CHEMISTRY LETTERS, pp. 867-870, 1992.

Molecular Structure of Phenyl[tris(trimethylsilyl)]ethylene Dilithium Complex. An Orthogonal Dianion[#,1]

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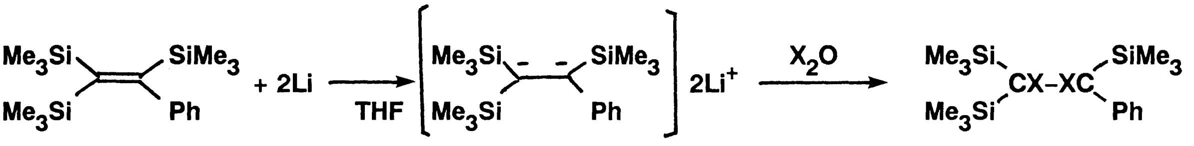
Phenyl[tris(trimethylsilyl)]ethylene bis(lithium dimethoxyethane) was prepared as black crystals. The molecular structure determined by the X-ray diffraction method shows several interesting features. One of the lithium atoms is located near the central two carbon atoms, while the other is above the benzene ring and the central C–C bond is twisted by 92°.

Structure and bonding of organolithium compounds are of considerable current interest.[2] In particular, 1,2-dilithioethane is a very interesting class of organolithiums in view of the theoretical and the experimental studies.[3] Very recently, we have reported synthesis and the molecular structure of 1,2-dilithio[tetrakis-(trimethylsilyl)]ethane as the first non-conjugated 1,2-dilithioethane derivative.[4] The structure determined by X-ray analysis revealed that the lithium atoms were bridged to the central two carbon atoms with the dihedral angle of 33.6°.[4b]

A theoretical calculation of 1,2-dilithioethane suggests that trans structures with partially or symmetrically lithium-bridged geometry are most stable.[3g,3l] The orthogonal structure with the dihedral angle of 90° is calculated to be much higher in energy than the trans bridged planar ones. Herein we report the phenyl[tris(trimethylsilyl)]ethylene dilithium complex as the first lithium salt of the orthogonal dianion.

Phenyl[tris(trimethylsilyl)]ethylene **1** (56 mg, 0.17 mmol) was allowed to react with excess lithium metal (ca. 70 mg) in dry oxygen-free THF (15 ml) at room temperature under argon. The solution immediately turned to dark red upon two-electron reduction. The reaction of the dianion with H_2O and D_2O led to the formation of phenyl[tris(trimethylsilyl)]ethane **2a**[5] and **2b**,[6] respectively, in quantitative yields.



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2a: X = H
2b: X = D

In ^{1}H NMR spectrum in THF-d_8 (255 K), the aryl protons were observed at 4.77 ppm as a triplet for para proton, at 5.82 and 6.25 ppm as two triplets for meta protons, and at 6.03 and 6.13 ppm as two doublets for ortho protons.[7] Correspondingly, aryl carbons were observed as six separate signals at 152.9 (ipso C),

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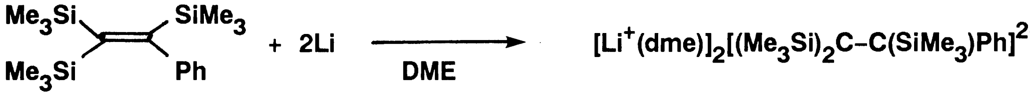
[#] This paper is dedicated to Professor Osamu Simamura in the occasion of his 80th birthday.

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 $(Me_3Si)_2C$ and 73.1 ppm for $Ph(Me_3Si)C$. 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 $[Li^+(dme)]_2[(Me_3Si)_2C\text{–}C(SiMe_3)Ph]^{2-}$ (**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)



1 **3**

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 pπ–σ*(Si–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 $LiCH(SiMe_3)_2$.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.

We are grateful for the financial support of the Ministry of Education, Science and Culture of Japan (Specially Promoted Research No. 02102004).

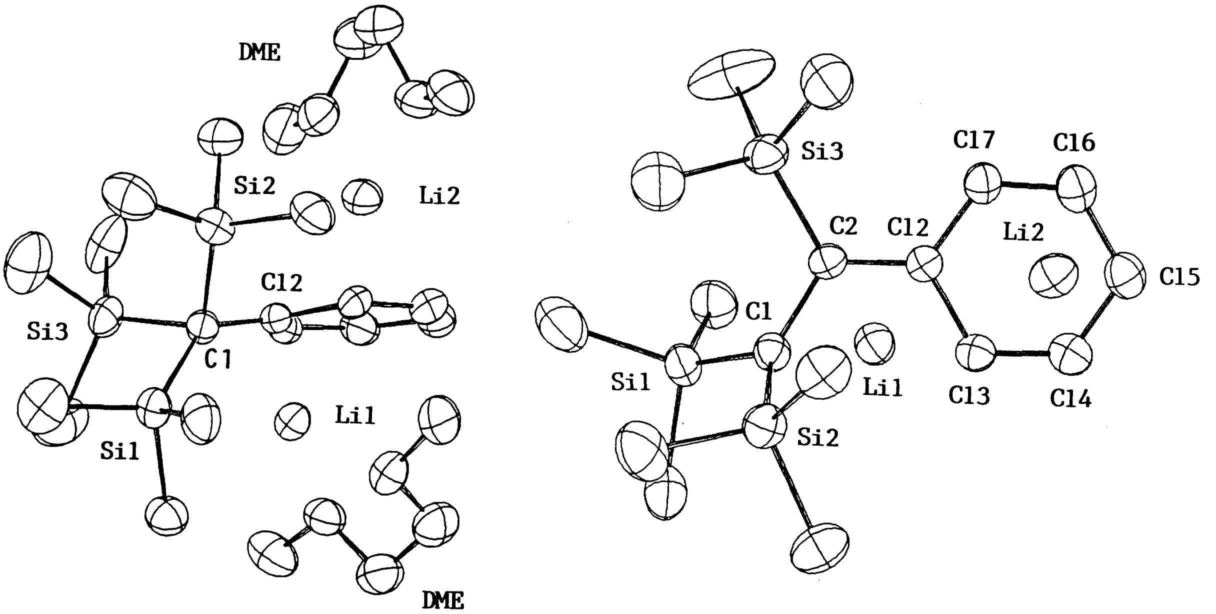


Fig. 1. ORTEP drawing of $[Li^+(dme)]_2[(Me_3Si)_2C-C(SiMe_3)Ph]^{2-}$ (**3**); side view through the C1-C2 bond (left) and top view (right, DME is omitted for the clarity). Selected bond lengths (Å); C(1)-C(2) 1.534(9), Si(1)-C(1) 1.810(6), Si(2)-C(1) 1.826(6), Si(3)-C(2) 1.867(6), C(2)-C(12) 1.398(9), 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).

References

1) Chemistry of Organosilicon Compounds 279.

2) J. L. Wardell, "Comprehensive Organometallic Chemistry," ed by G. Wilkinson, F. G. A. Stone, and E. W. Abel, Pergamon Press, New York (1982); P. v. R. Schleyer, *Pure Appl. Chem.*, **55**, 355 (1983); P. v. R. Schleyer, *ibid.*, **56**, 151 (1984); W. N. Setzer and P. v. R. Schleyer, *Adv. Organomet. Chem.*, **24**, 353 (1985); H. Günther, D. Moskau, P. Bast, and D. Schmalz, *Angew. Chem.,Int. Ed. Engl.*, **26**, 1212 (1987).

3) a) J. F. Garst, *J. Am. Chem. Soc.*, **93**, 6312 (1971); b) V. Rautenstrauch, *Angew. Chem. Int. Ed. Engl.*, **14**, 259 (1975); c) M. Walczak and G. D. Stucky, *J. Organomet. Chem.*, **97**, 313 (1975); d) M. Walczak and G. D. Stucky, *J. Am. Chem. Soc.*, **98**, 5531 (1976); e) W. E. Rhine, J. H. Davis, and G. D. Stucky, *J. Organomet. Chem.*, **134**, 139 (1977); f) B. Bogdanović and B. Wermeckes, *Angew. Chem., Int. Ed. Engl.*, **20**, 684 (1981); g) A. J. Kos, E. D. Jemmis, P. v. R. Schleyer, R. Gleiter, U. Fischbach, and J. A. Pople, *J. Am. Chem. Soc.*, **103**, 4996 (1981); h) L. Manceron and L. Andrews, *J. Phys. Chem.*, **90**, 4514 (1986);

i) A. Maercker and B. Grebe, *J. Organomet. Chem.*, **334**, C21 (1987); j) N. J. R. van E. Hommes, F. Bickelhaupt, and G. W. Klumpp, *Angew. Chem., Int. Ed. Engl.*, **27**, 1083 (1988); k) M. A. Fox and D. Shultz, *J. Org. Chem.*, **53**, 4386 (1988); l) S. P. So, *J. Organomet. Chem.*, **361**, 283 (1989).

4) a) H. Sakurai, Y. Nakadaira, and H. Tobita, *Chem. Lett.*, **1982**, 771; b) A. Sekiguchi, T. Nakanishi, C. Kabuto, and H. Sakurai, *J. Am. Chem. Soc.*, **111**, 3748 (1989).

5) Compound **2a**: ^{1}H 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 $C_{17}H_{34}Si_3$: 322.1968. Found: 322.1969.

6) Compound **2b**: ^{1}H 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 = 18Hz), 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 $C_{17}H_{32}D_2Si_3$: 324.2094. Found: 324.2094.

7) Proton and carbon resonances of the dianions were assigned by two dimensional NMR techniques (^{1}H–^{1}H COSY, ^{1}H–^{13}C COSY, and COLOC).

8) Compound **3**: ^{1}H NMR (300 MHz, toluene-d_8) (298 K) δ 0.31 (s, 18H, $SiMe_3$ x 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; ^{7}Li 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 x 0.4 x 0.3 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 CuKα radiation (λ = 1.5418 Å). A total of 6247 reflections within 2θ = 126° were collected by 2θ – ω scan method with a scan rate of 4°/min. Crystal data: M.F. = $C_{25}H_{52}O_4Si_3Li_2$, M. W. = 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, Dc = 0.935 g/cm^3. The final R factor was 0.093 for 4372 reflections Fo > 3σ (Fo).

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 $[Li(thf)_4][Li\{C(SiMe_3)_3\}_2]$ and $Li(thf)[C(SiMe_2Ph)_3]$ has been reported to be 2.18 Å and 2.12 Å, 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 Å, whereas C(2) carbon is below Si(3)–C(12)–C(1) plane by 0.095 Å.

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 $\{[Co(C_5Me_5)_2]\}^+{}_2[(NC)_2CC(CN)_2]^{2-}$, the dihedral angle of 87.1° is observed. D. A. Dixon and J. S. Miller, *J. Am. Chem. Soc.*, **109**, 3656 (1987).

(Received March 6, 1992)