Highly Twisted Ethylene Dianion Dilithium Stabilized by Phenyl and Silyl Groups

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Phenyl- and silyl-substituted ethylene dianion dilithiums, [1-phenyl-1,2,2-tris(trimethylsilyl)ethylene]{bis[(dimethoxyethane)lithium(I)]} (**2**) and [1,1-diphenyl-2,2-bis(trimethylsilyl)ethylene][tris(tetrahydrofuran)dilithium(I)] (**4**), were prepared and characterized by X-ray crystallography as well as NMR spectra. The crystal structures of **2** and **4** revealed interesting structural features. One of the lithium cations was located near to the two central carbon atoms, ipso and ortho carbons of the phenyl ring, while the other one was found above the benzene ring. The central C–C bond is twisted by ca. 90° for **2** and ca. 70° for **4**.

The structure and bonding of organolithium compounds are of considerable current interest.[1)] In particular, 1,2-dilithioethane is a very interesting class of organolithiums in view of theoretical and experimental studies.[2)] X-Ray analyses of the dilithium compounds of π-conjugated stilbene and bifluorenylidene have revealed that the lithium cations are connected to the central two carbon atoms to afford doubly bridged structures.[3)] In 1989, we reported on the synthesis and crystal structure of [1,1,2,2-tetrakis(trimethylsilyl)ethylene]{bis[(tetrahydrofuran)lithium(I)]} as the first non-conjugated 1,2-dilithioethane derivative.[4)] The structure determined by X-ray crystallography revealed that the lithium atoms were bridged to the central two anionic carbon atoms with a dihedral angle of 33.6°.[4a)] We recently disclosed that (2,2,2′,2′,5,5,5′,5′-octamethyl-2,2′,5,5′-tetrasilabicyclopentylidene){bis[(tetrahydrofuran)lithium(I)]} has a symmetrically double-bridged planar structure.[5)] We report herein on detailed studies of the synthesis, crystal structures, and spectroscopic properties of the orthogonal ethylene dianion dilithiums derived from 1-phenyl-1,2,2-tris(trimethylsilyl)ethylene (**1**) and 1,1-diphenyl-2,2-bis(trimethylsilyl)ethylene (**3**).[6)]

Results and Discussion

Synthesis and Crystal Structure of Dianion Dilithium (2). Our earlier paper reported on the successful preparation of several dianion dilithiums by the reaction of the silyl-substituted olefins or benzenes with lithium metal in THF.[4—7)] Similarly, [1-phenyl-1,2,2-tris(trimethylsilyl)ethylene]{bis[(dimethoxyethane)lithium(I)]} (**2**) and [1,1-diphenyl-2,2-bis(trimethylsilyl)ethylene][tris(tetrahydrofuran)dilithium(I)] (**4**) were synthesized by the reactions of 1-phenyl-1,2,2-tris(trimethylsilyl)ethylene (**1**) and 1,1-diphenyl-2,2-bis(trimethylsilyl)ethylene (**3**) with lithium metal in THF. Thus, compound **1** was allowed to react with excess lithium metal in dry oxygen-free THF at room temperature under argon. The solution immediately turned to dark red upon a two-electron reduction to give a solution of the dianion. Several attempts to obtain single crystals of the dianion dilithium prepared in THF for X-ray crystallography were unsuccessful. However, single crystals for X-ray analysis were obtained when the reduction of **1** by lithium metal was carried out in a mixture of 1,2-dimethoxyethane (DME) and THF. Evaporation of the solvent with a vacuum line afforded dark-black solids, which were recrystallized from hexane to give a pure **2** (Scheme 1). The crystals **2** were highly air and moisture sensitive, and immediately reverted to **1** upon exposure to air.

The molecular structure of **2** determined by X-ray crystallography is shown in Fig. 1. The bond lengths, bond angles, and torsion angles are given in Table 1. An X-ray crystallographic analysis of **2** has revealed several kinds of quite unusual structural features. The interesting point is the location of the lithium atoms. One of the lithium cations is located near to the central two carbons atoms, ipso and ortho carbons of the phenyl ring, and the other one is above the benzene ring. To each lithium atom, bidentate DME is bound.

The length of the central C–C bond is 1.534(9) Å.[8)] The bond distances of Si1–C1 (1.810(6) Å) and Si2–C1

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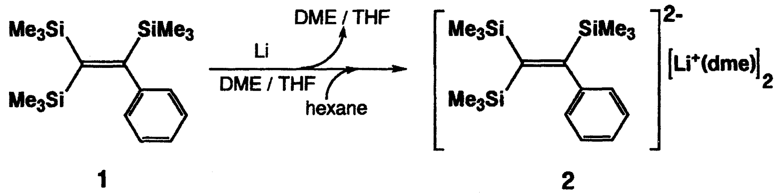


Scheme 1.

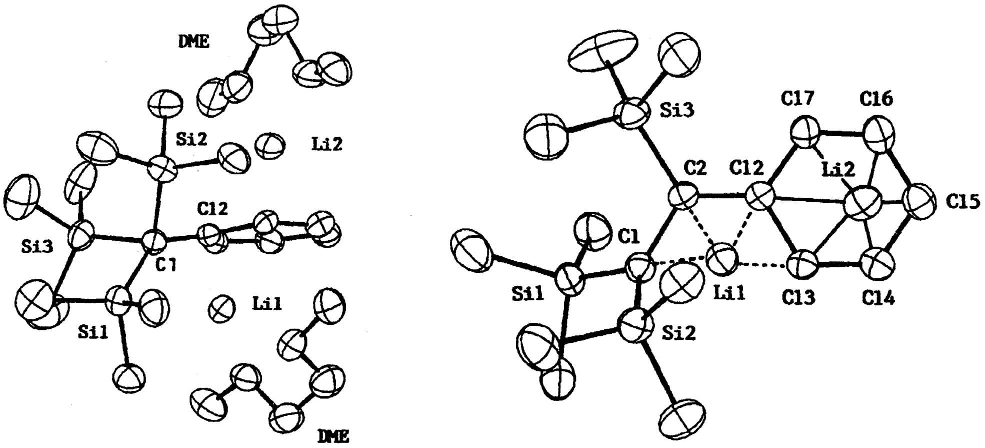


Fig. 1. ORTEP drawing of **2**: left, view through C1–C2 bond; right, top view (DME is omitted for clarity).

Table 1. Selected Bond Distances (Å), Angles (deg.), and Torsion Angles (deg.) of **2**

	Bond distances		
C1–C2	1.534(9)	Li1–C1	2.234(13)
C1–Si1	1.810(6)	Li1–C2	2.272(12)
C1–Si2	1.826(6)	Li1–C12	2.265(13)
C2–Si3	1.867(6)	Li1–C13	2.330(13)
C2–C12	1.398(9)	Li2–C12	2.594(15)
C12–C13	1.474(8)	Li2–C13	2.375(15)
C12–C17	1.455(9)	Li2–C14	2.289(14)
C13–C14	1.391(9)	Li2–C15	2.320(15)
C14–C15	1.389(10)	Li2–C16	2.354(14)
C15–C16	1.411(11)	Li2–C17	2.460(14)
C16–C17	1.366(10)		
	Bond angles		
Si1–C1–Si2	116.4(3)	C2–C12–C17	125.4(5)
Si1–C1–C2	122.5(4)	C12–C13–C14	121.9(5)
Si2–C1–C2	116.8(4)	C12–C17–C16	123.9(6)
Si3–C2–C1	118.7(4)	C13–C12–C17	111.7(5)
Si3–C2–C12	120.4(4)	C13–C14–C15	123.5(6)
C1–C2–C12	119.9(5)	C14–C15–C16	115.8(6)
C2–C12–C13	122.9(5)	C15–C16–C17	122.7(6)
	Torsion angles		
Si1–C1–C2–Si3	63.8(6)	Si3–C2–C12–C13	162.9(4)
Si1–C1–C2–C12	128.0(5)	Si3–C2–C12–C17	19.9(8)
Si2–C1–C2–Si3	92.0(5)	C1–C2–C12–C13	5.0(9)
Si2–C1–C2–C12	76.1(6)	C1–C2–C12–C17	172.2(5)

(1.826(6) Å) are shorter than the mean Si–C (1.88 Å). The shortening of Si1–C1 and Si2–C1 is suggestive of pπ–σ*(Si–C) bonding, and the anion for $C(SiMe_3)_2$ is stabilized by the two silyl groups. In contrast, the bond length of Si3–C2 (1.867(6) Å) is almost normal; this silyl group dose not participate in the stabilization of the anion for $CPh(SiMe_3)$. Instead, this anion is largely stabilized by the phenyl group. Thus, the C2–C12 bond distance (1.398(9) Å) is appreciably shortened, which indicates that the negative charge is delocalized over the aromatic ring. Although the benzene ring is essentially planar, all aromatic C–C bonds differ in distance. The distances of C13–C14 (1.391(9) Å) and C16–C17 (1.366(10) Å) are shortened to some extent, whereas those of C12–C13 (1.474(8) Å), C12–C17 (1.455(9) Å), and C15–C16 (1.411(11) Å) are stretched compared to the usual range of the aromatic C–C bond distance of 1.40 Å. However, the C14–C15 bond (1.389(10) Å) is unexpectedly shortened. C1, C2, Si3, and aromatic carbons are arranged almost in the same plane. Therefore, a planar conjugated system is produced.

Li1 and Li2 are in close contact with four carbon atoms (C1, C2, C12, C13) and six aromatic carbons (C12–C17), respectively. The distances of Li2 from the benzene ring ranges from 2.29(1) Å to 2.59(1) Å, which are typical distances for the π-complexed organolithium.[1] The Li2 is not located directly over the central position of the benzene ring, but is in rather close contact with the para position of the benzene ring. This is probably caused by an electrostatic attraction between the lithium cation and delocalized negative charge on the para position.

A quite interesting feature of the structure is the large torsion angles. The torsion angles of Si2–C1–C2–C12 and Si2–C1–C2–Si3 are 76.1° and 92.0°, respectively. The sum of the bond angles at C1 (355.7°) indicates that the anionic C1 carbon is slightly pyramidalized, whereas the C2 carbon is nearly planar (sum of the bond angle, 359.0°).[9)]

The dianion dilithium **2** is almost perpendicular, whereas the (octamethyl-2,2′,5,5′-tetrasilabicyclopentylidene){bis[(tetrahydrofuran)lithium(I)]} is completely planar.[5)] Since the anion is highly stabilized by the phenyl ring, one of the lithium must be located above the benzene ring. Since the conjugated benzene ring is coplanar to the central C–C bond, the steric repulsion in the planar structure is larger than that in the twisted structure. Consequently, the ethylene dianion dilithium **2** favors a twisted structure in order to relieve the steric repulsion as well as an electrostatic repulsion between the adjacent negative charges.[10)]

NMR Spectra of Dianion Dilithiums (2). The orthogonal structure of **2**, found by X-ray crystallography, is maintained in solution. The two ortho and meta protons as well as the carbons of the phenyl ring are nonequivalent, since the free rotation of the aryl group is frozen due to the fixed structure by lithium. In ^{1}H NMR spectrum in toluene-d_8 (298 K), the aryl protons were observed at δ=4.78 (1H, J=6.9 Hz) as a triplet for the para proton, δ=5.98 (1H, J=6.9 Hz) as a triplet for meta proton, δ=6.23 (1H, J=6.9 Hz) as a doublet for ortho proton, and δ=6.33—6.44 (2H, m) for the ortho and meta protons (Fig. 2).[11)] Correspondingly, aryl carbons were observed as six separate signals at δ=100.7 (*para* C), 118.4 (*ortho* C), 125.1 (*ortho* C), 131.7 (*meta* C), 137.6 (*meta* C), and 145.6 (*ipso* C). Extremely large upfield shifts of both the aromatic para proton and the para carbon are suggestive of a substantial delocalization of the negative change over the phenyl ring. The anionic carbons can be seen at δ=19.5 for $(Me_3Si)_2C$ and δ=88.4 for Ph$(Me_3Si)C$. The shift to the lower field of the latter carbon is caused by a substantial delocalization of the negative charge over the aromatic ring. Two sets of resonances for the trimethylsilyl groups can be observed; δ=0.50 (s, 18H) and 0.59 (s, 9H) in ^{1}H NMR, δ=4.6 (1×SiMe$_3$) and 6.9 (2×SiMe$_3$) in ^{13}C NMR, δ=−16.3 (2×SiMe$_3$) and −14.8 (1×SiMe$_3$) in ^{29}Si NMR. These spectroscopic data are in accordance with the orthogonal structure of the dianion in solution.

However, only one signal of the ^{6}Li NMR resonance was observed at δ=−2.48 at room temperature. By lowering the temperature, the ^{6}Li signal became wide, and ultimately a broad peak. At 200 K, sharp ^{6}Li resonances with the same intensity were observed at δ=−2.43 and −2.60 (Fig. 3). The dynamic process was reversible and the coalescence temperature (T_c) was 215 K, giving $\Delta G^{\ddagger}_{215\mathrm{K}}$=47 kJ mol^{-1} for the lithium interconversion.[12)] The small $\Delta G^{\ddagger}$ value implies a facile interconversion between Li1 and Li2. The orthogonal structure of **2** facilitates an interconversion between the two lithiums (Scheme 3).

Synthesis and Crystal Structure of Dianion Dilithium (4). The dianion solution was prepared by the reaction of 1,1-diphenyl-2,2-bis(trimethylsilyl)ethylene (**2**) with lithium in dry oxygen-free THF. After removing the solvent, recrystallization from pentane afforded [1,1-diphenyl-2,2-bis(trimethylsilyl)ethylene]-[tris(tetrahydrofuran)dilithium(I)] (**4**) as dark-red crystals suitable for X-ray crystallography (Scheme 2).

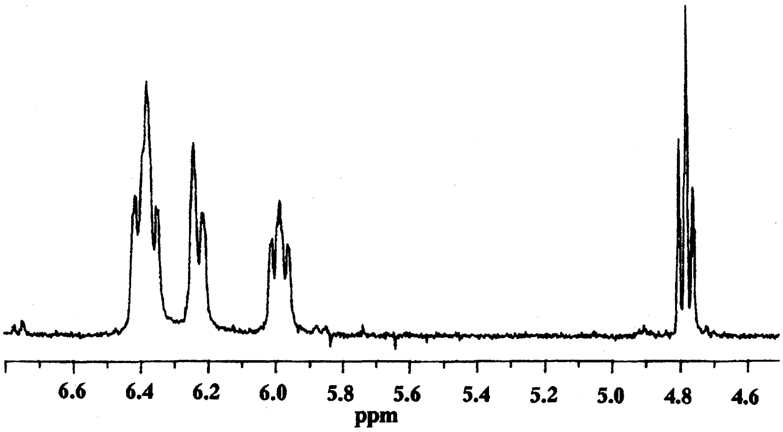
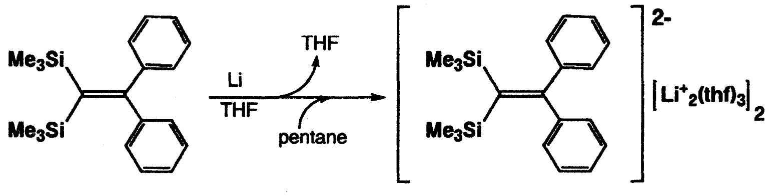


Fig. 2. ^{1}H NMR of **2** in toluene-d_8 at 298 K (aromatic region).



3 **4**

Scheme 2.

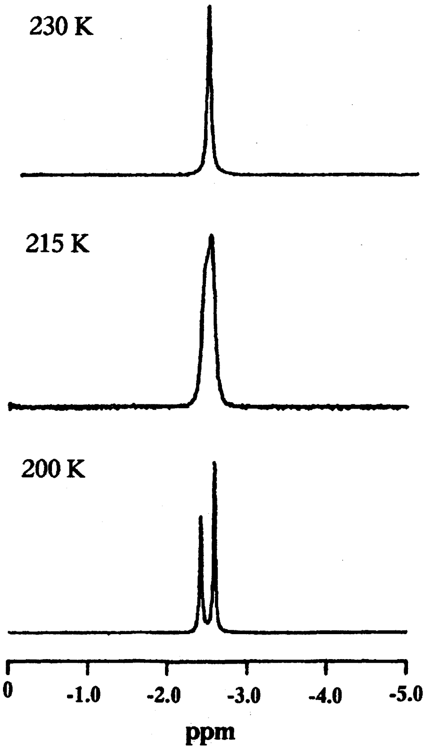
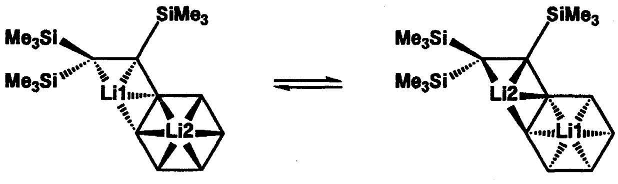


Fig. 3. Temperature dependent ^{6}Li NMR spectra of **2** in toluene-d_8.



Scheme 3.

Table 2. Selected Bond Distances (Å), Angles (deg.), and Torsion Angles (deg.) of **4**

	Bond distances		
C1–C2	1.517(7)	C23–C24	1.377(10)
C1–Si1	1.819(6)	C24–C25	1.379(10)
C1–Si2	1.827(6)	C25–C26	1.381(9)
C2–C11	1.400(7)	Li1–C1	2.116(12)
C2–C21	1.481(7)	Li1–C2	2.182(12)
C11–C12	1.457(7)	Li1–C11	2.260(12)
C11–C16	1.466(7)	Li1–C12	2.350(9)
C12–C13	1.387(7)	Li2–C11	2.681(9)
C13–C14	1.395(9)	Li2–C12	2.429(9)
C14–C15	1.398(9)	Li2–C13	2.379(12)
C15–C16	1.363(9)	Li2–C14	2.410(12)
C21–C22	1.393(7)	Li2–C15	2.453(11)
C21–C26	1.399(7)	Li2–C16	2.559(11)
C22–C23	1.369(9)		
	Bond angles		
Si1–C1–Si2	118.0(3)	C11–C16–C15	122.2(5)
Si1–C1–C2	116.5(3)	C12–C11–C16	112.4(4)
Si2–C1–C2	119.6(3)	C12–C13–C14	121.8(5)
C1–C2–C11	122.8(4)	C13–C14–C15	117.0(6)
C1–C2–C21	118.1(4)	C14–C15–C16	123.1(6)
C2–C11–C12	124.0(4)	C21–C22–C23	122.5(5)
C2–C11–C16	123.5(4)	C21–C26–C25	121.7(5)
C2–C21–C22	124.4(4)	C22–C21–C26	116.0(5)
C2–C21–C26	119.6(4)	C22–C23–C24	120.4(6)
C11–C2–C21	119.1(4)	C23–C24–C25	118.9(6)
C11–C12–C13	122.5(5)	C24–C25–C26	120.4(6)
	Torsion angles		
Si1–C1–C2–C11	137.7(4)	C1–C2–C11–C12	4.3(8)
Si1–C1–C2–C21	44.2(5)	C1–C2–C11–C16	178.9(4)
Si2–C1–C2–C11	69.8(6)	C1–C2–C21–C22	118.6(5)
Si2–C1–C2–C21	108.3(4)	C1–C2–C21–C26	58.6(6)

An ORTEP drawing of **4** is shown in Fig. 4. The bond lengths, angles, and torsion angles are listed in Table 2. As in **2**, one of the lithium atoms is located near to the central C–C bond, ipso and ortho carbons of the phenyl ring, and the other one is located above the benzene ring. Li1, located near to the central bond, is in contact with four carbon atoms (C1, C2, C11, C12), and one THF molecule is coordinated. Li2 above the benzene ring is in close contact with the para position of the benzene ring, as found in **2**, and two THF molecules

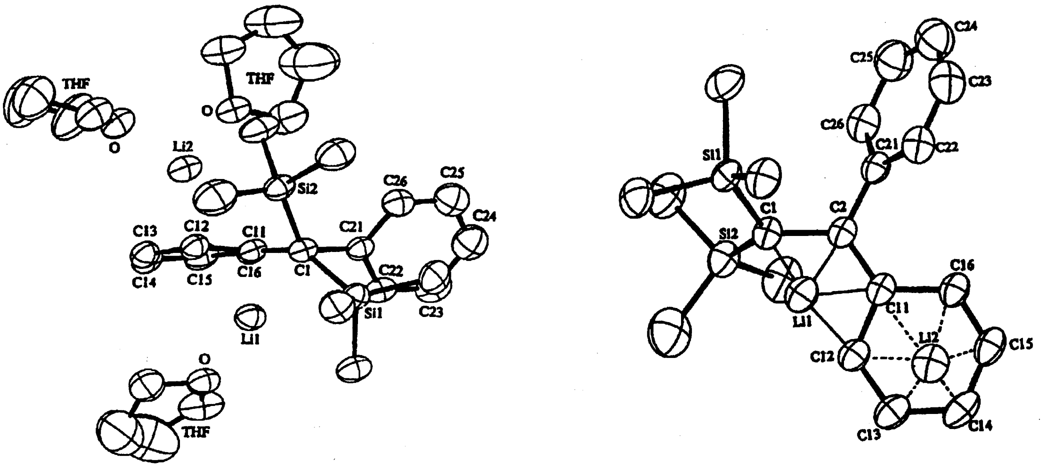
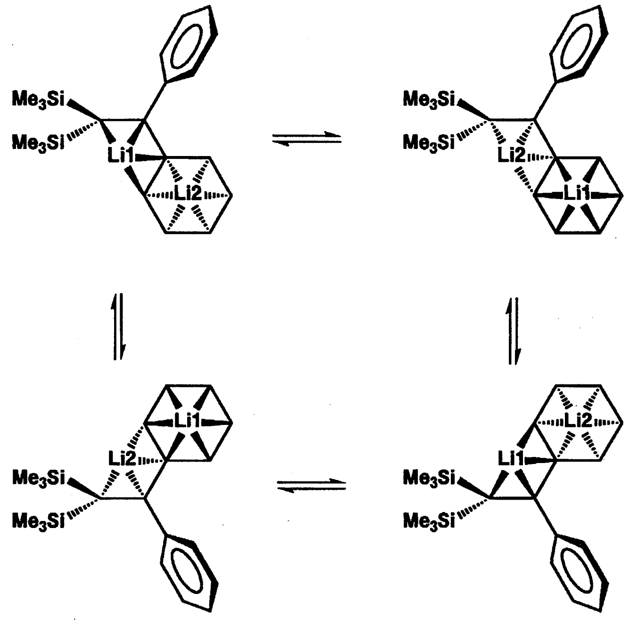


Fig. 4. ORTEP drawing of **4**: left, view through C1–C2 bond; right, top view (THF is omitted for clarity).

are coordinated. The molecular structure of **4** is very close to that of **2**. The length of the central C–C bond is 1.517(7) Å and twisted, as determined by the torsion angle of Si2–C1–C2–C11 (69.8°). The anionic carbons (C1 and C2) are arranged in the same plane of the benzene ring (C11–C16) (torsion angle of C1–C2–C11–C12, 4.3°). Delocalization of the negative charge into this benzene ring results in the double bond character of C2–C11 (1.400(7) Å) as well as the alternation of bond lengths of the aromatic ring. In contrast, the other benzene ring (C21–C26) is twisted by ca. 60°; such a bond alternation of the benzene ring can not be observed. The small pyramidalization at C1 carbon (sum of bond angles, 354.1°) can be seen, as found in **2**, whereas the anionic C2 carbon is completely planar.

NMR Spectra of Dianion Dilithium (4). The dianion **4** also has an orthogonal structure in solution. By contrast to **2**, the NMR spectra of **4** are very simple. Thus, in ^{1}H NMR of **4** in toluene-d_8 at 298 K, the aryl protons were observed at δ=5.79 (2H, t, J=6.7 Hz) for para protons, δ=6.69 (4H, dd, J=6.7 Hz, J=8.2 Hz) for meta protons, and δ=6.85 (4H, d, J=8.2 Hz) for ortho protons. Aryl carbons were observed at δ= 105.1 (*para* C), 117.7 (*ortho* C), 128.6 (*meta* C), and 140.4 (*ipso* C). The anionic carbons appeared at δ= 24.3 for $(Me_3Si)_2C$ and δ=103.4 for Ph_2C. ^{6}Li and ^{29}Si resonances were observed at δ=−2.12 and δ=−11.6, respectively. A single resonance peak due to trimethylsilyl groups is consistent with the orthogonal structure of **4**. The equivalence of the two phenyl groups and the two lithiums (Li1 and Li2) is reasonably explained by means of the rapid interconversion of the two lithiums through the two benzene rings (Scheme 4). As a result, two phenyl groups and two lithiums become equivalent on the NMR time scale. However, the ^{6}Li signal was not split out, even at 200 K.



Scheme 4.

Conclusion. The present X-ray studies as well as the spectroscopic properties of ethylene dianion dilithiums substituted by silyl and phenyl groups evidently provide the first structural characterization of the orthogonal dianions. The dianions described here are stabilized by both phenyl and silyl groups. The NMR data and crystal structure are suggestive of a substantial delocalization of negative charge into the phenyl ring. Consequently, one Li^+ should be preferentially localized above the benzene ring due to the electrostatic situation. Owing to the steric repulsion of the vicinal substituent and/or the electronic repulsion of the adjacent negative charge, the central C–C bond is highly twisted. However, the orthogonal structure would not destroy the effectiveness of conjugation within each half the molecule. For **2**, each half of a twisted dianion would give $(Me_3Si)_2C^-$ stabilized by the two silyl groups and $Ph(Me_3Si)C^-$ stabilized by phenyl group. For **4**, each half would give $(Me_3Si)_2C^-$ and Ph_2C^-. The interconversion of the two lithiums in solution readily occurs due to the orthogonal structure.

Experimental

General Procedure. All of the manipulations were carried out in an atmosphere of dry argon. All of the solvents were dried and degassed over a potassium mirror in vacuo prior to use. Lithium-6 (95 atom %) metal was commercially available (Aldrich Chemical Company). The ^{1}H NMR spectra were recorded on a Bruker AC-300 FT spectrometer. ^{13}C, ^{29}Si, and ^{6}Li NMR spectra were collected on a Bruker AC-300 at 75.5, 59.6, and 44.2 MHz, respectively. ^{1}H and ^{13}C resonances of the dianions were assigned based on two-dimensional NMR techniques. The chemical shifts of ^{6}Li NMR are in ppm with respect to LiCl in MeOH. The mass spectra and high-resolution mass spectra were obtained on a Shimadzu QP-1000 or a JEOL IMS D-300 mass spectrometer.

1-Phenyl-1,2,2-tris(trimethylsilyl)ethylene (1).[13] A hexane solution (10 ml) of bromine (1.76 g, 11.1 mmol) was added to 1,1,2,2-tetramethyl-3-phenyl-4-trimethylsilyl-1,2-disilacyclobut-3-ene[14] (3.52 g, 12.1 mmol) in hexane (20 ml) at 0 °C. To the resulting mixture, was added an ether solution (45 ml) of MeLi (0.86 M, 38.7 mmol, 1 M=1 mol dm^{-3}) at 0 °C. The reaction mixture was stirred for 0.5 h at 0 °C, and then overnight at room temperature. The usual work-up gave **1** in 75% yield, mp 51—52 °C. ^{1}H NMR ($CDCl_3$) δ=−0.28 (s, 9H, SiMe$_3$), 0.04 (s, 9H, SiMe$_3$), 0.29 (s, 9H, SiMe$_3$), 6.77—6.84 (m, 2H, ArH), 7.06—7.22 (m, 3H, ArH); ^{13}C NMR ($CDCl_3$) δ=2.4, 3.3, 4.3, 125.5, 127.2, 128.2, 149.1, 160.2, 176.9; ^{29}Si NMR ($CDCl_3$) δ=−9.1, −8.6, −6.8. HRMS Found: m/z 320.1898. Calcd for $C_{17}H_{30}Si_3$: M, 320.1810.

$[Li^+(dme)]_2[(Me_3Si)_2C{=}C(SiMe_3)Ph]^{2-}$ (2). After lithium metal (70 mg, 10 mmol) and **1** (140 mg, 0.44 mmol) were placed in a Schlenk flask, dry oxygen-free DME (5 ml) and THF (10 ml) were introduced by vacuum transfer. The mixture was stirred for 1 h at room temperature to give a dark-red solution of dianion. Evaporation of the solvent afforded **2** as dark-black solids. ^{1}H NMR (C_7D_8)

δ=0.50 (s, 18H, 2SiMe$_3$), 0.59 (s, 9H, SiMe$_3$), 2.97 (s, 8H, DME), 3.16 (s, 12H, DME), 4.78 (t, 1H, J=6.9 Hz, *p*-H), 5.98 (t, 1H, J=6.9 Hz, *m*-H), 6.23 (d, 1H, J=6.9 Hz, *o*-H), 6.33—6.44 (m, 2H, *o*-H, *m*-H); ^{13}C NMR (C$_7$D$_8$) δ=4.6 (SiMe$_3$), 6.9 (2SiMe$_3$), 19.5 (C–Li), 59.3 (DME), 70.6 (DME), 88.4 (C–Li), 100.7, 118.4, 125.1, 131.7, 137.6, 145.6; ^{29}Si NMR (C$_7$D$_8$) δ=−16.3 (SiMe$_3$), −14.8 (2SiMe$_3$); ^{6}Li NMR (C$_7$D$_8$) δ=−2.48.

1,1-Diphenyl-2,2-bis(trimethylsilyl)ethylene (3). This compound was prepared by the reaction of tris(trimethylsilyl)methyllithium (30 mmol) with benzophenone (5.4 g, 30 mmol) according to a method from the literature.[15)]

[Li$_2^+$(thf)$_3$][(Me$_3$Si)$_2$C=CPh$_2$]$^{2-}$ (4). The lithium derivative **4** was prepared by a procedure similar to that used in the synthesis of **2**. A mixture of **3** (308 mg, 0.95 mmol), Li (30 mg, 4.3 mmol), and THF (2 ml) was stirred for 0.5 h to give a dark-red solution of the dianion. Evaporation of the solvent afforded **4** as dark red-solids. ^{1}H NMR (C$_7$D$_8$) δ=0.37 (s, 18H, SiMe$_3$), 1.40—1.48 (m, 12H, THF), 3.51—3.59 (m, 12H, THF), 5.79 (t, 2H, J=6.7 Hz, *p*-H), 6.69 (dd, 4H, J=6.7 Hz, J=8.2 Hz, *m*-H), 6.85 (d, 4H, J=8.2 Hz, *o*-H); ^{13}C NMR (C$_7$D$_8$) δ=6.3 24.3 (C–Li), 25.7 (THF), 68.5 (THF), 103.4 (C–Li), 105.1 (*p*-C), 117.7 (*o*-C), 128.6 (*m*-C), 140.4 (ipso C); ^{29}Si NMR (C$_7$D$_8$) δ=−11.6; ^{6}Li NMR (C$_7$D$_8$) δ=−2.12.

X-Ray Crystallography. Single crystals of **2** and **4** for X-ray diffractions were grown from hexane and pentane, respectively. A single crystal was selected, cut to a suitable size, and sealed in a capillary glass tube in a globe box. The X-ray crystallographic experiments were performed on a Rigaku-Denki AFC 5R diffractometer equipped with graphite monochromatized Cu $K\alpha$ radiation (λ=1.5418 Å). Crystal data of **2**: MF=C$_{25}$H$_{52}$O$_4$Si$_3$Li$_2$, MW=514.8, monoclinic, a=30.064(3), b=11.646(1), c=20.949(2) Å, β=93.63(1)°, V=7319.8(2) Å^3, space group $I2/c$, Z=8, D_c=0.935 g cm^{-3}. The final R factor was 0.0932 (R_w=0.1374) for 4372 reflections $F_o > 3\sigma(F_o)$. Crystal data of **4**: MF=C$_{32}$H$_{52}$O$_3$Si$_2$Li$_2$, MW=554.8, triclinic, a=11.092(2), b=18.388(4), c=9.664(2) Å, α=99.17(2), β=113.36(2), γ=94.99(2)°, V=1761.7(8) Å^3, space group $P\bar{1}$, Z=2, D_c=1.046 g cm^{-3}. The final R factor was 0.0711 (R_w=0.0669) for 3465 reflections $F_o > 3\sigma(F_o)$. Tables of positional and thermal parameters and complete interatomic distances and angles have been deposited as Document No. 68063 at the Office of the Editor of Bull. Chem. Soc. Jpn.

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8) A relatively low level accuracy of the crystal structure for **2** is due to a problem of the crystals. Even taking into account for standard deviations, the elongation of the central C–C bond, the shortening of Si1–C1 and Si2–C2 bonds, and the bond alternation of the benzen ring are evident.

9) The anionic carbons are slightly pyramidalized. C1 carbon is located above Si1–Si2–C2 plane by 0.210 Å, whereas C2 carbon is below Si3–C12–C1 plane by 0.095 Å.

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