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Tetrasilyl-substituted cyclobutadiene dianion dilithium salt: synthesis and structure*,**

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The reaction of tetrakis(trimethylsilyl)cyclobutadienylcyclopentadienyl cobalt complex $(Me_3Si)_4C_4CoCp$ with lithium metal in THF yielded the dilithium salt of cyclobutadiene dianion CBD^{2-} stabilized by four trimethylsilyl groups, $Li^+{}_2[(Me_3Si)_4C_4]^{2-}$. The bridged CBD^{2-} dianion was also synthesized by a similar procedure starting from the bridged cobalt complex, which was prepared from the reaction of 2,2,5,5,8,8,11,11-octamethyl-2,5,8,11-tetrasilacyclododeca-1,6-diyne with $CpCo(CO)_2$ in refluxing octane. The aromaticity of the CBD^{2-} is discussed on the basis of the structural characteristics and magnetic properties.

Key words: aromaticity, cyclobutadiene cobalt complex, cyclobutadiene dianion, lithium compound, transmetallation.

Since the formation of cyclopentadienide was reported in 1900 by Thiele,[1] various anion species with a π-electron system having extra electrons in the molecule have been investigated in relation to their unique structures, properties, and reactivities.[2]

There are now many isolable cyclopentadienide derivatives, and they have been widely utilized for coordination chemistry. In contrast, the synthesis and chemistry of cyclobutadiene dianion (CBD^{2-}) have been rarely explored, despite its fundamental importance. Similarly to cyclopentadienide, Hückel's rule predicts CBD^{2-} to be aromatic because of its six π-electrons. 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-}.[3—9]

Ab initio calculations indicate that the parent CBD^{2-} ($C_4H_4{}^{2-}$) is a nonaromatic compound because of the considerable Coulomb repulsion between the two negative charges.[10] The optimized structure of $C_4H_4{}^{2-}$ is bent and approximates to C_s symmetry, consisting of an allyl anion and a localized carbanion. The stabilization of the Hückel-type D_{4h} geometry due to cyclic delocalization is not sufficient in this doubly charged system. Meanwhile, calculations of a dilithium salt of CBD^{2-} ($Li^+{}_2C_4H_4{}^{2-}$) suggest the possibility of experimental observation of a derivative with D_{4h} geometry.[11] The problem with D_{4h} CBD^{2-} is that four electrons must fill nonbonding π-MOs. It has been pointed out that complexation with counter lithium cations is very important to stabilize CBD^{2-}. The most recent theoretical calculations also indicate that lithium complexation appears to enhance the aromatic effects of the four-membered ring by reducing electron repulsion.[11d]

We recently succeeded in synthesizing the first aromatic CBD^{2-} species, a dilithium salt of tetrakis(trimethylsilyl)cyclobutadiene dianion, $Li^+{}_2[(Me_3Si)_4C_4{}^{2-}]$ (**1**).[12] The introduction of a silyl group to the π-electron system causes remarkable steric and electronic perturbations.[13] One of the most interesting features of the silyl-substituted π-electron system is its ability to form the corresponding anion species by reduction with alkali metals. We have previously reported the preparations of various dianion dilithium or tetraanion tetralithium derivatives of π-electron systems by taking advantage of the silyl groups.[13—15] In this paper, we report a detailed study of CBD^{2-} supported by four silyl groups.[12—16] The aromaticity of CBD^{2-} will be reported along with the structural features and magnetic properties.

Results and Discussion

Synthesis of cobalt complexes with the tetrasilyl-substituted CBD^{2-} dianion. Tetrasilyl-substituted cyclobutadiene (CBD) can be regarded as one of the best candidate precursors for CBD^{2-}.[17] However, the methods used to

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* This paper is dedicated to the memory of H. Watanane.

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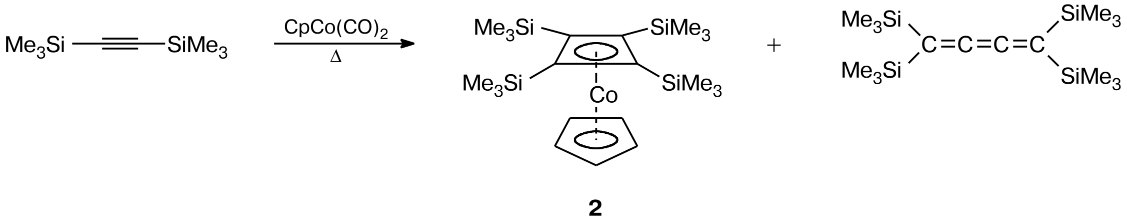
Scheme 1



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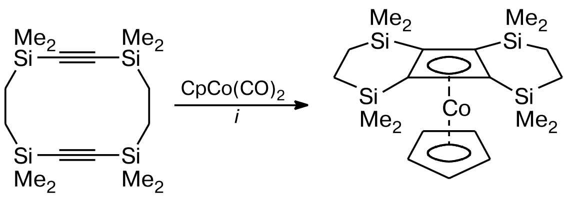
prepare CBD are sometimes very tedious and have undesirable side photoreactions.[18] Indeed, the persilylated CBD derivatives could not be isolated before our two-electron oxidation reaction to CBD^{2-}.[17] At the beginning of the work, we focused on the application of transition metal complexes of CBD as starting materials for CBD^{2-}. Tetrakis(trimethylsilyl)cyclobutadienylcyclopentadienylcobalt, $(Me_3Si)_4C_4CoCp$ (**2**)[19] was prepared according to the Vollhardt method.[19b] A mixture of bis(trimethylsilyl)acetylene and cyclopentadienyl(dicarbonyl) cobalt, $CpCo(CO)_2$, was refluxed for five days to produce yellow crystals of **2** in 55% yield and a small amount of tetrakis(trimethylsilyl)butatriene[20] (Scheme 1).

We have also prepared the cobalt complex bridged by the $Me_2Si(CH_2)_2SiMe_2$ chains (**3**) in a similar manner. The reaction of 2,2,5,5,8,8,11,11-octamethyl-2,5,8,11-tetrasilacyclododeca-1,6-diyne with $CpCo(CO)_2$ in refluxing octane produced **3** as yellow crystals in 16% yield (Scheme 2). The closely related reaction between cyclic diyne compounds and $CpCo(CO)_2$ has been investigated by Gleiter *et al.* who reported a variety of cobalt complexes, including metal-capped cyclobutadienosuperphanes.[21] Compounds **2** and **3** are thermally stable but slightly moisture sensitive, and slowly decompose in air.

Scheme 2



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i. Refluxing in octane.

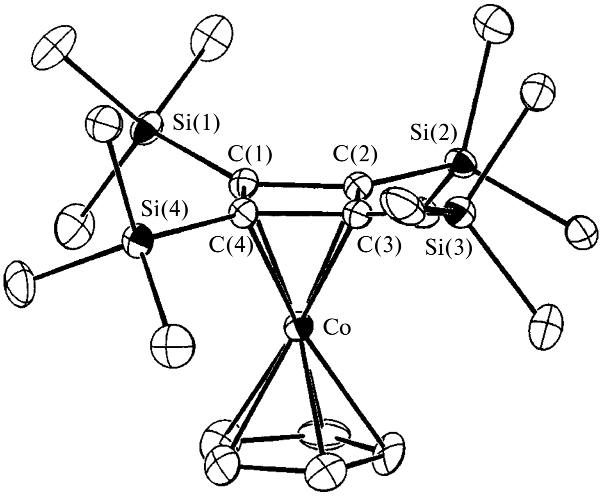


Fig. 1. Molecular structure of complex **2** (one of the four crystallographically independent molecules of compound **2** is presented). Hydrogen atoms are omitted for clarity.

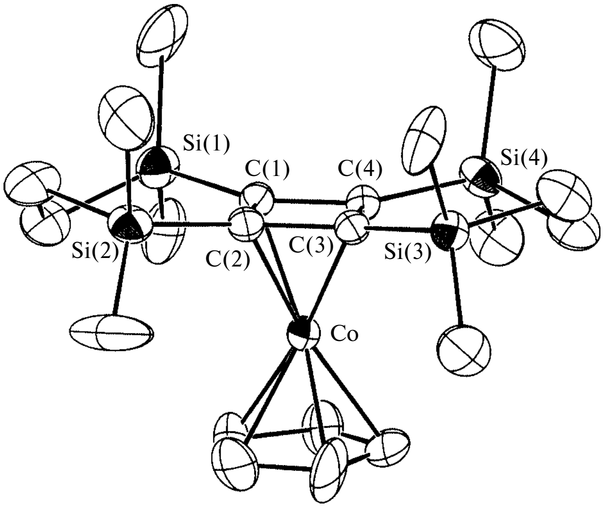


Fig. 2. Molecular structure of complex **3**. Hydrogen atoms are omitted for clarity.

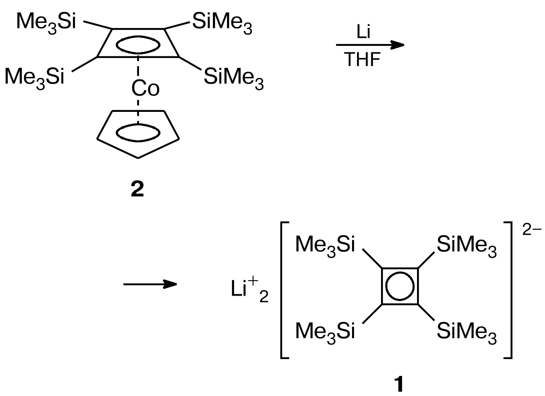
Structures of cobalt complexes with the tetrasilyl-substituted CBD^{2-} dianion. Complexes **2** and **3** are diamagnetic. They were characterized by NMR spectroscopy and their structures were determined by X-ray crystallography. The X-ray structures of *cis*- and *trans*-$[Ph_2(SiMe_3)_2C_4]Co(Cp)$ have been previously reported by Sakurai.[22] Figures 1 and 2 show the sandwich structures of compounds **2** and **3**, respectively. Spectroscopic evidence, as well as X-ray studies, show that free CBD and its derivatives generally adopt a rectangular structure. The four-membered ring of the tetrasilyl-substituted CBD derivatives, tetrakis(trimethylsilyl)cyclobutadiene and 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, also exhibit a planar rectangular structure with localized C=C double bonds, as determined by low-temperature X-ray analysis.[17] 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 crystal **2** at 120 K, an asymmetric unit consists of four crystallographically independent molecules. Since the four molecules are structurally very similar, only one of the molecules is presented in Fig. 1. The four-membered ring of the CBD ligand in **2** 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 four-membered C—C bond lengths are 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). Meanwhile, the four-membered ring of the CBD **3** is planar and slightly deformed to a rectangular structure, probably due to the $Me_2Si(CH_2)_2SiMe_2$ bridges (see Fig. 2). The internal bond angles are 89.84(16) to 90.19(16)° and the sum of the bond angles is 360°.

The C(1)—C(2) and C(3)—C(4) lengths (1.478(3) and 1.479(3) Å, respectively) are a little longer relatively to the C(2)—C(3) and C(1)—C(4) lengths (1.466(3) and 1.469(3) Å, respectively). The C—C bond lengths in **2** (on the average, 1.486 Å) are longer than those observed in **3** (on the average, 1.473 Å). The Si—C bond lengths in **2** (on the average, 1.870 Å) are also slightly long as compared with **3** (on the average, 1.854 Å). This might be due to the large steric repulsion between the trimethylsilyl groups.

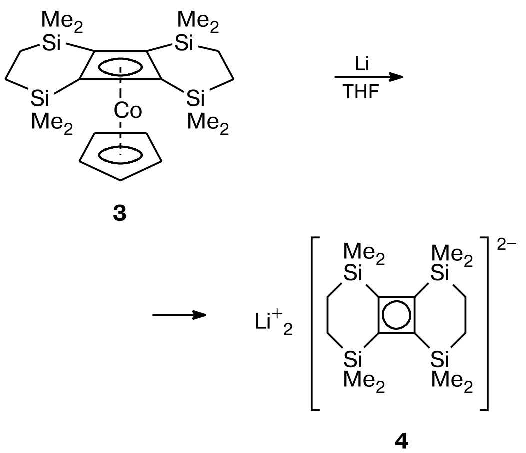
Transmetallation of tetrasilyl-substituted CBD^{2-} cobalt complexes with lithium. We investigated the transmetallation reaction of the CBD cobalt complex with alkali metals. A reaction tube was charged with cobalt complex **2**, excess amount of lithium metal, and dry, oxygen-free THF. The mixture was stirred vigorously at room temperature for 24 h to produce a dark brown solution containing the dilithium salt of tetrakis(trimethylsilyl)cyclobutadiene dianion, $Li^+{}_2[(Me_3Si)_4C_4]^{2-}$ (**1**) (Scheme 3). The choice of alkali metal is crucial in the transmetallation reaction, since alkali metals other than lithium (*e.g.*, sodium or potassium) do not work. The reaction solvent, THF, is also very important, as the reaction does not proceed in Et_2O or DME. After hexane was added to the reaction mixture, the residual lithium pieces and insoluble dark material were removed. Compound **1** containing THF molecules can be purified by recrystallization from hexane.

Scheme 3



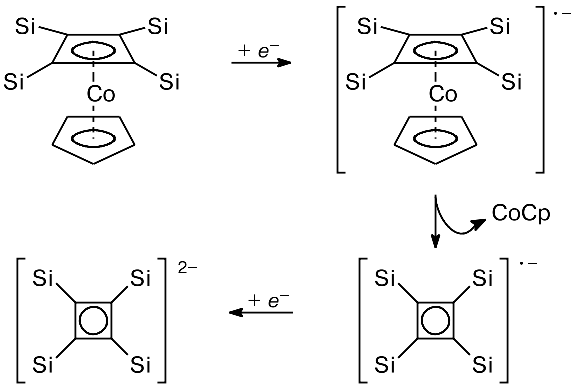
The bridged CBD^{2-} derivative (**4**) was also synthesized by a similar procedure, starting from the corresponding cobalt complex (**3**) (Scheme 4).

Scheme 4



The transmetallation reaction from transition metal complex to alkali metal complex is uncommon. It has been previously observed in the reductive cleavage of cobaltocene, Cp_2Co, with potassium under ethylene gas to yield $CpCo(C_2H_4)_2$, together with potassium cyclopentadienide (CpK) as a by-product.[23] We attempted to find lithium cyclopentadienide (CpLi) in THF-d_8 solution; however, no CpLi signal was observed in the ^{7}Li NMR spectrum. The ^{7}Li NMR of CpLi is reported to be −8.37 ppm in THF due to the strong shielding.[24] This suggests that the removal of cyclopentadienide from the cobalt center has not occurred in the present reaction system. Scheme 5 shows one of the more likely mechanisms of the transmetallation: (1) Electron-transfer reaction from lithium metal to the cobalt complex occurs to form a radical anion species of the cobalt complex. (2) CBD$^{\bullet -}$ radical anion is then removed from the cobalt center. (3) This CBD$^{\bullet -}$ 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. Cp_2Co is a stable 19-valence-electron (VE) complex and cyclopentadienide could be removed from a further reduced species.[23] In contrast, the 19-VE radical anion of the CBD cobalt complex may be unstable and the metal-ring bond therefore readily cleaved. Although the mechanism of the transmetallation remains unclear at this moment, it has permitted the preparation of the dilithium salts of CBD^{2-} incorporating four silyl groups.

Scheme 5



NMR studies on dilithium salts of the tetrasilyl-substituted CBD^{2-} dianion. The structures of 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 **1** in toluene-d_8 indicate the formation of very highly symmetric contact ion pairs (CIPs). In the ^{1}H NMR spectrum of **1**, only one signal is observed at δ 0.45 for the methyl protons along with the signals for THF. The ^{6}Li NMR spectrum of **1** displays only one signal at a chemical shift of δ –5.07. 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 $Li_2C_4R_4$ (R = H, Me, Bu^t) are around –3 ppm.[11d] The ^{13}C NMR signal of the ring carbon atoms appears at δ 104.1 as a quintet ($^1J_{Li,C}$ = 1.4 Hz) due to the coupling with two ^{6}Li nuclei ($I = 1$). These data indicate a structure in which the two counter lithium ions are above and below the center of the plane of the four-membered ring. In the ^{29}Si NMR spectrum, one signal appears at δ –23.7, which is shifted considerably upfield compared with the precursor **1** (δ –7.8, Δδ = –15.9). This suggests that the negative charge is largely stabilized by the silyl groups through pπ—σ* conjugation.[13]

Bridged CBD^{2-} **4** also shows a highly symmetrical CIPs formation in toluene-d_8. Only one signal for the methyl (δ 0.35) and one for the methylene (δ 1.19) groups are observed in the ^{1}H NMR spectrum. The ^{6}Li NMR spectrum of **4** shows a signal at δ –5.10, which is comparable to that of **1**. In the ^{13}C NMR spectrum, one signal for the cyclobutadienediide ring carbons appears at δ 102.1 as a quintet ($^1J_{Li,C}$ = 1.2 Hz). The ^{29}Si NMR spectrum of **4** shows one signal at δ –24.2, which is also shifted upfield compared with **3** (δ –9.0, Δδ = –15.2). The Li NMR studies were very useful for estimating the magnitude of the ring current, because the two lithium ions are located inside the aromatic-shielding region.[25] From a magnetic point of view, the tetrasilyl-substituted CBD^{2-} in solution clearly shows a strong diatropic ring current due to the delocalization of the six π-electrons. Thus, CBD^{2-} should be regarded as an aromatic compound that is stabilized not only by the aromatic 6π-electron system but also by the four silyl groups.

Crystal structure of dilithium salt of tetrasilyl-substituted CBD^{2-}. For a structural study, we performed a ligand exchange on the lithium ions from THF to DME. A single crystal of **1** containing two molecules of DME per unit cell suitable for X-ray analysis was obtained by recrystallization from hexane. The crystal structure of **1** is shown in Fig. 3. The dilithium salt has a monomeric structure and forms contact ion pairs 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 Li(1) and the four carbon atoms (C(1), C(2), C(3), and C(4)) range from 2.166(12) to 2.195(12) Å (on the average, 2.178 Å), and those for Li(2) are

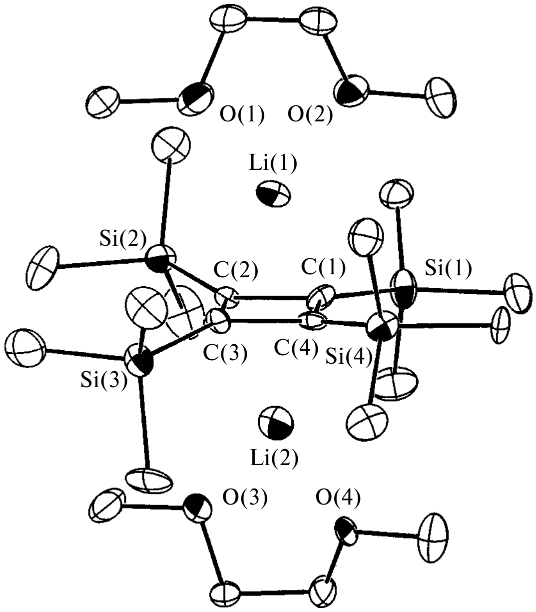


Fig. 3. Molecular structure of complex **1**. Hydrogen atoms are omitted for clarity.

2.152(11)—2.199(12) Å (on the average, 2.181 Å). The Li distances from the ring centroid are 1.90(1) Å.

The four-membered ring of **1** is planar and forms an almost square structure, as confirmed by the internal bond angles of 89.2(6) to 90.7(6)° and the sum of the bond angles (360.0°). The dihedral angles are 0.90(2)° for C(1)—C(2)—C(3)/C(1)—C(3)—C(4) and 0.89(2)° for C(2)—C(3)—C(4)/C(1)—C(2)—C(4). The C—C bond lengths are 1.496(3) Å for C(1)—C(2), 1.485(10) Å for C(2)—C(3), 1.493(4) Å for C(3)—C(4), and 1.507(9) Å for C(1)—C(4), giving diagonal distances of 2.12(1) Å for C(1)—C(3) and 2.11(1) Å for C(2)—C(4). No significant difference was found between the observed C—C bond lengths of **1** (on the average, 1.495 Å) and **2** (on the average, 1.486 Å). Meanwhile, the Si—C bond lengths in **1** (on the average, 1.836 Å) are noticeably shorter than those observed in **2** (on the average, 1.870 Å), which is attributed to the hyperconjugative interaction between the occupied p orbitals of the quaternary carbon atom and the σ* (Si—C_{Me}) orbital. Due to the large steric repulsion of the Me_3Si groups, the positions of the Si atoms deviate up and down alternately about the plane of the cyclobutadienediide ring. The angles between the central four-membered ring plane and the Si—C bond are 8.0—9.9°.

The structure of **1** containing DME is close to that predicted by a calculation of the corresponding $Li^+{}_2[C_4H_4]^{2-}$ with D_{4h} symmetry.[11] The observed C—C lengths (on the average, 1.495 Å) in the crystal are similar to the calculated value of 1.461 Å for $Li^+{}_2[C_4H_4]^{2-}$ (6-31G**). The Li distance from the ring centroid (1.90 Å) is relatively long in comparison 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 counter lithium ions. The observed diagonal distance of 2.11—2.12 Å is comparable to the calculated value of 2.069 Å.[11c]

Summing up, we have synthesized the dilithium salts of CBD^{2-} stabilized by four silyl groups (**1** and **4**) by the transmetallation of the CBD cobalt complexes (**2** and **3**) with lithium metal in THF. The present transmetallation is a unique and clean reaction, which permits the quantitative formation of CBD^{2-}. The present experimental observations by NMR spectroscopic and X-ray crystallographic studies satisfy the inherent definitions of aromaticity using the geometry criteria, *i.e.*, the planarity of the four-membered ring, the lack of bond alternation, and the highly shielded chemical shift in the Li NMR due to the diatropic ring current. The aromatic stabilization of CBD^{2-} competes with the electrostatic repulsion of the negative charge in the doubly-charged four-membered ring system, and complexation with lithium cations is very important to stabilize the CBD^{2-}. The two lithium ions stabilize the HOMO of CBD^{2-} through the vacant 2p-orbitals with η^4-coordination. 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.[26] The smaller lithium ions can approach more closely than other cations,[27] and counteract the serious Coulomb repulsion. Stabilization of the negative charge by silyl groups is also important to isolate CBD^{2-}.

Experimental

^1H NMR spectra were recorded on a Bruker AC-300 FT spectrometer. ^{13}C, ^{29}Si, ^6Li, and ^7Li NMR spectra were collected on a Bruker AC-300 at 75.5, 59.6, 44.2, and 116.6 MHz, respectively. ^6Li and ^7Li NMR spectra were referenced to 1 *M* solutions of LiCl in methanol/benzene-d_6, methanol/toluene-d_8, or THF-d_8. The sampling of **1** for X-ray analysis was carried out using an MBRAUN MB 150 B-G glovebox in an argon atmosphere. THF 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. Octane was dried and distilled from calcium hydride. DME, benzene-d_6, toluene-d_8, and THF-d_8 were dried over molecular sieves, and then transferred into a tube covered with a potassium mirror prior to use. Bis(trimethylsilyl)acetylene ($Me_3SiC{\equiv}CSiMe_3$) was prepared from the reaction of $BrMgC{\equiv}CMgBr$ with 2 equiv. Me_3SiCl in THF. 2,2,5,5,8,8,11,11-Octamethyl-2,5,8,11-tetrasilacyclododeca-1,6-diyne was prepared by the reported method.[28] Commercially available lithium rod (99.9%, Mitsuwa´s Pure Chemicals, Osaka, Japan) was pressed out from a stainless steel bottle with a hole to make the lithium wire (diameter *ca.* 1 mm), which was cut into small pieces under argon flow just before use. Lithium-6 (95 at.%) metal and $CpCo(CO)_2$ were obtained commercially (Aldrich Chemical Company).

Tetrakis(trimethylsilyl)cyclobutadienylcyclopentadienyl cobalt (2). A mixture of $Me_3SiC{\equiv}CSiMe_3$ (40 mL) and $CpCo(CO)_2$ (2.80 g, 15.6 mmol) was added dropwise slowly to refluxing $Me_3SiC{\equiv}CSiMe_3$ (50 mL). The reaction mixture was then heated under the refluxing temperature of $Me_3SiC{\equiv}CSiMe_3$ over a period of five days. Excess $Me_3SiC{\equiv}CSiMe_3$ was removed by vacuum transfer and the products were chromatographed on silica gel to produce yellow crystals of **2** in 55% yield (3.99 g, 8.58 mmol) with a small amount of orange crystals of tetrakis(trimethylsilyl)butatriene. Compound **2** had already been isolated by Sakurai *et al.* initially,[19a] and this procedure followed the subsequently reported Vollhardt´s method.[19b] M.p. 213—214 °C. ^1H NMR ($CDCl_3$), δ: 0.17 (s, 36 H, Me); 4.91 (s, 5 H, CH). ^{13}C NMR ($CDCl_3$), δ: 2.4 (Me); 79.5 (CH); 82.0 (C). ^{29}Si NMR ($CDCl_3$), δ: –7.8. UV (hexane), λ_{max}/nm (ε): 217 (30600), 237 sh (15700), 290 (9700), 404 (300).

{(η^4-1,2,7,8)-3,3,6,6,9,9,12,12-Octamethyl-3,6,9,12-tetrasilacyclo[6.4.0.0^{2,7}]dodeca-1,7-dienyl}cyclopentadienyl cobalt (3). A mixture of 3,3,6,6,9,9,12,12-octamethyl-3,6,9,12-tetrasilacyclododeca-1,7-diyne (501 mg, 1.49 mmol) and $CpCo(CO)_2$ (320 mg, 1.78 mmol) in octane (10 mL) was heated under the refluxing temperature of octane for five days. The reaction mixture was chromatographed on silica gel to produce yellow crystals of **3** in 16% yield (110 mg, 0.24 mmol). M.p. 252—254 °C. Found (%): C, 54.44; H, 8.14. $C_{21}H_{37}CoSi_4$. Calculated (%): C, 54.74; H, 8.09. ^1H NMR ($CDCl_3$), δ: 0.02 (s, 12 H, Me); 0.13 (s, 12 H, Me); 0.59—0.69 (m, 4 H, CH_2); 0.73—0.83 (m, 4 H, CH_2), 4.92 (s, 5 H, CH). ^{13}C NMR ($CDCl_3$), δ: –1.0, –0.3 (both Me); 8.6 (CH_2); 79.1 (CH); 80.6 (C). ^{29}Si NMR ($CDCl_3$), δ: –9.0. UV (hexane), λ_{max}/nm (ε): 218 (30500), 236 sh (15700), 262 (5500), 292 (8900), 410 (400).

Tetrakis(trimethylsilyl)cyclobutadiene dilithium salt (1). The crystals of **2** (49 mg, 0.105 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 (1.0 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** in an almost quantitative yield. The solvent was evaporated, and then degassed hexane (5.0 mL) was added to the reaction mixture by vacuum transfer. After 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 DME (*ca*. 0.3 mL) were introduced by vacuum transfer. The solution was cooled to produce air- and moisture-sensitive yellow crystals of **1** containing two molecules of DME, quantitatively.

Compound 1 (THF ligand). ^1H NMR (C_7D_8), δ: 0.45 (s, 36 H, Me); 1.26, 3.44 (both br.s, 8 H each, THF). ^{13}C NMR (C_7D_8), δ: 5.5 (Me); 25.5, 69.5 (both THF); 104.1 (quint, $^1J_{Li,C}$ = 1.4 Hz). ^{29}Si NMR (C_7D_8), δ: –23.7. ^6Li NMR (C_7D_8), δ: –5.07.

Compound 1 (DME ligand). ^1H NMR (C_7D_8), δ: 0.47 (s, 36 H, Me); 3.13 (s, 12 H, DME); 3.14 (s, 8 H, DME). ^{13}C NMR (C_7D_8), δ: 5.7 (Me); 59.3, 71.3 (both DME); 103.6 (C). ^{29}Si NMR (C_7D_8), δ: –24.4. ^6Li NMR (C_7D_8), δ: –5.01.

Compound 1. ^1H NMR (THF-d_8), δ: 0.09 (s, 36 H, Me). ^{13}C NMR (THF-d_8), δ: 5.1 (Me); 104.0 (C). ^{29}Si NMR (THF-d_8), δ: –24.3. ^7Li NMR (THF-d_8), δ: –4.92.

3,3,6,6,9,9,12,12-Octamethyl-3,6,9,12-tetrasilacyclo[6.4.0.0^{2,7}]dodeca-1,7-diene dilithium dianion salt (4). Dilithium dianion **4** was prepared by the same procedure as compound **1**, starting from **3** (49 mg, 0.106 mmol), and in an almost quantitative yield (THF ligand). Compound **4** (THF ligand). ^1H NMR (C_7D_8), δ: 0.35 (s, 24 H, Me); 1.19 (s, 8 H, CH_2); 1.34, 3.49 (both br.s, 8 H each, THF). ^{13}C NMR (C_7D_8), δ: 2.5 (Me); 12.4 (CH_2); 25.5, 68.7 (both THF); 102.1 (quint, $^1J_{Li,C}$ = 1.2 Hz). ^{29}Si NMR (C_7D_8), δ: –24.2. ^6Li NMR (C_7D_8), δ: –5.10.

X-ray crystallography. X-ray quality single crystals were obtained from hexane for **2** and **3** as yellow plates and from hexane/DME for **1** as yellow blocks. Diffraction data were collected on a MacScience DIP2030K image plate diffractometer using graphite-monochromatized MoKα radiation (λ = 0.71070 Å). The structure was solved by the direct method and refined by the full-matrix least-squares method using SHELXL-97 program. Crystal data for compound **2** at 120 K: molecular formula $C_{21}H_{41}Si_4Co$, M = 464.83, triclinic, a = 9.6330(2), b = 19.060(1), c = 30.721(1) Å, α = 105.601(2), β = 95.354(2), γ = 99.912(2)°, V = 5293.4(3) Å^3, space group $P1$ (No. 2), Z = 8, d_{calc} = 1.167 g cm^{-3}. The final R factor was 0.0457 for 19242 reflections with $I > 2\sigma(I)$ and wR_2 = 0.1231 for all data. GOF = 1.003. Crystal data for compound **3** at 120 K: molecular formula $C_{21}H_{37}Si_4Co$, M = 460.80, triclinic, a = 11.314(1), b = 15.948(1), c = 28.861(1) Å, β = 95.017(2)°, V = 5187.6(3) Å^3, space group $C2/c$ (No. 15), Z = 8, D_{calc} = 1.180 g cm^{-3}. The final R factor was 0.0444 for 5199 reflections with $I > 2\sigma(I)$ and wR_2 = 0.1302 for all data. GOF = 0.985. Crystal data for compound **1** (DME ligand) at 120 K: molecular formula $C_{24}H_{56}Li_2O_4Si_4$, M = 534.93, monoclinic, a = 18.741(1), b = 10.446(1), c = 19.270(1) Å, β = 114.640(4)°, V = 3429.0(4) Å^3, space group Cc (No. 9), Z = 4, d_{calc} = 1.036 g cm^{-3}. The final R factor was 0.0565 for 3460 reflections with $I > 2\sigma(I)$ and wR_2 = 0.1646 for all data. GOF = 1.026.

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