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Dimeric [3,3-Dimethyl-2-(trimethylsilyl)cyclopropenyl]-lithium−Tetramethylethylenediamine: Distortion of the Cyclopropenyl Geometry Due to Strong Rehybridization at the Lithiated Carbon

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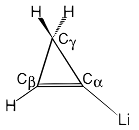
Abstract: The reaction of 3,3-dimethyl-1-(trimethylsilyl)cyclopropene with *n*-BuLi in the presence of 1 equiv of tetramethylethylenediamine (TMEDA) affords [3,3-dimethyl-2-(trimethylsilyl)cyclopropenyl]lithium (**2**). While NMR data reveal a monomer in tetrahydrofuran (THF) solution, **2** crystallizes as a dimeric TMEDA solvate, (**2**·TMEDA)$_2$. The structure was determined by single-crystal X-ray diffraction (crystal data: monoclinic, space group $P2_1/n$, $a = 1879.9(2)$ pm, $b = 1035.0(2)$ pm, $c = 2045.5(2)$ pm, $\beta = 113.198(9)°$, $V = 3.6580(8)$ nm^3, $Z = 4$, [$C_{28}H_{62}Li_2N_4Si_2$]). Although dimeric unsolvated cyclopropenyllithium was computed (Becke3LYP/6-31G*) to have two planar tetracoordinate carbon ($R^1R^2CLi_2$) fragments, (**2**·TMEDA)$_2$ adopts a perpendicular ("tetrahedral") structure due to lithium solvation and the steric crowding of the lithium ligands. Lithiation at C(α) of the cyclopropenyl ring in **2** lengthens the vicinal and shortens the distal C−C bonds due to the rehybridization at the lithiated carbon. This is confirmed both by the natural localized molecular orbital carbon hybridizations and by the large coupling constant, $^1J_{^{13}C-^6Li} = 17.6$ Hz, observed in THF solution (the usual range for organolithium monomers is 10 and 16 Hz). Despite the strong rehybridization and their relationship to the C(Li)X halogen and C(Li)O carbenoids, the lithiated cyclopropenes do not have carbenoid nature.

Introduction

The considerable strain in cyclopropene results in remarkable chemical properties.[1,2] Due to the large s-character of the vinylic C−H bonds, the acidity of cyclopropene resembles that of acetylene.[1,3,4] While lithiated cyclopropenes are useful synthetic reagents,[1,5] only computational structural information is available. Several ab initio studies predicted that the three-membered ring distorts markedly upon monolithiation:[6] the vicinal C(α)−C(γ) bond of 1-lithiocyclopropene (**1**) 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.[6c,d]



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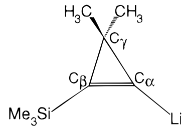

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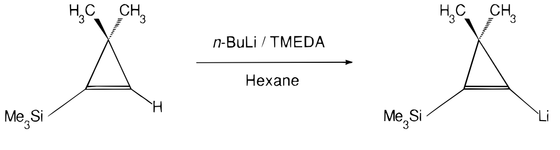
We now report the first X-ray structure of a lithiated cyclopropene, dimeric [3,3-dimethyl-2-(trimethylsilyl)cyclopropenyl]lithium−tetramethylethylenediamine (TMEDA), [(**2**·TMEDA)$_2$]. The distortion of the carbon ring in **2**, NMR data in THF solution, and higher level ab initio calculations all confirm the earlier theoretical predictions for 1-lithiocyclopropene.

Results and Discussion

The lithiated cyclopropene **2** was synthesized by metalation of the cyclopropene with *n*-butyllithium in hexane in the presence of 1 equiv of TMEDA (eq 1). Colorless crystals of (**2**·TMEDA)$_2$ were obtained by recrystallization of the crude product from hexane.



(1)

Structure of {[3,3-Dimethyl-2-(trimethylsilyl)cyclopropenyl]lithium−TMEDA}$_2$ [(2·TMEDA)$_2$] in the Solid State. The

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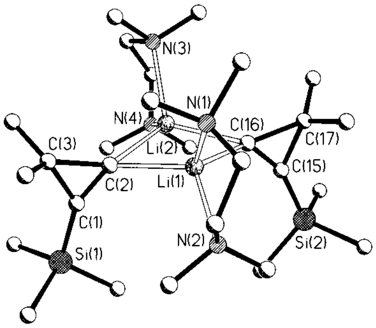

Figure 1. X-ray structure of dimeric [3,3-dimethyl-2-(trimethylsilyl)cyclopropenyl]lithium−TMEDA. The hydrogen atoms have been omitted for clarity.

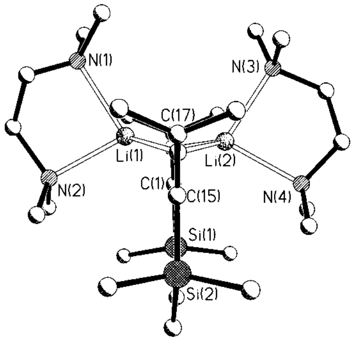

Figure 2. Plot of dimeric [3,3-dimethyl-2-(trimethylsilyl)cyclopropenyl]lithium−TMEDA along the C(16)−C(2) axis showing the cisoid structure and the tilting of the TMEDA molecules.

Table 1. Bond Distances (pm) and Angles (deg) of (**2**·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)

molecular structure of (**2**·TMEDA)$_2$ is shown in Figure 1; bond distances and angles are given in Table 1. The asymmetric unit contains two [3,3-dimethyl-2-(trimethylsilyl)cyclopropenyl]lithium and two TMEDA molecules. The two cyclopropenyl rings are nearly coplanar (deviation of 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 (**2**·TMEDA)$_2$ are typical of dimeric organolithium compounds.[7] Chelation by a TMEDA ligand results in a distorted tetrahedral geometry around the lithiums. The TMEDA ligands are disordered; similar interconversion between the two puckered conformations is often found.[8]

Although dimeric organolithium structures are well-known,[7,8b−d,9,10] the C_{2v} symmetry (not crystallographic) of (**2**·TMEDA)$_2$ and the cisoid orientation of the cyclopropenyl rings are remarkable (Figure 2). 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)$_2$,[9b] (2-lithiobenzothiophene−TMEDA)$_2$,[8d] (2-lithiothiophene−TMEDA)$_2$,[8d] (*n*-butyllithium-TMEDA)$_2$,[10a] and (*tert*-butyllithium−Et_2O)$_2$.[10b] 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 2) 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.

Interestingly, the lithiated cyclopropene dimer, (**1**)$_2$, like the phenyllithium dimer,[11] was computed to have two planar tetracoordinate carbon ($R^1R^2CLi_2$) fragments.[7a] At the Becke-3LYP/6-31G* level,[24] 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 3). 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 cyclopropene carbon natural charges[29] of planar (**1**)$_2$ (C(α), −0.57; C(β), −0.26; C(γ), −0.66) document the distribution[6c] of the negative charge over the three carbon centers of the cyclopropenyl ring and a high negative value of C(γ). However, the solid-state structure of (**2**·TMEDA)$_2$ reveals the "perpendicular" geometry of the solvated dimer: 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 1)). As was found with dimeric TMEDA-solvated phenyllithium,[9b] lithium solvation favors the "perpendicular" form[11] usually observed in dimeric organolithium compounds (in the dimers, solvation results in the preferred lithium tetracoordination).[7,12] Also, steric hindrance (see above) is lessened in the perpendicular ("tetrahedral") geometry of (**2**·TMEDA)$_2$.

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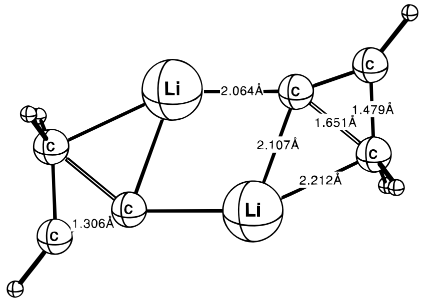
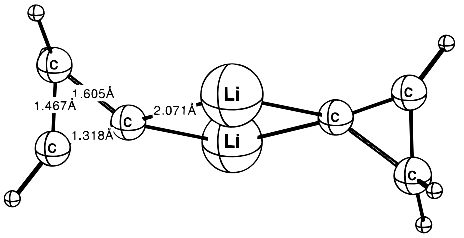


planar, C_{2h}, (0.0)



perpendicular, C_{2h}, (10.9)

Figure 3. Becke3LYP/6-31G* optimized structures of planar and perpendicular dimeric cyclopropenyllithium.

The most remarkable structural features of (**2**·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 1)). The non-olefinic C−C ring bond length in cyclopropene and its derivatives is about 151−152 pm in the gas phase (Figure 4)[4,13] (the mean of 11 crystal structures is 152.3 pm).[14] 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 (**2**·TMEDA)$_2$ show a similar 4 pm elongation: whereas the C=C bond length of 11 cyclopropenes is 129.2 pm (solid state, mean)[14] and the gas-phase value ranges between 129 and 130 pm (Figure 4),[4,13] 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 (**2**·TMEDA)$_2$ are shortened (C(1)−C(3), 148.9(2) pm; C(15)−C(17), 148.5(2) pm).

The distortion of the three-membered ring in 1-lithiocyclopropene (**1**) and its derivatives reflects the rehybridization at the lithiated carbon. According to Walsh[15a] and to Bent,[15b] 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[29] computed at Becke3LYP/6-311+G** [24] (Figure 5): the C(α) hybridization in **1** 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 **1** is even ca. 10 pm longer compared with cyclopropene (the Becke3LYP/6-311+G** [24] 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 **1** 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).[14] Consequently, the distal C(β)−C(γ) ring bond in **1** is shortened to 147.2 pm. The ring deformation in 1-lithiocyclopropene was predicted computationally;[6c] the rehybridization at the lithiated carbon demonstrated by the NLMO carbon hybridizations[29] (computed at Becke3LYP/6-311+G** [24]) now explains why the cyclopropenyl ring is distorted. Whereas the three-membered ring bond lengths and endocyclic angles in monolithiated cyclopropene (**1**) are strongly deformed, the balancing effect of the lithium and the electropositive silicon substituent in **2** results in smaller changes: the C(α)−C(γ) and the vinylic C(α)−C(β) ring bonds in (**2**·TMEDA)$_2$ show a

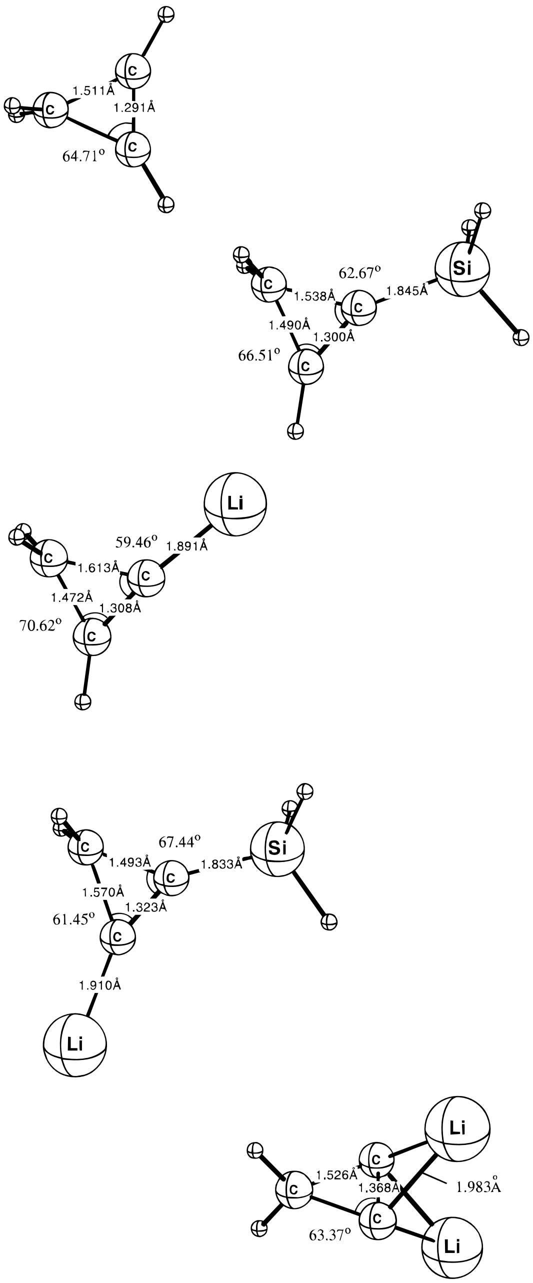


Figure 4. Becke3LYP/6-311+G** optimized structures (energy minima) of cyclopropene, 1-silylcyclopropene, (1-cyclopropenyl)-lithium, (2-silylcyclopropenyl)lithium and 1,2-dilithiocyclopropene. Note the distortion—bond lengths and endocyclic angles—of the three-membered rings. Lithium substitution dominates the distortion in (2-silylcyclopropenyl)lithium, originating from the less electropositive SiH_3 substituent.

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Table 2. Ring Distortion—Bond Lengths (pm) and Endocyclic Angles (deg)—of Substituted Cyclopropenes (and the 1-Cyclopropenyl Anion)[a]

compd	$C(\alpha)-C(\beta)$	$C(\alpha)-C(\gamma)$	$C(\beta)-C(\gamma)$	$C(\beta)C(\alpha)C(\gamma)$	$C(\alpha)C(\beta)C(\gamma)$	structural data
cyclopropene	129.1	151.1	151.1	64.71	64.71	Becke3LYP/6-311+G**
	129−130	151−152	151−152			gas-phase (cyclopropene and derivatives)[b]
	129.2	152.3	152.3	64.9	64.9	X-ray (mean of 11 structures)[c]
1-silylcyclopropene	130.0	153.8	149.0	62.67	66.51	Becke3LYP/6-311+G**
1-cyclopropenyl anion	132.2	163.3	147.4	58.73	71.25	Becke3LYP/6-311+G**
1-lithiocyclopropene (**1**)	130.8	161.3	147.2	59.46	70.62	Becke3LYP/6-311+G**
2	133.1(2)	156.0(2)	148.7(2)	61.30(11)	66.96(12)	X-ray (mean values in (**2**·TMEDA)$_2$)
(2-silylcyclopropenyl)lithium	132.3	157.0	149.3	61.45	67.44	Becke3LYP/6-311+G**
1,2-dilithiocyclopropene	136.8	152.6	152.6	63.37	63.37	Becke3LYP/6-311+G**

[a] C(α) is the lithiated carbon. [b] See refs 4 and 13. [c] See ref 14.

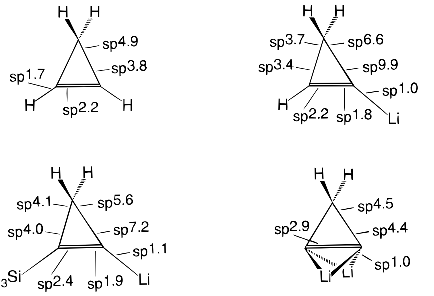

Figure 5. NLMO carbon hybridizations computed at Becke3LYP/6-311+G** of cyclopropene, (1-cyclopropenyl)lithium, (2-silylcyclopropenyl)lithium and 1,2-dilithiocyclopropene.

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**

species	point group	E_{tot}	ZPE[a]
cyclopropene	C_{2v}	−116.654 32	35.0 (0)
1-cyclopropenyl anion	C_s	−116.028 02	26.0 (0)
1-lithiocyclopropene (**1**)	C_s	−123.573 47	28.4 (0)
1-silylcyclopropene	C_s	−407.385 82	45.0 (0)
(2-silylcyclopropenyl)lithium	C_s	−414.306 58	38.4 (0)
1,2-dilithiocyclopropene	C_{2v}	−130.476 68	22.9 (0)

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

nearly equal elongation of 4 pm; the distal $C(\beta)-C(\gamma)$ 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 (**2**·TMEDA)$_2$ are less deformed: $\angle C(\beta)C(\alpha)C(\gamma)$ (C(1)C(2)C(3) and C(15)C(16)C(17), respectively) is decreased to 61.3° (mean), and $\angle C(\alpha)C(\beta)C(\gamma)$ (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**,[24] 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 (**2**·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[29] 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 with the values of cyclopropene (Table 2; the Becke3LYP/6-311+G** [24] optimized geometry of 1,2-dilithiocyclopropene 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[29] indicate the increase in p-character of the C═C bond (Figure 5).

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.[9b,16,17]

Structure in Solution. Crystals of the TMEDA solvate of **2**, enriched with 96% ^{6}Li, were dissolved in THF-d_8 (the 1:1 stoichiometry of TMEDA:**2** 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 THF-d_8 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 (the downfield shift of the ^{13}C NMR signal of the lithiated carbon in **2** relative to the δ (^{13}C(2)) of 3,3-dimethyl-1-(trimethylsilyl)cyclopropene, $\Delta\delta = 55.7$, is similar to values observed for monomeric vinyllithium derivatives[18]).[19,20a,b] The very large $^1J_{^{13}C-^{6}Li}$ coupling constant of 17.6 Hz in **2** indicates high s-character of the C(α) orbital (C−Li bond):[20a,b,21] the NLMO C(α) hybridization[29] in (1-silylcyclopropenyl)lithium is sp$^{1.1}$ compared with the sp$^{1.7}$ hybrid used in bonding to hydrogen (in cyclopropene (Figure 5)).

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[21] A three-line $^{13}C-^{6}Li$ coupling pattern is also observed for the lithiated carbon of [3,3-dimethyl-2-(1,1-diphenylmethoxymethyl)cyclopropenyl]lithium (**3**) (THF-d_8, −90 °C), as well as a similarly large coupling constant, $^1J^{13}C-^{6}Li = 16.8$ Hz, is found: Sorger, K.; Schleyer, P. v. R. Unpublished results.

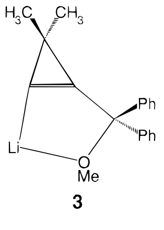

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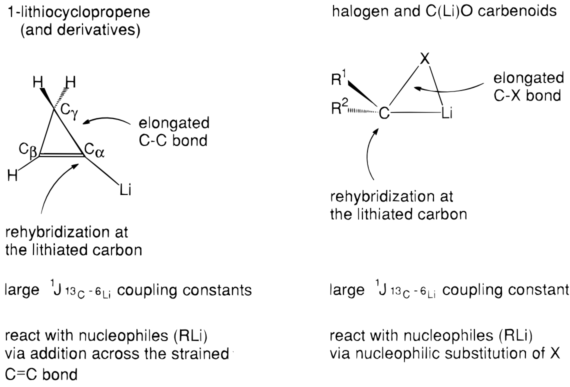
Chart 1. Characteristics of 1-Lithiocyclopropene (and Derivatives) and Carbenoids



Coupling constants of monomeric organolithium compounds usually range between 10 and 16 Hz;[19] larger magnitudes (16.3–17.2 Hz) have only been reported before for α-halogen-substituted organolithium compounds (carbenoids).[20a,b]

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 (Chart 1).[7g,20,22] This results in large $^1J_{^{13}\mathrm{C}-^6\mathrm{Li}}$ coupling constants (see above) as well as a decidedly elongated C–X bond.[20,22,23] Carbenoids easily react with nucleophiles, e.g. RLi, by metal-assisted nucleophilic substitution of 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[23b,c,e]).[22a,c,23d,e]

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 **1** (due to the balancing rehybridization effect of the lithium and the electropositive silicon substituent in **2**, only a ca. 4 pm elongation is found in the X-ray structure of (**2**·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.[1,2] While the $^1J_{^{13}\mathrm{C}-^6\mathrm{Li}}$ coupling constant of 17.6 Hz (16.8 Hz in [3,3-dimethyl-2-(1,1-diphenylmethoxymethyl)cyclopropenyl]lithium (**3**))[21] is as large as the values found for halogen carbenoids,[20a,b] 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.[5c] Despite the strong rehybridization relationship with carbenoids, lithiated cyclopropenes do not have Li/C carbenoid nature.

Conclusions

The TMEDA solvate of [3,3-dimethyl-2-(trimethylsilyl)-cyclopropenyl]lithium (**2**), synthesized by hydrogen–lithium exchange, adopts a cisoid dimeric structure in the solid state but is a monomer in THF solution. The cyclopropenyl ring of **2** 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 **2** can be attributed to rehybridization at the lithiated carbon which is confirmed both by the NLMO hybridizations and by the large coupling constant, $^1J_{^{13}\mathrm{C}-^6\mathrm{Li}} = 17.6$ Hz (the usual range for organolithium monomers is 10 and 16 Hz),[19] observed in THF solution. Although both the structural ring distortion in 1-lithiocyclopropene (and its derivative **2**) and the large $^1J_{^{13}\mathrm{C}-^6\mathrm{Li}}$ coupling constants in **2** and **3**[21] resemble carbenoids, lithiated cyclopropenes do not have carbenoid nature.

Computational Methods. Calculations were performed using the Gaussian 94 program package.[24] All geometries were optimized using the 6-31G* and 6-311+G** basis sets at the Becke3LYP level of the density functional theory (DFT)[25,26] and characterized as minima or transition structures by calculating the vibrational frequencies.[27] The Becke3LYP method is a hybrid of Hartree–Fock exchange with DFT exchange correlation.[26] DFT calculations on a varity of organolithium compounds have recently been shown to reproduce accurately high-level ab initio and experimental data.[28] Natural charges and natural localized molecular orbital carbon hybridizations were calculated by using the natural population analysis (NPA) method.[29]

Experimental Section

General Conditions. All experiments were carried out under an argon atmosphere by using standard Schlenk and needle/septum techniques. Hexane was freshly distilled from sodium/benzophenone prior to use. TMEDA was dried over CaH_2, distilled, and subsequently kept over Na/Pb alloy. 3,3-Dimethyl-1-(trimethylsilyl)cyclopropene was prepared according to Baird *et al.*[5i,j] and de Meijere *et al.*[5e]

NMR spectra were recorded on a JEOL GX spectrometer (frequencies: ^{1}H, 400 MHz; ^{13}C, 100.6 MHz). ^{1}H and ^{13}C chemical shifts are given with respect to TMS and are based on the THF-d_8 solvent signals (^{1}H, $\delta = 3.58$; ^{13}C, $\delta = 67.4$).

{[3,3-Dimethyl-2-(trimethylsilyl)cyclopropenyl]lithium–TMEDA}$_2$ [(2·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 (0.081 g, 0.58 mmol) and TMEDA (0.58 mmol, 0.09 mL) in 0.5 mL of hexane. This caused a white solid to precipitate, which dissolved on warming

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to room temperature (within 30 min). 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.[30] ^{1}H NMR (THF-d_8, −20 °C): $\delta = 1.02$ (6 H, s, CCH_3), 0.03 (9 H, s, SiCH_3); TMEDA signals at $\delta = 2.32$ (4 H, s, NCH_2), 2.19 (12 H, s, NCH_3). ^{13}C NMR (THF-d_8, −20 °C): $\delta = 192.19$ (C(1)), 139.73 (C(2)), 33.22 (CCH$_3$), 12.82 (C(3)), 1.17 (SiCH$_3$); TMEDA signals at $\delta = 58.26$ (NCH$_2$), 46.54 (NCH$_3$).

X-ray Data Collection. Crystal data of dimeric (**2**·TMEDA)$_2$, [$C_{28}H_{62}Li_2N_4Si_2$]: $M = 524.88$, monoclinic, space group $P2_1/n$, $a = 1879.9(2)$ pm, $b = 1035.0(2)$ pm, $c = 2045.5(2)$ pm, $\beta = 113.198(9)°$, $V = 3.6580(8)$ nm^3, $Z = 4$, $D_{\text{calcd}} = 0.953$ Mg/m^3, $F(000) = 1168$, $\lambda = 71.073$ pm, $T = 153(2)$ K, μ (Mo Kα) = 0.116 mm^{-1}, data were collected on a Stoe-Siemens-AED. Intensities of a 0.6 × 0.6 × 0.8 mm rapidly cooled crystal in an oil drop[30] were collected by the $2\theta/\omega$ method in the range $8° \leq 2\theta \leq 55°$. Of a total of 9413 refections, 8446 were independent and used to refine 431 parameters, largest difference peak and hole: 345 and −278 e/nm^3, $R1$ ($F > 4\sigma$ (F)) = 0.0491 and $wR2 = 0.1381$ (all data), with $R1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $wR2 = (\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2)^{0.5}$. The structure was solved with direct methods (SHELXS-90)[31] and refined by full-matrix least squares on F^2 (SHELXL-93).[32] 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.

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

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Supporting Information Available: A fully labeled figure of 50% anisotropic displacement parameters, tables of bond distances, bond angles, positional parameters, and thermal parameters for the X-ray structure of (2·TMEDA)$_2$ (9 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masterhead page for ordering information and Internet access instructions.

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