closely (17 and 30° twist angles). Bridging of the vinylic $C_\alpha-C_\beta$ bonds by the chelated lithiums in (**9**·2THF)$_2$ results in an unexpected feature, the nearly planar tetracoordinate environment of C_β (the cyclopropene carbon next to the lithiated site)! Becke3LYP/6-31G* calculations on mixed-anion (MeLi·LiOH)$_2$ model aggregates are consistent with the experimental findings that dimerization of both (**8**·TMEDA)$_2$ and of (**8**·2THF)$_2$ involves the Li−O rather than the Li−C bond. In contrast (but also consistent with the model computations and with the steric environments), the (**9**·2THF)$_2$ dimer is formed via Li−C rather than Li−N bond aggregation.

Introduction

Nearly two decades ago, computational studies revealed that two lithium atoms attached to the same carbon should result in a remarkable stabilization of planar tetracoordinate arrangements.[1,2] While planar and "tetrahedral" structures of dilithiomethane were found to be close in energy, 1,1-dilithiocyclopropane **1** was the first molecule calculated to prefer a planar tetracoordinate $R^1R^2CLi_2$ carbon geometry.[1,2] While 1,1-dilithio-2,2,3,3-tetramethylcyclopropane has been synthesized by a pyrolysis reaction, high reactivity and low solubility in inert solvents (evidently due to aggregation) have hampered X-ray structural investigations.[3,4] More experimental success resulting in planar tetracoordinate organolithium structures has been achieved by using a different strategy.

The "in plane" geometry of the unsolvated phenyllithium dimer **2** with planar tetracoordinate $R^1R^2CLi_2$ *ipso* carbons—similar to 1,1-dilithiocyclopropane **1**—was computed to be more stable than the "perpendicular" dimer **3**.[5] However, the X-ray structure of (phenyllithium·TMEDA)$_2$ showed that the lithium solvation present in the crystal resulted in the "perpendicular" arrangement **3** instead.[6] This problem might be overcome in systems with intramolecular lithium solvation (chelation).[5] Phenyllithium derivatives with heteroatom substituents (e.g., OR, NR_2, CH_2NR_2) have thus become intriguing synthetic target molecules for the realization of planar tetracoordinate carbon.[7,8]



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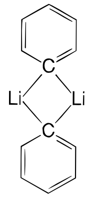

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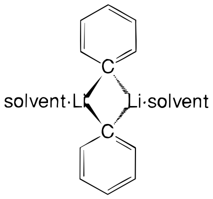

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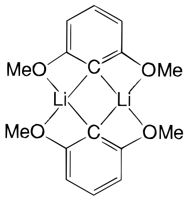

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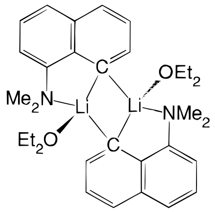

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[⊗] Abstract published in *Advance ACS Abstracts,* June 15, 1996.

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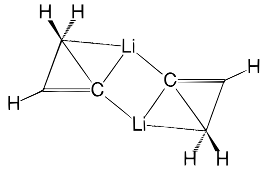
(7) (a) Jastrzebski, J. T. B. H.; van Koten, G.; Goubitz, K.; Arlen, C.; Pfeffer, M. *J. Organomet. Chem.* **1983**, *246*, C75. (b) Jastrzebski, J. T. B. H.; van Koten, G.; Konijn, M.; Stam, C. H. *J. Am. Chem. Soc.* **1982**, *104*, 5490. (c) Rietveld, M. H. P.; Wehman-Ooyevaar, I. C. M.; Kapteijn, G. M.; Grove, D. M.; Smeets, W. J. J.; Kooijman, H.; Spek, A. L.; van Koten, G. *Organometallics* **1994**, *13*, 3782 and references therein.

S0002-7863(96)00336-8 CCC: $12.00

Indeed, nearly planar $R^1R^2CLi_2$ *ipso* carbon arrangements can be discerned in the dimer units in the X-ray structure of (2,6-dimethoxyphenyl)lithium (**4**) (the twist angle between the Li−C_{ipso}−Li plane and the phenyl ring plane was found to be ca. 11°), although these dimer units have additional interactions and stack to form an unsymmetrical tetramer.[8b] Only one dimer—[8-(dimethylamino)-1-naphthyllithium·Et_2O]$_2$ (**5**)—had a $Li_2(C_{ipso})_2$ arrangement approaching planarity (with ca. 11° twist angles).[7c,9]



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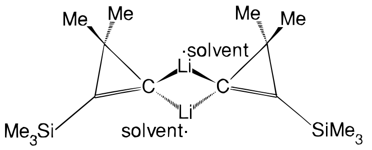

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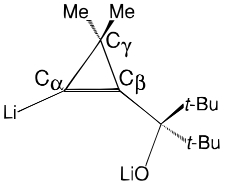

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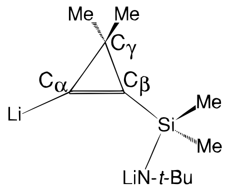

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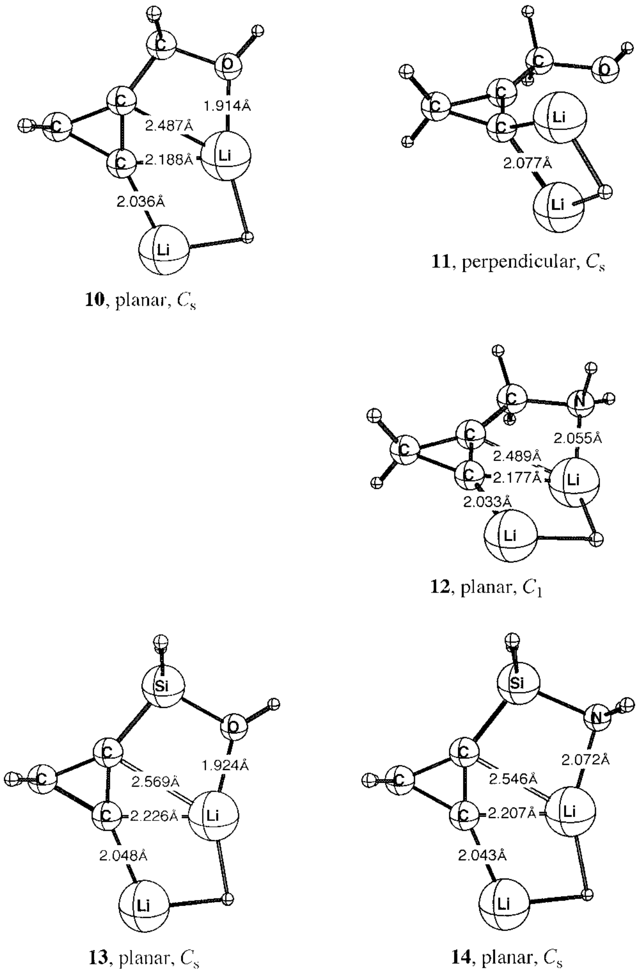
Unsolvated dimeric cyclopropenyllithium **6** was computed recently to prefer an “in plane” geometry with planar tetracoordinate $R^1R^2CLi_2$ carbons.[10,2b] However, as with the phenyllithium dimer **3**,[5,6] lithium solvation was shown to favor the “perpendicular” geometry in the X-ray structure of the dimeric TMEDA complex of [3,3-dimethyl-2-(trimethylsilyl)cyclopropenyl]lithium (**7**).[10] We now report the results of a deliberate attempt to realize planar tetracoordinate carbon arrangements in simple organolithium dimers. Based on the chelation strategy applied to phenyllithium dimers,[5] we computed cyclopropenyllithium model dimers with heteroatom substituents at the vinylic C_β atom. This pointed to suitable synthetic target molecules: lithium chelation by O^- (and N^-) moieties in the C_α and O dilithiated 1-(di-*tert*-butylhydroxymethyl)-3,3-dimethylcyclopropene (**8**) and in the C_α and N dilithiated 1-(*tert*-butylaminodimethylsilyl)-3,3-dimethylcyclopropene (**9**) resulted in nearly planar tetracoordinate carbon arrangements.

Results and Discussion

Computational Studies of Cyclopropenyllithium Model Dimers with Heteroatom Substituents. Cyclopropenes monosubstituted with the heteroatom (e.g., OR, NR_2) directly attached to the vinylic carbon of the three-membered ring were not considered to be promising since such molecules can be expected to have limited stability.[11] It would be better to employ CH_2X (X = OR, NR_2) substituents. These would form thermodynamically favorable five-membered chelate rings upon lithiation.[7b,12] Thus, the “in plane” dimer **6** should benefit from CH_2X (X = OR, NR_2) substituents at the vinylic C_β atom. Indeed, the planar structure of the [2-(hydroxymethyl)cyclopropenyl]lithium model dimer **10** is computed to be 14.2 kcal/mol more stable than the “perpendicular” isomer **11**. One cyclopropenyllithium monomer is substituted by LiH; the mixed dimer models the effect of a single heteroatom substituent (OH and NH_2 are computed in place of OR and NR_2, respectively). The optimized geometries of the planar and “perpendicular” model dimers are presented in Figure 1, the energies are listed in Table 1.



10, planar, C_s **11**, perpendicular, C_s **12**, planar, C_1 **13**, planar, C_s **14**, planar, C_s

Figure 1. Becke3LYP/6-31+G* optimized structures of heteroatom substituted cyclopropenyllithium model dimers.

Intramolecular solvation by the hydroxy group in the planar minimum **10** results in a Li−O contact (Li−O distance: 191.4 pm). In contrast, steric constraints in the “perpendicular” transition structure **11** preclude an effective electrostatic interaction between the Li^+ cation and the carbanion as well as the O atom of the CH_2OH substituent: the lithiums only are coordinated to the cyclopropenyl anion. The CH_2NH_2 substituent (NH_2 models NR_2) is more effective: the energy difference

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[8] (a) 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. (b) Harder, S.; Boersma, J.; Brandsma, L.; van Heteren A.; Kanters, J. A.; Bauer, W.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1988**, *110*, 7802.

[9] Neither this feature nor the twist angle was pointed out in the original report: see ref 7a.

[10] Sorger, K.; Schleyer, P. v. R.; Stalke, D. *J. Am. Chem. Soc.* **1996**, *118*, 1086.

[11] General introduction into the chemistry of cyclopropenes: (a) Halton, B.; Banwell, M. G. *The Chemistry of the Cyclopropyl Group*; Rappoport, Z., Ed.; Wiley: New York, 1987; Part 2, p 1223. (b) Baird, M. S. *Top. Curr. Chem.* **1988**, *144*, 137.

[12] For lithium chelation in heteroatom-facilitated lithiations, see e.g.: (a) Bauer, W; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1989**, *111*, 7191 and references therein. (b) Klumpp, G. W. *Rec. Trav. Chim. Pays-Bas* **1986**, *105*, 1. (c) Beak, P.; Meyers, A. I. *Acc. Chem. Res.* **1986**, *19*, 356.

Table 1. Total Energies (E_{tot}, hartrees), Zero-point Vibrational Energies (ZPE, kcal/mol) and Relative Energies (E_{rel}, kcal/mol) of Heteroatom Substituted Cyclopropenyllithium Model Dimers Computed at Becke3LYP/6-31+G*.

substituent	E_{tot}	ZPE[a]	E_{rel}[b]
CH_2OH			
planar, C_s, **10**	−246.260 52	55.0 (0)	0.0
perpendicular, C_s, **11**	−246.236 80	54.3 (1)	14.2
CH_2NH_2			
“planar”, C_1, **12**	−226.396 42	63.5 (0)	0.0
planar, C_s	−226.395 84	63.3 (1)	0.2
perpendicular, C_s	−226.367 83	62.1 (2)	16.5
SiH_2OH			
planar, C_s, **13**	−497.704 60	48.2 (0)	0.0
perpendicular, C_s	−497.679 57	47.1 (1)	14.7
SiH_2NH_2			
planar, C_s, **14**	−477.820 38	56.0 (0)	0.0
perpendicular, C_s	−477.794 77	54.6 (1)	14.6

[a] Number of imaginary frequencies given in parentheses. [b] Relative energies with ZPE correction.

between the planar structure (C_1) of the [2-(aminomethyl)-cyclopropenyl]lithium model dimer **12** and the “perpendicular” geometry is 16.5 kcal/mol (Figure 1, Table 1). Due to the eclipsed conformation of the CH_2NH_2 group, the planar C_s form is a transition structure only 0.2 kcal/mol above **12** and the “perpendicular” isomer a second order saddle point; the C_1-symmetric minimum has a slightly distorted planar $R^1R^2CLi_2$ arrangement. Computations find the SiH_2X substituent (X = OH, NH_2) to be similar effective in stabilizing the “in plane” geometry, due to the formation of LiO(N)SiCC five-membered chelate rings: the planar structure of the [2-(hydroxysilyl)-cyclopropenyl]lithium—LiH complex **13** is 14.7 kcal/mol lower in energy than the “perpendicular” form (Figure 1, Table 1); the planar arrangement of the [2-(aminosilyl)cyclopropenyl]-lithium model dimer **14** is favored by 14.6 kcal/mol (note that the planar C_s structure is a true minimum).

Interestingly, the planar geometries display weak Li−C interactions between the chelated lithiums and the vinylic C_β atoms (the Li−C_β contacts range from 248.7 pm in **10** to 256.9 pm in **13**). This implies lithium bridging of the cyclopropene double bond: the planar tetracoordinate arrangement at C_β results. These Li−C_β interactions are due to (1) formation of five-membered chelate rings and (2) distribution of the negative charge over the three carbon centers of the cyclopropenyl ring.[13] The calculated cyclopropene natural carbon charges[49] in **10** (C_α: −0.58, C_β: −0.20, C_γ: −0.50) indicate attractive electrostatic interactions between the chelated Li (natural charge: +0.80) and C_α as well as C_β. Since silicon stabilizes and thus localizes negative charge at an adjacent carbon center,[14] the vinylic C_β atoms in **13** and **14** are highly negatively charged (cyclopropene natural carbon charges in **13**: C_α: −0.51, C_β: −0.71, C_γ: −0.50; **14**: C_α: −0.52, C_β: −0.68, C_γ: −0.51). Consequently, the electrostatic Li−C_β interactions are even more important in the planar structures **13** and **14** (Li−C_β distances: **13**: 256.9 pm, **14**: 254.6 pm).

The “in plane” geometry of the cyclopropenyllithium dimer **6** is stabilized by heteroatom substituents at the vinylic C_β, due to the formation of favorable five-membered chelate rings. Heteroatom substitution even favors structures with Li bridged double bonds (planar tetracoordinate C_β, *vide infra*).

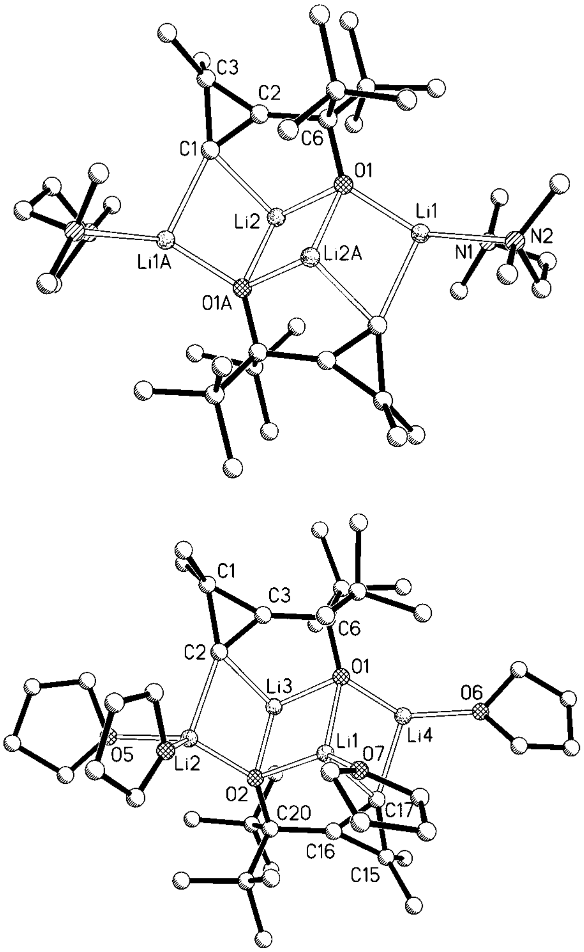
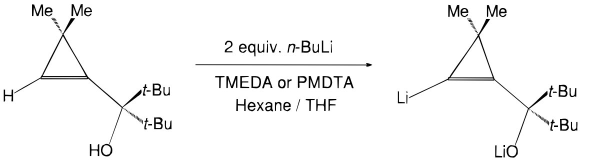


Figure 2. X-ray structures of (**8**·TMEDA)$_2$ (top) and (**8**·2THF)$_2$ (bottom). The hydrogen atoms have been omitted for clearity (labels with a letter identify atoms which are related by a center of inversion).

Syntheses and Structures of the TMEDA and THF Complexes of C_α and O Dilithiated 1-(Di-*tert*-butylhydroxymethyl)-3,3-dimethylcyclopropene, (8·TMEDA)$_2$ and (8·2THF)$_2$. The dilithium compound **8** was synthesized by metalation of 1-(di-*tert*-butylhydroxymethyl)-3,3-dimethylcyclopropene with 2 equiv of *n*-butyllithium in a hexane/THF mixture in the presence of 1 equiv of either TMEDA or PMDTA (eq 1). In the presence of the ligand TMEDA, compound **8** crystallizes as an amine complex, (**8**·TMEDA)$_2$; however, a crystalline THF solvate, (**8**·2THF)$_2$,[15] is formed in the presence of PMDTA.



(1)

Both (**8**·TMEDA)$_2$ and (**8**·2THF)$_2$ adopt self-assembled dimer structures in the solid state (depicted in Figure 2; bond distances and angles are given in Tables 2 and 3). The structure of (**8**·TMEDA)$_2$ consists of a crystallographically centrosymmetrical ladder-type arrangement of two monomeric units **8** with each peripheral lithium additionally solvated by a bidentate TMEDA ligand. In contrast, complex (**8**·2THF)$_2$, which displays a similar puckered ladder as the structural backbone, adopts an unsymmetrical dimeric structure: the lithium cations, differently solvated by THF, have distinct environments. The outer

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(13) Schleyer, P. v. R.; Kaufmann, E.; Spitznagel, G. W.; Janoschek, R.; Winkelhofer, G. *Organometallics* **1986**, *5*, 79.

(14) (a) Schleyer, P. v. R.; Clark, T.; Kos, A. J.; Spitznagel, G. W.; Rohde, C.; Arad, D.; Houk, K. N.; Rondan, N. G. *J. Am. Chem. Soc.* **1984**, *106*, 6467 and references therein. (b) Brinkman, E. A.; Berger, S.; Brauman, J. I. *J. Am. Chem. Soc.* **1994**, *116*, 8404.

(15) Preliminary communication: Sorger, K.; Schleyer, P. v. R.; Stalke, D. *J. Chem. Soc, Chem. Commun.* **1995**, 2279.

Table 2. Selected Bond Distances (pm) and Angles (deg) of (**8**·TMEDA)$_2$

C(1)−C(2)	132.3(2)	C(1)−C(3)	156.8(2)
C(2)−C(3)	147.9(2)	C(3)−C(4)	151.8(2)
C(3)−C(5)	151.9(2)	C(2)−C(6)	152.8(2)
C(6)−O(1)	141.8(2)	C(1)−Li(1A)	217.3(3)
C(1)−Li(2)	210.0(3)	C(2)−Li(2)	233.7(3)
O(1)−Li(1)	193.8(3)	O(1)−Li(2)	193.0(3)
O(1)−Li(2A)	189.1(2)	N(1)−Li(1)	241.5(3)
N(2)−Li(1)	221.7(3)		
C(1)C(2)C(3)	67.80(10)	C(2)C(1)C(3)	60.83(9)
C(1)C(3)C(2)	51.37(8)	C(1)C(2)C(6)	140.22(11)
C(2)C(6)O(1)	107.19(10)	C(6)O(1)Li(1)	135.59(10)
C(6)O(1)Li(2)	101.19(10)	C(6)O(1)Li(2A)	131.74(10)
C(1A)Li(1)O(1)	95.84(10)	C(1)Li(2)O(1)	96.92(11)
C(1)Li(2)O(1A)	99.82(11)	O(1)Li(2)O(1A)	107.95(11)
Li(1A)C(1)Li(2)	74.18(10)	Li(1)O(1)Li(2A)	84.60(11)
Li(2)O(1)Li(2A)	72.05(11)	N(1)Li(1)N(2)	79.61(9)

Table 3. Selected Bond Distances (pm) and Angles (deg) of (**8**·2THF)$_2$

C(1)−C(2)	158.2(8)	C(1)−C(3)	148.5(7)
C(2)−C(3)	134.4(8)	C(3)−C(6)	152.7(7)
C(6)−O(1)	141.5(7)	C(15)−C(16)	147.0(7)
C(15)−C(17)	153.6(8)	C(16)−C(17)	131.5(7)
C(16)−C(20)	153.8(7)	C(20)−O(2)	141.0(6)
C(2)−Li(2)	215.5(10)	C(2)−Li(3)	209.0(9)
C(3)−Li(3)	237.1(10)	C(17)−Li(1)	218.1(9)
C(17)−Li(4)	209.6(10)	C(16)−Li(1)	250.6(10)
Li(1)−O(1)	207.2(9)	Li(1)−O(2)	203.0(8)
Li(1)−O(7)	198.6(8)	Li(2)−O(2)	193.9(8)
Li(2)−O(5)	205.1(9)	Li(2)−O(8)	208.4(9)
Li(3)−O(1)	189.2(9)	Li(3)−O(2)	187.4(9)
Li(4)−O(1)	183.0(9)	Li(4)−O(6)	194.9(8)
C(1)C(2)C(3)	60.4(4)	C(1)C(3)C(2)	67.8(4)
C(2)C(1)C(3)	51.9(3)	C(2)C(3)C(6)	138.0(5)
C(3)C(6)O(1)	106.4(4)	C(15)C(16)C(17)	66.7(4)
C(15)C(17)C(16)	61.5(4)	C(16)C(15)C(17)	51.8(3)
C(17)C(16)C(20)	139.6(5)	C(16)C(20)O(2)	106.3(4)
Li(2)C(2)Li(3)	73.2(4)	Li(1)C(17)Li(4)	73.1(4)
Li(2)O(2)Li(3)	83.1(4)	Li(1)O(1)Li(4)	81.3(4)
Li(1)O(1)Li(3)	72.5(3)	Li(1)O(2)Li(3)	73.8(4)
C(2)Li(3)O(1)	95.9(4)	C(17)Li(1)O(2)	90.1(4)
C(2)Li(2)O(2)	98.3(4)	C(17)Li(4)O(1)	102.5(4)
C(2)Li(3)O(2)	102.7(4)	C(17)Li(1)O(1)	92.3(3)
O(1)Li(3)O(2)	113.2(4)	O(1)Li(1)O(2)	100.1(3)
O(5)Li(2)O(8)	97.4(3)	O(1)Li(4)O(6)	146.1(6)
C(17)Li(4)O(6)	111.0(5)		

lithiums both in (**8**·TMEDA)$_2$ and (**8**·2THF)$_2$ bridge between the carbanion and the oxygen anion of the two monomeric units. The inner lithiums are chelated by a C/O dianion; additional Li−O contacts to the second unit result in four-runged puckered ladders with central LiOLiO rings. Two five-membered LiOCCC chelate rings edge share both a Li−O and a Li−C bond of the ladder core each.

In (**8**·TMEDA)$_2$, the inner lithiums Li2 and Li2A are three-coordinate (trigonal pyramidal). The outer Li1 and Li1A are distorted "tetrahedrally". Both the long Li−N(TMEDA) bonds (Li1−N1: 221.7(3), Li1−N2: 241.5(3) pm) and the bending of the TMEDA ligands towards the adjacent cyclopropenyl moiety reflect the steric requirements of the *tert*-butyl as well as the TMEDA methyl groups. For the tetracoordinate Li1 and Li1A, the increased coordination number at the metals leads to longer C−Li bonds relative to the trigonal, inner Li2 and Li2A (217.3(3) versus 210.0(3) pm; *cf.* the 220.5(3)−221.9(3) pm values found in the dimeric TMEDA complex of [3,3-dimethyl-2-(trimethylsilyl)cyclopropenyl]lithium).[10] The Li−O distances range between 189.1(2) and 193.8(3) pm, values typical of lithium alkoxides[16] and enolates[16,17] in which three cations, respectively, are μ_3 bridged by the oxygen anions.

The Li−C distances in (**8**·2THF)$_2$ vary from 209.0(9) to 218.1(9) pm, the Li−O bond lengths even from 183.0(9) to 207.2(9) pm. This wide range of bond lengths is related to the selective THF solvation of the cations (and consequently the different cation coordination numbers). This gives rise to four nonequivalent lithium environments: both the Li2 and the Li3 coordination sphere in (**8**·2THF)$_2$ is similar to the TMEDA complex, (**8**·TMEDA)$_2$—the inner Li3 is trigonal pyramidal and the outer Li2, additionally solvated by two THF ligands, is tetrahedral; in contrast, the inner Li1 is approximately tetrahedral and Li4 is trigonal planar. The two cations coordinate to one THF molecule each.

Remarkably, the lithiated tetracoordinate R^{1}R^{2}CLi$_2$ cyclopropenyl carbons in (**8**·TMEDA)$_2$ and (**8**·2THF)$_2$ deviate fundamentally from the perpendicular ("tetrahedral") arrangement (Figure 2): in (**8**·TMEDA)$_2$, the twist angle between orthogonals of the Li1A−C1−Li2 plane and the C1−C2−C3 cyclopropenyl ring plane is 36.3°; the corresponding values in (**8**·2THF)$_2$ are 34.6° and 38.8°.[15,18] In contrast, the two lithium cations in {[3,3-dimethyl-2-(trimethylsilyl)cyclopropenyl]lithium·TMEDA}$_2$[10] and (phenyllithium·TMEDA)$_2$[6] are in the normal, perpendicular orientation (twist angles of ca. 90°). Shown by the computations of cyclopropenyllithium model dimers (*vide supra*), the chelation strategy in (**8**·TMEDA)$_2$ and (**8**·2THF)$_2$ resulted in R^{1}R^{2}CLi$_2$ carbon environments with a high degree of planarization. Even closer approaches to planar R^{1}R^{2}CLi$_2$ arrangements have only been found before in two aryl derivatives, [8-(dimethylamino)-1-naphthyllithium·Et$_2$O]$_2$[7a,c] (**5**) and in the dimer units **4** in the X-ray structure of [(2,6-dimethoxyphenyl)lithium]$_4$.[8b]

The distance between the chelated Li2 and the vinylic C$_\beta$ (C2) in (**8**·TMEDA)$_2$ (as well as Li2A−C2A in the dimer) is quite short (233.7(3) pm), due to the formation of five-membered chelate rings and the distribution of the negative charge over the three carbon centers of the cyclopropenyl ring (this was pointed out above, see structure **10**). Similar short Li−C$_\beta$ distances are found in the X-ray structures of (*n*-butyllithium)$_6$,[19] (*tert*-butyllithium)$_4$,[19] (isopropyllithium)$_6$,[20] (cyclohexyllithium)$_6$,[21] [(tetramethylcyclopropyl)methyllithium]$_6$,[22] and in the (*n*-BuLi·LiO-*t*-Bu)$_4$ complex.[23] The Li−C$_\beta$ distance in the C_i-symmetric structure of dimeric dilithiated 1-(hydroxymethyl)cyclopropene, computed at Becke3LYP/6-31G*, is 231.5 pm (the optimized structure is shown in Figure 3; note the good agreement between the calculated unsolvated model and the experimental structures): the 0.014 NLMO Li−C$_\beta$ bond order (Li−C$_\alpha$: 0.061; the small values are due to the highly ionic character of the C−Li bond) indicates attractive electrostatic interactions between Li and the negatively charged vinylic C$_\beta$ (natural charges: C$_\alpha$: −0.63, C$_\beta$: −0.17). Including Li2(Li2A) the vinylic C$_\beta$ atom C2(C2A) in (**8**·TMEDA)$_2$ is

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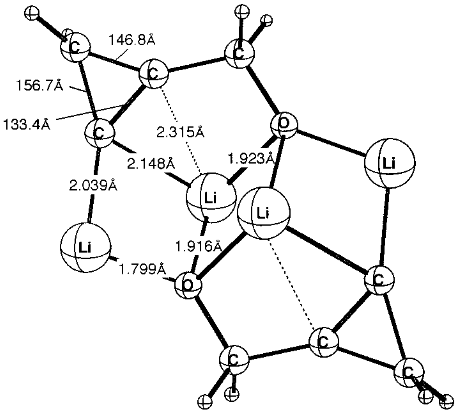


Figure 3. Becke3LYP/6-31G* optimized structure of dimeric dilithiated 1-(hydroxymethyl)cyclopropene (an energy minimum at HF/6-31G*).

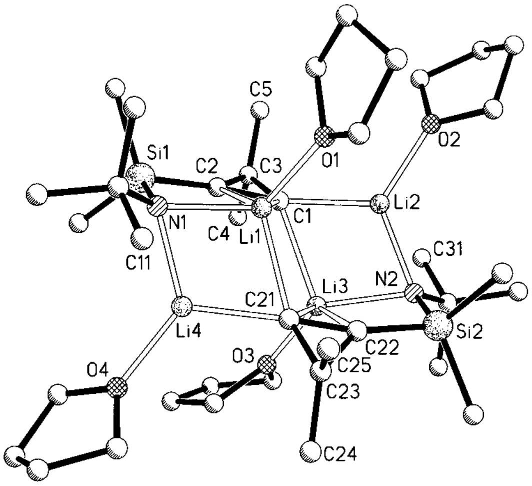


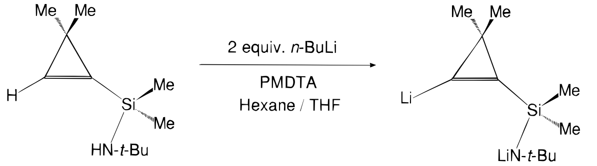
Figure 4. X-ray structure of ($\mathbf{9}$·2THF)$_2$. The hydrogen atoms are omitted for clearity.

tetracoordinate, but not planar (Figure 2): whereas C1, C2, C3, and C6 are coplanar (mean deviation from the best plane: 0.17 Å), the angle between the C1−Li2 vector and the C1−C2−C3−C6 plane is 29.9°. In ($\mathbf{8}$·2THF)$_2$, the Li−C$_\beta$ distance between Li3 and C3 has a similar value of 237.1(10) pm; however, Li1−C16 is much longer (250.6(10) pm), due to the additional coordination of THF.

The central $Li_4C_2O_2$ framework merits attention both in ($\mathbf{8}$·TMEDA)$_2$ and in ($\mathbf{8}$·2THF)$_2$ (Figure 2): two monomeric units combining organolithium and lithium alkoxide moieties dimerize along the Li−O bond to form a ladder-type or stair-shaped structure. A four-runged ladder core (with two Li−O bonds and two Li−N bonds) has recently been found in the structure of the complex between lithium diisopropylamide and a lithium alkoxide (the structure of a lithium diisopropylamide—lithium ketone enolate complex also consists of a ladder framework[24]).[25] Structural motifs typified by ($\mathbf{8}$·TMEDA)$_2$ and ($\mathbf{8}$·2THF)$_2$ also are well-known in the chemistry of lithium amides[16,26,27] and phosphides[16,27b,28] (the structure of a dilithium disiloxanediolate species adopts a similar puckered ladder[29]). The structures of ($\mathbf{8}$·TMEDA)$_2$ and ($\mathbf{8}$·2THF)$_2$ are unprecedented in that an organolithium moiety is incorporated in a ladder framework.[2b,30] TMEDA complexation in ($\mathbf{8}$·TMEDA)$_2$ occurs at the outer lithiums which is common with ladders having four Li−N rungs.[27c,d,31] In ($\mathbf{8}$·2THF)$_2$, however, the inner Li1 is solvated by THF; heteroatom solvation of a central lithium in a four-runged ladder has also been observed in the structures of a dilithium disiloxanediolate species[29] and a lithium amide—lithium alkoxide complex.[25]

For NMR studies, crystals of ($\mathbf{8}$·TMEDA)$_2$ and ($\mathbf{8}$·2THF)$_2$ were dissolved in THF-d_8 (the compounds are soluble only to a modest extent; the 1:1 stoichiometry of $\mathbf{8}$:TMEDA was confirmed by integration of the ^{1}H NMR signals[54]). At +30 °C, both the ^{1}H and the ^{13}C NMR spectra show no evidence for the presence of more than a single dilithium species. The spectra of the ($\mathbf{8}$·TMEDA)$_2$ and ($\mathbf{8}$·2THF)$_2$ solutions are identical indicating that the TMEDA ligands are not coordinated to the lithiums in THF solution. This has also been observed for TMEDA-containing THF solutions of *tert*-butyllithium,[32] 2,4,6-tri-*tert*-butylphenyllithium,[32] and (2-lithiophenyl)-*tert*-butylthioether.[33] The ^{7}Li spectrum of $\mathbf{8}$ displays only one resonance at +30 °C (δ = 0.99), due to rapid scrambling of the lithiums. In contrast to the unsymmetrical solid-state structure of ($\mathbf{8}$·2THF)$_2$, the NMR data indicate a time averaged symmetrical structure of $\mathbf{8}$ in THF solution.[34]

Synthesis and Structure of the THF Complex of C$_\alpha$ and N Dilithiated 1-(*tert*-Butylaminodimethylsilyl)-3,3-dimethylcyclopropene, ($\mathbf{9}$·2THF)$_2$. The dilithium compound $\mathbf{9}$ was synthesized by metalation of 1-(*tert*-butylaminodimethylsilyl)-3,3-dimethylcyclopropene with 2 equiv of *n*-butyllithium in a hexane/THF mixture in the presence of 1 equiv of PMDTA (eq 2) and crystallizes as a THF complex, ($\mathbf{9}$·2THF)$_2$.



(2)

The structure of ($\mathbf{9}$·2THF)$_2$ adopts a self-assembled unsymmetric dimer in the solid state which, similar to ($\mathbf{8}$·TMEDA)$_2$ and ($\mathbf{8}$·2THF)$_2$, consists of a ladder-type arrangement of two monomeric units $\mathbf{9}$ (the structure is illustrated in Figure 4; bond distances and angles are given in Table 4). Every cation is

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[34] The low solubility particularly at low temperatures has precluded aggregation studies.

Table 4. Selected Bond Distances (pm) and Angles (deg) of (**9**·2THF)$_2$

C(1)−C(2)	134.3(3)	C(1)−C(3)	155.8(3)
C(2)−C(3)	148.3(3)	C(2)−Si(1)	185.8(3)
Si(1)−N(1)	169.0(2)	N(1)−C(8)	147.3(3)
C(21)−C(22)	133.8(3)	C(21)−C(23)	155.7(3)
C(22)−C(23)	148.1(3)	C(22)−Si(2)	186.1(2)
Si(2)−N(2)	168.7(2)	N(2)−C(28)	147.4(3)
C(1)−Li(1)	220.5(4)	C(1)−Li(2)	212.4(5)
C(1)−Li(3)	235.9(5)	C(2)−Li(1)	238.1(4)
C(21)−Li(1)	227.3(4)	C(21)−Li(3)	229.8(4)
C(21)−Li(4)	210.3(5)	C(22)−Li(3)	240.0(4)
N(1)−Li(1)	207.2(4)	N(1)−Li(4)	199.4(4)
N(2)−Li(2)	199.2(4)	N(2)−Li(3)	207.0(4)
Li(1)−O(1)	198.6(4)	Li(2)−O(2)	198.3(4)
Li(3)−O(3)	197.0(4)	Li(4)−O(4)	199.7(4)
C(1)C(2)C(3)	66.7(2)	C(1)C(3)C(2)	52.4(2)
C(2)C(1)C(3)	60.9(2)	C(1)C(2)Si(1)	147.3(2)
C(2)Si(1)N(1)	103.94(10)	Si(1)N(1)C(8)	126.0(2)
C(21)C(22)C(23)	66.8(2)	C(21)C(23)C(22)	52.2(2)
C(22)C(21)C(23)	61.0(2)	C(21)C(22)Si(2)	149.3(2)
C(22)Si(2)N(2)	104.24(10)	Si(2)N(2)C(28)	124.4(2)
Li(1)C(1)C(2)	80.3(2)	Li(3)C(22)C(21)	69.3(2)
Li(1)N(1)Li(4)	76.2(2)	Li(2)N(2)Li(3)	76.5(2)
Li(1)C(21)Li(4)	69.8(2)	Li(2)C(1)Li(3)	68.0(2)
Li(1)C(1)Li(3)	78.7(2)	Li(1)C(21)Li(3)	78.6(2)
N(1)Li(1)C(21)	101.7(2)	N(2)Li(3)C(1)	101.3(2)
N(1)Li(4)C(21)	110.8(2)	N(2)Li(2)C(1)	112.8(2)
C(1)Li(1)C(21)	103.9(2)	C(1)Li(3)C(21)	98.4(2)

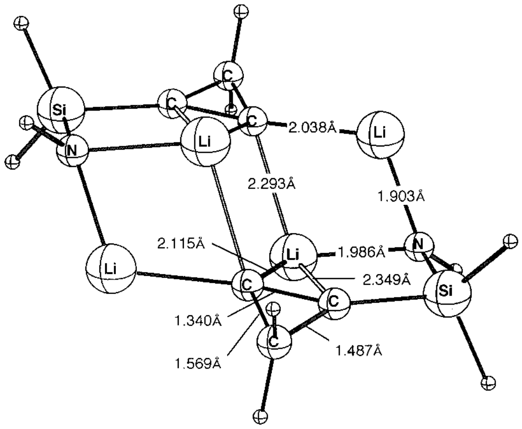

Figure 5. Becke3LYP/6-31G* optimized structure of dimeric dilithiated 1-(aminosilyl)cyclopropene (an energy minimum at HF/6-31G*).

solvated by THF. The outer lithiums bridge between the carbanion and the nitrogen anion of the two monomeric units and each lithium has an additional weak contact to the methyl carbon atom of the *tert*-butyl group (Li2−C31: 275.8(5), Li4−C11: 268.6(5) pm; similar Li−C_{methyl} contacts often are found in lithium amides with bulky alkyl or silyl groups[35]). The inner cations are chelated by a C/N dianion and have additional contacts to the carbanion of the second unit. This results in a puckered, four-runged ladder with two fused LiNSiCC five-membered chelate rings. The C−Li bond lengths within the ladder core widely range between 210.3(5) and 235.9(5) pm; *cf.* 220.5(3)−221.9(3) pm in {[3,3-dimethyl-2-(trimethylsilyl)cyclopropenyl]lithium·TMEDA}$_2$[10] and ca. 210−221 pm in (**8**·TMEDA)$_2$ and (**8**·2THF)$_2$. The Li−N distances to the outer lithium cations are shorter (Li2−N2: 199.2(4), Li4−N1:199.4(4) pm) than to the inner cations with the higher coordination numbers (Li1−N1: 207.2(4), Li3−N2: 207.0(4) pm). This is typically observed in lithium amides with cations in different coordination spheres.[16,26,27]

The stair-shaped four-runged ladder $Li_4C_2N_2$ core of (**9**·2THF)$_2$ is intriguing: whereas ladder structures are well-known in the chemistry of lithium amides[16,26,27,31] (for compounds exhibiting similar puckered ladder structures, see above), the combination of organolithium and lithium amide moieties to form a puckered ladder is unique.[2b,30] Both the outer and the inner Li cations are solvated by one THF ligand each. In contrast, only the outer cations are complexed in ladders having four Li−N rungs, due to steric factors.[27c,d,31]

Interestingly, the C−Li bonds between the two monomer units—the two C−Li rungs of the $Li_4C_2N_2$ ladder (Figure 4)—are on average significantly longer than the two C_α−Li bonds within a monomer unit—the C−Li edges of the ladder (rungs: 231.6(5), central edges: 225.2(4), outer edges: 211.4(5) pm; average values). This indicates weak electrostatic Li−C interactions between the two monomers: the dimer is held together mainly by strong Li−N interactions (the Li−N rungs are shorter than the Li−N edges, mean: 199.3(4) versus 207.1(4) pm). Considering the two C_α−Li bonds within each monomer unit in (**9**·2THF)$_2$, the lithium substituents Li1 and Li2 at C1 in the one monomer unit approach a planar $R^1R^2CLi_2$ arrangement closely, due to the lithium chelation: the twist angle between the Li1−C1−Li2 plane and the cyclopropenyl ring plane (C1−C2−C3) is only 17.4°; in the second monomer unit, the Li3−C21−Li4 plane is twisted by 29.7° with respect to the C21−C22−C23 plane (*cf.* the 34.6−38.8° twist angles in (**8**·TMEDA)$_2$ and (**8**·2THF)$_2$ and the ca. 11° twist angles in [8-(dimethylamino)-1-naphthyllithium·Et_2O]$_2$[7a,c] (**5**) and in the dimer units **4** in [(2,6-dimethoxyphenyl)lithium]$_4$[8b]). Although weak, additional Li−C interactions between the two monomer units result in pentacoordinate lithiated carbons in (**9**·2THF$_2$)$_2$. The C_i-symmetric structure of dimeric dilithiated 1-(aminosilyl)cyclopropene, computed as an unsolvated model at the Becke3LYP/6-31G* level, also displays weak Li−C interactions between the two monomeric units (the optimized structure is shown in Figure 5). The C−Li bonds between the two monomers are longer (229.3 pm) than the C_α−Li bonds within a monomer (211.5 and 203.8 pm). The $R^1R^2CLi_2$ arrangement in each unit—involving the two shorter C_α−Li bonds—is nearly planar. The C−Li bonding and the lithiated carbon environments in (**9**·2THF)$_2$ both resemble tetrameric (2,6-dimethoxyphenyl)lithium,[8b] which is comprised of two interacting dimer units **4**. The Li−C distances between the two dimer units **4** are somewhat longer than within the dimers; the $R^1R^2CLi_2$ *ipso* carbon environments in each dimer are nearly planar, although additional Li−C interactions between the dimers result in pentacoordinate *ipso* carbons.

A remarkable structural feature in (**9**·2THF)$_2$, the bridging of the vinylic C=C bonds by the inner lithium cations (Figure 4), is shown by the short contacts between the inner lithium cations and the vinylic C_β atoms (Li1−C2: 238.1(4), Li3−C22: 240.0(4) pm; these compare to the longer 231.6(5) pm (mean) Li−C_α distances; *cf.* the ca. 230−240 pm Li−C_β distances in *n*-BuLi,[19] *t*-BuLi,[19] *i*-PrLi,[20] *c*-$C_6H_{11}Li$,[21] (*c*-CHCMe$_2$CMe$_2$)CH$_2$Li,[22] and in the (*n*-BuLi·LiO-*t*-Bu)$_4$ complex[23]) and by the small Li−C_α−C_β angles (Li1−C1−C2: 80.3(2)°, Li3−C21−C22: 77.7(2)°). The Li1−C16 distance in (**8**·2THF)$_2$ is much longer (250.6(10) pm) and the Li1−C17−C16 angle much wider (87.9(4)°, Figure 2). The environment of Li1 with its additional THF ligand may be compared with that of the inner Li^+ cations in (**9**·2THF)$_2$. The bridging of the C=C bonds in (**9**·2THF)$_2$ is due to the formation of five-membered chelate rings (*cf.* structure **14**) and to the localization of negative charge at the vinylic C_β by the silicon substituent. The natural cyclopropene carbon charges in the computed dimer

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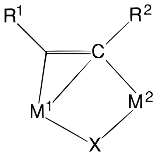
Table 5. Ring Distortion—Bond Lengths (pm) and Angles (deg)—of Lithiated Cyclopropenes[a]

compound	C(α)−C(*β*)	C(α)−C(*γ*)	C(*β*)−C(*γ*)	C(*β*)C(α)C(*γ*)	C(α)C(*β*)C(*γ*)	structural data
cyclopropene	129.1	151.1	151.1	64.71	64.71	Becke3LYP/6-311+G**[b]
	129−130	151−152	151−152			gas-phase (cyclopropene and derivatives)[b]
	129.2	152.3	152.3	64.9	64.9	X-ray (mean of 11 structures)[b]
(1-cyclopropenyl)lithium	130.8	161.3	147.2	59.46	70.62	Becke3LYP/6-311+G**[b]
[3,3-dimethyl-2-(trimethylsilyl)cyclopropenyl]lithium	133.1(2)	156.0(2)	148.7(2)	61.30(11)	66.96(12)	X-ray (mean values in the dimeric TMEDA complex)[b]
8	132.3(2)	156.8(2)	147.9(2)	60.83(9)	67.80(10)	X-ray (mean values in (**8**·TMEDA)$_2$)
8	133.0(8)	155.9(8)	147.8(7)	61.0(4)	67.3(4)	X-ray (mean values in (**8**·2THF)$_2$)
9	134.1(3)	155.8(3)	148.2(3)	60.9(2)	66.7(2)	X-ray (mean values in (**9**·2THF)$_2$)

[a] The lithiated carbon is C(α). [b] See ref 10.

(Figure 5) document the unexpectedly large negative C_β charge (C_α: −0.71, C_β: −0.54, C_γ: −0.50). The vinylic tetracoordinate C2 in (**9**·2THF)$_2$ is nearly planar (Figure 4): the twist angle between the Si1−C2−Li1 plane and the C1−C2−C3 ring plane is only 11.1° (the twist angle between the Si2−C22−Li3 plane and the cyclopropenyl ring plane is 27.2°).



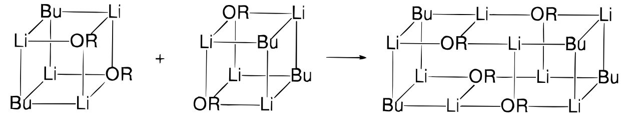
15

A planar tetracoordinate carbon also comprises part of a double bond in the bimetallic compounds **15**: within a five-membered M^1XM^2CC ring (M^1 = Cp_2Zr/Hf, M^2 = B/Al/GaR_2, X = H, Cl, Me, alkynyl), the transition metal bridges the C=C bond which results in a planar tetracoordinate carbon environment.[36] Similarly, a zirconium center in two cationic bis(zirconocene) complexes **15** (M^1, M^2 = Cp_2Zr, X = alkynyl) is bridged by a C=C bond.[37]

Both the ^{1}H and ^{13}C NMR spectra of **9** (crystals of (**9**·2THF)$_2$ were dissolved in THF-d_8; the compound is soluble only to a modest extent)[54] give no indications of more than a single dilithium species, at +30 °C. The ^{7}Li spectrum displays only one resonance (δ = 1.19), due to rapid scrambling of the lithiums. These data are consistent with a time averaged symmetrical structure in solution,[34] in contrast to the different Li environments observed in the crystal.

Distortion of the Cyclopropenyl Geometry in (8·TMEDA)$_2$, (8·2THF)$_2$ and (9·2THF)$_2$. Lithiation at the vinylic carbon both of 1-(di-*tert*-butylhydroxymethyl)-3,3-dimethylcyclopropene and 1-(*tert*-butylaminodimethylsilyl)-3,3-dimethylcyclopropene results in significant changes in the cyclopropene C−C bond lengths and endocyclic angles (the cyclopropenyl ring distortions observed in four X-ray structures of cyclopropenyllithium derivatives are summarized in Table 5): due to the rehybridization, the C=C and the C(α)−C(γ) bonds (vicinal bonds) in **8** and **9** are lengthened, and the C(β)−C(γ) (distal) bonds are shortened by several pm relative to the distances in cyclopropene.[10] Similar ring distortions, first predicted computationally,[13] also are found in the X-ray structure of {[3,3-dimethyl-2-(trimethylsilyl)cyclopropenyl]lithium·TMEDA}$_2$.[10]

Scheme 1



Theoretical Investigations Probing Ring vs Ladder vs Stack Structural Preferences of MeLi/LiOH and MeLi/LiNH$_2$ Mixed-Anion Aggregates. The (**8**·TMEDA)$_2$, (**8**·2THF)$_2$, and (**9**·2THF)$_2$ structures resemble one another. The three compounds display puckered ladder frameworks with fused five-membered chelate rings. In marked contrast to (**8**·TMEDA)$_2$ and (**8**·2THF)$_2$ which dimerize via the Li−O bonds, the (**9**·2THF)$_2$ dimer is formed by Li−C bond association but does not involve the Li−N bond. The structures of (**8**·TMEDA)$_2$, (**8**·2THF)$_2$, and (**9**·2THF)$_2$ show how an organolithium compound and a lithium alkoxide/amide can aggregate. Computations at the Becke3LYP/6-31G* level on unsolvated mixed-anion aggregates, i.e., (MeLi·LiOH)$_2$ and (MeLi·LiNH$_2$)$_2$, and PM3 calculations on the THF-solvated complexes of (MeLi·LiOMe)$_2$ and (MeLi·LiNMe$_2$)$_2$ were performed to probe the structural preferences of such aggregates further.

Three energy minima were calculated for (MeLi·LiOH)$_2$: a cubane-like structure (**16a**, X = OH, C_{2v}, a stack of MeLi and LiOH dimers), a C_i-symmetric ladder (**17a**) formed by lateral association of two (MeLi·LiOH) rings via the Li−O bond, and a planar eight-membered ring (**18a**, X = OH, C_{2h}). The structures of the aggregates are represented schematically in Figure 6; the energies of the optimized species are given in Table 6. The cube is favored over the ladder by 9.6 kcal/mol and over the ring arrangement by 12.9 kcal/mol. This stability order can readily be explained in terms of electrostatic interactions: due to the highly ionic character of the Li−O and the Li−C bonds,[2b] the maximum number of electrostatic Li−O and Li−C attractions are present in the cubane structure (tetrahedral arrangements are also preferred for the tetramers of MeLi[38] and LiOH[39]).[39] The ladder structure with a central LiOLiO ring has two more Li−O contacts compared with the planar eight-membered ring. The nonplanar structure of the ladder is due to orientation effects of the O lone pairs.[39] Since the Li cation prefers to interact with the small, highly electronegative oxygen anion, formation of the maximum number of Li−O contacts (six Li−O versus four Li−C interactions) results in the association of the two (MeLi·LiOH) rings along the Li−O bond to form a puckered ladder with a central LiOLiO ring; Li−C interactions are less important. Note that both (**8**·TMEDA)$_2$ and (**8**·2THF)$_2$ dimerize along the Li−O bond; the structural core of TMEDA-solvated trilithiated 2,5-dimethylphenol also is dictated by Li−O interactions.[40] Interestingly, Li−O interac-

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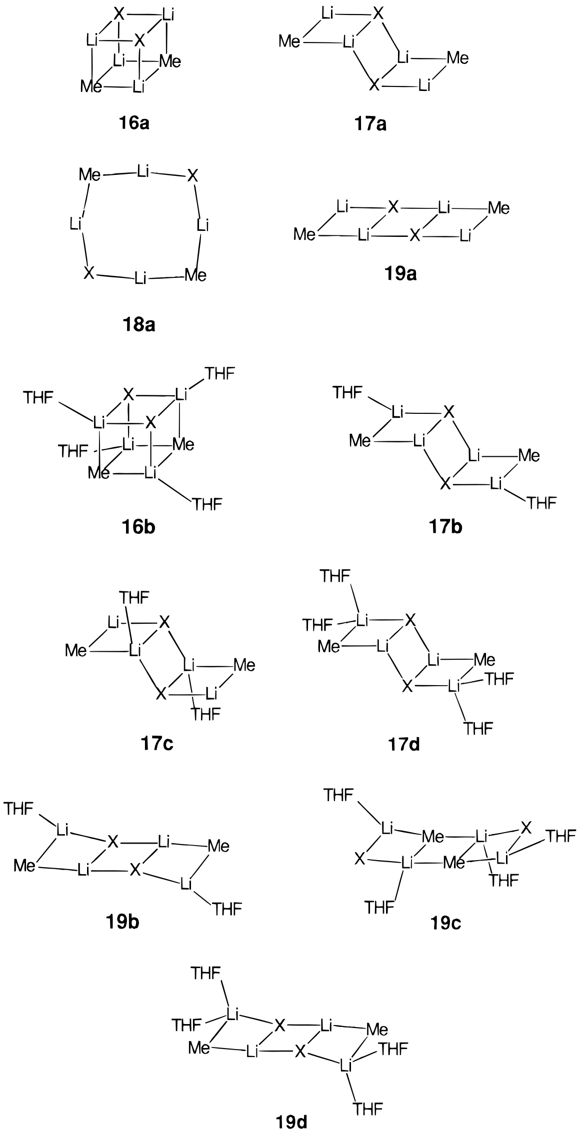

Figure 6. Schematic illustration of the Becke3LYP/6-31G* optimized structures (energy minima at HF/6-31G*) of unsolvated $(MeLi{\cdot}LiOH)_2$ and $(MeLi{\cdot}LiNH_2)_2$ mixed-anion aggregates (top, label *a* denotes the unsolvated species), as well as the PM3 optimized THF-solvated $(MeLi{\cdot}LiOMe)_2$ and $(MeLi{\cdot}LiNMe_2)_2$ aggregates (bottom).

Table 6. Total Energies (E_{tot}, hartrees), Zero-Point Vibrational Energies (ZPE, kcal/mol)[a] and Relative Energies (E_{rel}, kcal/mol) of Unsolvated Mixed-Anion Aggregates Computed at Becke3LYP/6-31G*

	point group	E_{tot}	ZPE[a]	E_{rel}[b]
		$(MeLi{\cdot}LiOH)_2$		
16a	C_{2v}	−261.810 29	61.6 (0)	0.0
17a	C_i	−261.793 86	60.9 (0)	9.6
18a	C_{2h}	−261.786 71	59.7 (0)	12.9
		$(MeLi{\cdot}LiNH_2)_2$		
18a	C_{2h}	−221.988 28	74.3 (0)	0.0
16a	C_{2v}	−221.988 28	74.9 (0)	0.6
19a	C_{2h}	−221.986 75	74.7 (0)	1.4

[a] Calculated at HF/6-31G* and scaled by 0.91. Number of imaginary frequencies given in parentheses. [b] Relative energies with ZPE correction.

Table 7. PM3 Heats of Formation (ΔH_f, kcal/mol) and Relative Energies (E_{rel}, kcal/mol) of Unsolvated and THF-Solvated Mixed-Anion Aggregates (Energy Minima)

	point group	ΔH_f	E_{rel}
	$(MeLi{\cdot}LiOMe)_2$		
cube, **16a**	C_{2v}	−168.2	0.0
planar ring, **18a**	C_{2h}	−164.7	3.5
puckered ladder, **17a**	C_i	−163.9	4.3
	$(MeLi{\cdot}LiOMe)_2{\cdot}2THF$		
17b	C_i	−274.4	0.0
17c	C_i	−251.3	23.1
	$(MeLi{\cdot}LiOMe)_2{\cdot}4THF$		
16b	C_2	−367.9	0.0
17d	C_i	−367.0	0.9
	$(MeLi{\cdot}LiNMe_2)_2$		
cube, **16a**	C_s	−55.7	0.0
planar ring, **18a**	C_{2h}	−54.2	1.5
planar ladder, **19a**	C_{2h}	−53.1	2.6
	$(MeLi{\cdot}LiNMe_2)_2{\cdot}2THF$		
19b	C_i	−164.5	
	$(MeLi{\cdot}LiNMe_2)_2{\cdot}4THF$		
19c	C_2	−263.6	0.0
19d	C_i	−261.3	2.3

tions also dominate the structure of the unsolvated $(n\text{-BuLi}{\cdot}\text{LiO-}t\text{-Bu})_4$ complex.[23] This may be described as a tetrameric stack: two $(n\text{-BuLi}{\cdot}\text{LiO-}t\text{-Bu})_2$ cubane units (the lowest energy $(MeLi{\cdot}LiOH)_2$ minimum **16a**) associate via Li−O interactions to form an aggregate with a partially opened Li_4O_4 cubic core (Scheme 1). Stacking of small $(RLi)_2$ subunits to form $[(RLi)_2]_n$ oligomers is a commonly observed structural principle in organolithium chemistry.[30,41] Both the bulky *tert*-butyl groups and the cosolvent present in the crystal in $(\mathbf{8}{\cdot}TMEDA)_2$ and $(\mathbf{8}{\cdot}2THF)_2$ preclude further aggregation.

Three different $(MeLi{\cdot}LiNH_2)_2$ structures were considered (Figure 6, Table 6): a cubic structure (**16a**, X = NH_2, C_{2v}), a planar ladder with a central LiNLiN ring (**19a**, C_{2h}), and an eight-membered planar ring (**18a**, X = NH_2, C_{2h}). In contrast to $(MeLi{\cdot}LiOH)_2$, the three energy minima are nearly equal in energy with the ring slightly favored over the cube (by 0.6 kcal/mol) and over the ladder (by 1.4 kcal/mol). As with $(LiNH_2)_4$, the best orientation of the N lone pairs prefers the planar ring and the planar ladder arrangement (recall that the $(MeLi{\cdot}LiOH)_2$ ladder is puckered) to the cube.[27d,39]

Differently THF-solvated structures were computed both for $(MeLi{\cdot}LiOMe)_2$ and $(MeLi{\cdot}LiNMe_2)_2$ in order to evaluate the influence of Li solvation. For $(MeLi{\cdot}LiOMe)_2{\cdot}2THF$, a ladder with THF coordinated to each of the two outer lithiums—the sterically easily accessible ladder ends—(**17b**, X = OMe, C_i) and a ladder with THF coordinated to each of the two inner lithiums (**17c**, X = OMe, C_i) are energy minima but are separated by ca. 23 kcal/mol. The structures of the aggregates are represented schematically in Figure 6; the energies of the optimized species are given in Table 7 which also lists the energies of the unsolvated compounds for comparison. That solvation occurs preferably at the ladder ends also is documented by the X-ray structures of $(\mathbf{8}{\cdot}TMEDA)_2$ and $(\mathbf{8}{\cdot}2THF)_2$, and also is found for the H_2O-solvated $(LiNH_2)_4$ ladder[27d] and for the THF-complexed $(i\text{-Pr}_2NLi{\cdot}LiCl)_2$ ladder.[42] With two solvated Li^+ cations, the planar eight-membered ring **18a** (X = OMe) optimized to the ladder structure **17b**.

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For $(MeLi{\cdot}LiOMe)_2{\cdot}4THF$, THF-complexation favors the ladder: the cubic arrangement **16b** (C_2) and the C_i-symmetric ladder **17d** (THF is coordinated only to the outer Li^+ cations) are minima and are separated by only 0.9 kcal/mol compared with the 4.3 kcal/mol energy difference between the unsolvated species (Table 7). A 9.6 kcal/mol energy difference between the cubic and ladder forms was computed for $(MeLi{\cdot}LiOH)_2$ (Table 6).

As with the H_2O-complexed $(LiNH_2)_4$ ladder,[27d] computations of the lithium-solvated $(MeLi{\cdot}LiNMe_2)_2$ species find the ladder structures to be stabilized (Figure 6, Table 7). For $(MeLi{\cdot}LiNMe_2)_2{\cdot}2THF$, the solvated planar eight-membered ring **18a** ($X = NMe_2$) optimized to the C_i-symmetric ladder structure **19b** (with THF coordinated only to the outer Li^+ cations). For $(MeLi{\cdot}LiNMe_2)_2{\cdot}4THF$, a cubic arrangement with every Li^+ cation solvated by THF (**16b**, $X = NMe_2$) optimized to a C_2-symmetric ladder **19c** with a central LiCLiC ring. However, a ladder structure with a central LiNLiN ring and the two outer lithiums solvated by two THF ligands, respectively (**19d**, $X = NMe_2$, C_i), is found to be only 2.3 kcal/mol higher in energy than **19c**. Solvation of the Li^+ cations results in a distortion of the ladder framework from a planar C_{2h} arrangement (this is typically observed for alkali metal amide ladders with additional ligands attached to the outer cations[27,43]).

Remarkably, the $(\mathbf{9}{\cdot}2THF)_2$ dimer, like the most stable $(MeLi{\cdot}LiNMe_2)_2{\cdot}4THF$ ladder arrangement **19c**, is formed via Li−C association but does not involve the Li−N bond. From a purely electrostatic point of view, formation of the maximum number of stronger Li−N contacts (as compared to Li−C interactions) would result in a central LiNLiN ring similar to the $(MeLi{\cdot}LiNMe_2)_2{\cdot}4THF$ ladder minimum **19d**. However, both the bulky *tert*-butyl substituent and the silyl methyl groups at the nitrogen anion preclude formation of the $(\mathbf{9}{\cdot}2THF)_2$ dimer along the Li−N bond. Instead, since the cyclopropene carbon atoms are tied back in the ring, the lithiated carbon (C_α) environment is sterically less demanding which results in the observed LiCLiC central ring (for **19c**, the H_3C^- moiety is sterically less demanding compared to the Me_2N^- moiety). This is also consistent with the unusual solvation of the cations in $(\mathbf{9}{\cdot}2THF)_2$ and **19c**: whereas, due to steric effects, only the outer lithiums are complexed in ladders having four Li−N rungs,[27c,d,31] the environment of the inner cations in $(\mathbf{9}{\cdot}2THF)_2$ and **19c** allows the additional coordination of one THF ligand per lithium. Whether the Li−N or the Li−C bond is involved depends on the steric requirement of the substituents at the carbanion vs the amide moieties.

Conclusions

Lithiated cyclopropenes bearing heteroatoms in appropriate vinylic C_β substituents are good candidates for realization of planar tetracoordinate carbon geometries. As with the chelation strategy applied to phenyllithium dimers,[5,7,8] planar tetracoordinate $R^1R^2CLi_2$ carbons in the "in plane" geometry of the cyclopropenyllithium dimer **6** can be stabilized successfully, which is confirmed by the X-ray structures of $(\mathbf{8}{\cdot}TMEDA)_2$, $(\mathbf{8}{\cdot}2THF)_2$, and $(\mathbf{9}{\cdot}2THF)_2$. Lithium chelation by O^- and N^- moieties in the dimers results in a high degree of planarization of the tetracoordinate carbon environments. Bridging of the vinylic $C(\alpha)-C(\beta)$ bonds by the chelated lithiums in $(\mathbf{9}{\cdot}2THF)_2$ results in a "bonus", a second, nearly planar tetracoordinate C_β! As with the $(n\text{-}BuLi{\cdot}LiO\text{-}t\text{-}Bu)_4$ complex[23] and the TMEDA solvate of trilithiated 2,5-dimethylphenol,[40] electrostatically favorable Li−O contacts (compared with Li−C interactions) dominate the $(\mathbf{8}{\cdot}TMEDA)_2$ and $(\mathbf{8}{\cdot}2THF)_2$ structures: the dimers, which show how an organolithium compound and a lithium alkoxide can aggregate to give puckered ladders, are formed via the Li−O bond. In contrast the $(\mathbf{9}{\cdot}2THF)_2$ structure dimerizes via the Li−C bond, due to the less steric requirement of the cyclopropenyl moiety.

Computational Methods. Density Functional Theory (DFT) calculations were performed using the Gaussian 94 program package.[44] All geometries were optimized using the 6-31G* and 6-31+G* basis sets at the Becke3LYP level of DFT[45,46] and characterized as minima or transition structures by calculating the vibrational frequencies (for the mixed anion aggregates, frequencies were calculated at HF/6-31G*).[47] The Becke3LYP method is a hybrid of Hartree−Fock exchange with DFT exchange-correlation.[46] DFT calculations on a variety of organolithium compounds have recently been shown to reproduce accurately high-level ab initio and experimental data.[48] Natural charges and bond orders were calculated by using the natural population analysis (NPA) method.[49] PM3 semiempirical calculations on the THF-solvated complexes were performed using the VAMP 5.0 program (the PM3 method was shown to reproduce well thermodynamical data—experimental and high-level ab initio—in particular of organolithium compounds[50b]).[50] Geometries were fully optimized without symmetry constraints. However, symmetric structures resulted on optimization. All stationary points were characterized to be minima by calculation of their vibrational frequencies.

Experimental Section

General Conditions. All experiments were carried out under an argon atmosphere by using standard Schlenk and needle/septum techniques. All solvents were freshly distilled from sodium/benzophenone prior to use. TMEDA and PMDTA were dried over CaH_2, destilled, and subsequently kept over Na/Pb alloy. NMR spectra were recorded on a JEOL GX spectrometer (frequencies: ^1H, 400 MHz; ^{13}C, 100.6 MHz; ^7Li, 155.3 MHz).

1-(Di-*tert*-butylhydroxymethyl)-3,3-dimethylcyclopropene was prepared by reaction of monolithiated 3,3-dimethylcyclopropene with 2,2,4,4-tetramethyl-3-pentanone as described by Cheskis *et al.*[51] as a colorless liquid (bp 83 °C at 1 mbar., 58%). ^1H NMR ($CDCl_3$) δ 6.97 (1H, s, vinylic H), 1.79 (1H, br s, OH), 1.24 (6H, s), 1.10 (9H, s); ^{13}C

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NMR (CDCl$_3$) δ 139.2 (C(1)), 116.0 (C(2)), 85.2 (COH), 40.6 (*C*(CH$_3$)$_3$), 29.1 (C(*C*H$_3$)$_3$), 28.0 (C(*C*H$_3$)$_2$), 22.0 (C(3)).

Dimeric TMEDA-Complexed Dilithiated 1-(Di-*tert*-butylhydroxymethyl)-3,3-dimethylcyclopropene, (8·TMEDA)$_2$. *n*-Butyllithium (0.8 mmol, 0.5 mL of 1.6 M hexane solution) was added to a solution of 1-(di-*tert*-butylhydroxymethyl)-3,3-dimethylcyclopropene (0.084 g, 0.4 mmol) and TMEDA (0.06 mL, 0.4 mmol) in a mixture of THF (0.15 mL) and hexane (1.0 mL) at −40 °C. The solution was then stirred for 30 min at this temperature and 2 h at 0 °C. The precipitated white solid dissolved on warming (ca. 40 °C). Cooling to 4 °C yielded the crude product which was washed (hexane) and dried. Recrystallization from Et$_2$O/THF mixtures at 4 °C resulted in the formation of colorless single crystals suitable for X-ray diffraction. The crystals were selected and transported to the diffractometer at −50 °C.[52] ^{1}H NMR (THF-*d*$_8$, +32 °C) δ 1.14 (6 H, s), 1.05 (18 H, s, *t*-Bu); TMEDA signals at δ 2.31 (4 H, s, NC*H*$_2$), 2.16 (12 H, s, NC*H*$_3$). ^{13}C NMR[53] (THF-*d*$_8$, +32 °C) δ 162.2 (C(β)), 158.2 (C(α)), 90.1 (COLi), 40.5 (*C*(CH$_3$)$_3$), 32.8 (C(*C*H$_3$)$_2$, 31.1 (C(*C*H$_3$)$_3$, 24.5 (C(γ)); TMEDA signals at δ 58.8 (NCH$_2$), 46.2 (NCH$_3$).

Dimeric THF-Complexed Dilithiated 1-(Di-*tert*-butylhydroxymethyl)-3,3-dimethylcyclopropene, (8·2THF)$_2$. *n*-Butyllithium (0.8 mmol, 0.5 mL of 1.6 M hexane solution) was added to a solution of 1-(di-*tert*-butylhydroxymethyl)-3,3-dimethylcyclopropene (0.084 g, 0.4 mmol) and PMDTA (0.07 mL, 0.4 mmol) in a mixture of THF (0.3 mL) and hexane (1.0 mL) at −50 °C. The solution was then stirred for 30 min. On warming to room temperature (within 20 min), the product, a white solid, dissolved. Cooling to 4 °C yielded the crude product which was washed (hexane) and dried. Recrystallization from THF/hexane mixtures at 4 °C resulted in the formation of colorless single crystals suitable for X-ray diffraction. The crystals were selected and transported to the diffractometer at −50 °C.[52] ^{1}H NMR[54] (THF-*d*$_8$, +30 °C) δ 1.09 (6H, s, CH$_3$), 1.00 (9H, s, *t*-Bu); ^{13}C NMR[53] (THF-*d*$_8$, +30 °C) δ 162.2 (C(β)), 158.3 (C(α)), 90.1 (COLi), 40.5 (*C*(CH$_3$)$_3$), 32.8 (C(*C*H$_3$)$_2$), 31.1 (C(*C*H$_3$)$_3$), 24.6 (C(γ)); ^{7}Li NMR (THF-*d*$_8$, +30 °C, referenced to 1 M LiBr in THF-*d*$_8$) δ 0.99.

1-(*tert*-Butylaminodimethylsilyl)-3,3-dimethylcyclopropene. 1-(Chlorodimethylsilyl)-3,3-dimethylcyclopropene (6.4 g, 40 mmol, prepared by reaction of (3,3-dimethylcyclopropenyl)lithium[55] with dichlorodimethylsilane) was added to a 40 °C solution of triethylamine (4.1 g, 40 mmol) and *tert*-butylamine (3.7 g, 50 mmol) in hexane (200 mL). The mixture was stirred for 0.5 h at 40 °C and 24 h at room temperature. The precipitated ammonium chloride was removed by filtration and washed with hexane (30 mL). Excess amine and solvent are removed under reduced pressure. The residual liquid is destilled under reduced pressure to give the product (52 °C at 5 mbar, 5.1 g, 65%). ^{1}H NMR (CDCl$_3$) δ 7.81 (1H, s, vinylic H), 1.16 (9H, s, N-*t*-Bu), 1.13 (6H, s, CCH$_3$), 0.74 (1H, br s, NH), 0.17 (6H, s, SiCH$_3$); ^{13}C NMR (CDCl$_3$) δ 135.6 (C(2)), 135.4 (C(1)), 49.4 (N*C*CH$_3$), 33.6 (NC*C*H$_3$), 28.7 (C*C*H$_3$), 17.7 (C(3)), 1.7 (SiCH$_3$).

Dimeric THF-Complexed Dilithiated 1-(*tert*-Butylaminodimethylsilyl)-3,3-dimethylcyclopropene (9·2THF)$_2$. *n*-Butyllithium (0.62 mmol, 0.39 mL of a 1.6 M solution in hexane) was added to a solution of 1-(*tert*-butylaminodimethylsilyl)-3,3-dimethylcyclopropene (0.06 g, 0.31 mmol), PMDTA (0.07 mL, 0.31 mmol) and THF (0.15 mL) in hexane (2.0 mL) at −60 °C. The solution was then stirred for 1 h which caused a white solid to precipitate. On warming to ca. 40 °C, THF (ca. 0.4 mL) was syringed until the product dissolved. Cooling the solution to 4 °C yielded the crude product which was washed (hexane) and dried. Recrystallization from THF/hexane mixtures at 4 °C resulted in the formation of colorless single crystals suitable for X-ray diffraction. The crystals were selected and transported to the diffractometer at −50 °C.[52] ^{1}H NMR[54] (THF-*d*$_8$, +32 °C) δ 1.22 (9H, s, N-*t*-Bu), 1.11 (6H, s, C(CH$_3$)$_2$), 0.13 (6H, s, SiMe$_2$); ^{13}C NMR[53] (THF-*d*$_8$, +32 °C) δ 178.0 (C(α)), 156.6 (C(β)), 53.2 (N*C*(CH$_3$)$_3$), 37.1 (NC(*C*H$_3$)$_3$), 32.6 (C(*C*H$_3$)$_2$), 12.5 (C(γ)), 7.9 (Si(CH$_3$)$_2$); ^{7}Li NMR (THF-*d*$_8$, +30 °C, referenced to 1 M LiBr in THF-*d*$_8$) δ 1.19.

X-ray Data. Data collection on a Stoe-Siemens AED four-circle diffractometer with graphite-monochromated Mo-K$_\alpha$ radiation (λ = 71.073 pm). The structures were solved with direct methods (SHELXS-90)[56] and refined by full-matrix least-squares on F^2 (SHELXL-93).[57] *R*-values: $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $wR2 = (\Sigma w\,(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2)^{0.5}$. All non-hydrogen atoms were refined anisotropically. A riding model was applied to refine the hydrogen atom positions.

Crystal Data of (8·TMEDA)$_2$. [C$_{20}$H$_{40}$Li$_2$N$_2$O] in the asymmetric unit, M = 338.42, triclinic, space group $P\bar{1}$, a = 875.6(2), b = 1105.8(2), c = 1249.5(3) pm, α = 104.92(3)°, β = 109.44(3)°, γ = 100.15(3)°, V = 1.0559(4) nm^3, Z = 2, D_c = 1.064 Mgm^{-3}, F(000) = 376, μ(Mo-K$_\alpha$) = 0.063 mm^{-1}, T = 173(2) K. Intensities of a 0.7 × 0.6 × 0.6 mm rapidly cooled crystal in an oil drop[52] were collected by the $2\theta/\omega$ method in the range of $4° \leq 2\theta \leq 55°$. Of a total of 7265 reflections, 4896 were independent and used to refine 242 parameters, largest difference peak and hole: 340 and −363 enm^{-3}, $R1(F > 4\sigma(F))$ = 0.0517 and $wR2$ = 0.1749 (all data).

Crystal Data of (8·2THF)$_2$. [C$_{22}$H$_{40}$Li$_2$O$_3$] in the asymmetric unit, M = 366.42, orthorhombic, space group $Pna2_1$, a = 1627.2(7), b = 2132.3(4), c = 1305.1(4) pm, V = 4.528(3) nm^3, Z = 8, D_c = 1.075 Mgm^{-3}, F(000) = 1616, μ(Mo-K$_\alpha$) = 0.067 mm^{-1}, T = 153(2) K. Intensities of a 1.4 × 0.8 × 0.8 mm rapidly cooled crystal in an oil drop[52] were collected by the $2\theta/\omega$ method in the range of $8° \leq 2\theta \leq 45°$. Of a total of 4918 reflections, 4339 were independent and, together with 531 restraints, used to refine 577 parameters, largest difference peak and hole: 315 and −222 enm^{-3}, $R1(F > 4\sigma(F))$ = 0.0682 and $wR2$ = 0.1909 (all data).

Crystal Data of (9·2THF)$_2$. [C$_{38}$H$_{74}$Li$_4$N$_2$O$_4$Si$_2$] in the asymmetric unit, M = 706.93, monoclinic, space group $P2_1/c$, a = 1710.8(5), b = 1557.5(4), c = 1723.6(4) pm, β = 102.95(3)°, V = 4.476(2) nm^3, Z = 4, D_c = 1.049 Mgm^{-3}, F(000) = 1552, μ(Mo-K$_\alpha$) = 0.115 mm^{-1}, T = 153(2) K. Intensities of a 1.2 × 1.1 × 0.9 mm rapidly cooled crystal in an oil drop[52] were collected by the $2\theta/\omega$ method in the range of $6° \leq 2\theta \leq 45°$. Of a total of 6482 reflections, 5832 were independent and 5829, together with 547 restraints, used to refine 494 parameters, largest difference peak and hole: 356 and −232 enm^{-3}, $R1(F > 4\sigma(F))$ = 0.0476 and $wR2$ = 0.1339 (all data).

Further details of the crystal structure investigations are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, GB-Cambridge CB2 1EW (U.K.), by quoting the full journal citation.

Acknowledgment. This work was supported by the Fonds der Chemischen Industrie, the Stiftung Volkswagenwerk (Erlangen), the Convex Computer Corporation (Erlangen) and the Deutsche Forschungsgemeinschaft. K.S. thanks the Freistaat Bayern for a scholarship.

Supporting Information Available: A fully labeled figure of 50% anisotropic displacement parameters and tables of bond distances, bond angles, positional parameters, and thermal parameters for the X-ray structures of (**8**·TMEDA)$_2$, (**8**·2THF)$_2$, and (**9**·2THF)$_2$ (28 pages). See any current masthead page for ordering and Internet access instructions.

JA9603362

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[53] An α-β-γ numbering was used for the carbon atoms of the cyclopropenyl ring (lithium is at C$_\alpha$).

[54] For (**8**·2THF)$_2$, and (**9**·2THF)$_2$, integration may indicate variable amounts of THF, as this is partially lost when the crystals are dried in vacuo.

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