Synthesis and Molecular Structure of a Dilithium Salt of the *cis*-Diphenylcyclobutadiene Dianion

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The *cis*-diphenyl-substituted cyclobutadiene cobalt complex (**1**), prepared from the reaction of 1,8-diphenyl-3,6-disila-1,7-octadiyne with $CpCo(CO)_2$, reacted with lithium metal in tetrahydrofuran (THF) to yield pale orange crystals of the dilithium salt of the *cis*-diphenylcyclobutadiene dianion (**2**). The structure was determined by spectroscopic methods and X-ray crystallography to reveal the aromatic character of the doubly-charged four-membered ring system.

Phenyl groups are very useful for the stabilization of carbanions with their large delocalization of negative charge. Structures of various anions stabilized by phenyl groups both in the solid state and in solution have been reported that include both solvated and contact ion pair (CIP).[1] As the phenyl-substituted cyclobutadiene dianion (CBD^{2-}), the dilithium salt of 1,2-diphenylbenzocyclobutadienediide[2] and the dipotassium salt of 1,2,3,4-tetraphenylcyclobutadienediide[3] have been reported, however, the stabilization by six π-electron delocalization remains unclear. The expected energy gain by delocalization of the negative charge in the aromatic system is offset by electron repulsion in the dianion.[4] As a result, a large amount of negative charge is distributed on the substituents. The problem of aromaticity in CBD^{2-} and its derivatives still remains open, both from experimental and theoretical points of view.[5] Quite recently, we have reported the first experimental evidence for the aromaticity of CBD^{2-} with a six π-electron system, the dilithium salt of tetrakis(trimethylsilyl)cyclobutadiene dianion, $2[Li^+]\cdot[(Me_3Si)_4C_4{}^{2-}]$.[6] Herein, we report the synthesis, characterization, and X-ray structure of the dilithium salt of the *cis*-diphenylcyclobutadiene dianion, which reveals the aromatic character of the doubly-charged four-membered ring system, stabilized by both phenyl and silyl groups.

As a precursor, we designed the *cis*-diphenyl-substituted cyclobutadiene cobalt complex (**1**), 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.[7] The molecular structure of **1** is shown in Figure 1.[8]

Crystals of **1** (36 mg, 0.076 mmol) and lithium metal (30 mg, 4.3 mmol) were placed in a reaction tube with a magnetic stirrer. Dry, oxygen-free THF (1.2 mL) was introduced by vacuum transfer, and the mixture was stirred at room temperature to give a dark brown solution containing **2** within 24 h. After the solvent was removed in vacuo, degassed hexane (5 mL) was introduced by vacuum transfer. Then, after the lithium and insoluble dark materials were removed, the solution was cooled to afford air- and moisture-sensitive pale orange crystals of **2** (THF ligand) in a quantitative yield (Scheme 1).[9] After ligand exchange on the Li^+ ions from THF to 1,2-dimethoxyethane (DME), crystallization from heptane at –30 °C afforded fine crystals of **2** containing two molecules of DME.

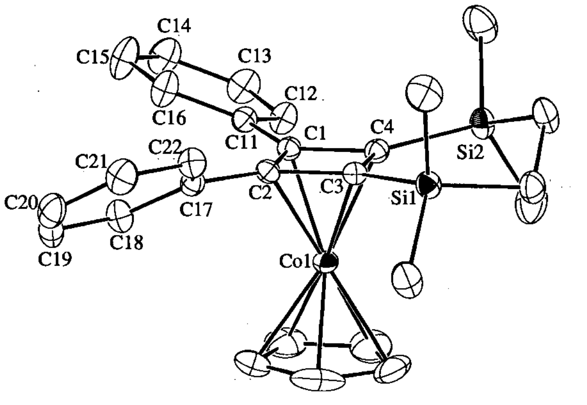
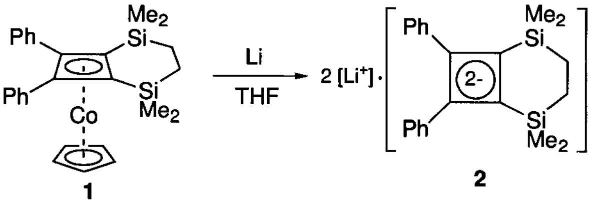


Figure 1. ORTEP drawing of **1** (hydrogen atoms are omitted for the clarity). Selected bond lengths (Å) : C1–C2 1.470(2), C1–C4 1.472(2), C1–C11 1.465(2), C2–C3 1.466(2), C2–C17 1.470(2), C3–C4 1.482(2), C3–Si1 1.857(1), C4–Si2 1.864(1), C1–Co1 1.986(1), C2–Co1 1.992(1), C3–Co1 2.001(1), C4–Co1 1.986(1). Selected bond angles (°): C2–C1–C4 90.2(1), C1–C2–C3 90.3(1), C2–C3–C4 90.0(1), C1–C4–C3 89.5(1).



Scheme 1.

The molecular structure of **2** was unequivocally determined by X-ray crystallography (Figure 2).[10] The molecule has a crystallographic two-fold axis on the four-membered ring (*C*2 symmetry). The dilithium salt **2** 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, in contrast to $2[Li^+]\cdot[(Me_3Si)_4C_4{}^{2-}]$ in which they are located above and below the center of the four-membered ring.[6] 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 **2** correspond well to the criteria of aromaticity; e.g., 1) the planarity of the four-membered ring; and 2) the lack of bond alternation.

The C1–C3 distance in **2** (1.448(5) Å) is slightly shortened in comparison with the corresponding distances in **1** (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 **2** (1.828(4) Å) is also shorter than the corresponding distances in **1** (av 1.861(1) Å) due to the p_{π}–σ^* conjugation.[11] 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)°).

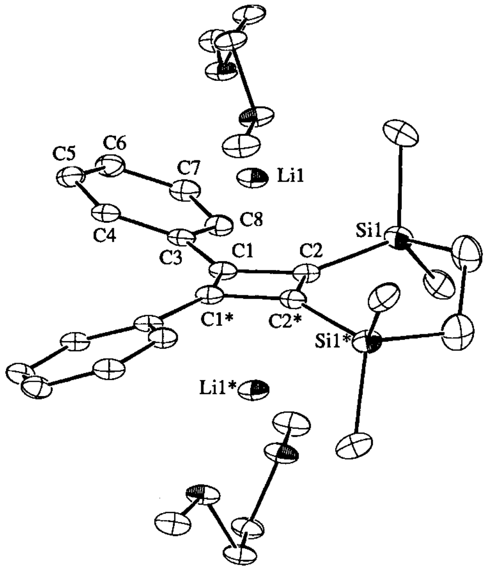


Figure 2. ORTEP drawing of 2 (hydrogen atoms are omitted for the clarity). Selected bond lengths (Å): C1–C1* 1.506(6), C1–C2 1.480(5), C1–C3 1.448(5), C2–C2* 1.493(6), C3–C4 1.419(5), C3–C8 1.401(5), C4–C5 1.387(5), C5–C6 1.392(5), C6–C7 1.387(5), C7–C8 1.404(5), C2–Si1 1.828(4), C1–Li1 2.208(6), C1*–Li1 2.186(6), C2–Li1 2.249(6), C2*–Li1 2.256(6). Selected bond angles (°): C1*–C1–C2 89.8(1), C1–C2–C2* 90.2(1).

We have also characterized the structure of **2** in solution on the basis of NMR spectroscopy.[9] Interestingly, in the ^{7}Li NMR spectrum of **2** in benzene-d_6, one signal was found at δ = –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 **2** in the crystal is maintained in solution. However, the signal of **2** (δ = –4.21) is slightly shifted to lower field compared with that of $2[Li^+]\cdot[(Me_3Si)_4C_4^{2-}]$ (δ = –5.07),[6] due to the decrease of the ring current by the introduction of phenyl groups.

The ^{13}C NMR spectrum of **2** shows two signals for the cyclobutadienediide ring carbons appearing at δ = 89.6 (Ph*C*) and 102.8 (Si*C*) together with the four signals for phenyl carbons (δ = 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 **1** (δ = 126.9 (*ortho*-) and 125.6 (*para*-)) due to delocalization of the negative charge on the phenyl ring. The ^{29}Si signal of **2** (δ = –21.3) is also shifted to higher field relative to that of **1** (δ = –7.0). The present experimental results clearly show that the negative charge is stabilized by both silyl and phenyl groups, but stabilization by the phenyl group is more effective.

References and Notes

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7 M.p. 56 °C; ^{1}H NMR ($CDCl_3$, δ) 0.16 (s, 6 H, CH_3), 0.42 (s, 6 H, CH_3), 0.72–0.84 (m, 2 H, C*H*H), 0.90–1.01 (m, 2 H, CH*H*), 4.65 (s, 5 H, CpH), 7.18–7.26 (m, 6 H, ArH), 7.40–7.44 (m, 4 H, ArH); ^{13}C NMR ($CDCl_3$, δ) –1.4 (CH_3), 1.2 (CH_3), 8.9 (CH_2), 66.5 (C), 81.4 (CH), 83.7 (C), 125.6 (CH), 126.9 (CH), 128.1 (CH), 139.3 (C); ^{29}Si NMR ($CDCl_3$, δ) –7.0; Anal. Calcd for $C_{27}H_{31}CoSi_2$: C, 68.90; H, 6.64%. Found: C, 68.45; H, 6.62%.

8 Crystal data for **1** at 120 K: $C_{27}H_{31}CoSi_2$, FW = 470.63, a = 9.770(2), b = 26.795(9), c = 10.188(4) Å, β = 113.093(2)°, V = 2453(1) Å^3, monoclinic, space group $P2_1/c$, Z = 4, ρ = 1.274 g·cm^{-3}. The final R_1 factor was 0.0348 for 5860 reflections with $I > 2\sigma(I)$ (wR_2 = 0.0936 for all data). GOF = 1.040.

9 ^{1}H NMR (C_6D_6, 298 K, δ) 0.53 (s, 12 H, CH_3), 1.19 (br.s, THF), 1.22 (s, 4 H, CH_2), 3.30 (br.s, THF), 6.74 (t, J = 7.2 Hz, 2 H, CH), 7.25 (t, J = 7.2 Hz, 4 H, CH), 7.62 (d, J = 7.2 Hz, 4 H, CH); ^{13}C NMR (C_6D_6, 298 K, δ) 2.9 (CH_3), 12.3 (CH_2), 25.4 (THF), 68.3 (THF), 89.6 (C), 102.8 (C), 117.4 (CH), 121.3 (CH), 128.5 (CH), 142.8 (C); ^{29}Si NMR (C_6D_6, 298 K, δ) –21.3; ^{7}Li NMR (C_6D_6, 298 K, δ) –4.21 (LiCl in MeOH, external).

10 Crystal data for **2** at 120 K: $C_{30}H_{46}Li_2O_4Si_2$, FW = 540.73, a = 22.291(2), b = 10.426(2), c = 15.513(2) Å, β = 117.085(7)°, V = 3209.9(8) Å^3, monoclinic, space group $C2/c$, Z = 4, ρ = 1.119 g·cm^{-3}. The final R_1 factor was 0.0757 for 3515 reflections with $I > 2\sigma(I)$ (wR_2 = 0.1943 for all data). GOF = 1.101.

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