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Synthesis and Structure of Air-Stable *trans*-1,1,4,4-Tetrakis(trimethylsilyl)-1,3-butadiene

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The reaction of $(CH_3)_3SiC{\equiv}CSi(CH_3)_3$ and B_5H_9 at 135–140 °C in a stainless-steel reactor produced the title compound III as an air-stable solid, along with the known compounds $\{[(CH_3)_3SiCH{=}CSi(CH_3)_3]_2BH\}_2$ (I) and *nido*-$[(CH_3)_3Si]_2C_2B_4H_6$ (II). Compound III was characterized by IR, mass, and ^1H, ^{13}C, and ^{29}Si NMR spectra and by single-crystal X-ray diffraction. Compound III crystallizes in the triclinic space group $P\bar{1}$ (no. 2) with $a = 6.466$ (1) Å, $b = 9.073$ (2) Å, $c = 10.965$ (2) Å, $\alpha = 74.29$ (2)°, $\beta = 85.72$ (1)°, $\gamma = 71.90$ (1)°, $U = 589$ (1) Å^3, and $Z = 1$. Final refinement converged at values $R = 0.0602$ and $R_w = 0.0699$. Under similar conditions, the pyrolysis of $[(CH_3)_3SiCH{=}CSi(CH_3)_3]_3B$ failed to produce III.

Introduction

A wide variety of alkenylsilanes, alkynylsilanes, and arylsilanes have been synthesized.[1] In most cases, spectroscopic data and theoretical calculations fail to provide enough information concerning the geometry of such derivatives. At present, X-ray diffraction is the method of choice for the characterization of silyl-substituted alkene derivatives.[2] Recently, the controversy concerning the geometry of 1,4-cyclohexadiene derivatives[3] has been resolved by the synthesis and crystal structure of *cis-* and *trans*-1,4-bis(trimethylsilyl)hexamethyl-1,4-disilacyclohexa-2,5-diene.[4] This provided an unambiguous proof of their preferred conformational geometries; the cis isomer has a slightly twisted boat conformation and the trans isomer adopts a nearly planar conformation.[4]

Another group of interesting silicon compounds, which has received much attention, is the trimethylsilyl-substituted 1,3-butadienes. The isomeric 1,2-, 1,4-, and 2,3-bis(trimethylsilyl)-1,3-butadienes and 1,1,3,4-tetrakis(trimethylsilyl)-1,3-butadiene have been synthesized by Bock and Seidl.[5] These workers determined the vertical ionization energies, characteristic vibrational frequencies, ^1H NMR spectra, half-wave reduction potentials, radical-anion ESR coupling constants, and electronic transitions for these compounds. However, attempts to synthesize 1,1,4,4-tetrakis(trimethylsilyl)-substituted 1,3-butadiene were unsuccessful. In addition, no crystal structures for any of these derivatives have been reported. We report herein the synthesis, spectroscopic data, and crystal structure of *trans*-1,1,4,4-tetrakis(trimethylsilyl)-1,3-butadiene.

Experimental Section

Materials. Pentaborane(9) was obtained from Callery Chemical Co., Callery, PA, and was checked for purity by IR spectroscopy and vapor pressure measurements before use. Bis(trimethylsilyl)acetylene (Petrarch Systems, Inc., Bristol, PA) was also checked for purity by IR, NMR, and vapor pressure measurements. Tris[1,2-bis(trimethylsilyl)ethenyl]borane was prepared by using the method described elsewhere.[6] All solvents were dried over 4–8 mesh molecular sieve (Davidson) and either saturated with dry argon or degassed before use. All other reagents were commercially obtained and used as received.

Instrumentation. Proton, boron-11, carbon-13, and silicon-29 pulse Fourier-transform NMR spectra at 200.13, 64.2, 50.3, and 39.76 MHz, respectively, were recorded on an IBM-200SY multinuclear NMR spectrometer. Unit resolution mass spectra were obtained on a Du Pont GC/mass spectrometer Model 321. Infrared spectra were recorded on a Perkin-Elmer Model 283 infrared spectrometer. Elemental analyses were obtained from Galbraith Laboratories, Knoxville, TN. The molecular weight determinations were made on Wescan Model 233 molecular weight apparatus.

X-ray Analysis of III. Large well-formed clear colorless crystals of III were grown by sublimation onto a glass surface. A suitable single crystal of dimensions 0.3 × 0.3 × 0.2 mm was glued to a glass fiber and mounted on an Enraf-Nonius CAD4-F diffractometer. Initial lattice parameters were determined from a least-squares fit to 15 accurately centered reflections $10.0 \leq 2\theta \leq 24.0°$ and subsequently refined using higher angle data. These indicated a triclinic lattice. Data were collected for one hemisphere, $+h{\pm}k{\pm}l$, using the ω–2θ scan method. The final scan speed for each reflection was determined from the net intensity gathered during an initial prescan and ranged from 2 to 7° min^{-1}. The ω-scan angle was determined for each reflection according to the

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Table I. Mass Spectrometric Data of III (EI, 70 eV)

m/e	% rel intensity	most intense peak	ion
345, 344, 342	2.06, 4.72, 15.78	342	$[(^{12}CH_3)_3{}^{28}Si]_2{}^{12}C{=}{}^{12}CH^{12}CH{=}{}^{12}C[^{28}Si(^{12}CH_3)_3]_2{}^+$
271, 270, 269, 268	2.07, 5.23, 15.40, 8.68	269	$[(^{12}CH_3)_3{}^{28}Si]_2{}^{12}C{=}{}^{12}CH^{12}CH{=}{}^{12}C[^{28}Si(^{12}CH_3)_3]^+$
256, 255, 254, 253	3.58, 7.49, 25.49, 7.49	254	$[(^{12}CH_3)_3{}^{28}Si]_2{}^{12}C{=}{}^{12}CH^{12}CH{=}{}^{12}C[^{28}Si(^{12}CH_3)_2]^+$
242, 241, 240, 239, 237	2.33, 14.80, 25.53, 46.12, 1.15	239	$[(^{12}CH_3)_3{}^{28}Si]_2{}^{12}C{=}{}^{12}CH^{12}CH{=}{}^{12}C[^{28}Si(^{12}CH_3)]^+$
197, 196, 195	1.69, 2.90, 16.17	195	$[(^{12}CH_3)_3{}^{28}Si]_2{}^{12}C{=}{}^{12}CH^{12}C{\equiv}{}^{12}C^+$
184, 183, 182, 181, 179	1.06, 9.20, 19.17, 50.00, 3.02	181	$[(^{12}CH_3)_2{}^{28}Si][(^{12}CH_3)_3{}^{28}Si]^{12}C{=}{}^{12}CH^{12}C{\equiv}{}^{12}CH^+$
169, 168, 167, 166, 165, 163	1.07, 0.86, 2.52, 5.01, 14.20, 0.69	165	$[(^{12}CH_3)^{28}Si][(^{12}CH_3)_3{}^{28}Si]^{12}C{=}{}^{12}CH^{12}C{\equiv}{}^{12}C^+$
157, 156, 155, 153	5.96, 7.23, 31.50, 1.58	155	$[(^{12}CH_3)^{28}Si][(^{12}CH_3)_3{}^{28}Si]^{12}C{=}{}^{12}CH^{12}CH_2{}^+$
85, 84, 83, 81	5.0, 3.86, 25.21, 1.42	83	$(^{12}CH_3)_2{}^{28}Si^{12}C{\equiv}{}^{12}CH^+$
75, 73	25.18, 100.00	73	$(^{12}CH_3)_3{}^{28}Si^+$
60, 59, 58, 57	2.44, 28.74, 8.32, 6.17	59	$(^{12}CH_3)_2{}^{28}SiH^+$
47, 46, 45, 44, 43	5.77, 10.05, 45.62, 19.28, 29.80	45	$(^{12}CH_3)^{28}SiH_2{}^+$

equation $A + B \tan\theta$ for which A and B were set at values 0.8 and 0.35°, respectively. Aperture settings were derived in a like manner with A = 4.0 and B = 1.0 mm. Two check reflections were measured every 30 min throughout the 28.5 h of data collection and showed a linear decay of 15.4%.

Data were corrected for the effects of Lorentz, polarization, and decay, but not for absorption (μ = 2.4 cm^{-1}). Merging of equivalent and duplicate reflections gave a total of 1862 unique measured data for which 1329 were considered observed, $I > 3.0\sigma(I)$. The structure was solved by using the direct methods program MULTAN, which revealed the positions of most of the non-hydrogen atoms. All others were revealed in a subsequent difference Fourier synthesis. The molecule resides on a crystallographic center of inversion confirming the choice of $P\bar{1}$ as the space group. All non-hydrogen atoms were refined by using anisotropic thermal parameters. Hydrogen atoms were placed in calculated positions, 0.95 Å from their respective carbon atoms, and included in the structure factor calculations. Final refinement using full-matrix, least-squares converged smoothly to values of R = 0.0602 and R_w = 0.0699. The highest peak in the final difference Fourier map was 0.0295 e/Å^3.

Synthetic Procedures. Except where otherwise indicated, all operations were conducted in vacuo. All room-temperature experiments were carried out in Pyrex glass round-bottom flasks of 250-mL capacity, containing a magnetic stirring bar, and fitted with high-vacuum Teflon valves. All high-temperature experiments were carried out in stainless-steel single ended cylinders of 500 mL capacity (obtained from Tech Controls, Inc., Dallas, TX) fitted with forged body shut-off valves of $^1/_4$ in. male npt and $^1/_4$ in. Swagelok fittings (obtained from Texas Valve and Fitting Co., Dallas, TX). Nonvolatile substances were manipulated in evacuable glovebags under an atmosphere of dry argon.

All known compounds among the products were identified by comparing their infrared and ^{1}H NMR spectra with those of authentic samples.

Synthesis of *trans*-1,1,4,4-Tetrakis(trimethylsilyl)-1,3-butadiene. Pentaborane (6.40 g, 100 mmol) and bis(trimethylsilyl)acetylene (78.0 g, 459 mmol) were condensed at −196 °C into a 500-mL single-ended stainless-steel reactor fitted with a high vacuum (10^{-6} torr) Swagelok shut-off valve. Extreme care was taken to keep the upper end of the reactor at room temperature by occasional warming with a heat gun during the condensation of the reactants. The mixture was later warmed to room temperature, after which the *lower half* of the reactor was immersed in an oil bath maintained at a temperature of 135–140 °C. The heating was continued for 48 h. After the mixture was cooled to −196 °C, accumulated noncondensable gas, presumably H_2 (4.00 mmol) was pumped out. After the most volatile products were transferred from the reactor into a vacuum line trap at −196 °C, the remaining mixture was heated to 70 °C. A low volatile, colorless liquid was distilled into a vacuum line trap at −78 °C over a period of 24 h. All the distillable and/or volatile products were transferred to the main vacuum line traps and were mixed and fractionated through traps, as described elsewhere,[6] to collect $\{[(CH_3)_3SiCH{=}CSi(CH_3)_3]_2BH\}_2$ (I) (0.81 g, 1.14 mmol), *nido*-$[(CH_3)_3Si]_2C_2B_4H_6$ (II) (12.67 g, 57.6 mmol), $(CH_3)_3SiH$ (90.0 mmol), and unreacted starting materials, B_5H_9 (20.0 mmol) and $(CH_3)_3SiC{\equiv}CSi(CH_3)_3$ (2.60 g, 15.3 mmol). The compounds I and II have been characterized as described elsewhere.[6] After removal of all the volatile and distillable products at 70 °C (in vacuo), the least volatile material remained in the stainless-steel reactor. This residue was heated to 180 °C in vacuo for 24 h and a white solid $[(CH_3)_3Si]_2C{=}CH{-}CH{=}C[Si(CH_3)_3]_2$ (III) collected in a detachable U trap at 0 °C, while polymeric material remained in the stainless-steel reactor. All the attempts to characterize this polymeric material were unsuccessful and hence this material was discarded.

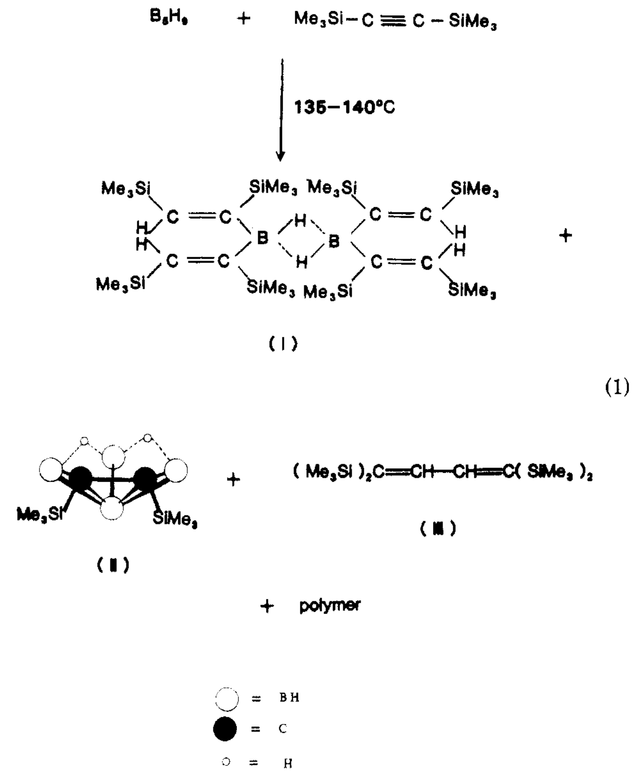
The solid III was resublimed under high vacuum at 78 °C into a second U-trap to give ca. 2.21 g (6.46 mmol, 2.91% yield based on $(CH_3)_3SiC{\equiv}CSi(CH_3)_3$ consumed) of pure III. The physical properties and characterization of III are as follows: mp 120 °C; solubility, highly soluble in CH_2Cl_2, $CDCl_3$, CCl_4, C_6H_6, THF, $(C_2H_5)_2O$, $(CH_3)_2CO$, C_2H_5OH, and C_6H_{14}. Anal. Calcd for $C_{16}H_{38}Si_4$: C, 56.14; H, 11.11; Si, 32.75. Found: C, 56.19; H, 11.14; Si, 32.68. NMR ($CDCl_3$): ^{1}H (relative to external Me_4Si) δ 7.38 [s (br), 1 H, olefinic H], 0.19 [s (br), 9 H, $Si(CH_3)_3$], 0.10 [s (br), 9 H, $Si(CH_3)_3$]; ^{13}C (relative to external Me_4Si) δ 153.17 [d, olefinic carbon (=CH), $^1J(^{13}C{-}^1H)$ = 153.0 Hz], 148.80 [s (br), olefinic carbon (=C(Si≡)$_2$), 1.95 [q, $(CH_3)_3Si$, $^1J(^{13}C{-}^1H)$ = 119.0 Hz], and 0.40 [q, $(CH_3)_3Si$, $^1J(^{13}C{-}^1H)$ = 119.0 Hz]; ^{29}Si (relative to external Me_4Si) δ −0.49 [m, $Si(CH_3)_3$, $^2J(^{29}Si{-}^1H)$ = 4.8 Hz], and −9.08 [m, $Si(CH_3)_3$, $^2J(^{29}Si{-}^1H)$ = 5.2 Hz]. Mass spectrum of III is listed in Table I. IR ($CDCl_3$ vs. $CDCl_3$): 2955 (m, s) and 2895 (w) (ν(C—H)), 1599 (w, br) (ν(C=C)), 1405 (w, br) (δ(CH), asym), 1251 (s) (δ(CH), sym), 1050 (m, br), 841 (vvs, br) (ρ(CH)), and 670 (m, br) (ν(Si–C)) cm^{-1}.

Pyrolysis of Tris[1,2-bis(trimethylsilyl)ethenyl]borane. A stainless-steel reactor was charged with 5.62 g (10.73 mmol) of $[(CH_3)_3SiCH{=}CSi(CH_3)_3]_3B$ (IV) and was evacuated. The trivinylborane derivative was then pyrolyzed at 135–140 °C under the same conditions as those employed in the preparation of III. The fractionation of all the volatile products gave $(CH_3)_3SiC{\equiv}CSi(CH_3)_3$ (1.04 g, 6.12 mmol) and I (2.12 g, 2.99 mmol), collected at −78 and 0 °C traps, respectively. A nonvolatile residue remained at the bottom of the reactor. This residue was then heated further at 180 °C over a period of 24 h while being pumped through a series of traps at −196 °C. During this period only traces of $(CH_3)_3SiH$ were collected in the traps, but not III. A polymeric material (not characterized) remaining in the reactor was discarded.

Results and Discussion

Synthesis. The reaction of pentaborane and bis(trimethylsilyl)acetylene at 135–140 °C produced not only the dimer of the hydroborated species and the *nido*-carborane as liquids but also a new, air-stable solid *trans*-1,1,4,4-tetrakis(trimethylsilyl)-1,3-butadiene. This reaction is shown in eq 1.

It has already been established that I is produced directly from its trivinylborane precursor $[(CH_3)_3SiCH{=}CSi(CH_3)_3]_3B$ (IV) at 135 °C in Pyrex-glass reactors.[6] Furthermore, the formation of IV even at 135 °C is believed to be the driving force in the preparation of II. However, the exact mechanism of the formation of III is not known. The presence of I and II among the products implies that the hydroboration of alkyne involving one BH_3 unit of B_5H_9 occurred in reaction 1. The formation of III requires a mechanism where C(sp^2)–B bond should be ruptured at 135 °C to form a reactive vinylsilyl fragment that could easily condense with another such fragment to



(1)

yield the 1,2,3,4-tetrakis(trimethylsilyl)-1,3-butadiene and eventually the 1,1,4,4-tetrakis(trimethylsilyl)-1,3-butadiene by thermal rearrangement or some other *intramolecular* rearrangement. However, this mechanism could be easily ruled out due to the fact that the trivinylborane precursor IV under similar conditions failed to produce either 1,2,3,4- or 1,1,4,4-silyl-substituted butadiene derivatives (see Experimental Section).

Scheme I outlines another plausible sequence by which two $(CH_3)_3SiC{\equiv}CSi(CH_3)_3$ molecules could link and then further undergo a regio- and stereoselective addition of $(CH_3)_3SiH$ across each of the carbon–carbon triple bonds. The presence of trimethylsilane in the products requires the rupture of a Si–C(sp) bond and the abstraction of a hydrogen atom. This scheme involves the high-temperature rupture of C(sp)–Si bond leading to the formation of a reactive alkyne radical and a trimethylsilyl radical which then could extract one of the pentaborane bridge hydrogen atoms forming trimethylsilane. If a side reaction such as the one shown in eq 2 occurs, then one could expect a formation of $(CH_3)_3SiC{\equiv}CH$ or the final carborane product $(CH_3)_3SiC_2B_4H_7$ via a similar reaction[6] shown in eq 1. However, neither $(CH_3)_3SiC{\equiv}CH$ nor $(CH_3)_3SiC_2B_4H_7$ has been identified among the products (see Experimental Section). Therefore, it is probable that the reactive alkyne fragment links directly with another such fragment to yield the 1,3-butadiyne derivatives.[7] Since this diacetylene has been found[5] to undergo regio- and stereoselective addition reactions with a variety of silanes in the presence of a suitable catalyst yielding alkenes with the silyl groups on the same olefinic carbon, it is reasonable to believe that such a reaction could be involved in the synthesis of III. This is further supported by the so-called β-effect[8] where the addition of an electrophile to a vinylsilane or silylacetylene results in the buildup of electrophilic character β to the carbon–silicon bond; such a species is said to be stabilized either by bridging or by so-called vertical stabilization (hyperconjugation).

$$[(CH_3)_3SiC{\equiv}C\cdot] + B_5H_9 \rightarrow (CH_3)_3SiC{\equiv}CH + [B_5H_8\cdot] \qquad (2)$$

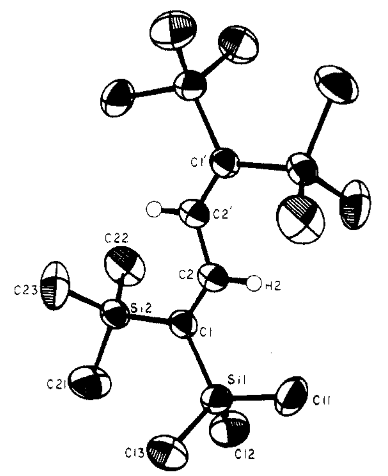
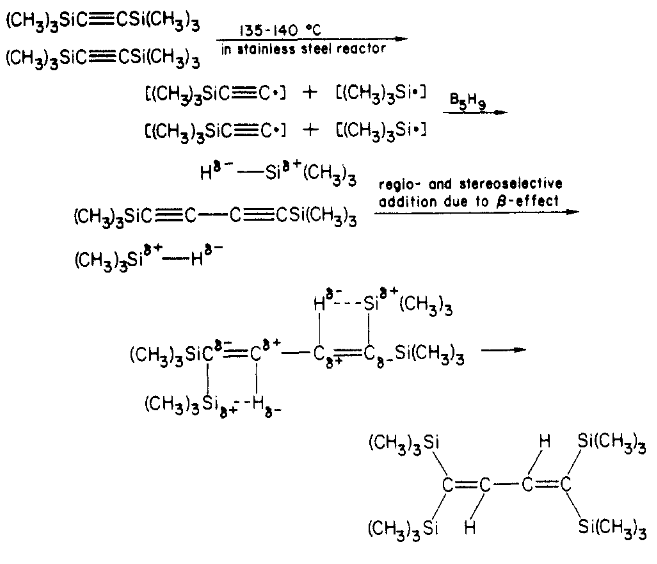


Figure 1. ORTEP view of III showing the atom numbering scheme and thermal ellipsoids at the 50% probability level.

Scheme I



Spectra. The IR and mass spectra, with assignments, are given in the Experimental Section and Table I, respectively. The IR assignments of III are in agreement with those of similar compounds reported by Bock and Seidl,[5] Hosmane et al.,[9] Seyferth and Vaughan,[10] and Mironor and Chumaevskii.[11] The electron-impact (EI) mass spectrum of III exhibits a grouping with an intense peak at *m/e* 342, corresponding to the parent ion $[(^{12}CH_3)_3{}^{28}Si]_2{}^{12}C{=}{}^{12}CH{}^{12}CH{=}{}^{12}C[{}^{28}Si({}^{12}CH_3)_3]_2{}^{+}$.

The ^1H, ^{13}C, and ^{29}Si FT NMR spectra (see Experimental Section) indicate the presence of two Me_3Si groups and one type of olefinic CH at expected chemical shifts.[12,13]

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Table II. Bond Distances (Å) for $(Me_3Si)_2C{=}CHCH{=}C(SiMe_3)_2$, III[a]

atom 1	atom 2	dist	atom 1	atom 2	dist	atom 1	atom 2	dist
Si(1)	C(1)	1.874 (5)	Si(1)	C(13)	1.864 (9)	Si(2)	C(22)	1.876 (8)
Si(1)	C(11)	1.860 (7)	Si(2)	C(1)	1.889 (5)	Si(2)	C(23)	1.879 (10)
Si(1)	C(12)	1.867 (8)	Si(2)	C(21)	1.895 (8)	C(1)	C(2)	1.351 (8)
						C(2)	C(2)′	1.456 (8)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Table III. Bond Angles (deg) for $(Me_3Si)_2C{=}CHCH{=}C(SiMe_3)_2$, III[a]

atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
C(1)	Si(1)	C(11)	110.7 (3)	C(12)	Si(1)	C(13)	109.3 (4)	C(21)	Si(2)	C(23)	107.8 (4)
C(1)	Si(1)	C(12)	111.6 (3)	C(1)	Si(2)	C(21)	110.2 (3)	C(22)	Si(2)	C(23)	112.5 (4)
C(1)	Si(1)	C(13)	110.2 (3)	C(1)	Si(2)	C(22)	110.2 (4)	Si(1)	C(1)	Si(2)	121.5 (3)
C(11)	Si(1)	C(12)	107.0 (4)	C(1)	Si(2)	C(23)	108.9 (3)	Si(1)	C(1)	C(2)	117.1 (4)
C(11)	Si(1)	C(13)	108.0 (3)	C(21)	Si(2)	C(22)	107.3 (4)	Si(2)	C(1)	C(2)	121.4 (4)
								C(1)	C(2)	C(2)′	127.6 (4)

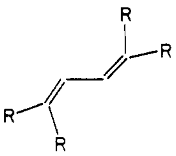
[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

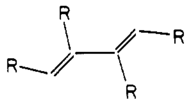
Table IV. Positional Parameters and Their Estimated Standard Deviations for $(Me_3Si)_2C{=}CHCH{=}C(SiMe_3)_2$, III[a]

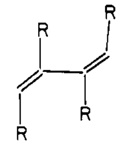
atom	*x*	*y*	*z*	*B*, Å^2
Si(1)	0.9202 (3)	0.2635 (2)	0.7958 (2)	3.73 (4)
Si(2)	1.6761 (3)	−0.3531 (2)	0.6731 (2)	4.00 (4)
C(1)	0.8777 (9)	0.4495 (6)	0.6618 (5)	3.2 (1)
C(2)	1.000 (1)	0.4367 (7)	0.5574 (5)	3.6 (1)
C(11)	1.125 (1)	0.0898 (8)	0.7531 (7)	5.9 (2)
C(12)	0.664 (1)	0.2077 (9)	0.8354 (7)	6.0 (2)
C(13)	1.023 (1)	0.2934 (9)	0.9391 (7)	5.7 (2)
C(21)	0.526 (2)	0.620 (1)	0.8289 (7)	8.4 (3)
C(22)	0.467 (1)	0.721 (1)	0.5430 (7)	6.7 (2)
C(23)	0.828 (1)	0.7941 (8)	0.6692 (8)	6.9 (2)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(^4/_3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

This is consistent with three possible structures, namely, 1,1,4,4-IIIa, 1,2,3,4-*cis*,*cis*-IIIb, and 1,2,3,4-*trans*,*trans*-IIIc illustrated below.


1, 1, 4, 4-IIIa


1, 2, 3, 4-*cis*, *cis*-IIIb


1, 2, 3, 4-*trans*, *trans*-IIIc

R=Me$_3$Si

Table V. Crystallographic Data for $(Me_3Si)_2C{=}CHCH{=}C(SiMe_3)_2$, III

formula	$C_{16}H_{38}Si_4$
fw	342.82
cryst system	triclinic
space group	$P\bar{1}$ (No. 2)
a/Å	6.466 (1)
b/Å	9.073 (2)
c/Å	10.965 (2)
α/deg	74.29 (2)
β/deg	85.72 (1)
γ/deg	71.90 (1)
V/Å^3	589 (1)
Z	1
ρ(calcd)/g cm^{-3}	0.967
λ(Mo Kα)/Å	0.71069 (graphite monochromator)
μ(Mo Kα)/cm^{-1}	2.4
2θ limits/deg	$2.0 \leq 2\theta \leq 50.0$
no. of unique data measd	1862
no. of data obsd	1329
data cutoff	$I > 3.0\sigma(I)$
no. of parameters varied	167
R	0.0602
R_w	0.0699

In order to differentiate between the two 1,2,3,4- and 1,1,4,4-substituted forms, an X-ray crystal structure determination was carried out for III. The results are shown in Figure 1 along with the adopted atom numbering scheme. The molecule resides on a crystallographic center of inversion located at the midpoint of the C(2)–C(2)′ vector. As a result, the carbon skeleton C(1)–C(2)–C(2)′–C(1)′ adopts a planar and transoid conformation. Each of the terminal C(1) carbons is bonded to two Me$_3$Si groups, C(1)–Si(1) = 1.874 (5) and C(1)–Si(2) = 1.889 (5) Å, thus establishing its identity on the 1,1,4,4-substituted isomer. The bond lengths within the skeleton reveal a substantial localization of double-bond character in the C(1)–C(2) bond. Thus the value C(1)–C(2) = 1.351 (8) Å is significantly shorter than the C(2)–C(2)′ bond length of 1.456 (8) Å. The angles at C(1) are in the normal range observed for olefinic carbon atoms; Si(1)–C(1)–C(2) = 117.1 (4), Si(2)–C(1)–C(2) = 121.4 (4), and Si(1)–C(1)–Si(2) = 121.5 (3)°. Note, however, that the angle Si(2)–C(1)–C(2) is some 4° larger than the value for Si(1)–C(1)–C(2). This is presumably a result of intramolecular steric effects since Si(2) is cis to C(2)′ while Si(1) is cis to the much smaller hydrogen atom H(1). The geometries of the Me$_3$Si group are unexceptional and deserve no special comment. Full listings of bond lengths, interbond angles, and atomic positional parameters are given in Tables II–IV respectively, while pertinent crystallographic data are collected in Table V.

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Registry No. I, 96346-86-0; II, 91686-41-8; III, 96293-10-6; IV, 95691-42-2; $(CH_3)_3SiC{\equiv}CSi(CH_3)_3$, 14630-40-1; pentaborane, 19624-22-7.

Supplementary Material Available: Tables of calculated hydrogen position, thermal parameters, and observed and calculated structure factors (Supplementary Tables 1–3) (8 pages). Ordering information is given on any current masthead page.