Realization of unusual structures: planar tetracoordinate carbon

Den naturwissenschaftlichen Fakultäten

der Friedrich-Alexander Universität Erlangen-Nürnberg

zur

Erlangung des Doktorgrades

vorgelegt von

Klas Sorger

aus Erlangen

Als Dissertation genehmigt von den Naturwissenschaftlichen Fakultäten der Universität Erlangen-Nürnberg

Tag der mündlichen Prüfung:	28.6.1996
Vorsitzender der Promotionskommission:	
	Prof. Dr. D. Kölzow
Erstberichterstatter:	Prof. Dr. P. v. R. Schleyer
Zweitberichterstatter:	Prof. Dr. M. Feigel
Drittberichterstatter:	Prof. Dr. A. Streitwieser

Meinen Eltern

Die vorliegende Arbeit entstand in der Zeit von Mai 1993 bis Januar 1996 am Institut für Organische Chemie der Friedrich-Alexander Universität Erlangen-Nürnberg

Danksagung

Sie gilt:

Meinem Doktorvater, Herrn *Professor Dr. Paul von Ragué Schleyer*, für die Unterstützung dieser Arbeit, seinem großen Interesse und seiner stetigen Diskussionsbereitschaft. Die gewährte „akademische Freiheit" trug wesentlich zum Gelingen dieser Arbeit bei.

Herrn *Prof. Dr. Dietmar Stalke* (Würzburg) nicht nur für sein Fingerspitzengefühl bei der Anfertigung der Röntgenstrukturanalysen, sondern auch für seine Gastfreundschaft in Göttingen und Würzburg.

Herrn *Prof. Dr. H. F. Schaefer* (Athens, Georgia, U.S.A.) für den herzlichen Empfang und die Gastfreundlichkeit während eines Forschungsaufenthaltes.

Herrn *Priv.-Doz. Dr. Walter Bauer* für seinen Einsatz bei den NMR-Messungen.

Herrn *Dr. Nico van Eikema Hommes* für stetige Beantwortung zahlreicher „Computerfragen".

Meinen „Laborgenossen" *Bernd Goldfuss* und *Holger Bettinger* für zahlreiche anregende Diskussionen und ein freundschaftliches Arbeitsklima.

Meinen „Mitstreitern von erster Stunde" *Dr. Peter Schreiner* und *Dr. Horst Sulzbach* für viele chemische und „außerakademische" Aktivitäten.

Allen nicht namentlich genannten Kolleginnen und Kollegen sowie den Angestellten des Instituts für Organische Chemie, die zum Gelingen dieser Arbeit beigetragen haben.

Dem Freistaat Bayern bin ich für die finanzielle Unterstützung durch ein Promotionsstipendium zu großem Dank verpflichtet.

Contents

Abbreviations

Becke3LYP	Hybrid method using Becke's three parameter functional with correlation provided by the functional of Lee, Young, and Parr
DFT	Density functional theory
DMF	Dimethylformamide
DMSO	Dimethylsulfoxide
HOESY	Heteronuclear Overhauser effect spectroscopy
LDA	Lithium diisopropylamide
NIMAG	Number of imaginary frequencies
NLMO	Natural localized molecular orbital
NPA	Natural population analysis
PMDTA	N,N,N',N'',N''-Pentamethyldiethylenetriamine
TMEDA	N,N,N',N'-Tetramethylethylenediamine
ZPE	Zero point energy

List of Publications

Contributions to Journals

1) „α-Ethoxyvinyllithium: an unexpected polymeric structure—tetrameric subunits linked by Li-Cπ interactions", K. Sorger, W. Bauer, P. v. R. Schleyer, D. Stalke, *Angew. Chem.* **1995**, *107*, 1766-1768; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1594-1596.

2) „Towards planar tetracoordinate carbon in the puckered ladder structure of dilithiated 1-(di-*tert*-butylhydroxymethyl)-3,3-dimethylcyclopropene", K. Sorger, P. v. R. Schleyer, D. Stalke, *J. Chem. Soc., Chem. Commun.* **1995**, 2279-2280.

3) „Planar and inherently non-tetrahedral tetracoordinate carbon: a status report", K. Sorger, P. v. R. Schleyer, *J. Mol. Struct., Theochem* **1995**, *338*, 317-346.

4) „Dimeric [3,3-dimethyl-2-(trimethylsilyl)cyclopropenyl]lithium—tetramethylethylenediamine: distortion of the cyclopropenyl geometry due to strong rehybridization at the lithiated carbon", K. Sorger, P. v. R. Schleyer, D. Stalke, *J. Am. Chem. Soc.* **1996**, *118*, 1086-1091.

5) „Towards planar tetracoordinate carbon in the puckered ladder structures of chelated cyclopropenyllithium aggregates", K. Sorger, P. v. R. Schleyer, R. Fleischer, D. Stalke, *J. Am. Chem. Soc.*, in press.

6) „A $[Li_2Na_2C_2]^{2+}$ ion cluster in the novel octahedral structure of a mixed lithium—sodium aggregate comprising fused cyclopropenyl anion—amide moieties", K. Sorger, P. v. R. Schleyer, D. Stalke, *Chem. Eur. J.*, in preparation.

7) „Lithiated di-*tert*-butyl-(3,3-dimethylcyclopropenyl)methoxide—X-ray structural and ab initio investigations on the first unsolvated lithium alkoxide trimer“, K. Sorger, P. v. R. Schleyer, D. Stalke, in preparation.

Published Contributions to Conferences

8) P. v. R. Schleyer, K. Sorger, (**1994**): Upon reexamination, weird structures of lithium compounds become even weirder, First International Conference on the Chemistry of the Alkali and Alkaline Earth Metals, Cambridge, U.K., September 1994, Lecture Abstracts.

9) P. v. R. Schleyer, K. Sorger, (**1995**): Quest for planar tetracoordinate carbon—a deliberate realization, International Chemical Congress of Pacific Basin Societies, Honolulu, Hawaii, U.S.A., December 1995, 0366 (paper number).

Lebenslauf

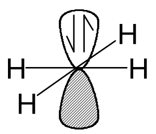
Name:	Klas Mathias Sorger
Geburtsdatum:	17. Mai 1967
Geburtsort:	Erlangen
Familienstand:	ledig
Wohnort:	Hofmannstr. 118, 91052 Erlangen
Eltern:	Dr. med. Günther Sorger, Arzt für Urologie, Dr. med. Ursel Sorger, geb. Lemke, Ärztin für Neurologie
Schulbesuch:	1973-75 Volksschule Pestalozzischule, Erlangen 1975-77 Volksschule Schießstättenschule, Neumarkt/Opf., 1977-86 humanistisch-neusprachliches Ostendorfer Gymnasium, Neumarkt/Opf.—Juni 1986 Abitur.
Bundeswehr:	1. Juli 1986 bis 30. September 1987, Nachschubsoldat im Grundwehrdienst
Studium:	November 1987 bis März 1993 Studium der Chemie an der an der Friedrich-Alexander Universität Erlangen-Nürnberg November 1989 Diplomchemiker-Vorprüfung Juli 1992 Diplomchemiker-Hauptprüfung September 1992 bis März 1993 Diplomarbeit über planar tetra-koordinierten Kohlenstoff unter Anleitung von Prof. Dr. P. v. R. Schleyer am Institut für Organische Chemie seit Mai 1993 Doktorarbeit über Realisation ungewöhnlicher Strukturen am Beispiel von planar tetrakoordiniertem Kohlenstoff unter Anleitung von Prof. P.v.R. Schleyer am Institut für Organische Chemie von April 1993 bis September 1993 angestellt als wissenschaftliche Hilfskraft von Oktober 1993 bis September 1995 Stipendiat des Freistaates Bayern seit Oktober 1995 angestellt als wissenschaftliche Hilfskraft
Forschungsaufenthalt:	1.Oktober bis 12.November 1994 University of Georgia, Athens, GA, U.S.A. (Prof. Dr. H. F. Schaefer)

Introduction

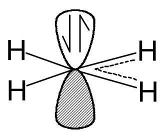
1.1 Background

In 1874, van't Hoff and Le Bel concluded independently that tetracoordinate carbon prefers tetrahedral (or nearly tetrahedral) arrangements of the four substituents.[i,ii] This fundamental idea introduced the third dimension into chemists' perceptions of molecular structures. In the late 1960's chemists started considering the possibility that compounds might be found with *planar* (rather than tetrahedral) tetracoordinate carbons („anti-van't Hoff systems").[iii] The stereomutation of tetrahedral compounds through a planar or nearly planar transition state is of considerable chemical interest.[iv,v]

The most basic organic molecule, methane, has often served as a model to investigate the considerable resistance toward geometrical deformation. Hoffmann, Alder and Wilcox pointed out the qualitative electronic structure of square planar D_{4h} methane (**1**).[vi] As the carbon is sp^2 hybridized, D_{4h} methane lacks electrons in the σ system and only six electrons are involved in four C-H bonds. The remaining two electrons occupy a nonbonding carbon p orbital. This lone pair is orthogonal to the molecular plane and can participate in π bonding to appropriate substituents. Distortion from D_{4h} to planar C_{2v} (**2**) does not change the nature of the lone pair, but leads to two „normal" C-H bonds and one three–center, two–electron bond. The latter is formed from a carbon sp^2



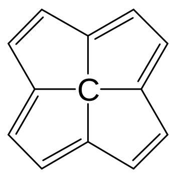
1



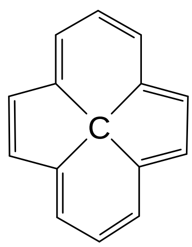
2

hybrid and two hydrogen s orbitals. Quantitative energy differences have been computed theoretically many times,[iv,vd-l,vii] recent ab initio calculations at very high levels indicate D_{4h} singlet planar methane to be 130.5 kcal/mol less stable than the tetrahedral minimum and to have four imaginary frequencies.[vl] The planar C_{2v} form is 121.6 kcal/mol higher in energy than T_d methane and is neither a minimum nor a transition structure, since it has two imaginary frequencies.[vl] Since the energy required for C-H bond cleavage is only 103.2 kcal/mol,[viii] planar singlet methane, either D_{4h} or C_{2v}, is not a viable species.

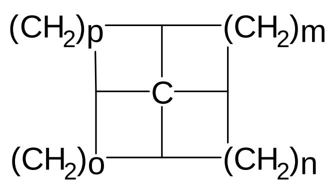
One strategy to construct „anti-van't Hoff" arrangements would be to force the planar tetracoordinate carbon to adopt extreme angular distortions by incorporation into a strained polycyclic environment. Steric constraints would thus force the central tetracoordinate carbon to be nearly planar. This strategy has been pursued both experimentally and computationally.



3



4

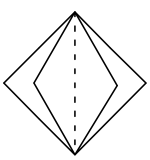


5

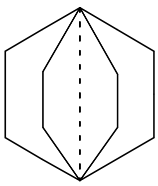
Hoffmann et al.[vi] and later Keese et al.[ix] suggested that such unusual arrangements might be achieved by locking a central carbon atom into an appropriate annulene perimeter. The unsaturated fenestranes[x] **3** and **4** were proposed as possible candidates. However, semiempirical MO computations did not agree:[xi] the planar geometries were indicated to be unstable towards distortion into nonplanar arrangements. Compounds **3** and **4** were indicated to be polyolefinic systems lacking significant aromatic character. Even the most stable forms with essentially tetrahedral coordination around the central carbon are highly strained and, thus, would tend to be highly reactive species.

Likewise, in the family of compounds named fenestranes[x] by Georgian and Salzman,[xii] steric constraints force the central carbon to distort considerably from tetrahedral geometries. These systems, represented by **5**, possess fused carbon rings connected by a single common carbon atom. The connection between the rings can either be cis or trans. Planarizing distortions at the central tetracoordinate carbon in fenestranes are due to the opening of opposite bond angles. Keese's analysis[xc,xiii] defines structural requirements for the opening of these angles which influence the geometry at the central carbon and increase the strain of these systems. Since experimental heats of combustion are lacking for the fenestranes, semiempirical and ab initio computations provide insight into the strain and stability of these compounds.[x,xiv] These reveal nice relationships among structure, strain, and the planarizing distortions of the tetracoordinate carbons. However, only compounds possessing a moderate distortion of the tetrahedral environment of the central carbon have been prepared.[x,xv]

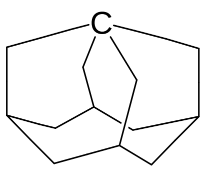
Small ring „paddlanes" (e.g. **6a** and **6b**) are another family of polycyclic hydrocarbons suggested to be attractive synthetic targets for realization of planar tetracoordinate carbon.[xvi] However, both semiempirical and ab initio calculations indicate pyramidal rather than planar geometries at the bridgehead carbon atoms.[xvie,g] Furthermore, paddlane systems (**6a** and **6b**) were calculated to be highly strained and unstable themodynamically.



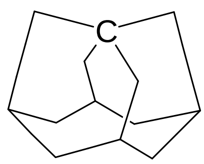
6a



6b



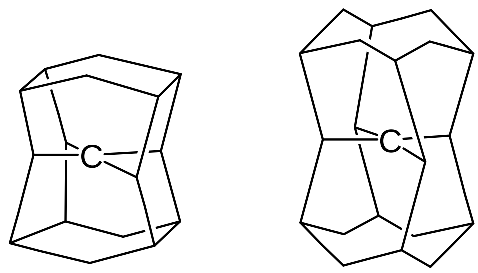
7a



7b

To reduce the strain in [1.1.1.1]paddlane **6a**, one bridgehead carbon atom might be replaced by an eight-membered ring: „bowlane“ **7** results.[xb] MM2 calculations indicated a structure (**7a**) with C_{4v} symmetry and a strain energy which was not excessive.[xviia] However, ab initio HF/6-31G* calculations showed the C_{4v} structure **7a** to be a transition state connecting two equivalent C_{2v} minima **7b**.[xviib] At correlated levels, **7b** is about 25 kcal/mol lower in energy than C_{4v} **7a**. In the C_{2v} minimum structure **7b**, the opposite bond angles of the quaternary bridgehead carbon are 148.1° and 170.9°; these are not far from the 180° planar limit. The calculated strain energy of **7b** is high (166 kcal/mol)[xviib] but is comparable to that of other systems which have already been synthesized but are highly strained (e.g., the strain energies of [3]prismane and cubane have been estimated to be 149 and 165 kcal/mol, respectively).[xviii] Hence, bowlane is judged to be a prospective hydrocarbon candidate for the realization of planar tetracoordinate carbon.

More recently, Radom has explored computationally a class of neutral saturated hydrocarbons, the alkaplanes, which contain a potentially planar tetracoordinate carbon.[xix] Extending the bowlane principle to higher symmetry, hexaplane **8** and octaplane **9** were constructed by capping a planar $C(C)_4$ arrangement with cycloalkanes. S_4-symmetric oktaplane **9**, a local minimum at the HF/6-31G* level, has a CCC angle of 168.8° at the quaternary carbon. This deviates only slightly from the ideal 180° value for planarity. Strain energies per carbon atom (22 and 15 kcal/mol for **8** and **9**, respectively),[xixa] calculated at correlated levels, are not larger than those of known strained hydrocarbons (25 and 21 kcal/mol for [3]prismane and cubane, respectively).[xviii]



8 **9**

A different strategy, to employ bonding principles, rather than just strain, is based on Hoffmann's qualitative analysis of the electronic structure of planar methane.[vi] The unusual bonding of planar tetracoordinate carbon might be stabilized by a suitable combination of stereoelectronic effects: (1) delocalization of the planar carbon lone pair, (2) further incorporation of this lone pair into an aromatic 4n + 2 π system, and (3) replacing hydrogen by more electropositive substituents, i.e. metals. In 1976, Collins, Dill, Jemmis, Apeloig, Schleyer, Seeger and Pople calculated the energies of planar versus tetrahedral[1] geometries of a remarkably extensive set of simple molecules.[iv] These ab initio computations confirmed that electropositive σ donor and π acceptor substituents are particularly effective in stabilizing planar arrangements.[iii,iv] Multiple metal substitution provides further stabilization: planar and „tetrahedral" structures of *cis*-dilithiomethane were found to be very close in energy. The planar tetracoordinate carbon **10** structure of 1,1-dilithiocyclopropane actually was calculated to be more stable than the „tetrahedral" form (Chart 1). The three-membered ring favors

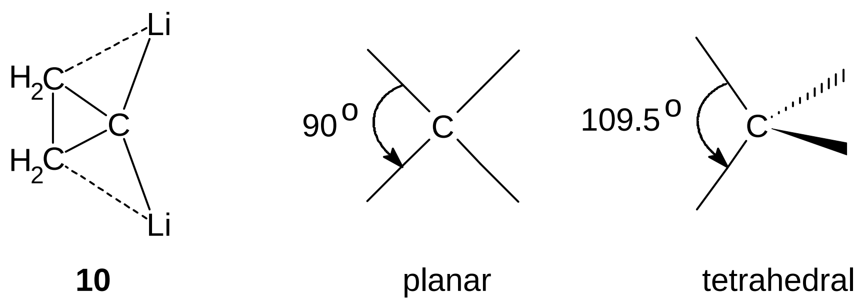


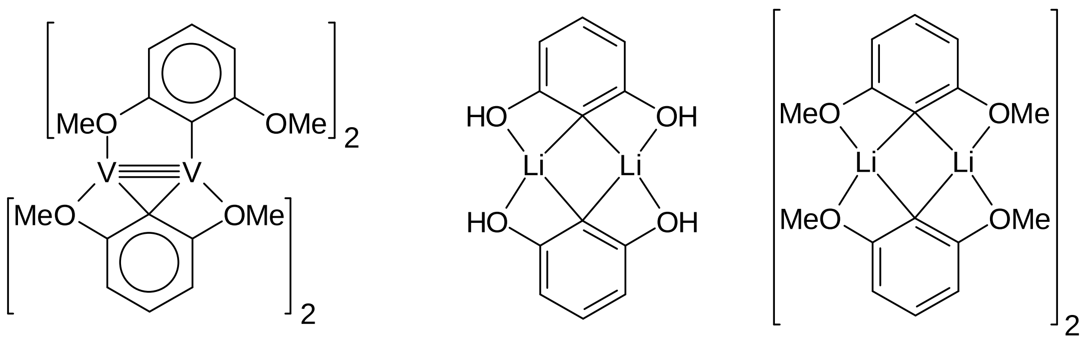
Chart 1. 1,1-Dilithiocyclopropane (**10**) overcomes the steric problem—angle strain—in planar tetracoordinate carbon structures

---

[1] Exact tetrahedral geometry, for example in T_d methane, is seldom encountered. In the following text, „tetrahedral" will be employed loosely to describe nearly tetrahedral geometry.

the planar arrangement **10**: the steric problems in achieving planarity are reduced since the carbon atoms are tied back in the three-membered ring.[iii,iv,xx]

Experimentally verified polarorganometallic compounds with this exceptional „anti-van't Hoff" arrangement are accumulating slowly.[xxi] The first molecule with a planar tetracoordinate carbon was synthesized in 1979.[xxia] The X-ray structure of the divanadium complex **11**, shown in Figure 1, contains two differently coordinated 2,6-dimethoxyphenyl ligands. One of these bridges the two vanadium atoms symmetrically. Intramolecular chelation of both metal centers by the methoxy groups encourages the aryl ligand and the vanadium atoms to lie in the same plane. Consequently, the metal-bound phenyl carbons, C_1 and C_7, have planar tetracoordinate environments.



11 **12a** **12b**

The effectiveness of oxygen-lithium chelation in stabilizing such planar tetracoordinate geometries was shown by a MNDO study of a dimeric model compound **12a**.[xxii] The planar form was computed to be 29.1 kcal/mol more stable than the „perpendicular" arrangement. The X-ray structure of the methoxy derivative, **12b**, synthesized later, shows a tetramer comprised of two planar tetracoordinate carbon dimer units.[xxib,c]

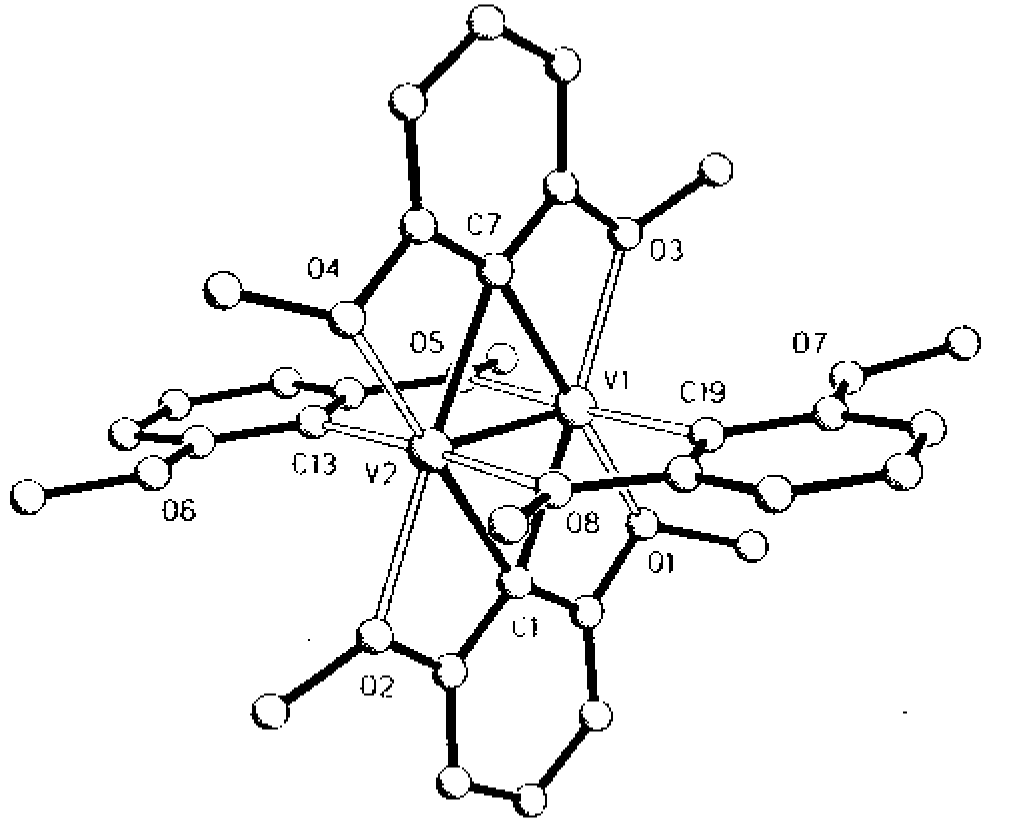
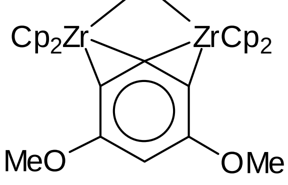


Fig. 1: Crystal structure of the $V_2[2,6\text{-}(OMe)C_6H_4]_4$ complex (**11**).

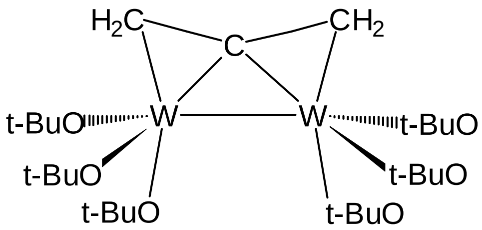
The dimetallic zirconium complex **13**, which contains an in-plane bridging aryl ligand, is another polarorganometallic compound with an unusual geometry.[xxid] A recent theoretical study of both **11** and **13** indicated that the planar tetracoordinate carbons in the bridging phenyl groups should be described as a phenyl anion with the σ lone pair pointing towards the center of the metal-metal



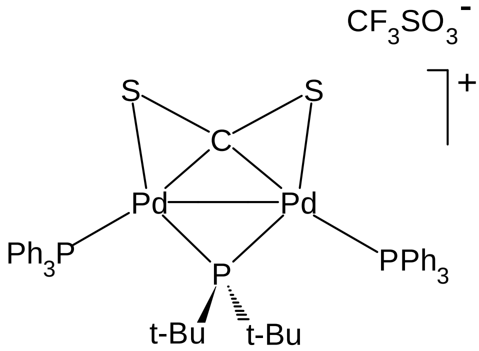
13

axis.[xxiii] These σ lone pairs are stabilized by delocalization into metal d orbitals with predominatly metal-metal bonding character.

Parallel-bridging ligands characerize the complexes **14** and **15**.[xxif-h] The coordination of the central carbon of the ligand—an allene fragment in **14** and a CS_2 molecule in **15**—to both metal atoms results in a planar tetra-coordinate environment.

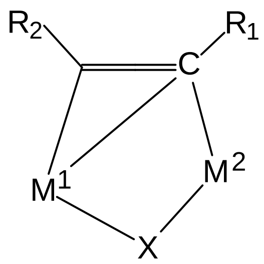


14

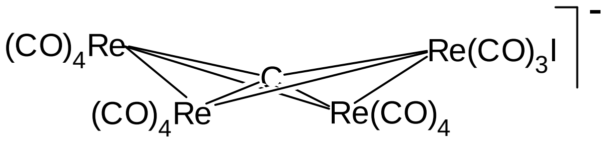


15

A class of dimetallic compounds in which planar tetracoordinate carbon is stabilized by the interaction with both a transition and a main group metal was reported recently.[xxii-k] In compounds **16** (M^1 = Cp_2Zr/Hf, M^2 = B/Al/GaR_3, X = H, Cl, Me, alkynyl), where the main group metal can either be aluminium, gallium or even boron, a planar tetracoordinate carbon comprises part of a double bond. Ab initio as well as extended-Hückel calculations indicated the planar arrangement to be mainly stabilized by σ interactions between C_1 and the strong σ acceptor zirconium (in a d^0 zirconocene fragment).[xxiv]



16



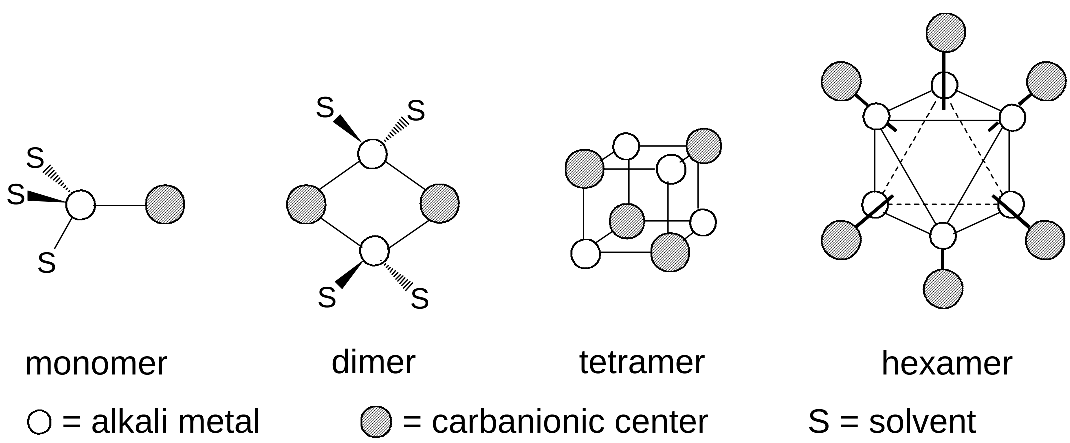
17

The carbidoclusteranion $[Re_4C(CO)_{15}I]^-$ **17** exemplifies a tetrametalla-[3.3.3.3]fenestrane.[xxii] The nearly planar tetracoordinate environment of the central carbido carbon atom includes three $Re(CO)_4$ groups and one $Re(CO)_3I^-$ moiety.

Compounds **10** - **17** all confirm nicely that Hoffmann's concept of stereoelectronic stabilization of this unusual carbon bonding situation can be applied successfully to polarorganometallic systems.

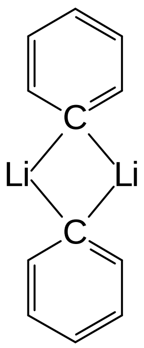
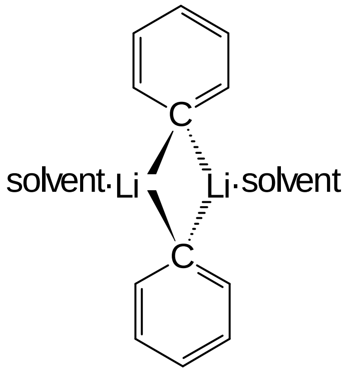
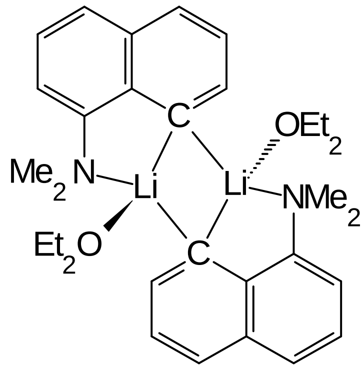
1.2 Planar tetracoordinate carbon in organolithium compounds—the aim of this thesis

Organolithium compounds are widely used synthetic reagents both in organic and inorganic chemistry.[xxv] Due to the highly ionic character of the C-Li bond, organolithium species usually form closely associated ion pairs.[xxvi,xxvii] Also, polar organometallic compounds like alkyl- or aryllithium derivatives associate and solvate: the metal may coordinate to more than one carbanion center in the aggregated species.[xxvb,xxvi-xxviii] In the last two decades, single crystal X-ray diffraction has provided detailed structural information of lithium and the heavier alkali metal compounds.[xxvb,xxvia,b,xxvii-xxix] Scheme 1 presents important structure types. Monomers, dimers, tetramers, oligomers, and polymers are typically observed aggregates. If the cations are coordinated by solvent molecules, smaller aggregates may occur, e.g. monomers or dimers. Lithium prefers a tetracoordinate environment and often adopts a „tetrahedral" geometry.



Scheme 1. Important aggregation types of polar organometallic compounds.

Schleyer and coworker's early survey of the energies of planar versus „tetrahedral" geometries of tetracoordinate molecules by ab initio calculations demonstrated that the electropositive lithium strongly favors the planar arrangement.[iii,iv,xx] The finding that 1,1-dilithiocyclopropane prefers a planar tetracoordinate $R^1R^2Ci_2$ carbon geometry (**10**) attracted attention to the synthesis of such species.[xxx] 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) has hampered X-ray structural invesigations.[xxxi] However, aggregation can be used to advantage: the „in plane" geometry of the unsolvated phenyllithium dimer **18a** with planar tetracoordinate $R^1R^2CLi_2$ *ipso* carbons—similar to 1,1-dilithiocyclopropane **10**—was computed to be more stable than the „perpendicular" dimer **18b**.[xxii] However, the X-ray structure of (phenyllithium•TMEDA)$_2$ showed that the lithium solvation present in the crystal resulted in the „perpendicular" arrangement **18b** instead.[xxxii] This problem might be overcome in systems with intramolecular lithium solvation (chelation).[xxii] 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.[xxib,xxxiii,xxxiv] Indeed, nearly planar $R^1R^2CLi_2$ *ipso* carbon arrangements can be discerned in the dimer units **12b** in the X-ray structure of (2,6-dimethoxyphenyl)lithium (the twist angle between the Li-C_{ipso}-Li plane and the phenyl ring plane was found to be ca. 11^o); however, these dimer units have additional interactions and stack to form an unsymmetrical tetramer.[xxib,c] Only one dimeric aryl derivative, [8-(dimethylmino)-1-naphthyllithium•Et_2O]$_2$ (**19**), had an $Li_2(C_{ipso})_2$ arrangement approching planarity—with ca. 11° twist angles (neither this feature nor the twist angle was pointed out in the original report[xxxiiia]).[xxxiiia,c]

18a **18b** **19**

The propensity of organolithium compounds to solvate and aggregate has thus often frustated experimental realization of gas phase theoretical planar tetracoordinate carbon predictions.

The aim of this work was to realize planar tetracoordinate carbon structures—an unusual carbon environment—deliberately. Prior examples of planar tetracoordinate carbon arrangements (*cf.* compounds **11** - **17**, **19**) were obtained largely by chance rather than by design. As lithium is particularly effective in stabilizing planar geometries,[iii,iv,xx] attention was called to organolithium compounds as „anti-van't Hoff" prospects. Computations provided information concerning geometries and energies of differently substituted cyclopropenyllithium dimers which pointed to suitable synthetic target molecules. X-ray analyses of internally solvated cyclopropenyllithium aggregates revealed puckered ladder structures with nearly planar tetracoordinate carbon environments. The nature of the species in solution was investigated by NMR methods.

The unusual structures of an unsolvated lithium alkoxide and a carbenoid, α-ethoxyvinyllithium, were elucidated. Cation solvation by cyclopropene

C=C bonds in the lithium alkoxide trimer—a rarely observed structure type for LiOR species—was found to be important in stabilizing lithium cations in a low coordination number. The C(Li)O carbenoid character of α-ethoxyvinyllithium was confirmed by computations, X-ray structure analysis, as well as NMR studies.

The influence of different alkali metals on the structure of a metalated cyclopropene compound was investigated both experimetally and computationally. Combining fused carbanion and amide moieties the mixed Li/Na species represents a model for the synthetically valuable „super bases“.

1.3 Computational methods

Computations were performed using the Gaussian 92 and Gaussian 94 programs.[xxxv,xxxvi] Geometry optimizations and energy calculations were carried out at the Becke3LYP level of Density Functional Theory (DFT).[xxxvii,xxxviii] The BeckeLYP method is a hybrid of Hartree-Fock exchange with DFT exchange-correlation.[xxxviii] DFT calculations on a varity of organolithium compounds have recently been shown to reproduce accuratly high-level ab initio and experimental data.[xxxix]

All geometries were optimized using the 6-31G*, 6-31+G*, and 6-311+G** standard Pople basis sets and characterized as minima (NIMAG=0), transition structures (NIMAG=1), or higher saddle points (NIMAG>1) by calculating the vibrational frequencies.[xl] Frequency calculations were carried out at the HF and Becke3LYP levels.

Natural charges, bond orders, and natural localized molecular orbital (NLMO) carbon hybridizations were calculated by using the natural population analysis (NPA) method.[xli]

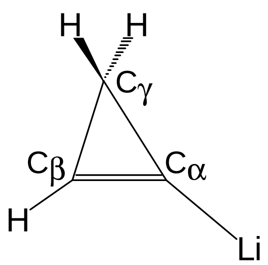
PM3 semiempirical calculations on THF-solvated $(MeLi \cdot LiNMe_2)_2$ and $(MeLi \cdot LiOMe)_2$ complexes were performed using the VAMP 5.0 program.[xlii,xliii] The PM3 method was shown to reproduce well thermodynamical data—experimental and high-level ab initio—in particular of organolithium compounds.[xliib] 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.[xl]

Results

2 Dimeric cyclopropenyllithium—tetracoordinate carbon in a planar environment?

2.1 Introduction

The monolithiated cyclopropene dimer, $(\mathbf{20})_2$, like the phenyllithium dimer (**18**),[xxii] was computed to have two planar tetracoordinate carbon ($R^1R^2CLi_2$) fragments.[xx,xxvii] At the Becke3LYP/6-31G* level, the planar geometry is 10.9 kcal/mol lower in energy than the perpendicular form with „tetrahedral" tetracoordinate carbon (geometries of the optimized cyclopropenyllithium dimers are shown in Figure 2).[xliv] The preference for the planar dimer is due to attractive electrostatic Li^+-$C(\gamma)^{\delta-}$ interactions which are very much reduced in the „perpendicular" isomer. The natural cyclopropene carbon charges of planar $(\mathbf{20})_2$ (C(α): -0.57, C(β): -0.26, C(γ): -0.66) document the distribution[xlviic] of the negative charge over the three carbon centers of the cyclopropenyl ring, and a high negative charge of C(γ). Also, the three-membered rings in $(\mathbf{20})_2$ overcome the steric problems in achieving planarity (see Chart 1). Lithiated cyclopropenes are thus judged to be prospective candidates for the

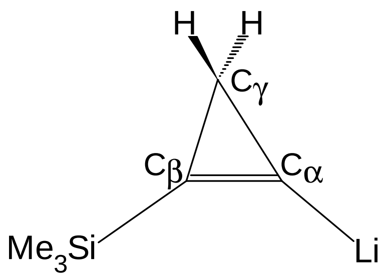


20

realization of planar tetracoordinate carbon arrangements in a simple organolithium dimer.[xx]

Fig. 2. Becke3LYP/6-31G* optimized structures of planar and perpendicular dimeric cyclopropenyllithium.

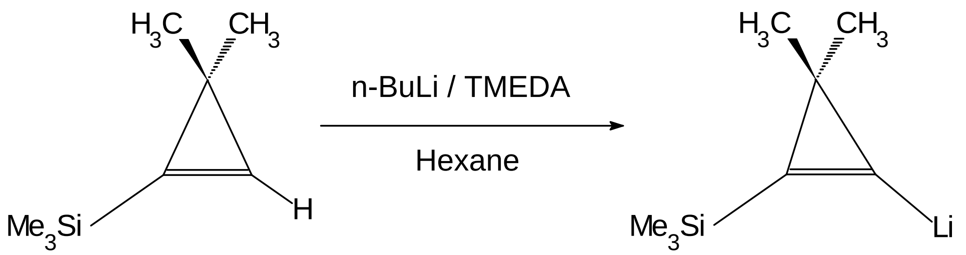
While lithiated cyclopropenes are useful synthetic reagents,[xlv,xlvi] only computational structural information is available. Several ab initio studies predicted that the three-membered ring distorts markedly upon monolithiation:[xlvii] the vicinal C(α)-C(γ) bond of 1-lithiocyclopropene **20** is found to be much longer (157 pm) than in cyclopropene (about 151 pm, see below), whereas the C(β)-C(γ) (distal) bond shortens to 146 pm.[xlviic,d] The first X-ray structure of a lithiated cyclopropene, dimeric [3,3-dimethyl-2-(trimethylsilyl)cyclopropenyl]lithium—TMEDA, (**21**·TMEDA)$_2$, NMR data in THF solution, and DFT computations are presented in the following chapter.



21

2.2 The structure of [3,3-dimethyl-2-(trimethylsilyl)cyclopropenyl]lithium as eluciated by X-ray, NMR, and DFT investigations

The lithiated cyclopropene **21** was synthesized by metalation of the cyclopropene with *n*-butyllithium in hexane in the presence of one equivalent of TMEDA (eq 1).[xx,xliv] Colorless crystals of (**21**·TMEDA)$_2$ were obtained by recystallization of the crude product from hexane.



(1)

Structure of {[3,3-dimethyl-2-(trimethylsilyl)cyclopropenyl]lithium — TMEDA}$_2$, (21·TMEDA)$_2$, in the solid state. The molecular structure of (**21**·TMEDA)$_2$ is shown in Figure 3; bond distances and angles are given in Table 1. The asymmetric unit contains two [3,3-dimethyl-2-(trimethyl-silyl)cyclopropenyl]lithium and two TMEDA molecules (Figure 3, top). The two cyclopropenyl rings are nearly coplanar (deviation: 2.1°) and are bridged quite symmetrically by the two lithiums in the dimer (note the small range of C-Li distances: 220.5(3) - 221.9(3) pm). The Li-C-Li angles in the two monomer units are 67.8(1) and 68.0(1)°, respectively. Both the C-Li bond lengths and the acute Li-C-Li angles in (**21**·TMEDA)$_2$ are typical of dimeric organolithium compounds.[xxvia,b,xxvii-xxix] Chelation by a TMEDA ligand results in a distorted tetrahedral geometry around the lithiums. The TMEDA

Fig. 3. X-ray structure of dimeric {[3,3-dimethyl-2-(trimethylsilyl)cyclopropenyl]lithium-TMEDA}$_2$ (top). The hydrogen atoms have been omitted for clearity. Plot along the C(16)-C(2) axis showing the cisoid structure and the tilting of the TMEDA molecules (bottom).

ligands are disordered; similar interconversion between the two puckered conformations is often found.[xlviii]

Table 1. Bond distances (pm) and angles (deg.) of (**21**·TMEDA)$_2$.

C(1)-C(2)	133.3(2)	C(1)-C(3)	148.9(2)
C(2)-C(3)	156.1(2)	C(3)-C(4)	151.2(3)
C(3)-C(5)	150.9(3)	C(15)-C(16)	132.9(2)
C(15)-C(17)	148.5(2)	C(16)-C(17)	155.9(2)
C(17)-C(18)	151.1(3)	C(17)-C(19)	150.8(3)
C(1)-Si(1)	181.8(2)	C(15)-Si(2)	181.8(2)
C(2)-Li(1)	221.9(3)	C(2)-Li(2)	220.7(3)
C(16)-Li(1)	220.5(3)	C(16)-Li(2)	220.9(3)
N(1)-Li(1)	217.9(3)	N(2)-Li(1)	214.1(3)
N(3)-Li(2)	214.4(3)	N(4)-Li(2)	216.6(3)
C(1)C(2)C(3)	61.34(11)	C(2)C(1)C(3)	66.88(12)
C(1)C(3)C(2)	51.78(10)	C(2)C(1)Si(1)	154.90(14)
C(15)C(16)C(17)	61.26(11)	C(16)C(15)C(17)	67.04(12)
C(15)C(17)C(16)	51.71(10)	C(16)C(15)Si(2)	158.66(14)
Li(1)C(2)Li(2)	67.76(11)	Li(1)C(16)Li(2)	67.96(11)
C(2)Li(1)C(16)	110.16(13)	C(2)Li(2)C(16)	110.46(13)
N(1)Li(1)N(2)	85.86(12)	N(3)Li(2)N(4)	85.53(11)

Although dimeric organolithium structures are well-known,[xxvia,b,xxvii,xxviii,xxixa-c,xlviiib-d,xlix] the C_{2v} symmetry (not crystallographic) of (**21**·TMEDA)$_2$ and the cisoid orientation of the cyclopropenyl rings are remarkable (Figure 3, bottom). The central, equilateral C_2Li_2 four-membered ring is folded: the angle between the C(2)Li(1)Li(2) and the C(16)Li(1)Li2) plane is 163.1°. A few organolithium dimers provide precedents: (phenyllithium-TMEDA)$_2$,[xxxii] (2-lithiothiophene-TMEDA)$_2$,[xlviiid] (2-lithiobenzothiophene-TMEDA)$_2$,[xlviiid] (*n*-butyllithium-TMEDA)$_2$,[xlixa] and (*tert*-butyllithium-Et_2O)$_2$.[xlixb] The TMEDA molecules are tilted on the C(2)-

C(16) vector (the angle between the Li(1)C(2)C(16) and the Li(2)C(2)C(16) plane is 155.3°; Figure 3) to minimize steric repulsions between the N(2), N(4) and the silyl methyl groups. Additional folding of the central C_2Li_2 ring by 16.9° avoids short contacts between the N(1),N(3) and the cyclopropenyl methyl groups.

Although [3,3-dimethyl-2-(trimethylsilyl)cyclopropenyl]lithium adopts the „expected" dimer arrangement in the crystal, the X-ray structure of the TMEDA-solvated complex reveals the „perpendicular" geometry: the Li(1)-Li(2) vector is nearly perpendicular to the plane of the cyclopropenyl rings (the twist angles between the C(2)Li(1)Li(2) and C(16)Li(1)Li(2) planes and the planes of the three-membered rings are 94.1 and 92.0°, respectively; Figure 3, top). As with dimeric TMEDA-solvated phenyllithium,[xxxii] lithium solvation favors the „perpendicular" form usually observed in dimeric organolithium compounds (in the dimers, solvation results in the preferred lithium tetracoordination). Also, steric hindrance (see above) is lessened the perpendicular („tetrahedral") geometry of (**21**·TMEDA)$_2$.

Remarkable structural features of (**21**·TMEDA)$_2$ are the distortions of the lithiated cyclopropenyl rings: the vicinal C(α)-C(γ) bonds in the dimer, C(2)-C(3) and C(16)-C(17), are elongated by about 4 pm (to 156.1(2) and 155.9(2) pm, respectively; Figure 3, top). The non-olefinic C-C ring bond length in cyclopropene and its derivatives is about 151 - 152 pm in the gas-phase (Figure 4),[l] (the mean of 11 crystal structures is 152.3 pm).[li] The distortions of the three-membered ring in substituted cyclopropenes—computed and experimental data—are presented in Table 2. The vinylic C(α)-C(β) bonds of (**21**·TMEDA)$_2$ show a similar 4 pm elongation: whereas the C=C bond length of 11 cyclopropenes is 129.2 pm (solid-state, mean)[li] and the gasphase value ranges between 129 and 130 pm (Figure 4),[l] the C(1)-C(2) and C(15)-C(16) bond lengths are 133.3(2) and 132.9(2) pm, respectively. In contrast, the distal C(β)-C(γ) ring bonds of (**21**·TMEDA)$_2$ are shortened (C(1)-C(3): 148.9(2) pm; C(15)-C(17): 148.5(2) pm).

Fig. 4. Becke3LYP/6-311+G** optimized structures (energy minima) of cyclopropene, 1-silylcyclopropene and 1-(cyclopropenyl)lithium. Lithium substitution dominates the distortion in (2-silylcyclopropenyl)lithium, originating from the less elektropositive SiH_3 substituent.

Fig. 4 (contd.). Becke3LYP/6-311+G** optimized structures of (2-silylcyclopropenyl)lithium and 1,2-dilithiocyclopropene. Note the distortion—bond lengths and endocyclic angles—of the three-membered rings.

The distortion of the three-membered ring in 1-lithiocyclopropene (**20**) and its derivatives reflects the rehybridization at the lithiated carbon. According to Walsh[liia] and to Bent,[liib] the s-character of a C-H orbital is increased when hydrogen is substituted by lithium. This is demonstrated by the natural localized molecular orbital (NLMO) C(α)-H or Li hybridizations[xli] computed at Becke3LYP/6-311+G** (Figure 5): the C(α) hybridization in **20** is $sp^{1.0}$ compared with the $sp^{1.7}$ hybrid used in bonding to

hydrogen (in cyclopropene). Consequently, the p-character and the length of the C(α)-C(γ) ring bond—and less the C(α)-C(β) bond—are increased (Table 2): the C(α)-C(γ) ring bond in **20** is even ca. 10 pm longer compared with cyclopropene (the Becke3LYP/6-311+G** optimized geometries of cyclopropene and 1-lithiocyclopropene are shown in Figure 4; energies are given in Table 3). This increased p-character contracts the endocyclic angle at the lithiated carbon: the C(β)C(α)C(γ) angle of **20** is decreased to 59.5°, whereas < C(α)C(β)C(γ) is 70.6°. The mean endocyclic CC(vinyl)C(vinyl) angle of 11 cyclopropenes (solid-state) is 64.9° (Table 2, Figure 4).[li] Consequently, the distal C(β)-C(γ) ring bond in **20** is shortened to 147.2 pm. The ring deformation in 1-lithiocyclopropene was predicted computationally;[xlviic] the rehybridization at the lithiated carbon demonstrated by the NLMO carbon hybridizations[xli] (computed at Becke3LYP/6-311+G**) now explains why the cyclopropenyl ring is distorted. Whereas the three-membered ring bond lengths and endocyclic angles in monolithiated cyclopropene (**20**) are strongly deformed, the balancing effect of the lithium and the electropositive silicon substituent in **21** results in smaller changes: the C(α)-C(γ) and the vinylic C(α)-C(β) ring bonds in (**21**·TMEDA)$_2$ show a nearly equal elongation of 4 pm; the distal C(β)-C(γ) bond is shortened to 148.7(2) pm (compare the corresponding bond lengths in 1-lithiocyclopropene and in cyclopropene; Table 2, Figure 4). Also, the endocyclic angles of the three-membered rings of (**21**·TMEDA)$_2$ are less deformed: < C(β)C(α)C(γ) (C(1)C(2)C(3) and C(15)C(16)C(17), respectively) is decreased to 61.3° (mean), and < C(α)C(β)C(γ) (C(2)C(1)C(3) and C(16)C(15)C(17), respectively) is 67.0° (mean). Monomeric (2-silylcyclopropenyl)lithium, computed as a model system at Becke3LYP/6-311+G**, exhibits a ring distortion—C-C bond lengths and endocyclic angles—which agrees well with the experimental values found in the solid-state structure of (**21**·TMEDA)$_2$ (Table 2, the optimized geometries of 1-silylcyclopropene and its lithium derivative are shown in Figure 4, energies are given in Table 3; note that the electropositive SiH_3 substituent also alters the ring geometry). The NLMO carbon hybridizations[xli] in (2-silylcyclopropenyl)lithium demonstrate the balancing effect of the Li and the SiH_3 substituent (Figure 5). Two lithiums at the vinylic C=C bond in cyclopropene, i.e. 1,2-dilithiocyclopropene, result in an even less deformation of the three-membered ring: due to the balancing rehybridization effect, both the non-olefinic C-C bond lengths (152.6 pm) and the endocyclic angles (63.4°) compare to the values of cyclopropene (Table 2; the Becke3LYP/6-311+G** optimized geometry of 1,2-dilithio-cyclopropene is shown in Figure 4; for energies, see Table 3). However, the vinylic C=C bond in the dilithium derivative is now elongated by ca. 7 pm (compared to cyclopropene, Table 2, Figure 4). The computed NLMO carbon hybridizations[xli] indicate the increase in p-character of the C=C bond (Figure 5).

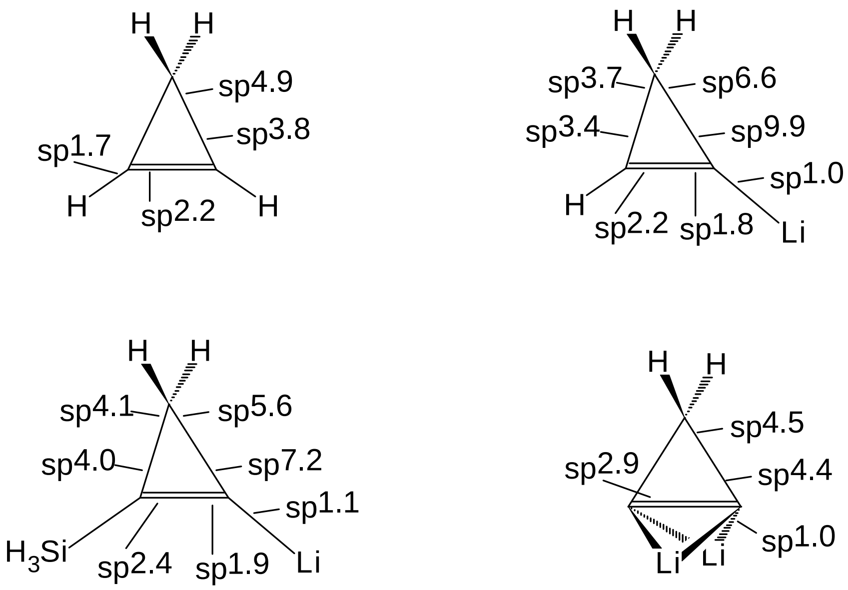


Fig. 5. NLMO carbon hybridizations computed at Becke3LYP/6-311+G** of cyclopropene, (1-cyclopropenyl)lithium, (2-silylcyclopropenyl)lithium und 1,2-di-lithiocyclopropene.

Table 3. Total energies ($E_{tot.}$, hartrees), and zero-point vibrational energies (ZPE, kcal/mol) of cyclopropene, the 1-cyclopropenyl anion, and substituted cyclopropenes computed at Becke3LYP/6-311+G**.

compound	point group	$E_{tot.}$	ZPE [a]
cyclopropene	C_{2v}	-116.65432	35.0 (0)
1-cyclopropenyl anion	C_s	-116.02802	26.0 (0)
1-lithiocyclopropene	C_s	-123.57347	28.4 (0)
1-silylcyclopropene	C_s	-407.38582	45.0 (0)
(2-silylcyclopropenyl)lithium	C_s	-414.30658	38.4 (0)
1,2-dilithiocyclopropene	C_{2v}	-130.47668	22.9 (0)

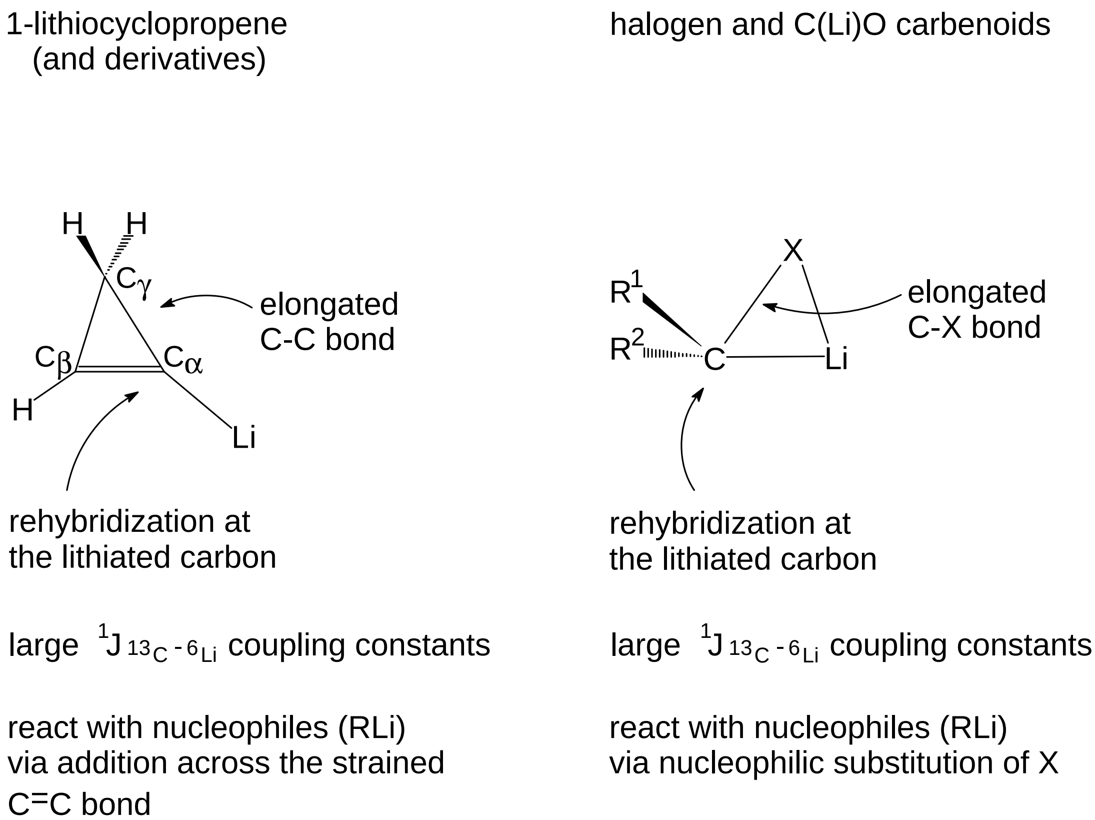
[a] The number of imaginary frequencies is given in parentheses.

The deviation of regular hexagonal geometry of the benzene ring in PhM compounds, i.e. elongation of the C(ipso)-C bond distances and angle contraction at the ipso position, when M is an electropositive element (e.g. Li-Cs), is also related to rehybridization at the metalated carbon.[xxxii,xxxiiic,liii]

Structure in Solution. Crystals of the TMEDA solvate of **21**, enriched with 96% ^{6}Li, were dissolved in [D$_8$]THF (the 1:1 stoichiometry of TMEDA:**21** was confirmed by integration of the ^{1}H NMR signals). A low temperature spectrum reveals that the dimeric solid-state structure is not retained in [D$_8$]THF solution. At -90°C, a well resolved ^{13}C 1:1:1 *three-line* coupling pattern due to ^{13}C-^{6}Li scalar coupling, is observed for the lithiated carbon of the monomer (Figure 6)(the downfield shift of the ^{13}C NMR signal of the lithiated carbon in **21** relative to the δ (^{13}C(2)) of 3,3-dimethyl-1-(trimethylsilyl)cyclopropen, $\Delta\delta$ = 55.7, compares to values observed for monomeric vinyllithium derivatives[liv]).[lv,lvi] The very large $^{1}J_{^{13}C\text{-}^{6}Li}$ coupling constant of 17.6 Hz in **21** indicates high s-character of the C(α) orbital (C-Li bond):[lvib,lviia] the NLMO C(α) hybridization[xli] in (2-silylcyclopropenyl)-lithium is $sp^{1.1}$ compared with the $sp^{1.7}$ hybrid used in bonding to hydrogen (in cyclopropene, Figure 5). Coupling constants of monomeric organolithium compounds usually range between 10 and 16 Hz;[lv] larger magnitudes (16.3 to 17.2 Hz) have only been reported before for α-halogen substituted organolithium compounds (carbenoids).[lvib,lviia]

Fig. 6. ^{13}C NMR signal of the lithiated carbon in **21**-^{6}Li (-90°C, [D_8]THF, 1 equiv. TMEDA).

Is cyclopropenyllithium a carbenoid? Carbenoids, $R^1R^2C(Li)X$ (X= halogen, OR), are strongly rehybridized at the carbenoid carbon, due to the presence of both an electropositive and an electronegative substituent at the same carbon (Scheme 2).[xxviiib,c,lvib,lvii,lviii] This results in large $^{1}J_{^{13}C\text{-}^{6}Li}$ coupling constants (see above) as well as a decidedly elongated C-X bond.[lvib,lvii-lix] Carbenoids easily react with nucleophiles, e.g. RLi, by metal-assisted nucleophilic substitution of the the leaving group X (the substitution is already indicated by the elongated C-X bond; also, the lithium bridges the C-O bond in C(Li)O carbenoids and increases its ionicity[lixb,c,e]).[lviiia,c,lixd,e]



Scheme 2. Characteristics of 1-lithiocyclopropene (and derivatives) and carbenoids.

Cyclopropenyllithium and its derivatives „pretend" to be carbenoids (C/Li carbenoids): the computed ca. 10 pm elongation of the C(α)-C(γ) bond in the three-membered ring of **20** (due to the balancing rehybridization effect of the lithium and the electropositive silicon substituent in **21**, only a ca. 4 pm is found in the X-ray structure of (**21**·TMEDA)$_2$) fulfill the structural prerequisite shown by halogen and C(Li)O carbenoids. But in contrast to carbenoids, the strong rehybridization at the lithiated carbon in cyclopropenyllithium and its derivatives is due to the unusual bonding within the cyclopropenyl ring, i.e. the large strain.[xlv,lx] While the $^{1}J_{^{13}C\text{-}^{6}Li}$ coupling constant of 17.6 Hz is as large as the values found for halogen carbenoids,[lvib,lviia] a nucleophilic substitution reaction with RLi as the „chemical" criterion has not been reported for lithiated cyclopropenes (this would result in the opening of the three-membered ring with a carbanion as the leaving group). Instead, phenyllithium was found to add across the strained C=C bond of both 1-lithiocyclopropene and 1,2-dilithiocyclopropene.[xlvic] Despite the strong rehybridization relationship with carbenoids, lithiated cyclopropenes do not have Li/C carbenoid nature.

2.3 Conclusions

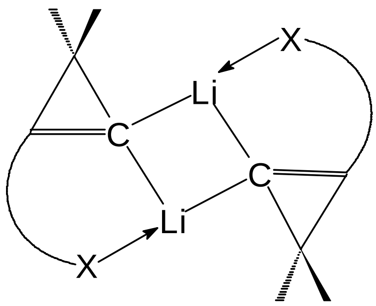
Dimeric unsolvated cyclopropenyllithium was computed (Becke3LYP/6-31G*) to prefer a planar geometry with planar tetracoordinate $R^1R^2CLi_2$ carbons. The TMEDA solvate of [3,3-dimethyl-2-(trimethylsilyl)cyclopropenyl]lithium **21**, synthesized by hydrogen-lithium exchange, adopts a cisoid dimer in the solid state. However, the X-ray structure reveals the perpendicular dimer with „tetrahedral" $R^1R^2CLi_2$ fragments instead, due to the lithium solvation present in the crystal. In THF solution, **21** is a monomer.

The cyclopropenyl ring of **21** is distorted: the vicinal C(α)-C ring bonds are elongated (4 pm), the endocyclic angle at the lithiated carbon is contracted, and the distal C-C ring bond is shortened. The distortion of the carbon skeleton of **21** can be attributed to rehybridization at the lithiated carbon which is confirmed both by the NLMO hybridizations and by the large coupling constant, $^{1}J_{^{13}C\text{-}^{6}Li}$ = 17.6 Hz (the usual range for organolithium monomers is 10 and 16 Hz),[lv] observed in THF solution. Although both the structural ring distortion in 1-lithiocyclopropene (and its derivative **21**) and the large $^{1}J_{^{13}C\text{-}^{6}Li}$ coupling constant in **21** resemble carbenoids, lithiated cyclopropenes do not have carbenoid nature.

3 Planar tetracoordinate carbon in chelated cyclopropenyllithium aggregates

3.1 Introduction

The X-ray structures of (**21**·TMEDA)$_2$[xliv] and (phenyllithium·-TMEDA)[xxxii] show that lithium solvation in the crystal favors the perpendicular dimer with „tetrahedral“ tetracoordinate $R^1R^2CLi_2$ carbons (see Fig. 3 and formula **18b**). The propensity of the organolithium dimers to solvate complicated the quest for planar tetracoordinate carbon. Can solvation be used to advantage? Incorporation of the solvent in the molecule might overcome this problem:[xxii] the planar arrangement in a suitably heteroatom substituted cyclopropenyllithium dimer **22** (X = OR, NR_2) could be stabilized by lithium chelation. The chelation strategy has been applied successfully to phenyllithium dimers: nearly planar tetracoordinate $R^1R^2CLi_2$ *ipso* carbon arrangements can be discerned in the dimer units **12b** (although these dimer units stack to form an unsymmetrical tetramer).[xxib,c] The dimeric aryl derivative **19** shows *ipso* carbon environments with a high degree of planarization.[xxxiiia,c] Computations of cyclopropenyllithium model dimers with heteroatom substituents at the vinylic C_β atom are reported in the following chapter. These calculations pointed to suitable synthetic target molecules.



22

3.2 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.[xlv] It would be better to employ CH_2X (X = OR, NR_2) substituents. These would form thermodynamically favorable five-membered chelate rings upon lithiation.[xxxiiib,lxi] Thus, the „in plane" dimer **22** 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 **23a** is computed to be 14.2 kcal/mol more stable than the „perpendicular" isomer **23b**. 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 7, the energies listed in Table 4.

Intramolecular solvation by the hydroxy group in the planar minimum **23a** results in a Li-O contact (Li-O distance: 191.4 pm). In contrast, steric constraints in the „perpendicular" transition structure **23b** 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 between the planar structure (C_1) of the [2-(aminomethyl)cyclopropenyl]lithium model dimer **24** and the „perpendicular" geometry is 16.5 kcal/mol (Figure 7, Table 4). 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 **24** 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 **25** is 14.7 kcal/mol lower in energy than the „perpendicular“ form (Figure 7, Table 4); the planar arrangement of the [2-(aminosilyl)cyclopropenyl]lithium model dimer **26** is favored by 14.6 kcal/mol (note that the planar C_s structure is a true minimum).

Table 4. 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, **23a**	-246.26052	55.0 (0)	0.0
perpendicular, C_s, **23b**	-246.23680	54.3 (1)	14.2
CH_2NH_2			
„planar“, C_1, **24**	-226.39642	63.5 (0)	0.0
planar, C_s	-226.39584	63.3 (1)	0.2
perpendicular, C_s	-226.36783	62.1 (2)	16.5
SiH_2OH			
planar, C_s, **25**	-497.70460	48.2 (0)	0.0
perpendicular, C_s	-497.67957	47.1 (1)	14.7
SiH_2NH_2			
planar, C_s, **26**	-477.82038	56.0 (0)	0.0
perpendicular, C_s	-477.79477	54.6 (1)	14.6

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

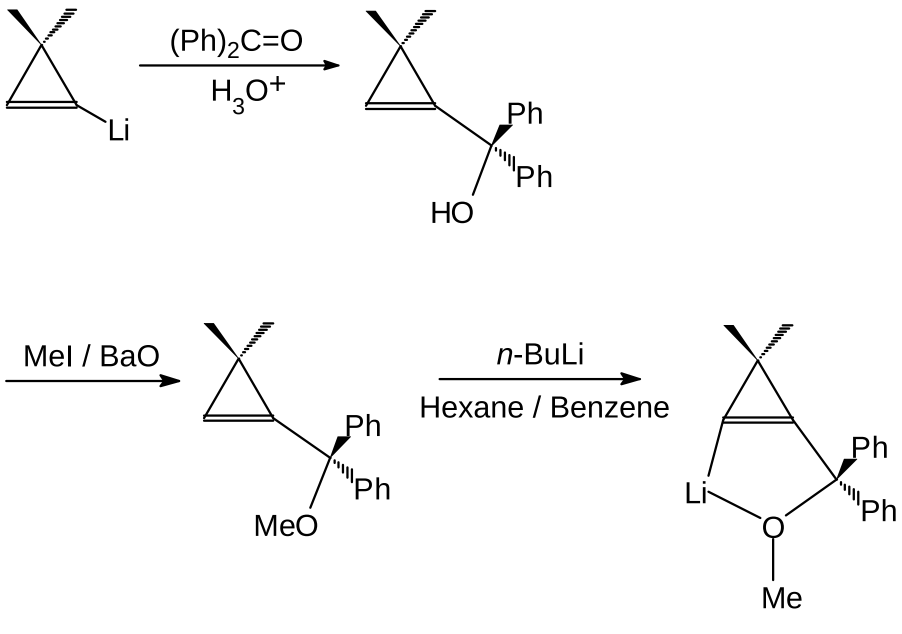
Fig. 7. Becke3LYP/6-31+G* optimized geometries of heteroatom substituted cyclopropenyllithium model dimers.

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 **23a** to 256.9 pm in **25**). 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.[xlviic] The calculated cyclopropene natural carbon charges in **23a** (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,[lixb,lxii] the vinylic C_β atoms in **25** and **26** are highly negatively charged (cyclopropene natural carbon charges in **25**: C_α: -0.51, C_β: -0.71, C_γ: -0.50; **26**: 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 **25** and **26** (Li-C_β distances: **25**: 256.9 pm, **26**: 254.6 pm).

The „in plane“ geometry of the cyclopropenyllithium dimer (**20**)$_2$ 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 lithium bridged double bonds (planar tetracoordinate C_β), as is shown in the next chapters.

3.3 Intramolecular lithium solvation by OR substituents

[3,3-Dimethyl-2-(1,1-diphenylmethoxymethyl)cyclopropenyl]lithium (**27**), synthesized by metalation of the cyclopropene with *n*-butyllithium in apolar solvents (eq 2), provides the solvation internally.



27

(2)

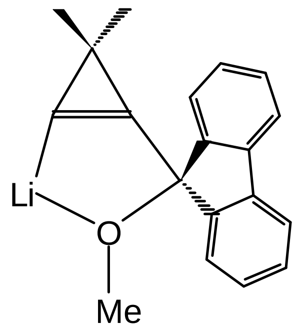
Crystals of **27** were obtained from hexane/benzene mixtures in the absence of cosolvents; however, the crystals were not suited for X-ray diffraction. NMR experiments indicated that a chelate ring formed upon lithiation. In THF solution (using [D_6]acetone as external standard), a ^{13}C NMR spectrum shows that the methoxy signal in **27** is shifted *upfield* relativ zu δ $^{13}C(OCH_3)$ of 3,3-dimethyl-1-(1,1-diphenylmethoxymethyl)cyclopropene ($\Delta\delta$ = 1.4). Due to close contacts between lithium and the methoxy group (i.e. chelation), the electric field produced by lithium results in an upfield shift of the $^{13}C(OCH_3)$ signal.[lxiii] Similar upfield shifts also are found for the

^{13}C(OCH$_3$) signal of (2,6-dimethoxyphenyl)lithium[xxib] (**12b**) and the ^{13}C(OCH$_2$) signal of α-ethoxyvinyllithium (see chapter 4);[lixc] intramolecular lithium solvation in the two compounds both in the solid state and in solution was confirmed by X-ray analyses and NMR studies. A low temperature ^{13}C NMR spectrum of [3,3-dimethyl-2-(1,1-diphenylmethoxy-methyl)cyclopropenyl]lithium (**27**-^{6}Li) reveals a monomer in THF solution.

Fig. 8. ^{13}C NMR signal of the lithiated carbon in **27**-^{6}Li ([D$_8$]THF, -90°C).

At -90°C, a well resolved ^{13}C 1:1:1 *three-line* coupling pattern due to ^{13}C-^{6}Li scalar coupling, is observed for the lithiated carbon of **27** (Figure 8).[lv,lvi,lviia] The large $^{1}J_{^{13}C-^{6}Li}$ coupling constant of 16.8 Hz in **27** indicates high s-character of the C(α) orbital (C-Li bond) and thus confirms the strong rehybridization at the lithiated carbon observed for **21** (*cf.* the 17.6 Hz $^{1}J_{^{13}C-^{6}Li}$ coupling constant in **21**).[xliv,lvib,lviia]

The cyclopropenyllithium derivative 9-(3,3-dimethyl-2-lithiocyclopropenyl)-9-methoxyfluoren (**28**) was synthesized in order to obtain crystals suitable for X-ray analysis. However, the lithium derivative **28** was found to be nearly insoluble in apolar and polar solvents, even in the presence of co-ligands (e.g. TMEDA, PMDTA). The very low solubility compared to the phenyl substituted species **27** may be attributed to the rigidity of the fluorenyl-chelate moiety.



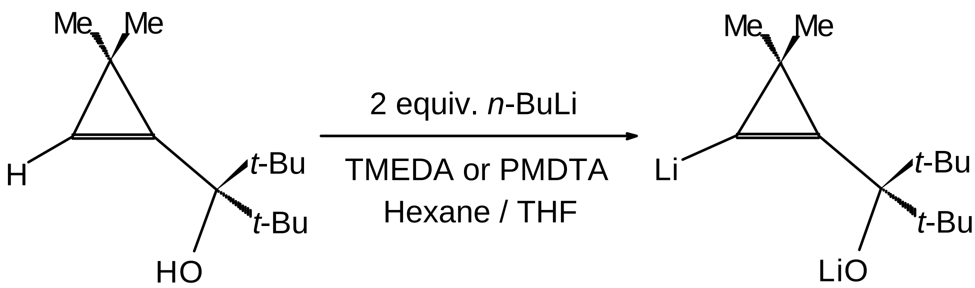
28

Although the lithium cations in the cyclopropenyllithium derivatives **27** and **28** are internally solvated by the heteroatom, the experimental achievement of planar tetracoordinate carbon failed. However, lithium chelation by C/O and C/N dianions resulted in planar $R^1R^2CLi_2$ environments.

3.4 Lithium chelation by C/O and C/N dianions

3.4.1 Nearly planar $R^1R^2CLi_2$ arrangements: syntheses and structures of the TMEDA and THF complexes of dilithiated 1-(di-*tert*-butylhydroxymethyl)-3,3-dimethylcyclopropene

Dilithiated 1-(di-*tert*-butylhydroxymethyl)-3,3-dimethylcyclopropene **29** was synthesized by metalation of the cyclopropene with two equivalents of *n*-butyllithium in a hexane/THF mixture in the presence of one equivalent of either TMEDA or PMDTA (eq 3). In the presence of the ligand TMEDA, compound **29** crystallizes as an amine complex, (**29** • TMEDA)$_2$; however, a crystalline THF solvate, (**29** • 2THF)$_2$,[lxiva] is formed in the presence of PMDTA.[lxivb]



29

(3)

Both (**29** • TMEDA)$_2$ and (**29** • 2THF)$_2$ adopt self-assembled dimer structures in the solid state (depicted in Figures 9, 10; bond distances and angles are given in Tables 5, 6). The structure of (**29** • TMEDA)$_2$ consists of a crystallographically centrosymmetrical ladder-type arrangement of two monomeric units **29** with each peripheral lithium additionally solvated by a bidentate TMEDA ligand. In contrast, complex (**29**·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 lithiums both in (**29**·TMEDA)$_2$ and (**29**·2THF$_2$)$_2$ 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.

Table 5. Selected bond distances (pm) and angles (deg.) of (**29**·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)

Fig. 9. X-ray structure of (**29** · TMEDA)$_2$. The hydrogen atoms have been omitted for clearity (labels with a letter identify atoms which are related by a center of inversion).

Fig. 10. X-ray structure of $(\mathbf{29} \cdot 2THF)_2$. The hydrogen atoms have been omitted for clearity.

Table 6. Selected bond distances (pm) and angles (deg.) of ($\mathbf{29} \cdot 2THF)_2$.

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)		

In ($\mathbf{29} \cdot TMEDA)_2$, the inner lithiums Li2 and Li2A are three-coordinate (trigonal pyramidal)(Figure 9). 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, (**21**·TMEDA)$_2$).[xliv] The Li-O distances range between 189.1(2) and 193.8(3) pm, values typical of lithium alkoxides[lxv] and enolates[xxixc,lxv] in which three cations, respectively, are μ_3 bridged by the oxygen anions.

The Li-C distances in (**29**·2THF$_2$)$_2$ 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 (Figure 10, Table 6). 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 non-equivalent lithium environments: both the Li2 and the Li3 coordination sphere in (**29**·2THF$_2$)$_2$ is similar to the TMEDA complex, (**29**·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 $R^1R^2CLi_2$ cyclopropenyl carbons in (**29**·TMEDA)$_2$ and (**29**·2THF$_2$)$_2$ deviate fundamentally from the perpendicular („tetrahedral“) arrangement (Figures 9 - 11): in (**29**·-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 (**29**·2THF$_2$)$_2$ are 34.6° and 38.8° (Figure 11).[lxiv,lxvi] In contrast, the two lithium cations in (**21**·TMEDA)$_2$)[xliv] and (phenyllithium·TMEDA)$_2$[xxxii] 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 (**29**·TMEDA)$_2$ and (**29**·2THF$_2$)$_2$ resulted in $R^1R^2CLi_2$ carbon environments with a high degree of planarization. Even closer approaches to planar $R^1R^2CLi_2$ arrangements have only been found before in two aryl derivatives, [8-(dimethylamino)-1-naphtyllithium $\cdot$ Et_2O]$_2$[xxxiiia,c] (**19**) and in the dimer units **12b** in the X-ray structure of [(2,6-dimethoxyphenyl)lithium]$_4$.[xxib,c]

Fig. 11. Repesentative parts of the X-ray structure of (**29** $\cdot$ 2THF)$_2$ showing the nearly planar tetracoordinate lithiated C(2) environment (top) and the puckered ladder framework (bottom).

The distance between the chelated Li2 and the vinylic C_β (C2) in (**29**·TMEDA)$_2$ (as well as Li2A-C2A in the dimer) is quite short (233.7(3) pm)(Figure 9), 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 **23a**). Similar short Li-C_β distances are found in the X-ray structures of (*n*-butyllithium)$_6$,[xlixa] (*tert*-butyllithium)$_4$,[xlixa] (isopropyllithium)$_6$,[lxvii] (cyclohexyllithium)$_6$·(benzene)$_2$,[lxviii] [(tetramethylcyclopropyl)methyllithium]$_6$,[lxix] and in the (*n*-BuLi·LiO-*t*-Bu)$_4$ complex.[lxx] The Li-C_β 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 12; note the good agreement between the calculated unsolvated model and the experimental structures): the 0.014 NLMO Li-C_β bond order (Li-C_α: 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_β (natural charges: C_α: -0.63, C_β: -0.17). Including Li2(Li2A) the vinylic C_β atom C2(C2A) in (**29**·TMEDA)$_2$ is tetracoordinate, but not planar (Figure 9): 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 (**29**·2THF$_2$)$_2$, the Li-C_β 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 (Figure 10).

Fig. 12. Becke3LYP/6-31G* optimized structure of dimeric dilithiated 1-(hydroxymethyl)cyclopropene (an energy minimum at HF/6-31G*).

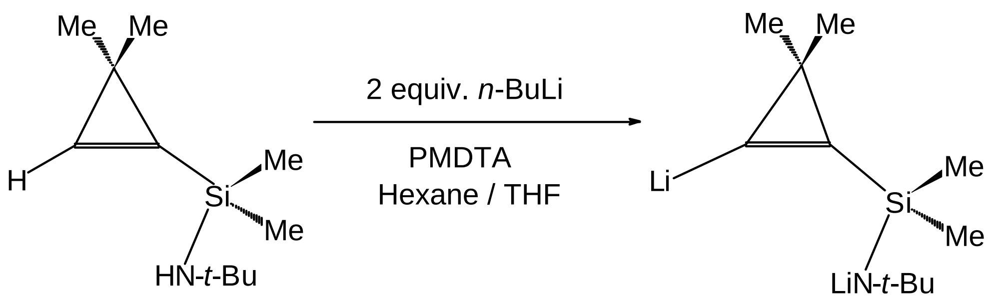
The central $Li_4C_2O_2$ framework merits attention both in (**29**·TMEDA)$_2$ and in (**29**·2THF$_2$)$_2$ (Figure 11): two monomeric units combining organolithium and lithium alkoxide moieties dimerize along the Li-O bond to form a ladder-type or stair-shaped structure. A four-runged ladder core (with 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[lxxi]).[lxxii] Structural motifs typified by ($\mathbf{29}\cdot$TMEDA)$_2$ and ($\mathbf{29}\cdot$2THF$_2$)$_2$ also are well-known in the chemistry of lithium amides[lxv,lxxiii,lxxiv] and phosphides[lxv,lxxivb,lxxv] (the structure of a dilithium disiloxanediolate species adopts a similar puckered ladder[lxxvi]). The structures of ($\mathbf{29}\cdot$TMEDA)$_2$ and ($\mathbf{29}\cdot$2THF$_2$)$_2$ are unprecedented in that an organolithium moiety is incorporated in a ladder framework.[xxvia,b,xxvii,xxviii,xxixa-c] TMEDA complexation in ($\mathbf{29}\cdot$TMEDA)$_2$ occurs at the outer lithiums which is common with ladders having four Li-N rungs (Figure 9).[lxxivc,d,lxxvii] In ($\mathbf{29}\cdot$2THF$_2$)$_2$, however, the inner Li1 is solvated by THF (Figure 10); heteroatom solvation of a central lithium in a four-runged ladder has also been observed in the structures of a dilithium disiloxanediolate species[lxxvi] and a lithium amide—lithium alkoxide complex.[lxxii]

For NMR studies, crystals of ($\mathbf{29}\cdot$TMEDA)$_2$ and ($\mathbf{29}\cdot$2THF$_2$)$_2$ were dissolved in [D$_8$]THF (the compounds are soluble only to a modest extent; the 1:1 stoichiometry of **29**:TMEDA was confirmed by integration of the ^{1}H NMR signals[cxxxviii]). At +30 C^o, 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 ($\mathbf{29}\cdot$TMEDA)$_2$ and ($\mathbf{29}\cdot$2THF$_2$)$_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,[lxxviii] 2,4,6-tri-*tert*-butylphenyllithium,[lxxviii] and (2-lithiophenyl)-*tert*-butylthioether.[xxxiv] The ^{7}Li spectrum of **29** displays only one resonance at +30 ^{o}C (δ = 0.99; Figure 13, top), due to rapid scrambling of the lithiums. In contrast to the unsymmetrical solid-state structure of ($\mathbf{29}\cdot$2THF$_2$)$_2$, the NMR data indicate a time averaged symmetrical structure of **29** in THF solution.[lxxix]

Fig. 13. ^{7}Li spectra of (**29**$\cdot$2THF)$_2$ (top) and (**30**$\cdot$2THF$_2$)$_2$ (bottom) ([D$_8$]THF, +30 ^{o}C, referenced to 1 *M* LiBr in [D$_8$]THF).

3.4.2 Planar tetracoordinate carbon: synthesis and structure of the THF complex of dilithiated 1-(*tert*-butylaminodimethylsilyl)-3,3-dimethylcyclopropene

Dilithiated 1-(*tert*-butylaminodimethylsilyl)-3,3-dimethylcyclopropene **30** was synthesized by metalation of the cyclopropene with two equivalents of *n*-butyllithium in a hexane/THF mixture in the presence of one equivalent of PMDTA (eq 4) and crystallizes as a THF complex, (**30**·2THF)$_2$.



30

(4)

The structure of (**30**·2THF)$_2$ adopts a self-assembled unsymmetric dimer in the solid state which, similar to (**29**·TMEDA)$_2$ and (**29**·2THF)$_2$, consists of a ladder-type arrangement of two monomeric units **30** (the structure is illustrated in Figure 14; bond distances and angles are given in Table 7). Every cation is 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[lxxx]). 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,

Fig. 14. X-ray structure of $(\mathbf{30}\cdot 2THF)_2$. The hydrogen atoms have been omitted for clearity.

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-(trimethyl-silyl)cyclopropenyl]lithium—TMEDA}$_2$, $(\mathbf{21}\cdot TMEDA)_2$,[xliv] and ca. 210 - 221 pm in $(\mathbf{29}\cdot TMEDA)_2$ and $(\mathbf{29}\cdot 2THF)_2$. 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.[lxv,lxxiii,lxxiv]

Table 7. Selected bond distances (pm) and angles (deg.) of (**30**·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)

Fig. 15. Representative parts of the X-ray structure of (**30**·2THF)$_2$ showing the tetracoordinate C(1) and C(2) arrangements (top) and the ladder framework (bottom).

The stair-shaped four-runged ladder $Li_4C_2N_2$ core of (**30**·2THF)$_2$ is intriguing (Figure 15, bottom): whereas ladder structures are well known in the chemistry of lithium amides[lxv,lxxiii,lxxiv,lxxvii] (for compounds exhibiting similar puckered ladder structures, see above), the combination of organolithium and lithium amide moieties to form a puckered ladder is unique.[xxvia,b,xxvii,xxviii,xxixa-c] 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.[lxxivc,d,lxxvii]

Interestingly, the C-Li bonds between the two monomer units—the two C-Li rungs of the $Li_4C_2N_2$ ladder (Figures 14 and 15, bottom)—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 (**30**•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 (Figure 15, top): 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 (**29**•TMEDA)$_2$ and (**29**•2THF$_2$)$_2$ and the ca. 11° twist angles in [8-(dimethylamino)-1-naphthyllithium•Et_2O]$_2$[xxxiiia,c] (**19**) and in the dimer units **12b** in [(2,6-dimethoxyphenyl)lithium]$_4$[xxib,c]). Although weak, additional Li-C interactions between the two monomer units result in pentacoordinate lithiated carbons in (**30**•2THF)$_2$ (Figure 14). 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 16). 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 (**30**·2THF)$_2$ both resemble tetrameric (2,6-dimethoxy-phenyl)lithium, which is comprised of two interacting dimer units **12b**.[xxib,c] The Li-C distances between the two dimer units **12b** 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.

Fig. 16. Becke3LYP/6-31G* optimized structure of dimeric dilithiated 1-(amino-silyl)cyclopropene (an energy minimum at HF/6-31G*).

A remarkable structural feature in ($\mathbf{30}\cdot$2THF)$_2$, the bridging of the vinylic C=C bonds by the inner lithium cations (Figure 14), is shown by the short contacts between the inner lithium cations and the vinylic C_β atoms (Li1-C2: 238.1(4), Li3-C22: 240.0(4) pm; these compare to the longer 231.6(5) pm (mean) Li-C_α distances; *cf* the ca. 230 - 240 pm Li-C_β distances in *n*-BuLi,[xlixa] *t*-BuLi,[xlixa] *i*-PrLi,[lxvii] *c*-C_6H_{11}Li,[lxviii] (*c*-CHCMe$_2$CMe$_2$)-CH$_2$Li,[lxix] and in the (*n*-BuLi$\cdot$LiO-*t*-Bu)$_4$ complex[lxx]) and by the small Li-C_α-C_β angles (Li1-C1-C2: 80.3(2)^o, Li3-C21-C22: 77.7(2)^o). The Li1-C16 distance in ($\mathbf{29}\cdot$2THF)$_2$ is much longer (250.6(10) pm) and the Li1-C17-C16 angle much wider (87.9(4)^o)(Figure 10). The environment of Li1 with its additional THF ligand may be compared with that of the inner Li$^+$ cations in ($\mathbf{30}\cdot$2THF)$_2$. The bridging of the C=C bonds in ($\mathbf{30}\cdot$2THF)$_2$ is due to the formation of five-membered chelate rings (*cf.* structure **26**) 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 (Figure 16) 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 ($\mathbf{30}\cdot$2THF)$_2$ is nearly planar (Figure 15, top): the twist angle between the Si1-C2-Li1 plane and the C1-C2-C3 ring plane is only 11.1^o (the twist angle between the Si2-C22-Li3 plane and the cyclopropenyl ring plane is 27.2^o).

A planar tetracoordinate carbon also comprises part of a double bond in the bimetallic compounds **16**: within a five-membered M^1XM^2CC ring (M^1 = Cp$_2$Zr/Hf, M^2 = B/Al/GaR$_3$, X = H, Cl, Me, alkynyl), the transition metal bridges the C=C bond which results in a planar tetracoordinate carbon environment.[xxii,j] Similarly, a zirconium center in two cationic bis(zirco-nocene) complexes **16** (M^1, M^2 = Cp$_2$Zr, X = alkynyl) is bridged by a C=C bond.[xxie,k]

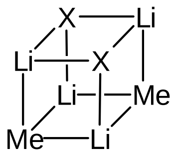
Both the ^{1}H and ^{13}C NMR spectra of **30** (crystals of ($\mathbf{30}\cdot$2THF)$_2$ were dissolved in [D$_8$]THF; the compound is soluble only to a modest extent)[cxxxviii] give no indications of more than a single dilithium species, at +30 ^{o}C. The ^{7}Li spectrum displays only one resonance (δ = 1.19)(Figure 13, bottom), due to rapid scrambling of the lithiums. These data are consistent with a time averaged symmetrical structure in solution,[lxxix] in contrast to the different Li environments observed in the crystal.

3.4.3 Distortion of the cyclopropenyl geometry in (**29**·TMEDA)$_2$, (**29**·2THF)$_2$, and (**30**·2THF)$_2$

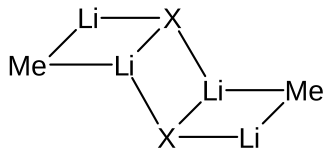
Lithiation at the vinylic carbon both of 1-(di-*tert*-butylhydroxymethyl)-3,3-dimethylcyclopropene and 1-(*tert*-butylaminodimethylsilyl)-3,3-dimethyl-cyclopropene results in significant changes in the cyclopropene C-C bond lengths and endocyclic angles (the cyclopropenyl ring distortions observed in four X-ray structures of cyclopropenyllithium derivatives are summarized in Table 8): due to the rehybridization, the C=C and the C(α)-C(γ) bonds (vicinal bonds) in **29** and **30** are lengthened and the C(β)-C(γ) (distal) bonds are shortened by several pm relative to the distances in cyclopropene.[xliv] Similar ring distortions, first predicted computationally,[xlviic] also are found in the X-ray structure of {[3,3-dimethyl-2-(trimethylsilyl)cyclopropenyl]-lithium·TMEDA}$_2$, (**21**·TMEDA)$_2$.[xliv]

3.4.4 Theoretical investigations probing ring vs ladder vs stack structural preferences of C/O and C/N mixed-anion aggregates

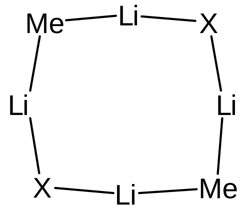
The (**29**·TMEDA)$_2$, (**29**·2THF)$_2$, and (**30**·2THF)$_2$ structures resemble one another. The three compounds display puckered ladder frameworks with fused five-membered chelate rings. In marked contrast to (**29**·TMEDA)$_2$ and (**29**·2THF)$_2$ which dimerize via the Li-O bonds, the (**30**·2THF)$_2$ dimer is formed by Li-C bond association but does not involve the Li-N bond. The structures of (**29**·TMEDA)$_2$, (**29**·2THF)$_2$, and (**30**·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.



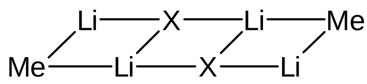
31a



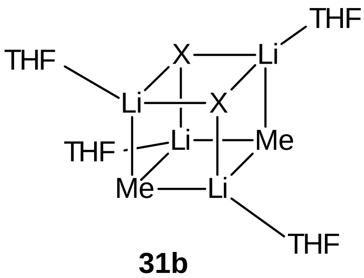
32a



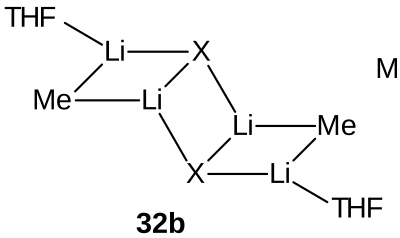
33a



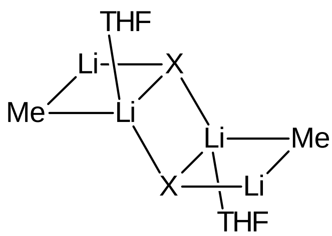
34a



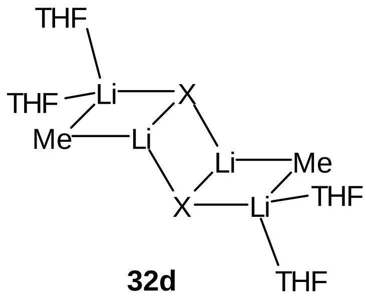
31b



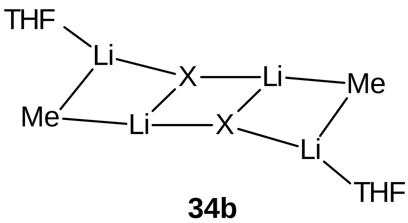
32b



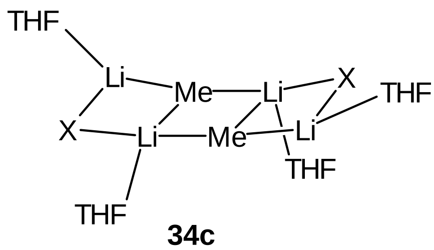
32c



32d



34b



34c

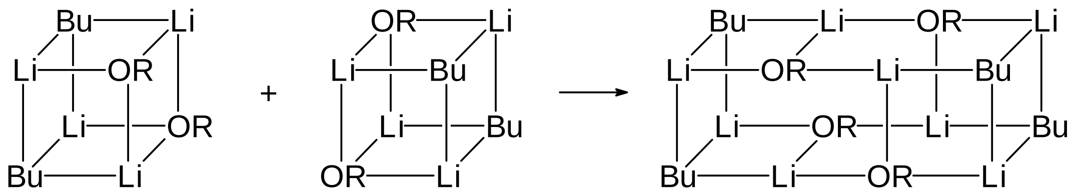
Fig. 17. Schematic illustration of the Becke3LYP/6-31G* optimized structures (energy minima at HF/6-31G*) of unsolvated $(MeLi \cdot LiOH)_2$ and $(MeLi \cdot LiNH_2)_2$ mixed anion aggregates (top, label *a* denotes the unsolvated species), as well as the PM3 optimized THF-solvated $(MeLi \cdot LiOMe)_2$ and $(MeLi \cdot LiNMe_2)_2$ aggregates (bottom).

Table 8. 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 • LiOH)$_2$				
31a	C_{2v}	-261.81029	61.6 (0)	0.0
32a	C_i	-261.79386	60.9 (0)	9.6
33a	C_{2h}	-261.78671	59.7 (0)	12.9
(MeLi • LiNH$_2$)$_2$				
33a	C_{2h}	-221.98828	74.3 (0)	0.0
31a	C_{2v}	-221.98828	74.9 (0)	0.6
34a	C_{2h}	-221.98675	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.

Three energy minima were calculated for (MeLi • LiOH)$_2$: a cubane-like structure (**31a**, X = OH, C_{2v}, a stack of MeLi and LiOH dimers), a C_i-symmetric ladder (**32a**) formed by lateral association of two (MeLi • LiOH) rings via the Li-O bond and a planar eight-membered ring (**33a**, X = OH, C_{2h}). The structures of the aggregates are represented schematically in Figure 17; the energies of the optimized species are given in Table 8. 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,[xxvia,b,xxvii] 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[lxxxi] and LiOH[lxxxii]).[lxxxii] The ladder structure with a central LiOLiO ring has two more Li-O contacts compared with the planar eight-membered ring. The non-planar structure of the ladder is due to orientation effects of the O lone pairs.[lxxxii] 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 (**29**•TMEDA)$_2$ and (**29**•2THF)$_2$ dimerize along the Li-O bond; the structure of the core of TMEDA-solvated trilithiated 2,5-dimethylphenol also is dictated by Li-O interactions.[lxxxiii] Interestingly, Li-O interactions also dominate the structure of the unsolvated (*n*-BuLi•LiO-*t*-Bu)$_4$ complex.[lxx] This may be described as a tetrameric stack: two (*n*-BuLi•LiO-*t*-Bu)$_2$ cubane units (the lowest energy (MeLi•LiOH)$_2$ minimum **31a**) associate via Li-O interactions to form an aggregate with a partially opened Li_4O_4 cubic core (Scheme 3). Stacking of small $(RLi)_2$ subunits to form $[(RLi)_2]_n$ oligomers is a commonly observed structural principle in organolithium chemistry.[xxvia,b,xxvii,xxviii,xxixa-c,lxxxiv] Both the bulky *tert*-butyl groups and the cosolvent present in the crystal in (**29**•TMEDA)$_2$ and (**29**•2THF$_2$)$_2$ preclude further aggregation.



Scheme 3. Stacking of two (*n*-BuLi•LiO-*t*-Bu)$_2$ cubane units to form the (*n*-BuLi•LiO-*t*-Bu)$_4$ complex.

Three different $(MeLi \cdot LiNH_2)_2$ structures were considered (Figure 17, Table 8): a cubic structure (**31a**, X = NH_2, C_{2v}), a planar ladder with a central LiNLiN ring (**34a**, C_{2h}), and an eight-membered planar ring (**33a**, 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 prefer the planar ring and the planar ladder arrangement (recall that the $(MeLi \cdot LiOH)_2$ ladder is puckered) to the cube.[lxxivd,lxxxii]

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 (**32b**, X = OMe, C_i)—the sterically easily accessible ladder ends—and a ladder with THF coordinated to each of the two inner lithiums (**32c**, X = OMe, C_i) are energy minima but are seperated by ca. 23 kcal/mol. The structures of the aggregates are represented schematically in Figure 17; the energies of the optimized species are given in Table 9 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 $(\mathbf{29} \cdot TMEDA)_2$ and $(\mathbf{29} \cdot 2THF_2)_2$, and also is found for the H_2O-solvated $(LiNH_2)_4$ ladder[lxxivd] and for the THF-complexed $(i\text{-}Pr_2NLi \cdot LiCl)_2$ ladder.[lxxxv] With two solvated Li^+ cations, the planar eight-membered ring **33a** (X = OMe) optimized to the ladder structure **32b**.

For $(MeLi \cdot LiOMe)_2 \cdot 4THF$, THF-complexation favors the ladder: the cubic arrangement **31b** (C_2) and the C_i-symmetric ladder **32d** (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 9). A 9.6 kcal/mol energy difference between the cubic and ladder forms was computed for $(MeLi \cdot LiOH)_2$ (Table 8).

Table 9. 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, **31a**	C_{2v}	-168.2	0.0
planar ring, **33a**	C_{2h}	-164.7	3.5
puckered ladder, **32a**	C_i	-163.9	4.3
$(MeLi \cdot LiOMe)_2 \cdot 2THF$			
32b	C_i	-274.4	0.0
32c	C_i	-251.3	23.1
$(MeLi \cdot LiOMe)_2 \cdot 4THF$			
31b	C_2	-367.9	0.0
32d	C_i	-367.0	0.9
$(MeLi \cdot LiNMe_2)_2$			
cube, **31a**	C_s	-55.7	0.0
planar ring, **33a**	C_{2h}	-54.2	1.5
planar ladder, **34a**	C_{2h}	-53.1	2.6
$(MeLi \cdot LiNMe_2)_2 \cdot 2THF$			
34b	C_i	-164.5	
$(MeLi \cdot LiNMe_2)_2 \cdot 4THF$			
34c	C_2	-263.6	0.0
32d	C_i	-261.3	2.3

As with the H_2O-complexed $(LiNH_2)_4$ ladder,[lxxivd] computations of the lithium-solvated $(MeLi \cdot LiNMe_2)_2$ species find the ladder structures to be stabilized (Figure 17, Table 9). For $(MeLi \cdot LiNMe_2)_2 \cdot 2THF$, the solvated planar eight-membered ring **33a** (X = NMe_2) optimized to the C_i-symmetric ladder structure **34b** (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 (**31b**, X = NMe_2) optimized to a C_2-symmetric ladder **34c** 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 (**32d**, X = NMe_2, C_i), is found to be only 2.3 kcal/mol higher in energy than **34c**. 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[lxxiv,lxxxvi]).

Remarkably, the (**30**·2THF)$_2$ dimer, like the most stable (MeLi·-LiNMe$_2$)$_2$·4THF ladder arrangement **34c**, is formed via Li-C association but does not involve the Li-N bond (Figure 14). 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·LiNMe$_2$)$_2$·2THF ladder minimum **32d**. However, both the bulky *tert*-butyl substituent and the silyl methyl groups at the nitrogen anion preclude formation of the (**30**·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 **34c**, 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 (**30**·2THF)$_2$ and **34c**: whereas, due to steric effects, only the outer lithiums are complexed in ladders having four Li-N rungs,[lxxivc,d,lxxvii] the environment of the inner cations in (**30**·2THF)$_2$ and **34c** 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.

3.5 Conclusion

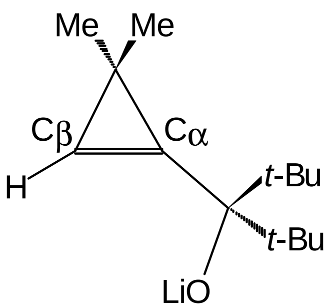
Lithiated cyclopropenes bearing heteroatoms in appropriate vinylic C_β substituents are good candidates for realization of planar tetracoordinate carbon geometries, due to the five-membered ring intramolecular lithium solvation. As with the chelation strategy applied to phenyllithium dimers,[xxib,xxii,xxxiii,xxxiv] planar tetracoordinate $R^1R^2CLi_2$ carbons in the „in plane“ geometry of the cyclopropenyllithium dimer (**20**)$_2$ can be stabilized successfully, which is confirmed by the X-ray structures of (**29**·TMEDA)$_2$, (**29**·2THF)$_2$, and (**30**·2THF)$_2$ (the cyclopropenyllithium derivatives **27** and **28** provide the solvation internally; however, single crystal X-ray diffraction failed). Lithium chelation by C/O and C/N dianions in the dimers results in a high degree of planarization of the tetracoordinate carbon environments. Bridging of the vinylic C(α)-C(β) bonds by the chelated lithiums in (**30**·2THF)$_2$ results in a „bonus“, a second, nearly planar tetracoordinate C_β! As with the (*n*-BuLi·LiO-*t*-Bu)$_4$ complex[lxx] and the TMEDA solvate of trilithiated 2,5-dimethylphenol,[lxxxiii] electrostatically favorable Li-O contacts (compared with Li-C interactions) dominate the (**29**·TMEDA)$_2$ and (**29**·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. Although Li-N interactions are electrostatically prefered to Li-C contacts, the (**30**·2THF)$_2$ structure dimerizes via the Li-C bond, due to the less steric requirement of the cyclopropenyl moiety.

4 Unusual structures of lithium compounds

4.1 Lithium di-*tert*-butyl-(3,3-dimethylcyclopropenyl)methoxide: the importance of cation solvation by cyclopropene C=C bonds in an unsolvated lithium alkoxide trimer

4.1.1 Introduction

Lithium compounds exhibit remarkable structural variety.[xxvia,b,xxvii,xxviii,xxixa-c,lxv,lxxiva,b] Due to the highly ionic character of such species, closely associated ion pairs are formed which associate and often solvate.[xxvia,b,xxvii,xxviii,lxxiva] Whereas dimers, tetramers, hexamers, and polymers are typically observed aggregates (see Scheme 1), trimers are only rarely found.[lxxxvii-lxxxix] Heteroatom substituents in the few examples of organolithium and lithium alkoxide trimers coordinate intramolecularly to the lithium cations and saturate their coordination sphere.[lxxxvii,lxxxviii] Electrostatic interactions between the lithiums and the phenyl carbons of the benzyl moieties in unsolvated dibenzylamidolithium, $[(PhCH_2)_2NLi]_3$, were found to contribute to the cation coordination sphere in the trimer arrangement.[lxxxixd] The first X-ray structure of an unsolvated lithium alkoxide trimer, lithium di-*tert*-butyl-(3,3-dimethylcyclopropenyl)methoxide (**35**), is reported in the following section. The importance of lithium bridging of the cyclopropene

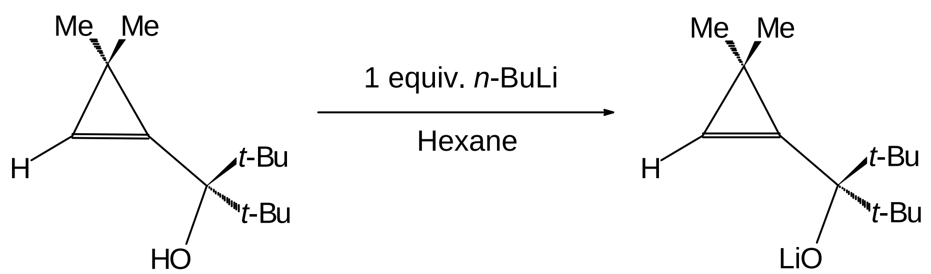


35

C=C bond in stabilizing lithium cations in a low coordination number is shown both by X-ray structural and theoretical density functional theory (DFT) studies.

4.1.2 Synthesis, crystal structure, and computational studies of lithium di-*tert*-butyl-(3,3-dimethylcyclopropenyl)methoxide

Reaction of *n*-butyllithium with 1-(di-*tert*-butylhydroxymethyl)-3,3-dimethylcyclopropene in hexane in a 1:1 molar ratio afforded the lithium methoxide derivative **35** (eq 5). Although, due to the large s-character of the vinylic C-H bonds,[xliv,la,xc] cyclopropenes can easily be metalated,[xliv-xlvi] only the alkoxide species was formed. Colorless crystals of **35** were obtained from hexane in the absence of cosolvents.



(5)

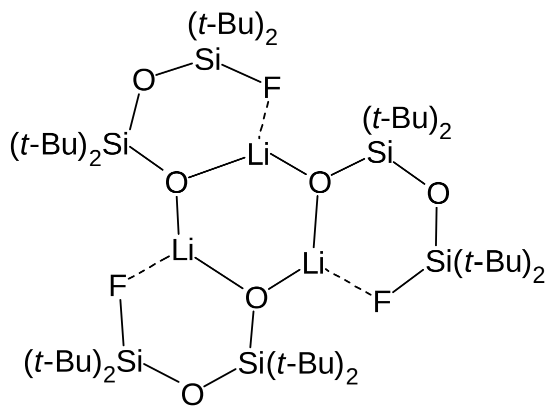
The structure of **35** adopts a trimer in the solid state. The molecular structure of $(\mathbf{35})_3$ is shown in Figure 18a; important average bond distances and angles are depicted in Figure 18 b. The asymmetric unit contains two crystallographically independent trimeric molecules which differ in the orientation of the cyclopropenyl rings (Figure 18 c). The core of the two molecules consists of a nearly planar Li_3O_3 six-membered ring (maximum least-squares deviation in the two molecules: 1.3 and 5.3 pm, respectively)(Figure 18 a). The Li-O-Li and O-Li-O angles are in the ranges of 105.0(4) - 109.0(4) (mean: 106.7(5)°) and 130.8(6) - 135.7(5)° (mean: 133.1(6)°), respectively, and compare to values found for solvated lithium alkoxide trimers.[lxxxviii]

Fig. 18. Crystal structure of trimeric lithium di-*tert*-butyl-(3,3-dimethylcyclo-propenyl)methoxide (**35**). The hydrogen atoms of the methyl groups have been omitted for clarity. a) Plot perpendicular to the Li_3O_3 plane.

Fig. 18 (contd.). b) Monomeric subunit depicting average bond lengths and angles. c) Plot along the Li_3O_3 plane showing the differently orientated cyclopropenly moieties in the two trimers.

A remarkable structural feature, the bridging of the cyclopropene C=C bonds by the lithium cations, is shown by the short contacts between Li^+ and the vinylic C_α atoms (248.0(11) - 259.5(10) pm, mean: 254.8(11) pm), as well as the vinylic C_β atoms (246.9(11) - 257.9(12) pm, mean: 252.3(12) pm)(*cf.* the average 280 pm distances between the lithiums and the phenyl α- and *ortho*-carbons of the benzyl units in the unsolvated dibenzylamidolithium trimer[lxxxixd]). These distances are similar to Li-C bond lengths observed for lithiums π-bonded to π-delocalized carbanionic moieties (e.g., in benzyl-lithium[xci]).[xxvia,b,xxviii,xxixa] Several computational studies on the ethylene—Li^+ (or LiH) π complex pointed out that lithium coordination to the π system is favored energetically.[xcii,xciii] Electrostatic interactions between the Li^+ cations and the cyclopropene C=C bond in $(\mathbf{35})_3$ increase the cation coordination number to four—two Li-O and two Li-C contacts—and thus stabilize the lithiums in the unsolvated trimer arrangement. The internal lithium π-complexation in $(\mathbf{35})_3$ may be compared with intramolecular lithium solvation (chelation) by heteroatom substituents.

The lithium bridging involves interesting structural features (Figure 18 a): firstly, the cyclopropenyl rings are bent towards the adjacent lithium cations of the Li_3O_3 ring in order to „solvate“ the lithiums effectively. This is demonstrated by the distinctly smaller $(t\text{-Bu})_2$C-O-Li angles within each monomer unit (mean: 110.5(4)°) compared to the corresponding angles to the lithiums of the neighbouring unit (141.4(4)°). Similar bending of the aryl moieties towards the neighbouring lithium cations is found for $[(PhCH_2)_2NLi]_3$.[lxxxixd] Secondly, lithium π-complexation results in longer Li-O bonds within each monomer unit (mean: 182.4(11) pm) compared to the Li-O distances between the monomer units (mean: 177.8(10) pm). Even larger Li-O bond alternations are observed in the Li_3O_3 core of a lithium disiloxanolate trimer, $[LiOSi(t\text{-Bu})_2OSi(t\text{-Bu})_2F]_3$ (**36**).[lxxxviiib] Due to lithium chelation by the fluorine atoms, the Li-O bonds within the three six-membered Li-O-Si-O-Si-F chelate rings are much longer than the Li-O distances between the single units.



36

The importance of internal lithium solvation by the cyclopropene double bonds in (**35**)$_3$ is substantiated by theoretical DFT calculations. The C_1-symmetric structure of the lithium cyclopropenylmethoxide model trimer, computed at Becke3LYP/6-31G*, displays the lithium bridging of the C=C bond: the distances between Li^+ and the vinylic α-carbon as well as the vinylic β-carbon are 258.0 pm and 259.2 pm, respectively (the optimized structure is shown in Figure 19; note the good agreement between the calculated model and the experimental structures). The 0.014 NLMO Li-C_β and 0.009 Li-C_α bond orders indicate attractive electrostatic interactions between Li^+ (natural charge: +0.85) and the negatively charged vinylic carbons (natural charges: C_β: -0.28, C_α: -0.05). As Li^+-O^- interactions are favored electrostatically, the Li-O bond orders are larger (0.051 - 0.067; in general, the small values are due to the highly ionic character of the C-Li and O-Li bonds). The lithium bridging of the C=C bond in the computed model trimer results in structural features also observed in the solid-state structure of (**35**)$_3$: (1) a largely reduced H_2C-O-Li angle (108.3°) within the monomer unit indicates the bending of the cyclopropenyl ring towards the adjacent lithium cation (the 143.6° angle to the neighbouring lithium is much larger); (2) the Li-O bond within the monomer with its bridged lithium is ca. 6 pm longer than the remaining Li-O distances (183.8 versus ca. 177 pm).

Fig. 19. Becke3LYP/6-31G* optimized structure of the lithium cyclopropenyl-methoxide model trimer (an energy minimum at HF/6-31G*).

Interestingly, lithium cations can coordinate to cyclopropenyl rings in different ways. In the most stable C_s-symmetric minimum **37**, computed at Becke3LYP/6-311+G**, the lithium cation does not coordinate to the cyclopropene π bond but bridges a C-C single bond instead (the optimized geometries of the cyclopropene—Li^+ complex are shown in Figure 20; energies are given in Table 10)! The planar tetracoordinate carbon arrangement results. The preference for the bridging of the σ bond is due to attractive electrostatic Li^+-$C_\gamma^{\delta-}$ interactions: the cyclopropen carbon natural charges (C_α: -0.24; C_β: -0.06; C_γ: -0.60; Li: +0.86) document a high negative value of C_γ. Both the lithium bridging and the tetracoordinate C_α environment in **37** resemble the planar geometry of the unsolvated 1-lithiocyclopropene dimer (**20**)$_2$ (Figure 2). Structure **38** (C_s) represents the transition structure (with an activation barrier of 1.1 kcal/mol) between two equivalent minima **37**. The Li^+ cation in **38** is positioned above the three-membered ring which results in three Li-C contacts as well as an additional contact to the C-H bond of the CH_2 group. A second C_s-symmetric minimum **39**, reminiscent of doubly bridged 1,2-dilithiocyclopropene,[xliv] is 2.4 kcal/mol higher in energy than **37**. The Li^+ cation „binds“ η^2 to the vinylic C=C bond (the angle between the lithium-midpoint(C=C) vector and the plane of the three-membered ring is 113.1°)(Figure 20). The C_{2v}-symmetic transition structure **40** lies 3.6 kcal/mol above the global cyclopropene—Li^+ minimum **37** and connects two minimum structures **39**. The cyclopropene C=C bond is „in-plane“-bridged by the σ-bound lithium: the vinylic tetracoordinate carbons are planar.

Fig. 20. Becke3LYP/6-311+G** optimized geometries (energy minima) of the cyclopropene—Li^+ complex.

Table 10. Total energies ($E_{tot.}$, hartrees), zero-point vibrational energies (ZPE, kcal/mol) and relative energies ($E_{rel.}$, kcal/mol) of different cyclopropene—Li^+ structures computed at Becke3LYP/6-311+G**.

	point group	$E_{tot.}$	ZPE [a]	$E_{rel.}$ [b]
37	C_s	-123.97448	35.6 (0)	0.0
38	C_s	-123.97311	35.9 (1)	1.1
39	C_s	-123.97100	35.8 (0)	2.4
40	C_{2v}	-123.96918	35.9 (1)	3.6

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

The lithium bridging of a cyclopropene C-C single bond—similar to the lowest energy cyclopropene–Li^+ structure **37**—is not observed in the solid-state structure of (**35**)$_3$ (Figures 18a,c). While the lithium cation in **39** is η^2-coordinated to the cyclopropene π bond, geometrical restraints in (**35**)$_3$ prevent an effective lithium π-complexation. A coordination mode intermediary between structures **39** and **40** is adopted instead: the angles between the lithium-midpoint(C=C) vector and the cyclopropenyl ring planes in (**35**)$_3$ range between 142 and 148^o (mean: 145^o; *cf.* the 113^o angle in **39** and the 180^o angle in planar **40**). Intramolecular lithium solvation (chelation) even favors the planar arrangement **40**: bridging of the vinylic C_α-C_β bonds by the chelated lithiums in the X-ray structure of (**30**$\cdot$2THF)$_2$ results in the planar tetracoordinate C_β environment (Figure 14).

Internal lithium π coodination to an olefinic C=C bond has also been observed for organolithium compounds:[xciv] while early NMR data on but-3-enyllithium provided evidence for intramolecular Li-C π interactions in the apolar solvent cyclopentane only,[xcv] a recent NMR study showed that a 5-hexenyllithium derivative exits in the polar solvent THF as a mixture of THF-solvated and intramolecularly π-complexed species.[xciii] Similarly, internal lithium π coordination to the C=C bond was indicated to dominate the stereoselectivities of ring closure reactions of substituted 5-hexenyl-lithiums.[xciic]

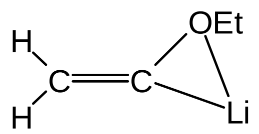
4.1.3 Conclusions

Unsolvated lithium di-*tert*-butyl-(3,3-dimethylcyclopropenyl)methoxide (**35**) adopts a trimeric structure in the solid state. The lithium cations in each monomer subunit in $(\mathbf{35})_3$ are internally complexed by the cyclopropene C=C bonds. Structural characteristics in both the solid-state and the computed model structures—Li-O bond alternation and the bending of the cyclo-propenyl moieties towards the neighbouring lithium—stress the importance of cation solvation by the vinylic C=C bonds.

4.2 α-Ethoxyvinyllithium: the unusual structure of a carbenoid

4.2.1 Introduction

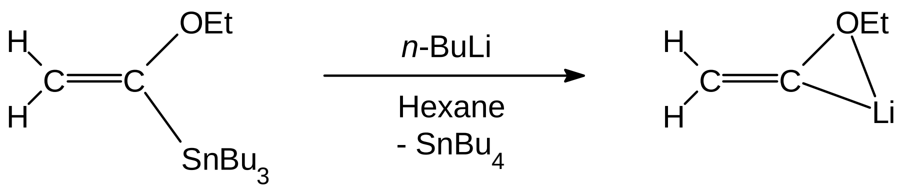
Serving as an acyl anion equivalent, α-ethoxyvinyllithium (**41**) is a widely-used synthetic reagent.[xcvi] In general, α-halogen or oxygen substituted organolithium systems (R^1R^2CXLi) have „carbenoid“ character, with bridging lithium and elongated C-X bonds (see Scheme 2).[xlviiid,lvib,lvii-lix,xcvii,xcviii] The complex X-ray structure of unsolvated **41**, as well as NMR evidence for its nature in THF solution are presented in the following section.



41

4.2.2 Synthesis and crystal structure of α-ethoxyvinyllithium

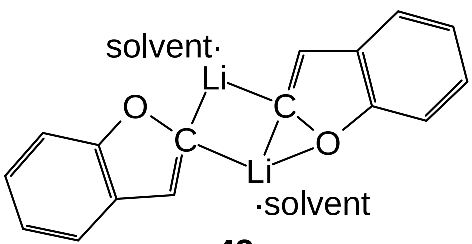
α-Ethoxyvinyllithium (**41**) was synthesized by tin/lithium exchange (eq 6). Crystals of **41** were obtained from hexane in the absence of cosolvents.



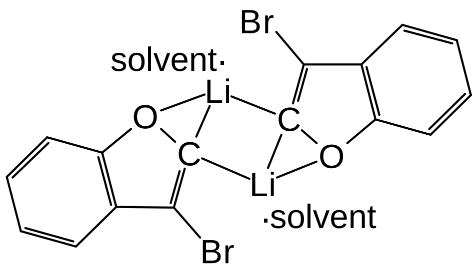
(6)

The structure of **41** adopts a self-assembled, polymeric chain in the solid state (depicted in Figure 21; selected bond lengths and angles are given in Table 11). The asymmetric unit contains six $CH_2=C(Li)OEt$ molecules. Four of them are aggregated to form a distorted cubic Li_4C_4 tetramer, the remaining two generate a second tetramer by a C_2 axis (Fig. 21, top).

The Li/oxygen carbenoid character of **41** is shown by the elongated C_α-O bond (142.1(6) - 143.6(6) pm, mean: 142.8(7) pm).[lixb-d,xcvii,xcviiia] The C_{vinyl}-O bond length is about 136 pm in vinylethers (Fig. 16).[xcix] Similar 6.8 and 8.5 pm elongations were observed in 2-lithiobenzofuran[xlviiid] **42** and 3-bromo-2-lithiobenzofuran[lixe] **43**. The C_α-O bond of monomeric α-methoxyvinyllithium (computed at the Becke3LYP/6-311+G** level) is even longer (13 pm, Fig. 22) due to the absence of other lithium ligands. Due to the unfavorable lone pair repulsions in the *s-cis*-form, the favored *s-trans* conformation of the α-methoxyvinyl anion (Fig. 22) differs both from that of its lithium derivative and from that of the parent ether. The 7.5 pm C-O bond elongation in the anion is much less than computed for the lithium derivative. This emphasizes the effect of ion pairing.[xxvia,b]



42



43

Fig. 21. Crystal structure of polymeric **41** showing the monoclinic unit cell (top). For clarity, the methylene and methyl hydrogen atoms of the ethoxy groups have been omitted (the labels with a letter identify atoms which are related by a C_2 axis). Chain structure of polymeric **41** showing the tetrameric subunits linked by Li-C π interactions (bottom).

Table 11. Selected bond distances (pm) and angles (deg.) of **41**.

Li(1)-O(1)	183.6(9)	Li(1)-O(2)	189.8(9)
Li(1)-C(2)	216.8(11)	Li(1)-C(6)	245.9(10)
Li(1)-C(6a)	222.1(10)	Li(2)-C(2)	223.4(10)
Li(2)-C(2a)	232.1(10)	Li(2)-C(6)	227.9(11)
Li(2)-C(9)	244.6(10)	Li(2)-C(10)	253.1(10)
Li(3)-C(10)	225.1(11)	Li(3)-C(14)	231.3(10)
Li(3)-C(22)	227.4(10)	Li(3)-C(5)	244.8(10)
Li(3)-C(6)	251.8(10)	Li(4)-C(10)	236.6(10)
Li(4)-C(14)	223.0(10)	Li(4)-C(18)	227.2(11)
Li(4)-C(13a)	242.5(10)	Li(4)-C(14a)	251.5(10)
Li(5)-O(4)	186.0(10)	Li(5)-O(5)	188.0(10)
Li(5)-C(14)	234.1(11)	Li(5)-C(18)	230.1(12)
Li(5)-C(22)	221.4(11)	Li(6)-O(3)	187.9(9)
Li(6)-O(6)	186.6(10)	Li(6)-C(10)	231.3(11)
Li(6)-C(18)	214.4(10)	Li(6)-C(22)	228.3(11)
Li bridged C=C (mean)	133.3(8)	non-bridged C=C (mean)	131.9(8)
C=C-O (mean)	117.7	C(1)-C(2)-Li(1)	172.1(5)
C(5)-C(6)-Li(1)	149.0(4)	C(9)-C(10)-Li(6)	156.5(5)
C(13)-C(14)-Li(5)	156.2(5)	C(17)-C(18)-Li(5)	163.8(6)
C(21)-C(22)-Li(6)	158.0(5)		

Fig. 22. Becke3LYP/6-311+G** optimized C_s geometries (energy minima) of monomeric α-methoxyvinyllithium, the *s-trans* α-methoxyvinyl anion, and *s-cis* methylvinylether. Note the different conformational preferences and the C-O bond lengths.

The lithium cations in the polymeric solid-state structure of **41** bridge the C-O bonds in notable ways: two lithiums in each tetramer coordinate simultanously to *two* oxygen atoms, i.e. Li1 to O1 and O2, Li1a to O1a and O2a, Li5 to O4 and O5, Li6 to O3 and O6 (Li-O distance: 183.6(9) - 189.8(9), mean: 187.0(10) pm) (Fig. 21, top). Pentacoordinate lithiums result. Similar double-coordination of lithium to two heteroatoms is found in 1-lithio-2-methoxybenzene,[c] where lithium bridges between carbon and a β-oxygen atom.

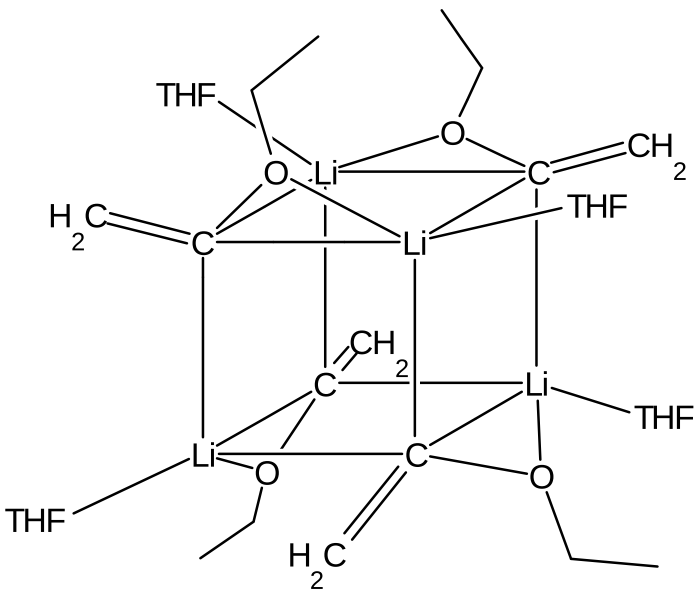
The two other lithium cations in each tetramer, Li2 and Li2a (as well as Li3 and Li4 in the polymeric chain), do *not* have oxygen contacts. Instead, these cations exhibit π interactions to the C=C double bonds of α-ethoxy-vinyllithium units in the neighbouring tetramer (Fig. 21). Consequently, these lithiums are σ-bonded to three vinylic carbon atoms (C-Li distance: 223.4(10) - 236.6(10) pm) and are η^2-coordinated to a C-C π bond. Hence, there are two different lithium environments in polymeric **41**: penta-coordination involving two oxygens and pentacoordination to five carbons, two of them π-bound.

The unusual manner in which neighbouring tetrameric subunits are connected—via Li-C_{vinyl} η^2-interactions—is intriguing (Fig. 21, bottom).[xxvia,b,xxvii,xxviii,xxixa-c] The Li-C π contacts in the solid-state structure of **41** saturate the lithium coordination sphere and link the tetramers into a polymeric chain. In contrast, the Li_4C_4 tetramers in polymeric [(PhC≡CLi)$_4$-(tetramethylhexanediamine)$_2$][ci] are joined by the diamine ligands to form helices. Since the π electrons are polarized towards the terminal carbon (C_β) upon lithiation (i.e., ethylvinylether vs **41**),[lvib] the C-Li distances to C_β are shorter (242.5(10) - 244.8(10) pm) than to C_α (251.5(10) - 253.1(10) pm). However, both distances are within the range of C-Li bond lengths observed for π-bonded lithiums.[xxvia,b,xxvii,xxviii,xxixa-c,cii]

Consistent with computational findings,[xciia,b] the lithium-bridged C=C bonds (average: 133.3(8) pm) are 1.4 pm (marginally but systematically) *longer* than the non-bridged C=C bonds (average: 131.9(8) pm]. At

Becke3LYP/6-311+G**, the C=C bond elongation in the Li^+—ethylene C_{2v} π complex is 1.2 pm.

4.2.3 Structure of α-ethoxyvinyllithium in THF solution



44

A low temperature ^{13}C NMR spectrum of α-ethoxyvinyllithium (**41**) reveals that the solid-state structure is not retained in [D_8]THF solution. At -90°C, a well resolved seven-line ^{13}C multiplet due to ^{13}C-^{6}Li scalar coupling is observed for the lithiated carbon (Figure 23, top). This is consistent with a *static* tetrameric aggregate **44**[ciii] ($^{1}J_{^{13}C\text{-}^{6}Li}$ = 5.0 Hz).[lv,lvi,lviia] The lithiated carbon, C_α, couples with three *equivalent* lithium cations.[lv,lvi,lviia] Coupling

Fig. 23. ^{13}C NMR spectra of **41**-^{6}Li at various temperatures ([D$_8$]THF, c = 3.4).

of $^{13}C_{\alpha}$ with the remote diagonal ^{6}Li nucleus in **44** is not observed. Raising the temperature to -70°C results in scrambling of the septet (Figure 23, top). However, resplitting of the ^{13}C NMR signal is not observed at still higher temperatures (Figure 23, bottom): due to rapid intraaggregate exchange of the lithium sites in the tetrameric cluster **44**, coupling of ^{13}C with *all four* ^{6}Li nuclei would result in a nine-line multiplet. Static and dynamic aggregates have been found for the vinyllithium[civ] and the *tert*-butyllithium tetramers.[cv]

A tetramer **44** with lithium bridging the C-O bond is confirmed by ^{6}Li-^{1}H heteronuclear Overhauser effect spectroscopy (HOESY; this NMR technique allows the detection of short contacts (< 3.5 Å) betweeen ^{6}Li and ^{1}H nucei and has become an effective tool for elucidation of the structure in solution of lithium compounds):[cvi] in [D_8]THF solution at -90°C, however in the presence of one equivalent of [H_8]THF per lithium, ^{6}Li cross peaks with nearly identical intensities to *all* hydrogens of **41**, as well as to the THF hydrogens are found (Figure 24). Close contacts between lithium and the methylene, and even the methyl hydrogens of the ethoxy group, demonstrate the lithium bridging of the C_{α}-O bond, in solution. Close contacts between lithium and the THF hydrogens indicate the coordination of an additional THF molecule to lithium.

A ^{13}C NMR spectrum of **41** shows that the methylene signal of the ethoxy group is shifted *upfield* relativ zu δ $^{13}C(OCH_2)$ of ethylvinylether, Δδ = 3.8. Due to close contacts between lithium and the ethoxy group (i.e. lithium bridging of the C_{α}-O bond), the electric field produced by lithium results in an upfield shift of the $^{13}C(OCH_2)$ signal (*cf.* the upfield shift of the $^{13}C(OCH_3)$ signal in **27**, Δδ = 1.4).[lxiii]

The downfield shift of the ^{13}C NMR signal of the lithiated carbon in **41** relative to the δ $^{13}C(1)$ of CH_2=CHOEt, Δδ = 60.7,[cvii] is typically large for carbenoids.[lvib,lvii,lviiic,lixe,cviii] This downfield shift exceeds that of „non-carbenoid“ tetrameric vinyllithium[cvib] (Δδ = 54.4).

Fig. 24. ^{1}H-^{6}Li HOESY, contour plot, of **41**-^{6}Li ([D_8]THF, -90°C, *c* = 3.4, mixing time τ = 1.2 sec).

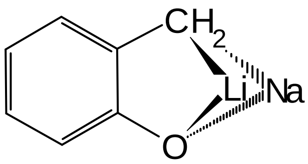
4.2.4 Conclusions

α-Ethoxyvinyllithium (**41**) adopts a novel polymeric structure in the solid state. Whereas Li_4C_4 tetramers in polymeric $[(PhC{\equiv}CLi)_4(\text{tetramethyl-hexanediamine})_2]$[ci] are joined by the diamine ligands, tetrameric subunits in **41** are linked by Li-C_{vinyl} π interactions. In THF solution, the polymeric chain is broken in THF-solvated tetrameric aggregates **44**. The lithium cation in **41** bridges the C_α-O bond both in the solid state and in THF solution. The C(Li)O carbenoid character of **41** is confirmed both by the C-O bond elongation and by the ^{13}C NMR characteristics.

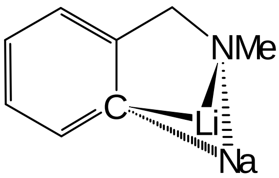
5 A mixed lithium—sodium aggregate comprising fused cyclopropenyl anion—amide moieties: the structure of a model super base

5.1 Introduction

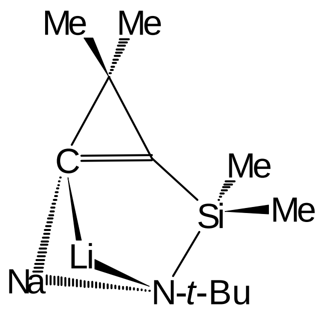
Super bases—mixtures of different bases—are valuable organometallic reagents.[xxvd,e,cix-cxiii] Wittig first reported the enhanced reactivity of a phenyllithium—phenylsodium combination compared to phenyllithium.[cx] Nearly three decades ago, Lochmann[cxi] and Schlosser[cxii] showed that mixing organolithium compounds with potassium (or sodium) alkoxides resulted in very strong bases (termed „LICKOR“ reagents). Similarly, addition of sodium or potassium alkoxides to lithium or sodium amides was found to increase the proton abstracting ability of the amide base.[cxiii] Because of their high ionic character alkali metal compounds are commonly aggregated.[xxvia,b,xxvii,xxviii,xxix] Structural evidence shows that the unimetal combinations $NaNH_2 \cdot NaO$-*t*-Bu,[cxiva] *n*-BuLi$\cdot$LiO-*t*-Bu,[lxx,cxivb] *n*-BuLi$\cdot$LiO-*n*-Bu,[cxivc] and lithium amide—lithium alkoxide/enolate mixtures[lxxi,lxxii,cxv] form complexes both in the solid state and in solution. However, the structure and the nature of the reactive species in solution for „LICKOR“ reagents are still speculative.[cxvi] Several experiments pointed to the pure potassium (or cesium[cxvi]) compound as being the metalating reagent.[cxiia,cxvi,cxvii] The superbasic species may well exist as an organometal—alkoholate combination.[cxviii] A recent theoretical study indicated that mixed alkali metal model dimers may be favored electrostatically.[cxix] Several X-ray structures of species with different alkali metals have been identified.[cxx] However, alkali metal complexes combining both carbanion and alkoxide or amide residues as well as different cations are rare.[cxxi] The X-ray structure of lithium 4,6-dimethyl-2-sodiomethylphenoxide (**45**) revealed a tetrameric TMEDA-solvated aggregate in which the C/O dianions chelate both the Li^+ and the Na^+ cations: the central Li_4O_4 cubic core with benzyl sodium side arms stresses the importance of Li-O bonding.[cxxia] Both Li-N and Li-C interactions were found to dominate the structural framework of the Li/Na phenyl anion/amide species **46** which also adopts a TMEDA-solvated tetramer in the solid state.[cxxib] The two complexes of carbanion and alkoxide/amide moieties represent super base models. The X-ray analysis of a heterobimetallic Li/Na compound **47** combining fused cyclopropenyl anion and amide moieties are reported in the following section. Its structure will be compared with that of its dilithium congener **30**.[lxiv]



45



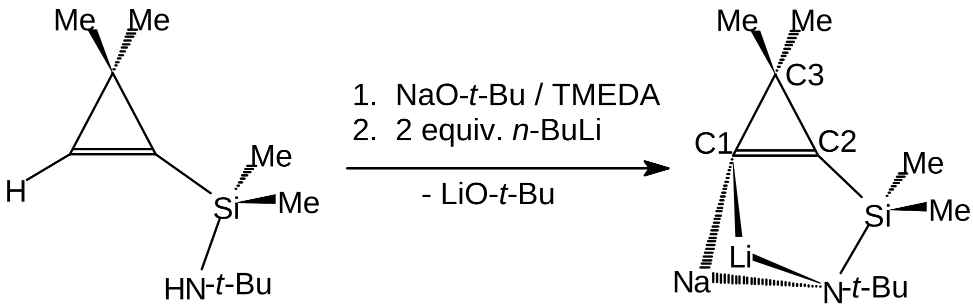
46



47

5.2 Synthesis and crystal structure of the mixed lithium—sodium species **47**

Equimolar amounts of 1-(*tert*-butylaminodimethylsilyl)-3,3-dimethyl-cyclopropene, NaO-*t*-Bu, and TMEDA were dissolved in THF. Subsequent dimetalation using two equivalents of *n*-butyllithium in hexane, yielded the bimetallic compound **47** (eq 7) which crystallizes as a THF solvate, (**47** • 2THF)$_2$.



(7)

The structure of (**47** • 2THF)$_2$ adopts a self-assembled, crystallographically centrosymmetric dimer in the solid state (depicted in Figure 25; bond distances and angles are given in Table 12). No complex between compound **47** and the resulting LiO-*t*-Bu could be isolated (eq 7); however, the Li/Na species **47** represents an internally mixed aggregate.

Fig. 25. X-ray structure of (**41**·2THF)$_2$. The hydrogen atoms have been omitted for clearity.

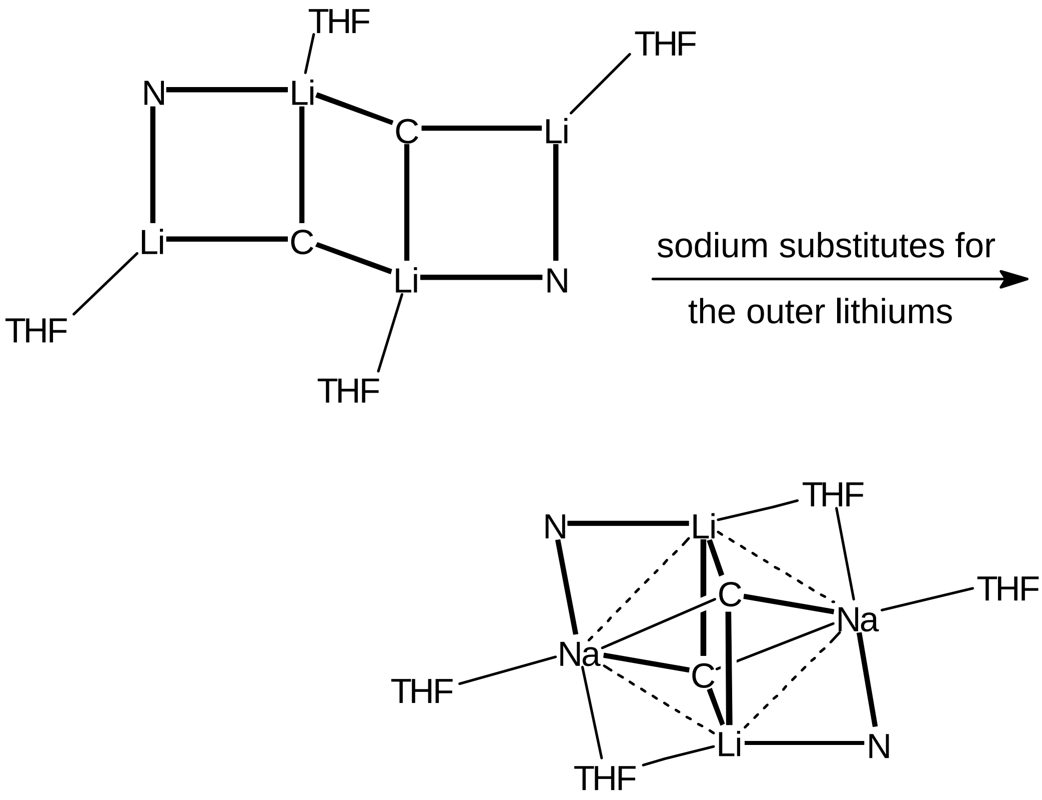
Table 12. Selected bond distances (pm) and angles (deg.) of $(\mathbf{47}\cdot 2THF)_2$.

C(1)-C(2)	133.5(4)	C(1)-C(3)	154.7(3)
C(2)-C(3)	148.5(2)	C(2)-Si(1)	184.9(3)
Si(1)-N(1)	168.1(2)	N(1)-C(8)	147.2(3)
C(1)-Li(1)	237.8(4)	C(1)-Li(1A)	218.4(4)
C(1)-Na(1)	307.9(3)	C(1)-Na(1A)	257.6(3)
N(1)-Li(1)	203.0(4)	N(1)-Na(1)	242.7(2)
O(20)-Na(1)	237.0(12)	O(30)-Na(1)	254.5(2)
O(30)-Li(1A)	201.1(4)		
C(1)C(2)C(3)	66.3(2)	C(2)C(1)C(3)	61.5(2)
C(1)C(3)C(2)	52.2(2)	C(1)C(2)Si(1)	143.1(2)
C(2)Si(1)N(1)	101.53(10)	Li(1)C(1)Li(1A)	85.4(2)
Na(1)C(1)Na(1A)	107.80(8)	C(1)Li(1)C(1A)	94.6(2)
C(1)Na(1)C(1A)	72.20(8)	Li(1)N(1)Na(1)	71.22(12)
Li(1A)O(30)Na(1)	78.23(12)	O(20)Na(1)O(30)	84.9(7)

Remarkably, an *octahedral* $[Li_2Na_2C_2]^{2+}$ ion cluster comprises the structural core of $(\mathbf{47}\cdot 2THF)_2$. The two Li-C and the two Na-C distances both differ significantly in length: Li1-C1A [218.4(4) pm] is similar to the ca. 220 pm values found in the dimeric TMEDA-solvate of [3,3-dimethyl-2-(trimethylsilyl)cyclopropenyl]lithium, $(\mathbf{21}\cdot TMEDA)_2$;[xliv] Na1-C1A [257.6(3) pm] is comparable to Na-C distances in the mixed compound $[\{Na(TMEDA)\}_3][LiPh_4]$ (*cf.* the ca. 267 pm distances in a phenyl sodium dimer[cxxii]).[cxxg] The decidedly longer Li1-C1 and Na1-C1 bonds in $(\mathbf{47}\cdot 2THF)_2$ (237.8(4) and 307.9(3) pm, respectively) reflect the weaker C-M bonding in a monomer unit. Each C/N dianion chelates both a Li^+ and a Na^+ cation: the amide anions bridge two opposite Li-Na edges of the $[Li_2Na_2C_2]^{2+}$ unit which fuses five-membered chelate rings to four edges of the octahedron. The Li-N and the Na-N bond lenghts (203.0(4) and 242.7(2)pm, respectively) compare to values found for the μ_2 N-bridged cations in the two mixed Li/Na amides, $\{LiNa[N(CH_2Ph)_2]_2\cdot OEt_2\}_2$[cxxe] and $\{LiNa[N(SiMe_3)_2]_2\cdot 3THF\}$.[cxxf]

One of the two THF ligands per monomer unit coordinates simultanously to *two* cations, i.e. O30(THF) to Li1A and Na1 [O30-Li1A: 201.1(4), O30-Na1: 254.5(2) pm]. Whereas μ_2-bridging oxygen is well-known in alkali metal alkoxide and enolate structures,[xxixc,lxv] the rare μ_2 coordination mode of the ether oxygen in (**47**·2THF)$_2$ has only been reported before in the ladder structure of a lithium anilide solvate[cxxiii] and in the X-ray structures of three potassium compounds.[cxxiv] As the cation coordination depends on the ionic radius, μ_2-bridging THF results in bissolvation of the larger Na^+ (additionally coordinated by a disordered THF molecule) and monosolvation of the smaller Li^+.[cxxf,cxxii]

The intriguing octahedral structure of (**47**·2THF)$_2$ is unprecedented in alkali and mixed alkali metal compounds.[xxvia,b,xxvii,xxviii,xxix,cxx,cxxi] However, the $Li_2Na_2C_2$ octahedron with its two N-bridged Li-Na edges is closely related to the ladder-type core of the dilithium derivative **30** (Scheme 4, left); the structure of **30** also consists of a dimeric THF-solvate in the solid state, (**30**·2THF)$_2$(Figure 14).[lxiv] The structural influence of the larger Na^+ cations may be explained as follows: sodium substitutes for the outer lithium cations of the four-runged ladder core of (**30**·2THF)$_2$ (Scheme 4, left; note that the Na^+ cations are also positioned in the outer rungs in the ladder structure of the mixed Li/Na amide $\{LiNa[N(CH_2Ph)_2]_2\cdot OEt_2\}_2$[cxxe]). Subsequently, the ladder is twisted in a manner that the Na^+ cations obtain additional contacts to the central carbanions (Scheme 4, right; the twisted ladder framework is marked in bold type). This results in the octahedral structure of (**47**·2THF)$_2$ (Figure 25). As the lithiums in (**47**·2THF)$_2$ and the inner lithiums in (**30**·2THF)$_2$ are tetracoordinate—a preferred lithium environment, the additional Na1-C1 and Na1A-C1A contacts in (**47**·2THF)$_2$ thus increase the coordination number of the larger sodium cations to five (vs three-coordinate outer lithiums in (**30**·2THF)$_2$; Scheme 4, left).



Scheme 4. Comparison of the octahedral core of (**47**•2THF$_2$)$_2$ (right) with the ladder framework of its dilithium congener (**30**•2THF$_2$)$_2$ (left). The ladder framework is marked in bold type.

The dimeric structure of (**47**•2THF)$_2$, reminiscent of the $[Ba_6Li_3O_2]^{11+}$ polyion aggregate wrapped lipophilically by *tert*-butylate ions and THF molecules,[cxxv] can also be viewed as an eight-membered [Na-N-Li-O]$_2$ ring with the Li_2Na_2 metal core capped by the two cyclopropenyl anions (Figure 26): *four* cations are bound to the hexacoordinate cyclopropenyl carbons. Such high unsaturated carbon coordination numbers generally are found only in higher aggregates (tetramers, hexamers, polymers).[xxvia,b,xxvii,xxviii,xxix,cxx,cxxi]

Fig. 26. Part of the X-ray structure of (**47**$\cdot$2THF)$_2$ showing the eight-membered [Na-N-Li-O]$_2$ ring capped by the carbanionic moieties.

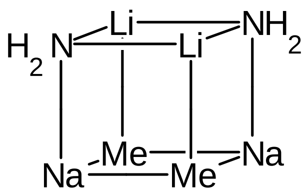
5.3 Theoretical investigations probing structural preferences of super base MeLi/$NaNH_2$ complexes

The structure of the mixed Li/Na phenyl anion/amid compound **46** adopts a tetrameric aggregate in which the lithium cations are positioned at the center, while the Na^+ cations occupy the outer regions.[cxxia] This results in the formation of the maximum number of electrostatically favorable Li-N and Li-C interactions. In contrast, contacts to the larger sodium over the Li^+ cations appear to be most important in the structural framework of (**47**·2THF)$_2$. Computations at the Becke3LYP/6-311+G** level on unsolvated aggregates of (MeLi·$NaNH_2$)$_2$ were performed to probe the structural preferences of super base complexes further.

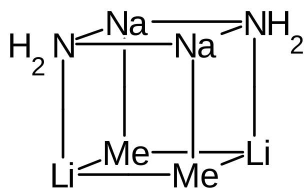
Table 13. Total energies ($E_{tot.}$, hartrees), zero-point vibrational energies (ZPE, kcal/mol) [a] and relative energies ($E_{rel.}$, kcal/mol) of unsolvated (MeLi·$NaNH_2$)$_2$ aggregates computed at Becke3LYP/6-311+G**.

	point group	$E_{tot.}$	ZPE [a]	$E_{rel.}$ [b]
48a	C_{2v}	-531.58699	72.8 (0)	0.0
48b	C_{2v}	-531.58578	72.6 (0)	0.5
49a	C_{2h}	-531.57976	72.6 (0)	4.3
49b	C_{2h}	-531.58097	72.5 (0)	3.4
50	C_{2h}	-531.57931	72.4 (0)	4.4

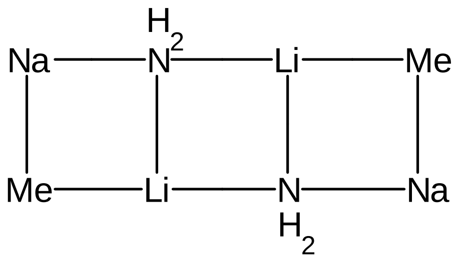
[a] Calculated at HF/6-31G* and scaled by 0.91. Number of imaginary frequencies given in parentheses. [b] Relative energies with ZPE correction.



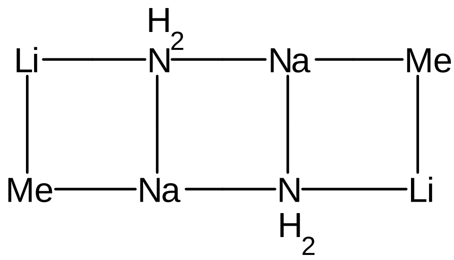
48a



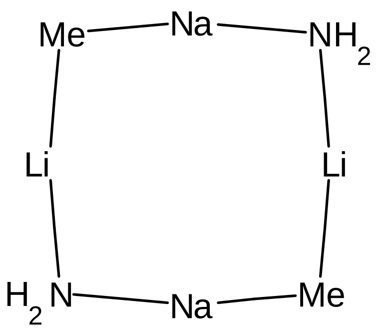
48b



49a



49b



50

Fig. 27. Schematic illustration of the Becke3LYP/6-311+G** optimized structures (energy minima at HF/6-31G*) of unsolvated aggregates of $(MeLi \cdot NaNH_2)_2$.

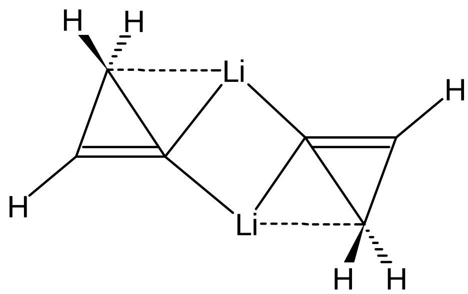
Five energy minima were calculated: two C_{2v}-symmetric cubane-like structures (the stack of $LiNH_2$ and MeNa dimers, **48a**, and the stack of MeLi and $NaNH_2$ dimers, **48b**), two planar ladders formed by lateral association of two $MeLi \cdot NaNH_2$ dimeric rings along the Li-N and Na-N bonds, respectively (**49a** and **49b**, C_{2h}), and a planar eight-membered ring (**50**, C_{2h}). The structures of the aggegates are represented schematically in Figure 27; the energies of the optimized species are given in Table 13. The aggregates are close in energy with the cube **48a** sightly favored over the cubic arrangement **48b** (by 0.5 kcal/mol), over the two ladders **49a** and **49b** (by 4.3 and 3.4 kcal/mol, respectively), and over the ring **50** (by 4.4 kcal/mol). Due to the highly ionic character of the M-N and M-C bonds (M = Li, Na),[xxvia,b,xxvii,cxxvi] the maximum number of electrostatic M-N/C attractions results in the cuban-like stacks **48a** and **48b**. However, the planar structures are only about 3-4 kcal/mol higher in energy. As was found with $(LiNH_2)_4$[lxxivd,lxxxii] and $(MeLi \cdot LiNH_2)_2$,[lxivb] the best orientation of the nitrogen lone pairs prefer the planar ring and the planar ladder arrangement to the cube. In contrast, the MeLi tetramer strongly favors a tetrahedral arrangement.[lxxxi,lxxxii] Interestingly, although the maximum number of Li-N contacts is present in the cubic structure **48a** (four Li-N vs two Na-N bonds), the cube **48b** is only 0.5 kcal/mol less stable. This indicates that Li-N bonding is only slightly preferred to Na-N bonding. The ladder structure **49a** has two more Li-N contacts, but is ca. 1 kcal/mol less stable than **49b** which can be attributed to stronger Li-N bonding within each $MeLi \cdot NaNH_2$ subunit in **49b**.[lxxivd,cxix] Whereas strong Li-O bonds (compared to Na-O bonds[cxix]) dominate the core of the mixed Li/Na carbanion/alkoxide species (**45**·TMEDA)$_4$[cxxib] and the unimetal super base *n*-BuLi·LiO-*t*-Bu,[lxx] as well as lithium amide—lithium alkoxide/enolate complexes,[lxxii,lxxxv,cxva] the small computed energy differences for $(MeLi \cdot NaNH_2)_2$ aggregates indicate that Li-N bonding is only favored slightly to Na-N interactions. While the structure of (**46**·TMEDA)$_4$ is dominated by the Li^+ cation interaction,[cxxia] the Na^+ cations dictate the octahedral core of (**47**·2THF)$_2$.

5.4 Conclusions

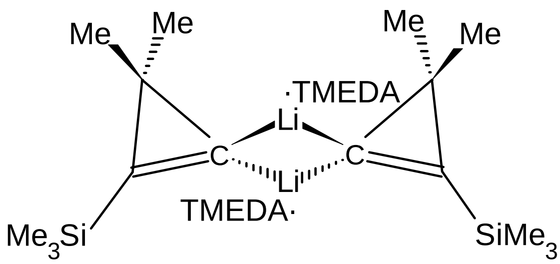
The structure of ($\mathbf{47}\cdot$2THF)$_2$ shows how a superbasic mixture of an organolithium compound and a sodium amide can aggregate. Whereas the structural framework of the intramolecular organosodium—lithium alkoxide super base **45**[cxxib] and of the unimetal *n*-BuLi$\cdot$LiO-*t*-Bu combination[lxx] are dictated by strong Li-O bonds,[cxix] Li-N interactions are less dominant in the structures of mixed Li/Na carbanion—amide complexes. While the structural core of ($\mathbf{46}\cdot$TMEDA)$_4$ is dictated by both carbanion and amide bonding to the lithium cations,[cxxia] the sodium cation interaction appears to be most important in determining the octahedral feature of ($\mathbf{47}\cdot$2THF)$_2$. The larger size of sodium over the lithium cations is responsible as is shown by comparison with the structure of the dilithium congener ($\mathbf{30}\cdot$2THF)$_2$.

Zusammenfassung

Ziel dieser Arbeit war es, ungewöhnliche Strukturen am Beispiel des planar tetrakoordinierten Kohlenstoffs zu realisieren. Da die wenigen experimentell verifizierten Beispiele mit planar tetrakoordiniertem Kohlenstoff („anti-van't Hoff-Systeme")—es handelt sich um polare Organometallverbindungen[xxi]—fast ausnahmslos dem Zufall zu verdanken sind, sollten gezielt Verbindungen mit dieser für Kohlenstoff ungewöhnlichen Umgebung synthetisiert werden. Aufmerksamkeit galt hierbei lithiumorganischen Verbindungen, da nach theoretischen Untersuchungen von Schleyer et al. das elektropositive Lithium die planare Geometrie des tetrakoordinierten Kohlenstoffs begünstigt[iii,iv].

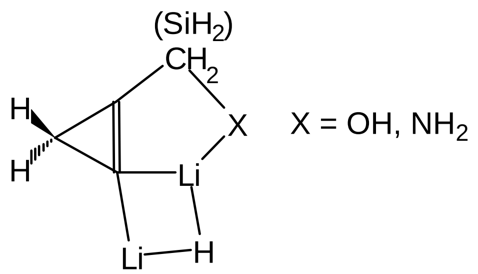


(**20**)$_2$

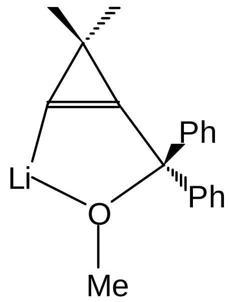


(**21**·TMEDA)$_2$

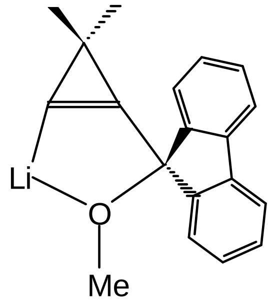
Rechnungen zeigten, daß für dimeres unsolvatisiertes 1-Lithiocyclopropen (**20**)$_2$ eine planare Struktur mit zwei planar tetrakoordinierten $R^1R^2CLi_2$-Fragmenten energetisch begünstigt ist (Kap. 2). Die Kristallstruktur einer Cyclopropenyllithiumverbindung, [3,3-Dimethyl-2-(trimethylsilyl)cyclopropenyl]lithium, ergab ein dimeres TMEDA-solvatisiertes Aggregat, (**21**·TMEDA)$_2$, das im Gegensatz zu (**20**)$_2$ aber keine planare Struktur mit planar tetrakoordinierten $R^1R^2CLi_2$-Fragmenten annimmt. Die Bevorzugung der „tetraedrischen“ Koordinationsgeometrie in (**21**·TMEDA)$_2$ läßt sich auf Solvatisierung der Li^+-Kationen durch die TMEDA-Liganden und sterische Wechselwirkungen zurückführen.



23 - 26



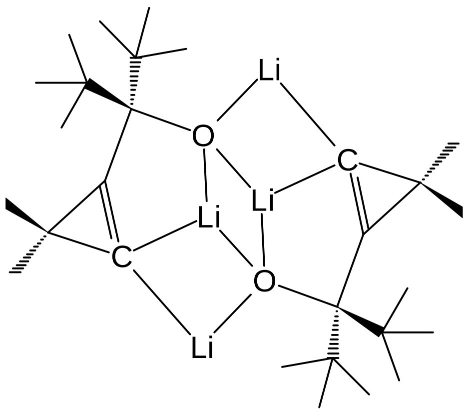
27



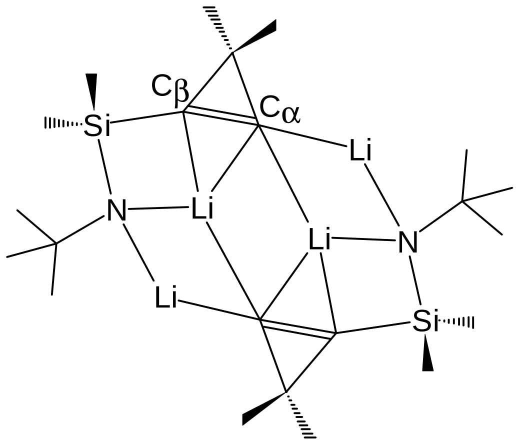
28

Durch „Einbau“ einer zusätzlichen Li^+-Koordinationsstelle in das Cyclopropenmolekül sollte das Problem der Solvatisierung gelöst werden: Rechnungen ergaben, daß die planaren Geometrien dimerer Modellverbindungen mit Heteroatomsubstituenten am olefinischen C_β-Atom (**23** - **26**) infolge intramolekularer Solvatisierung (Chelatisierung) der Li^+-Kationen wesentlich stabilisiert sind (Kap 3.2). Zwei Cyclopropenyllithiumderivate mit OR-Liganden wurden synthetisiert (**27** und **28**, Kap. 3.3). Obwohl NMR-Experimente für **27** die Bildung eines fünfgliedrigen Chelatringes anzeigten, konnte die Kristallstruktur beider Verbindungen nicht bestimmt werden.

Daß Chelatisierung die planare Struktur (**20**)$_2$ begünstigt, konnte in zwei Verbindungen gezeigt werden (Kap 3.4). Chelatisierung von Li^+ durch ein C/O-Dianion wurde in dilithiiertem 1-(Di-*tert*-butylhydroxymethyl)-3,3-dimethylcyclopropen realisiert. Zwei Kristallstrukturen der Dilithioverbindung zeigen ein dimeres Aggregat, (**29**·TMEDA)$_2$ und (**29**·2THF)$_2$, mit tetrakoordinierten $R^1R^2CLi_2$-Fragmenten, die nicht weit von planar tetrakoordiniertem Kohlenstoff entfernt sind (TMEDA- oder THF-Liganden sind aus Gründen der Übersicht weggelassen). Durch Ausbildung eines fünfgliedrigen OCCCLi-Chelatringes wird die planare Form begünstigt. Im dimeren Aggregat von dilithiiertem 1-(*tert*-Butyldimethylsilyl)-3,3-dimethylcyclopropen (**30** • 2THF)$_2$ liegen fast planar tetrakoordinierte $R^1R^2C_\alpha Li_2$-Umgebungen vor—die inneren Li^+-Kationen werden von C/N-Dianionen chelatisiert. Schwache Li-C-Kontakte zur zweiten Monomereinheit resultieren aber in pentakoordinierten C_α-Atomen. Infolge NSiCCLi-Chelatringbildung und Ladungslokalisation durch die Silylgruppe sind die C_β-Atome planar tetrakoordiniert.

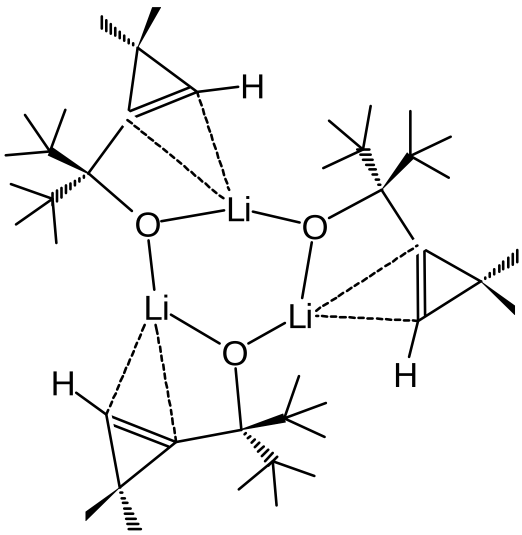


(**29**·TMEDA)$_2$
(**29**·2THF)$_2$

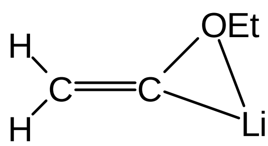


(**30**·2THF)$_2$

Neben Strukturen mit planar tetrakoordiniertem Kohlenstoff konnte die ungewöhnliche Struktur eines unsolvatisierten Lithiumalkoholats, Lithium-[di-*tert*-butyl-(3,3-dimethylcyclopropenyl)]methylat (**35**), aufgeklärt werden (Kap. 4.1). Im Kristall liegt **35** als Trimer (**35**)$_3$ vor—ein für Lithiumverbindungen seltener Aggregationsgrad. Strukturelle Charakteristika des Trimers —alternierende Li-O-Bindungslängen und auf benachbarte Li^+-Kationen hingebogene Cyclopropenylringe—zeigten die Bedeutung von Li^+-„Solvatisierung“ durch die Cyclopropen-C=C-Bindung für die Stabilisierung von Kation in niedrigen Koordinationszahlen auf. Dies wurde durch Dichtefunktional-Rechnungen bestätigt.

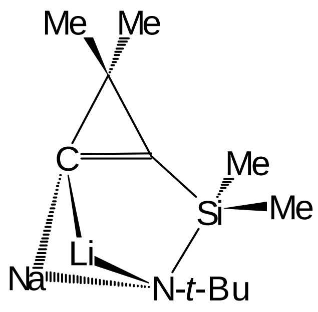


$(\mathbf{35})_3$



41

Die ungewöhnliche Struktur von α-Ethoxyvinyllithium (**41**) wurde durch Röntgenspektroskopie aufgeklärt (Kap. 4.2). Zwei unterschiedliche Li-Umgebungen kennzeichnen die solvensfreie, polymere Struktur von **41**: die Tetramerenkette wird durch Li-Atome aufgebaut, die durch zwei O- und drei C- bzw. durch fünf C-Atome koordiniert sind. In THF liegt **41** dagegen tetramer vor. Der C(Li)O-carbenoide Charakter von **41** äußert sich einer deutlich verlängerten C_α-O-Bindung und in überbrückendem Lithium, was durch theoretische Untersuchungen untermauert werden konnte.



47

Am Beispiel einer Cyclopropenmetallverbindung mit Carbanion- und Amid-Funktionalitäten (**47**) wurde der strukturelle Einfluß unterschiedlicher Alkalimetalle untersucht (Kap. 5). Dies lieferte Hinweise auf die Strukturen der synthetisch wichtigen „Superbasen“. Während stabile Li-O-Bindungen[cxix] die Würfelstuktur einer Organonatrium—Lithiumalkoxid-Verbindung (**45**)[cxxia] und die Kristallstruktur des (n-BuLi $\cdot$ LiO-t-Bu)$_4$ Aggregats beherrschen[lxx], zeigten Dichtefunktional-Berechnungen, daß Li-N-Wechselwirkungen in gemischten (MeNa $\cdot$ -LiNH$_2$)$_2$-Komplexen keine ähnlich dominierende Rolle spielen. Elektrostatische Wechselwirkungen zu den größeren Natrium-Kationen bestimmen sogar den „Oktaederkern“ von (**47** $\cdot$ 2THF)$_2$, wie ein Vergleich mit der Struktur des Dilithium-Derivats ((**30** $\cdot$ 2THF)$_2$) zeigte.

Experimental Section

General Conditions. All metalation experiments were carried out under an argon atmosphere by using standard Schlenk and needle/septum techniques. Solvents were freshly destilled from sodium/benzophenone ketyl prior to use. — NMR spectra were recorded on a JEOL GX 400 spectrometer; ^1H and ^{13}C chemical shifts are given with respect to TMS and are based on the solvent signals ($CDCl_3$: δ = 7.24/77.0, C_6D_6: δ = 7.15/128.0, [D_8]toluene: δ = 7.19/127.80, [D_8]THF: δ = 3.58/67.4, [D_6]acetone: δ = 2.04/206.30). — IR spectra were recorded on a Beckman AccuLab 1.3.

1 Syntheses of 3,3-dimethyl-1-(trimethylsilyl)cyclopropene and [3,3-dimethyl-2-(trimethylsilyl)cyclopropenyl]lithium (**21**)

3,3-Dimethyl-1-(trimethylsilyl)cyclopropen was prepared according to de Meijere et al.[xlvie] (method A) and Baird et al.[xlvii,j] (method B).

<u>Method A (4 steps):</u> Cyclopropanation of isobutene with bromoform afforded 1,1-dibromo-2,2-dimethylcyclopropane which was reduced to 1-bromo-2,2-dimethylcyclopropane. Dehydrobromination resulted in 3,3-dimethylcyclopropen which was transformed to the lithium derivative. Reaction with trimethylsilyl chloride gave 3,3-dimethyl-1-(trimethylsilyl)cyclopropen.

1,1-Dibromo-2,2-dimethylcyclopropane [cxxvii]

At ca. + 10°C, aqueous 50% NaOH solution (200 ml) was added dropwise during 1 h to a stirred mixture of isobutene (150 g, 2.6 mol), bromoform (126 g, 0.5 mol), 20 ml EtOH, 260 ml CH_2Cl_2, and benzyltriethylammonium chloride (1 g). The resultant mixture was stirred for 5 h. On warming to room temperature overnight excess isobutene evaporated. The residue was poured into 700 ml water. The mixture was extracted with CH_2Cl_2 (4 x 200 ml), the organic extract washed with 100 ml 5% HCl and 400 ml water, and dried over Na_2SO_4. The solvent was removed under vaccuum and the residual liquid destilled. The product was obtained as a colorless liquid, yield 103.4 g (90%); b.p. 60°C/20 torr.

^{1}H-NMR (400 MHz, $CDCl_3$, RT): δ = 1.45 (s, 2H, CH_2), 1.41 (s, 6H, CH_3); ^{13}C-NMR (100.6 MHz, $CDCl_3$, RT): δ = 39.7 (CBr_2), 35.0 (CH_2), 26.3 (*C*CH_3), 25.3 (CH_3); IR (liquid): 3010, 2980, 2945, 1465, 1450, 1440, 1050, 690.

1-Bromo-2,2-dimethylcyclopropane [cxxviii]

During 6 h, tri-*n*-butyltin hydride (132.0 g, 0.45 mol) was added dropwise to 1,1-dibromo-2,2-dimethylcyclopropane (103.4 g, 0.45 mol) with stirring under nitrogen. The temperature was maintained below +50°C. The mixture was then stirred at 30°C for 2 h. Destillation at reduced pressure gave 48.2 g product (71%) as a colorless liquid; b.p. 35°C/20 torr.

^{1}H-NMR (400 MHz, $CDCl_3$, RT): δ = 2.82 (dd, 1H, CHBr), 1.26 (s, 3H, *cis*-CH_3), 1.12 (s, 3H, *trans*-CH_3), 0.97 (dd, 1H, *cis*-H) 0.64 (dd, 1H, *trans*-H); ^{13}C-NMR (100.6 MHz, $CDCl_3$, RT): δ = 30.4 (CHBr), 24.8 (CH_2), 23.2 (*cis*-CH_3), 22.8 (*trans*-CH_3), 17.4 (*C*CH_3); IR (liquid): 3080, 2960, 2930, 2880, 1450, 1380, 1210, 690.

3,3-Dimethylcyclopropene [cxxix]

At 90°C, a solution of KO-*t*-Bu (36.1 g, 0.32 mol) in 120 ml DMSO was added dropwise to 1-bromo-2,2-dimethylcyclopropane (48.0 g, 0.32 mol) during 5 h. The mixture was heated to 90 - 100°C for 3 h. The gaseous product was collected in a cooled (-78°C) tube as a colorless liquid (21.9 g, 65%) and purified by recondensation.

^{1}H-NMR (400 MHz, $CDCl_3$, 0°C): δ = 7.41 (s, 2H, =CH), 1.16 (s, 6H, CH_3); ^{13}C-NMR (100.6 MHz, $CDCl_3$, 0°C): δ = 123.8 (=C), 28.6 (CH_3), 16.0 (*C*CH_3); IR (gas): 3120, 2980, 2950, 2890, 1635, 1010.

3,3-Dimethyl-1-(trimethylsilyl)cyclopropene (21) [xlvie,cxxx]

At -60°C, *n*-butyllithium (0.027 mol, 16.9 ml of a 1.6 M hexane solution) was added dropwise to a solution of diisopropylamine (2.7 g, 0.027 mol) in 20 ml Et_2O. The mixture was stirred and allowed to warm to room temperature (within 30 min). At -76°C, the LDA solution was added dropwise to a mixture of 3,3-dimethylcyclopropene (1.82 g, 0.027 mol), 40 ml Et_2O, and TMEDA (4 ml, 0.027 mol). The mixture was stirred for 2 h and was then allowed to warm to room temperature (within 30 min). After cooling to - 50°C, chlorotrimethylsilane (3.6 g, 0.028 mol, 5% excess) in 10 ml Et_2O was added, the mixture stirred at room temperature overnight, and then hydrolysed with 10 ml of satd. NH_4Cl solution. After separation, the organic phase was washed with satd. NH_4Cl solution (3 x 10 ml), and dried over Na_2SO_4. Destillation gave the product as a colorless liquid, yield 1.86 g (49%); b.p. 50°C/70 torr.

^{1}H-NMR (400 MHz, $CDCl_3$, RT): δ = 7.85 (s, 1H, =CH), 1.11 (s, 6H, CH_3), 0.13 (s, 9H, $SiCH_3$); ^{13}C-NMR (100.6 MHz, $CDCl_3$, RT): δ = 136.5 (C(2)), 134.1 (C(1)), 28.8 (C*C*H_3), 16.9 (C(3)), -1.0 ($SiCH_3$); IR (liquid): 3105, 2965, 2940, 1675, 1245, 855, 830.

Method B (3 steps): Cyclopropanation of 1-bromo-2-methylpropen with bromoform afforded 1,1,3-tribromo-2,2-dimethylcyclopropane. Reaction with MeLi gave 1-lithio-3,3-dimethylcyclopropene which was trapped with chlorotrimethylsilane to form 3,3-dimethyl-1-(trimethylsilyl)cyclopropene.

1-Bromo-2-methylpropene [cxxxi]

At ca. 130°C, 1,2-dibromo-2-methylpropane (130 g, 0.60 mol; obtained by reaction of bromine with *t*-BuOH [cxxxi]) was added dropwise to a stirred mixture of KOH (45 g, 0.80 mol) in 120 ml ethylene glycol. The product destilled and was collected, washed with 5% KOH (10 ml) and water (3 x 10 ml), dried over Na_2SO_4, and destilled through a Vigreux column. The product (40g, 49%) was obtained as a colorless liquid; b.p. 94°C/760 torr.

^{1}H-NMR (400 MHz, $CDCl_3$, RT): δ = 5.85 (m, 1H, =CH), 1.80 (s, 6H, *cis*- und *trans*-CH_3); ^{13}C-NMR (100.6 MHz, $CDCl_3$, RT): δ = 138.0 (=CHBr), 100.5 (=*C*CH_3), 24.1 (*cis*-CH_3), 20.7 (*trans*-CH_3); IR (liquid): 3080, 2980, 2930, 1630, 1275, 1150, 1050, 750, 700.

1,1,3-Tribromo-2,2-dimethylcyclopropane [xlvii,j]

Improved synthesis: At room temperature, NaOH (60 g) in 60 ml water was added over 1 h to a rapidly stirred solution of 1-bromo-2-methyl-propene (40 g, 0.30 mol), bromoform (90 ml, 1.03 mol), 170 ml CH_2Cl_2, 14 ml EtOH, and benzyltriethylammonium chloride (0.8 g). The mixture was heated for 7 h and then poured into 450 ml water. After separation, the aqueous phase was extracted with CH_2Cl_2 (3 x 100 ml), the combined organic layers were washed with 2% HCl and dried over Na_2SO_4. The solvent was removed and the residue destilled under vacuum. The product was obtained as a colorless liquid, yield 46.3 g (51%); b.p. 52°C/0.15 torr.

^{1}H-NMR (400 MHz, $CDCl_3$, RT): δ = 3.47 (s, 1H, CHBr), 1.51 (s, 6H, *trans*-CH_3), 1.37 (s, 6H, *cis*-CH_3); ^{13}C-NMR (100.6 MHz, $CDCl_3$, RT): δ =

42.9 (CBr_2), 42.6 (CHBr), 25.6 (*trans*-CH_3), 22.7 (*cis*-CH_3); IR (liquid): 3040, 2970, 2930, 1440, 1235, 980, 770, 670.

3,3-Dimethyl-1-(trimethylsilyl)cyclopropene [xlvii]

At ca. -80°C, methyllithium (0.073 mol, 45.6 ml of a 1.6 M Et_2O solution) was added over 30 min to a stirred solution of 1,1,3-tribromo-2,2-dimethylcyclopropane (9 g, 0.029 mol) in 80 ml Et_2O. The mixture was allowed to warm to room temperature and, after 30 min, was cooled again to -50°C. Trimethylsilyl chloride (4.3 ml, 0.034 mol) was added over 10 min. After 20 min, the mixture was warmed to room temperature, stirred for 2 h, and hydrolyzed with 40 ml cold water. After separation, the aqueous phase was extracted with Et_2O (3 x 30 ml) and the combined organic layers were dried over Na_2SO_4. The solvent was removed under vacuum at 0°C and the residue destilled. The product was obtained as a colorless liquid, yield 2.5 g (62%); b.p. 45°C/65 torr.

(for spectoscopic data, see above).

Synthesis und crystal structure of {[3,3-dimethyl-2-(trimethylsilyl)-cyclopropenyl]lithium-TMEDA}$_2$, (21 · TMEDA)$_2$

At ca. -60 °C, *n*-butyllithium (0.58 mmol, 0.36 ml of a 1,6 M hexane solution) was added dropwise to a well-stirred solution of 3,3-dimethyl-1-(trimethylsilyl)cyclopropene (0.081g, 0.58 mmol) and TMEDA (0.09 ml, 0.58 mmol) in 0.5 ml hexane. This caused a white solid to precipitate, which dissolved on warming to room temperature (within 30 minutes). Evaporization of the solvent at 0°C yielded crude product which was recrystallized from *n*-hexane by cooling the solutions to +4 °C. Thus, colorless crystals suitable for X-ray structure analysis were obtained. The crystals were selected and transported to the diffractometer at -50°C [cxxxii]. ^1H NMR ([D$_8$]THF, -20°C): δ = 1.02 (6 H, s, CH_3), 0.03 (9 H, s, SiCH_3); TMEDA signals at δ = 2.32 (4 H, s, NCH_2), 2.19 (12 H, s, NCH_3). ^{13}C NMR ([D_8]THF, -20°C): δ = 192.19 (C(1)), 139.73 (C(2)), 33.22 (CCH$_3$), 12.82 (C(3)), 1.17 (SiCH$_3$); TMEDA signals at δ = 58.26 (NCH$_2$), 46.54 (NCH$_3$).

Crystal data of (21 · TMEDA)$_2$: [$C_{28}H_{62}Li_2N_4Si_2$] in the asymmetric unit, M = 524.88, monoclinic, space group $P2_1$/n, a = 1879.9(2), b = 1035.0(2), c = 2045.5(2) pm, β = 113.198(9) °, V = 3.6580(8) nm^3, Z = 4, D_{calc} = 0.953 Mg/m^3, F(000) = 1168, λ = 71.073 pm, T = 153(2) K, μ (Mo-K$_\alpha$) = 0.116 mm^{-1}, data were collected on a Stoe-Siemens-AED. Intensities of a 0.6 x 0.6 x 0.8 mm rapidly cooled crystal in an oil drop [cxxxii] were collected by the 2θ /ω method in the range of 8 ° ≤ 2θ ≤ 55 °. Of a total of 9413 refections, 8446 were independent and used to refine 431 parameters, largest difference peak and hole: 345 and -278 enm^{-3}, $R1$ (F > 4σ (F)) = 0.0491 and $wR2$ = 0.1381 (all data), with $R1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$ and $wR2 = (\Sigma w (F_o^2 - F_c^2)^2 / \Sigma w (F_o^2)^2)^{0.5}$. The structure was solved with direct methods (SHELXS-90 [cxxxiii]) and refined by full-matrix least-squares on F^2 (SHELXL-93 [cxxxiv]). A riding model was applied to refine the hydrogen atom positions. The twist disorder of the TMEDA ethylene bridges and the TMEDA methyl groups has successfully been refined in two positions.

2 Syntheses of 3,3-dimethyl-1-(1,1-diphenylmethoxymethyl)-cyclopropene and [3,3-dimethyl-1-(1,1-diphenylmethoxymethyl)-cyclopropenyl]lithium (**27**)

3,3-Dimethyl-1-(1,1-diphenylmethoxymethyl)cyclopropene was synthesized in two steps: reaction of (3,3-dimethylcyclopropenyl)lithium with benzophenone afforded the alcohol which was transformed to the corresponding methylether.

3,3-Dimethyl-1-(1,1-diphenylhydroxymethyl)cyclopropen

At -60°C, *n*-butyllithium (0.033 mol, 20.6 ml of a 1.6 M hexane solution) was added dropwise to a solution of diisopropylamine (4.6 ml, 0.033 mol) in 14 ml THF. The mixture was stirred and allowed to warm to room temperature (within 30 min). At ca. -80°C, the LDA solution was added dropwise to a mixture of 3,3-dimethylcyclopropene (2.30 g, 0.033 mol), 17 ml THF, and TMEDA (5.0 ml, 0.033 mol) (for the preparation of similar compounds, see ref [cxxxv]). After 2 h, the mixture was allowed to warm to room temperature, stirred for 30 min, and then cooled to -40°C. Benzophenone (6.0 g, 0.033 mol) dissolved in 7 ml THF was added dropwise. The mixture was stirred for 2 h, warmed to room temperature, and hydrolyzed with 15 ml satd. NH_4Cl solution. After separation, the organic phase was washed with 10 ml NH_4Cl solution and 10 ml water and dried over Na_2SO_4. The solvent was removed under vacuum to give 5.4g (66%) of product as a yellow oil. This was used in the subsequent reaction without further purification.

^{1}H-NMR (60 MHz, $CDCl_3$, RT): δ = 7.30 (br, 10H, *Phenyl*-H), 7.20 (s, 1H, =CH), 2.53 (br, 1H, OH), 1.13 (s, 6H, CH_3).

3,3-Dimethyl-1-(1,1-diphenylmethoxymethyl)cyclopropene

The mixture of 3,3-dimethyl-1-(1,1-diphenylhydroxymethyl)cyclopropene (5.4g, 0.022 mol), iodomethane (12.2 g, 0.088 mol), powdered BaO (7 g, 0.045 mol), and 20 ml DMSO was gently heated to ca. 60°C during 30 min (analogous to ref [cxxxvi]). After an induction period, a rapid reaction occurred (boiling of iodomethane). The mixture was cooled to ca. +30°C, stirred for 4 h, diluted with 50 ml $CHCl_3$, and hydrolysed with 40 ml satd. NH_4Cl solution. Hexane (40 ml) was added. After separation, the organic layer was washed with water (2 x 20 ml) to remove residual DMSO and dried over Na_2SO_4. The solvent was removed and the resulting yellow oil purified by column chromatography (SiO_2, $CCl_4/CHCl_3$ = 5/1) to afford 3.52 g (60%) of product as a colorless oil.

^{1}H-NMR (400 MHz, $CDCl_3$, RT): δ = 7.41 (d, 4H, *ortho*-H), 7.32 (s, 1H, =CH), 7.29 (t, 4H, *meta*-H), 7.24 (t, 2H *para*-H), 3.23 (s, 3H, OCH_3), 1.08 (s, 6H, CCH_3); ^{13}C-NMR (100.6 MHz, $CDCl_3$, RT): δ = 143.5 (*ipso*-C), 136.3 (C(1)), 127.9 (*ortho*-C), 127.4 (*meta*-C), 127.2 (*para*-C), 118.7 (C(2)), 83.6 (*C*OCH_3), 52.4 (OCH_3), 27.2 (C*C*H_3), 21.2 (C(3)); IR (liquid): 3060, 3030, 2965, 2940, 1730, 1600, 1450, 1070, 750, 695.

[3,3-Dimethyl-1-(1,1-diphenylmethoxymethyl)cyclopropenyl]lithium (27)

At ca. -60 °C, *n*-butyllithium (0.35 mmol, 0.21 ml of a 1.6 M hexane solution) was added dropwise to a well-stirred solution of 3,3-dimethyl-1-(1,1-diphenylmethoxymethyl)cyclopropene (0.092 g, 0.35 mmol) in 0.6 ml hexane and 0.2 ml benzene. A white solid precipitated within 15 min. The mixture was stirred for 1.5 h and was then allowed to warm to room temperature. After the solid had dissolved, the slightly yellow solution was stirred for 5 min. Crystals suitable for NMR studies were obtained by cooling the solution to ca. -20°C.

^{1}H-NMR (400 MHz, [D$_8$]THF, RT): δ = 7.66 (d, 4H, *ortho*-H), 7.13 (4H, *meta*-H), 7.05 (2H, *para*-H), 3.17 (OCH_3), 0.97 (6H, CCH_3); ^{13}C-NMR (100.6 MHz, [D$_8$]THF, -40°C): δ = 168.5 (C(1)), 149.0 (*ipso*-C), 143.6 (C(2)), 129.0 (*ortho*- and *meta*-C), 127.3 (*para*-C), 84.7 (C(Ph)$_2$), 51.4 (OCH_3), 31.7 (C*C*H$_3$), 15.7 (C(3)).

3 Syntheses of 9-(3,3-dimethylcyclopropenyl)-9-methoxyfluorene and 9-(3,3-dimethyl-2-lithiocyclopropenyl)-9-methoxyfluorene (**28**)

9-(3,3-Dimethylcyclopropenyl)-9-methoxyfluorene was synthesized as described for 3,3-dimethyl-1-(1,1-diphenylmethoxymethyl)cyclopropene.

9-(3,3-Dimethylcyclopropenyl)-9-hydroxyfluorene

At ca. -80°C, a LDA solution in hexane/THF (0.026 mol, obtained as described above) was added dropwise to a mixture of 3,3-dimethylcyclopropene (1.74 g, 0.026 mol), 15 ml THF, and TMEDA (3.9 ml, 0.026 mol) (for the preparation of similar compounds, see ref [cxxxv]). After 2 h, the mixture was allowed to warm to room temperature, stirred for 30 min, and then cooled to -40°C. Fluorenone (4.6 g, 0.026mol) dissolved in 7 ml THF was added dropwise. The mixture was stirred for 2 h, warmed to room temperature, and hydrolyzed with 20 ml satd. NH_4Cl solution. After separation, the organic phase was washed with water (3 x 10 ml) and dried over Na_2SO_4. The solvent was removed under vacuum to give 3.9g (61%) of product as a red oil. This was used in the subsequent reaction without further purification.

[1]H-NMR (60 MHz, $CDCl_3$, RT): δ = 7.40 (br, 8H, *fluorenyl*-H), 6.95 (s, 1H, =CH), 2.00 (br, 1H, OH), 0.95 (s, 6H, CH_3).

9-(3,3-Dimethylcyclopropenyl)-9-methoxyfluorene

The mixture of 9-(3,3-dimethylcyclopropenyl)-9-hydroxyfluorene (3.9 g, 0.016 mol), iodomethane (8.9 g, 0.063 mol), powdered BaO (4.8 g, 0.032 mol), and 17 ml DMF was gently heated to ca. 70°C (analogous to ref [cxxxvi]). After an induction period, a rapid reaction occurred (boiling of iodomethane). The mixture was cooled to ca. +30°C, stirred for 4 h, diluted with 100 ml $CHCl_3$, and hydrolysed with 40 ml satd. Na_2CO_3 solution. After separation, the organic layer was washed with 40 ml satd. Na_2CO_3 solution and 20 ml satd. $Na_2S_2O_3$ solution, and dried over Na_2SO_4. The solvent was removed under vacuum and the resulting red oil purified by flash chromatography (SiO_2, CH_2Cl_2/hexane = 3/1) to afford 2.52 g (56%) of product as a red oil.

[1]H-NMR (400 MHz, $CDCl_3$, RT): δ = 7.66 (d, 2H, H(1,8), 7.48 (d, 2H, H(4,5), 7.37 (t, 2H, H(2,7)), 7.28 (t, 2H H(3,6), 7.09 (s, 1H, =CH), 2.97 (s, 3H, OCH_3), 0.97 (s, 6H, CCH_3); [13]C-NMR (100.6 MHz, $CDCl_3$, RT): δ = 143.7 (C(8a,9a)), 140.4 (C(4a,4b), 135.4 (*cyclopropene*-C(1)), 129.3 (C(1,8)), 127.6 (C(4,5)), 125.2 (C(2,7)), 120.1 (C(3,6)), 115.2 (*cyclopropene*-C(2)), 86.1 (C(9)), 51.4 (OCH_3), 27.0 (C*C*H_3), 21.9 (*cyclopropene*-C(3)); IR (liquid): 3060, 2920, 1750, 1605, 1445, 1115, 1090, 760, 745, 730.

9-(3,3-Dimethyl-2-lithiocyclopropenyl)-9-methoxyfluorene (**28**) was synthesized as described for [3,3-dimethyl-1-(1,1-diphenylmethoxymethyl)-cyclopropenyl]lithium; the lithium compound could not be characterized, due to its low solubility.

4 Syntheses of 1-(di-*tert*-butylhydroxymethyl)-3,3-dimethylcyclopropene, 1-(*tert*-butylaminodimethylsilyl)-3,3-dimethylcyclopropene, and their dilithium derivatives **29** and **30**

1-(Di-*tert*-butylhydroxymethyl)-3,3-dimethylcyclopropene

The cyclopropene derivative was prepared by reaction of monolithiated 3,3-dimethylcyclopropene with 2,2,4,4-tetramethyl-3-pentanone as described by Cheskis et al. [cxxxv] (see above, synthesis of 3,3-dimethyl-1-(1,1-diphenylhydroxymethyl)cyclopropene) as a colorless liquid (bp 83°C /1 mbar., 58%).

^{1}H NMR (400 MHz, $CDCl_3$, RT): δ = 6.97 (s, 1H, vinylic H), 1.79 (br s, 1H, OH), 1.24 (s, 6H, $C(CH_3)_2$), 1.10 (s, 9H, *tert*-butyl); ^{13}C NMR (100.6 MHz, $CDCl_3$, RT): δ = 139.2 (C(1)), 116.0 (C(2)), 85.2 (COH), 40.6 ($\mathit{C}(CH_3)_3$), 29.1 ($C(\mathit{C}H_3)_3$), 28.0 ($C(\mathit{C}H_3)_2$), 22.0 (C(3)); IR (liquid): 3630, 2960, 2920, 1720, 1480, 1365, 990, 715.

Dimeric TMEDA-complexed dilithiated 1-(di-*tert*-butylhydroxymethyl)-3,3-dimethylcyclopropene, (29 · 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_2O/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. [cxxxii]

^{1}H NMR (400 MHz, [D$_8$]THF, +32°C): δ = 1.14 (s, 6 H, C(CH$_3$)$_2$), 1.05 (s, 18 H, *tert*-butyl); TMEDA signals at δ 2.31 (s, 4H, NC*H*$_2$), 2.16 (s, 12 H, NC*H*$_3$). ^{13}C NMR [cxxxvii] (100.6 MHz, [D$_8$]THF, +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, (29 · 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. [cxxxii]

^{1}H NMR [cxxxviii] (400 MHz, [D$_8$]THF, +30°C): δ = 1.09 (s, 6H, CH$_3$), 1.00 (s, 9H, *tert*-butyl); ^{13}C NMR [cxxxvii] (100.6 MHz, [D$_8$]THF, +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 (155.3 MHz, [D$_8$]THF, +30 °C, referenced to 1 M LiBr in [D$_8$]THF): δ = 0.99.

1-(*tert*-Butylaminodimethylsilyl)-3,3-dimethylcyclopropene was synthesized in two steps: reaction of (3,3-dimethylcyclopropenyl)lithium with dichlorodimethylsilane afforded 1-(chlorodimethylsilyl)-3,3-dimethylcyclopropen which was reacted with *tert*-butylamine.

1-(Chlorodimethylsilyl)-3,3-dimethylcyclopropen

At ca. -80°C, methyllithium (0.16 mol, 100 ml of a 1.6 M Et_2O solution) was added over 45 min to a stirred solution of 1,1,3-tribromo-2,2-dimethylcyclopropane (24.05 g, 0.078 mol) in 150 ml Et_2O (analogous to ref [xlvii]). The solution was stirred for 30 min at this temperature and then allowed to warm to room temperature (within 1 h). The solution was concentrated by removal of solvent (ca. 100 ml) under vacuum (at ca. +15°C) and then added dropwise over 45 min to a solution of dichlorodimethylsilane (9.5 ml, 0.078 mol) in 80 ml Et_2O at -30°C. The mixture was allowed to warm to room temperature (within 1 h), stirred for 2 h, and heated under reflux for 1.5 h. The precipitated LiCl was removed by filtration and washed with pentane (4 x 20 ml). The solvent was removed under vacuum at 0°C and the residue destilled. The product was obtained as a colorless liquid, yield 6.4 g (51%); b.p. 58-60°C/50 torr.

^{1}H NMR (400 MHz, $CDCl_3$, RT): δ = 8.14 (s, 1H, vinylic H), 1.18 (s, 6H, CCH_3), 0.55 (s, 6H, $SiCH_3$); ^{13}C NMR (100.6 MHz, $CDCl_3$, RT): δ = 140.8 (C(2)), 131.3 (C(1)), 28.3 (*C*CH_3), 19.4 (C(3)), 2.7 ($SiCH_3$).

1-(*tert*-Butylaminodimethylsilyl)-3,3-dimethylcyclopropene

1-(Chlorodimethylsilyl)-3,3-dimethylcyclopropen (6.4 g, 40 mmol) 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 residue was destilled under reduced pressure to give the product as a colorless liquid (5.1 g, 65 %); b.p. 52°C/5 mbar.

^{1}H NMR (400 MHz, $CDCl_3$, RT): δ = 7.81 (s, 1H, vinylic H), 1.16 (s, 9H, N-*t*-Bu), 1.13 (s, 6H, $C(CH_3)_2$), 0.74 (br s, 1H, NH), 0.17 (s, 6H, $SiCH_3$); ^{13}C NMR (100.6 MHz, $CDCl_3$, RT): 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 (29 · 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-dimethylcyclo-propene (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. Recrystalli-zation 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. [cxxxii]

^{1}H NMR [cxxxviii] (400 MHz, [D_8]THF, +32°C): δ = 1.22 (s, 9H, N-*t*-Bu), 1.11 (s, 6H, $C(CH_3)_2$), 0.13 (s, 6H, $SiMe_2$); ^{13}C NMR [cxxxvii] (100.6 MHz, [D_8]THF, +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 (155.3 MHz, [D_8]THF, +30 °C, referenced to 1 M LiBr in [D_8]THF): δ = 1.19.

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

Crystal data of (29·TMEDA)₂. [$C_{20}H_{40}Li_2N_2O$] in the asymmetric unit, M = 338.42, triclinic, space group $P1$, 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_α) = 0.063 mm^{-1}, T = 173(2) K. Intensities of a 0.7 x 0.6 x 0.6 mm rapidly cooled crystal in an oil drop [cxxxii] were collected by the 2θ/ω method in the range of 4 ° ≤ 2θ ≤ 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 (29·2THF)₂. [$C_{22}H_{40}Li_2O_3$] in the asymmetric unit, M = 366.42, orthorombic, 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_α) = 0.067 mm^{-1}, T = 153(2) K. Intensities of a 1.4 x 0.8 x 0.8 mm rapidly cooled crystal in an oil drop [cxxxii] were collected by the 2θ/ω method in the range of 8° ≤ 2θ ≤ 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 (30·2THF)₂. [$C_{38}H_{74}Li_4N_2O_4Si_2$] 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_α) = 0.115 mm^{-1}, T = 153(2) K. Intensities of a 1.2

x 1.1 x 0.9 mm rapidly cooled crystal in an oil drop [cxxxii] were collected by the 2θ/ω method in the range of $6^{o} \leq 2\theta \leq 45^{o}$. 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).

5 Synthesis and crystal structure of lithium di-*tert*-butyl-(3,3-dimethylcyclopropenyl)methoxide (**35**)

n-Butyllithium (1.8 mmol, 1.15 ml of 1.6 M hexane solution) was added to a solution of 1-(di-*tert*-butylhydroxymethyl)-3,3-dimethylcyclopropene (0.388 g, 1.8 mmol) in hexane (0.5 ml) at 0°C. The solution was stirred for 2 h at this temperature and 1 h at room temperature. The precipitated white solid dissolved on warming. Solvent was removed at 0°C. The crude product was recrystallized from *n*-hexane at 4°C. A second recrystallization from *n*-hexane at -30°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. [cxxxii]

^{1}H NMR (400 MHz, [D$_6$]benzene, +32°C): δ = 7.11 (s, 1 H, vinylic H), 1.33 (s, 6H, CH_3); 1.14 (s, 18 H, *tert*-butyl). ^{13}C NMR (100.6 MHz, [D$_6$]benzene, +32°C): δ = 149.7 (C(1)), 115.2 (C(2)), 87.8 (COLi), 41.2 (C(CH$_3$)$_2$, 30.4 (C(CH$_3$)$_3$, 28.7 (C(CH$_3$)$_3$), 25.6 (C(3)).

Crystal data of trimeric (35)$_3$. $[LiOC_{14}H_{25}]_6$ in the asymmetric unit, M = 216.28, triclinic, space group P-1, a = 1318.1(11), b = 1323.4(8), c = 2777(2) pm, $\alpha = 89.28(4)^{o}$, $\beta = 83.01(6)^{o}$, $\gamma = 60.86(3)^{o}$, $V = 64.194(5)$ nm^3, Z = 12, $D_{calc.}$ = 1.028 Mg/m^3, F(000) = 1440, λ = 71.073 pm , μ (Mo-K$_\alpha$) = 0.066 mm^{-1}, T = 153 (2) K, data were collected on a Stoe-Siemens-AED. Intensities of a 0.8 x 0.7 x 0.7 mm rapidly cooled crystal in an oil drop [cxxxii] were collected by the 2θ /ω method in the range of $5° \leq 2\theta \leq 45°$. Of a total of 11378 refections, 10936 were independent and 10929 used to refine 929 parameters, largest difference peak and hole: 396 and -340 enm^{-3}, $R1$ ($F > 4\sigma$ (F)) = 0.093 and $wR2$ = 0.285 (all data), with $R1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$ and $wR2 = (\Sigma w (F_o^2 - F_c^2)^2 / \Sigma w (F_o^2)^2)^{0.5}$. The structure was solved with direct methods (SHELXS-90 [cxxxiii]) and refined by full-matrix least-squares on F^2 (SHELXL-93 [cxxxiv]). A riding model was applied to refine the hydrogen atom positions of the other groups.

6 Syntheses of 1-ethoxyvinyltributylstannane and α-ethoxyvinyllithium (**41**)

1-Ethoxyvinyltributylstannane was prepared by reaction of α-ethoxyvinylpotassium [cxxxix] with tri-*n*-butyltin chloride [xcvie]

Ethylvinylether (43.3 g, 0.6 mol) was added to a solution of *t*-BuOK (24 g, 0.21 mol) in 180 ml THF at ca. 0°C. The mixture was cooled to -90°C and *n*-butyllithium (0.21 mol, 131 ml of a 1.6 M hexane solution) was added dropwise over 1 h. The temperature was kept between -70 and - 80°C during the addition. The mixture was then stirred for 30 min at this temperature and 10 min at -50°C. At ca. -70°C, tri-*n*-butyltin chloride (55 ml, 0.20 mol) was added dropwise over 10 min. This caused a white solid (KCl) to precipitate. The mixture was allowed to warm to room temperature (within 2 h), stirred overnight, and poured into 400 ml water. After separation, the aqueous phase was extracted with Et_2O (2 x 100 ml), the combined organic layers were washed with satd. NH_4Cl solution (2 x 100 ml) and 100 ml water, and dried over Na_2SO_4. Excess ethylvinylether and solvents were removed and the residue was destilled under vacuum through a Vigreux column to give the product as a colorless liquid (63 g, 84%); b.p. 93°C/0.15 torr.

^{1}H NMR (400 MHz, $CDCl_3$, RT): δ = 4.67 (s, 1H, H(trans), 4.04 (s, 1H, H(cis)), 3.69 (q, 2H, OCH_2), 1.53 (m, 6H, β-CH_2), 1.32 (m, 6H, γ-CH_2), 1.25 (t, 3H, O-CH_3), 0.94 (m, 9H, CH_3), 0.89 (t, 6H, α-CH_2); ^{13}C NMR (100.6 MHz, $CDCl_3$, RT): δ = 172.9 (C(α)), 95.4 (C(β)), 62.0 (OCH_2), 29.0 (β-CH_2), 27.3 (γ-CH_2), 14.6 (O-CH_3), 13.7 (CH_3), 9.8 (α-CH_2); IR (liquid): 3080, 2940, 2910, 1565, 1460, 1375, 1180, 1040, 805.

Synthesis and crystal structure of α-ethoxyvinyllithium (41)

n-Butyllithium (3.30 mmol, 2.06 ml of a 1.6 M hexane solution) was added to a solution of 1-ethoxyvinyltributylstannane (1.19 g, 3.30 mmol) in 17.0 ml hexane at -40 °C. The solution was then stirred for 5 h at 0°C. The product, a white precipitate, was warmed into solution (50°C). Cooling to +8°C yielded the crude product which was recrystallized from *n*-hexane at room temperature. This resulted in the formation of long, but very thin, colorless needles, which, under these conditions, are stable only for about 12 h. After several temptations, a single crystal suitable for X-ray analysis was obtained. The crystal was selected and transported to the diffractometer at -50°C. [cxxxii]

^{1}H NMR [cxl] (400 MHz, [D_8]THF, *c* = 3.4, -50°C): δ = 4.85 (s, 1H, H_{trans}), 3.96 (s, 1H, H_{cis}), 3.58 (q, ^{3}J (H,H) = 13.4 Hz, 2H, CH_2), 1.29 (t, ^{3}J (H,H) = 13.4 Hz, 3H, CH_3); ^{13}C-NMR [cvii] (100.6 MHz, [D_8]THF, *c* = 3.4, -50°C): δ = 212.6 (C(1)), 95.2 (C(2)), 58.4 (CH_2), 15.7 (CH_3); ^{6}Li-NMR ([D_8]THF, *c* = 3.4, -90°C, reference to 1 M LiBr in [D_8]THF): δ = -0.20 (s).

Crystal data of polymeric 41. $[LiC_4H_7O]_6$ in the asymmetric unit, M = 468.22, monoclinic, space group $C2/c$, a = 3322(2), b = 976.7(7), c = 2491(2) pm, β = 130.47 (3)°, V = 6.149(8) nm^3, Z = 8, $D_{calc.}$ = 1.011 Mg/m^3, $F(000)$ = 2016, λ = 71.073 pm , μ (Mo-$K_α$) = 0.066 mm^{-1}, T = 153 K, data were collected on a Stoe-Siemens-AED. Intensities of a 0.9 x 0.1 x 0.05 mm rapidly cooled crystal in an oil drop [cxxxii] were collected by the 2θ /ω method in the range of $8° \leq 2\theta \leq 45°$. Of a total of 5121 refections, 4028 were independent and 4024 used to refine 368 parameters, largest difference peak and hole: 223 and -195 enm^{-3}, $R1$ ($F > 4\sigma$ (F)) = 0.079 and $wR2$ = 0.230 (all data), with $R1 = \Sigma || F_o | - | F_c || / \Sigma | F_o |$ and $wR2 = (\Sigma w (F_o^2 - F_c^2)^2 / \Sigma w (F_o^2)^2)^{0.5}$. The structure was solved with direct methods (SHELXS-90 [cxxxiii]) and refined by full-matrix least-squares on F^2 (SHELXL-93 [cxxxiv]). The hydrogen atom positions of the CH_2 groups were refined freely with the C-H bond length restrained to be the same while a riding model was applied to refine the hydrogen atom positions of the other groups.

7 Synthesis und crystal structure of the mixed lithium—sodium species (**47**·2THF)$_2$

Preparation of (47·2THF)$_2$

n-Butyllithium (0.62 mmol, 0.39 ml of a 1.6 M solution in hexane) was added to a stirred solution of 1-(*tert*-butylaminodimethylsilyl)-3,3-dimethyl-cyclopropene (0.31 mmol, 0.06 g), NaO-*t*-Bu (0.31 mmol, 0.03 g) in hexane (0.8 ml), and THF (0.8 mL) at -70°C. When the solution was stirred for 30 min, a solid precipitated. On warming to 0°C, the solid dissolved. Evaporization of the solvent yielded crude product which was recrystallized from *n*-hexane/THF at +4°C. A second recrystallization resulted in colorless crystals suitable for X-ray analysis. The crystal was selected for X-ray analyis and transported to the diffractometer at -50°C [cxxxii].

^{1}H NMR (400 MHz, [D_8]THF, +32°C): δ = 1.16 (s, 9H, NCCH_3), 1.05 (s, 6H, CCH_3), 0.05 (s, 6H, SiCH_3); ^{13}C NMR (100.6 MHz, [D_8]THF, +32°C): δ = 181.1 (C(1)), 158.3 (C(2)), 52.8 (N*C*CH_3), 38.2 (NC*C*H_3), 33.2 (C*C*H_3), 12.7 (C(3)), 8.2 (SiCH_3).

X-ray data of (47·2THF)$_2$: [$C_{19}H_{37}LiNaO_2Si$] in the asymmetric unit, M = 369.52, monoclinic, $P2_1/n$, a = 1122.2(2), b = 2011.8(4), c = 1125.3(2) pm, β = 115.58(2) °, V = 2.2915(8) nm^3, Z = 4, D_c = 1.071 Mgm^{-3}, $F(000)$ = 808, λ = 71.073 pm, μ(Mo-K$_\alpha$) = 0.067 mm^{-1}, T = 153(2) K, data were collected on a Stoe-Siemens-AED four-circle diffractometer. Intensities of a 1.5 x 1.0 x 0.9 mm rapidly cooled crystal in an oil drop [cxxxii] were collected by the $2\theta/\omega$ method in the range of $4^\circ \leq 2\theta \leq 45^\circ$. Of a total of 4423 refections, 2989 were independent and used to refine 279 parameters, largest difference peak and hole: 220 and -309 e nm^{-3}, $R1(F>4\sigma(F))$ = 0.0458 and $wR2$ = 0.1744 (all data) with $R1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$ and $wR2 = (\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2)^{0.5}$. The structure was solved with direct methods (SHELXS-90) [cxxxiii] and refined by full-matrix least-squares on F^2 (SHELXL-93) [cxxxiv]. A riding model was applied to refine the hydrogen atom positions. The non-bridging THF molecule has successfully been refined in two positions.

References

[i] J. H. van't Hoff, Arch. Neerl. Sci. Exactes Nat. **1874**, *9*, 445.

[ii] J. A. Le Bel, Bull. Soc. Chim. Fr. **1874**, *22*, 337.

[iii] Recent review: K. Sorger, P. v. R. Schleyer, *J. Mol. Struct., Theochem* **1995**, *338*, 317.

[iv] J. B. Collins, J. D. Dill, E. D. Jemmis, Y. Apeloig, P. v. R. Schleyer, R. Seeger, J. A. Pople, *J. Am. Chem. Soc.* **1976**, *98*, 5419.

[v] a) R. Hoffmann, *J. Chem. Phys.* **1963**, *39*, 1397; b) J. A. Pople, D. P. Santry, G. A. Segal, *J. Chem. Phys.* **1965**, *43*, 5129; c) J. A. Pople, G. A. Segal, *J. Chem. Phys.* **1965**, *43*, 5136; d) H. J. Monkhorst, *J. Chem. Soc., Chem. Commun.* **1968**, 1111; e) W. A. Lathan, W. J. Hehre, L. A. Curtiss, J. A. Pople, *J. Am. Chem. Soc.* **1971**, *93*, 6377; f) S. Durmaz, J. N. Murrell, J. B. Pedley, *J. Chem. Soc., Chem. Commun.* **1972**, 933; g) R. Firestone, *J. Chem. Soc., Chem. Commun.* **1973**, 163; h) M.-B. Krogh-Jespersen, J. Chandrasekhar, E.-U. Würthwein, J. B. Collins, P. v. R. Schleyer, *J. Am. Chem. Soc.* **1980**, *102*, 2263; i) D. C. Crans, J. P. Snyder, *J. Am. Chem. Soc.* **1980**, *102*, 7152; j) J. Moc, Z. Latajka, J. M. Rudzinski, H. J. Ratajczak, J. Chem. Soc., Perkin Trans. 2 **1989**, 131; k) M. S. Gordon, M. W. Schmidt, *J. Am. Chem. Soc.* **1993**, *115*, 7486; l) M. J. M. Pepper, I. Shavitt, P. v. R. Schleyer, M. N. Glukhovtsev, R. Janoschek, M. Quack, *J. Comput. Chem.* **1994**, *15*, 1.

[vi] R. Hoffmann, R. G. Alder, C. F. Wilcox, *J. Am. Chem. Soc.* **1970**, *92*, 4992. See also: R. Hoffmann, *Pure Appl. Chem.* **1971**, *28*, 181.

[vii] W. J. Hehre, L. Radom. P. v. R. Schleyer, J. A. Pople, *Ab Initio Molecular Orbital Theory*, Wiley, New York, **1986**, p 429.

[viii] D. M. Golden, R. Walsh, S. W. Benson, *J. Am. Chem. Soc.* **1965**, *87*, 4053.

[ix] R. Keese, A. Pfenninger, A. Roesle, *Helv. Chim. Acta* **1979**, *62*, 326.

[x] For reviews concerning chemistry and planarizing distortion of tetracoordinate carbon in the fenestrane-family, see: a) B. R. Venepalli, W. C. Agosta, *Chem. Rev.* **1987**, *87*, 399; b) W. C. Agosta, *The Chemistry of Alkanes and Cycloalkanes*, S. Patai, Z. Rappoport, Eds., Wiley, Chichester, **1992**, p 927; c) W. Luef, R. Keese, *Advances in Strain of Organic Compounds*, JAI Press, Greenwich, CT, **1993**, Vol. 3, p 229.

[xi] a) M. C. Böhm, R. Gleiter, P. Schang, *Tetrahedron Lett.* **1979**, *28*, 2575; b) J. Chandrasekhar, E.-U. Würthwein, P. v. R. Schleyer, *Tetrahedron* **1981**, *37*, 921.

[xii] V. Georgian, M. Salzman, *Tetrahedron Lett.* **1972**, 4315.

[xiii] a) W. Luef, R. Keese, H.-B. Buergi, *Helv. Chim. Acta* **1987**, *70*, 534; b) W. Luef, R. Keese, *Helv. Chim. Acta* **1987**, *70*, 543; c) W. Luef, R. Keese, *J. Mol. Struct., Theochem.* **1992**, *257*, 353.

[xiv] a) K. B. Wiberg, J. J. Wendoloski, *J. Am. Chem. Soc.* **1982**, *104*, 5679; b) J. M. Schulman, M. L. Sabio, R. L. Disch, *J. Am. Chem. Soc.* **1983**, *105*, 743.

[xv] a) W. T. Hoeve, H. Wynberg, *J. Org. Chem.* **1980**, *45*, 2925, 2930; b) R. Keese, *Nachr. Chem. Tech. Lab.* **1982**, *30*, 844; c) K. Krohn, *Nachr. Chem. Tech. Lab.* **1987**, *35*, 264; d) R. Keese, *Angew. Chem.* **1992**, *104*, 307; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 344.

[xvi] a) K. B. Wiberg, J. E. Hiatt, G. Burgmaier, *Tetrahedron Lett.* **1968**, 5855; b) E. H. Hahn, H. Bohm, D. Ginsburg, *Tetrahedron Lett*. **1973**, 507; c) F. Vögtle, P. K. T. Mew, *Angew. Chem.* **1978**, *90*, 58; *Angew. Chem. Int. Ed. Engl.* **1978**, *17*, 60; d) K. B. Wiberg, M. J. O'Donnell, *J. Am. Chem. Soc.* **1979**, *101*, 6660; e) E.-U. Würthwein, J. Chandrasekhar, E. J. Jemmis, P. v. R. Schleyer, *Tetrahedron Lett*. **1981**, *22*, 843; f) P. E. Eaton, B. D. Leipzig, *J. Am. Chem. Soc.* **1983**, *105*, 1656; g) K. B. Wiberg, *Tetrahedron Lett.* **1985**, 5967.

[xvii] a) H. Dodziuk, *J. Mol. Struct., Theochem* **1990**, *239*, 167; b) M. P. McGrath, L. Radom, H. F. Schaefer III, *J. Org. Chem.* **1992**, *57*, 4847.

[xviii] a) J. M. Schulman, R. L. Disch, *J. Am. Chem. Soc.* **1985**, *107*, 5059; b) R. L. Disch, J. M. Schulman, *J. Am. Chem. Soc.* **1988**, *110*, 2102.

[xix] a) M. P. McGrath, L. Radom, *J. Am. Chem. Soc.* **1993**, *115*, 3320; b) J. E. Lyons, D. R. Rasmussen, M. P. McGrath, R. H. Nobes, L. Radom, *Angew. Chem.* **1994**, *106*, 1722; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1667.

[xx] K. Sorger, *Diplomarbeit*, Universität Erlangen-Nürnberg, **1993**.

[xxi] a) F. A. Cotton, M. Millar, *J. Am. Chem. Soc.* **1977**, *99*, 7886; b) S. Harder, J. Boersma, L. Brandsma, A. v. Heteren, J. A. Kanters, W. Bauer, P. v. R. Schleyer, *J. Am. Chem. Soc.* **1988**, *110*, 7802; c) H. Dietrich, W. Mahdi, W. J. Storch, *J. Organomet. Chem.* **1988**, *349*, 1; d) S. L. Buchwald, E. A. Lucas, W. M. Davies, *J. Am. Chem. Soc.* **1989**, *111*, 397; e) A. D. Horten, A. G. Orpen, *Angew. Chem.* **1992**, *104*, 902; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 876; f) R. H. Cayton, S. T. Chacon, M. H. Chrisholm, M. J. Hampden-Smith, J. C. Huffman, K. Folting, P. D. Ellis, B. A. Huggins, *Angew. Chem.* **1989**, *101*, 1547; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 1523; g) S. T. Chacon, M. H. Chisholm, K. Folting, J. C. Huffman, M. J. Hampden-Smith, *Organometallics* **1991**, *10*, 3722; h) P. Leoni, M. Pasquali, G. Pieri, A. Albinati, P. S. Pregosin, H. Rüegger, *Organometallics* **1995**, *14*, 3143; i) G. Erker, R. Zwettler, C. Krüger, R. Noe, S. Werner, *J. Am. Chem. Soc.* **1990**, *112*, 9620; j) M. Albrecht, G. Erker, C. Krüger, *Synlett* **1993**, 441; k) D. Röttger, G. Erker, R. Fröhlich, M. Grehl, S. J. Silverio, I. Hyla-Kryspin, R. Gleiter, *J. Am. Chem. Soc.* **1995**, *117*, 10503 and references therein.; l) T. Beringhelli, G. Ciani, G. D'Alfonso, A. Sironi, M. Freni, *J. Chem. Soc, Chem. Commun.* **1985**, 978.

[xxii] J. Chandrasekhar, P. v. R. Schleyer, *J. Chem. Soc., Chem. Commun.* **1981**, 260.

[xxiii] C. N. Poumbga, M. Bénard, I. Hyla-Kryspin, *J. Am. Chem. Soc.* **1994**, *116*, 8259.

[xxiv] R. Gleiter, I. Hyla-Kryspin, S. Niu, G. Erker, *Angew. Chem.* **1993**, *105*, 753; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 754.

[xxv] Recent reviews: a) *Comprehensive Organic Synthesis*, B. M. Trost, I. Fleming, Eds., Pergamon Press, Oxford, **1991**, Vol. 1, 3; b) J. L. Wardell, *Comprehensive Organometallic Chemistry*, G. Wilkinson, F. G. A. Stone, E. W. Abel, Eds., Pergamon Press, Oxford, **1982**, Vol. 1, p 43; c) B. J. Wakefield,

Comprehensive Organometallic Chemistry, G. Wilkinson, F. G. A. Stone, E. W. Abel, Eds., Pergamon Press, Oxford, **1982**, Vol. 7, p 1; d) L. Brandsma, H. Verkruijsse, *Preparative Polar Organometallic Chemistry*, Springer, Berlin, **1987**, Vol. 1; e) L. Brandsma, *Preparative Polar Organometallic Chemistry*, Springer, Berlin, **1990**, Vol. 2; f) B. J. Wakefield, *Organolithium Methods*, Academic Press, London, **1988**.

[xxvi] Reviews: a) C. Lambert, P. v. R. Schleyer, *Angew. Chem.* **1994**, *106*, 1187; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1129; b) C. Lambert, P. v. R. Schleyer, *Methoden Org. Chem. (Houben-Weyl) 4th Ed. 1952-*, M. Hanack, Ed., Thieme, Stuttgart, **1993**, Vol. E19d, p 1; c) M. Schlosser, *Struktur und Reaktivität polarer Organometalle*, Springer, Berlin, **1973**.

[xxvii] Review: A. Streitwieser, S. M. Bachrach, A. Dorigo, P. v. R. Schleyer, *Lithium Chemistry*, A.-M. Sapse, P. v. R. Schleyer, Eds., Wiley, New York, **1995**, p 1.

[xxviii] a) W. N. Setzer, P. v. R. Schleyer, *Adv. Organomet. Chem.* **1985**, *24*, 353; b) P. v. R. Schleyer, *Pure Appl. Chem.* **1983**, *55*, 355; c) P. v. R. Schleyer, *Pure Appl. Chem.* **1984**, *56*, 151.

[xxix] a) E. Weiss, *Angew. Chem.* **1993**, *105*, 1565; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1501; b) G. Boche, *Angew. Chem.* **1989**, *101*, 286; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 277; c) D. Seebach, *Angew. Chem.* **1988**, *100*, 1685; *Angew. Chem. Int. Ed. Engl.* **1990**, *27*, 1624; d) C. Schade, P. v. R. Schleyer, *Adv. Organomet. Chem.* **1987**, *27*, 169; e) P. Jutzi, *Adv. Organomet. Chem.* **1986**, *26*, 217.

[xxx] Review: A. Maercker, *Top. Curr. Chem.* **1987**, *138*, 1.

[xxxi] Flash vaporization mass spectroscopy showed monomers and dimers to be present in the gas phase: H. Kawa, B. C. Manley, R. Lagow, *J. Am. Chem. Soc.* **1985**, *107*, 5313.

[xxxii] D. Thoennes, E. Weiss, *Chem. Ber.* **1978**, *111*, 3157.

[xxxiii] a) J. T. B. H. Jastrzebski, G. van Koten, K. Goubitz, C. Arlen, M. Pfeffer, *J. Organomet. Chem.* **1983**, *246*, C75; b) J. T. B. H. Jastrzebski, G. van Koten, M. Konijn, C. H. Stam, *J. Am. Chem. Soc.* **1982**, *104*, 5490; c) M. H. P.

Rietveld, I. C. M. Wehman-Ooyevaar, G. M. Kapteijn, D. M. Grove, W. J. J. Smeets, H. Kooijman, A. L. Spek, G. van Koten, *Organometallics* **1994**, *13*, 3782 and references therein.

[xxxiv] W. Bauer, P. A. A. Klusener, S. Harder, J. A. Kanters, A. J. M. Duisenberg, L. Brandsma, P. v. R. Schleyer, *Organometallics* **1988**, *7*, 552.

[xxxv] GAUSSIAN 92/DFT, Revision G.2, M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. W. Wong, J. B. Foresman, M. A. Robb, M. Head-Gordon, E. S. Replogle, R. Gomberts, J. L. Andres, K. Raghavachari, J. S. Binkley, C. Gonzalez, R. L. Martin, D. J. Fox, D. J. Defrees, J. Baker, J. J. P. Stewart, J. A. Pople, Gaussian, Inc., Pittsburgh PA, **1993**.

[xxxvi] GAUSSIAN 94, Revision B.2, M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, J. A. Pople, Gaussian, Inc., Pittsburgh PA, **1995**.

[xxxvii] a) J. W. Labanowski, J. Andzelm, *Density Functional Methods in Chemistry*, Springer, New York, **1991**; b) R. G. Parr, W. Yang, *Density Functional Theory of Atoms and Molecules*, Oxford University Press, New York, **1989**.

[xxxviii] For the Becke3LYP hybrid method, see: a) P. J. Stephens, F. J. Devlin, C. F. Chabalowski, M. J. Frisch, *J. Phys. Chem.* **1994**, *98*, 11623 and references therein; b) M. J. Frisch, A. Frisch, J. B. Foresman, *Gaussian 94 User's Reference*, Gaussian, Inc., Pittsburgh PA, **1994**.

[xxxix] L. M. Pratt, I. M. Khan, *J. Comp. Chem.* **1995**, *16*, 1067.

[xl] See ref [vii] p 1.

[xli] a) A. E. Reed, R. B. Weinstock, F. Weinhold, *J. Chem. Phys.* **1985**, *83*, 735; b) A. E. Reed, L. A. Curtis, F. Weinhold, *Chem. Rev.* **1988**, *88*, 889.

[xlii] a) PM3: J. J. P. Stewart, *J. Comp. Chem.* **1989**, *10*, 209, 221; **1991**, *12*, 320; b) PM3-Li-parametrization: E. Anders, R. Koch, P. Freunscht, *J. Comp. Chem.* **1993**, *14*, 1301.

[xliii] VAMP 5.0 (Vectorized Ampac): G. Rauhut, A. Alex, J. Chandrasekhar, T. Steinke, T. Clark, Erlangen, **1993**.

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

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

[xlvi] a) G. L. Closs, L. E. Closs, *J. Am. Chem. Soc.* **1961**, *83*, 1003; **1963**, *85*, 99; b) A. J. Schipperijn, *Recl. Trav. Chim. Pays-Bas* **1971**, *90*, 1110; c) D. E. Applequist, E. C. Saurborn, *J. Org. Chem.* **1972**, 37, 1676; d) A. Padwa, M. J. Pulwer, R. J. Rosenthal, *J. Org. Chem.* **1984**, *49*, 856; e) M. A. Kirms, H. Primke, M. Stohlmeier, A. de Meijere, *Recl. Trav. Chim. Pays-Bas* **1986**, *105*, 462; f) S. Untiedt, A. de Meijere, *Chem. Ber.* **1994**, *127*, 1511; g) N. I. Yakushkina, G. R. Zhurina, L. S. Surmina, Y. K. Grishin, D. V. Bazhenov, V. V. Plemenkov, G. I. Bolesov, *Zh. Obshch. Khim.* **1982**, *52*, 1604; *J. Gen. Chem. USSR (Engl. Übersetzung)* **1982**, *52*, 1417; h) P. Binger, P. Müller, R. Wenz, R. Mynott, *Angew. Chem.* **1990**, *102*, 1070; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 1037; i) M. S. Baird, H. H. Hussain, W. Nethercott, *J. Chem. Soc., Perkin Trans. I* **1986**, 1845; j) M. S. Baird, W. Nethercott, *Tetrahedron Lett.* **1983**, *24*, 605.

[xlvii] a) E. D. Jemmis, J. Chandrasekhar, P. v. R. Schleyer, *J. Am. Chem. Soc.* **1979**, *101*, 2848; b) P. v. R. Schleyer, J. Chandrasekhar, A. J. Kos, T. Clark, G. W. Spitznagel, *J. Chem. Soc., Chem. Commun.* **1981**, 882; c) P. v. R. Schleyer, E. Kaufmann, G. W. Spitznagel, R. Janoschek, G. Winkelhofer, *Organometallics* **1986**, *5*, 79; d) The computed bond length differences in the 1-cyclopropenyl anion are even greater, see: W.-K. Li, *Croat. Chem. Acta* **1988**, *61*, 833 and Table 2.

[xlviii] a) J.J. Brooks, G. D. Stucky, *J. Am. Chem. Soc.* **1972**, *94*, 7333; b) P. R. Zerger, G. D. Stucky, *J. Chem. Soc., Chem. Commun.* **1973**, 44; c) R. Amstutz, T. Laube, W. B. Schweizer, D. Seebach, J. D. Dunitz, *Helv. Chim. Acta* **1984**, *67*, 224; d) S. Harder, J. Boersma, L. Brandsma, J. A. Kanters, W. Bauer, P. v. R. Schleyer, H. Schöllhorn, U. Thewalt, *Organometallics* **1989**, *8*, 1688.

[xlix] a) T. Kottke, D. Stalke, *Angew. Chem.* **1993**, *105*, 619; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 580; b) M. A. Nichols, P. G. Williard, *J. Am. Chem. Soc.* **1993**, *115*, 1568.

[l] a) F. H. Allen, *Tetrahedron*, **1982**, *38*, 645; b) E. Hirota, T. Iijima, K. Kuchitsu, W. J. Lafferty, D. A. Ramsay, *Structure Data of Free Molecules (Landolt-Börnstein)*, K. Kuchitsu, Ed., Springer, Berlin, **1992**, Vol. II/21.

[li] Cambridge Structural Database. Structures of cyclopropenes with π-acceptors at C(3) have not been considered since it is known that these lengthen the vicinal bonds and shorten the distal (C=C) bond; see ref. [la] and: C. J. Cheer, D. Bernstein, A. Greenberg, P.-C. Lyu, *J. Am. Chem. Soc.* **1988**, *110*, 226.

[lii] a) A. D. Walsh, *Discuss. Faraday Soc.* **1947**, *2*, 118; b) H. A. Bent, *Chem. Rev.* **1961**, *61*, 275.

[liii] a) D. Hoffmann, W. Bauer, F. Hampel, N. J. R. van Eikema Hommes, P. v. R. Schleyer, P. Otto, U. Pieper, D. Stalke, D. S. Wright, R. Snaith, *J. Am. Chem. Soc.* **1994**, *116*, 528 and references therein; b) S. Harder, P. F. Ekhart, L. Brandsma, J. A. Kanters, A. J. M. Duisenberg, P. v. R. Schleyer, *Organometallics* **1992**, *11*, 2623; c) D. Stalke, K. J. Whitmire, *J. Chem. Soc., Chem. Commun.* **1990**, 833; d) U. Schümann, U. Behrens, E. Weiss, *Angew. Chem.* **1989**, *101*, 481; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 476; e) T. Maetzke, D. Seebach, *Helv. Chim. Acta* **1989**, *72*, 624; f) H. Hope, P. P. Power, *J. Am. Chem. Soc.* **1983**, *105*, 5320.

[liv] R. Knorr, J. Freudenreich, K. Polborn, H. Nöth, G. Linti, *Tetrahedron* **1994**, *50*, 5845 and references therein.

[lv] For recent reviews on NMR spectroscopy of organolithium comounds, see: a) H. Günther, D. Moskau, D. Schmak, *Angew. Chem.* **1987**, *99*, 1242; *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 1212; b) W. Bauer, P. v. R. Schleyer, in *Advances in Carbanion Chemistry*, V. Snieckus, Ed., JAI Press, Greenwich, CT, **1992**, Vol. 1, p 89.

[lvi] For early ^{13}C NMR studies of ^{6}Li enriched compounds, see: a) G. Fraenkel, A. M. Fraenkel, M. J. Geckle, F. Schloss, *J. Am. Chem. Soc.* **1979**, *101*, 4745; b) D. Seebach, R. Hässig, J. Gabriel, *Helv. Chim. Acta* **1983**, *66*, 308.

[lvii] a) D. Seebach, H. Siegel, J. Gabriel, R. Hässig, *Helv. Chim. Acta* **1980**, *63*, 2046; b) D. Seebach, H. Siegel, K. Müllen, K. Hiltbrunner, *Angew. Chem.* **1979**,

91, 844; *Angew. Chem. Int. Ed. Engl.* **1979**, *18*, 784; c) H. Siegel, K. Hiltbrunner, D. Seebach, *Angew. Chem.* **1979**, *91*, 845; *Angew. Chem. Int. Ed. Engl.* **1979**, *18*, 785.

[lviii] For reviews on carbenoids, see: a) G. Köbrich, *Angew. Chem.* **1972**, *84*, 557; *Angew. Chem. Int. Ed. Engl.* **1972**, *11*, 473; b) H. Siegel, *Top. Curr. Chem.* **1982**, *106*, 55; c) A. Maercker, *Angew. Chem.* **1993**, *105*, 1072; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1023 and references therein.

[lix] a) T. Clark, P. v. R. Schleyer, *J. Chem. Soc., Chem. Commun.* **1979**, 883; *J. Am. Chem. Soc.* **1979**, *101*, 7747; *Tetrahedron Lett.* **1979**, 4963; b) P. v. R. Schleyer, T. Clark, J. A. Kos, G. W. Spitznagel, C. Rohde, D. Arad, K. N. Houk, *J. Am. Chem. Soc.* **1984**, *106*, 6467; c) K. Sorger, W. Bauer, P. v. R. Schleyer, D. Stalke, *Angew. Chem.* **1995**, *107*, 1766; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1594 and references therein; d) G. Boche, M. Marsch, A. Müller, K. Harms, *Angew. Chem.* **1993**, *105*, 1081; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1032; e) G. Boche, F. Bosold, J. C. W. Lohrenz, A. Opel, P. Zulauf, *Chem. Ber.* **1993**, *126*, 1873.

[lx] For the strain in cyclopropene, see: a) N. C. Baird, M. J. S. Dewar, *J. Am. Chem. Soc.* **1967**, *89*, 3966; b) P. v. R. Schleyer, J. E. Williams, K. R. Blanchard, *J. Am. Chem. Soc.* **1970**, *92*, 2377; c) R. C. Bingham, M. J. S. Dewar, D. H. Lo, *J. Am. Chem. Soc.* **1975**, *97*, 1294.

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

[lxii] E. A. Brinkman, S. Berger, J. I. Brauman, *J. Am. Chem. Soc.* **1994**, *116*, 8404.

[lxiii] J. I. Musher, *J. Chem. Phys.* **1962**, *37*, 34.

[lxiv] a) K. Sorger, P. v. R. Schleyer, D. Stalke, *J. Chem. Soc, Chem. Commun.* **1995**, 2279; b) K. Sorger, P. v. R. Schleyer, R. Fleischer, D. Stalke, *J. Am. Chem. Soc.*, accepted.

[lxv] Review: F. Pauer, P. P. Power, *Lithium Chemistry*, A.-M. Sapse, P. v. R. Schleyer, Eds., Wiley, New York, **1995,** p 295.

[lxvi] For planarizing distortions in hydrocarbons, see refs [xb,c], [xiii].

[lxvii] U. Siemeling, T. Redecker, B. Neumann, H.-G. Stammler, *J. Am. Chem. Soc.* **1994**, *116*, 5507.

[lxviii] R. Zerger, W. Rhine, G. Stucky, *J. Am. Chem. Soc.* **1974**, *96*, 6048.

[lxix] A. Maercker, M. Bsata, W. Buchmeier, B. Engelen, *Chem. Ber.* **1984**, *117*, 2547.

[lxx] M. Marsch, K. Harms, L. Lochmann, G. Boche, *Angew. Chem.* **1990**, *102*, 334; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 308.

[lxxi] P. G. Williard, M. J. Hintze, *J. Am. Chem. Soc.* **1987**, *109*, 5539.

[lxxii] K. W. Henderson, D. S. Walther, P. G. Williard, *J. Am. Chem. Soc.* **1995**, *117*, 8680.

[lxxiii] The dilithium salts of two chelating bis(amido) compounds adopt similar puckered ladder structures: H. Chen, R. A. Bartlett, H. V. R. Dias, M. M. Olmstead, P. P. Power, *Inorg. Chem.* **1991**, *30*, 2487.

[lxxiv] For ring laddering in lithium amides, see: a) K. Gregory, P. V. R. Schleyer, R. Snaith, *Adv. Inorg. Chem.* **1991**, *37*, 47; b) R. E. Mulvey, *Chem. Soc. Rev.* **1991**, *20*, 167; c) D. R. Amstrong, D. Barr, W. Clegg, R. E. Mulvey, D. Reed, R. Snaith, K. Wade, *J. Chem. Soc., Chem. Commun.* **1986**, 869; d) D. R. Amstrong, D. Barr, W. Clegg, S. M. Hodgson, R. E. Mulvey, D. Reed, R. Snaith, D. S. Wright, *J. Am. Chem. Soc.* **1989**, *111*, 4719.

[lxxv] R. A. Jones, A. L. Stuart, T. C. Wright, *J. Am. Chem. Soc.* **1983**, *105*, 7459.

[lxxvi] M. B. Hursthouse, M. A. Hossain, M. Motevalli, M. Sanganee, A. C. Sullivan, *J. Organomet. Chem.* **1990**, *381*, 293.

[lxxvii] G. Boche, I. Langlotz, M. Marsch, N. E. S. Nudelman, *Angew. Chem.* **1992**, *104*, 1239; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1205.

[lxxviii] W. Bauer, W. R. Winchester, P. v. R. Schleyer, *Organometallics* **1987**, *6*, 2371.

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

[lxxx] a) M. Veith, F. Goffing, V. Huch, *Chem. Ber.* **1988**, *121*, 943; b) I. Hemme, B. Tecklenburg, M. Noltemeyer, U. Klingebiel, *Chem. Ber.* **1995**, *128*, 343.

[lxxxi] E. Kaufmann, K. Raghavachari, A. E. Reed, P. v. R. Schleyer, *Organometallics*, **1988**, *7*, 1597.

[lxxxii] A.-M. Sapse, K. Raghavachari, P. v. R. Schleyer, E. Kaufmann, *J. Am. Chem. Soc.* **1985**, *107*, 6483.

[lxxxiii] S. Harder, M. Lutz, A. Streitwieser, *J. Am. Chem. Soc.* **1995**, *117*, 2361.

[lxxxiv] M. Geissler, J. Kopf, B. Schubert, E. Weiss, W. Neugebauer, P. v. R. Schleyer. *Angew. Chem.* **1987**, *99*, 569; *Angew. Int. Ed. Engl.* **1987**, *26*, 587.

[lxxxv] F. E. Romesberg, D. B. Collum, *J. Am. Chem. Soc.* **1994**, *116*, 9187.

[lxxxvi] D. R. Baker, R. E. Mulvey, W. Clegg, P. A. O'Neil, *J. Am. Chem. Soc.* **1993**, *115*, 6472.

[lxxxvii] Organolithium trimers: a) S. Harder, J. Boersma, L. Brandsma, J. A. Kanters, W. Bauer, P. v. R. Schleyer, *Organometallics* **1989**, *8*, 1696; b) S. Harder, J. Boersma, L. Brandsma, J. A. Kanters, A. J. M. Duisenberg, J. H. v. Lenthe, *Organometallics* **1991**, *10*, 1623; c) S. Harder, P. F. Ekhart, L. Brandsma, J. A. Kanters, A. J. M. Duisenberg, P. v. R. Schleyer, *Organometallics* **1992**, *11*, 2623.

[lxxxviii] Lithium alkoxide trimers: a) M. S. Korobov, V. I. Minkin, L. E. Nivorozhkin, O. E. Kompan, Y. T. Struchkov, *Zh. Obshch. Khim.* **1989**, *59*, 429; *J. Gen. Chem. URSS* **1989**, *59*, (engl. translation); b) D. Schmidt-Bäse, U. Klingebiel, *Chem. Ber.* **1990**, *123*, 449; c) P. A. van den Schaaf, M. P. Hogenheide, D. Grove, A. L. Spek, G. van Koten, *J. Chem. Soc., Chem. Commun.* **1992**, 1703.

[lxxxix] Lithium amide trimers: a) D. Mootz, A. Zinnius, B. Böttcher, *Angew. Chem.* **1969**, *81*, 398; *Angew. Int. Ed. Engl.* **1969**, *8*, 378; b) R. D. Rogers, J. L. Atwood, R. Grüning, *J. Organomet. Chem.* **1978**, *157*, 229; c) M. Rannenberg, H. D. Hausen, J. Weidlein, *J. Organomet. Chem.* **1989**, *376*, C27; d) D. Barr, W. Clegg, R. E. Mulvey, R. Snaith, *J. Chem. Soc., Chem. Commun.* **1984**, 285, 287; e) D. R. Armstrong, R. E. Mulvey, G. T. Walker, D. Barr, R. Snaith, W. Clegg, D. Reed, *J. Chem. Soc, Dalton Trans.* **1988**, 617.

[xc] a) K. B. Wiberg, W. J. Bartley, *J. Am. Chem. Soc.* **1960**, *82*, 6375; b) G. L. Closs, R. B. Larrabee, *Tetrahedron Lett.* **1965**, 287.

[xci] a) S. P. Patterman, I. L. Karle, G. D. Stucky, *J. Am. Chem. Soc.* **1970**, *92*, 1150; b) M. A. Beno, H. Hope, M. M. Olmstead, P. P. Power, *Organometallics* **1985**, *4*, 2117; c) W. Zarges, M. Marsch, K. Harms, G. Boche, *Chem. Ber.* **1989**, *122*, 2303.

[xcii] a) J. E. Del Bene, M. J. Frisch, K. H. Raghavachari, J. A. Pople, P. v. R. Schleyer, *J. Phys. Chem.* **1983**, *87*, 73; b) K. N. Houk, N. G. Rondan, P. v. R. Schleyer, E. Kaufmann, T. Clark, *J. Am. Chem. Soc.* **1985**, *107*, 2821; c) W. F. Bailey, A. D. Khanolkar, K. Gavaskar, T. V. Ovaska, K. Rossi, Y. Thiel, K. B. Wiberg, *J. Am. Chem. Soc.* **1991**, *113*, 5720; d) J. W. Caldwell, P. A. Kollman, *J. Am. Chem. Soc.* **1995**, *117*, 4177.

[xciii] For computations on the propene—LiH complex, see: T. Rölle, R. W. Hoffmann, *J. Chem. Soc., Perkin Trans 2* **1995**, 1953.

[xciv] For Li-C π interactions in a vinyllithium derivative, α-ethoxyvinyllithium, see ref [lixc].

[xcv] J. P. Oliver, J. B. Smart, M. T. Emerson, *J. Am. Chem. Soc.* **1966**, *88*, 4101.

[xcvi] a) Review: O. W. Lever, *Tetrahedron* **1976**, *32*, 1943 (see p 1958 and references therein); b) U. Schöllkopf, P. Hänssle, *Justus Liebigs Ann. Chem.* **1972**, *763*, 208; c) I. Hoppe, U. Schöllkopf, *Liebigs Ann. Chem.* **1080**, 1474; d) J. E. Baldwin, G. A. Höfle, O. W. Lever, Jr., *J. Am. Chem. Soc.* **1974**, *96*, 7125; e) J. A. Soderquist, A. Hassner, *J. Am. Chem. Soc.* **1980**, *102*, 1577; f) T. Takahashi, H. Yamada, J. Tsuji, *J. Am. Chem. Soc.* **1981**, *103*, 5259; g) M. Shimano, A. I. Meyers, *J. Am. Chem. Soc.* **1994**, *116*, 10815; h) R. R. Schmidt, R. Betz, *Synthesis* **1982**, 748; i) P. G. Mc Dougal, J. G. Rico, D. VanDerveen, *J. Org. Chem.* **1986**, *51*, 4492; j) R. K. Boeckman, Jr., K. J. Bruza, *Tetrahedron*, **1981**, *37*, 3997; k) S. J. Gould, B. D. Remillard, *Tetrahedron Lett.* **1978**, 4353; l) E. J. Corey, D. L. Boger, *Tetrahedron Lett.* **1978**, 13; m) P. Lesimple, J.-M. Beau, G. Jaurand, P. Sinay, *Tetrahedron Lett.* **1986**, 6201.

[xcvii] T. Clark, P. v. R. Schleyer, K. N. Houk, N. G. Rondan, *J. Chem. Soc., Chem. Commun.* **1981**, 579. See also: B. Wang, C. Deng, *Chem. Phys. Lett.* **1988**, *147*, 99; B. Wang, C. Deng, L. Xu, T. Tao, *Chem. Phys. Lett.* **1989**, *161*, 388.

[xcviii] a) G. Boche, K. Harms, M. Marsch, A. Müller, *J. Chem. Soc., Chem. Commun.* **1994**, 1393; b) G. Boche, A. Opel, M. Marsch, K. Harms, F. Haller, J. C. W. Lohrenz, C. Thümmler, W. Koch, *Chem. Ber.* **1992**, *125*, 2265; c) C. Lambert, P. v. R. Schleyer, E.-U. Würthwein, *J. Org. Chem.* **1993**, *58*, 6377; d) S. Harder, J. Boersma, L. Brandsma, J. A. Kanters, W. Bauer, R. Pi, P. v. R. Schleyer, H. Schöllhorn, U. Thewalt, *Organometallics* **1989**, *8*, 1688; e) G. Boche, M. Marsch, J. Harbach, K. Harms, B. Ledig, F. Schubert, J. C. W. Lohrenz, H. Ahlbrecht, *Chem. Ber.* **1993**, *126*, 1887.

[xcix] R. Amstutz, W. B. Schweizer, D. Seebach, J. D. Dunitz, *Helv. Chim. Acta* **1981**, *64*, 2617.

[c] S. Harder, J. Boersma, L. Brandsma, G. P. M. van Mier, J. A. Kanters, *J. Organomet. Chem.* **1989**, *364*, 1.

[ci] B. Schubert, E. Weiss, *Angew. Chem.* **1983**, *95*, 499; *Angew. Chem. Int. Ed. Engl.* **1983**, *22*, 496.

[cii] R. Amstutz, J. D. Dunitz, T. Laube, W. B. Schweizer, D. Seebach, *Chem. Ber.* **1986**, *119*, 434.

[ciii]Li-O_{ethoxy} bond scrambling must be rapid on the NMR time scale.

[civ]W. Bauer, C. Griesinger, *J. Am. Chem. Soc.* **1993**, *115*, 10871 and references therein.

[cv] R. D. Thomas, M. T. Clarke, R. M. Jensen, T. C. Young, *Organometallics* **1986**, *5*, 1851.

[cvi]a) Review: W. Bauer, *Lithium Chemistry*, A.-M. Sapse, P. v. R. Schleyer, Eds., Wiley, New York, **1995**, p 125; b) W. Bauer, F. Hampel, *J. Chem. Soc., Chem. Commun.* **1992**, 903 and references therein.

[cvii] F. T. Oakes, J. F. Sebastian, *J. Org. Chem.* **1980**, *45*, 4959.

[cviii] $\Delta\delta$ values of 56.6 and 57.2 have been determined for the closely related *a*-lithio-2,3-dihydrofuran and *a*-lithio-2,3-dihydro-4H-pyran, the carbenoid character of which is well established [lixe]: see ref [cvii].

[cix]For reviews of synthetic applications, see: a) M. Schlosser, *Pure Appl. Chem.* **1988**, *60*, 1627; *Mod. Synth. Methods* **1992**, *6*, 227 and references therein; b) L. Lochmann, J. Trekoval, *Collect. Czech. Chem. Commun.* **1988**, *53*, 76; c) A. Mordini in *Advances in Carbanion Chemistry*, *Vol. 1* (Ed.: V. Snieckus), JAI Press,

London, **1988**, p 1; d) P. Caubère, *Chem. Rev.* **1993**, *93*, 2317. See also: L. Brandsma, H. D. Verkruijsse, C. Schade, P. von R. Schleyer, *J. Chem. Soc, Chem. Commun.* **1986**, 260 and P. A. A. Klusener, L. Brandsma, H. D. Verkruijsse, P. v. R. Schleyer, T. Friedl, R. Pi, *Angew. Chem.* **1986**, *98*, 458; *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 465.

[cx] a) G. Wittig, R. Ludwig, R. Polster, *Chem. Ber.* **1955**, *88*, 294; b) G. Wittig, F. Bickelhaupt, *Chem. Ber.* **1958**, *91*, 865; c) G. Wittig, E. Benz, *Chem. Ber.* **1958**, *91*, 873.

[cxi]a) L. Lochmann, J. Pospíšil, J. Vodnansky, J. Trekoval, D. Lím, *Collect. Czech. Chem. Commun.* **1965**, *30*, 2187; b) L. Lochmann, J. Pospíšil, D. Lím, *Tetrahedron Lett.* **1966**, 257; c) L. Lochmann, J. Petránek, *Tetrahedron Lett.* **1991**, 1483.

[cxii] a) M. Schlosser, *J. Organomet. Chem.* **1967**, *8*, 9; b) M. Schlosser, S. Strunk, *Tetrahedron Lett.* **1984**, 741.

[cxiii] a) P. Caubère, *Acc. Chem. Res.*, **1974**, *7*, 301; *Top. Curr. Chem.* **1978**, *73*, 50; b) S. Raucher, G. A. Koolpe, *J. Org. Chem.* **1978**, *43*, 3794; c) B. Renger, H. Hügel, W. Wykypiel, D. Seebach, *Chem. Ber.* **1978**, *111*, 2630; d) L. Lochmann, J. Trekoval, *J. Organomet. Chem.* **1979**, *179*, 123; e) C. Margot, M. Schlosser, *Tetrahedron Lett.* **1985**, 1035.

[cxiv] a) P. Palmas, P. Tekely, B. Jamart-Grégoire, P. Caubère, D. Canet, *J. Am. Chem. Soc.* **1994**, *116*, 11604; b) V. Halaška, L. Lochmann, *Collect. Czech. Chem. Commun.* **1973**, *38*, 1780; c) J. F. McGarrity, C. A. Ogle, *J. Am. Chem. Soc.* **1985**, *107*, 1805.

[cxv] a) P. G. Williard, Q.-Y. Liu, *J. Am. Chem. Soc.* **1993**, *115*, 3380; b) P. G. Williard, M. J. Hintze, *J. Am. Chem. Soc.* **1990**, *112*, 8602; c) A. S. Galiano-Roth, Y.-J. Kim, J. H. Gilchrist, A. T. Harrison, D. J. Fuller, D. B. Collum, *J. Am. Chem. Soc.* **1991**, *113*, 5053; d) P. L. Hall, J. H. Gilchrist, D. B. Collum, *J. Am. Chem. Soc.* **1991**, *113*, 9571.

[cxvi] Review: W. Bauer, L. Lochmann, *J. Am. Chem. Soc.* **1992**, *114*, 7482 and references therein.

[cxvii] a) R. Pi, W.Bauer, B. Brix, C. Schade, P. v. R. Schleyer, *J. Organomet. Chem.* **1986**, *306*, C1; b) L. Lochmann, D. Lím, *J. Organomet. Chem.* **1971**, *28*, 153; c) L. Lochmann, *Collect. Czech. Chem. Commun.* **1987**, *52*, 2710.

[cxviii] a) E. M. Arnett, K. D Moe, *J. Am. Chem. Soc.* **1991**, *113*, 7068; b) M. Schlosser, J. H. Choi, S. Takagishi, *Tetrahedron* **1990**, *46*, 5633; c) R. Lehmann, M. Schlosser, *Tetrahedron Lett.* **1984**, *25*, 745.

[cxix] T. Kremer, S. Harder, M. Junge, P. v. R. Schleyer, *Organometallics* **1996**, *15*, 585.

[cxx] a) K. W. Henderson, P. G. Willard, P. R. Bernstein, *Angew. Chem.* **1995**, *107*, 1218; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1117; b) D. R. Baker, W. Clegg, L. Horsburgh, R. E. Mulvey, *Organometallics* **1994**, *13*, 4170 and references therein; c) H. Gornitzka, D. Stalke, *Angew. Chem.* **1994**, *106*, 695; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 693; d) S. Freitag, W. Kolodziejski, F. Pauer, D. Stalke, *J. Chem. Soc., Dalton Trans.* **1993**, 3479; e) D. R. Baker, R. E. Mulvey, W. Clegg, P. A. O'Neil, *J. Am. Chem. Soc.* **1993**, *115*, 6472; f) P. G. Willard, M. A. Nichols, *J. Am. Chem. Soc.* **1991**, *113*, 9671 and references therein; g) U. Schümann, E. Weiss, *Angew. Chem.* **1988**, *100*, 573; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 584.

[cxxi] a) S. Harder, M. Lutz, T. Kremer, *Organometallics* **1995**, *14*, 2133; b) S. Harder, A. Streitwieser, *Angew. Chem.* **1993**, *105*, 1108; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1067. For the structure of a mixed lithium pinacolonate—KO-*t*-Bu complex, see: P. G. Williard, G. J. MacEwan, *J. Am. Chem. Soc.* **1989**, *111*, 7671.

[cxxii] U. Schümann, U. Behrens, E. Weiss, *Angew. Chem.* **1989**, *101*, 481; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 476.

[cxxiii] W. Clegg, L. Horsburgh, F. M. Mackenzie, R. E. Mulvey, *J. Chem. Soc., Chem. Commun.* **1995**, 2011.

[cxxiv] a) S. Brooker, F. T. Edelmann, T. Kottke, H. W. Roesky, G. M. Sheldrick, D. Stalke, K. H. Whitmire, *J. Chem. Soc., Chem. Commun.* **1991**, 144; b) K. Dippel, U. Klingebiel, T. Kottke, F. Pauer, G. M. Sheldrick, D. Stalke, *Chem. Ber.* **1990**, *123*, 237; c) N. Hu, L. Gong, Z. Jin, W. Chen, *J. Organomet. Chem.* **1988**, *352*, 61.

[cxxv] H. Bock, T. Hauck, C. Näther, N. Rösch, M. Staufer, O. D. Häberlen, *Angew. Chem.* **1995**, *107*, 1439; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1353.

[cxxvi] a) H. Horn, R. Ahlrichs, *J. Am. Chem. Soc.* **1990**, *112*, 2121; b) J. P. Ritchie, S. M. Bachrach, *J. Am. Chem. Soc.* **1987**, *109*, 5909.

[cxxvii] O. A. Nesmeyanova, T. Y. Rudashevskaya, A. I. Dyachenko, S. F. Savilova, O. M. Nefedov, *Synthesis* **1982**, 296.

[cxxviii] D. Seyferth, H. Yamazaki, D. L. Alleston, *J. Org. Chem.* **1963**, *28*, 703.

[cxxix] P. Binger, *Synthesis* **1974**, 190.

[cxxx] R. Walsh, S. Untiedt, M. Stohlmeier, A. de Meijere, *Chem. Ber.* **1989**, *122*, 637.

[cxxxi] E. A. Braude, E. A. Evans, *J. Chem. Soc.* **1955**, 3328.

[cxxxii] T. Kottke, D. Stalke, *J. Appl. Crystallogr.* **1993**, *26*, 615.

[cxxxiii] SHELXS-90, G. M. Sheldrick, *Acta Crystallogr. Sect. A* **1990**, *46*, 467.

[cxxxiv] SHELXL-93, G. M. Sheldrick, program for crystal structure refinement, Göttingen, **1993**.

[cxxxv] B. A. Cheskis, A. M. Moiseenkov, T. Y. Rudashevskaya, O. A. Nesmeyanova, A. V. Semenovskii, *Izv. Akad. Nauk. SSSR* **1982**, 1084; *Bull. Acad. Sci. URSS, Div. Chem. Sci. (engl. translation)* **1982**, 965.

[cxxxvi] R. Kuhn, H. H. Baer, A. Seeliger, *Justus Liebigs Ann. Chem.* **1958**, *611*, 236.

[cxxxvii] An α-β-γ numbering was used for the carbon atoms of the cyclopropenyl ring (lithium is at C_α).

[cxxxviii] For (**29**·2THF)$_2$, and (**30**·2THF)$_2$, integration may indicate variable amounts of THF, as this is partially lost when the crystals are dried in vacuo.

[cxxxix] H. D. Verkruijsse, L. Brandsma, P. v. R. Schleyer, *J. Organomet. Chem.* **1987**, *332*, 99.

[cxl] ^{1}H NMR chemical shifts of the vinylic protons in **35**: R. Knorr, T. von Roman, *Angew. Chem.* **1984**, *96*, 349; *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 366.