Bull. Chem. Soc. Jpn., 77, 211–226 (2004)

Award Accounts

The Chemical Society of Japan Award for Young Chemists for 2002

Cyclobutadiene Dianion

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In this account, we present the synthesis and chemistry of the dilithium salts of the cyclobutadiene dianion (CBD^{2-}), which contains a doubly charged four-membered ring system. The transmetalation reaction of tetrasilyl-substituted cyclobutadiene (CBD) cobalt complexes (**5**,**6**) with lithium metal led to the formation of the corresponding dilithium salts of CBD^{2-} (**10**,**11**). The aromaticity of the CBD^{2-} species has been studied on the basis of structural characteristics and magnetic properties. The dilithium salts of CBD^{2-} stabilized by both phenyl and silyl groups (**12**–**14**) were also prepared by a similar procedure, starting from the corresponding CBD cobalt complexes (**7**–**9**). The CBD^{2-} species have been fully characterized by NMR studies and X-ray crystallography. The two-electron oxidation reaction of the tetrasilyl-CBD^{2-} (**10**,**11**) with 1,2-dibromoethane produced the neutral CBD derivatives (**17**,**22**). The structures, properties, and reactivities of the tetrasilyl-substituted CBD are also reviewed here. Tetrakis(trimethylsilyl)tetrahedrane (**26**) was synthesized by irradiation of tetrakis(trimethylsilyl)cyclobutadiene (**17**). The structure and properties of tetrahedrane (**26**) are presented.

π-Electron systems with alternating carbon–carbon single and double bonds are fundamental and essential species in organic chemistry. Various types of π-electron systems are known, with their properties depending primarily on the number and arrangement of double bonds. The basic concepts concerning π-electron systems, such as conjugation, aromaticity, and Hückel's rule, have been established from both theoretical and experimental viewpoints.

Benzene, with a 6C/6π-electron system, can be written as a resonance hybrid of two Kekulé structures (Chart 1).[1] This representation suggests that the π-electrons are delocalized with a bond order of 1.5 between adjacent carbon atoms. The molecular structure of benzene is a planar equilateral hexagon, in which each sp^2 carbon atom has an unhybridized p orbital perpendicular to the ring plane, and six electrons occupy this circle of p orbitals. The special stability of benzene is called aromaticity.[2,3] An aromatic compound is a cyclic compound containing a particular number of conjugated double bonds with an unusually large resonance energy. In general, aromatic compounds are those that conform to the following criteria. 1) The structure must be cyclic and contain a particular number of conjugated π-bonds. Hückel's rule predicts benzene, with a 6π-electron system, to be aromatic, as it is a $(4N + 2)$ system, with $N = 1$. 2) Each atom in the ring must have an unhybridized p orbital. The ring atoms are usually sp^2 hybridized, or occasionally sp hybridized. 3) The unhybridized p orbitals must overlap to form a continuous ring of parallel orbitals. In most cases, the structure should be planar or nearly planar for effective overlap. 4) Delocalization of the π-electrons over the ring must result in a lowering of the electronic energy.

Chart 1.

Since the formation of a cyclopentadienide with a 5C/6π-electron system was reported in 1900 by Thiele,[4] a variety of anion species with a π-electron system having extra electrons in the molecule have been investigated from the viewpoint of their unique structures, properties, and reactivities.[5] Anion species with a π-electron system have many interesting and important characteristics: delocalization of π-electrons, distribution of negative charge, complexation with metal cations, formation of ion pairs, solvation of counter cations, and so on. A negative charge on a cyclopentadienide is delocalized over five ring carbon atoms; the structure is a planar, equilateral pentagon. Thus, cyclopentadienide is a stable, closed-shell anion species stabilized by an aromatic 6π-electron system. There are now many isolable cyclopentadienide derivatives, and they have been widely utilized in coordination chemistry.

In contrast, the synthesis and chemistry of the cyclobutadiene dianion (CBD^{2-}), with a 4C/6π-electron system, have been rarely explored, despite their fundamental importance. As with cyclopentadienide, Hückel's rule predicts the 6π-electrons of CBD^{2-} to be aromatic. Over the years, many efforts have been directed toward studying CBD^{2-}; however, there has been no clear evidence for the aromaticity of CBD^{2-}. "*Aromatic or non-aromatic; that is the question!*"

Published on the web February 10, 2004; DOI 10.1246/bcsj.77.211

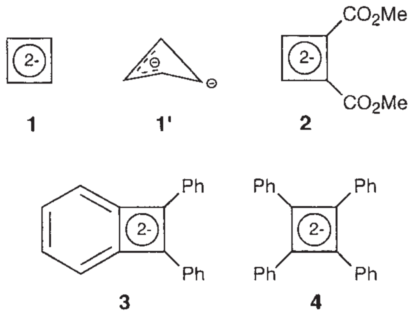


Chart 2.

In 1982, McKennis et al. obtained the first evidence for the formation of CBD^{2-} (**1**). However, they characterized it as being highly reactive, since it apparently abstracted protons from tetrahydrofuran (THF).[6] In 1978, Garratt et al. successfully used ester groups to delocalize the negative charge so extensively that the dianion (**2**) was stable at room temperature (Chart 2).[7] Measurements of pK_a indicate that the dianion **2** does not experience any aromatic stabilization; only 40% of the negative charge remains in the four-membered ring. In 1982, NMR studies of the dilithium salt of the 1,2-diphenylbenzocyclobutadiene dianion (**3**) and the dipotassium salt of tetraphenylcyclobutadiene dianion (**4**) were reported by Boche et al.[8,9] The negative charge of **4** resides predominantly on the phenyl groups (64%). Later, they also reported the X-ray structure of **3** with two molecules of tetramethylethylenediamine (TMEDA).[10] Although two types of molecular structures were found in the crystal, additional stabilization by Hückel delocalization of the six π-electrons could not be detected.

Elaborate calculations show that the parent CBD^{2-} ($C_4H_4{}^{2-}$, **1**) should be regarded as a nonaromatic compound because of destabilizing 1,3-interactions. The charge density per carbon unit of $C_4H_4{}^{2-}$ is -0.5, which is 2.5 times larger than that of $C_5H_5{}^{-}$ (-0.2). Optimization of $C_4H_4{}^{2-}$ by ab initio MO methods was found to give a bent structure with C_s symmetry (**1′**), which was composed of an allyl anion and a localized negative charge (Chart 2).[11] 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 because of cyclic delocalization is not sufficient in this doubly charged system. In 1980, Kos and Schleyer pointed out the importance of the counter cation for the stabilization of $C_4H_4{}^{2-}$.[12] They reported 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. Recent theoretical calculations on the dilithium salt $Li^{+}{}_2C_4H_4{}^{2-}$ also suggest the possibility of experimental observation of a derivative with D_{4h} geometry.[13]

In 2000, we reported the first experimental evidence for the aromaticity of CBD^{2-}. The dilithium salt of tetrakis(trimethylsilyl)cyclobutadiene dianion, $[Li^{+}{}_2]\cdot[(Me_3Si)_4C_4{}^{2-}]$ (**10**), was prepared by reaction of the tetrakis(trimethylsilyl)cyclobutadiene cobalt complex, $(Me_3Si)_4C_4CoCp$ (**5**) with lithium metal in THF.[14] The introduction of a silyl group to the π-electron system causes remarkable steric and electronic perturbations.[15] One of the most interesting features of the silyl-substituted π-electron system is the ability to form the corresponding anion species by reduction with alkali metals. We have previously reported the preparation of a variety of dianion dilithium or tetraanion tetralithium salts of π-electron systems by taking advantage of the silyl groups.[16,17] The α-effect of a silyl group is well known as a very important electronic effect stabilizing the negative charge; the anion on the atom that is located at an α-position to the silicon atom is stabilized by the antibonding σ^* orbital of the silicon–carbon bond of the alkylsilyl group (Fig. 1). When alkylsilyl group is substituted by the π-electron system, the level of LUMO of π-electron system is stabilized by the interaction between the antibonding σ^* orbital of the silicon–carbon bond and π^* orbital of π-electron system. It is a σ^*–π^* conjugation. Subsequently, we have also reported the successful preparation of the dilithium salts of CBD^{2-} species stabilized by both phenyl and silyl groups (**12**–**14**).[18] In the present account, we summarize our recent studies on a series of dilithium salts of CBD^{2-} (**10**–**14**, Chart 3). We will review here the synthesis, structures, properties, and reactivities of the CBD^{2-}, together with the chemistry of tetrasilyl-substituted cyclobutadiene (CBD)[19] and tetrahedrane.[20]

1 Synthesis of Dilithium Salts of CBD^{2-}

1.1 Synthesis of CBD Cobalt Complexes. At the beginning of the work, we focused on the application of transition metal complexes of CBD as starting materials for CBD^{2-}, because of the lack of tetrasilyl-substituted CBD derivatives. Tetrakis(trimethylsilyl)cyclobutadienyl(cyclopentadienyl)cobalt, $[(Me_3Si)_4C_4CoCp]$ (**5**),[21] was prepared according to Vollhardt's method.[21b] A mixture of bis(trimethylsilyl)acetylene and cyclopentadienyl(dicarbonyl)cobalt $[CpCo(CO)_2]$ was refluxed for five days to produce yellow crystals of **5** in 55% yield with a small amount of tetrakis(trimethylsilyl)butatriene[22] (Scheme 1). We have also prepared the cobalt complex bridged by $Me_2Si(CH_2)_2SiMe_2$ chains (**6**) in a similar manner. The re-

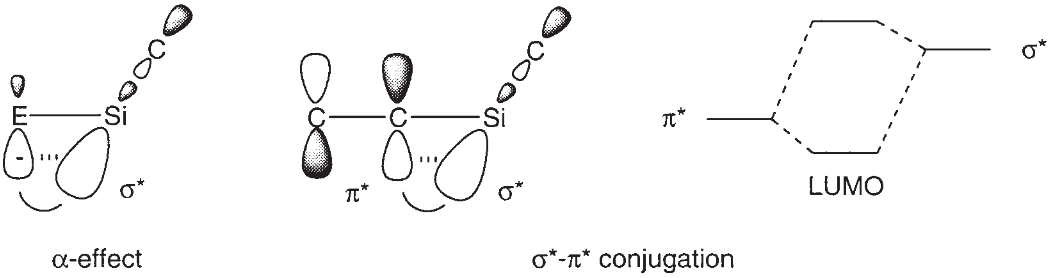


Fig. 1. α-Effect of silyl group and σ^*–π^* conjugation.

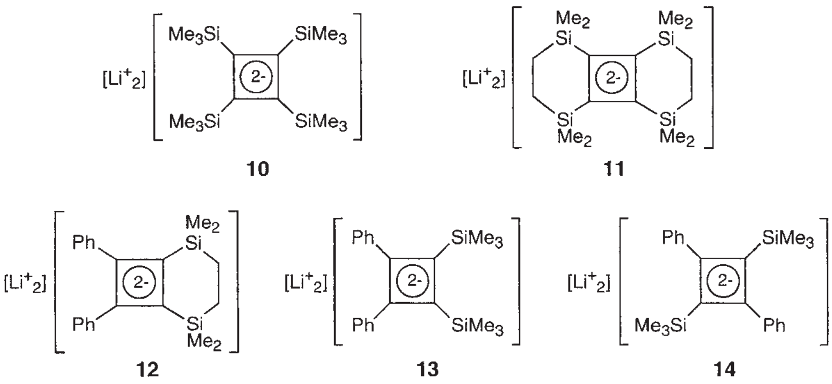
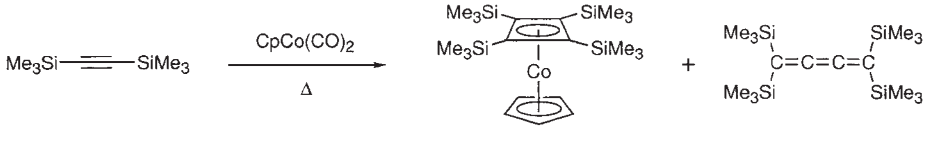
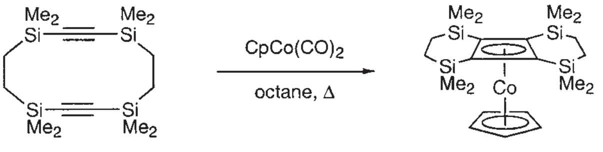


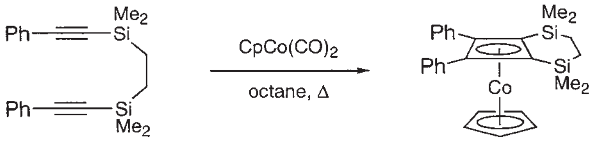
Chart 3.



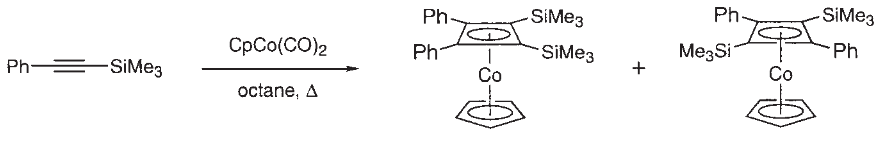
Scheme 1.



Scheme 2.



Scheme 3.



Scheme 4.

action of 3,3,6,6,9,9,12,12-octamethyl-3,6,9,12-tetrasilacyclododeca-1,7-diyne[23] with [CpCo(CO)$_2$] in refluxing octane produced **6** in 16% yield (Scheme 2). The closely related reactions between cyclic diyne compounds and [CpCo(CO)$_2$] have been investigated by Gleiter et al. They reported various cobalt complexes, such as metal-capped cyclobutadienosuperphanes.[24]

We have designed the *cis*-diphenyl-substituted CBD cobalt complex (**7**) as a precursor of the CBD^{2-} species supported by both phenyl and silyl groups. A mixture of 1,8-diphenyl-3,6-disila-1,7-octadiyne and [CpCo(CO)$_2$] was refluxed in octane to give **7** in 86% yield (Scheme 3). In this reaction, we obtained complex **7** with the *cis* arrangement of the substituents as the sole product. On the other hand, the reaction of phenyl(trimethylsilyl)acetylene with [CpCo(CO)$_2$] in refluxing octane for seven days produced a mixture of *cis*- and *trans*-[{Ph$_2$(SiMe$_3$)$_2$C$_4$}Co(Cp)] (**8** and **9**) in 84% yield (Scheme 4).[25] The mixture was chromatographed on silica gel with hexane to separate the species. Compounds **5**–**9** are thermally stable but slightly moisture-sensitive, and they slowly decompose in air.

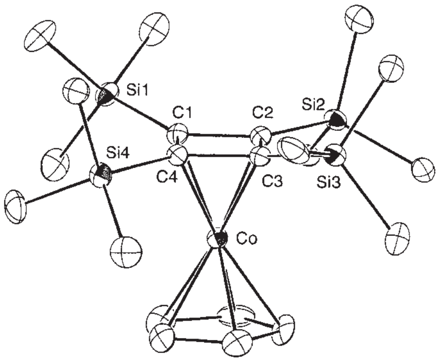


Fig. 2. ORTEP drawing of **5**.

1.2 Structures of CBD Cobalt Complexes. Complexes **5**–**9** are diamagnetic and have been characterized by NMR spectroscopy. In addition, the structures of **5**–**7** were determined by X-ray crystallography.[18a,26] The X-ray structures of *cis*- and *trans*-[{Ph$_2$(SiMe$_3$)$_2$C$_4$}Co(Cp)] (**8** and **9**) were previously reported by Sakurai et al.[25] Figures 2 and 3 show the π-sandwich

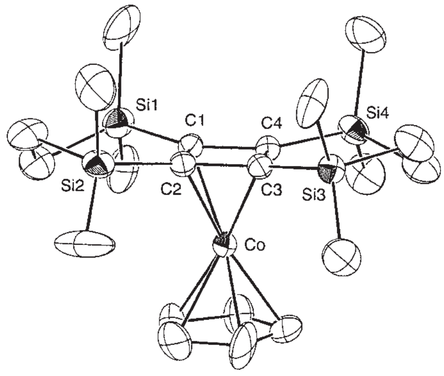


Fig. 3. ORTEP drawing of **6**.

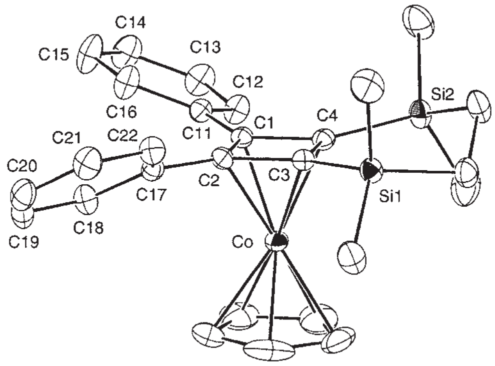
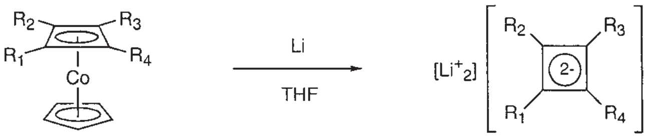


Fig. 4. ORTEP drawing of **7**.



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

10 (R_1, R_2, R_3, R_4 = $SiMe_3$)
11 (R_1, R_2 = R_3, R_4 = $Me_2SiCH_2CH_2SiMe_2$)
12 (R_1, R_2 = Ph, R_3, R_4 = $Me_2SiCH_2CH_2SiMe_2$)
13 (R_1, R_2 = Ph, R_3, R_4 = $SiMe_3$)
14 (R_1, R_3 = Ph, R_2, R_4 = $SiMe_3$)

Scheme 5.

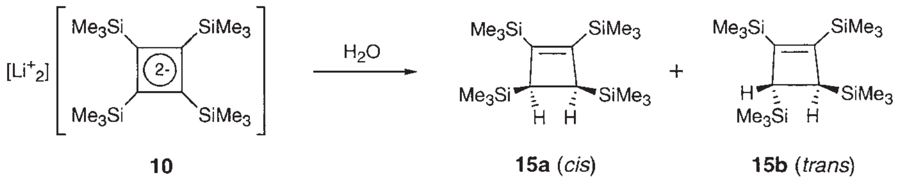
structures of **5** and **6** having a tetrasilyl-substituted CBD ligand, respectively. Spectroscopic evidence and X-ray analysis show that free CBD and its derivatives adopt a rectangular structure. In contrast, η^4-coordination of the CBD ligand in transition metal complexes shows a square configuration. CBD has four π-electrons and four π-MOs. The square CBD possesses two degenerate singly occupied π-MOs, which can interact with singly occupied metal orbitals of matching symmetry.

According to X-ray analysis of **5** at −120 °C, an asymmetric unit consists of four crystallographically independent molecules. Because the four molecules are structurally very similar, only one molecule is presented in Fig. 2. The four-membered ring of the CBD ligand in **5** is planar and forms an almost square structure, as confirmed by the internal bond angles of 89.59(19) to 90.20(19)° and the sum of the bond angles (359.99°). The C–C bond lengths range from 1.480(3) to 1.486(3) Å, thus being intermediate between the typical C–C double bond length (1.34 Å) and single bond length (1.54 Å). On the other hand, the geometry of the CBD ligand of **6** is planar and slightly deformed from a rectangular structure, probably because of the $Me_2Si(CH_2)_2SiMe_2$ bridges (Fig. 3). The internal bond angles are 89.86(17) to 90.18(17)° and the sum of the bond angles is 359.99°. The C1–C2 and C3–C4 distances (1.478(3) and 1.479(3) Å) are slightly elongated relative to the C2–C3 and C1–C4 distances (1.466(3) and 1.470(3) Å). The C–C bond lengths in **5** (av. 1.483 Å) are slightly longer than those observed in **6** (av. 1.473 Å). The Si–C bond lengths in **5** (av. 1.870 Å) are also elongated compared with those in **6** (av. 1.854 Å). This might be due to the large steric repulsion between the trimethylsilyl groups.

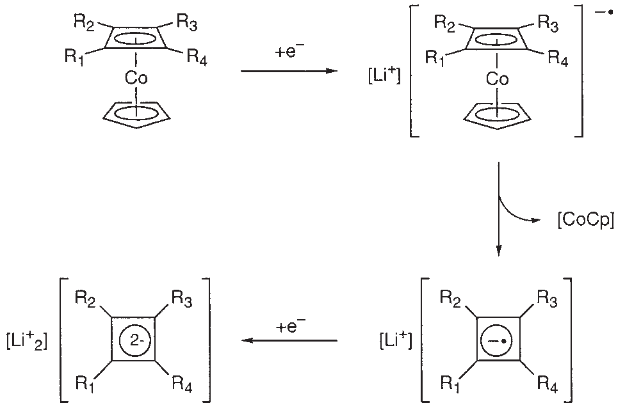
Figure 4 shows a similar π-sandwich structure of **7** in the crystal. The four-membered ring is planar and the sum of the bond angles is 359.99°. The geometry of the CBD ligand exhibits a slightly trapezoidal structure (C1–C2: 1.470(2), C2–C3: 1.466(2), C3–C4: 1.482(2), C1–C4: 1.472(2) Å). The elongation of the C3–C4 bond might be due to the *cis* arrangement of the substituents. This tendency is more noticeable in *cis*-$[\{Ph_2(SiMe_3)_2C_4\}Co(Cp)]$ **8**.[25] The Si–C distances in **7** are 1.8570(16) Å for Si1–C3 and 1.8638(16) Å for Si2–C4.

1.3 Transmetalation of CBD Cobalt Complexes with Lithium. We have investigated the transmetalation reaction of the CBD cobalt complex with alkali metals. A reaction tube was charged with the cobalt complex **5**, an excess amount of lithium metal, and dry, oxygen-free THF. The mixture was stirred vigorously at room temperature for 24 h to produce a dark brown solution containing the dilithium salt of tetrakis(trimethylsilyl)cyclobutadiene dianion, $[Li^+{}_2]\cdot[(Me_3Si)_4C_4{}^{2-}]$ (**10**) (Scheme 5). The choice of alkali metal is very important in the transmetalation reaction, because alkali metals other than lithium (e.g., sodium or potassium) do not work. The reaction solvent, THF, is also important; the reaction does not proceed in Et_2O or 1,2-dimethoxyethane (DME). After hexane was added to the reaction mixture, the residual lithium pieces and insoluble dark material were removed. The CBD^{2-} **10**, containing THF molecules, could be purified by recrystallization from hexane. The $Me_2Si(CH_2)_2SiMe_2$ bridged CBD^{2-} (**11**) was also synthesized by a similar procedure starting from the corresponding cobalt complex (**6**). We have found that the dilithium salts of diphenyl-disilyl-CBD^{2-} derivatives (**12**–**14**) can also be prepared by reaction of the corresponding CBD cobalt complexes (**7**–**9**) with lithium metal in THF.

The reaction of **10** with water led to the almost quantitative



Scheme 6.



Scheme 7.

formation of a mixture of 1,2-adducts, *cis*- and *trans*-1,2,3,4-tetrakis(trimethylsilyl)cyclobutene **15a** (*cis*) and **15b** (*trans*) in an approximately 1:2 ratio (Scheme 6). No 1,3-adducts with the bicyclo[1.1.0]butane skeleton were found in this reaction. The ^{1}H NMR spectrum of the mixture shows that both diastereomers correspond to a symmetrical conformation in solution (C_s for **15a** and C_2 for **15b**). The methine proton signals are observed at $\delta = 2.91$ and 2.41 ppm. According to PM3 calculations,[27] the *trans* isomer is lower in energy than the *cis* isomer. The optimized structure of **15a** exhibits large steric repulsion between the trimethylsilyl groups in the *cis*-arrangement. Thus, the major isomer can be assigned to **15b** (*trans*).

The transmetalation reaction from transition metal complex to alkali metal complex is uncommon. It has previously been observed in the reductive cleavage of cobaltocene, Cp_2Co with potassium under ethylene gas to yield $[CpCo(C_2H_4)_2]$, together with the formation of potassium cyclopentadienide (CpK) as a by-product.[28] We tried to observe a lithium cyclopentadienide (CpLi) in THF-d_8 solution; however, no CpLi signal was observed in the ^{7}Li NMR spectrum. The ^{7}Li NMR signal of CpLi was reported to be -8.37 ppm in THF because of the strong shielding.[29] This suggests that removal of cyclopentadienide from the cobalt center has not occurred in the present reaction. Scheme 7 shows one of the more likely mechanisms for the transmetalation. 1) The radical anion species 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 CBD radical anion may be removed from the cobalt center. 3) This CBD radical anion is further reduced by lithium metal to form the stable CBD^{2-} species. The residual insoluble dark material, which is flammable in air, might be the anion species of CpCo fragments. As mentioned above, Cp_2Co is a stable 19 valence electron (VE) complex and cyclopentadienide could be removed from a further reduced species.[28] In contrast, the 19 VE radical anion of the CBD cobalt complex may be unstable and the metal–carbon bond of the cyclobutadienyl ligand is readily cleaved. Although the precise mechanism of the transmetalation remains unclear at this moment, it has permitted the preparation of the dilithium salts of the CBD^{2-} in high yields.

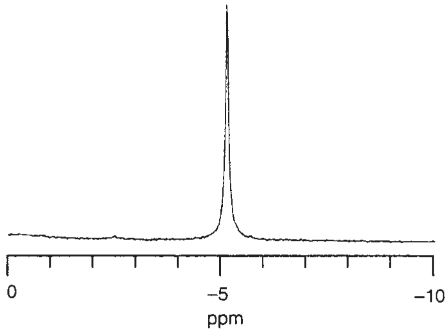


Fig. 5. ^{6}Li NMR spectrum of **10** (44.2 MHz, toluene-d_8, 298 K).

2 Structural Characterization of Dilithium Salts of Tetrasilyl-CBD^{2-} [14]

2.1 NMR Studies on Dilithium Salts of Tetrasilyl-CBD^{2-}. The structures of the tetrasilyl-CBD^{2-} in solution were characterized by ^{1}H, ^{6}Li, ^{13}C, and ^{29}Si NMR spectroscopy. The NMR data on the structure of the dilithium salt of tetrakis(trimethylsilyl)cyclobutadiene dianion (**10**) in toluene-d_8 indicate the formation of very highly symmetric contact ion pairs (CIPs). In the ^{1}H NMR spectrum of **10**, only one signal is observed at $\delta = 0.45$ ppm for the methyl protons along with the signals for THF. The ^{6}Li NMR spectrum of **10** displays only one signal at a chemical shift of $\delta = -5.07$ ppm (Fig. 5). The considerable upfield shift is apparently caused by the strong shielding effect of the diatropic ring current resulting from the 6π-electron system. Schleyer et al. reported that the computed Li chemical shifts in $Li^{+}{}_2C_4R_4{}^{2-}$ (R = H, Me, *t*-Bu) are around -3 ppm.[12] The ^{13}C NMR signal of the ring carbon atoms appears at $\delta = 104.1$ ppm as a quintet ($^{1}J_{^{6}\mathrm{Li}-^{13}\mathrm{C}} = 1.4$ Hz) because of the coupling with two ^{6}Li nuclei ($I = 1$) (Fig. 6). The NMR data point to a structure in which the two counter lithium ions reside above and below the center of the plane of the four-membered ring. In the ^{29}Si NMR spectrum, one signal appears at $\delta = -23.7$ ppm, which is shifted upfield compared with the precursor **5** ($\delta = -7.8$ ppm, $\Delta\delta = -15.9$ ppm). This suggests that the negative charge is largely stabilized by the silyl groups through the pπ–σ^* conjugation.[15]

The bridged tetrasilyl-CBD^{2-} **11** also shows a highly symmetrical CIPs formation in toluene-d_8. Only one signal for the methyl ($\delta = 0.35$ ppm) and methylene ($\delta = 1.19$ ppm) groups is observed in the ^{1}H NMR spectrum. The ^{6}Li NMR spectrum of **11** shows a signal at $\delta = -5.10$ ppm, which is comparable to that of **10** ($\delta = -5.07$ ppm). In the ^{13}C NMR

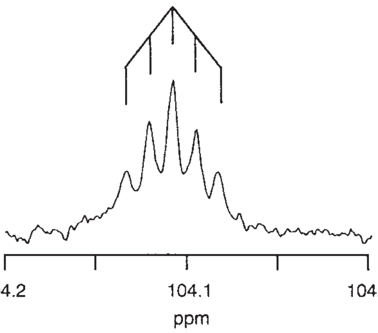


Fig. 6. ^{13}C NMR signal of the ring carbons of **10** (77.5 MHz, toluene-d_8, 298 K).

spectrum, one signal for the cyclobutadienediide ring carbons appeared at $\delta = 102.1$ ppm as a quintet ($^1J_{^6\text{Li}-^{13}\text{C}} = 1.2$ Hz). The ^{29}Si NMR spectrum of **11** shows one signal at $\delta = -24.2$ ppm, which is also shifted upfield compared with **6** ($\delta = -9.0$ ppm, $\Delta\delta = -15.2$ ppm).

The Li NMR studies are very useful for estimating the magnitude of the ring current, because the two lithium ions are located inside the aromatic-shielding region.[30] From the magnetic point of view, the tetrasilyl-substituted CBD^{2-} species in solution clearly show a strong diatropic ring current due to the delocalization of six π-electrons. It is considered that the degree of the stabilizing cyclic electron delocalization of CBD^{2-} is a good indicator of the intensity of the diatropic current. Thus, the CBD^{2-} should be regarded as aromatic compounds. It is expected that the four-membered ring of **11** will adopt a more planar structure relative to that of **10** because of the bridge building of $Me_2Si(CH_2)_2SiMe_2$. However, no significant difference of ^{6}Li chemical shift between **10** and **11** could be found in the spectra. The extent of the aromaticity of the CBD^{2-}, **10** and **11**, is nearly equal; they are stabilized not only by the four silyl groups but also by the aromatic 6π-electron system.

2.2 Crystal Structure of Dilithium Salts of Tetrasilyl-CBD^{2-}. For a structural study, we performed a ligand exchange on the lithium ions from THF to DME. A single crystal of **10** containing two molecules of DME suitable for X-ray analysis was obtained by recrystallization from hexane. The crystal structure of **10** is shown in Fig. 7. The dilithium salt has a monomeric structure and forms CIPs in the crystal. One DME molecule is coordinated to each lithium atom. The two lithium atoms are located above and below the approximate center of the cyclobutadienediide ring and are bonded to the four ring carbon atoms (η^4-coordination). The distances between Li1 and the four carbon atoms (C1, C2, C3, and C4) range from 2.166(12) to 2.195(12) Å (av. 2.178 Å), and those of Li2 are 2.152(11)–2.199(12) Å (av. 2.181 Å). The Li1 and Li2 distances from the ring centroid are 1.90(1) Å.

The geometry of the four-membered ring of **10** is planar. The ring forms an almost square structure, as confirmed by the internal bond angles of 89.2(6)–90.7(6)° and the sum of the bond angles (360.0°) (Fig. 8). The dihedral angles are 0.90(2)° for C1–C2–C3/C1–C3–C4 and 0.89(2)° for C2–C3–C4/C1–C2–C4. The C–C bond lengths are 1.496(3) Å for C1–C2, 1.485(10) Å for C2–C3, 1.493(4) Å for C3–C4, and 1.507(9) Å for C1–C4, giving diagonal distances of 2.12(1) Å for C1–C3 and 2.11(1) Å for C2–C4. No significant difference is found between the observed C–C bond lengths of **10** (av. 1.495 Å) and those of the precursor **5** (av. 1.483 Å). On the other hand, the Si–C bond lengths in **10** (av. 1.836 Å) are characteristically shorter than those observed in **5** (av. 1.870 Å); this is attributed to the negative hyperconjugative interaction between the occupied p orbitals of the quaternary carbon atom and the σ^* (Si–C$_{\text{Me}}$) orbital. Because of the large steric repulsion of the SiMe$_3$ groups, the positions of the Si atoms deviate up and down alternately about the plane of the cyclobutadienediide ring. The angles between the central four-membered ring plane and the Si–C bond are 8.0–9.9°.

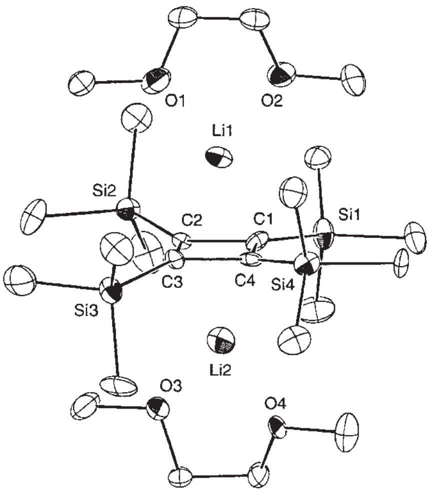


Fig. 7. ORTEP drawing of **10**.

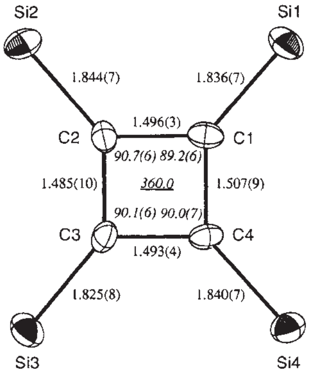


Fig. 8. Selected structural parameters of **10** (Å, deg).

The structure of **10** containing DME is close to that predicted by a calculation on the corresponding $\text{Li}^+{}_2\text{C}_4\text{H}_4{}^{2-}$ with D_{4h} symmetry.[13] The observed C–C distances (av. 1.495 Å) in the crystal are similar to the value of 1.461 Å calculated for $\text{Li}^+{}_2\text{C}_4\text{H}_4{}^{2-}$ (6-31G**). The Li distance from the ring centroid (1.90 Å) is rather long when compared with the calculated value of 1.770 Å. The influence of the coordination by DME weakens the interaction between the negatively charged four-membered framework and the counter lithium ions. The observed diagonal distance of 2.11–2.12 Å is comparable to the calculated value of 2.069 Å.[11] The present experimental observations by X-ray crystallographic analysis and NMR spectroscopy for **10** 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

Li NMR signals because of the diatropic ring current.

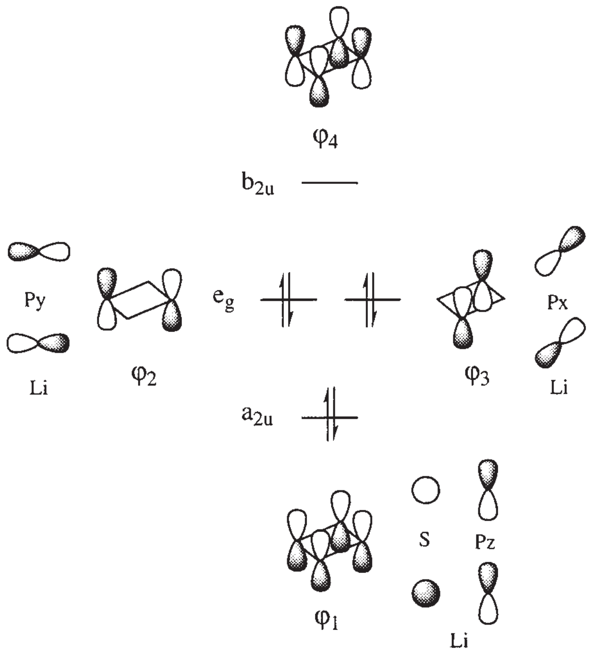


Fig. 9. π-MOs of the D_{4h} $Li^{+}{}_{2}C_4H_4{}^{2-}$.

2.3 MO Consideration of Dilithium Salts of CBD^{2-}.[31] The problem with D_{4h} CBD^{2-} is that four electrons have to go into nonbonding π-MOs. It is believed that complexation with counter cations is very important for stabilizing the CBD^{2-}. The CBD^{2-} have a monomeric structure and form 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 stability of the dilithium complex of 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 (Fig. 9). It is believed that the two Li^{+} ions counteract the large Coulomb repulsion in CBD^{2-}. The small Li^{+} ions can approach more closely than other cations.[32] Indeed, the use of lithium metal is crucial in the transmetalation reaction.

A simple calculation shows that the aromatic CBD^{2-} has six π-electrons and four π-orbitals (a_{2u}, e_g, and b_{2u} orbitals) as shown in Fig. 9. In general, annulenes have degenerate HOMO and LUMO, nondegenerate HOMO and degenerate LUMO, or nondegenerate HOMO and LUMO. The D_{4h} CBD^{2-}, having degenerate HOMO and nondegenerate LUMO, is a very unusual electronic configuration. For elucidation of the electronic structure of CBD^{2-} (**10**), we used UV–visible absorption and magnetic circular dichroism (MCD) spectroscopies simultaneously. More than 20 years ago, Michl proposed that the $^1A_{1g} \rightarrow {}^1E_u$ transitions of an aromatic CBD^{2-} species would be a good example of a characteristic negative Faraday A term, because of excitation from the degenerate e_g orbitals to the nondegenerate b_{2u} orbital.[33] However, no one has yet succeeded in presenting experimental evidence of this, because of the unavailability of stable CBD^{2-}.

The tetrasilyl-CBD^{2-} **10** showed an intense absorption band at 289 nm in the electronic absorption spectrum (Fig. 10).[31] In the MCD spectrum of **10**, two intense peaks of opposite sign are found at 274.5 and 298 nm. The inflection point in the MCD spectrum coincides with the absorption maximum within experimental error. These spectroscopic data are characteristic of a Faraday A term, indicating a degenerate excited state.[33] Thus, they can be reasonably assigned to degenerate $^1A_{1g} \rightarrow {}^1E_u$ transitions. Because the two MCD peaks at 298 and 274.5 nm show positive and negative signs, the sign of the Faraday A term is clearly negative. The corresponding negative Faraday A term is interpreted by excitation from the degenerate e_g orbitals to the nondegenerate b_{2u} orbital, providing experimental evidence for the theoretical prediction by Michl.[29] This is the first clear demonstration of a negative Faraday A term, which is theoretically predicted for aromatic organic compounds.[34,35] This study is important not only as a rare example of a negative Faraday A term but also to illustrate the effectiveness of MCD spectroscopy in elucidating the chemistry of the CBD^{2-} species.

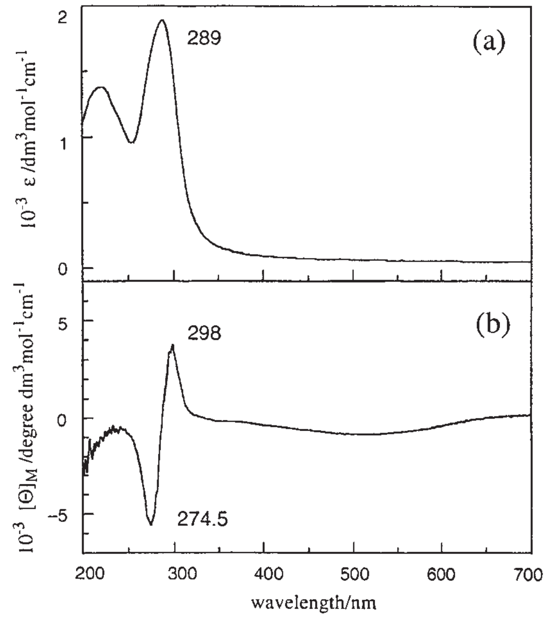
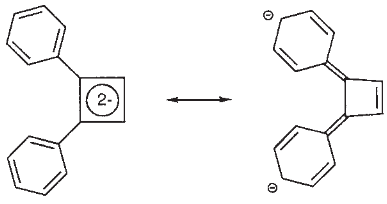


Fig. 10. Electronic absorption (a) and MCD (b) spectra of **10**.

3 Structural Characterization of Dilithium Salts of Diphenyl-Disilyl-CBD^{2-}[18]

3.1 NMR Studies on Dilithium Salts of Diphenyl-Disilyl-CBD^{2-}. Phenyl groups are very useful for the stabilization of carbanions with extensive delocalization of negative charge. The structures of various anion species stabilized by phenyl groups in the solid state and in solution have been reported, including both solvated and contact ion pair formation.[5] The electronic effect of the phenyl group is quite different from that of the silyl group. The former involves conjugation, whereas the latter is based on negative hyperconjugation (pπ–σ^* conjugation). We have examined the structures and properties of dilithium salts of CBD^{2-} involving both phenyl and silyl groups. There are two contributions in the *cis*-diphenyl-substituted CBD^{2-}: one is a square structure (**16a**) with aromatic stabilization by delocalization of six π-electrons, and the other is a quinoid structure (**16b**) resulting from delocalization of the negative charge onto the phenyl groups because of electron repulsion (Chart 4).

We have characterized the structure of the *cis*-diphenyl-



16a **16b**

Chart 4.

CBD^{2-} **12** in solution on the basis of NMR spectroscopy.[18a] In the ^{7}Li NMR spectrum of **12** in benzene-d_6, one signal was found at $\delta = -4.21$ ppm. The ^{13}C NMR spectrum of **12** shows two signals for the quaternary ring carbons that appear at $\delta =$ 89.6 ppm (Ph*C*) and 102.8 ppm (Si*C*), together with the four signals for phenyl carbons ($\delta = 117.4$ ppm (*para*-), 121.3 ppm (*ortho*-), 128.5 ppm (*meta*-), and 142.8 ppm (*ipso*-)). The ^{13}C signals of *ortho*- and *para*-carbons are shifted to somewhat higher field relative to those signals in **7** ($\delta = 126.9$ ppm (*ortho*-) and 125.6 ppm (*para*-)) because of delocalization of the negative charge. The ^{29}Si signal of **12** ($\delta = -21.3$ ppm) is also shifted to higher field compared with that of **7** ($\delta = -7.0$ ppm, $\Delta\delta = -14.3$ ppm). Thus, the doubly charged four-membered ring system is stabilized not only by the phenyl groups but also by the silyl groups.

In the ^{7}Li NMR spectrum of the dilithium salt of 1,2-diphenyl-3,4-bis(trimethylsilyl)cyclobutadiene dianion (**13**) in benzene-d_6, one signal appeared at $\delta = -4.24$ ppm; this signal is similar to that observed in **12** ($\delta = -4.21$ ppm).[18c] The ^{7}Li NMR signal of **14** was observed at $\delta = -4.44$ ppm. These signals are shifted to somewhat lower field compared with those of the tetrasilyl-CBD^{2-} ($\delta = -5.07$ ppm (**10**) and $\delta = -5.10$ ppm (**11**)). As mentioned above, the chemical shift of the Li NMR signal indicates the magnitude of the diatropic ring current resulting from the 6π-electron system. The above data suggests that the ring current should be decreased by the introduction of phenyl groups. In addition, the *trans*-diphenyl-CBD^{2-} **14** has a slightly stronger ring current than do those of the *cis*-diphenyl-CBD^{2-} **12** and **13**, presumably because of the symmetrical arrangement of the substituents.

In the ^{13}C NMR spectrum of **13** and **14** in benzene-d_6, two signals for the cyclobutadienediide ring carbons appear, at $\delta =$ 83.8 ppm (Ph*C*) and 106.1 ppm (Si*C*) for **13** and at $\delta = 84.0$ ppm (Ph*C*) and 110.1 ppm (Si*C*) for **14**. Phenyl carbons are observed at $\delta = 119.4$ ppm (*para*-), 125.2 ppm (*ortho*-), 128.3 ppm (*meta*-), and 142.1 ppm (*ipso*-) for **13**, and at $\delta = 117.6$ ppm (*para*-), 123.9 ppm (*ortho*-), 127.7 ppm (*meta*-), and 143.3 ppm (*ipso*-) for **14**. 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 shifted to higher fields relative to those signals observed in **8** ($\delta = 127.5$ ppm, $\Delta\delta = -2.3$ ppm (*ortho*-) and $\delta = 125.9$ ppm, $\Delta\delta = -6.5$ ppm (*para*-)) and **9** ($\delta = 127.5$ ppm, $\Delta\delta = -2.3$ ppm (*ortho*-) and $\delta = 125.9$ ppm, $\Delta\delta = -6.5$ ppm (*para*-)). In the ^{29}Si NMR spectra of **13** and **14**, only one signal appeared, at $\delta = -20.7$ ppm for **13** and $\delta = -23.1$ ppm for **14**. These ^{29}Si signals are shifted upfield compared with their precursors ($\delta = -5.7$ ppm, $\Delta\delta = -15.0$ ppm for **8**, and $\delta = -7.1$ ppm, $\Delta\delta = -16.0$ ppm for **9**).

On the basis of the NMR data, we can conclude that all of the CBD^{2-} (**12**–**14**) in solution exhibit a strong diatropic ring current resulting from delocalization of the 6π-electron system. Thus, the diphenyl-disilyl-substituted CBD^{2-} derivatives should be regarded as aromatic compounds from the point of view of magnetic properties in solution. The aromatic stabilization in the doubly charged four-membered ring system remains rather strong despite the considerable electrostatic repulsion. The Li NMR studies show that the extent of the aromaticity of the CBD^{2-} can be represented approximately as **10** and **11** ($\delta = -5.07$ and -5.10 ppm) $>$ **14** ($\delta = -4.44$ ppm) $\geq$ **12** and **13** ($\delta = -4.21$ and -4.24 ppm). Interestingly, the stabilizing cyclic electron delocalization of CBD^{2-} decreases on the introduction of aromatic benzene rings. The negative charge of the CBD^{2-} is stabilized by both phenyl and silyl groups; however, stabilization by phenyl groups is more effective.

3.2 Crystal Structure of Dilithium Salts of Diphenyl-Disilyl-CBD^{2-}. The molecular structures of the CBD^{2-} (**12**–**14**) have been determined by X-ray crystallography. Figures 11, 13, and 15 show ORTEP drawings of **12**–**14**, respectively. Each of the dilithium salts has a monomeric structure and forms CIPs in the crystals. One DME molecule is coordinated to each lithium atom.

The molecules of **12** have a crystallographic two-fold axis on the four-membered ring with C_2 symmetry (Fig. 11).[18a] 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 $[\mathrm{Li}^{+}{}_{2}]\cdot[(\mathrm{Me}_3\mathrm{Si})_4\mathrm{C}_4{}^{2-}]$ (**10**) in which they are located above and below the center of the four-membered ring. 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 Å).

Selected structural parameters of **12** are depicted in Fig. 12. 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

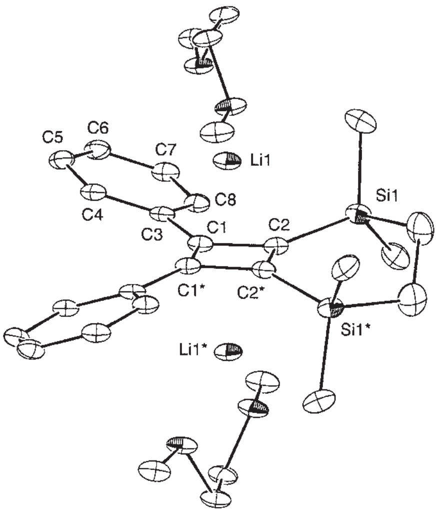


Fig. 11. ORTEP drawing of **12**.

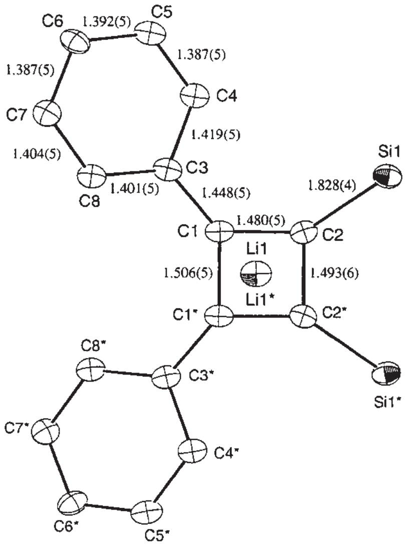


Fig. 12. Selected bond lengths of **12** (Å).

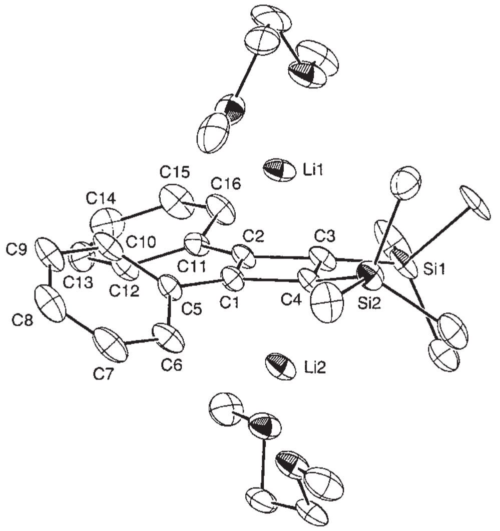


Fig. 13. ORTEP drawing of **13**.

12 correspond well to the criteria of aromaticity, namely: 1) the planarity of the four-membered ring, and 2) the lack of bond alternation. The C1–C3 distance in **12** (1.448(5) Å) is slightly shorter than the corresponding distance in **7** (av. 1.468 Å) because of delocalization of the negative charge on the phenyl ring. However, the quinoid structure (**16b**) of the phenyl ring is not observed (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 **12** is also shorter than the corresponding distance in **7** (av. 1.861 Å) because of the pπ–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)°).

The dilithium salt of 1,2-diphenyl-3,4-bis(trimethylsilyl)cyclobutadiene dianion (**13**) has C_1 symmetry in the crystal (Fig. 13).[18c] 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 Å), and those of Li2 range from 2.172(6) to 2.218(6) Å (av. 2.196 Å). The Li distances from the ring centroid are 1.927(5) Å for Li1 and 1.928(6) Å for Li2.

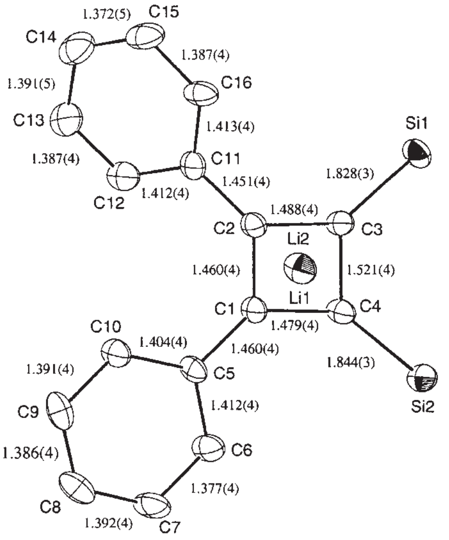


Fig. 14. Selected bond lengths of **13** (Å).

The four-membered ring of **13** 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 trapezoidal 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)°, Fig. 14). The elongation of the C3–C4 bond results from the large steric repulsion between the two trimethylsilyl groups. Such a trapezoidal structure has never been observed in the CBD^{2-} **10** and **12**. 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 **10** (av. 1.836(7) Å) and **12** (av. 1.828(4) Å). The C1–C5 and C2–C11 distances in **13** are 1.460(4) and 1.451(4) Å, respectively.

The dilithium salt of 1,3-diphenyl-2,4-bis(trimethylsilyl)cyclobutadiene dianion (**14**) has an inversion center at the center of the C1–C2–C1*–C2* four-membered ring (C_i symmetry, Fig. 15).[18c] 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 Å). The Li distances from the ring centroid (2.070(4) Å) are longer than those observed in **10** (av. 1.90 Å), **12** (1.959(6) Å), and **13** (av. 1.928 Å). This indicates that the interaction (electrostatic or covalent or both) between the Li^+ ions and the charged ring of **14** is not as strong as it is for the other CBD^{2-} (**10**, **12**, and **13**).

Interestingly, the geometry of the four-membered ring of **14** shows a planar and slightly rhomboidal structure (Fig. 16). 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 rhomboidal structure might be due to the *trans* arrangement of the substituents. The C2–C3

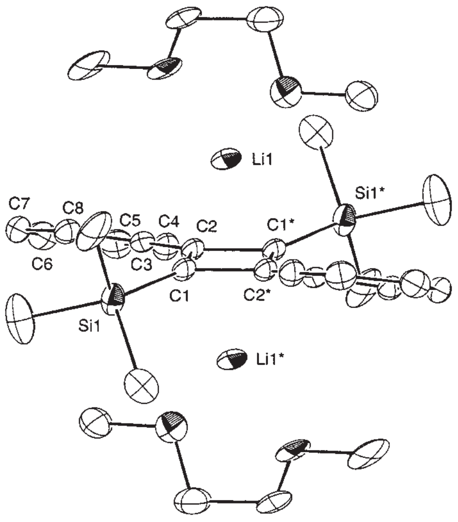


Fig. 15. ORTEP drawing of **14**.

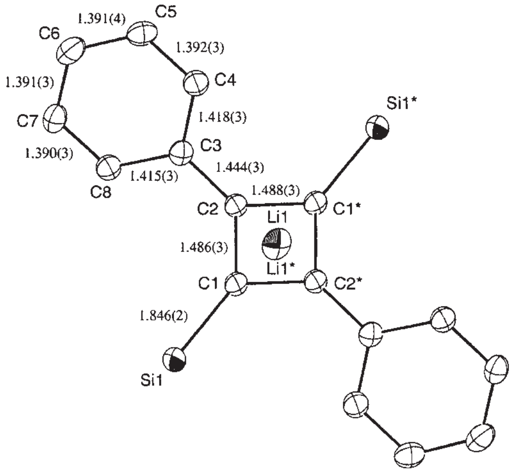


Fig. 16. Selected bond lengths of **14** (Å).

distance (1.444(3) Å) is comparable to that observed in **12** (1.448(5) Å) and **13** (av. 1.456 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.

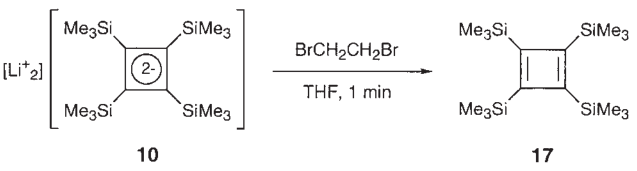
CBD^{2-} has a considerable electrostatic repulsion between the two negative charges. In addition, the planar four-membered ring has a large ring strain. Thus, the stabilizing cyclic electron delocalization of CBD^{2-} is quite interesting, and it is very difficult to comprehend its nature. From the X-ray crystal structure, the CBD^{2-} (**10**, **12**–**14**) are cyclic and nearly planar in the ring, although the geometries of the cyclobutadienediide rings are almost square structures for **10** and **12**; the geometry is a pronounced trapezoidal structure for **13** and is a slightly rhomboidal structure for **14**. These structural characteristics of the four-membered rings in CBD^{2-} (**10**, **12**–**14**) are very similar to those of the precursor cobalt complexes (**5**, **7**–**9**).

4 Tetrasilyl-Substituted CBD[19]

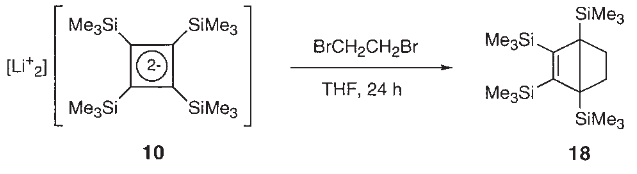
4.1 Two-Electron Oxidation Reaction of Dilithium Salts of Tetrasilyl-CBD^{2-}. The fascinating chemistry of cyclobutadiene and its derivatives has been studied in relation to their structures, properties, and reactivities.[5e,36] In the 1970s, the parent CBD (C_4H_4) was *Mona Lisa* in organic chemistry. Many chemists have tried to synthesize free CBD, but no one has been successful because of the antiaromaticity resulting from the 4π-electron system. The parent molecule, CBD, was initially generated by the oxidative treatment of $[(\eta^4\text{-}C_4H_4)Fe(CO)_3]$ with Ce^{IV} ions.[37] Then, it was observed—through the use of photochemical reactions—at low temperature in inert matrices,[2b] and at room temperature in a hemicarcerand.[38] According to the spectroscopic evidence obtained by matrix isolation, free CBD is not square but has a rectangular structure, and is not a triplet but a singlet species, owing to the Jahn–Teller effect. On the other hand, some CBD derivatives, stabilized by steric effects, have been isolated, and parts of their molecular structures have been determined by X-ray crystallography.[39] These compounds show the rectangular structure of the four-membered ring with considerably elongated carbon–carbon single bonds. However, the methods used to prepare CBD are sometimes very tedious and have undesirable side photoreactions.[40]

An interesting aspect is that CBD^{2-} is one of the best candidate precursors for CBD. We chose 1,2-dibromoethane ($BrCH_2CH_2Br$) for the oxidation of the dilithium salts of tetrasilyl-CBD^{2-}. The reaction of **10** with excess $BrCH_2CH_2Br$ in THF at room temperature produced tetrakis(trimethylsilyl)cyclobutadiene (**17**) in 64% yield (Scheme 8). The reaction time (ca. 1 min) for this transformation was very important for obtaining pure CBD **17**. The Diels–Alder cycloaddition product (**18**) with ethylene generated from $BrCH_2CH_2Br$ was also produced at longer reaction times. A reaction time longer than 24 h led to the quantitative formation of the bicyclic compound **18** (Scheme 9).

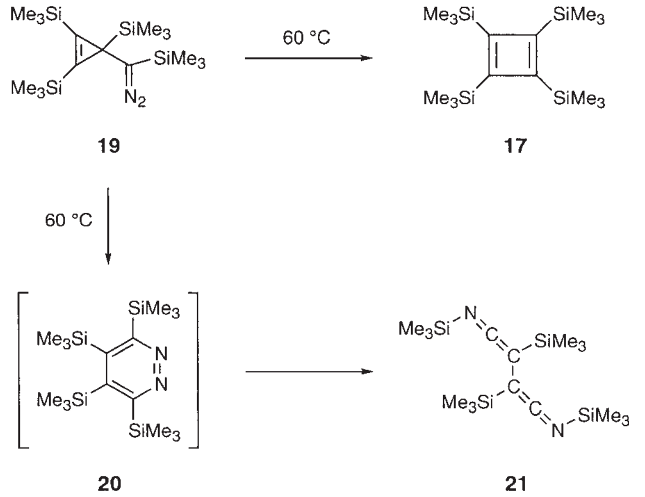
Pure compound **17** has been isolated as air-sensitive red crystals by vacuum sublimation (ca. 80 °C/0.02 mmHg). Compound **17**, the first CBD derivative with four heteroatomic substituents, was characterized by NMR spectroscopy. Only one signal at $\delta = 0.15$ ppm was observed for the methyl groups in the ^{1}H NMR spectrum of **17** in benzene-d_6. The ^{29}Si NMR spectrum showed a signal at $\delta = -16.7$ ppm, which was shifted downfield relative to that of the tetrasilyl-CBD^{2-} **10** ($\delta = -23.7$ ppm, $\Delta\delta = 7.0$ ppm). Two signals appeared at $\delta =$ 0.0 ppm (methyl carbon atoms) and $\delta = 172.1$ ppm (quaternary carbon atoms) in the ^{13}C NMR spectrum of **17**. The signal at $\delta = 172.1$ ppm was also shifted downfield relative to that of



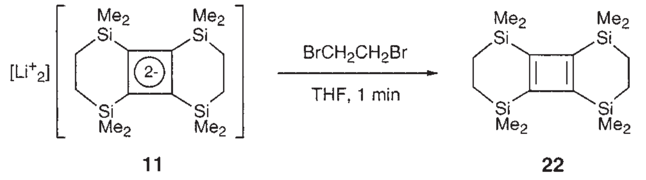
Scheme 8.



Scheme 9.



Scheme 10.



Scheme 11.

10 ($\delta = 104.1$ ppm, $\Delta\delta = 68.0$ ppm) by the two-electron oxidation.

An alternative route to CBD **17** was reported by Maier et al. (Scheme 10).[41] The thermal reaction of trimethylsilyl[1,2,3-tris(trimethylsilyl)-2-cycloprop-1-enyl]diazomethane (**19**) produced a mixture of CBD **17** and bis(ketenimine) (**21**). During the course of the reaction, diazomethane **19** partly isomerizes into pyridazine (**20**), which undergoes a ring opening to produce bis(ketenimine) **21** concurrent with the migration of trimethylsilyl groups.

We also prepared the bridged CBD derivative, 3,3,6,6,9,9,12,12-octamethyl-3,6,9,12-tetrasilatricyclo[6.4.0.0^{2,7}]dodeca-1(8),2(7)-diene (**22**). The CBD^{2-} **11** reacted with $BrCH_2CH_2Br$ in THF to produce CBD **22** in 81% yield (Scheme 11). In the ^{1}H NMR spectrum of **22** in toluene-d_8, the methyl and methylene signals are observed at $\delta = 0.07$ ppm and $\delta = 0.77$ ppm, respectively. The ^{13}C NMR spectrum shows one signal for the ring carbons at $\delta = 173.4$ ppm; this was shifted downfield relative to that of **11** ($\delta = 102.1$ ppm, $\Delta\delta = 71.3$ ppm) by the two-electron oxidation. The ^{29}Si NMR spectrum of **22** shows one signal at $\delta = -18.8$ ppm, which is also shifted downfield compared with **11** ($\delta = -24.2$ ppm, $\Delta\delta = 5.4$ ppm).

4.2 Crystal Structure of Tetrasilyl-CBD. The molecular structures of the tetrasilyl-substituted CBD derivatives (**17** and **22**) have been determined by X-ray diffraction. Unfortunately, a suitably sized single crystal of **17** has not yet been obtained. Although the refinement was unsatisfactory because of the poor quality of the crystals (the final R factor was 0.132 ($I > 2\sigma(I)$), $R_w = 0.328$ (all data), GOF = 0.965), preliminary X-ray analysis of **17** at 120 K shows a rectangular structure for the cyclobutadiene ring (Fig. 17).[42] The C–C double bond lengths are 1.37(1) Å for C1–C2 and 1.39(1) Å for C3–C4. The C–C single bond lengths are 1.58(1) Å for C1–C4 and 1.58(1) Å for C2–C3. The internal bond angles of the cyclobutadiene ring are 89.0(8)–91.0(9)° and the sum of the bond angles is 359.7°. The Si–C bond lengths are 1.86(1)–1.88(1) Å. The positions of the Si atoms deviate up and down alternately about the plane of the cyclobutadiene ring because of the steric repulsion of the trimethylsilyl groups.

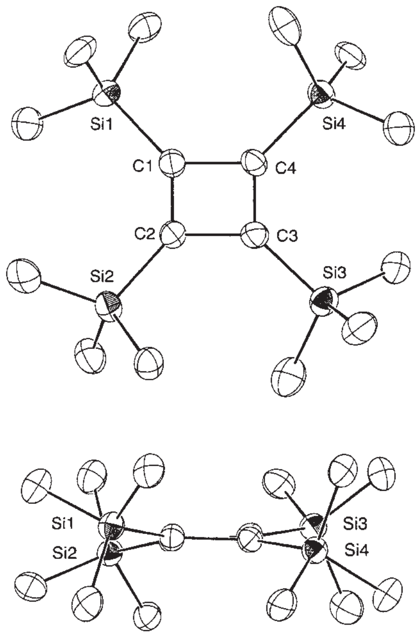


Fig. 17. ORTEP drawing of **17**: upper, top view; below, side view.

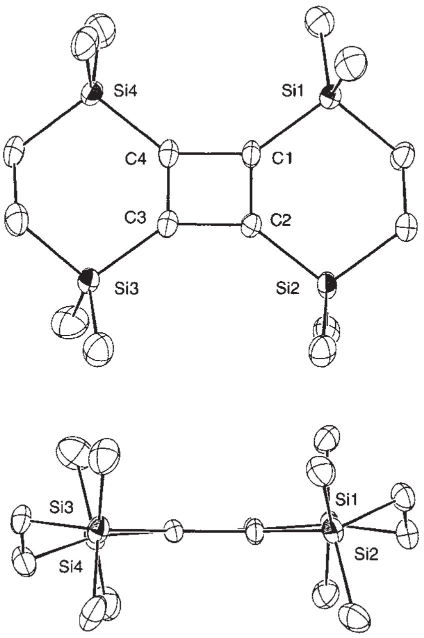
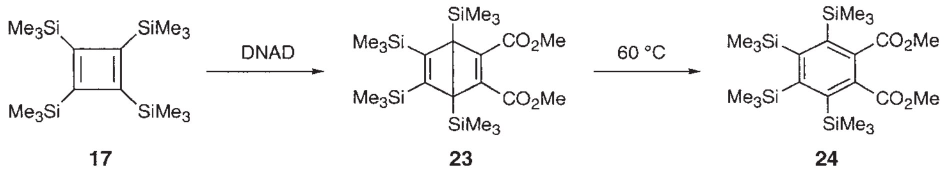


Fig. 18. ORTEP drawing of **22**: upper, top view; below, side view.

Figure 18 shows the ORTEP drawing of **22**. The X-ray diffraction data were collected at 105 K. The central four-membered ring of **22** exhibits a planar rectangular structure with localized C–C double bonds. The internal bond angles of the



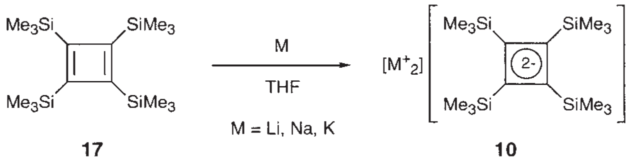
Scheme 12.

four-membered ring range from 89.5(4) to 90.3(4)° and the sum of the bond angles is 360.0°. The central four-membered ring is planar, as determined by the dihedral angles of 1.1(4)° for C1–C2–C3/C1–C3–C4 and 1.0(4)° for C1–C2–C4/C2–C3–C4. The C–C double bond lengths (C1–C2, 1.364(7) Å; C3–C4, 1.353(7) Å) are comparable to the typical value for a C–C double bond (1.34 Å). In contrast, the C–C single bond lengths (C1–C4, 1.587(6) Å; C2–C3, 1.583(6) Å) are longer than the typical value for a C–C single bond (1.54 Å).

The main cause of the elongation of the single bonds may be the steric repulsion between the methyl groups on the Si atoms. Similar structural features were observed in cyclobutadiene fused to two seven-membered rings in 3,3,7,7,10,10,14,14-octamethyl-5,12-dithiatricyclo[7.5.0.$0^{2,8}$]tetradeca-1(9),2(8)-diene (1.344 and 1.600 Å),[39b] and in 3,3,7,7,10,10,14,14-octamethyltricyclo[7.5.0.$0^{2,8}$]tetradeca-1(9),2(8)-diene (1.339 and 1.597 Å).[39j] The Si–C (quaternary carbon atoms) bond lengths of **22** (1.854(5)–1.863(5) Å) are quite normal. The positions of the four Si atoms slightly deviate from the plane of the four-membered ring (C1–C2–C3–C4), as determined by the vector plane angles between the C1–C2–C3–C4 plane and the Si–C bond (0.97(2)–3.70(2)°). The molecules of **22** adopt a more planar structure compared with those of **10** because of the $Me_2Si(CH_2)_2SiMe_2$ bridges.

4.3 Reactivities of Tetrasilyl-CBD. As mentioned above, CBD **17** readily reacted with ethylene to produce **18** (Scheme 9). The reaction of **17** with dimethyl acetylenedicarboxylate (DMAD) yielded a 1:1 adduct, the Dewar benzene **23**, quantitatively (Scheme 12). Such Diels–Alder cycloaddition reactions of free CBD and its derivatives are well known. Compound **23** was heated at 90 °C to produce the dimethyl ester of tetrakis(trimethylsilyl)phthalic acid **24**.[41]

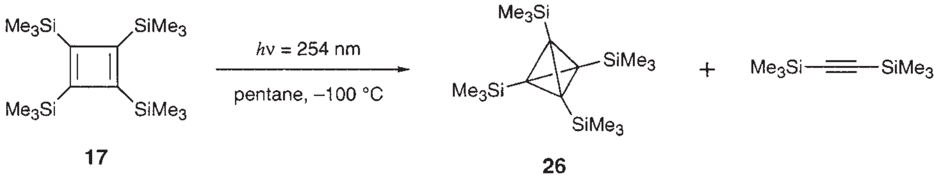
Because the present CBD derivatives are highly perturbed by the four silyl groups, we have examined their further reactivities. The two-electron reduction of **17** and **22** with lithium metal in THF resulted in the quantitative formation of the dilithium salts of CBD^{2-} **10** and **11** within a few hours. Thus, we can now easily perform the interconversion between a CBD and its corresponding CBD^{2-}. CBD **17** also reacted with lithium in DME to produce CBD^{2-} **10**. In addition, the reduction of **17** with sodium or potassium metal in THF led to the successful preparation of the dialkali metal salts of CBD^{2-} derivatives (Scheme 13).[42] The dialkali metal complexes of CBD^{2-} (**10**, M = Na, K) have been characterized by NMR spectroscopy. In the ^{13}C NMR spectra of **10** (M = Na, K) in benzene-d_6, the signal due to cyclobutadienediide ring carbons was observed at $\delta = 105.6$ ppm (M = Na) and 108.9 ppm (M = K) ($\delta = 104.1$ ppm (M = Li) in toluene-d_8). In the ^{29}Si NMR spectra in benzene-d_6, one signal appeared at $\delta = -30.0$ ppm (M = Na) and -31.3 ppm (M = K) ($\delta = -23.7$ ppm (M = Li) in toluene-d_8). This higher field change of the ^{29}Si resonance might be due to an increase in the ionic character.[16d] In contrast, the ^{13}C resonance of the cyclobutadienediide ring carbons moves in the opposite direction. This is reasonably explained by the polarizing effect of the counter cation; the electron density at the anionic carbons is proportional to the size of the cation.[43]



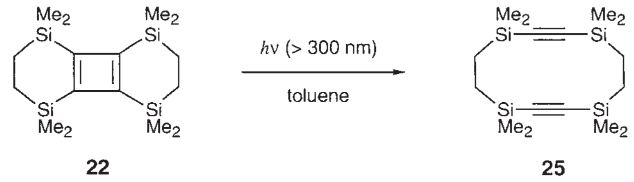
Scheme 13.

5 Tetrasilyl-Substituted Tetrahedrane[20]

5.1 Photoreaction of Tetrasilyl-CBD. Irradiation of CBD **17** in toluene-d_8 with a 500-W high-pressure mercury lamp with a filter ($\lambda > 300$ nm) at room temperature yielded bis(trimethylsilyl)acetylene through cleavage of the C–C bonds. In contrast, long-time irradiation ($\lambda = 254$ nm) of **17** in pentane at −100 °C produced tetrahedrane **26** together with bis(trimethysilyl)acetylene (Scheme 14). Compound **26** is very stable in air. Recrystallization from ethanol gave pure colorless crystals of **26** in 10% yield. The structure of **26** has been characterized by NMR spectroscopy. The ^{1}H NMR spectrum of **26** shows only one signal for methyl groups at $\delta = 0.10$ ppm. In the ^{13}C NMR spectrum, the characteristic signal for the ring carbon atoms is observed at $\delta = -20.46$ ppm,[5d,39d,39l,39n,44] along with the signal due to methyl groups ($\delta = -0.03$ ppm). In the ^{29}Si NMR spectrum, only one signal appears at $\delta = -1.55$ ppm. The hybridization of the bonds in **26** can be estimated from the NMR coupling constants.[45] $^1J_{Si\text{–}C} = 96.1$ Hz for the bond between the silicon atom and the quaternary carbon atom, which is much larger than that of bis(trimethylsilyl)acetylene ($^1J_{Si\text{–}C} = 78.4$ Hz), indicates the enhanced s-character of the



Scheme 14.



Scheme 15.

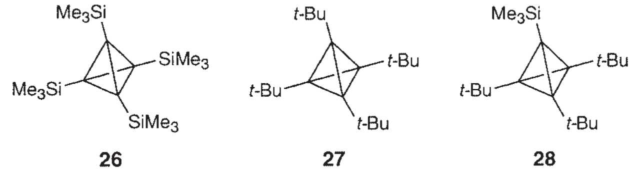


Chart 5.

exocyclic bonds.

In the case of **22**, the cyclic diyne compound, 3,3,6,6,9,9,12,12-octamethyl-3,6,9,12-tetrasilacyclododeca-1,7-diyne (**25**)[23] was produced after irradiation (Scheme 15). The macrocyclic diyne compound **25** is the starting material for the cobalt complex **6**. The CBD ring system of **22** undergoes an interconversion of the two rectangular forms in solution at room temperature. This bond-switching process is completely blocked in the crystal at 105 K.

5.2 Crystal Structure of Tetrakis(trimethylsilyl)tetrahedrane. There have been eight isolable tetrahedrane derivatives. They are tetra-*t*-butyltetrahedrane (**27**)[5d,39d,44] and seven additional candidates in which one *t*-butyl group is replaced by one of the following substituents: $SiMe_3$ (**28**)[39l,39n] $SiMe_2$-Ph,[39o,46] $SiMe_2OCHMe_2$,[39o,46] $SiHMe_2$,[39o,46] $GeMe_3$,[39p] $CHMe_2$,[39t] and adamantyl (Chart 5).[39t] Tetrakis(trimethylsilyl)tetrahedrane **26** is the ninth member in this series, and is the first tetrahedrane derivative having four heteroatomic substituents.

The molecular structure of tetrahedrane **26** has been clearly determined by X-ray analysis. Only two examples of the crystal structure of tetra-*tert*-butyltetrahedrane **27** and tri-*tert*-butyl(dimethylphenylsilyl)tetrahedrane are known.[39o,47] However, major disorder problems affected the quality of the structure elucidation. We have succeeded in determining the X-ray structure of tetrahedrane **26** without disorder phenomena for the first time. X-ray-quality single crystals were obtained by crystallization from ethanol at 5 °C. Diffraction data were collected at −120 °C. An asymmetric unit consists of three crystallographically independent molecules. Because the three molecules are structurally very similar, an ORTEP drawing of only one molecule is shown in Fig. 19. The C–C bond lengths of the skeleton range from 1.495(4) to 1.508(4) Å (av. 1.501 Å), such lengths are similar to those of **27** (av. 1.497 Å). The lengths of the exocyclic Si–C bonds are 1.823(3)–1.829(3) Å (av. 1.826 Å), which are appreciably shorter than normal Si–C(sp^3) bond lengths (1.88 Å). The distances are even smaller than the value for Si–C(sp) bond lengths (1.837 Å).[48] The bond lengths between silicon atoms and methyl carbons are normal (av. 1.865 Å).

5.3 Thermal Stability of Tetrakis(trimethylsilyl)tetrahedrane. All of the previously reported tetrahedrane derivatives lie higher in energy than the corresponding CBD. For example, colorless crystals of tetra-*t*-butyltetrahedrane **27** melt at 135 °C with red coloration due to isomerization into tetra-*t*-butylcyclobutadiene. Tri-*t*-butyl(trimethylsilyl)tetrahedrane **28** is more stable than **27**. The melting point of **27** is 179 °C, at which temperature transformation to the corresponding CBD begins. In contrast, tetrakis(trimethylsilyl)tetrahedrane **26** is thermally very stable and melts at 202 °C without decomposition. Tetrahedrane **26** was heated at 300 °C to yield bis(trimethylsilyl)acetylene quantitatively. The higher stability of **26** compared with **27** and **28** is consistent with ab initio calculations at the HF/6-31G(d) level.[39l,39n] Cremer et al. previously pointed out the influence of σ-donors and π-acceptors on the stability of small ring systems.[49] These theoretical calculations suggest that the trimethylsilyl group enhances the stability of the tetrahedron skeleton.[2e,49]

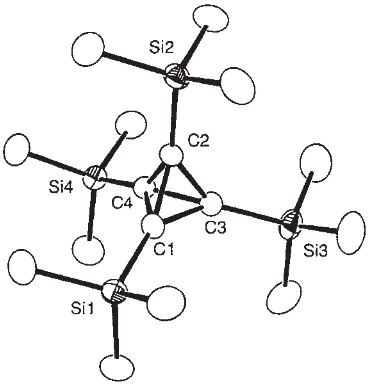
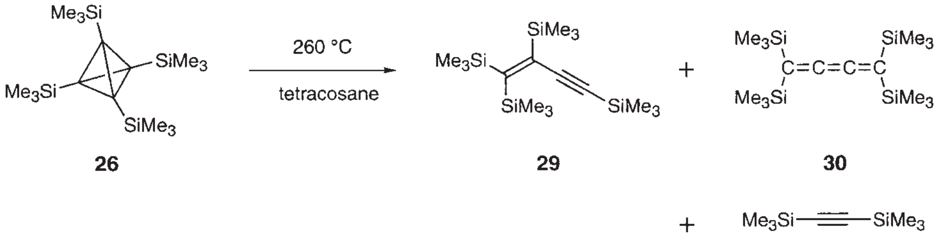


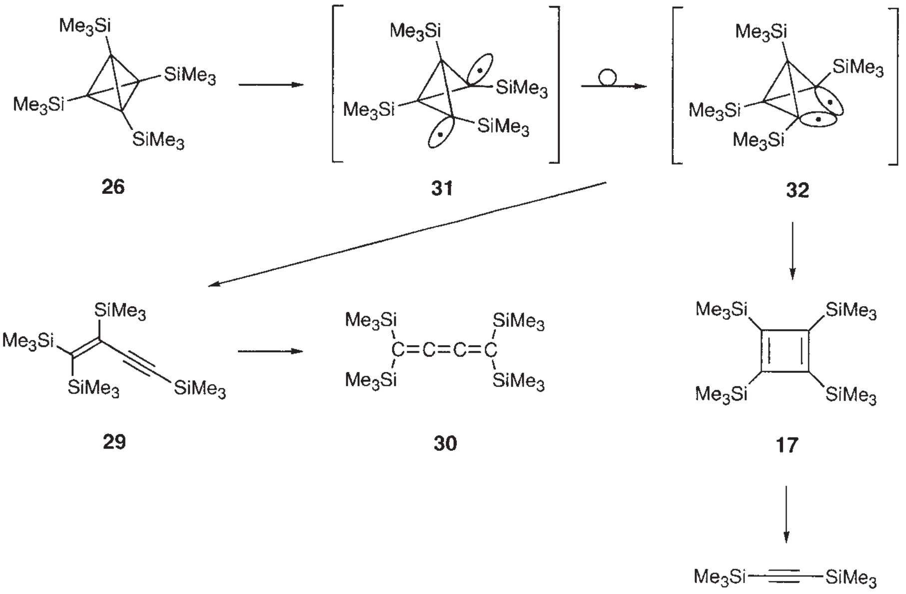
Fig. 19. ORTEP drawing of **26**.

Thermolysis of **26** in solution is quite different from that of molten tetrahedrane. Heating of **26** in perdeuterated tetracosane at 280 °C produced new signals due to vinylacetylene **29**[50] in the NMR spectra. After **26** was heated for several hours, the signals of butatriene **30**[22] appeared with a decrease in the signals of **29**. After 11 h, the signals of tetrahedrane **26** disappeared completely and, after one day, the signals due to butatriene **30** were mainly observed in the NMR spectrum, together with the signals of a small amount of bis(trimethylsilyl)acetylene. No signal of CBD **17** could be detected through the reaction. We have also performed thermolysis of **26** in tetracosane on a preparative scale. Tetrahedrane **26** was heated at 260 °C for 9 h to produce 50% vinylacetylene **29**, 19% butatriene **30**, and 31% bis(trimethylsilyl)acetylene (Scheme 16). On the other hand, thermal reaction of CBD **17** under the same conditions produced bis(trimethylsilyl)acetylene as the sole product. This indicates that CBD **17** is not an intermediate in the isomerization of tetrahedrane **26** into vinylacetylene **29** and butatriene **30**.

A possible mechanism of the thermolysis of **26** is summarized in Scheme 17. First, the central strained C–C bond of **26** is cleaved to generate the biradical species, *exo*,*exo*-bicyclobutane-2,4-diyl (**31**). At this stage, two reaction pathways can compete. One pathway is the isomerization of **31** into the *endo*,*endo* isomer (**32**). This step is rate determining and is very sensitive to steric repulsion of the large substituents, because of the narrowing of the groups in **32**. The *endo*,*endo* biradical **32** undergoes additional bond cleavage to give CBD **17**. According to a theoretical calculation at the B3LYP/6-31G(d)



Scheme 16.



Scheme 17.

level, CBD **17** is 8.8 kcal mol^{-1} higher in energy than tetrahedrane **26**. CBD **17** cannot be detected, thus giving exclusively bis(trimethylsilyl)acetylene. The other pathway involves the double C–C bond cleavage of biradicals **31** and **32**. The intermediate tetrakis(trimethylsilyl)butadiene-biradical was generated, and then vinylacetylene **29** was formed concurrent with the 1,3-migration of a trimethylsilyl group. The closely related reaction of the parent species has been reported: matrix irradiation of the dimer of acetylene generates 1,3-butadiene-1,4-diyl, which leads to vinylacetylene by a 1,3 hydrogen shift.[51] Finally, butatriene **30** was formed via isomerization of vinylacetylene **29**.

Conclusion

We have described our recent results concerning isolable CBD^{2-} in this account. Our transmetalation reaction of the CBD cobalt complex with lithium metal has permitted the preparation of a variety of dilithium salts of the CBD^{2-}. The molecular structures of the tetrasilyl-substituted CBD^{2-} (**10**) and the diphenyl-disilyl-substituted CBD^{2-} (**12–14**) have been clearly determined by X-ray diffraction. 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 6π-electron system. The aromatic stabilization of the CBD^{2-} competes with Coulomb repulsion of the negative charge in the doubly charged four-membered ring system, and stabilization of the negative charge by the phenyl groups is more effective than that by the silyl groups. The present experimental observations by NMR spectroscopic and X-ray crystallographic studies 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 Li NMR signals due to the diatropic ring current. We have developed a new and easy synthetic route from CBD^{2-} to CBD derivatives that proceeds by the two-electron oxidation reaction. Irradiation of tetrakis(trimethylsilyl)cyclobutadiene (**17**) produces tetrakis(trimethylsilyl)-tetrahedrane (**26**). Compounds **17** and **26**, the first CBD and tetrahedrane derivatives having four heteroatomic substituents, were characterized by NMR studies, and their molecular structures were confirmed by X-ray analyses. The chemistry of these compounds has just begun and further investigations are needed in order to understand their properties and reactivities.

This work was partially supported by Grants-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology. The experiments discussed in this article have been performed with many collaborators. Reports on CBD^{2-} have been summarized with M. Tanaka, T. Mizue, and the late H. Watanabe of the University of Tsukuba. Research on MCD spectroscopy of CBD^{2-} was undertaken with Prof. N. Kobayashi and Dr. K. Ishii of Tohoku University. The results of tetrahedrane were published together with Prof. G. Maier, Dr. J. Neudert, Dr. O. Wolf, and Dr. D.

Pappusch of Justus-Liebig-Universität. The authors wish to express their thanks to all of them for their kind collaboration.

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