3,7,10-Trichalcogenaoctasila[3.3.3]propellanes

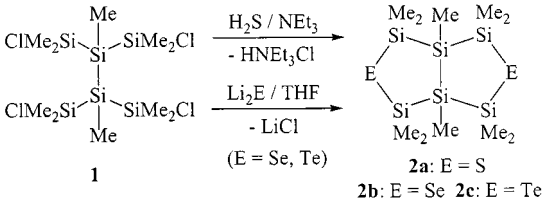
U. Herzog*[a] and G. Rheinwald[b]

Keywords: Silanes / Sulfur / Selenium / Tellurium / Polycycles

The reaction of hexakis(trimethylsilyl)disilane with acetyl chloride and aluminum chloride yields hexakis(chlorodimethylsilyl)disilane (**5a**) under carefully controlled reaction conditions. Treatment of **5a** with either H_2S/NEt_3 or Li_2E (E = Se, Te) gives the dodecamethyl-3,7,10-trichalcogenaoctasila-[3.3.3]propellanes $Si_2(SiMe_2)_6E_3$ (**6a** E = S, **6b** E = Se, **6c** E = Te). The products have been characterized by multinuclear NMR spectroscopy (^1H, ^{13}C, ^{29}Si, ^{77}Se, ^{125}Te). The central silicon atoms are very deshielded in comparison with other compounds containing an $Si(Si)_4$ unit due to their incorporation into three five-membered rings. The molecular structures of **5a** and **6a** are reported revealing an elongated central Si–Si bond in **5a** of 2.3865(11) Å and three different spatial orientations of the $SiMe_2Cl$ groups in each $Si(SiMe_2Cl)_3$ unit. In **6a** all three five-membered rings Si_4S adopt *envelope* conformations with the four silicon atoms in one plane. A view of the Si_8S_3 skeleton along the central silicon–silicon bond of **6a** resembles a three-blade propeller.

Introduction

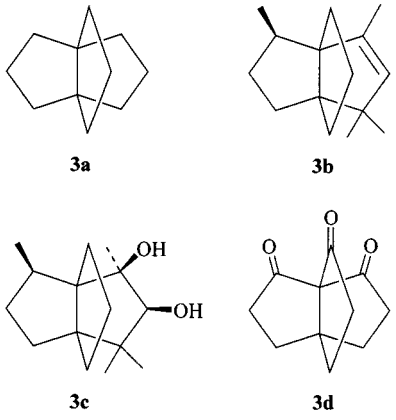
In previous investigations we have shown that the reaction of 1,1,2,2-tetrakis(chlorodimethylsilyl)dimethyldisilane (**1**) with either H_2S/NEt_3 or Li_2E (E = Se, Te) yields exclusively the 3,7-dichalcogenahexasilabicyclo[3.3.0]octanes [**2a**–**c**; Equation (1)].[1]



(1)

The formation of these compounds underlines the general observation that the formation of five-membered heterocycles is preferred in the systems silicon-sulfur, -selenium and -tellurium.[2,3] The facile formation of the bicyclic systems tempted us to apply these reactions to the synthesis of the corresponding tricyclic ring systems, which can be described as [3.3.3]propellanes (**3a**, Scheme 1).

It should be mentioned that carbon-based [3.3.3]propellanes have been known for some time[4,5] and even a naturally occurring sesquiterpene, modhephene (**3b**),[6,7] containing this tricyclic skeleton has been described. Molecular structures have been reported for modhephenediol (**3c**, 2,3-dihydroxy-2,4,4,8-tetramethyl[3.3.3]propellane,[6]) and [3.3.3]-propellane-2,8,9-trione (**3d**).[8]

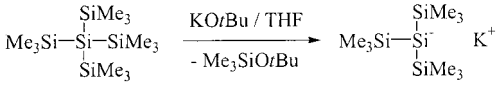


Scheme 1

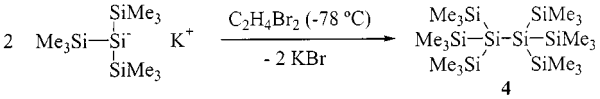
Results and Discussion

Formation and Structure of Hexakis(chlorodimethylsilyl)disilane (5a)

The formation of 3,7,10-trichalcogenaoctasila[3.3.3]propellanes requires an octasilane skeleton with six chlorodimethylsilyl units connected to a central disilane. This compound, hexakis(chlorodimethylsilyl)disilane (**5a**), can be prepared in three steps starting from tetrakis(trimethylsilyl)-silane by the formation of hypersilylpotassium developed by Marschner[9] [Equation (2)] and a subsequent oxidative dimerization of the hypersilanyl anion [Equation (3)].



(2)



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[a] Institut für Anorganische Chemie der TU Bergakademie Freiberg,
Leipziger Str. 29, 09596 Freiberg, Germany
[b] Institut für Chemie, Lehrstuhl Anorganische Chemie,
TU Chemnitz,
Straße der Nationen 62, 09111 Chemnitz, Germany

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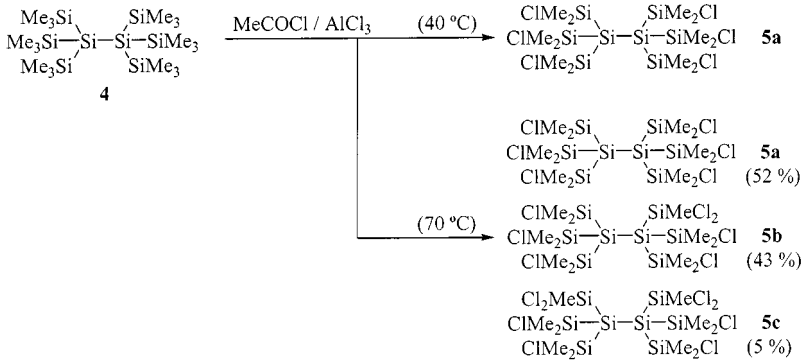


(4)

The molecular structure of the formed hexakis(trimethylsilyl)disilane (**4**) has been reported previously[10,11] revealing an elongated central Si−Si bond of 2.40 Å.

The treatment of **4** with acetyl chloride and aluminum chloride in hexane yields the desired hexachlorinated octasilane **5a** under optimized reaction conditions. Slightly higher reaction temperatures also led to the formation of the higher chlorinated octasilanes **5b** and **5c** [Equation (4)].

The molecular structure of **5a** is shown in Figure 1 and 2 and selected bond lengths and angles are summarized in Table 1. The structure of **5a** is a rare example of a successful crystal structure determination of a methylchlorooligosilane because most compounds of this class are liquids or low melting solids which are highly soluble in all organic solvents. The central silicon−silicon bond of **5a** (Si1−Si5) is, at 2.3865(11) Å, longer than the other Si−Si bonds but slightly shorter than that in **4**. In both $Si(SiMe_2Cl)_3$ units one chlorine substituent occupies a more axial position with respect to the central Si−Si bond (Cl3, Cl4) while the other two are equatorial. This reduces the steric overcrowding resulting in a slightly shorter central Si−Si bond than in **4**. A closer look reveals that in each $Si(SiMe_2Cl)_3$ unit there are three different $SiMe_2Cl$ groups which can be distinguished by their different dihedral angles Cl−Si−Si−Si (see Table 1). A comparison of the two $Si(SiMe_2Cl)_3$ units shows that the silyl units containing Si(2) and Si(8) have a similar orientation, as is the case for Si(3) and Si(7) and Si(4) and Si(6). A look at the Si−Si−Si angles shows that all the Si−Si(1)−Si(5) ands Si(1)−Si(5)−Si angles are larger than the tetrahedral angle of 109.5°, while all the Si−Si−Si angles within each $Si(SiMe_2Cl)_3$ unit are smaller. This is a result of the mutual repulsion of the two $Si(SiMe_2Cl)_3$ units connected by the central Si−Si bond. By comparing the angles C−Si−C (107.93−112.18°, average 109.68°) and C−Si−Si (112.18−117.41°, average 114.30°) with the angles C−Si−Cl (104.94−107.03°, average 106.00°) and Cl−Si−Si (102.97−109.18°, average 105.68°) it can be clearly seen that a methyl group occupies more space than a chlorine substituent.

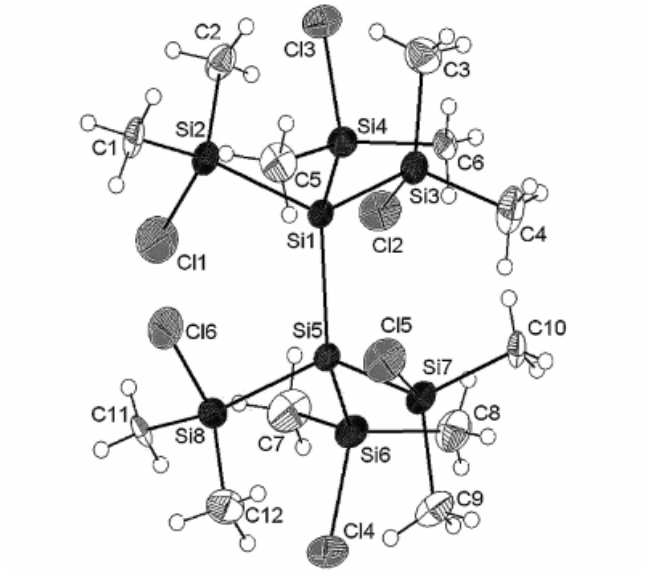


Figure 1. Molecular structure of **5a**

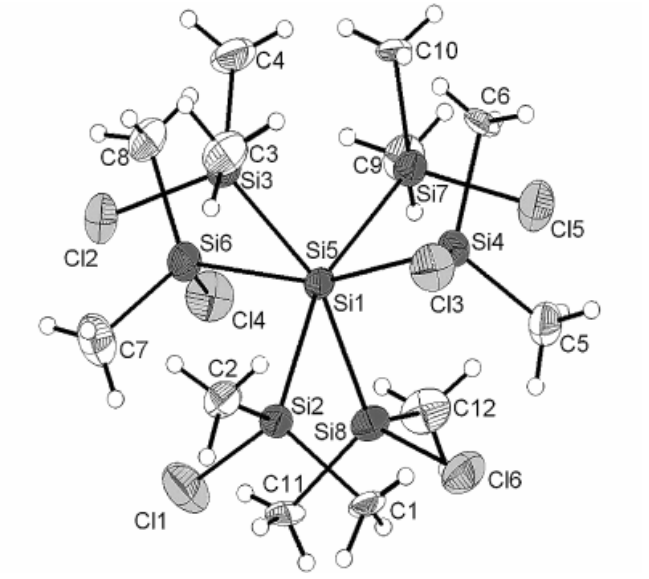
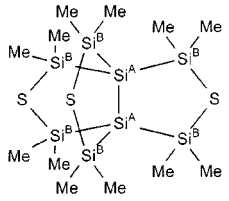
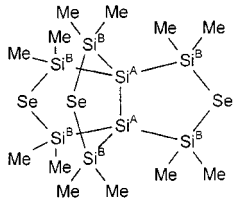
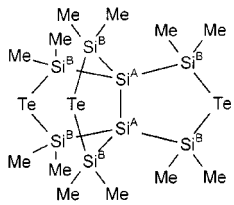


Figure 2. Molecular structure of **5a** viewed along the Si1−Si5 bond

Table 1. Selected bond lengths (Å) and angles (°) of **5a**

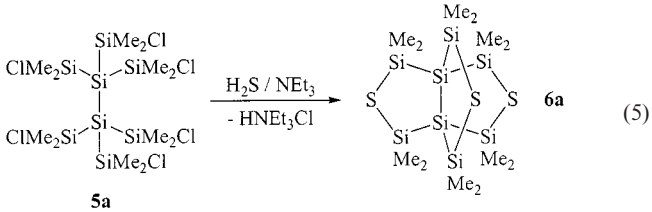
Atoms	Distances	Atoms	Angles
Si(1)−Si(2)	2.3754(11)	Si(2)−Si(1)−Si(3)	104.64(4)
Si(1)−Si(3)	2.3597(12)	Si(2)−Si(1)−Si(4)	104.27(4)
Si(1)−Si(4)	2.3597(10)	Si(3)−Si(1)−Si(4)	105.31(4)
Si(1)−Si(5)	2.3865(11)	Si(2)−Si(1)−Si(5)	117.20(4)
Si(5)−Si(6)	2.3658(10)	Si(3)−Si(1)−Si(5)	110.48(4)
Si(5)−Si(7)	2.3676(11)	Si(4)−Si(1)−Si(5)	113.88(4)
Si(5)−Si(8)	2.3617(12)	Si(6)−Si(5)−Si(1)	116.16(4)
Si(2)−Cl(1)	2.0621(12)	Si(7)−Si(5)−Si(1)	112.14(4)
Si(3)−Cl(2)	2.0911(11)	Si(8)−Si(5)−Si(1)	112.50(4)
Si(4)−Cl(3)	2.0865(11)	Si(6)−Si(5)−Si(7)	105.57(4)
Si(6)−Cl(4)	2.1002(12)	Si(6)−Si(5)−Si(8)	104.09(4)
Si(7)−Cl(5)	2.0778(11)	Si(7)−Si(5)−Si(8)	105.45(4)
Si(8)−Cl(6)	2.0764(12)	Si(1)−Si(2)−Cl(1)	109.18(5)
Si(2)−C(1)	1.883(3)	Si(1)−Si(3)−Cl(2)	104.78(5)
Si(2)−C(2)	1.879(3)	Si(1)−Si(4)−Cl(3)	103.21(4)
Si(3)−C(3)	1.857(4)	Si(5)−Si(6)−Cl(4)	102.97(5)
Si(3)−C(4)	1.854(4)	Si(5)−Si(7)−Cl(5)	106.98(5)
Si(4)−C(5)	1.849(4)	Si(5)−Si(8)−Cl(6)	106.97(5)
Si(4)−C(6)	1.885(3)	Si(4)−Si(1)−Si(5)−Si(6)	−157.81(5)
Si(6)−C(7)	1.849(4)	Si(3)−Si(1)−Si(5)−Si(7)	81.97(5)
Si(6)−C(8)	1.867(4)	Si(2)−Si(1)−Si(5)−Si(8)	−39.67(5)
Si(7)−C(9)	1.856(4)	Si(5)−Si(1)−Si(2)−Cl(1)	−31.78(6)
Si(7)−C(10)	1.882(3)	Si(5)−Si(1)−Si(3)−Cl(2)	68.92(5)
Si(8)−C(11)	1.870(3)	Si(5)−Si(1)−Si(4)−Cl(3)	−174.49(5)
Si(8)−C(12)	1.861(3)	Si(1)−Si(5)−Si(8)−Cl(6)	−33.29(6)
		Si(1)−Si(5)−Si(7)−Cl(5)	68.48(6)
		Si(1)−Si(5)−Si(6)−Cl(4)	−167.52(5)

Table 2. ^{29}Si, ^{77}Se, ^{125}Te, ^{13}C and ^{1}H NMR spectroscopic data (ppm, Hz) of the [3.3.3]propellanes $Si_2(SiMe_2)_6E_3$ (E = S, Se, Te)

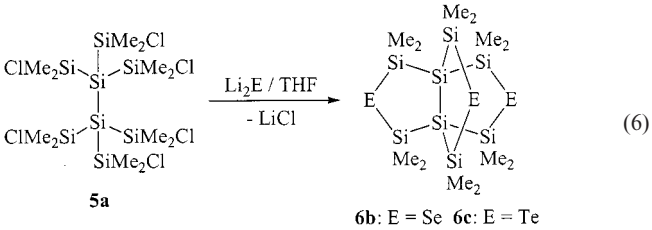
	compound	δ_{Si}	δ_E	δ_C	δ_H
6a		A: −84.52 B: 19.78 $^1J_{SiSi}$: 54.2	–	6.11 $^1J_{SiC}$: 47.5	0.61
6b		A: −73.22 B: 14.96 $^1J_{SiSi}$: 48.6	Se: −189 $^1J_{SiSe}$: 110.8 $^2J_{SiSe}$: 24.8 $^3J_{SiSe}$: 13.6	5.89	0.72
6c		A:−52.36 B: −5.26 $^1J_{SiSi}$: 45.3	Te: −622 $^1J_{SiTe}$: 284.3	5.64	0.99

3,7,10-Trichalcogenaoctasila[3.3.3]propellanes

The reaction of **5a** with either H_2S/NEt_3 in hexane or Li_2E (E = Se, Te) prepared in situ from the chalcogens and $LiBEt_3H$ in THF yielded the expected dodecamethyl-3,7,10-trichalcogenaoctasila[3.3.3]propellanes **6a−c** [Equation (5) and (6)]:



(5)



(6)

The NMR spectroscopic data of the propellanes **6a−c** are given in Table 2. While the δ_{Si} values of the $SiMe_2$ units are similar to those in the corresponding monocyclic five-membered rings $(SiMe_2)_4E$[12] and the bicyclo[3.3.0]octanes **2a−c**, the NMR chemical shifts of the central Si atoms are remarkable. Compared with other compounds containing $Si(Si)_4$ units like $Si(SiMe_3)_4$ (δ_{Si} = −135.5[13]), $Si_2(SiMe_3)_6$ (**4**, δ_{Si} = −129.5[9]) or even chloro-substituted derivatives like $Si(SiMe_2Cl)_4$ (δ_{Si} = −113.9[14]) and $Si_2(SiMe_2Cl)_6$ (**5a**, δ_{Si} = −111.62) the chemical shifts found in the propellanes **6a−c** are shifted significantly to lower field, especially in the cases of the heavier chalcogens (Se, Te; see Figure 3).

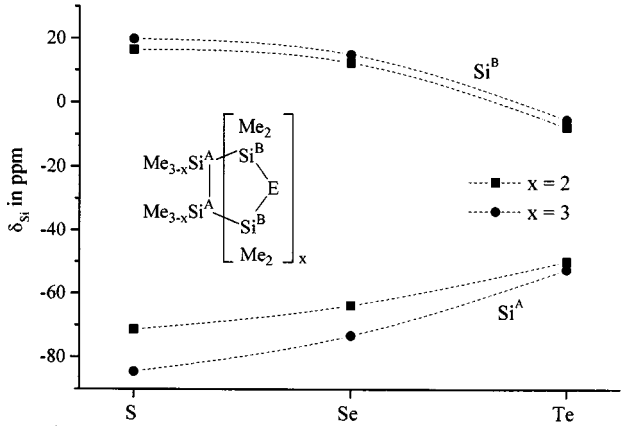


Figure 3. ^{29}Si NMR chemical shifts in bicyclo[3.3.0]octanes (**2a−c**) [1] and [3.3.3]propellanes (**6a−c**) for E = S, Se, Te

It has been observed before that the formation of five-membered rings in the silicon chalcogen systems is always accompanied by a strong low-field shift of the ^{29}Si NMR signals, which increases from sulfur to tellurium in the case of oligosilanyl units.[3] In the cases of the central silicon atoms in the propellanes **6a−c** these atoms are incorporated into three five-membered rings causing these unusual low-

field shifts. Furthermore, compared to the bicyclo[3.3.0]octanes **2b**−**c**[1] the ^{77}Se and the ^{125}Te NMR signals of the propellanes **6b**−**c** are shifted to lower field by 89 ppm (Se) and 114 ppm (Te), despite the same first and second coordination sphere around the chalcogen atoms.

Compound **6a** was characterized by its mass spectrum and also by an X-ray structure analysis. Figure 4 shows the molecular structure of **6**, and some bond lengths and angles are given in Table 3.

In contrast to **5a** all the Si−Si bond lengths are in the usual range. All three five-membered rings adopt almost ideal envelope conformations with dihedral angles Si−Si(1)−Si(5)−Si of −4.8 to −5.2° and envelope angles of 44.57(6)° [Si_4S ring including S(1)], 46.52(6)° [Si_4S ring including S(2)] and 45.28(8)° [Si_4S ring including S(3)]. This is slightly more than in the organic [3.3.3]propellane modhephenediol (**3c**) with envelope angles of 37−42°[6] and close to the envelope angles in the bicyclo[3.3.0]octane derivative **2a** [42.34(4)° and 44.35(3)° [1]]. In contrast to the structure of **2a**, however, all three five-membered rings in **6a** are folded in the same rotatory sense resembling an almost ideal three-blade propeller (Figure 5). The angles at the sulfur atoms in **6a** are, at 101.5−102.4°, close to the values in **2a**. The same holds for the Si−Si and the Si−S bond lengths. Due to the formation of the five-membered rings all Si−Si−Si angles including the Si(1)−Si(5) bond are smaller than the tetrahedral angle (101.5−102.6°) resulting in Si−Si−Si angles of more than 109.5° within the $Si_3Si(1)$ and $Si_3Si(5)$ units (in the range of 115.1−116.4°).

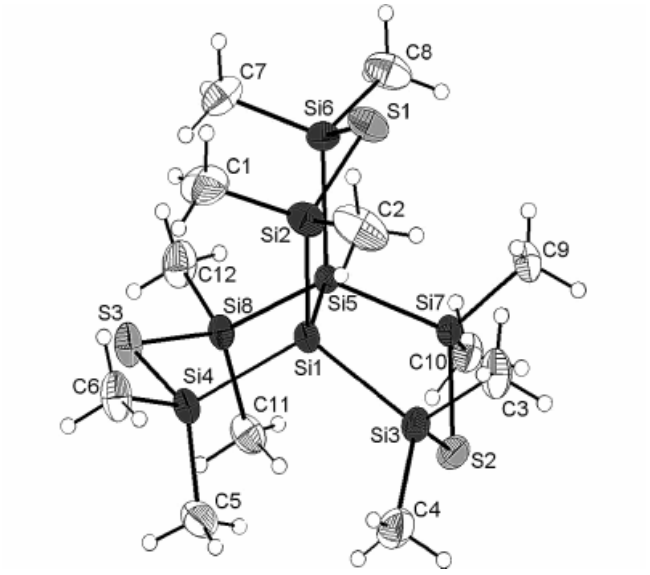


Figure 4. Molecular structure of **6a**

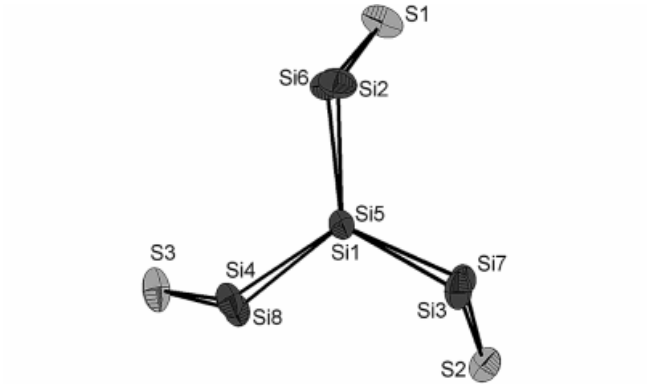


Figure 5. The silicon and sulfur skeleton of **6a** viewed along the central Si−Si bond

Table 3. Selected bond and distances (Å) and angles (°) of **6a**

Atoms	Distances	Atoms	Angles
Si(1)−Si(2)	2.3564(17)	Si(2)−S(1)−Si(6)	102.40(7)
Si(1)−Si(3)	2.3543(15)	Si(3)−S(2)−Si(7)	101.53(6)
Si(1)−Si(4)	2.3621(17)	Si(4)−S(3)−Si(8)	101.65(7)
Si(1)−Si(5)	2.3487(16)	Si(2)−Si(1)−Si(3)	115.41(7)
Si(5)−Si(6)	2.3416(15)	Si(2)−Si(1)−Si(4)	116.39(7)
Si(5)−Si(7)	2.3416(16)	Si(3)−Si(1)−Si(4)	115.24(6)
Si(5)−Si(8)	2.3395(17)	Si(2)−Si(1)−Si(5)	101.89(6)
Si(2)−S(1)	2.1501(18)	Si(3)−Si(1)−Si(5)	102.60(6)
Si(3)−S(2)	2.1541(18)	Si(4)−Si(1)−Si(5)	102.02(6)
Si(4)−S(3)	2.1492(16)	Si(6)−Si(5)−Si(1)	102.58(6)
Si(6)−S(1)	2.1479(18)	Si(7)−Si(5)−Si(1)	101.55(6)
Si(7)−S(2)	2.1543(15)	Si(8)−Si(5)−Si(1)	101.80(6)
Si(8)−S(3)	2.1401(18)	Si(6)−Si(5)−Si(7)	115.15(6)
Si(2)−C(1)	1.871(5)	Si(6)−Si(5)−Si(8)	116.37(6)
Si(2)−C(2)	1.854(5)	Si(7)−Si(5)−Si(8)	115.91(6)
Si(3)−C(3)	1.856(5)	Si(1)−Si(2)−S(1)	106.34(7)
Si(3)−C(4)	1.868(4)	Si(1)−Si(3)−S(2)	105.49(6)
Si(4)−C(5)	1.864(4)	Si(1)−Si(4)−S(3)	106.15(7)
Si(4)−C(6)	1.861(5)	Si(5)−Si(6)−S(1)	104.89(6)
Si(6)−C(7)	1.855(4)	Si(5)−Si(7)−S(2)	104.80(6)
Si(6)−C(8)	1.868(5)	Si(5)−Si(8)−Cl(6)	105.50(7)
Si(7)−C(9)	1.860(4)	Si(4)−Si(1)−Si(5)−Si(8)	−4.95(7)
Si(7)−C(10)	1.865(4)	Si(3)−Si(1)−Si(5)−Si(7)	−5.21(8)
Si(8)−C(11)	1.867(4)	Si(2)−Si(1)−Si(5)−Si(8)	−4.79(7)
Si(8)−C(12)	1.868(4)		

Experimental Section

General: All NMR spectra were recorded on a Bruker DPX 400 in $CDCl_3$ solution and TMS as internal standard for ^{1}H, ^{13}C and ^{29}Si. External Ph_2Se_2 (δ_{Se} = 460) and Ph_2Te_2 (δ_{Te} = 422) in $CDCl_3$ were used as standards for ^{77}Se and ^{125}Te. In order to obtain a sufficient signal-to-noise ratio of ^{29}Si NMR spectra for obtaining $^1J_{SiC}$, $^1J_{SiSi}$, $^{1,2,3}J_{SiSe}$ or $^1J_{SiTe}$ satellites ^{29}Si INEPT spectra were also recorded. ^{77}Se and ^{125}Te spectra were determined using an IGATED pulse program.

Mass spectra were measured on a Hewlett Packard 5971 (ionization energy: 70 eV, column: 30 m × 0.25 mm × 0.25 μm, phenylmethylpolysiloxane, column temperature: 80 °C (3 min)/20 K/min, flow: He 0.5 mL/min).

Starting Materials: H_2S (N25, Air Liquide), Se, Te, triethylamine, 1 M $LiBEt_3H$ in THF (Super Hydride), were commercially available. $Si(SiMe_3)_4$ was prepared as described in ref.[21] THF was distilled from sodium/potassium alloy prior to use. The other solvents were dried over KOH or sodium wire. All reactions were carried out under argon using standard Schlenk techniques.

Crystal Structure Analysis: X-ray structure analysis measurements were performed on a Bruker SMART CCD. Crystal data of **5a** and

Table 4. Crystal data of **5a** and **6a** as well as data collection and refinement details

	5a	**6a**
Chemical formula	$C_{12}H_{36}Cl_6Si_8$	$C_{12}H_{36}S_3Si_8$
Molecular weight	617.83	501.31
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$C2/c$
Unit cell dimensions, Å, °	a = 10.9820(6)	a = 14.6972(19)
	b = 17.0125(10)	b = 12.0174(14)
	c = 17.2780(11)	c = 31.930(4)
	β = 100.401(2)	β = 100.812(2)
Volume in Å^3; Z	3175.0(3); 4	5539.4(12); 8
Density (calcd.) in g/cm^3	1.292	1.202
Linear absorption coeff., mm^{-1}	0.845	0.612
Radiation used	Mo-K_α	Mo-K_α
Temperature	173(2) K	173(2) K
Scan method	ω scans	ω scans
Absorption correction	empirical	empirical
Max./min. transmission	0.9202/0.6773	0.9138/0.8144
Measured reflections	14079	12037
Independent reflections	6291	6510
Observed reflections	4435	3151
Index range	$-13 \le h \le 12$	$-19 \le h \le 19$
	$-23 \le k \le 4$	$-16 \le k \le 8$
	$-22 \le l \le 22$	$-15 \le l \le 42$
R(int)	0.0341	0.0713
θ range for collection, °	1.69−29.36	1.30−29.47
Completeness to θ_{max} %	72.1	84.6
Refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
Final R_1/wR^2 [$I > 2\,\sigma(I)$][a]	0.0368/0.0900	0.0532/0.1030
R_1/wR^2 (all data) [a]	0.0643/0.1008	0.1493/0.1279
No. of reflections/parameters used	6291/379	6510/220
H-locating and refining	difmap/refall	geom./constr.
Goodness-of-fit (S)[b] on F^2	1.000	0.904
Max./min. e-density in e/Å^3	0.472/-0.410	0.545/-0.421

[a] $R_1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$, $wR^2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma(wF_o^4)]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$, a = 0.0530, b = 0.5866 (**5a**), a = 0.053, b = 0 (**6a**). − [b] $S = [\Sigma w(F_o^2 - F_c^2)^2]/(n - p)^{1/2}$, n = number of reflections, p = parameters used.

6a as well as data collection and refinement details are given in Table 4. The unit cell dimensions were determined with the program SMART.[15] The program SAINT[15] was used for data integration and refinement of the unit cell parameters. The space group was determined with the aid of the programs ABSEN[16] (**5a**) and XPREP[15] (**6a**). All data were corrected for absorption using SADABS.[17] The structures were solved using direct methods [SIR97[18] (**5a**), SHELX97[19] (**6a**)], refined using least-squares methods (SHELX-97) and drawn using Diamond.[20] The ellipsoids of the non-hydrogen atoms are at the 50% probability level. The hydrogen atoms on the methyl groups in **6a** were refined as constrained groups, whereas all hydrogen atoms in **5a** could be located from the difference map and fully refined.

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-164379 (**5a**) and -164380 (**6a**). Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44-1223/336-033, E-mail: deposit@ccdc.cam.ac.uk].

Hexakis(trimethylsilyl)disilane, $Si_2(SiMe_3)_6$ (4): $Si(SiMe_3)_4$ was reacted in THF with KO*t*Bu and the resulting $KSi(Me_3Si)_3$ solution was treated with $C_2H_4Br_2$ as described in ref.[9] After removal of the solvent the product was a mixture of **4** and approximately 25% $Si(SiMe_3)_4$. The two compounds were separated by sublimation in vacuo at 130 °C for 6 h. The residue of the sublimation was almost pure **4** in 72% yield, which could be used without further purification. ^{1}H NMR: δ = 0.274; ^{13}C NMR: δ = 4.38 ($^1J_{SiC}$ = 42.3 Hz); ^{29}Si NMR: δ = −9.55 ($SiMe_3$, $^1J_{SiSi}$ = 53.0 Hz), −130.13 ($SiSi_4$). − GC/MS: *m*/*z* (%) = 494 (4) [M$^+$], 479 (4) [M − Me], 421 (3) [$Me_{15}Si_7$], 406 (5) [$Me_{14}Si_7$], 305 (2) [$Me_{11}Si_5$], 273 (11) [Me_7Si_6], 247 (22) [Me_9Si_4], 232 (100) [Me_8Si_4], 199 (15), 173 (12) [$Me_5Si_3CH_2$], 131 (13) [Me_5Si_2], 73 (62) [Me_3Si].

Hexakis(chlorodimethylsilyl)disilane, $Si_2(SiMe_2Cl)_6$ (5a): Compound **4** (1.36 g, 2.75 mmol) was dissolved in 20 mL hexane and anhydrous aluminum chloride (3.00 g, 22.5 mmol) was added. Acetyl chloride (1.6 g, 20 mmol) was slowly added to this stirred mixture. After stirring overnight the reaction mixture was heated to 40 °C for one hour and the hexane phase was separated. Removal of the solvent in vacuo yielded 0.70 g (1.13 mmol, 41%) of pure crystalline **5a**, m.p.: 257 °C; ^{1}H NMR: δ = 0.845; ^{13}C NMR: δ = 8.05 ($^1J_{SiC}$ = 48.7 Hz); ^{29}Si NMR: δ = 29.06 ($SiMe_2Cl$, $^1J_{SiSi}$ = 56.9 Hz), −111.62 ($SiSi_4$). − GC/MS: *m*/*z* (%) = 601 (2) [M − Me], 581 (1) [M − Cl], 523 (44) [$Me_{10}Cl_5Si_7$], 488 (21) [$Me_{10}Cl_4Si_7$], 395 (9) [$Me_8Cl_3Si_6$], 380 (15) [$Me_7Cl_3Si_6$], 309 (13) [$Me_6Cl_3Si_4$], 272 (42) [$Me_6Cl_2Si_4$], 209 (18) [Me_6ClSi_3], 174 (13) [Me_6Si_3], 131 (26) [Me_5Si_2], 93 (37) [Me_2ClSi], 73 (100) [Me_3Si].

If the reaction mixture was heated to 70 °C, a mixture of **5a** (52%), $(ClMe_2Si)_3Si-Si(SiClMe_2)_2(SiCl_2Me)$ (**5b**; 43%) and

$(Cl_2MeSi^C)(ClMe_2Si^B)_2Si^A-Si^A(Si^BClMe_2)_2(Si^CCl_2Me)$ (**5c**; 5%) was obtained after removal of the solvent hexane.

$(ClMe_2Si^C)_3Si^A-Si^B(Si^DClMe_2)_2(Si^ECl_2Me)$ (5b): ^{13}C NMR: δ = 8.03 (Si^CMe_2), 7.69 (Si^DMe_2), 13.02 (Si^EMe); ^{29}Si NMR: δ = −111.23 (Si^A), −104.08 (Si^B), 28.88 (Si^C), 27.85 (Si^D), 36.98 (Si^E). − GC/MS: *m*/*z* (%) = 623 (2) [M − Me], 543 (27) [$Me_9Cl_6Si_7$], 508 (28) [$Me_9Cl_5Si_7$], 415 (10) [$Me_7Cl_4Si_6$], 400 (24) [$Me_6Cl_4Si_6$], 309 (31) [$Me_6Cl_3Si_4$], 272 (13) [$Me_6Cl_2Si_4$], 209 (19) [Me_6ClSi_3], 159 (22) [Me_5Si_3], 131 (29) [Me_5Si_2], 93 (61) [Me_2ClSi], 73 (100) [Me_3Si].

$(Cl_2MeSi^C)(ClMe_2Si^B)_2Si^A-Si^A(Si^BClMe_2)_2(Si^CCl_2Me)$ (5c): ^{29}Si NMR: δ = −111.23 (Si^A), 27.75 (Si^B), 36.21 (Si^C).

Dodecamethyl-3,7,10-trithiaoctasila[3.3.3]propellane, $Si_2(SiMe_2)_6S_3$ (6a): Compound **5a** (0.23 g, 0.37 mmol) was dissolved in 30 mL hexane and NEt_3 (0.35 mL, 2.5 mmol) was added while a stream of dried H_2S was bubbled through the stirred solution. After stirring overnight the reaction mixture was filtered. Removal of the solvent from the filtrate yielded 0.14 g (0.28 mmol, 76%) of pure **6a** as a colorless crystalline residue. Single crystals of **6a** were grown from a solution in hexane, m.p.: 225 °C (decomp.).

6a: GC/MS: *m*/*z* (%) = 500 (25) [M^+], 485 (6) [M − Me], 441 (8) [$Me_9Si_7S_3CH_2$], 427 (29) [$Me_9Si_7S_3$], 395 (3) [$Me_9Si_7S_2$], 351 (6) [$Me_7Si_6S_2CH_2$], 337 (7) [$Me_7Si_6S_2$], 293 (6) [$Me_5Si_5S_2CH_2$], 277 (10) [Me_7Si_5S], 262 (8) [Me_6Si_5S], 247 (15) [Me_5Si_5S], 233 (11) [$Me_5Si_4SCH_2$], 189 (11) [Me_7Si_3], 131 (13) [Me_5Si_2], 73 (100) [Me_3Si].

Dodecamethyl-3,7,10-triselenaoctasila[3.3.3]propellane, $Si_2(SiMe_2)_6Se_3$ (6b) and Dodecamethyl-3,7,10-tritelluraoctasila[3.3.3]propellane, $Si_2(SiMe_2)_6Te_3$ (6c): A solution of **5a** (0.31 g, 0.50 mmol) in 1 mL THF was slowly added to a suspension of Li_2E (E = Se, Te) prepared from 1.5 mmol elemental E and 3 mL of a 1 M solution of $Li[BEt_3H]$ in THF. In the case of the tellurium compound the reaction was carried out at −30 °C to prevent Si−Si bond cleavage reactions. After stirring for 30 min the solvent was removed in vacuo and replaced by 10 mL hexane. Filtration from precipitated lithium salts and removal of the solvents yielded the propellanes **6b** and **6c** as colorless crystalline residues in 62 and 25% yield, respectively.

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