3,7,10-Trichalcogenaoctasila[3.3.3]propellanes

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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 H₂S/NEt₃ or Li₂E (E = Se, Te) gives the dodecamethyl-3,7,10-trichalcogenaoctasila=[3.3.3]propellanes Si₂(SiMe₂)₆E₃ (**6**a E = S, **6b** E = Se, **6c** E = Te). The products have been characterized by multinuclear NMR spectroscopy (¹H, ¹³C, ²⁹Si, ⁷⁷Se, ¹²⁵Te). The central silicon atoms are very deshielded in comparison with other

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]







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 (**5**a), 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)].

$$Me_{3}Si \xrightarrow{SiMe_{3}}_{i}Si \xrightarrow{KOrBu / THF}_{-Me_{3}SiOrBu} \xrightarrow{Me_{3}Si}_{i}Si \xrightarrow{K^{+}}_{i}K^{+}$$
(2)

$$2 \operatorname{Me_{3}Si}_{SiMe_{3}}^{SiMe_{3}} \operatorname{K}^{+} \xrightarrow{C_{2}H_{4}Br_{2} (-78 \ ^{\circ}C)}_{- 2 \ ^{\circ}KBr} \xrightarrow{Me_{3}Si}_{Me_{3}Si-Si-Si-SiMe_{3}}_{Me_{3}Si} (3)$$

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]

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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(SiMe₂Cl)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(SiMe₂Cl)₃ unit there are three different SiMe₂Cl groups which can be distinguished by their different dihedral angles Cl-Si-Si-Si (see Table 1). A comparison of the two Si(SiMe₂Cl)₃ units shows that the silvl 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) and 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(SiMe₂Cl)₃ unit are smaller. This is a result of the mutual repulsion of the two Si(SiMe₂Cl)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.



C4

Figure 1. Molecular structure of 5a

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

Distances

2.3754(11)

2.3597(12)

2.3597(10)

2.3865(11)

2.3658(10)

2.3676(11)

2.3617(12)

2.0621(12)

2.0911(11)

2.0865(11)

2.1002(12)

2.0778(11)

2.0764(12)

1.883(3)

1.879(3)

1.857(4)

1.854(4)

1.849(4)

1.885(3)

1.849(4)

1.867(4)

1.856(4)

1.882(3)

1.870(3)

1.861(3)

Atoms

Si(1) - Si(2)

Si(1) - Si(3)

Si(1) - Si(4)

Si(1) - Si(5)

Si(5) - Si(6)

Si(5) - Si(7)

Si(5) - Si(8)

Si(2)-Cl(1)

Si(3)-Cl(2)

Si(4) - Cl(3)

Si(6) - Cl(4)

Si(7) - Cl(5)

Si(8) - Cl(6)

Si(2) - C(1)

Si(2) - C(2)

Si(3) - C(3)

Si(3) - C(4)

Si(4) - C(5)

Si(4) - C(6)

Si(6) - C(7)

Si(6) - C(8)

Si(7) - C(9)

Si(7)-C(10)

Si(8) - C(11)

Si(8) - C(12)

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

Atoms

Si(2) - Si(1) - Si(3)

Si(2) - Si(1) - Si(4)

Si(3) - Si(1) - Si(4)

Si(2) - Si(1) - Si(5)

Si(3)-Si(1)-Si(5)

Si(4) - Si(1) - Si(5)

Si(6) - Si(5) - Si(1)

Si(7) - Si(5) - Si(1)

Si(8) - Si(5) - Si(1)

Si(6) - Si(5) - Si(7)

Si(6) - Si(5) - Si(8)

Si(7) - Si(5) - Si(8)

Si(1) - Si(2) - Cl(1)

Si(1) - Si(3) - Cl(2)

Si(1) - Si(4) - Cl(3)

Si(5) - Si(6) - Cl(4)

Si(5) - Si(7) - Cl(5)

Si(5)-Si(8)-Cl(6)

Si(4) - Si(1) - Si(5) - Si(6)

Si(3) - Si(1) - Si(5) - Si(7)

Si(2) - Si(1) - Si(5) - Si(8)

Si(5) - Si(1) - Si(2) - Cl(1)

Si(5) - Si(1) - Si(3) - Cl(2)

Si(5) - Si(1) - Si(4) - Cl(3)

Si(1) - Si(5) - Si(8) - Cl(6)

Si(1) - Si(5) - Si(7) - Cl(5)

Si(1) - Si(5) - Si(6) - Cl(4)

Angles

-167.52(5)

C (1	C'M/		
1 ot the		1143410	

The NMR spectroscopic data of the propellanes 6a-care given in Table 2. While the δ_{Si} values of the SiMe₂ units are similar to those in the corresponding monocyclic fivemembered rings (SiMe₂)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 $Si(SiMe_3)_4$ ($\delta_{Si} = -135.5^{[13]}$), $Si_2(SiMe_3)_6$

		compound	δ_{Si}	δ_{E}	δ _C	δ_{H}
104.64(4)	6a	Me Me	A: -84.52	_	6.11	0.61
104.27(4)			e D. 10.79		11 . 47.5	
105.31(4)			B: 19.70		J _{SiC} . 47.5	
117.20(4)			$J_{\rm SiSi}: 54.2$			
110.48(4)		∖ J_si^.	5			
113.88(4)		Si ^B Si ^B				
116.16(4)		Me Me Me M	e			
112.14(4)		Me Me				
112.50(4)	0	Me Me	A. 72.22	Sec. 190	5.90	0 72
105.57(4)	6b	Me Me Me	le A: -/3.22	Se: -189	5.89	0.72
104.09(4)		Me_si ^B /Si ^B	B: 14.96	$^{1}J_{\rm SiSe}$: 110.8		
105.45(4)		/ Sin \	$^{-1}L_{\rm exc}$ 48.6	$^{2}I_{a:a} \cdot 24.8$		
109.18(5)		Se Se	Se 5551 40.0	3 SiSe. 2 1.0		
104.78(5)		Si ^B Si ^C Si ^B		$^{3}J_{SiSe}$: 13.6		
103.21(4)		Me Si ^B	10			
102.97(5)		Me Me				
106.98(5)						
100.97(5)	6c	Me Me	A:-52.36	Te: -622	5.64	0.99
-137.81(3)			B. −2.26	¹ <i>J</i> ₆₀₇ : 284.3		
-30.67(5)			D. 0.20	0 Sile. 20 110		
-31.78(6)			'J _{SiSi} : 45.3			
68 92(5)		sin /				
-17449(5)						
-33.29(6)		Me Me Me M	1e			
68,48(6)		Me Me				
	-					

3,7,10-Trichalcogenaoctasila[3.3.3] propellanes

The reaction of 5a with either H₂S/NEt₃ in hexane or Li_2E (E = Se, Te) prepared in situ from the chalcogens and LiBEt₃H in THF yielded the expected dodecamethyl-3,7,10-trichalcogenaoctasila[3.3.3]propellanes 6a-c [Equation (5) and (6)]:

 Me_2 Si Me_2 SiMe₂Cl Me_2 SiMe₂Cl ClMe₂Si H₂S / NEta 6a (5)- HNEt₃Cl ClMe₂Si⁻ SiMe₂Cl S SiMe₂Cl Me_2 Si Me₂ Me₂ 5a Me_2 Me_2 Si Me_2 SiMe₂Cl Si -Si ClMe₂Si-∠SiMe₂Cl Li2E / THF F - LiCl (6) ClMe₂Si² SiMe₂Cl Me_2 Me₂ SiMe₂Cl Ši. Me₂ 5a **6b**: E = Se **6c**: E = Te

It has been observed before that the formation of fivemembered rings in the silicon chalcogen systems is always accompanied by a strong low-field shift of the ²⁹Si 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-

Figure 3. ²⁹Si NMR chemical shifts in bicyclo[3.3.0]octanes (2a-c)

[1] and [3.3.3] propellanes (6a-c) for E = S, Se, Te



(4, $\delta_{Si} = -129.5^{[9]}$) or even chloro-substituted derivatives

like $Si(SiMe_2Cl)_4$ ($\delta_{Si} = -113.9^{[14]}$) and $Si_2(SiMe_2Cl)_6$ (5a, $\delta_{Si} = -111.62$) 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).

field shifts. Furthermore, compared to the bicyclo[3.3.0]octanes $2b-c^{[1]}$ the ⁷⁷Se and the ¹²⁵Te 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.

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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



Figure 4. Molecular structure of 6a

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)		

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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)° [Si₄S ring including S(1)], 46.52(6)° [Si₄S ring including S(2)] and $45.28(8)^{\circ}$ [Si₄S ring including S(3)]. This is slightly more than in the organic [3.3.3]propellane modhephenediol (3c) with envelope angles of $37-42^{\circ[6]}$ 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 $101.5-102.4^{\circ}$, 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 $115.1-116.4^\circ$).



Figure 5. The silicon and sulfur skeleton of $\mathbf{6a}$ viewed along the central Si-Si bond

Experimental Section

General: All NMR spectra were recorded on a Bruker DPX 400 in CDCl₃ solution and TMS as internal standard for ¹H, ¹³C and ²⁹Si. External Ph₂Se₂ ($\delta_{Se} = 460$) and Ph₂Te₂ ($\delta_{Te} = 422$) in CDCl₃ were used as standards for ⁷⁷Se and ¹²⁵Te. In order to obtain a sufficient signal-to-noise ratio of ²⁹Si NMR spectra for obtaining ¹J_{SiC}, ¹J_{SiSi}, ^{1,2,3}J_{SiSe} or ¹J_{SiTe} satellites ²⁹Si INEPT spectra were also recorded. ⁷⁷Se and ¹²⁵Te spectra were determined using an IGATED pulse program.

Mass spectra were measured on a Hewlett Packard 5971 (ionization energy: 70 eV, column: 30 m \times 0.25 mm \times 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 LiBEt₃H in THF (Super Hydride), were commercially available. Si(SiMe₃)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 ₆ Si ₈	C ₁₂ H ₃₆ S ₃ Si ₈
Molecular weight	617.83	501.31
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	C2/c
Unit cell dimensions, A, °	a = 10.9820(6)	a = 14.6972(19)
	b = 17.0125(10)	b = 12.0174(14)
	c = 17.2780(11)	c = 31.930(4)
	$\beta = 100.401(2)$	$\beta = 100.812(2)$
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	$Mo-K_a$	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 $R_1 / w R^2 [I > 2 \sigma(I)]^{[a]}$	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	ō.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 SAD-ABS.^[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, Si₂(SiMe₃)₆ (4): Si(SiMe₃)₄ was reacted in THF with KOtBu and the resulting KSi(Me₃Si)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(SiMe₃)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. ¹H NMR: $\delta = 0.274$; ¹³C NMR: $\delta = 4.38$ (¹ $J_{SiC} = 42.3$ Hz); ²⁹Si NMR: $\delta = -9.55$ (SiMe₃, ¹ $J_{SiSi} = 53.0$ Hz), -130.13 (*SiSi*₄). - GC/MS: *m/z* (%) = 494 (4) [M⁺], 479 (4) [M - Me], 421 (3) [Me₁₅Si₇], 406 (5) [Me₁₄Si₇], 305 (2) [Me₁₁Si₅], 273 (11) [Me₇Si₆], 247 (22) [Me₉Si₄], 232 (100) [Me₈Si₄], 199 (15), 173 (12) [Me₅Si₃CH₂], 131 (13) [Me₅Si₂], 73 (62) [Me₃Si].

Hexakis(chlorodimethylsilyl)disilane, Si₂(SiMe₂Cl)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; ¹H NMR: $\delta = 0.845$; ¹³C NMR: $\delta = 8.05$ (¹*J*_{SiC} = 48.7 Hz); ²⁹Si NMR: $\delta = 29.06$ (SiMe₂Cl, ¹*J*_{SiSi} = 56.9 Hz), -111.62 (*Si*Si₄). - GC/MS: *m*/*z* (%) = 601 (2) [M - Me], 581 (1) [M - Cl], 523 (44) [Me₁₀Cl₅Si₇], 488 (21) [Me₁₀Cl₄Si₇], 395 (9) [Me₈Cl₃Si₆], 380 (15) [Me₇Cl₃Si₆], 309 (13) [Me₆Cl₃Si₄], 272 (42) [Me₆Cl₂Si₄], 209 (18) [Me₆ClSi₃], 174 (13) [Me₆Si₃], 131 (26) [Me₅Si₂], 93 (37) [Me₂ClSi], 73 (100) [Me₃Si].

If the reaction mixture was heated to 70 °C, a mixture of **5a** (52%), (ClMe₂Si)₃Si-Si (SiClMe₂)₂(SiCl₂Me) (**5b**; 43%) and

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 $\label{eq:cl_2MeSi} \begin{array}{ll} (Cl_2MeSi^C)(ClMe_2Si^B)_2Si^A - Si^A(Si^BClMe_2)_2(Si^CCl_2Me) & (\textbf{5c}; \ 5\%) \\ \text{was obtained after removal of the solvent hexane.} \end{array}$

 $\begin{array}{l} (\mathbf{CIMe_2Si^C})_3\mathbf{Si^A} - \mathbf{Si^B}(\mathbf{Si^DCIMe_2})_2(\mathbf{Si^ECl_2Me}) \ (\mathbf{5b}): \ ^{13}\mathbf{C} \ \mathrm{NMR}: \ \delta = \\ 8.03 \ (\mathrm{Si^CMe_2}), \ 7.69 \ (\mathrm{Si^DMe_2}), \ 13.02 \ (\mathrm{Si^EMe}); \ ^{29}\mathbf{Si} \ \mathrm{NMR}: \ \delta = \\ -111.23 \ (\mathrm{Si^A}), \ -104.08 \ (\mathrm{Si^B}), \ 28.88 \ (\mathrm{Si^C}), \ 27.85 \ (\mathrm{Si^D}), \ 36.98 \ (\mathrm{Si^E}). \\ - \ GC/MS: \ m/z \ (\%) = \ 623 \ (2) \ [\mathrm{M} - \ \mathrm{Me}], \ 543 \ (27) \ [\mathrm{Me_3Cl_6Si_7}], \ 508 \\ (28) \ [\mathrm{Me_9Cl_5Si_7}], \ 415 \ (10) \ [\mathrm{Me_7Cl_4Si_6}], \ 400 \ (24) \ [\mathrm{Me_6Cl_4Si_6}], \ 309 \\ (31) \ [\mathrm{Me_6Cl_3Si_4}], \ 272 \ (13) \ [\mathrm{Me_6Cl_2Si_4}], \ 209 \ (19) \ [\mathrm{Me_6Cl_Si_3}], \ 159 \ (22) \\ [\mathrm{Me_5Si_3}], \ 131 \ (29) \ [\mathrm{Me_5Si_2}], \ 93 \ (61) \ [\mathrm{Me_2ClSi}], \ 73 \ (100) \ [\mathrm{Me_3Si}]. \end{array}$

(Cl₂MeSi^C)(ClMe₂Si^B)₂Si^A-Si^A(Si^BClMe₂)₂(Si^CCl₂Me) (5c): ²⁹Si NMR: $\delta = -111.23$ (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 NEt₃ (0.35 mL, 2.5 mmol) was added while a stream of dried H₂S 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) [Me₉Si₇S₃CH₂], 427 (29) [Me₉Si₇S₃], 395 (3) [Me₉Si₇S₂], 351 (6) [Me₇Si₆S₂CH₂], 337 (7) [Me₇Si₆S₂], 293 (6) [Me₅Si₅S₂CH₂], 277 (10) [Me₇Si₅S], 262 (8) [Me₆Si₅S], 247 (15) [Me₅Si₅S], 233 (11) [Me₅Si₄SCH₂], 189 (11) [Me₇Si₃], 131 (13) [Me₅Si₂], 73 (100) [Me₃Si].

Dodecamethyl-3,7,10-triselenaoctasila[3.3.3]propellane, Si₂(Si-Me₂)₆Se₃ (6b) and Dodecamethyl-3,7,10-tritelluraoctasila[3.3.3]propellane, Si₂(SiMe₂)₆Te₃ (6c): A solution of 5a (0.31 g, 0.50 mmol) in 1 mL THF was slowly added to a suspension of Li₂E (E = Se, Te) prepared from 1.5 mmol elemental E and 3 mL of a 1 M solution of Li[BEt₃H] 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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