5652 *J. Am. Chem. Soc.* **2000,** *122,* 5652−5653

Synthesis and Characterization of a Cyclobutadiene Dianion Dilithium Salt: Evidence for Aromaticity

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Received February 3, 2000

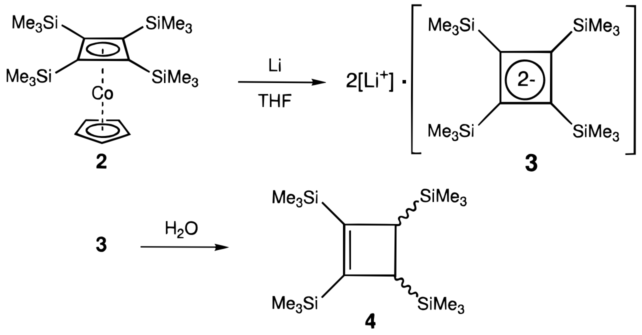
The fundamental Hückel's rule for aromaticity has stimulated considerable research into the synthesis of various unsaturated cyclic compounds.[1] Hückel's rule predicts the cyclobutadiene dianion (CBD^{2-}, **1**) to be aromatic. The aromaticity of the cyclobutadiene dianion has been experimentally challenged. There have been some studies on the transient cyclobutadiene dianion[2] and its derivatives stabilized by ester[3] or phenyl groups;[4] however, a preferred cyclic delocalization with formation of a 6 π-electron system has not been observed. Elaborate calculations on CBD^{2-} by ab initio MO methods lead to a preference for the distorted structure (**1′**, Chart 1).[5−7] The destabilizing character of **1** was attributed to substantial negative charges on the carbons, the short diagonal distance, and to a considerable Coulombic repulsion between the diagonal carbons. Accordingly, D_{4h} geometry (**1**) is not to be expected and the problem of the aromaticity in CBD^{2-} and its derivatives still remains open. Neither the planar CBD^{2-} itself nor its derivative with D_{4h} symmetry was reported.

Chart 1

However, theoretical calculations on the dilithium salt of the cyclobutadiene dianion ($Li^{+}{}_2C_4H_4{}^{2-}$) suggest the possibility of experimental observation of a derivative with D_{4h} geometry.[7] We have successfully synthesized various dilithium salts of silyl-substituted ethylene[8] and benzene derivatives.[9] These examples indicate that the electronic and steric effects of silyl groups are very important for stabilizing the dianion dilithium derivatives with π-electron systems.

We report here the isolation and structure of a dilithium salt of tetrakis(trimethylsilyl)cyclobutadiene dianion (**3**), which provides experimental verification of the aromatic nature of the 6 π-electron cyclobutadiene dianion. Treatment of the tetrakis(trimethylsilyl)cyclobutadiene cobalt complex (**2**)[10] with lithium in dry oxygen-free tetrahydrofuran (THF) at room temperature led to the formation of a dark brown solution from which the dilithium salt of tetrakis(trimethylsilyl)cyclobutadiene dianion (**3**) was isolated as air- and moisture-sensitive pale yellow crystals (Scheme 1).[11] The choice of alkali metals is crucial; alkali metals other than lithium (e.g. Na or K) do not work. The dianion **3** readily reacts quantitatively with water to give a mixture of *trans*- and *cis*-1,2,3,4-tetrakis(trimethylsilyl)cyclobutenes (**4**).

Scheme 1



Compound **3**, containing THF molecules, was purified by recrystallization from hexane. Evidence for the four-membered ring was given by the ^{13}C NMR spectrum: δ 104.1 for the ring carbon atoms as a quintet ($^{1}J_{^{6}\mathrm{Li}-^{13}\mathrm{C}} = 1.4$ Hz) due to the coupling with two ^{6}Li nuclei ($I = 1$). Of particular interest is the ^{6}Li signal appearing at a chemical shift of δ −5.07.[12] The appreciable upfield shift is evidently caused by the strong shielding effect of the diatropic ring current resulting from the 6 π-electron system.[13,14] This points to a structure in which the two Li^{+} ions reside above and below the center of the plane of the four-membered ring, that is, in the shielding region of the aromatic ring current.

To determine the exact structure of **3** by X-ray crystallography, we performed a ligand exchange on the Li^{+} ion from THF to 1,2-dimethoxyethane (DME).[15] A single crystal of **3** containing DME suitable for X-ray diffraction analysis was obtained by a

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(8) For silyl-substituted ethylene dianion dilithium derivatives, see: (a) Sekiguchi, A.; Nakanishi, T.; Kabuto, C.; Sakurai, H. *J. Am. Chem. Soc.* **1989**, *111*, 3748. (b) Sekiguchi, A.; Ichinohe, M.; Kabuto, C.; Sakurai, H. *Organometallics* **1995**, *14*, 1092. (c) Sekiguchi, A.; Ichinohe, M.; Takahashi, M.; Kabuto, C.; Sakurai, H. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1533.

(9) For silyl-substituted benzene dianion dilithium derivatives, see: (a) Sekiguchi, A.; Ebata, K.; Kabuto, C.; Sakurai, H. *J. Am. Chem. Soc.* **1991**, *113*, 1464. (b) Sekiguchi, A.; Ebata, K.; Kabuto, C.; Sakurai, H. *J. Am. Chem. Soc.* **1991**, *113*, 7081. (c) Ebata, K.; Setaka, W.; Inoue, T.; Kabuto, C.; Kira, M.; Sakurai, H. *J. Am. Chem. Soc.* **1998**, *120*, 1335.

(10) The cobalt complex **2** was prepared by reaction of CpCo(CO)$_2$ with bis(trimethylsilyl)acetylene, see: Fritch, J. R.; Vollhardt, K. P. C.; Thompson, M. R.; Day, V. W. *J. Am. Chem. Soc.* **1979**, *101*, 2768.

(11) Compound **3** was synthesized by the following procedure: Crystals of **2** (102 mg, 0.22 mmol) and Li (30 mg, 4.3 mmol) were placed in a reaction tube and degassed. Dry oxygen-free THF (0.5 mL) was introduced by vacuum transfer and the solution was stirred at room temperature for 24 h to give a dark brown solution. After the solvent was removed in vacuo, degassed hexane (5.0 mL) was introduced by vacuum transfer and cooled to afford yellow crystals of **3**, quantitatively. ^{1}H NMR (C_7D_8) δ 0.45 (s, 36 H), 1.26 (br. s, 8 H, THF), 3.44 (br. s, 8 H, THF); ^{13}C NMR (C_7D_8) δ 5.5, 25.5 (THF), 69.5 (THF), 104.1 (quintet, $^{1}J_{^{6}\mathrm{Li}-^{13}\mathrm{C}} = 1.4$ Hz); ^{29}Si NMR (C_7D_8) δ −23.7; ^{6}Li NMR (C_7D_8) δ −5.07.

(12) The computed Li chemical shifts in the $Li_2C_4R_4$ are around −3 ppm, see ref 7b. This paper also reports NICS (nucleus-independent chemical shifts) and discusses the aromaticity of the dications, $C_4R_4{}^{2+}$, dianions, $C_4R_4{}^{2-}$, and dilithiated species, $Li_2C_4R_4$ (R = H, Me, *t*-Bu). We thank professor Schleyer for informing us of this recent paper.

(13) The use of the chemical shift of Li^{+} complexed to ring faces as an aromaticity probe has been reported, see ref 7b. (a) Paquette, L. A.; Bauer, W.; Sivik, M. R.; Bühl, M.; Feigel, M.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1990**, *112*, 8776. (b) Jiao, H.; Schleyer, P. v. R. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1760.

(14) For comparison, the Li NMR chemical shift of lithium cyclopentadienide (LiCp) was reported to be δ −8.60 in diethyl ether due to the strong shielding, see: Elschenbroich, Ch.; Salzer, A. *Organometallics*; VCH Verlagsgesellschaft: Weinheim, 1989; pp 24−27. For Li NMR chemical shifts of [Li(ligand)·$C_5(SiMe_2H)_5$], δ −7.51 (THF ligand), δ −8.24 (DME ligand), see: Sekiguchi, A.; Sugai, Y.; Ebata, K.; Kabuto, C.; Sakurai, H. *J. Am. Chem. Soc.* **1993**, *115*, 1144. In contrast, a large deshielding effect of Li NMR for $Li_2(DME)_2$·(1,2,4,5-$(Me_3Si)_4C_6H_2$) appearing at δ 10.7 as an antiaromatic system has been reported (ref 9b).

(15) Spectral data for **3** (DME ligand): ^{1}H NMR (C_7D_8) δ 0.47 (s, 36 H), 3.13 (s, 12 H, DME), 3.14 (s, 8 H, DME); ^{13}C NMR (C_7D_8) δ 5.7, 59.3 (DME), 71.3 (DME), 103.6; ^{29}Si NMR (C_7D_8) δ −24.4; ^{6}Li NMR (C_7D_8) δ −5.01.

10.1021/ja0004175 CCC: $19.00

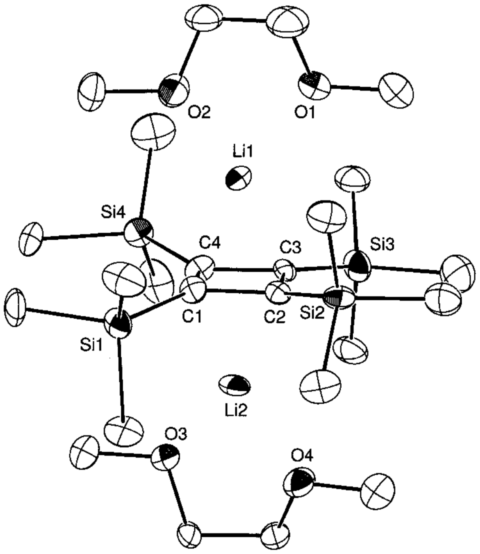

Figure 1. ORTEP drawing of **3**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): C1−C2 1.496(3), C1−C4 1.507(9), C2−C3 1.485(10), C3−C4 1.493(4), C1−Si1 1.836(7), C2−Si2 1.844(7), C3−Si3 1.825(8), C4−Si4 1.840(7), C1−Li1 2.178(12), C2−Li1 2.195(12), C3−Li1 2.174(12), C4−Li1 2.166(12), C1−Li2 2.175(11), C2−Li2 2.199(12), C3−Li2 2.197(11), C4−Li2 2.152(11). Selected bond angles (deg): C2−C1−C4 89.2(6), C3−C2−C1 90.7(6), C2−C3−C4 90.1(6), C3−C4−C1 90.0(7), C2−C1−Si1 131.1(7), C4−C1−Si1 138.3(5), C1−C2−Si2 129.1(7), C3−C2−Si2 138.6(5), C4−C3−Si3 128.4(7), C2−C3−Si3 140.1(5), C1−C4−Si4 137.6(6), C3−C4−Si4 131.0(7).

recrysallization from hexane, and the molecular structure was determined by X-ray crystallography (Figure 1).[16] The dilithium salt **3** contains two molecules of DME. The two lithium atoms (Li1 and Li2) are located above and below the approximate center of the four-membered ring (C1−C2−C3−C4), and are bonded to the four ring carbon atoms as well as to the two oxygen atoms of the DME molecules. The distances between the Li^+ ions and the carbon atoms (C1, C2, C3, and C4) range from 2.166(12) to 2.195(12) Å (av 2.178 Å) for Li1 and 2.152(11) to 2.199(12) Å (av 2.181 Å) for Li2, respectively. The Li distance from the ring centroid is 1.90(1) Å.

The four-membered ring is planar and almost square, as determined by the internal bond angles of 89.2(6) to 90.7(6)° (av 90.0°) and the dihedral angles (0.90(2)° for C1−C2−C3/C1−C3−C4 and 0.89(2)° for C2−C3−C4/C1−C2−C4). The average of the C−C bond lengths (Å) in the four-membered ring is 1.495 (C1−C2, 1.496(3); C1−C4, 1.507(9); C2−C3, 1.485(10); C3−C4, 1.493(4)), giving diagonal distances of 2.12(1) Å for C1−C3 and 2.11(1) Å for C2−C4. The observed C−C bond lengths are intermediate between the typical C═C double bond length (1.34 Å) and the C−C single bond length (1.54 Å). The Si−C bond lengths (Å) (Si1−C1, 1.836(7); Si2−C2, 1.844(7); Si3−C3, 1.825(8); Si4−C4, 1.840(7)) are shorter than the usual bond lengths (1.88 Å). Due to the large steric repulsion of the Me_3Si groups, the positions of the Si atoms deviate up and down alternately about the plane of the four-membered ring, as determined by the angles between the central four-membered ring plane and the Si−C bond (8.0−9.9°).

The structure of **3** containing DME is very close to that predicted by a calculation of the corresponding $Li^+{}_2C_4H_4{}^{2-}$ with D_{4h} symmetry.[7] The observed average C−C length is 1.495 Å compared with the calculated value of 1.461 Å (6-31G**) for $Li^+{}_2C_4H_4{}^{2-}$. The Li distance from the ring centroid (1.90 Å) is relatively long in comparison with the calculated value of 1.770 Å due to the influence of the coordination by DME that weakens the interaction between the negatively charged four-membered framework and Li^+ ions. The observed diagonal distance of 2.11−2.12 Å is similar to the calculated value of 2.069 Å.[6] The present experimental observations by X-ray crystallographic analysis and NMR spectroscopy for **3** satisfy the inherent definitions of aromaticity for the geometry criteria, i.e., the planarity of the four-membered ring, the lack of bond alternation, and the highly shielded chemical shift of ^6Li NMR due to the diatropic ring current.

Acknowledgment. This work was supported by a Grant-in-Aid for Scientific Research (Nos. 10304051, 12020209, 12042213) from the Ministry of Education, Science and Culture of Japan, and TARA (Tsukuba Advanced Research Alliance) fund.

Supporting Information Available: Tables of crystallographic data including atomic positional and thermal parameters for **3** (DME ligand) (PDF). These materials are available free of charge via the Internet at http://pubs.acs.org.

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[16] Crystal data for **3** (DME ligand) at 120 K: MF = $C_{24}H_{56}Li_2O_4Si_4$, MW = 534.93, monoclinic, *Cc*, $a = 18.741(1)$ Å, $b = 10.446(1)$ Å, $c = 19.270(1)$ Å, $\beta = 114.640(4)°$, $V = 3429.0(4)$ Å^3, $Z = 4$, $D_{calcd} = 1.036$ g·cm^3. The final *R* factor was 0.0565 for 3460 reflections with $I_o > 2\sigma(I_o)$ ($R_w = 0.1646$ for all data). GOF = 1.026.