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Tetrakis(trimethylsilyl)tetrahedrane[+]

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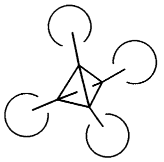
Abstract: Tetrakis(trimethylsilyl)tetrahedrane **3** has been synthesized upon irradiation of tetrakis(trimethylsilyl)cyclobutadiene **8**, which can be prepared either by thermal nitrogen elimination from trimethylsilyl-[1,2,3-tris(trimethylsilyl)-2-cycloprop-1-enyl]diazomethane **7** or by mild oxidation of cyclobutadiene dianion **9** with 1,2-dibromoethane. The structural characterization of tetrahedrane **3** has been achieved by X-ray crystallography. The surprising thermal stability of **3** − which is stable up to 300 °C − is discussed.

Introduction

Tetrakis(trimethylsilyl)tetrahedrane **3** is of interest in several respects. The "corset effect", that is, the stabilization by the accumulation of four voluminous substituents,[1] should be smaller in **3**[2] than in the tetra-*tert*-butyl derivative **1**, the first stable tetrahedrane,[1] because of the longer C−Si bonds. On the other hand, the four σ-donor substituents in **3** should particularly favor the tetrahedrane ring skeleton, an observation that we have made before in the case of tri-*tert*-butyl(trimethylsilyl)tetrahedrane **2**.[3] These influences will add up to a high thermal stability for tetrahedrane **3** despite the enormous strain energy expected for a tetrahedral skeleton. Another aspect is even more enticing: the high s-character of the bonds pointing from the ring skeleton to the substituents should enable the trimethylsilyl groups of **3** to be easily replaced.[1c,4] On this basis, a route to tetralithiotetrahedrane[5] − and perhaps even to the unsubstituted tetrahedrane **19** − can be envisaged.



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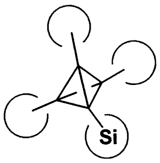

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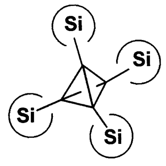

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One apparent procedure for the synthesis of tetrahedrane **3** is the photoisomerization of tetrakis(trimethylsilyl)cyclobutadiene **8**. By analogy with tetra-*tert*-butyl-[6] and tri-*tert*-butyl(trimethylsilyl)cyclobutadiene,[3] the photochemical precursors for tetrahedranes **1** and **2**, compound **8** can be prepared by the "cyclopropenyldiazomethane route" starting with diazo compound **7**.[7] Another route to **8** has been found by the Japanese group[8] via the mild oxidation of the corresponding cyclobutadiene dianion **9**. In this paper, we describe the synthesis of cyclobutadiene **8** and its isomerization into tetrahedrane **3** upon irradiation. The structural elucidation of tetrahedrane **3** and its astonishing thermal properties are also discussed.

Results and Discussion

Cyclobutadiene 8 via Diazo Compound 7. Trimethylsilyl-[1,2,3-tris(trimethylsilyl)-2-cycloprop-1-enyl]diazomethane **7** can be isolated as a yellow oil in 11% yield by the coupling of tris(trimethylsilyl)cyclopropenylium hexachloroantimonate **4**[9]

[+] Small Rings, Part 95. For Part 94, see ref 7.

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(1) (a) Maier, G.; Pfriem, S.; Schäfer, U.; Matusch, R. *Angew. Chem.* **1978**, *90*, 552−553; *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 520−521. (b) Maier, G.; Pfriem, S.; Schäfer, U.; Malsch, K.-D.; Matusch, R. *Chem. Ber.* **1981**, *114*, 3965−3987. (c) Summary: Maier, G. *Angew. Chem.* **1988**, *100*, 317−341; *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 309−332.

(2) Maier, G.; Lage, H. W.; Reisenauer, H. P. *Angew. Chem.* **1981**, *93*, 1010−1011; *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 976−977 and references therein.

(3) (a) Maier, G.; Born, D. *Angew. Chem.* **1989**, *101*, 1085−1087; *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1050−1052. (b) Maier, G.; Born, D.; Bauer, I.; Wolf, R.; Boese, R.; Cremer, D. *Chem. Ber.* **1994**, *127*, 173−189.

(4) Loerzer, T.; Malinek, R.; Lüttke, W.; Franz, L. H.; Malsch, K.-D.; Maier, G. *Angew. Chem.* **1983**, *95*, 914; *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 878−879.

(5) (a) Rauscher, G.; Clark, T.; Poppinger, D.; Schleyer, P. v. R. *Angew. Chem.* **1978**, *90*, 306; *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 276. (b) Citation 19 in ref 1c.

(6) Maier, G.; Fleischer, F. *Liebigs Ann.* **1995**, 169−172.

(7) Maier, G.; Neudert, J.; Wolf, O. *Angew. Chem.* **2001**, *113*, 1719−1720; *Angew. Chem., Int. Ed.* **2001**, *40*, 1674−1675 (preliminary communication).

(8) Sekiguchi, A.; Tanaka, M.; Matsuo, T.; Watanabe, H. *Angew. Chem.* **2001**, *113*, 1721−1723; *Angew. Chem., Int. Ed.* **2001**, *40*, 1675−1677 (preliminary communication).

(9) Maier, G.; Volz, D.; Neudert, J. *Synthesis* **1992**, 561−564.

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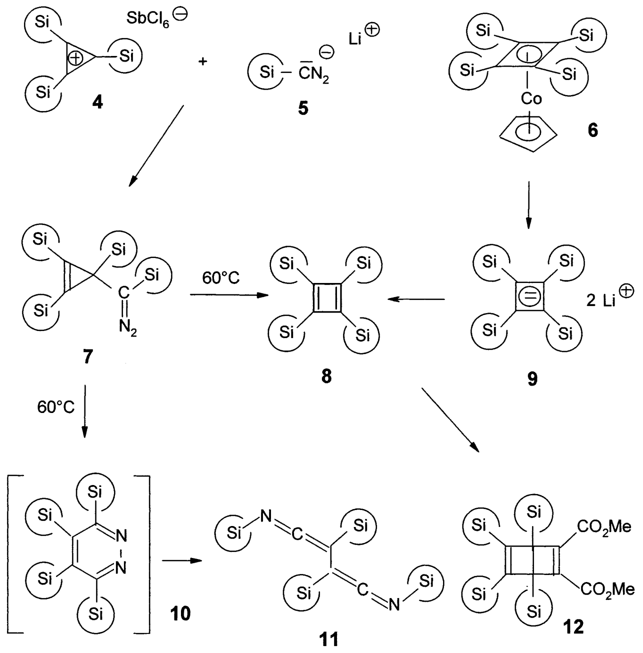
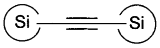


with lithiated (trimethylsilyl)diazomethane **5**. In addition, six further products, **13**−**18**, are formed.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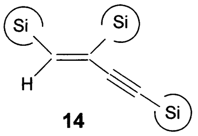
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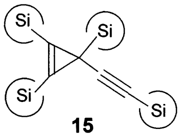
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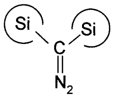
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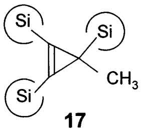
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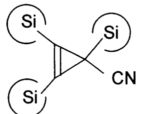
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As is shown below, bis(trimethylsilyl)acetylene **13** and tris(trimethylsilyl)vinylacetylene **14** are typical degradation products of diazo compound **7**. In an independent experiment, we have found that the anion **5** of (trimethylsilyl)diazomethane upon reaction with bis(trimethylsilyl)acetylene **13** yields bis(trimethylsilyl)diazomethane **16** and the anion of (trimethylsilyl)acetylene. This observation explains the formation of side products **15** and **16**. Because anion **5** was prepared by the reaction of (trimethylsilyl)diazomethane with methyllithium,[10] it is no surprise that methylcyclopropene **17** could also be isolated. Again, we prepared this compound separately by the reaction of salt **4** with methyllithium. In an analogous reaction with lithium aluminum hydride, 1,2,3-tris(trimethylsilyl)cyclopropene was formed. Less obvious is the mechanism that leads to 3-cyano-1,2,3-tris(trimethylsilyl)cyclopropene **18**, a compound that was already familiar to us from earlier studies.[11]

Many attempts were needed to find the appropriate conditions for the transformation of **7** into cyclobutadiene **8**. Neither the photochemical[6] nor the CuCl-catalyzed thermal[3] nitrogen elimination succeeded. Irradiation of **7** in benzene with a light of wavelength $\lambda > 300$ nm exclusively yielded acetylene **13**. The same result was observed when **7** was stirred in benzene together with Cu(acac)$_2$ (precipitation of copper) or Cu powder. After treatment of **7** with CuCl in chloroform at 0 °C, a mixture of **13** and vinylacetylene **14** could be isolated. Several rhodium and chromium catalysts had the same effect. The surprisingly easy loss of a trimethylsilyl group during deazotization of **7** during formation of tris(trimethylsilyl)vinylacetylene **14** seems to be a preferred pathway, especially if traces of acids are present. This is substantiated by the observation that **14** is the main product in the reaction of **7** with acids (CF_3CO_2H or gaseous HCl). Presumably, the cyclopropenylcarbinyl cation derived from diazo compound **7** plays a decisive role in this transformation.

However, cyclobutadiene **8** is formed (according to NMR spectroscopic analysis; in 45% yield) upon warming **7** in an inert medium (benzene, cyclohexane, methylcyclohexane) to 60 °C. Surprisingly, bis(ketenimine) **11** is observed as a second product, which means that on thermal excitation diazo compound **7** partly splits off nitrogen, and the carbene thus generated undergoes a ring expansion to cyclobutadiene **8**. Parallel to this reaction, an isomerization of cyclopropenyl diazomethane **7** into tetrakis(trimethylsilyl)pyridazine **10** occurs, which under these reaction conditions immediately undergoes a ring opening accompanied by migration of two trimethylsilyl groups to give 2,3-bis(trimethylsilyl)-1,3-butadienedione-bis(trimethylsilyl)imine **11**. This reaction reminds one of the isomerization of hexakis(trimethylsilyl)benzene to the thermodynamically more stable 1,1,3,4,6,6-hexakis(trimethylsilyl)-1,2,4,5-hexatetraene, reported by Sakurai and Sekiguchi et al.[12] Similarly, according to semiempirical PM3 calculations,[13] bis(ketenimine) **11** is 20 kcal mol^{-1} lower in energy than the aromatic pyridazine **10**.

Both of the thermolysis products **8** and **11** are sensitive to air and moisture. This fact complicates their separation into the pure components. The presence of cyclobutadiene **8** can be proven not only by the NMR spectra, but also by the following experiment: the addition of dimethyl acetylenedicarboxylate to the reaction mixture after the thermolysis of diazo compound **7** enables one to isolate adduct **12**, which at 90 °C quantitatively gives the dimethyl ester of tetrakis(trimethylsilyl)phthalic acid. After evaporation of the solvent of the solution of **8** and **11** in vacuo, it is possible to capture preferentially the more volatile bis(ketenimine) **11** under high vacuum conditions. The IR spectrum of **11**, obtained using this procedure, and measured in an argon matrix at 10 K, showed a band at 2112 cm^{-1}, that is, in a region typical for a ketenimine. Together with the NMR data, and the fact that hydrolysis yields the dinitrile of 2,3-bis(trimethylsilyl)succinic acid,[7] the structure of **11** can be taken as established.

It should be noted that we (German group) tried 20 years ago[2] to prepare cyclobutadiene **8** via our "cyclopentadienone route".[1] However, tetrakis(trimethylsilyl)cyclopentadienone[2] behaved completely differently as compared with the analogous tetra-*tert*-butyl-substituted derivative.[1]

Another candidate molecule for the synthesis of cyclobutadiene **8** could be complex **6**. However, the oxidative liberation of **8** upon treatment of **6** with ammonium cerium(IV) nitrate,[14]

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(10) Colvin, E. W.; Hamill, B. J. *J. Chem. Soc., Perkin Trans.* **1977**, *1*, 869−874.

(11) Volz, D. Doctoral Dissertation, Universität Giessen, 1987.

(12) (a) Sakurai, H.; Ebata, K.; Kabuto, C.; Sekiguchi, A. *J. Am. Chem. Soc.* **1990**, *112*, 1799−1803. (b) Sekiguchi, A.; Ebata, K.; Terui, Y.; Sakurai, H. *Chem. Lett.* **1991**, 1417−1420.

(13) Wolf, O. Doctoral Dissertation, Universität Giessen, 2000.

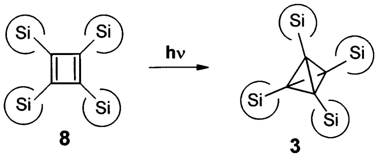
(14) Lage, H. W. Doctoral Dissertation, Universität Giessen, 1982.

used by Pettit et al.[15] in the preparation of the parent cyclobutadiene from the tricarbonyliron complex, and other oxidizing reagents,[16] failed. The situation is dramatically changed if one applies a reductive alternative, as is described in the following.

Cyclobutadiene 8 via Dianion 9. Recently, we (Japanese group) have succeeded in synthesizing the dilithium salt of the tetrakis(trimethylsilyl)cyclobutadiene dianion **9**, the first aromatic cyclobutadiene anion with a six π-electron system, by the reaction of the tetrakis(trimethylsilyl)cyclobutadiene cobalt complex **6** with lithium metal in tetrahydrofuran.[17] The precursor **6** is obtained by the reaction of bis(trimethyl)silylacetylene **13** with $CpCo(CO)_2$[18] or $CpCo(H_2C{=}CH_2)_2$.[19] It was found that dianion **9** is an excellent candidate precursor for cyclobutadiene **8**. This new and easy synthetic route from **9** to **8** consists of a two-electron oxidation reaction. We chose 1,2-dibromoethane ($BrCH_2CH_2Br$) as the oxidizing agent. The reaction of the dilithium salt of the tetrakis(trimethylsilyl)cyclobutadiene dianion **9**, with excess $BrCH_2CH_2Br$ in tetrahydrofuran at room temperature, produced tetrakis(trimethylsilyl)cyclobutadiene **8** in 64% yield. The reaction time (ca. 1 min) was quite important to obtain pure **8**. The Diels–Alder cycloaddition product with ethylene, generated from $BrCH_2CH_2Br$, was also produced at longer reaction times. With dimethyl acetylenedicarboxylate, the 1:1 adduct **12** was obtained in quantitative yield.

Tetrakis(trimethylsilyl)cyclobutadiene **8** was isolated, as air-sensitive pale red crystals, by vacuum sublimation at ca. 80 °C under 0.02 mmHg. Compound **8**, the first cyclobutadiene derivative having four heteroatomic substituents, was characterized by NMR spectroscopy. In the ^{1}H NMR spectrum of **8** in benzene-d_6, only one signal for the methyl groups was observed at $\delta = 0.15$. The ^{29}Si NMR spectrum showed a signal at $\delta = -16.7$, which was shifted downfield relative to that of dianion **9** ($\delta = -23.7$, $\Delta\delta = 7.0$).[17a] In the ^{13}C NMR spectrum of cyclobutadiene **8**, two signals appeared at $\delta = 0.0$ (methyl carbons of $SiMe_3$) and $\delta = 172.1$ (C=C). The signal at $\delta = 172.1$ was also significantly shifted downfield relative to that of dianion **9** ($\delta = 104.1$, $\Delta\delta = 68.0$)[17a] by the two-electron oxidation.

Synthesis of Tetrakis(trimethylsilyl)tetrahedrane 3. The search for tetrahedrane **3** began with **8** prepared by the "cyclopropenyldiazomethane" route. The many attempts to photoisomerize **8** into **3** under variation of wavelength, temperature, and solvent demanded great persistence. Practically all variants led to a fragmentation into two molecules of bis(trimethylsilyl)acetylene **13**. The exception was as follows: long-time irradiation of the mixture of **8** and **11** in deuterated methylcyclohexane at −130 °C in a photoreactor (254 nm) produced signals in the NMR spectra that, in comparison with those measured for **2**,[3] could arise from tetrakis(trimethylsilyl)tetrahedrane **3**. The final proof for the successful photochemically induced transformation of **8** into **3** could be achieved with a pure sample of cyclobutadiene **8** gained by the "dianion" route. Upon irradiation for 70 h under the above-mentioned conditions, the NMR signals of **8** had nearly disappeared. The newly formed NMR signals of practically equal intensities had to be attributed to bis(trimethylsilyl)acetylene **13** [^{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 large upfield shift of the ring C atoms is typical of tetrahedranes.[1,3]



Analogous long-time irradiation of **8** in pentane at −100 °C followed by evaporation of the low-boiling solvent and sublimation of the highly volatile tetrahedrane **3** at 30 °C under 0.02 mmHg allowed its isolation on a preparative scale (ca. 20 mg scale). Recrystallization from ethanol afforded pure **3** as colorless crystals. The tetrahedrane **3** is stable in air and highly soluble in the principal organic solvents (hexane, benzene, acetone, etc.).

Structural Characterization of Tetrakis(trimethylsilyl)tetrahedrane 3. Until now, eight isolable tetrahedranes have been synthesized, the tetra-*tert*-butyl derivative **1** (together with two isotopomers)[1c] and seven additional candidates[20] in which one *tert*-butyl group of **1** is replaced by the following substituents: $SiMe_3$ (**2**),[3] $SiMe_2Ph$,[21] $SiMe_2OCHMe_2$,[21] $SiHMe_2$,[21] $GeMe_3$,[22] $CHMe_2$,[23] and adamantyl.[23] The title compound **3** is the ninth member in this series. Nevertheless, this compound shows some peculiar properties. First, **3** is extremely thermally stable (see below). Second, **3** represents the first example of a tetrahedrane that lies lower in energy than the corresponding cyclobutadiene (see below). Third, for the first time a structural elucidation of a tetrahedrane could be carried out without being confronted with disorder effects.

Until now, X-ray analyses have only been applied to two tetrahedranes. After many unsuccessful attempts with the room-temperature modification of tetra-*tert*-butyltetrahedrane **1** (plastic, i.e., soft and easily deformed crystals), Irngartinger et al.[24a] succeeded in growing a more highly ordered modification at −60 °C. Later, the same authors found that this low-temperature form was stabilized by entrapped N_2 molecules.[24b] The best analysis was achieved with the corresponding Ar-clathrate of **1**.[24b] The bond lengths in the tetrahedron are relatively short (1.497 Å) in comparison with normal single bonds (1.54 Å), a consequence of the bending of the bonds. The deformation

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(15) Watts, L.; Fitzpatrick, J. D.; Pettit, R. *J. Am. Chem. Soc.* **1965**, *87*, 3253–3254.

(16) Neudert, J. Doctoral Dissertation, Universität Giessen, 1992.

(17) (a) Sekiguchi, A.; Matsuo, T.; Watanabe, H. *J. Am. Chem. Soc.* **2000**, *122*, 5652–5653. (b) Matsuo, T.; Mizue, T.; Sekiguchi, A. *Chem. Lett*. **2000**, 896–897. (c) Ishii, K.; Kobayashi, N.; Matsuo, T.; Tanaka, M.; Sekiguchi, A. *J. Am. Chem. Soc.* **2001**, *123*, 5356–5357. (d) Sekiguchi, A.; Matsuo, T.; Tanaka, M. *Organometallics* **2002**, *21*, 1072–1076.

(18) Fritch, J R.; Vollhardt, K. P. C.; Thompson, M. R.; Day, V. W. *J. Am. Chem. Soc.* **1979**, *101*, 2768–2770.

(19) (a) Binger, P.; Milczarek, R.; Mynott, R.; Regitz, M. *J. Organomet. Chem.* **1987**, *323*, C35–C38. (b) Marimoto, Y.; Higuchi, Y.; Wakamatsu, K.; Oshima, K.; Utimoto, K.; Yasuoka, N. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 639–641.

(20) Summaries: (a) Reference 1c. (b) Maier, G.; Rang, H.; Born, D. In *Cage Hydrocarbons*; Olah, G. A., Ed.; Wiley: New York, 1990; pp 219–259. (c) Maier, G.; Wolf, R.; Fleischer, F. *GIT Fachz. Lab*. **1992**, 506–511.

(21) (a) Maier, G.; Wolf, R.; Kalinowski, H.-O. *Angew. Chem.* **1992**, *104*, 764–766; *Angew. Chem., Int. Ed. Engl*. **1992**, *31*, 738–740. (b) Maier, G.; Wolf, R.; Kalinowski, H.-O.; Boese, R. *Chem. Ber.* **1994**, *127*, 191–200.

(22) Maier, G.; Wolf, R.; Kalinowski, H.-O. *Chem. Ber.* **1994**, *127*, 201–207.

(23) Maier, G.; Fleischer, F.; Kalinowski, H.-O. *Liebigs Ann.* **1995**, 173–186.

(24) (a) Irngartinger, H.; Goldmann, A.; Jahn, R.; Nixdorf, M.; Rodewald, H.; Maier, G.; Malsch, K.-D.; Emrich, R. *Angew. Chem.* **1984**, *96*, 967–968; *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 993–994. (b) Irngartinger, H.; Jahn, R.; Maier, G.; Emrich, R. *Angew. Chem.* **1987**, *99*, 356–357; *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 356–357.

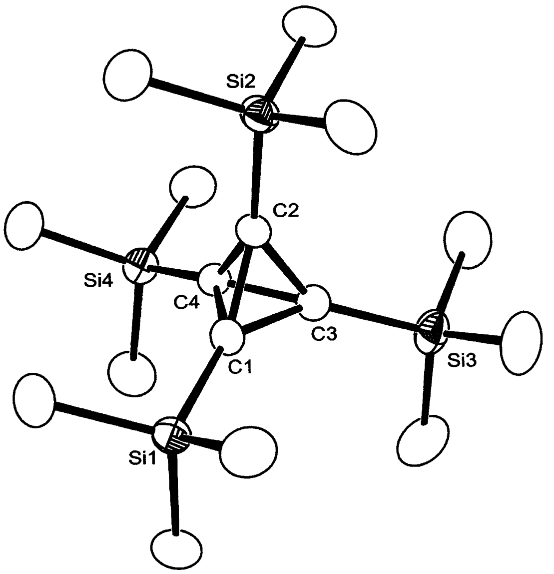

Figure 1. ORTEP drawing of the structure of **3**. The unit cell contains six molecules (two pairs of molecules A, B, and C). Because the three molecules are structurally very similar, an ORTEP drawing of molecule A only is shown.

densities demonstrate a deviation of the bonds by 26°.[24b] Enforced by the rotation of the *tert*-butyl groups, tetrahedrane **1** possesses only T- and not T_d-symmetry. The second molecule studied is tri-*tert*-butyl(dimethylphenylsilyl)tetrahedrane.[21b] Again, disorder phenomena influenced the quality of the structure determination. The tetrahedron skeleton is distorted (C_s-symmetry). The average lengths of the two sets of three bonds each are 1.47 Å (bonds opposite to the carbon atom bearing the silyl substituent) and 1.51 Å (bonds connected with the silyl-substituted ring position). Obviously, the $SiMe_2Ph$ group elongates the tetrahedral bonds pointing to the same ring position. The bond distance from this carbon atom to the silicon atom is 1.81 Å.

These results are nicely confirmed by the structural data of tetrahedrane **3**. Single crystals of **3** suitable for X-ray diffraction were grown from an ethanol solution at 5 °C. The X-ray structure determination was carried out at −120 °C. The unit cell contains six molecules (two pairs of molecules A, B, and C). Because the three molecules are structurally very similar, an ORTEP drawing of molecule A only is shown in Figure 1. Selected bond lengths and bond angles of molecule A are listed in Table 1. The averages of the selected bond lengths of molecules A, B, and C are summarized in Table 2. The C−C bond lengths of the skeleton are 1.495(4)−1.508(4) Å (av. 1.501(4) Å) for molecule A, 1.496(4)−1.510(4) Å (av. 1.502(4) Å) for molecule B, and 1.496(4)−1.510(4) Å (av. 1.502(4) Å) for molecule C, which are similar to those of **1** (av. 1.497 Å). The lengths of the exocyclic C−Si bonds (1.823(3)−1.829(3) Å (av. 1.826(3) Å) for molecule A, 1.816(3)−1.829(3) Å (av. 1.825(3) Å) for molecule B, and 1.817(3)−1.829(3) Å (av. 1.825(3) Å) for molecule C) are appreciably shortened as compared with normal C(sp^3)−Si bond lengths (1.88 Å). The distances are even smaller than the value for C(sp)−Si bond lengths (1.837 Å).[25] The bond lengths between silicon atoms and methyl carbons are normal (av. 1.865(4) Å for molecule A, av. 1.863(4) Å for molecule B, and av. 1.864(4) Å for molecule C).

Table 1. Selected Bond Lengths (Å) and Bond Angles (deg) of **3** (Molecule A)[a]

	Bond Lengths		
C1−C2	1.508(4)	C3−C4	1.500(4)
C1−C3	1.500(3)	C1−Si1	1.826(3)
C1−C4	1.504(4)	C2−Si2	1.823(3)
C2−C3	1.498(4)	C3−Si3	1.826(3)
C2−C4	1.495(4)	C4−Si4	1.829(3)
	Bond Angles		
C2−C1−C3	59.75(17)	C2−C1−Si1	143.1(2)
C2−C1−C4	59.52(17)	C3−C1−Si1	147.1(2)
C3−C1−C4	59.91(17)	C4−C1−Si1	144.3(2)
C1−C2−C3	59.87(17)	C1−C2−Si2	145.2(2)
C1−C2−C4	60.11(17)	C3−C2−Si2	143.4(2)
C3−C2−C4	60.15(17)	C4−C2−Si2	145.5(2)
C1−C3−C2	60.39(17)	C1−C3−Si3	144.9(2)
C1−C3−C4	60.18(17)	C2−C3−Si3	144.5(2)
C2−C3−C4	59.82(17)	C4−C3−Si3	144.6(2)
C1−C4−C2	60.37(17)	C1−C4−Si4	143.2(2)
C1−C4−C3	59.91(17)	C2−C4−Si4	144.5(2)
C2−C4−C3	60.03(17)	C3−C4−Si4	146.2(2)

[a] Atomic numbers are given in Figure 1. Standard deviations are in parentheses.

Table 2. Average of the Selected Bond Lengths (Å) of **3** (Molecules A, B, and C)

	molecule A	molecule B	molecule C	average (A, B, and C)
C−C	1.501(4)	1.502(4)	1.502(4)	1.502(4)
Si−C	1.826(3)	1.825(3)	1.824(3)	1.825(3)
Si−Me	1.865(4)	1.863(4)	1.864(4)	1.864(4)

The electronic situation in **3** can be derived from the NMR spectra. NMR coupling constants represent a spectroscopic quantity with which the electron distribution of the involved bonds can be characterized. By these means, the hybridization of the bonds in tetra-*tert*-butyltetrahedrane **1** could be estimated.[4] The experimental value $^1J_{\mathrm{Cr-Cq}} = 64.0$ Hz for the bond between the ring C-atom and the quaternary C-atom of the *tert*-butyl group is very close to $^1J_{\mathrm{Cacet-Cq}} = 66.1$ in *tert*-butylacetylene. So it can be concluded that the hybrid orbitals pointing in **1** from the Cr to the Cq atoms are practically s,p-hybridized. In good agreement with this observation, the enhanced s-character of the exocyclic C−Si bonds in **3** is also reflected by the NMR data ($^1J_{\mathrm{C-Si}} = 96.1$ Hz), which astonishingly is much larger than that of bis(trimethylsilyl)acetylene **13** ($^1J_{\mathrm{C-Si}} = 78.4$ Hz). The calculated hybridizations of the tetrahedranes C_4R_4 (R = H, Me, SiH_3, $SiMe_3$) at the NBO/B3LYP/6-31G(d) level further support the increased s-character of orbitals directed toward the exocyclic substituents and the higher p-character of the orbitals building up the skeleton on changing from H and Me to SiH_3 and $SiMe_3$: $sp^{1.46}$ (C_4H_4, **19**), $sp^{1.45}$ (C_4Me_4), $sp^{1.26}$ ($C_4(SiH_3)_4$), and $sp^{1.16}$ ($C_4(SiMe_3)_4$, **3**) for the exocyclic C−R bonds; $sp^{4.08}$ (C_4H_4, **19**), $sp^{4.11}$ (C_4Me_4), $sp^{4.39}$ ($C_4(SiH_3)_4$), and $sp^{4.59}$ ($C_4(SiMe_3)_4$, **3**) for the C−C bonds of the skeleton.

Thermal Stability of Tetrakis(trimethylsilyl)tetrahedrane 3. Tetra-*tert*-butyltetrahedrane **1** forms colorless crystals, stable in air and melting at 135 °C with red coloration; that is, at this temperature, **1** is transformed into the valence isomeric cyclobutadiene. In view of a record value of strain enthalpy for **1** (around 130 kcal mol^{-1}; estimated from the comparison of the experimental enthalpy of formation with the calculated value for the strain-free molecule on the basis of group increments[1]),

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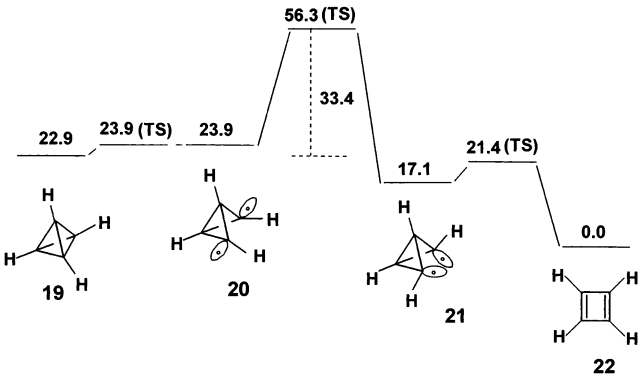
(25) Allen, F. H.; et al. *International Tables for Crystallography*; 1995; Vol. 3.

Scheme 1



this high thermal stability appeared to make a tetrahedrane structure very unlikely. The surprising kinetic stability of **1** was interpreted to be the result of a steric effect (see Introduction). The repulsion between the four bulky groups should be smaller in the case of tetrahedrane **2**, because a C−Si bond is longer than a C−C bond. However, **2** is even more stable than **1**. The melting point of **2**, at which isomerization to the corresponding cyclobutadiene begins, is 179 °C. Hence, an additional, even stronger factor plays a role, the electronic stabilization of the tetrahedron skeleton by the $SiMe_3$ substituent.[3] The higher stability of **2** as compared to **1** was in agreement with calculations [HF/6-31G(d)][3] and was consistent with earlier computational results of Cremer,[26] which illustrate the influence of σ-donors and π-acceptors on the stability of small ring compounds. According to theory, a $SiMe_3$ group should enhance the stability of the tetrahedron skeleton.[26,27]

One should expect that tetrahedrane **3** on thermal excitation isomerizes to the corresponding cyclobutadiene **8**. For the parent compound **19**, the reaction pathway leading to cyclobutadiene **22** was followed computationally already in 1981, using MINDO/3.[28] Newer results (MP2/6-311G**) are presented in Scheme 1.[29] The activation enthalpy for the cleavage of a ring bond in unsubstituted tetrahedrane **19** under formation of *exo*,*exo*-bicyclobutane-2,4-diyl **20** (radical centers pointing outward) is expected to be very small, and the transition state for the ring opening has practically the same energy. So the question arises whether diradical **20** has to be considered at all as an intermediate along the reaction coordinate leading from **19** to **22**. The barrier for the isomerization of **19** into cyclobutadiene **22** is governed by the slow inversion rate of diradical **20** (assuming that it is a real minimum) into the *endo*,*endo* isomer **21**.

What might be the situation in the tetrakis(trimethylsilyl) series? For tetrahedrane **3**, a strong electronic stabilization is expected, originating from the σ-donor effect of the four electropositive $SiMe_3$ groups and the π-acceptor effect of the same substituents (electron donation from the "banana bonds" of the tetrahedral skeleton into the σ*-orbital of the Si−Me bonds). As soon as 1979, Dill et al.[30] calculated the reduction of ring strain in corner-lithiated tetrahedrane by similar additive stabilizing interactions of the hydrocarbon framework with the electropositive lithium atoms. They found a striking reduction in the height of 115.4 kcal mol^{-1}. This value has to be compared with the strain in parent tetrahedrane **19**, which according to calculations on the G2 level of theory amounts to 136 kcal mol^{-1}.[31]

Yet in **3** not only the electronic stabilization should be taken into account. Another important factor might be kinetic hindrance in the ring-opening reaction, caused by the four bulky substituents ("corset effect"). This kinetic stabilization plays a decisive role for tetrahedrane **1** and is documented in the activation parameters for the transformation of **1** into tetra-*tert*-butylcyclobutadiene ($\Delta G^{\ddagger} = 28.6$ kcal mol^{-1}).[1c] Directly after our synthesis of tetrahedrane **1** in 1978, Mislow[32] studied − using a force field approach − not only the interactions of the four *tert*-butyl groups in the system tetra-*tert*-butyltetrahedrane **1**/tetra-*tert*-butylcyclobutadiene but also of the four trimethylsilyl substituents in **3** and **8**. Whereas in the tetra-*tert*-butyl series a strong preference for the tetrahedrane form (by 43.8 kcal mol^{-1}) was found, such an effect was calculated to be practically absent in the system **3**/**8**.

The stabilizing electronic effect of a trimethylsilyl group, already mentioned above for the case of tetrahedrane **2**, finds further support in the observation that the activation energy for the ring cleavage of tri-*tert*-butyl(isopropoxydimethylsilyl)-tetrahedrane is rather high ($E_A = 37-47$ kcal mol^{-1}; derived from the curve of a differential scanning calorimeter).[33]

To get a final answer about the net sum of electronic and steric effects of the four $SiMe_3$ groups in **3** and **8**, we decided to calculate these species at the same level of theory as it was done by Balci, McKee, and Schleyer[34] for the tetra-*tert*-butylated derivatives. They calculated [B3LYP/6-311+G(d)//B3LYP/6-31G(d)] that tetra-*tert*-butyltetrahedrane **1** prefers T over T_d symmetry (as was found before by Mislow[35] using a variety of force fields) and is supposed to be 1.5 kcal mol^{-1} more stable than tetra-*tert*-butylcyclobutadiene. Yet experiment[1] shows that **1** is disfavored in comparison with its valence isomer. Anyway, the energy difference between the two valence isomers must be small.

According to the strong stabilization effect of the $SiMe_3$ groups, the situation in the system **3**/**8** should be different. Indeed, when we calculated in completion of Schleyer's computations[34] the silyl- and trimethylsilyl-substituted derivatives, the power of the "silyl-trick"[1c] became quite obvious. The effect of substituents R (using for comparison purposes the same level as in Schleyer's work) was derived from the homodesmotic reaction formulated in eq 1. The results are quite convincing (Table 3). If a hydrogen atom in tetrahedrane **19** or cycobutadiene **22** is replaced by a methyl, silyl, or trimethylsilyl group, the C_4R_4 molecules are stabilized. The greatest effect is caused by the $SiMe_3$ substituent. In the tetra-*tert*-butyl system, only the tetrahedrane is lowered in energy; the cyclobutadiene isomer

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(26) Cremer, D.; Kraka, E. *J. Am. Chem. Soc.* **1985**, *107*, 3800−3810, 3811−3819.

(27) Minkin, V. I.; Glukhovtsev, M. N.; Simkin, B. Ya. *Aromaticity and Antiaromaticity*; Wiley: New York, 1994.

(28) Kollmar, H.; Carrion, F.; Dewar, M. J. S.; Bingham, C. *J. Am. Chem. Soc.* **1981**, *103*, 5292−5303.

(29) Lautz, C. Doctoral Dissertation, Universität Giessen, 1999.

(30) Dill, J. D.; Greenberg, A.; Liebman, J. F. *J. Am. Chem. Soc.* **1979**, *101*, 1, 6814−6826.

(31) Glukhovtsev, M. N.; Laiter, S.; Pross, A. *J. Phys. Chem.* **1995**, *99*, 6828−6831.

(32) Mislow, K.; Hounshell, W. D., private communication. The collaboration with Prof. Mislow is gratefully acknowledged.

(33) Belichmeier, J. A.; Cammenga, H. K.; Schneider, P. B.; Steer, A. *Thermochim. Acta* **1998**, *310*, 147−151.

(34) Balci, M.; McKee, M. L.; Schleyer, P. V. R. *J. Phys. Chem. A* **2000**, *104*, 1246−1255.

(35) Hounshell, W. D.; Mislow, K. *Tetrahedron Lett.* **1979**, 1205−1208.

Table 3. Effect of Substituent R on Energies (kcal mol^{-1}) and C−C Bond Distances (Å) of C_4R_4 Isomers, Calculated from Reaction 1 at the B3LYP/6-31G(d) Level

C_4R_4	R = H	R = Me	R = *t*-Bu	R = SiH_3	R = $SiMe_3$
tetrahedrane	0	−23.5	−17.1	−45.2	−76.7
	(1.479)	(1.487)	(1.495)	(1.494)	(1.498)
cyclobutadiene	0	−30.6	8.5	−23.8	−43.6
	(1.578)	(1.583)	(1.608)	(1.587)	(1.596)
	(1.334)	(1.341)	(1.354)	(1.355)	(1.361)

Table 4. Relative Energies (kcal/mol) of Cyclobutadienes and Tetrahedranes at the B3LYP/6-31G(d) Level

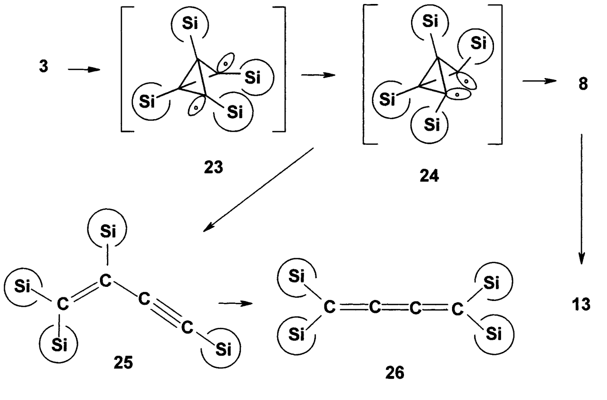
C_4R_4	R = H	R = Me	R = *t*-Bu	R = SiH_3	R = $SiMe_3$
tetrahedrane	24.3	31.4	−1.2	2.9	−8.8
cyclobutadiene	0.0	0.0	0.0	0.0	0.0

experiences a destabilization (in accordance with force field calculations[32]).

$$C_4H_4 + 4\,CH_3R \rightarrow C_4R_4 + 4\,CH_4 \tag{1}$$

From the substituent effects given in Table 4, the relative energies of the substituted tetrahedranes related to the corresponding cyclobutadienes were deduced (in comparison to the parent compounds). It turns out that tetrahedrane **3** should be 8.8 kcal mol^{-1} lower in energy than **8**. Because it can be assumed that the computational error is smaller than this number, **3** turns out to be the first case where the tetrahedrane is preferred to the cyclobutadiene isomer. As a consequence, a peculiar thermal behavior of **3** could be expected.

In the case of tetrahedrane **3**, the *exo,exo* diradical **23** must be formed in the first step, which can then isomerize to the *endo,endo* diradical **24.** This step should be rate determining. Because of the narrowing of the groups in **24**, this step may also be very sensitive to steric repulsion of the large substituents. The sequence should end with the formation of cyclobutadiene **8**.



What is the fate of **3** upon heating? Two observations are remarkable. First, **3** melts at 202 °C without decomposition. Second, neat tetrahedrane **3** is thermally extremely stable. Only at 300 °C does neat **3** begin to react, and bis(trimethylsilyl)acetylene **13** is formed quantitatively. Third, the thermal behavior of **3** is partly different in solution. If the thermolysis is followed in perdeuterated tetracosane at 280 °C spectroscopically by NMR, no signal of cyclobutadiene **8** can be detected. The new signals which slowly appear belong to tetrakis(trimethylsilyl)vinylacetylene **25**[36] (main product) and bis(trimethylsilyl)acetylene **13**. After 2.5 h, the signals of tetrakis(trimethylsilyl)butatriene **26**[18,19] appear. At the same time, the signals of **25** diminish. It takes almost 11 h until tetrahedrane **3** has disappeared completely. One day later, only the signals of mainly butatriene **26** and a small amount of acetylene **13** are observed. The same sequence was followed upon a more preparative scale. Heating of 49 mg of **3** in tetracosane at 260 °C for 9 h produced 50% vinylacetylene **25**, 19% butatriene **26**, and 31% acetylene **13**. Surprisingly, thermolysis of **8** in tetracosane yielded only bis(trimethylsilyl)acetylene **13**. Neither **25** nor **26** was found. Therefore, cyclobutadiene **8** cannot be an intermediate in the transformation of tetrahedrane **3** into **25** and **26**.

As far as the mechanism of the thermal ring opening of **3** in solution is concerned, one can assume that the first step is the central bond cleavage of **3** leading to diradical **23**. Now two reaction pathways can compete. One alternative is that **23** isomerizes to diradical **24**, which undergoes the additional bond cleavage to give **8**. Because cyclobutadiene **8** is higher in energy than tetrahedrane **3**, it cannot be detected, but produces exclusively bis(trimethylsilyl)acetylene **13**. The second pathway involves the cleavage of two strained C−C bonds in **23** or **24**, followed by 1,3-migration of a trimethylsilyl group in the thus formed tetrakis(trimethylsilyl)butadiene-diradical, generating tetrakis(trimethylsilyl)vinylacetylene **25**. Again there is a parallel in the parent series: matrix irradiation of the dimer of acetylene generates 1,3-butadiene-1,4-diyl, which leads to vinylacetylene by a 1,3 hydrogen shift.[37] Finally, vinylacetylene **25** is thermally transformed into butatriene **26**.[38] This step **25** → **26** is no surprise. It is a common observation that trimethylsilyl groups prefer vinylic positions. For instance, tetrakis(trimethylsilyl)butatriene **26** is the only product when tetrakis(trimethylsilyl)cyclopentadienone is irradiated in an organic matrix.[2]

Conclusions

Irradiation of tetrakis(trimethylsilyl)cyclobutadiene **8**, which has been synthesized by the German and Japanese group using two completely different routes, at low temperature for a long time affords tetrakis(trimethylsilyl)tetrahedrane **3**. The properties of **3** are absolutely opposite to the expectation for the unsubstituted tetrahedrane **19**, for which an extremely high strain energy is predicted.

Experimental Section

General. Tsukuba: ^{1}H NMR spectra were recorded on a Bruker AC-300 FT spectrometer. ^{13}C and ^{29}Si NMR spectra were collected on a Bruker AC-300 at 75.5 and 59.6 MHz, respectively. High-resolution mass spectra (HRMS) were obtained on a JMS-SX 102A. Tetrahydrofuran and hexane were dried and distilled from sodium benzophenone ketyl. These solvents were further dried and degassed over a potassium mirror in vacuo prior to use. 1,2-Dibromoethane was dried over molecular sieves and then over calcium hydride. Commercially available lithium rod (99.9%, Mitsuwa's Pure Chemicals) was pressed out from a stainless steel bottle with a hall to make the lithium wire (diameter ca. 1 mm), which was cut into small pieces under argon flow just before use. Giessen: ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker

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(36) Kusumoto, T.; Hiyama, T. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 3103−3110.
(37) Maier, G.; Lautz, C. *Eur. J. Org. Chem.* **1998**, *769*, 9−776.
(38) At this moment, it is not obvious why thermolysis of molten tetrahedrane **3** differs from that in solution.

AC-200 and AM-400 FT spectrometer. Mass spectra were obtained on a Varian Mat 111 and 311-A.

Trimethylsilyl[1,2,3-tris(trimethylsilyl)-2-cycloprop-1-enyl]diazomethane 7. To the yellow solution of (trimethylsilyl)diazomethane (9.9 mmol) in 120 mL of dry ether was added methyllithium (10.5 mmol) at 0 °C under argon. After 30 min, the temperature was lowered to −90 °C, and tris(trimethylsilyl)cyclopropenylium hexachloroantimonate **4** (6.0 g, 10.17 mmol) was added. The dark brown mixture was warmed slowly to −20 °C, and diisopropylamine (269 mg, 2 mmol) and pentane (200 mL) were added. The crude product was washed two times with 300 mL of ice-cold saturated NaCl solution and two times with water, and was then separated from the water. Removal of the solvent in vacuo at 0 °C gave a yellow crude product, which on high vacuum evaporation yielded bis(trimethylsilyl)acetylene **13** (390 mg, 23.2%) and bis(trimethylsilyl)diazomethane **16** (225 mg, 12.2%). The residue was separated by chromatography (aluminum oxide neutral, low activity, −25° C, pentane) to give five fractions:

Trimethylsilyl[1,2,3-tris(trimethylsilyl)-2-cycloprop-1-enyl]diazomethane 7 (390 mg, 10.7%) as a yellow oil. ^{1}H NMR (CDCl$_3$): δ −0.03 (s, 9H, SiMe$_3$), 0.15 (s, 9H, SiMe$_3$), 0.26 (s, 18H, SiMe$_3$). ^{13}C NMR (toluene-*d*$_8$): δ −0.4, −0.35, −0.1 (SiMe$_3$), 16.5 (quart. C), 38.6 (C═N$_2$), 141.1 (C═C). IR (film): 2960, 2900, 2020, 1705, 1250, 840 cm^{-1}. MS: *m*/*z* 368 (M$^+$), 340 (M$^+$ − N$_2$), 255, 155, 73 (SiMe$_3$). HRMS calcd for $C_{16}H_{36}N_2Si_4$ 368.1898, found 368.1955.

Tris(trimethylsilyl)vinylacetylene 14 (410 mg, 15.5%) as a colorless liquid. ^{1}H NMR (CDCl$_3$): δ 0.11 (s, 9H, SiMe$_3$), 0.16 (s, 18H, SiMe$_3$), 6.54 (s, 1H, ═CH). ^{13}C NMR (CDCl$_3$): δ −2.1, −1.0, −0.1 (SiMe$_3$), 103.7, 107.1, 145.4, 155.4. IR (CCl$_4$): 2960, 2900, 2130, 1405, 1250, 1050, 845 cm^{-1}. MS: *m*/*z* 268 (M$^+$), 253 (M$^+$ − CH$_3$), 195 (M$^+$ − SiMe$_3$), 180, 165, 155, 73 (SiMe$_3$). HRMS calcd for $C_{13}H_{28}Si_3$ 268.1499, found 268.1508.

[1,2,3-Tris(trimethylsilyl)-2-cyclopropen-1-yl](trimethylsilyl)acetylene 15 (460 mg, 13.1%) as a colorless liquid. ^{1}H NMR (CDCl$_3$): δ −0.03 (s, 9H, SiMe$_3$), 0.05 (s, 9H, SiMe$_3$), 0.24 (s, 18H, SiMe$_3$). ^{13}C NMR (CDCl$_3$): δ −2.3, −1.1, 0.5 (SiMe$_3$), 6.1 (quart. C), 73.9, 117.8 (acetylenic C), 132.2 (C═C). IR (film): 2980, 2945, 2135, 1745, 1255, 845 cm^{-1}. MS: *m*/*z* 352 (M$^+$), 337 (M$^+$ − CH$_3$), 264, 249, 155, 73 (SiMe$_3$). HRMS calcd for $C_{17}H_{36}Si_4$ 352.1894, found 352.1882.

3-Cyano-1,2,3-tris(trimethylsilyl)cyclopropene 18 (250 mg, 9%) as colorless crystals. ^{1}H NMR (CDCl$_3$): δ 0.1 (s, 9H, SiMe$_3$), 0.35 (s, 18H, SiMe$_3$). ^{13}C NMR (CDCl$_3$): δ −2.4, −1.5 (SiMe$_3$), 1.1 (quart. C), 126.6 (CN), 127.5 (C═C). IR (CCl$_4$): 2200, 1750, 1250, 850 cm^{-1}. HRMS calcd for $C_{13}H_{27}NSi_3$ 281.1451, found 281.1473. In some cases, cyclopropene **17** was found.

3-Methyl-1,2,3-tris(trimethylsilyl)cyclopropene 17 could also be prepared in the following way: To a suspension of tris(trimethylsilyl)cyclopropenylium hexachloroantimonate **4** (100 mg, 0.17 mmol) in 3 mL of dry ether was added methyllithium (0.32 mmol) under argon at −78° C. After the mixture was stirred for 15 min, the temperature was raised to 0 °C, and a small amount of water was added. The residue was extracted with ether, dried over MgSO$_4$, and the solvent was evaporated. High vacuum distillation gave the cyclopropene **17** (30 mg, 65%) as a colorless liquid. ^{1}H NMR (CDCl$_3$): δ 0.11 (s, 9H, SiMe$_3$), 0.14 (s, 18H, SiMe$_3$), 0.92 (s, 3H, CH$_3$). ^{13}C NMR (CDCl$_3$): δ −2.00, −0.65 (SiMe$_3$), 10.92 (quart. C), 25.8 (CH$_3$), 141.84 (C═C). IR (film): 2970, 2915, 2860, 1715, 1255, 840 cm^{-1}. MS: *m*/*z* 270 (M$^+$), 255 (M$^+$ − CH$_3$), 197 (M$^+$ − SiMe$_3$), 73 (SiMe$_3$). HRMS calcd for $C_{13}H_{30}Si_3$ 270.1640, found 270.1655.

1,2,3-Tris(trimethylsilyl)cyclopropene. To a suspension of tris(trimethylsilyl)cyclopropenylium hexachloroantimonate **4** (140 mg, 0.24 mmol) in 15 mL of dry ether was added lithium aluminum hydride (10 mg, 0.26 mmol) under argon. After being stirred for 30 min, the mixture was cooled to 0 °C and hydrolyzed with water. The residue was filtered, washed with 20 mL of ether, and dried over MgSO$_4$. The solvent was evaporated, and high vacuum distillation gave 1,2,3-tris(trimethylsilyl)cyclopropene (50 mg, 81%) as a pale yellow liquid. ^{1}H NMR (CDCl$_3$): δ −0.15 (s, 9H, SiMe$_3$), −0.06 (s, 1H, CH, proved by COSY experiment), 0.15 (s, 18H, SiMe$_3$). ^{13}C NMR (CDCl$_3$): δ −1.5, −1.1 (SiMe$_3$), 5.8 (CH), 132.7 (C═C). IR (film): 2960, 2900, 1730, 1250, 840 cm^{-1}. MS: *m*/*z* 256 (M$^+$), 241 (M$^+$ − CH$_3$), 183 (M$^+$ − SiMe$_3$), 168, 153, 73 (SiMe$_3$). HRMS calcd for $C_{12}H_{28}Si_3$ 256.1499, found 256.1513. These spectroscopic data differ from those reported by Garratt.[39]

Tetrakis(trimethylsilyl)cyclobutadiene 8 (via Diazo Compound 7). A sample of diazomethane **7** (30 mg, 0.0815 mmol) in 1 mL of benzene-*d*$_6$ or methylcyclohexane-*d*$_{14}$ was degassed in a tube by four vacuum freeze−thaw cycles, and then the tube was sealed under argon. Heating to 60 °C for 8 h gave a red-brown solution of **8** (according to NMR spectroscopy analysis 45% yield) and the bis(ketenimine) **11**.

Tetrakis(trimethylsilyl)cyclobutadiene 8. ^{1}H NMR (C$_7$D$_{14}$): δ 0.09 (s, 36H, SiMe$_3$). ^{13}C NMR (C$_7$D$_{14}$): δ 0.08 (SiMe$_3$), 171.59 (C═C). MS: *m*/*z* 340 (M$^+$), 268 (M$^+$ − SiMe$_3$). Under high vacuum conditions, it is possible to capture preferentially imine **11**.

2,3-Bis(trimethylsilyl)-1,3-butadienedione-bis(trimethylsilyl)imine 11 was isolated as a colorless oil. ^{1}H NMR (C$_6$D$_6$): δ 0.20 (s, 18H, SiMe$_3$), 0.35 (s, 18H, SiMe$_3$). ^{13}C NMR (C$_6$D$_{12}$): δ 0.4, 0.5 (SiMe$_3$), 26.3 (*C*═C═N), 177.1 (C═*C*═N). IR (argon-matrix, 10 K): 2961.4, 2907.0, 2112.1, 1254.7, 1249.0, 863.8, 839.2, 754.5, 747.5 cm^{-1}. MS: *m*/*z* 368 (M$^+$), 296 (M$^+$ − SiMe$_3$), 73 (SiMe$_3$). HRMS calcd for $C_{16}H_{36}N_2Si_4$ 368.1956, found 368.1963.

2,3-Bis(methoxycarbonyl)-1,4,5,6-tetrakis(trimethylsilyl)bicyclo[2.2.0]hexa-2,5-diene 12. Diazomethane **7** (162 mg, 0.44 mmol) in 1.5 mL of benzene-*d*$_6$ was heated to 70 °C for 100 min. The red-brown solution was cooled to room temperature, and dimethyl acetylenedicarboxylate (0.7 mL, 0.57 mmol) in 2 mL of benzene-*d*$_6$ was added under argon. Upon stirring for 1.5 h, the color changed to yellow, and purification by HPLC (first run: CN-phase, 10% *tert*-butylmethyl ether/90% hexane; second run: CN-phase, 5% *tert*-butylmethyl ether/95% hexane) gave **12** as colorless crystals (16.7 mg, 0.0346 mmol), mp 95 °C. ^{1}H NMR (CDCl$_3$): δ 0.20 (s, 18H, SiMe$_3$), 0.21 (s, 18H, SiMe$_3$), 3.56 (s, 6H, OCH$_3$). ^{13}C NMR (CDCl$_3$): δ 1.3, 1.5 (SiMe$_3$), 51.3 (OCH$_3$), 65.3 (C$_1$,C$_4$), 148.0 (C═C), 163.0 (C═C), 171.9 (CO). IR (KBr): 2950.5, 2901.4, 2840.2, 1716, 1625.9, 1262.8, 1108.8, 843.3 cm^{-1}. MS: *m*/*z* 482 (M$^+$), 467 (M$^+$ − CH$_3$), 451 (M$^+$ − OCH$_3$), 409 (M$^+$ − SiMe$_3$). HRMS calcd for $C_{22}H_{42}O_4Si_4$ 482.2160, found 482.2130.

Dimethyl Tetrakis(trimethylsilyl)phthalate. Dewarbenzene **12** (10 mg) was heated to 90 °C for 5.5 h. The phthalate was obtained quantitatively as colorless crystals, mp 165 °C. ^{1}H NMR (CDCl$_3$): δ 0.28 (s, 18H, SiMe$_3$), 0.32 (s, 18H, SiMe$_3$), 3.79 (s, 6H, OCH$_3$). ^{13}C NMR (CDCl$_3$): δ 3.4, 4.6 (SiMe$_3$), 52.2 (OCH$_3$), 135.7, 144.9, 166.9 (C═C), 171.3 (CO). IR (KBr): 2992.6, 2949.2, 2902.7, 1733.4, 1250.0, 1105.9, 847.1 cm^{-1}. MS: *m*/*z* 482 (M$^+$), 467 (M$^+$ − CH$_3$), 451 (M$^+$ − OCH$_3$), 409 (M$^+$ − SiMe$_3$). HRMS calcd for $C_{22}H_{42}O_4Si_4$ 482.2160, found 482.2180.

Tetrakis(trimethylsilyl)cyclobutadiene 8 (via Dianion 9). The crystals of tetrakis(trimethylsilyl)cyclobutadiene cobalt complex **6** (3.0 g, 6.5 mmol) and an excess amount of lithium metal (1.0 g, 0.14 mol) were placed in a reaction tube with a magnetic stirrer and degassed. Dry oxygen-free THF (30 mL) was introduced by vacuum transfer, and the mixture was stirred at room temperature for 24 h to give a dark brown solution containing tetrakis(trimethylsilyl)cyclobutadiene dianion **9**. The solvent was evaporated, and then degassed hexane (40 mL) was introduced by vacuum transfer. After the filtration of the residual lithium pieces and insoluble dark materials in a glovebox, degassed THF (10 mL) and 1,2-dibromoethane (2.1 g, 11 mmol) were introduced by vacuum transfer. The mixture was stirred for a short time (ca. 1 min). The solvent was removed in vacuo, and then again degassed hexane (5 mL) was introduced by vacuum transfer. After

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(39) Garratt, P. J.; Tsotinis, A. *J. Org. Chem.* **1990**, *55*, 84−88.

lithium bromide was filtered off in a glovebox, the filtrate was concentrated. The resulting residue was sublimated at 80 °C under 0.02 mmHg to afford pale red crystals of **8** (350 mg, 15%). When the reaction was carried out after the isolation of **9**, the yield of **8** increased to 64%, mp 122−123 °C. ^{1}H NMR (C_6D_6): δ 0.15 (s, 36H, $SiMe_3$). ^{13}C NMR (C_6D_6): δ 0.0 ($SiMe_3$), 172.1 (C=C). ^{29}Si NMR (C_6D_6): δ −16.7. UV/vis λ_{max} (hexane): 226, 452 nm. HRMS calcd for $C_{16}H_{36}Si_4$ 340.1894, found 340.1891.

Tetrakis(trimethylsilyl)tetrahedrane 3. The crystals of **8** (200 mg, 0.58 mmol) were placed in a quartz reaction tube. Dry oxygen-free pentane (2.0 mL) was introduced by vacuum transfer, and the tube was sealed. The solution was irradiated with a low-pressure mercury lamp (λ = 254 nm) at −100 °C for 70 h to give a mixture of tetrakis(trimethylsilyl)tetrahedrane **3** (~50%), tetrakis(trimethylsilyl)butatriene (**26**, ~5%), and bis(trimethylsilyl)acetylene (**13**, ~45%; determined by ^{1}H NMR). After the solvent was removed in vacuo, the resulting residue was sublimated at 30 °C under 0.02 mmHg to give crude crystals of **3**. Recrystallization from ethanol afforded pure **3** (20 mg, 10%) as colorless crystals, mp 202 °C. ^{1}H NMR (C_6D_6): δ 0.10 (s, 36H, $SiMe_3$). ^{13}C NMR (C_6D_6): δ −20.46 (ring C), −0.03 ($SiMe_3$). ^{29}Si NMR (C_6D_6): δ −1.55. HRMS calcd for $C_{16}H_{36}Si_4$ 340.1894, found 340.1889.

Thermolysis of Tetrakis(trimethylsilyl)tetrahedrane 3. (a) In substance. The crystals of **3** (10 mg, 0.029 mmol) were placed in a reaction tube and sealed. The tetrahedrane **3** remained unchanged when the tube was heated at 250 °C for 15 h. Heating at 300 °C for 10 h produced bis(trimethylsilyl)acetylene **13** quantitatively. (b) In solution. The crystals of **3** (49 mg, 0.14 mmol) and tetracosane (300 mg, 0.89 mmol) were placed in a reaction tube. After the reaction tube had been degassed, the tube was sealed. Upon heating at 260 °C for 9 h, the tetrahedrane **3** was transformed into tetrakis(trimethylsilyl)vinylacetylene[36] **25** (50%), tetrakis(trimethylsilyl)butatriene[19] **26** (19%), and bis(trimethylsilyl)acetylene **13** (31%). Compound **25**, ^{1}H NMR ($CDCl_3$): δ 0.15 (s, 9H, $SiMe_3$), 0.20 (s, 9H, $SiMe_3$), 0.25 (s, 9H, $SiMe_3$), 0.26 (s, 9H, $SiMe_3$). ^{13}C NMR ($CDCl_3$): δ −0.3 (CH_3), 1.7 (CH_3), 2.0 (CH_3), 3.0 (CH_3), 106.9 (C), 110.2 (C), 156.1 (C), 176.8 (C). ^{29}Si NMR ($CDCl_3$): δ −19.1, −6.7, −6.4, −6.3. The vinylacetylene **25** was thermally isomerized to **26** upon prolonged heating.

Thermolysis of Tetrakis(trimethylsilyl)cyclobutadiene 8. The crystals of **8** (20 mg, 0.06 mmol) and tetracosane (200 mg, 0.59 mmol) were placed in a reaction tube. After the reaction tube had been degassed, the tube was sealed. Upon heating at 250 °C for 1 h, the cyclobutadiene **8** was quantitatively transformed into bis(trimethylsilyl)acetylene **13**. Neither **25** nor **26** was found.

X-ray Structure Determination of 3. Single crystals of **3** suitable for X-ray diffractions were grown from an ethanol solution at 5 °C. A single crystal of **3** with approximate dimensions of 0.35 × 0.20 × 0.15 mm was mounted by a nylon loop, which was set on a Rigaku Mercury CCD system with graphite monochromatized Mo Kα radiation (λ = 0.71070 Å) under a cold nitrogen stream. The structure was solved by the direct method and refined on F^2 by the full-matrix least-squares method using the Crystal Structure software package. Anisotropic refinement was applied to all non-hydrogen atoms, and all of the hydrogen atoms were put at calculated positions. Crystal data for **3** at 153 K: MF = $Si_4C_{16}H_{36}$, FW = 340.80, triclinic $a = 9.7923(8)$, $b = 14.5753(11)$, $c = 25.180(2)$ Å, $\alpha = 89.960(7)$, $\beta = 89.964(7)$, $\gamma = 89.928(7)$, $V = 3593.8(4)$ Å^3, space group = P-1 (No. 2), $Z = 6$, $d_{calc} = 0.945$ g cm^{-3}. The final R factor was 0.0710 for 15 686 reflections with $I > 2\sigma(I)$ and wR_2 = 0.1880 for all data; GOF = 1.034.

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

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