Table 1. NMR spectroscopic data of compounds **6**–**11**.[a]

6: yellow oil; ^{1}H NMR ($CDCl_3$): $\delta = 0.26$ (18H), 0.15 (9H), -0.03 (9H); ^{13}C NMR ([D$_8$]toluene): $\delta = 141.1$ (C=C), 38.6 ($C{=}N_2$), 16.4 (ring-C), -0.1 (2SiMe$_3$), -0.35 (SiMe$_3$), -0.4 (SiMe$_3$)

7: colorless oil; ^{1}H NMR (C_6D_6): $\delta = 0.35$ (18H), 0.20 (18H); ^{13}C NMR (C_6D_{12}): $\delta = 177.1$ (C=C=N), 26.3 (C=C=N), 0.5 (SiMe$_3$), 0.4 (SiMe$_3$)

8: red-brown crystals; ^{1}H NMR (C_7D_{14}): $\delta = 0.09$ (36H); ^{13}C NMR (C_7D_{14}): $\delta = 171.59$ (ring-C), 0.08 (SiMe$_3$)

9: colorless solid (m.p. 139 °C); ^{1}H NMR (C_6D_6): $\delta = 1.46$ (2H), 0.06 (18H); ^{13}C NMR (C_6D_{12}): $\delta = 119.3$ ($C{\equiv}N$), 16.4 (C-H), -3.2 (SiMe$_3$)

10: colorless solid (m.p. 95 °C); ^{1}H NMR ($CDCl_3$): $\delta = 3.56$ (6H), 0.21 (18H), 0.20 (18H); ^{13}C NMR ($CDCl_3$): $\delta = 171.9$ (C=O), 163.0 (C=C), 148.0 (C=C), 65.3 (ring-C), 51.3 (OMe), 1.5 (SiMe$_3$), 1.3 (SiMe$_3$)

11: colorless solid (m.p. 165 °C); ^{1}H NMR ($CDCl_3$): $\delta = 3.79$ (6H), 0.32 (18H), 0.28 (18H); ^{13}C NMR ($CDCl_3$): $\delta = 171.3$ (C=O), 166.9 (C=C), 144.9 (C=C), 135.7 (C=C), 52.2 (OMe), 4.6 (SiMe$_3$), 3.4 (SiMe$_3$)

[a] ^{1}H NMR: 400.1 MHz, ^{13}C NMR: 100.6 MHz, chemical shifts are relative to TMS. All compounds gave correct elemental analyses or high resolution mass spectra.

Together with the NMR data and the fact that hydrolysis yields the dinitrile **9** of 2,3-bis(trimethylsilyl)succinic acid, the structure of **7** can be assumed with confidence.

The many attempts to photoisomerize **8** into tetrahedrane **3** by variation of the wavelength, temperature, and solvent demanded high persistence. Practically all variants led to a fragmentation into two molecules of bis(trimethylsilyl)acetylene. However, there was one exception: Irradiation of the mixture of **7** and **8** in deuterated methylcyclohexane at −130 °C in a photoreactor (254 nm) for a long time resulted in the appearance of signals in the NMR spectra, which, by comparison with those measured for **2**,[3] could arise from tetrakis(trimethylsilyl)tetrahedrane (**3**). The final proof of the successful photochemically induced transformation of **8** into **3** was achieved with a pure sample of cyclobutadiene **8** which was given to us by Sekiguchi.[7, 10] The NMR signals of **8** had nearly disappeared after irradiation of the sample for 70 hours under the above-mentioned conditions. The newly formed NMR signals of practically equal intensities can be attributed to bis(trimethylsilyl)acetylene [^{1}H: $\delta = 0.12$; ^{13}C: $\delta = 0.01$ (SiMe$_3$), 113.48 (acetylenic-C)] and tetrakis(trimethylsilyl)tetrahedrane (**3**) [^{1}H: $\delta = 0.10$; ^{13}C: $\delta = -0.03$ (SiMe$_3$), -20.46 (ring-C)]. The strong upfield shift of the ring-C atoms is typical for tetrahedranes.[1, 3]

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From a Cyclobutadiene Dianion to a Cyclobutadiene: Synthesis and Structural Characterization of Tetrasilyl-Substituted Cyclobutadiene**

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The fascinating chemistry of cyclobutadiene (CBD) and its derivatives has been studied from the point of view of their structures, properties, and reactivities.[1, 2] 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.[3] After that, it was observed—through the use of photochemical reactions—at low temperature in inert matrices,[4] and at room temperature in a hemicarcerand.[5] In contrast, some CBD derivatives, stabilized by steric effects, have been isolated, and parts of their molecular structures determined by X-ray crystallography.[6] For the most part, these compounds were prepared by the photolysis of cyclopentadienone derivatives or diazo compounds. However, the methods used to prepare CBD are sometimes very tedious and have undesirable side photoreactions.[7]

Recently, we succeeded in synthesizing the dilithium salt of the tetrakis(trimethylsilyl)cyclobutadiene dianion, the first aromatic CBD^{2-} ion with a six π-electron system, by the reaction of the cobalt complex of CBD derivative **2** with lithium metal in THF.[8] An interesting aspect is that CBD^{2-} is one of the best candidate precursors for CBD. Herein we report on a new and easy synthetic route from a CBD dianion to a CBD derivative that proceeds by a two-electron oxidation reaction.

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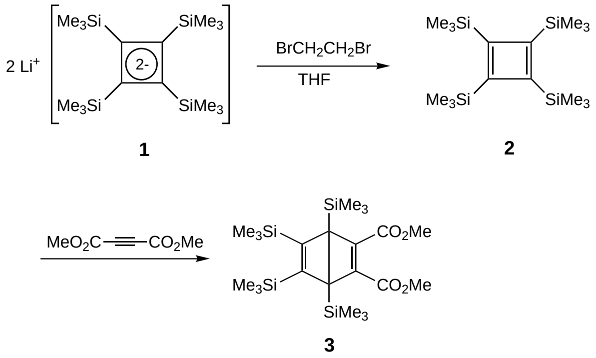
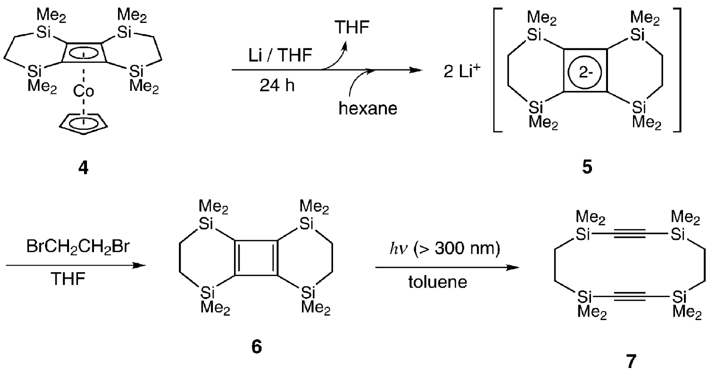
We chose 1,2-dibromoethane ($BrCH_2CH_2Br$) for the oxidation of the anion of **1**. The reaction of **1** with excess $BrCH_2CH_2Br$ in THF at room temperature produced tetrakis(trimethylsilyl)cyclobutadiene (**2**) in 64% yield (Scheme 1).[15] The reaction time (ca. 1 min) for this transformation was quite important to obtain pure CBD **2**. The Diels–Alder cycloaddition product with ethylene generated from $BrCH_2CH_2Br$ was also produced at longer reaction times. CBD **2** readily reacted with dimethyl acetylenedicarboxylate to yield quantitatively a 1:1 adduct, the Dewar benzene derivative **3**.[9]



Scheme 1. Synthesis and reaction of tetrakis(trimethylsilyl)cyclobutadiene (**2**).

Pure compound **2** was isolated as air-sensitive pale red crystals by vacuum sublimation (ca. 100 °C/0.01 Torr). Compound **2**, the first CBD derivative with four heteroatomic substituents, was characterized by NMR spectroscopy. Only one signal at $\delta = 0.15$ was observed for the methyl groups in the ^1H NMR spectrum of **2** in [D$_6$]benzene. The ^{29}Si NMR spectrum showed a signal at $\delta = -16.7$, which was shifted downfield relative to that of compound **1** ($\delta = -23.7$, $\Delta\delta = 7.0$). Two signals appeared at $\delta = 0.0$ (methyl carbon atoms) and $\delta = 172.1$ (quaternary carbon atoms) in the ^{13}C NMR spectrum of compound **2**. The signal at $\delta = 172.1$ was also significantly shifted downfield relative to that of compound **1** ($\delta = 104.1$, $\Delta\delta = 68.0$) by the two-electron oxidation. Single crystals of a size suitable for characterization by X-ray diffraction have not yet been obtained.[10]

Next, we designed 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 (**6**) to investigate any structural information that may be obtained when the cyclobutadiene ring is fixed with two six-membered rings. A new precursor **5** was prepared by the reaction of the cobalt complex **4** with lithium metal in THF.[11, 12] The reaction of **5** with $BrCH_2CH_2Br$ in THF occurred readily to give the cyclobutadiene derivative **6** (Scheme 2). CBD **6** was fully characterized by NMR spectroscopic and X-ray crystallographic analysis.



Scheme 2. Synthesis and photochemical reaction of octamethyl-3,6,9,12-tetrasilatricyclo[6.4.0.0^{2,7}]dodeca-1(8),2(7)-diene (**6**).

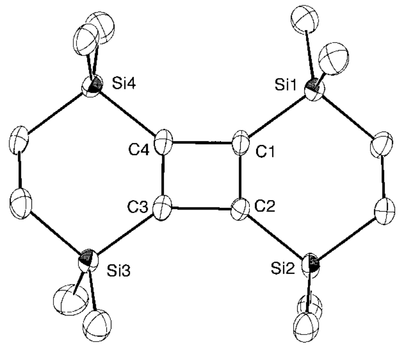


Figure 1. ORTEP drawing of the structure of **6** with thermal ellipsoids shown at the 50% probability level (hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: C1-C2 1.364(7), C1-C4 1.578(6), C2-C3 1.583(6), C3-C4 1.353(7), C1-Si1 1.863(5), C2-Si2 1.854(5), C3-Si3 1.861(5), C4-Si4 1.859(5); C2-C1-C4 90.1(4), C2-C1-Si1 126.5(4), C4-C1-Si1 143.4(4), C1-C2-C3 89.5(4), C1-C2-Si2 128.4(4), C3-C2-Si2 142.0(4), C4-C3-C2 90.3(4), C4-C3-Si3 126.7(4), C2-C3-Si3 142.9(4), C3-C4-C1 90.1(4), C3-C4-Si4 128.0(4), C1-C4-Si4 141.9(4).

The X-ray diffraction data were collected at 105 K. An ORTEP drawing of compound **6** is shown in Figure 1.[13] The central four-membered ring of **6** shows a planar rectangular structure with localized C–C double bonds. The internal bond angles of the four-membered ring range from 89.5(4) to 90.3(4)° (av 90.0°) and the sum of the bond angles is 360.0°. The central four-membered ring is essentially 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), 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 1.578(6), 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 the 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),[6b] 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).[6i] The Si–C (quaternary carbon atoms) bond lengths of compound **6** (1.854(5)–1.863(5) Å; av 1.859 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)°).

Since the present cyclobutadiene derivatives are highly perturbed by the four silyl groups, we have also examined their reactivities. The two-electron reduction of **2** and **6** with lithium metal in THF afforded the quantitative formation of the corresponding dianions **1** and **5** within a few hours. Thus, we can now easily perform the interconversion between the CBD and the CBD^{2-} ion. Irradiation of CBD **2** in [D$_8$]toluene 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 bond. No tetrahedrane derivative was observed under these conditions. Interestingly, in the case of **6**, the cyclic diyne compound 2,2,5,5,8,8,11,11-octamethyl-2,5,8,11-tetrasilacyclododeca-1,6-diyne (**7**)[14] was produced after irradiation (Scheme 2). Thus, the cyclobutadiene ring system of **6** undergoes an interconversion of the two rectangular forms in solution at room temperature. It is likely that this bond-switching process is completely blocked in the crystalline lattice at 105 K.

Experimental Section

2: Crystals of **1** (160 mg, 0.32 mmol) were placed in a reaction tube with a magnetic stirrer and then evacuated. Degassed THF (3 mL) and 1,2-dibromoethane (1.88 g, 10 mmol) were introduced by vacuum transfer, and the solution was stirred for a short time (1 min). The solvent was removed in vacuo, and then degassed hexane (3 mL) was introduced by vacuum transfer. The lithium bromide was removed by filtration and the filtrate was concentrated. The residue was then sublimed (ca. 100 °C/0.01 Torr) to afford pale red crystals of **2** (70 mg, 64 %). M.p. 122–123 °C; ^{1}H NMR ([D$_6$]benzene, TMS): $\delta = 0.15$ (s, 36 H; CH$_3$); ^{13}C{^{1}H} NMR ([D$_6$]benzene, TMS): $\delta = 0.0$ (CH$_3$), 172.1 (C); ^{29}Si{^{1}H} NMR ([D$_6$]benzene, TMS): $\delta = -16.7$; HR-MS calcd for $C_{16}H_{36}Si_4$: 340.1894; found: 340.1891.

Compound **6** was prepared by an analogous procedure as compound **2**, but starting from compound **4**, and in 81 % yield. ^{1}H NMR ([D$_8$]toluene, TMS): $\delta = 0.07$ (s, 24 H; CH$_3$), 0.77 (s, 8 H; CH$_2$); ^{13}C{^{1}H} NMR ([D$_8$]toluene, TMS): $\delta = -3.1$ (CH$_3$), 8.2 (CH$_2$), 173.4 (C); ^{29}Si{^{1}H} NMR ([D$_6$]benzene, TMS): $\delta = -18.8$; HR-MS calcd for $C_{16}H_{32}Si_4$: 336.1581; found: 336.1581.

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[9] Spectroscopic data for **3**: colorless crystals; m.p. 92–93 °C; ^{1}H NMR ([D$_6$]benzene, TMS): $\delta = 0.31$ (s, 18 H; CH$_3$), 0.32 (s, 18 H; CH$_3$), 3.37 (s, 6 H; CH$_3$); ^{13}C{^{1}H} NMR ([D$_6$]benzene, TMS): $\delta = 1.6$ (CH$_3$), 1.7 (CH$_3$), 51.0 (CH$_3$), 65.7 (C), 148.1 (C=C), 163.3 (C=C), 172.7 (C=O); ^{29}Si{^{1}H} NMR ([D$_6$]benzene, TMS): $\delta = -11.0, -3.2$.

[10] Preliminary X-ray diffraction analysis of **2** at 120 K showed a rectangular structure for the cyclobutadiene ring. However, the refinement was unsatisfactory as a result of the poor quality of the crystals.

[11] Spectroscopic data for **4**: yellow crystals; m.p. 252–254 °C; ^{1}H NMR ([D$_1$]chloroform, TMS): $\delta = 0.02$ (s, 12 H; CH$_3$), 0.13 (s, 12 H; CH$_3$), 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{^{1}H} NMR ([D$_1$]chloroform, TMS): $\delta = -1.0$ (CH$_3$), -0.3 (CH$_3$), 8.6 (CH$_2$), 79.1 (CH), 80.6 (C); ^{29}Si{^{1}H} NMR ([D$_1$]chloroform, TMS): $\delta = -9.0$.

[12] Spectroscopic data for **5**: pale yellow crystals; ^{1}H NMR ([D$_8$]toluene, TMS): $\delta = 0.35$ (s, 24 H; CH$_3$), 1.19 (s, 8 H; CH$_2$), 1.34 (br s, 8 H; THF), 3.49 (br s, 8 H; THF); ^{13}C{^{1}H} NMR([D$_8$]toluene, TMS): $\delta = 2.5$ (CH$_3$), 12.4 (CH$_2$), 25.5 (THF), 68.7 (THF), 102.1 (C, quint, $J(^{13}C,^{6}Li) = 1.2$ Hz); ^{29}Si{^{1}H} NMR ([D$_8$]toluene, TMS): $\delta = -24.2$; ^{6}Li{^{1}H} NMR ([D$_8$]toluene, TMS): $\delta = -5.1$.

[13] Crystal structure analysis of **6**: A single crystal ($0.40 \times 0.30 \times 0.20$ mm) was sealed in a capillary glass tube for the data collection. Diffraction data were collected at 105 K on a MacScience DIP2030K Image Plate Diffractometer employing graphite-monochromated Mo$_{K\alpha}$ radiation ($\lambda = 0.71070$ Å). Crystal data: $C_{16}H_{32}Si_4$, $M_r = 336.78$, monoclinic, space group $P2_1/c$, $a = 9.5770(6)$, $b = 19.631(2)$, $c = 12.184(1)$ Å, $\beta = 113.116(4)°$, $V = 2106.8(3)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.062$ g cm^{-3}, GOF = 1.129. The final R factor was 0.0980 ($R_w = 0.2550$) for 4736 reflections with $I_o > 2\sigma(I_o)$. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-152460. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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