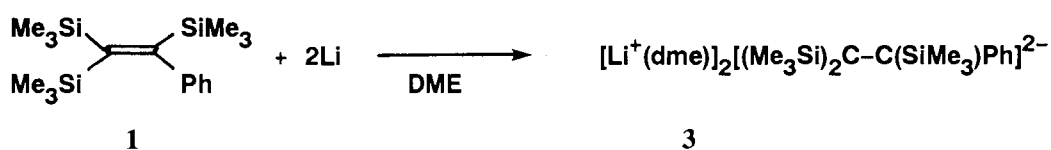


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[#] This paper is dedicated to Professor Osamu Simamura in the occasion of his 80th birthday.

103.3 (ortho C), 121.0 (ortho C), 125.6 (meta C), 131.9 (meta C), and 97.3 ppm (para C). Thus the two ortho and meta protons as well as the carbons of the phenyl ring are magnetically nonequivalent since the rotation of the aryl group is frozen. Extremely large upfield shifts of both aromatic protons and carbons are suggestive of substantial delocalization of the negative charge into the phenyl ring. The anionic carbons can be seen at 18.7 ppm for $(\text{Me}_3\text{Si})_2\text{C}$ and 73.1 ppm for $\text{Ph}(\text{Me}_3\text{Si})\text{C}$. It should be noted that two sets of the resonance of the trimethylsilyl groups can be observed; -0.12 (s, 18H) and 0.00 ppm (s, 9H) in ^1H NMR, 4.08 and 6.77 ppm in ^{13}C NMR, and -17.3 and -16.3 ppm in ^{29}Si NMR.

Although several attempts to obtain single crystals of the dianion prepared in THF for the X-ray analysis were unsuccessful, reduction of **1** with lithium in 1,2-dimethoxyethane (DME) worked as well to give the dianion and evaporation of the solvent with a vacuum line afforded dark black solids which were recrystallized from hexane to give $[\text{Li}^+(\text{dme})]_2[(\text{Me}_3\text{Si})_2\text{C}-\text{C}(\text{SiMe}_3)\text{Ph}]^{2-}$ (**3**) as metallic plates. The structure of **3** was determined by X-ray analysis as well as ^1H , ^{13}C and ^{29}Si NMR spectra.⁸⁾



The molecular structure of **3** determined by the X-ray diffraction method is shown in Fig. 1.⁹⁾ The quite unusual structural features can be seen at a glance. An interesting feature is the location of the lithium atoms. One of the lithium atoms is located between the central C-C bond, and the other is above the benzene ring. To each lithium atom, bidentate DME is bound. The length of the central C-C bond is 1.534 Å. The bond distances of Si(1)-C(1) (1.810 Å) and Si(2)-C(1) (1.826 Å) are shorter than the mean Si-C (1.88 Å), suggestive of $\pi\pi-\sigma^*(\text{Si}-\text{C})$ bonding. In contrast, the bond length of the Si(3)-C(2) (1.867 Å) is almost normal. The C(2)-C(12) bond distance (1.398 Å) is appreciably shortened, which indicates that the negative charge is largely delocalized into the aromatic ring.

The benzene ring is essentially planar, but all aromatic C-C bonds differ in distance. It should be noted that C(12)-C(13) (1.474 Å) and C(12)-C(17) (1.455 Å) bonds are elongated compared with other aromatic C-C bonds. C(1), C(2), Si(3), and aromatic carbons are arranged nearly in the same plane. Therefore, a planar conjugated system is maintained.

Li(1) and Li(2) atoms are in close contact with four carbon atoms [C(1), C(2), C(12), C(13)] and six aromatic carbons [C(12) - C(17)], respectively. The Li-C bonds (2.23 - 2.59 Å) are longer than those of σ -bonded alkyl lithium, for example 2.13 Å of the pentamethyldiethylenetriamine complex of $\text{LiCH}(\text{SiMe}_3)_2$.¹⁰⁾ Another interesting feature of the structure is a large torsional angle, the dihedral angle of Si(2)-C(1)-C(2)-Si(3) being 92.0° , almost perpendicular.¹¹⁾

The present X-ray studies evidently provide the first structural characterization of the orthogonal dianion.¹²⁾ NMR and crystal structural data indicate substantial delocalization of the negative charge into the benzene ring. As a result, one Li^+ preferentially localized above the benzene ring due to the electrostatic attraction. Related works are in progress.

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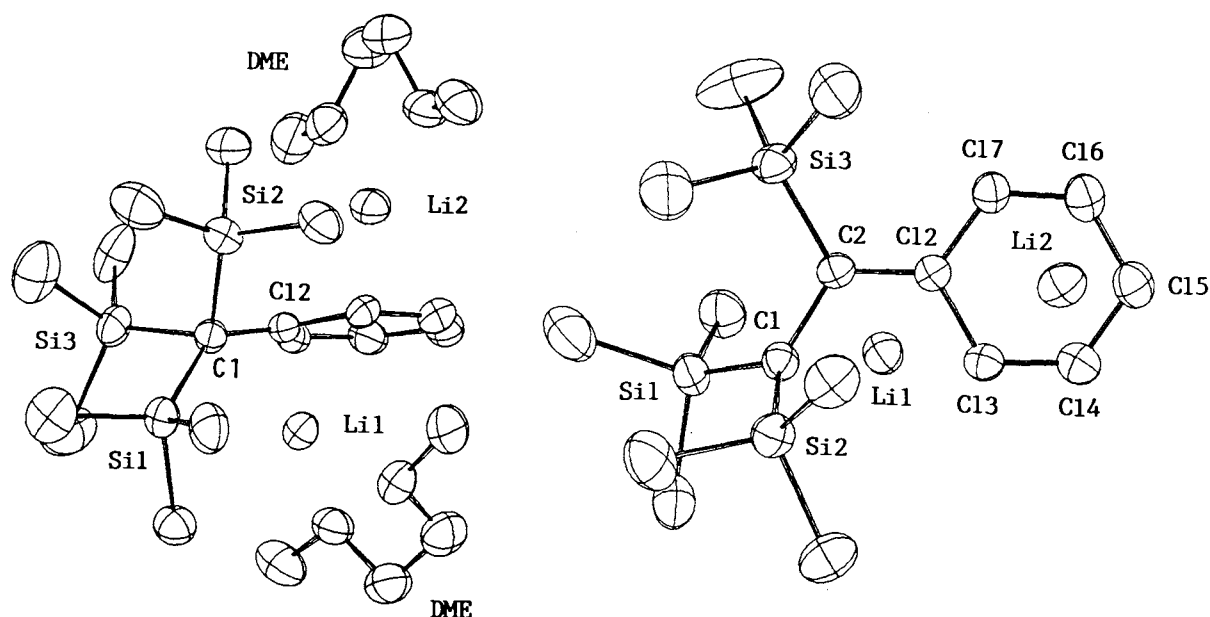


Fig. 1. ORTEP drawing of $[\text{Li}^+(\text{dme})]_2[(\text{Me}_3\text{Si})_2\text{C}-\text{C}(\text{SiMe}_3)\text{Ph}]^{2-}$ (**3**); side view through the C1-C2 bond (left) and top view (right, DME is omitted for the clarity). Selected bond lengths (Å); C(1)-C(2) 1.534(9), Si(1)-C(1) 1.810(6), Si(2)-C(1) 1.826(6), Si(3)-C(2) 1.867(6), C(2)-C(12) 1.398(9), C(12)-C(13) 1.474(8), C(13)-C(14) 1.391(9), C(14)-C(15) 1.389(10), C(15)-C(16) 1.411(11), C(16)-C(17) 1.366(10), C(17)-C(12) 1.455(9), Li(1)-C(1) 2.234(13), Li(1)-C(2) 2.272(12), Li(1)-C(12) 2.265(13), Li(1)-C(13) 2.330(13), Li(2)-C(12) 2.594(15), Li(2)-C(13) 2.375(15), Li(2)-C(14) 2.289(14), Li(2)-C(15) 2.320(15), Li(2)-C(16) 2.354(14), Li(2)-C(17) 2.460(14). Selected bond angles (°); Si(1)-C(1)-Si(2) 116.4(3), Si(1)-C(1)-C(2) 122.5(4), Si(2)-C(1)-C(2) 116.8(4), Si(3)-C(2)-C(1) 118.7(4), Si(3)-C(2)-C(12) 120.4(4), C(1)-C(2)-C(12) 119.9(5). Torsion angles (°); Si(1)-C(1)-C(2)-Si(3) 63.8(6), Si(1)-C(1)-C(2)-C(12) 128.0(5), Si(2)-C(1)-C(2)-Si(3) 92.0(5), Si(2)-C(1)-C(2)-C(12) 76.1(6), Si(3)-C(2)-C(12)-C(13) 162.9(4), Si(3)-C(2)-C(12)-C(17) 19.9(8), C(1)-C(2)-C(12)-C(13) 5.0(9), C(1)-C(2)-C(12)-C(17) 172.2(5).

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- 5) Compound **2a**: ^1H NMR (300 MHz, CDCl_3) δ -0.03 (s, 9H, SiMe_3), 0.03 (s, 9H, SiMe_3), 0.04 (s, 9H, SiMe_3), 0.49 (d, 1H, $J = 1.9$ Hz, CH), 2.68 (d, 1H, $J = 1.9$ Hz, CH), 7.0–7.3 (m, 5H, ArH); ^{13}C NMR (75.5 MHz, CDCl_3) δ -0.79, 1.71, 2.99, 17.2 (CH), 34.6 (CH), 124.9, 128.0, 130.2, 144.4; ^{13}Si NMR (59.6 MHz, CDCl_3) δ -0.05, 3.72, 5.90; High resolution MS: Calcd for $\text{C}_{17}\text{H}_{34}\text{Si}_3$: 322.1968. Found: 322.1969.
- 6) Compound **2b**: ^1H NMR (300 MHz, CDCl_3) δ -0.04 (s, 9H, SiMe_3), 0.02 (s, 9H, SiMe_3), 0.03 (s, 9H, SiMe_3), 7.0–7.3 (m, 5H, ArH); ^{13}C NMR (75.5 MHz, CDCl_3) δ -0.83, 1.67, 2.66, 17.1 (t, CD, $J = 18$ Hz), 34.5 (t, CD, $J = 18$ Hz), 124.9, 128.0, 130.2, 144.4; ^{29}Si NMR (59.6 MHz, CDCl_3) δ -0.04, 3.72, 5.92; High resolution MS: Calcd for $\text{C}_{17}\text{H}_{32}\text{D}_2\text{Si}_3$: 324.2094. Found: 324.2094.
- 7) Proton and carbon resonances of the dianions were assigned by two dimensional NMR techniques (^1H - ^1H COSY, ^1H - ^{13}C COSY, and COLOC).
- 8) Compound **3**: ^1H NMR (300 MHz, toluene- d_8) (298 K) δ 0.31 (s, 18H, $\text{SiMe}_3 \times 2$), 0.42 (s, 9H, SiMe_3), 2.93 (s, DME), 3.07 (s, DME), 4.76 (t, 1H, p-H), 5.93 (t, 1H, m-H), 6.11 (d, 1H, o-H), 6.27–6.36 (m, 2H, o-H, m-H); ^{13}C NMR (75.5 MHz, toluene- d_8 , 298 K) δ 4.65, 6.85, 18.6 (C-Li), 59.3 (DME), 70.5 (DME), 89.8 (C-Li), 101.1, 118.7, 125.1, 131.7, 137.6, 146.9; ^{29}Si NMR (59.6 MHz, toluene- d_8 , 308 K) δ -16.3, -14.8; ^7Li NMR (116.6 MHz, toluene- d_8 , 298 K) δ -2.43.
- 9) Being extremely air and moisture sensitive, a crystal of a sizes of $0.7 \times 0.4 \times 0.3 \text{ mm}^3$ was sealed in a capillary glass tube and was used for data collection on a Rigaku-Denki AFC 5R diffractometer with graphite monochromatized $\text{CuK}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). A total of 6247 reflections within $2\theta = 126^\circ$ were collected by $2\theta - \omega$ scan method with a scan rate of $4^\circ/\text{min}$. Crystal data: M.F. = $\text{C}_{25}\text{H}_{52}\text{O}_4\text{Si}_3\text{Li}_2$, M. W. = 514.8, monoclinic, $a = 30.064 (3)$, $b = 11.646 (1)$, $c = 20.949 (2) \text{ \AA}$, $\beta = 93.63^\circ(1)$, $V = 7319.8 (2) \text{ \AA}^3$, space group $I2/c$, $Z = 8$, $D_c = 0.935 \text{ g/cm}^3$. The final R factor was 0.093 for 4372 reflections $F_o > 3\sigma(F_o)$.
- 10) M. F. Lappert, L. M. Engelhardt, C. L. Raston, and A. H. White, *J. Chem. Soc., Chem. Commun.*, **1982**, 1323. The Li-C bonds of $[\text{Li}(\text{thf})_4][\text{Li}\{\text{C}(\text{SiMe}_3)_3\}_2]$ and $\text{Li}(\text{thf})[\text{C}(\text{SiMe}_2\text{Ph})_3]$ has been reported to be 2.18 \AA and 2.12 \AA , respectively. See: C. Eaborn, P. B. Hitchcock, J. D. Smith, and A. C. Sullivan, *J. Chem. Soc., Chem. Commun.*, **1983**, 827, 1390.
- 11) The anionic carbons are slightly pyramidalized. C(1) carbon is located above Si(1)-Si(2)-C(2) plane by 0.210 \AA , whereas C(2) carbon is below Si(3)-C(12)-C(1) plane by 0.095 \AA .
- 12) The molecular structure of disodium tetraphenylethylene dianion with dihedral angle of 56° has recently been reported. H. Bock, K. Ruppert, and D. Fenske, *Angew. Chem., Int. Ed. Engl.*, **28**, 1685 (1989). In the dianion of tetracyanoethylene, the charge-transfer salt of decamethylcobaltcene tetracyanoethylene $\{[\text{Co}(\text{C}_5\text{Me}_5)_2]\}^+ {}_2[(\text{NC})_2\text{CC}(\text{CN})_2]^{2-}$, the dihedral angle of 87.1° is observed. D. A. Dixon and J. S. Miller, *J. Am. Chem. Soc.*, **109**, 3656 (1987).

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