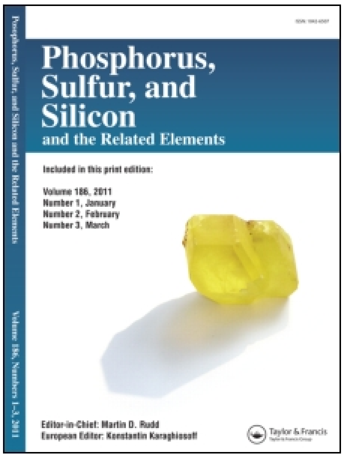

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Cyclobutadiene Dianion Dilithium: a New Aromatic Ring System

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The reaction of tetrakis(trimethylsilyl)- (or *cis*-diphenyl) cyclobutadiene cobalt complexes with lithium metal in THF at room temperature produced the dilithium salts of tetrakis(trimethylsilyl)- (or *cis*-diphenyl) cyclobutadiene dianion, which were isolated as pale yellow (or pale orange) solids stable in the absence of air. NMR spectra and X-ray crystallography of these dianions provide the evidence for an aromatic character with a six π-electron system.

Keywords: aromaticity; cyclobutadiene; cyclobutadiene dianion

INTRODUCTION

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-}) to be aromatic. There are some studies on the transient cyclobutadiene dianion[2] and its derivatives stabilized by ester[3] or

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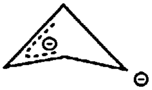
phenyl groups,[4] however, a preferred cyclic delocalization with formation of a six π-electron system has not been observed. *Ab initio* calculations on CBD^{2-} lead to a preference for the distorted structure **B**.[5-7] The destabilizing character of a delocalized structure **A** was attributed to substantial negative charges on the carbons, the short diagonal distance, and to a considerable Coulombic repulsion between the diagonal carbons. Accordingly, D_{4h} geometry 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.

A



B

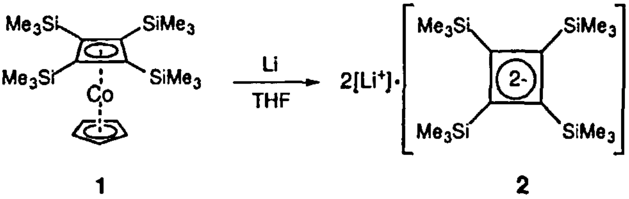
However, theoretical calculations on the dilithium salt of the cyclobutadiene dianion Li$^{+}_{2}$CBD^{2-} suggest the possibility of experimental observation of a derivative with D_{4h} geometry.[7]

We report here the isolation and structure of the dilithium salts of tetrakis(trimethylsilyl)- and *cis*-diphenylcyclobutadiene dianion, which provide experimental verification of the aromatic nature of the six π-electron cyclobutadiene dianion.

I. SYNTHESIS OF TETRAKIS(TRIMETHYLSILYL)-CYCLOBUTADIENE DIANION DILITHIUM SALT

Treatment of the tetrakis(trimethylsilyl)cyclobutadiene cobalt complex

(**1**), prepared by reaction of $CpCo(CO)_2$ and bis(trimethylsilyl)-acetylene, with lithium in dry oxygen-free THF at room temperature led to the formation of a dark brown solution from which the dilithium salt of tetrakis(trimethylsilyl)cyclobutadiene dianion (**2**) was isolated as air- and moisture-sensitive pale yellow crystals.[8]



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 ($^1J_{^6Li-^{13}C}$ = 1.4 Hz) due to the coupling with two ^6Li nuclei (I = 1). Of particular interest is the ^6Li signal appearing at -5.07 ppm. The appreciable upfield shift is evidently caused by the strong shielding effect of the diatropic ring current resulting from the six π-electron system. 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.

In order to determine the exact structure of **2** by X-ray crystallography, we performed a ligand exchange on the Li^+ ion from THF to 1,2-dimethoxyethane (DME). A single crystal of **2** containing DME suitable for X-ray diffraction analysis was obtained by a recrysallization from hexane, and the molecular structure was determined by X-ray crystallography (Fig. 1). The dilithium salt **2** 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.

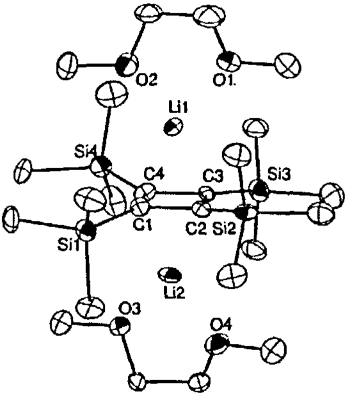


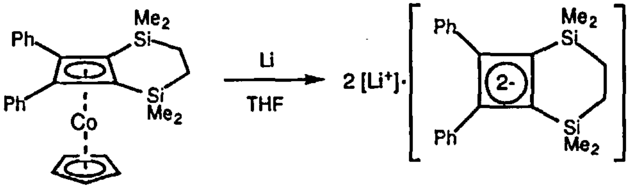
Figure 1. Molecular Structure of 2.

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 in the four-membered ring is 1.495 Å (C1-C2, 1.496(3); C1-C4, 1.507(9); C2-C3, 1.485(10); C3-C4, 1.493(4) Å), 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). 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 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 present experimental observations by X-ray crystallography and NMR spectroscopy for **2** satisfy the definitions of aromaticity, *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.

II. SYNTHESIS OF *cis*-DIPHENYLCYCLOBUTADIENE DIANION DILITHIUM SALT

Phenyl groups are very useful for the stabilization of carbanions with their large delocalization of negative charge. We used for the precursor of dianion species the *cis*-diphenyl- cyclobutadiene cobalt complex (**3**), which was prepared by the reaction of 1,8-diphenyl-3,6-disila-1,7-octadiyne with $CpCo(CO)_2$ in refluxing octane in 63% yield.

Reaction of **3** and lithium metal in dry, oxygen-free THF at room temperature produced a dark brown solution containing the dilithium salt of *cis*-diphenylcyclobutadiene dianion **4** within 24 h. [9]



3 **4**

After ligand exchange on the Li^+ ions from THF to DME, crystallization from heptane at –30 °C afforded fine crystals of **4** containing two molecules of DME (Figure 2).

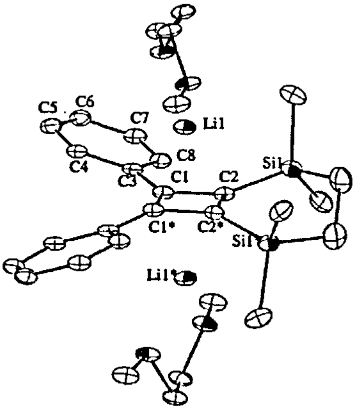


Figure 2. Molecular structure of **4**.

The dilithium salt **4** is monomeric and forms contact ion pairs (CIPs) in the crystal. One DME molecule is coordinated to each lithium atom. Li1 and Li1* are located above and below the plane of the four-membered ring (C1-C2-C2*-C1*). The two Li atoms are not located at the center of the four-membered ring, but are slightly shifted in the direction of the phenyl groups. The distances between Li1 and the four carbon atoms (C1, C2, C1*, and C2*) range from 2.186(6) to 2.256(6) Å (av 2.225(6) Å).

The four-membered ring is planar and forms an almost square structure, as confirmed by the internal bond angles (C1*-C1-C2, 89.8(1); C1-C2-C2*, 90.2(1)°) and the sum of the bond angles (360.0°). The average of the C-C distances in the four-membered ring is 1.490 Å (C1-C2, 1.480(5); C1-C1*, 1.506(6); C2-C2*, 1.493(6)

Å). These structural features of **4** correspond well to the criteria of aromaticity; eg. 1) the planarity of the four-membered ring; and 2) the lack of bond alternation.

The C1-C3 distance in **4** (1.448(5) Å) is slightly shortened in comparison with the corresponding distances in **3** (av 1.468(2) Å), due to the delocalization of the negative charge on the phenyl ring. However, the quinoid structure of the phenyl ring is not found (C3-C4, 1.419(5); C3-C8, 1.401(5); C4-C5, 1.387(5); C5-C6, 1.392(5); C6-C7, 1.387(5); C7-C8, 1.404(5) Å). The Si1-C2 distance in **4** (1.828(4) Å) is also shorter than the corresponding distances in **3** (av 1.861(1) Å) due to the $p\pi$-σ^* conjugation. The positions of the Si atoms and the *ipso*-carbon atoms deviate up (Si1 and C3) and down (Si1* and C3*) about the plane of the four-membered ring (C1-C2-C2*-C1*/C2-Si1, 12.14(2); C1-C2-C2*-C1*/C1-C3, 9.40(2)°).

We have also characterized the structure of **4** in solution on the basis of NMR spectroscopy. Interestingly, in the ^{7}Li NMR spectrum of **4** in benzene-d_6, one signal was found at $\delta = -4.21$. This considerable upfield shift is evidently caused by the strong shielding effect of the diatropic ring current resulting from the six π-electron system. This suggests that the molecular structure of **4** in the crystal is maintained in solution. However, the signal of **4** ($\delta = -4.21$) is slightly shifted to lower field compared with that of **2** ($\delta = -5.07$) due to the decrease of the ring current by the introduction of phenyl groups.

The ^{13}C NMR spectrum of **4** shows two signals for the cyclobutadienediide ring carbons appearing at $\delta = 89.6$ (Ph*C*) and 102.8 (Si*C*) together with the four signals for phenyl carbons ($\delta =$ 117.4 (*para*-), 121.3 (*ortho*-), 128.5 (*meta*-), and 142.8 (*ipso*-)). The

^{13}C signals of *ortho*- and *para*-carbons are shifted to higher field relative to those signals in **3** (δ = 126.9 (*ortho*-) and 125.6 (*para*-)) due to delocalization of the negative charge on the phenyl ring. The ^{29}Si signal of **4** (δ = –21.3) is also shifted to higher field relative to that of **3** (δ = –7.0). Thus, the doubly charged four-membered ring system is stabilized not only by the phenyl groups but also by the silyl groups.

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