Aromaticity of the Cyclobutadiene Dianion: Structural Characteristics and Magnetic Properties

Akira Sekiguchi,* Tsukasa Matsuo,[†] and Masanobu Tanaka

Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki 305-8571, Japan

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The dilithium salts of cyclobutadiene dianions (CBD^{2-}), 1,2-diphenyl-3,4-bis(trimethylsilyl)cyclobutadiene dianion dilithium (**3**), and 1,3-diphenyl-2,4-bis(trimethylsilyl)cyclobutadiene dianion dilithium (**4**) have been synthesized by the reaction of the corresponding cyclobutadiene cobalt complexes with lithium metal in tetrahydrofuran (THF). The dilithium salts were isolated as air- and moisture-sensitive crystals, and their molecular structures, containing two molecules of 1,2-dimethoxyethane (DME), were determined by X-ray crystallography. Each of the CBD^{2-} has a monomeric structure and forms contact ion pairs (CIPs) in the crystal. The two Li^+ ions are located above and below the plane of the four-membered ring and are bonded to the four quaternary carbon atoms. The cyclobutadienediide ring of the *cis*-diphenyl CBD^{2-} (**3**) shows a conspicuous trapezoid structure, whereas that of the *trans*-diphenyl CBD^{2-} (**4**) shows a slightly rhomboid structure. The ^7Li NMR spectra of the CBD^{2-} indicate that the two lithium atoms are considerably shielded by a diatropic ring current, resulting from the six-π-electron system.

Introduction

Over the years, many efforts have been directed toward studying the aromaticity of the cyclobutadiene dianion (CBD^{2-}).[1,2] In 1972, McKennis et al. obtained the first evidence for formation of CBD^{2-}. However, they characterized it as being highly reactive, since it apparently abstracted protons from tetrahydrofuran (THF).[3] In 1978, Garratt et al. successfully used ester groups to delocalize the negative charge so extensively that the dianion was stable at room temperature.[4] In 1982, NMR studies of the dilithium salt of 1,2-diphenylbenzocyclobutadiene dianion and the dipotassium salt of tetraphenylcyclobutadiene dianion were reported by Boche et al.[5,6] Later, they also reported the X-ray crystal structure of 1,2-diphenylbenzocyclobutadiene dianion dilithium with two molecules of tetramethylethylenediamine (TMEDA).[7]

Elaborate calculations indicate that the parent CBD^{2-} ($C_4H_4^{2-}$) should be regarded as a nonaromatic compound because of destabilizing 1,3-interactions. Optimization of $C_4H_4^{2-}$ by ab initio MO methods was found to give a bent structure with C_s symmetry, which was composed of an allyl anion and a localized negative charge.[8] Thus, the expected energy gain by delocalization of the negative charge in the aromatic system is offset by the considerable Coulomb repulsion between the diagonal carbons. In other words, stabilization of the Hückel-type D_{4h} geometry due to cyclic delocalization is not sufficient in this doubly charged system. In 1980, Kos and Schleyer pointed out the importance of the countercation for the stabilization of $C_4H_4^{2-}$.[9] They reported the theoretical calculations on $Li^+{}_2C_4H_4^{2-}$ with D_{4h} geometry, which was considered to be a derivative of the 6π cyclobutadiene dianion $C_4H_4^{2-}$, interacting on the top and bottom faces with two Li^+ ions. The most recent theoretical calculations on the dilithium salt of $Li^+{}_2C_4H_4^{2-}$ also suggest the possibility of experimental observation of a derivative with D_{4h} geometry.[10]

Recently, we reported the first experimental evidence for the aromaticity of CBD^{2-}, the dilithium salt of tetrakis(trimethylsilyl)cyclobutadiene dianion (**1**), which was prepared by reaction of the tetrakis(trimethylsilyl)cyclobutadiene cobalt complex (**5**) with lithium metal in THF.[11] Silyl groups are very useful in stabilizing the CBD^{2-} with $p\pi-\sigma^*$ conjugation.[12] In this paper, we report a detailed study of CBD^{2-} stabilized by both

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[†] Present address: Institute for Molecular Science, Myodaiji, Okazaki 444-8585, Japan.

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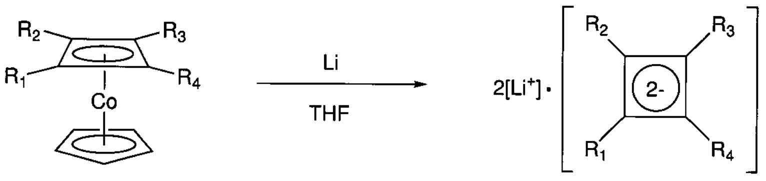
Scheme 1



5 (R_1, R_2, R_3, R_4 = $SiMe_3$)
6 (R_1, R_2 = Ph, R_3, R_4 = $Me_2SiCH_2CH_2SiMe_2$)
7 (R_1, R_2 = Ph, R_3, R_4 = $SiMe_3$)
8 (R_1, R_3 = Ph, R_2, R_4 = $SiMe_3$)

1 (R_1, R_2, R_3, R_4 = $SiMe_3$)
2 (R_1, R_2 = Ph, R_3, R_4 = $Me_2SiCH_2CH_2SiMe_2$)
3 (R_1, R_2 = Ph, R_3, R_4 = $SiMe_3$)
4 (R_1, R_3 = Ph, R_2, R_4 = $SiMe_3$)

phenyl and silyl groups.[13] Herein, we report the isolation and structural characterization of the dilithium salts of CBD^{2-}, 1,2-diphenyl-3,4-bis(trimethylsilyl)cyclobutadiene dianion dilithium (**3**), and 1,3-diphenyl-2,4-bis(trimethylsilyl)cyclobutadiene dianion dilithium (**4**). The nature of the CBD^{2-} will be reported on the basis of the structural features, as well as of the magnetic properties.

Results

Synthesis. The reaction of phenyl(trimethylsilyl)acetylene with $CpCo(CO)_2$ in refluxing octane for 7 days produced a mixture of *cis*- and *trans*-(Cp)Co[$Ph_2C_4(SiMe_3)_2$] (**7** and **8**) in 84% yield.[14] The mixture was chromatographed on silica gel with hexane to separate the species. Compound **7** and excess lithium metal were placed in a reaction tube with a magnetic stirrer. Dry, oxygen-free tetrahydrofuran (THF) was introduced by vacuum transfer, and the mixture was stirred vigorously at room temperature for 24 h to give a dark brown solution containing the dilithium salt of 1,2-diphenyl-3,4-bis(trimethylsilyl)cyclobutadiene dianion (**3**, THF ligand) in almost quantitative yield (Scheme 1). Next, after degassed hexane was added to the reaction mixture by vacuum transfer, the residual lithium pieces and insoluble dark material were removed in a glovebox. Then, after the solvent was removed in vacuo, once again degassed hexane and a small amount of 1,2-dimethoxyethane (DME) were introduced by vacuum transfer. The solution was cooled to afford air- and moisture-sensitive yellow-orange crystals of **3** containing two molecules of DME. The dilithium salt of 1,3-diphenyl-2,4-bis(trimethylsilyl)cyclobutadiene dianion (**4**) was prepared by the same procedure as for **3**, starting from **8**. The CBD^{2-} **4** containing two molecules of DME was isolated as red crystals.

Crystal Structure. The molecular structures of the CBD^{2-} **3** and **4** have been determined by X-ray crystallography. Figures 1 and 2 show ORTEP drawings of **3** and **4**, respectively. Each of the dilithium salts has a monomeric structure and forms contact ion pairs (CIPs) in the crystals. One DME molecule is coordinated to each lithium atom.

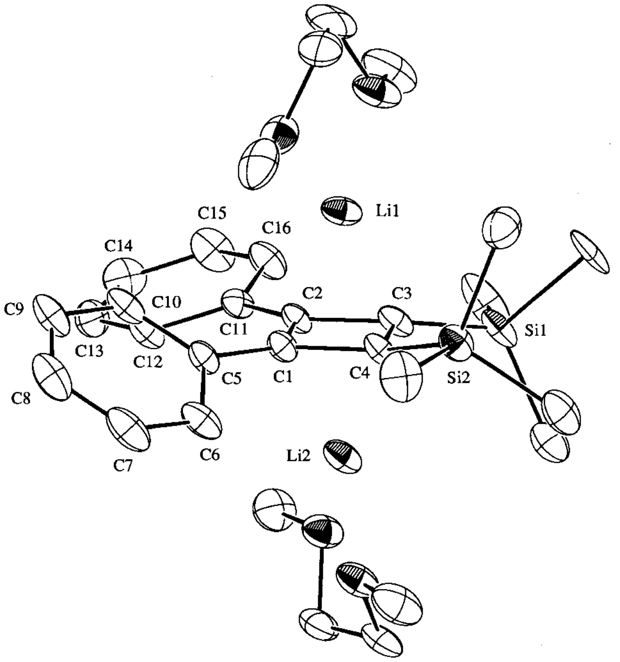


Figure 1. Molecular structure of **3** with thermal ellipsoids drawn at the 50% level (hydrogen atoms are omitted for clarity). Selected bond distances [Å]: C1−C2 1.462(4), C1−C4 1.479(4), C2−C3 1.488(4), C3−C4 1.521(4), C1−C5 1.460(4), C2−C11 1.451(4), C3−Si1 1.828(3), C4−Si2 1.844(3), C1−Li1 2.240(6), C2−Li1 2.174(6), C3−Li1 2.159(6), C4−Li1 2.216(6), C1−Li2 2.197(6), C2−Li2 2.218(6), C3−Li2 2.197(6), C4−Li2 2.172(6). Selected bond angles [deg]: C2−C1−C4 90.9(2), C2−C1−C5 134.7(2), C4−C1−C5 134.1(2), C1−C2−C3 91.4(2), C1−C2−C11 134.2(2), C3−C2−C11 134.1(2), C2−C3−C4 88.3(2), C2−C3−Si1 140.3(2), C4−C3−Si1 128.5(2), C1−C4−C3 89.5(2), C1−C4−Si2 136.3(2), C3−C4−Si2 129.9(2).

The *cis*-diphenyl CBD^{2-} **3** has C_1 symmetry. The two Li^+ ions (Li1 and Li2) are located above and below the approximate center of the plane of the cyclobutadienediide ring and are bonded to the four quaternary carbon atoms (η^4-coordination). The distances between Li1 and the four carbon atoms (C1, C2, C3, and C4) range from 2.159(6) to 2.240(6) Å (av 2.197(6) Å), and those of Li2 are 2.172(6)−2.218(6) Å (av 2.196(6) Å). The Li distances from the ring centroid are 1.927(5) Å for Li1 and 1.928(6) Å for Li2.

The four-membered ring is planar and the sum of the bond angles is 360.0°. However, the geometry of the four-membered ring does not show a square structure, but a trapezoid structure (C1−C2, 1.462(4); C2−C3, 1.488(4); C3−C4, 1.541(4); C1−C4, 1.479(4) Å; C4−C1−C2, 90.9(2)°; C1−C2−C3, 91.4(2)°; C2−C3−C4, 88.3(2)°; C3−C4−C1, 89.5(2)°, Figure 3). The elongation of the C3−C4 bond results from the large steric repulsion

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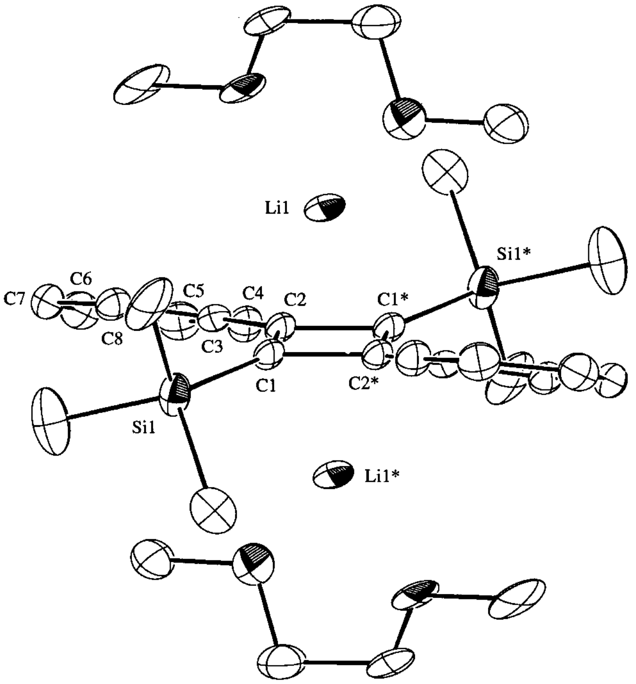

Figure 2. Molecular structure of **4** with thermal ellipsoids drawn at the 50% level (hydrogen atoms are omitted for the clarity). Selected bond distances [Å]: C1−C2 1.486(3), C1−C2* 1.488(3), C2−C3 1.444(3), C1−Si1 1.846(2), C1−Li1 2.242(5), C2−Li1 2.191(5), C1−Li1* 2.190(5), C2−Li1* 2.206(5). Selected bond angles [deg]: C2−C1−C2* 88.0(2), C2−C1−Si1 140.3(2), C2*−C1−Si1 130.8(2), C1−C2−C1* 92.0(2), C1−C2−C3 134.0(2), C1*−C2−C3 133.6(2).

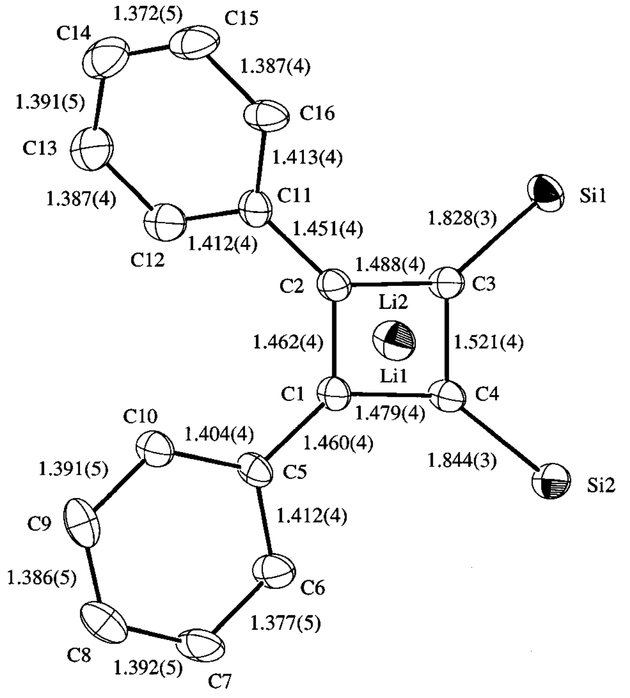

Figure 3. Section from the structure of **3** with selected lengths [Å].

between the two trimethylsilyl groups. Such a trapezoid structure has never been observed in the previously reported CBD^{2-}, 2[Li$^+$]·[(Me$_3$Si)$_4$C$_4$$^{2-}$] (**1**)[11] and the *cis*-diphenyl-substituted cyclobutadiene dianion bridged by a [−SiMe$_2$(CH$_2$)$_2$SiMe$_2$−] chain (**2**).[13] The silicon−carbon bond lengths (Si1−C3, 1.828(3); Si2−C4, 1.844(3) Å) are shorter than usual (1.88 Å) and are almost the same as those observed in **1** (av 1.836(7) Å) and **2** (1.828(4) Å), because of delocalization of the negative charge onto the silicon centers by pπ−σ* conjugation.[12] The C1−C5 and C2−C11 distances in **3** are 1.460(4) and 1.451(4) Å, respectively.

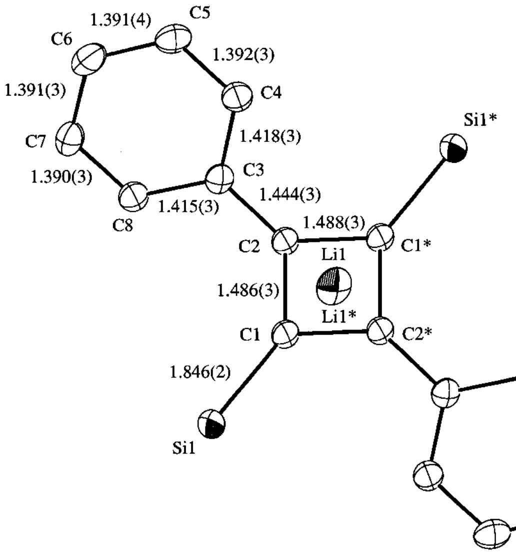

Figure 4. Section from the structure of **4** with selected lengths [Å].

The *trans*-diphenyl CBD^{2-} **4** has an inversion center at the center of the C1−C2−C1*−C2* four-membered ring (C_i symmetry). There are two independent half molecules in the unit cell, and the two half molecules have almost the same geometry. The two Li$^+$ ions (Li1 and Li1*) are bonded to the four carbon atoms (C1, C2, C1*, and C2*) with the distances ranging from 2.190(5) to 2.242(5) Å (av 2.207(5) Å). The Li distances from the ring centroid (2.070(4) Å) are longer than those observed in **1** (av 1.90(1) Å),[11] **2** (1.959(6) Å),[13] and **3** (av 1.928(6) Å). This indicates that the interaction (electrostatic or covalent, or both) between the Li$^+$ ions and the charged ring of **4** is not as strong as it is for the other CBD^{2-} (**1**, **2**, and **3**).

Interestingly, the geometry of the four-membered ring of **4** shows a planar and slightly rhomboid structure (Figure 4). The bond angles are 88.0(2)° for C2−C1−C2* and 92.0(2)° for C1−C2−C1*, and the bond distances are 1.486(3) Å for C1−C2 and 1.488(3) Å for C1−C2*. Such a rhomboid structure might be due to the *trans* arrangement of the substituents. The C2−C3 distance (1.444(3) Å) is comparable to that observed in **2** (1.448(5) Å)[13] and **3** (av 1.456(4) Å). This bond length between two quaternary ring carbons indicates the degree of delocalization of the negative charge over the phenyl ring. The Si1−C1 bond distance is 1.846(2) Å.

Structure in Solution. We have also investigated the structure of the CBD^{2-} in solution using NMR spectroscopy. In the ^{7}Li NMR spectrum of **3** in benzene-d_6, one signal appeared at $\delta = -4.24$, which is similar to that observed in **2** ($\delta = -4.21$).[13] The ^{7}Li signal of **4** was observed at $\delta = -4.44$. These signals of the CBD^{2-} are somewhat shifted to lower field compared with that of **1** ($\delta = -5.07$).[11] The chemical shift of the Li NMR signal indicates the magnitude of the diatropic ring current resulting from the six-π-electron system, because the two Li$^+$ ions of the CBD^{2-} are located in the shielding region due to the ring current.[15] From the above data, the ring current should be decreased by the introduction of phenyl groups. In addition, the *trans*-diphenyl CBD^{2-} **4** has a slightly stronger ring current compared with those of the *cis*-diphenyl CBD^{2-} **2** and **3**, presumably due to the symmetrical arrangement of the substituents.

The ^{13}C NMR spectra of **3** and **4** in benzene-d_6 show two signals for the cyclobutadienediide ring carbons at $\delta = 83.8$ (Ph*C*) and 106.1 (Si*C*) for **3** and $\delta = 84.0$ (Ph*C*) and 110.1 (Si*C*) for **4**. Phenyl carbons are observed at $\delta = 119.4$ (*para*-), 125.2 (*ortho*-), 128.3 (*meta*-), and 142.1 (*ipso*-) for **3** and $\delta = 117.6$ (*para*-), 123.9 (*ortho*-), 127.7 (*meta*-), and 143.3 (*ipso*-) for **4**. These ^{13}C NMR data show that the negative charges of the CBD^{2-} are delocalized onto the phenyl rings. Thus, the ^{13}C signals of *ortho*- and *para*-carbons are somewhat shifted to higher field relative to those signals observed in **7** ($\delta = 127.5$, $\Delta\delta = -2.3$ (*ortho*-) and $\delta = 125.9$, $\Delta\delta = -6.5$ (*para*-)) and **8** ($\delta = 127.3$, $\Delta\delta = -3.4$ (*ortho*-) and $\delta = 125.9$, $\Delta\delta = -8.3$ (*para*-)).

In the ^{29}Si NMR spectra of **3** and **4**, only one signal appeared, at $\delta = -20.7$ for **3** and $\delta = -23.1$ for **4**. These ^{29}Si signals are considerably shifted upfield compared with their precursors ($\delta = -5.7$, $\Delta\delta = -15.0$ for **7** and $\delta = -7.1$, $\Delta\delta = -16.0$ for **8**).

Discussion

The transmetalation reaction from transition metal complex to alkali metal complex is uncommon. The mechanism of the transmetalation remains unclear at this moment. One of the most plausible mechanisms is as follows. (1) The radical anion of the cobalt complex is formed by an electron-transfer reaction from the lithium metal to the cobalt complex at the initial stage. (2) The cyclobutadiene radical anion may be removed from the cobalt center. (3) This cyclobutadiene radical anion is further reduced by lithium metal to form the aromatic CBD^{2-}. We tried to see a lithium cyclopentadienide (CpLi) in THF-d_8 solution; however, no CpLi signal was observed in the ^{7}Li NMR spectrum.[15] This suggests that removal of cyclopentadienide from the cobalt center has not occurred. The residual insoluble dark material, which is flammable in air, might be the anion species of CpCo fragments.

CBD^{2-} has a considerable electrostatic repulsion between the two negative charges. In addition, the planar four-membered ring has a large ring strain. Thus, the stabilizing cyclic electron delocalization of CBD^{2-} is quite interesting, and it is very difficult to comprehend its nature. From the X-ray crystal structure, both **3** and **4** are cyclic and nearly planar in the ring, although the geometries of the cyclobutadienediide rings are almost square structures for **1** and **2**, a conspicuous trapezoid structure for **3**, and a slightly rhomboid structure for **4**. From the magnetic point of view, all of the CBD^{2-} in solution show a strong diatropic ring current resulting from delocalization of the six-π-electron system. Thus, the CBD^{2-} should be regarded as aromatic compounds. As mentioned above, the ^{7}Li NMR studies are very useful for estimating the magnitude of the ring current, because the two Li$^+$ ions are located inside the aromatic shielding region.[16] It is considered that the degree of the stabilizing cyclic electron delocalization is a good indicator of the intensity of the diatropic ring current. Thus, the degree of the aromaticity of the CBD^{2-} can be represented approximately as **1** ($\delta = -5.07$) > **4** ($\delta = -4.44$) ≥ **2** and **3** ($\delta = -4.21$ and -4.24).[17] Interestingly, the stabilizing cyclic electron delocalization of CBD^{2-} decreases on the introduction of benzene rings. The negative charge of the CBD^{2-} is stabilized by both silyl and phenyl groups; however, stabilization by phenyl groups is more effective.

The problem with D_{4h} CBD^{2-} is that four electrons have to go into nonbonding π-MOs. It is considered that complexation with counter lithium cations is important to stabilize the CBD^{2-}. Each CBD^{2-} has a monomeric structure and forms CIPs in the condensed phase. Thus, the two Li$^+$ ions stabilize the HOMO of CBD^{2-} through the vacant 2p orbitals with η^4-coordination. The dilithium complex of the CBD^{2-} with D_{4h} geometry should be explained by the interaction of the two degenerate nonbonding π-MOs with lithium ion orbitals of matching symmetry.[18] The Li$^+$ ions counteract the serious Coulomb repulsion. The smaller Li$^+$ ions can approach more closely than other cations.[19] Indeed, the choice of alkali metals is quite important in the transmetalation reaction, since alkali metals other than lithium (e.g., sodium or potassium) do not work.

Conclusion

Our transmetalation reaction of the cyclobutadiene cobalt complex with lithium metal has permitted the preparation of a variety of dilithium salts of the CBD^{2-}. The molecular structures of the phenyl-substituted CBD^{2-} (**3** and **4**) have been unambiguously determined by X-ray diffraction, and their structural parameters compared with the previously reported CBD^{2-} (**1** and **2**). The structures of the CBD^{2-} in solution were also fully characterized by NMR studies. All of the CBD^{2-} show a strong diatropic ring current resulting from the six-π-electron system. The aromatic stabilization of the CBD^{2-} competes with the electrostatic repulsion of the negative charge in the doubly charged four-membered ring system, and the stabilization of the negative charge by the phenyl groups is more effective than by the silyl groups. Changing the countercations of CBD^{2-} from lithium to other alkali metals (e.g., sodium or potassium) is in progress, and the synthesis of CBD^{2-} with

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[15] The ^{7}Li NMR chemical shifts of organolithiums (RLi, R = Me, Et, ^{n}Bu, ^{t}Bu, Ph) range from 0.4 to 1.6 ppm. The ^{7}Li NMR of lithium cyclopentadienide LiCp was reported to be −8.60 ppm in Et$_2$O due to the strong shielding. Elschenbroich, C.; Salzer, A. *Organometallics*; VCH Verlagsgesellschaft: Weinheim, 1989; pp 26−27. In contrast, a large deshielding effect of Li NMR for Li$_2$(DME)$_2$·(1,2,4,5-(Me$_3$Si)$_4$C$_6$H$_2$) appearing at δ 10.7 as an antiaromatic system has been reported, see: Sekiguchi, A.; Ebata, K.; Kabuto, C.; Sakurai, H. *J. Am. Chem. Soc.* **1991**, *113*, 7081.

[16] The computed Li chemical shifts in the Li$_2$C$_4$R$_4$ are around −3 ppm, see ref 10b. This paper also discusses the aromaticity of dianions C$_4$R$_4$$^{2-}$ and Li$_2$C$_4$R$_4$ (R = H, Me, ^{t}Bu).

[17] The use of the chemical shift of Li$^+$ complexed to ring faces as an aromaticity probe has been reported, see ref 10b. (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.

[18] Ishii, K.; Kobayashi, N.; Matsuo, T.; Tanaka, M.; Sekiguchi, A. *J. Am. Chem. Soc.* **2001**, *123*, 5356.

[19] The essential stabilization of polyanions by lithium and other counterions was extensively discussed and reviewed by Lambert and Schleyer, see: Lambert, C.; Schleyer, P. v. R. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1129.

solvent-separated ion pairs (SSIPs) is one of the most challenging further goals.

Experimental Section

General Procedures. ^{1}H NMR spectra were recorded on a Bruker AC-300 FT spectrometer. ^{13}C, ^{29}Si, and ^{7}Li NMR spectra were collected on a Bruker AC-300 at 75.5, 59.6, and 116.6 MHz, respectively. ^{7}Li NMR spectra are referenced to 1 M (1 M = 1 mol dm^{-3}) LiCl in methanol/benzene-d_6 or 1 M LiCl in THF-d_8. The sampling of **3** and **4** for X-ray crystallography was carried out by using a MBRAUN MB 150B-G glovebox in argon atmosphere. Tetrahydrofuran and hexane were dried and distilled from sodium benzophenone ketyl. These solvents were further dried and degassed over a potassium mirror in vacuo prior to use. Benzene-d_6 and THF-d_8 were dried over molecular sieves and then transferred into a tube covered with potassium mirror prior to use. The cobalt complexes *cis*- and *trans*-(Cp)Co[$Ph_2C_4(SiMe_3)_2$] (**7** and **8**) were prepared by the reported method.[14] Commercially available lithium rod (99.9%, Mitsuwa's Pure Chemicals) was pressed out from a stainless bottle with a hall to make the lithium wire (ca. diameter 1 mm), which was cut into small pieces under argon flow just before use.

1,2-Diphenyl-3,4-bis(trimethylsilyl)cyclobutadiene Dianion Dilithium (3). The crystals of *cis*-(Cp)Co[$Ph_2C_4(SiMe_3)_2$] (**7**, 50 mg, 0.092 mmol) and an excess amount of lithium metal (30 mg, 4.3 mmol) were placed in a reaction tube with a magnetic stirrer. After the tube had been degassed, dry, oxygen-free THF (1.5 mL) was introduced by vacuum transfer, and the mixture was stirred vigorously at room temperature for 24 h to give a dark brown solution containing 1,2-diphenyl-3,4-bis(trimethylsilyl)cyclobutadiene dianion dilithium (**3**, THF ligand) in almost quantitative yield. The solvent was evaporated, and then degassed hexane (5.0 mL) was added to the reaction mixture by vacuum transfer. After the filtration of the residual lithium pieces and insoluble dark materials in a glovebox, the solvent was removed in vacuo, and once again degassed hexane (3.0 mL) and a small amount of 1,2-dimethoxyethane (DME, ca. 0.3 mL) were introduced by vacuum transfer. The solution was cooled to afford air- and moisture-sensitive yellow-orange crystals of **3** containing two molecules of DME in 87% yield (50 mg, 0.092 mmol). NMR spectral data of **3** (THF ligand): ^{1}H NMR (C_6D_6, δ) 0.57 (s, 18 H, CH_3), 1.26 (br s, 8 H, THF), 3.39 (br s, 8 H, THF), 6.83 (t, $J = 7.5$ Hz, 2 H, CH), 7.22 (t, $J = 7.5$ Hz, 4 H, CH), 7.53 (d, $J = 7.5$ Hz, 4 H, CH); ^{13}C NMR (C_6D_6, δ) 5.3 (CH_3), 25.4 (THF), 68.4 (THF), 83.8 (C), 106.1 (C), 119.4 (CH), 125.2 (CH), 128.3 (CH), 142.1 (C); ^{29}Si NMR (C_6D_6, δ) −20.7; ^{7}Li NMR (C_6D_6, δ) −4.24.

1,3-Diphenyl-2,4-bis(trimethylsilyl)cyclobutadiene Dianion Dilithium (4). Dianion dilithium **4** was prepared by the same procedure as compound **3**, but starting from *trans*-(Cp)Co[$Ph_2C_4(SiMe_3)_2$] (**8**, 50 mg, 0.106 mmol), and had an almost quantitative yield (THF ligand). Compound **4** containing two molecules of DME was obtained as air- and moisture-sensitive red crystals (50 mg, 0.092 mmol, 87%). NMR spectral data of **4** (THF ligand): ^{1}H NMR (C_6D_6, δ) 0.61 (s, 18 H, CH_3), 1.27 (br s, 8 H, THF), 3.37 (br s, 8 H, THF), 6.74 (t, $J = 7.3$ Hz, 2 H, CH), 7.21 (t, $J = 7.3$ Hz, 4 H, CH), 7.41 (d, $J = 7.3$ Hz, 4 H, CH); ^{13}C NMR (C_6D_6, δ) 4.7 (CH_3), 25.5 (THF), 68.4 (THF), 84.0 (C), 110.1 (C), 117.6 (CH), 123.9 (CH), 127.7 (CH), 143.3 (C); ^{29}Si NMR (C_6D_6, δ) −23.1; ^{7}Li NMR (C_6D_6, δ) −4.44.

X-ray Crystal Structure Analyses. Single crystals of **3** and **4** suitable for X-ray diffractions were grown from a hexane solution. Diffraction data were collected on a Mac Science DIP2030K image plate diffractometer employing graphite-monochromatized Mo Kα radiation ($\lambda = 0.71070$ Å). The structure was solved by the direct method and refined by the full-matrix least-squares method using the SHELXL-97 program. Crystal data for **3** at 120 K: MF = $C_{30}H_{48}Li_2O_4Si_2$, fw = 542.75, triclinic, $a = 11.115(1)$ Å, $b = 11.032(1)$ Å, $c = 15.661(1)$ Å, $\alpha = 74.980(6)°$, $\beta = 70.856(6)°$, $\gamma = 63.375(5)°$, $V = 1607.4(3)$ Å^3, space group = $P\bar{1}$, $Z = 2$, $d_{calc} = 1.121$ g·cm^{-3}. The final R factor was 0.0671 for 4395 reflections with $I > 2\sigma(I)$ and $wR_2 = 0.1824$ for all data. GOF = 1.047. Crystal data for **4** at 120 K: MF = $C_{30}H_{48}Li_2O_4Si_2$, fw = 542.75, triclinic, $a = 10.686(1)$ Å, $b = 10.943(1)$ Å, $c = 15.885(1)$ Å, $\alpha = 77.443(3)°$, $\beta = 72.937(4)°$, $\gamma = 70.247(4)°$, $V = 1656.8(2)$ Å^3, space group = $P\bar{1}$, $Z = 2$, $d_{calc} = 1.088$ g·cm^{-3}. The final R factor was 0.0659 for 5580 reflections with $I > 2\sigma(I)$ and $wR_2 = 0.1827$ for all data. GOF = 1.028.

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Supporting Information Available: Tables giving the details of the X-ray structure determination, thermal ellipsoid plots, fractional atomic coordinates, anisotropic thermal parameters, bond lengths, and bond angles for **3** and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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