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X-ray Crystal and Molecular Structures of Hexacosamethylcyclotridecasilane, $(Me_2Si)_{13}$, and Dotriacontamethylcyclohexadecasilane, $(Me_2Si)_{16}$

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Abstract: The crystal and molecular structures of hexacosamethylcyclotridecasilane, $(Me_2Si)_{13}$ (**1**), and dotriacontamethylcyclohexadecasilane, $(Me_2Si)_{16}$ (**2**), have been determined by X-ray crystallography. The conformations of **1** and **2** in the solid state are quite different from those of cycloalkanes or other known 13- or 16-membered rings. Both **1** and **2** exhibit abnormal torsional angles far from 60° (gauche) or 180° (trans), and **1** contains unusually large Si-Si-Si angles averaging 115.2°. These distortions probably relieve unfavorable transannular methyl-methyl interactions. Crystals of **1** and **2** are both monoclinic, with space groups $P2_1/n$ ($a = 16.656$ Å, $b = 13.278$ Å, $c = 24.044$ Å, $\beta = 103.82°$) and $P2_1/c$ ($a = 15.338$ Å, $b = 13.946$ Å, $c = 15.451$ Å, $\beta = 110.58°$), respectively.

The cyclic polysilanes show unusual features which arise from electron delocalization in the Si-Si σ framework.[1] Their properties include UV absorption,[2] formation of charge-transfer complexes,[3] and reduction to delocalized anion[4] and cation[5] radicals. Among the many linear and cyclic polysilanes now known, the family of permethylated silicon rings $[Si(CH_3)_2]_n$ (where $n = 4$–35) have been studied most extensively, but relatively little structural information has been reported for those compounds. X-ray structures are known for two rings in this series, $(Me_2Si)_4$[6] and $(Me_2Si)_6$,[7] and we have recently reported the crystal structure and conformational analysis of $(Me_2Si)_7$.[8]

In this paper, the solid state structures of two large rings in the permethylcyclopolysilane series, hexacosamethylcyclotridecasilane, $(Me_2Si)_{13}$ (**1**), and dotriacontamethylcyclohexadecasilane, $(Me_2Si)_{16}$ (**2**), are reported, and their structures are compared with those of hydrocarbon analogues and other known 13- and 16-membered rings.

ORTEP diagrams for **1** and **2** as determined by X-ray diffraction are shown in Figures 1 and 2, respectively. Figures 3 and 4 present different views of **1** and **2**, as stereo pairs. Important bond lengths and angles are given in Tables I, ,II, and III.

To compare the structures of the cyclosilanes with those of corresponding cycloalkanes, it will be helpful to consider the 16-membered rings first. A diamond-lattice model is usually employed to describe idealized geometries of macrocyclic carbon rings with an even number of carbon atoms.[9] Cycloalkanes $(CH_2)_{2n}$ with $n > 6$ generally fit this pattern, having square or rectangular conformations with two or three carbon atoms connecting two sides together.

For cyclohexadecane, semiquantitative strain energy calculations[10,11] suggest that the diamond-lattice "square" or [4444][12] conformation is distinctly lower in energy than any other, and the infrared spectrum of the crystalline hydrocarbon as well as its ^{13}C NMR spectrum are consistent with the [4444] conformation.[13] X-ray crystal structures for 1,1,9,9-tetramethylcyclohexadecane,[14] (**3**), and for several tetraoxacyclohexadecanes,[15] show that all of these 16-rings adopt the [4444] arrangement. The next lowest energy conformation for cyclohexadecane is predicted to be the rectangular [3535] conformation.[10,11]

The structures of **2** (Figures 2 and 4) are quite unlike either the [4444] or [3535] conformations. In the usual formalism it could be described as [224224] or as two-cornered [88] with detailed structure [2121221212]. However, these designations do not take into account the abnormal torsional angles observed for **2**. As shown in Table III, the torsional angles for **3** are all within 10° of either 60° or 180°, the ideal gauche and trans angles, respectively. The torsional angles for **2** fall into two groups of six, with values clustering around 92 and 165°; thus the "gauche" angles are much larger, and the "trans" angles are much smaller than the normally expected values.

Abnormal values for torsional angles are more likely for **2** than for hydrocarbons because of the very low barrier to rotation around the Si-Si bond in methylsilanes.[16] However, this does not explain why **2** adopts its unusual conformation. Insight into this question is provided by the data for intramolecular methyl-methyl distances given in Table IV. In **2** there are no less than 20 carbon-carbon distances (for methyl groups on different silicon atoms) in the range from 359 to 400 pm (the latter value is the usual limit for van der Waals' forces between methyls).[17] We believe that these distances and the resulting conformation in the crystals reflect a balance of attractive and repulsive forces[18] between the methyl

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[1] For a review, see: West, R. *Pure Appl. Chem.* **1982**, *54*, 1041.

[2] (a) Pitt, C. G. In *Homoatomic Rings, Chains and Macromolecules of Main-Group Elements*; Rheingold, A., Ed.; Elsevier: Amsterdam, 1977; p 203. (b) Brough, L. F.; West, R. *J. Am. Chem. Soc.* **1981**, *103*, 3049. (c) Brough, L. F.; West, R. *J. Organomet. Chem.* **1980**, *194*, 139.

[3] Traven, V. F.; West, R. *J. Am. Chem. Soc.* **1973**, *95*, 6824.

[4] (a) Wadsworth, C. L.; West, R. *Organometallics* **1985**, *4*, 1664 and references cited therein. (b) Carberry, E.; West, R.; Glass, G. E. *J. Am. Chem. Soc.* **1969**, *91*, 5446.

[5] Bock, H.; Kaim, W.; Kira, M.; West, R. *J. Am. Chem. Soc.* **1979**, *101*, 7667.

[6] Kratky, C.; Schuster, H. G.; Hengge, E. *J. Organomet. Chem.* **1983**, *247*, 253.

[7] Carrell, H. L.; Donohue, J. *Acta Crystallogr. Sect. B: Struct. Crystallogr. Cryst. Chem.* **1972**, *B28*, 1566.

[8] Shafiee, F.; Damewood, J. R., Jr.; Haller, K. J.; West, R. *J. Am. Chem. Soc.* **1985**, *107*, 6950 and references cited therein.

[9] (a) Groth, P. *Acta Chem. Scand. A* **1976**, *30*, 155. (b) Groth, P. *Ibid.* **1979**, *33*, 199. (c) Kay, H. F.; Newman, B. A. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1968**, *B24*, 615.

[10] (a) Dale, J. *Acta Chem. Scand.* **1973**, *27*, 1115. (b) Alliger, A. L.; Gorden, B.; Profeta, J. *Tetrahedron* **1980**, *36*, 859. (c) Dale, J. *J. Chem. Soc.* **1968**, *93*. Dale, J.; Ekeland, T. *Acta Chem. Scand.* **1973**, *27*, 1519.

[11] In this shorthand notation for conformational type, the numbers within brackets each represent the number of bonds in one "side", starting with the shortest. The direction around the ring is so chosen that the following number is the smallest possible; the sum of all numbers within the bracket give the ring size.

[12] Borgen, G.; Dale, J. *Chem. Commun.* **1970**, 1340.

[13] Anet, F. A. L.; Cheng, A. K. *J. Am. Chem. Soc.* **1975**, *97*, 2420 and references cited therein.

[14] Groth, P. *Acta Chem. Scand. A* **1974**, *25*, 808 and references cited therein.

[15] (a) Groth, P. *Acta Chem. Scand.* **1975**, *29*, 642. (b) Groth, P. *Ibid.* **1971**, *25*, 725. (c) Borgen, G.; Dale, J.; Teien, G. *Ibid.* **1979**, *33*, 15.

[16] Damewood, J. R., Jr.; West, R. *Macromolecules* **1985**, *18*, 159 and references cited therein.

[17] Eliel, E.; Allinger, N. L.; Angyal, S. J.; Morrison, G. A. In *Conformational Analysis*; Interscience: New York, 1966; Chapter 7. (b) Westheimer, F. H.; Newman, M. S., Ed.; *Steric Effects in Organic Chemistry*; Wiley: New York, 1956, Chapter 12.

0002-7863/86/1508-5478$01.50/0

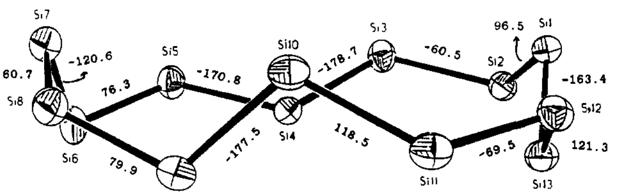

Figure 1. A different ORTEP view of $(Me_2Si)_{13}$, **1**, giving the numbering scheme used in the tables. Methyl groups have been eliminated for clarity. Values indicated at each bond are torsion angles between planes each defined by three atoms.

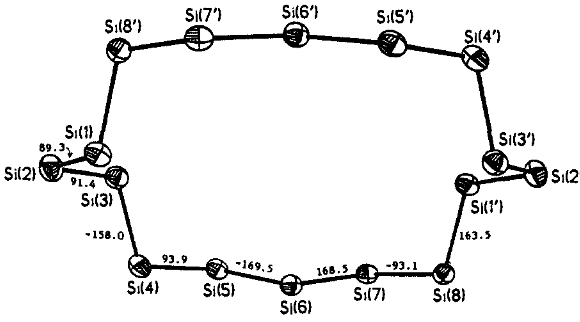

Figure 2. A different ORTEP view of $(Me_2Si)_{16}$, **2**, giving the numbering scheme used in the tables. Values indicated at each bond are torsion angles between planes each defined by three atoms. Methyl groups are eliminated for clarity.

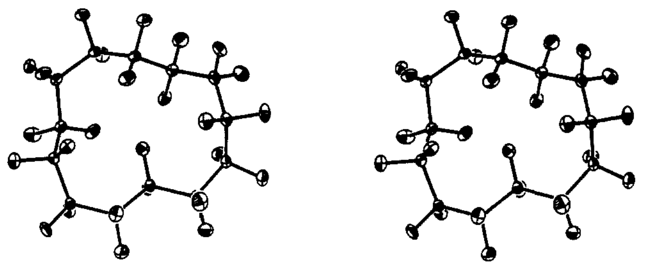

Figure 3. A stereoscopic pair of ORTEP views of $(Me_2Si)_{13}$, **1**. Hydrogen atoms have been removed for clarity. Thermal ellipsoids are drawn at the 50% probability level.

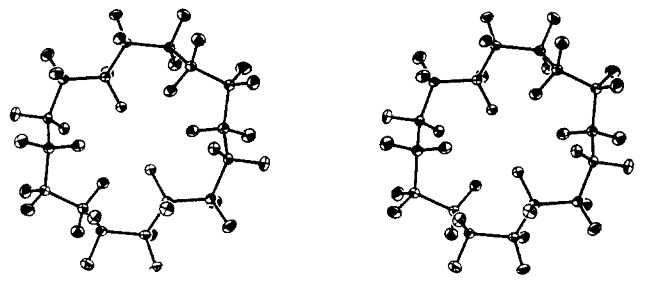

Figure 4. A stereoscopic pair of ORTEP views of $(Me_2Si)_{16}$, **2**. Hydrogen atoms have been removed for clarity. Thermal ellipsoids are drawn at the 50% probability level.

groups; that is, that the molecule adopts a conformation which maximizes attractive CH_3–CH_3 interactions while minimizing repulsive interactions. Packing forces probably play a secondary role in establishing the conformation of **2** in the solid. Table IV also lists intermolecular C–C distances for **2**; there are eight contacts at distances between 381 and 400 pm.

Table I. Selected Bonding Parameters for $(Me_2Si)_{13}$ (**1**)

Bond Lengths, pm			
Si–Si			
Si(1)–Si(2)	236.1 (3)	Si(8)–Si(9)	234.2 (4)
Si(2)–Si(3)	236.0 (3)	Si(9)–Si(10)	235.7 (3)
Si(3)–Si(4)	234.1 (3)	Si(10)–Si(11)	237.1 (4)
Si(4)–Si(5)	232.9 (3)	Si(11)–Si(12)	235.6 (4)
Si(5)–Si(6)	234.3 (4)	Si(12)–Si(13)	236.3 (3)
Si(6)–Si(7)	237.7 (4)	Si(13)–Si(1)	236.1 (3)
Si(7)–Si(8)	235.7 (3)	Si–Si(avg)	235.5
Si–C			
Si(1)–C(1)	190.0 (9)	Si(8)–C(15)	188.7 (10)
Si(1)–C(2)	191.3 (10)	Si(8)–C(16)	188.5 (11)
Si(2)–C(3)	188.8 (10)	Si(9)–C(17)	187.0 (10)
Si(2)–C(4)	189.6 (9)	Si(9)–C(18)	185.2 (10)
Si(3)–C(5)	188.7 (11)	Si(10)–C(19)	187.6 (10)
Si(3)–C(6)	187.4 (10)	Si(10)–C(20)	189.2 (10)
Si(4)–C(7)	187.8 (8)	Si(11)–C(21)	189.2 (10)
Si(4)–C(8)	189.1 (10)	Si(11)–C(22)	190.3 (8)
Si(5)–C(9)	188.3 (9)	Si(12)–C(23)	188.6 (10)
Si(5)–C(10)	188.7 (12)	Si(12)–C(24)	193.2 (9)
Si(6)–C(11)	184.9 (12)	Si(13)–C(25)	189.4 (11)
Si(6)–C(12)	190.5 (10)	Si(13)–C(26)	187.8 (9)
Si(7)–C(13)	188.4 (10)	Si–C(avg)	188.8
Si(7)–C(14)	189.3 (10)		
Bond Angles			
Si–Si–Si			
Si(13)–Si(1)–Si(2)	114.1 (1)	Si(7)–Si(8)–Si(9)	125.6 (1)
Si(1)–Si(2)–Si(3)	116.5 (1)	Si(8)–Si(9)–Si(10)	115.6 (1)
Si(2)–Si(3)–Si(4)	114.0 (1)	Si(9)–Si(10–Si(11)	112.4 (1)
Si(3)–Si(4)–Si(5)	114.3 (1)	Si(10)–Si(11)–Si(12)	117.9 (1)
Si(4)–Si(5)–Si(6)	110.5 (1)	Si(11)–Si(12)–Si(13)	117.1 (1)
Si(5)–Si(6)–Si(7)	113.9 (1)	Si(12)–Si(13)–Si(1)	114.9 (1)
Si(6)–Si(7)–Si(8)	117.8 (1)	Si–Si–Si(avg)	115.7
C–Si–C			
C(1)–Si(1)–C(2)	106.4 (4)	C(15)–Si(8)–C(16)	107.7 (5)
C(3)–Si(2)–C(4)	106.9 (5)	C(17)–Si(9)–C(18)	106.9 (5)
C(5)–Si(3)–C(6)	107.9 (5)	C(19)–Si(10)–C(20)	105.9 (5)
C(7)–Si(4)–C(8)	111.2 (4)	C(21)–Si(11)–C(22)	105.7 (4)
C(9)–Si(5)–C(10)	108.3 (5)	C(23)–Si(12)–C(24)	107.8 (4)
C(11)–Si(6)–C(12)	106.8 (5)	C(25)–Si(13)–C(26)	105.9 (5)
C(13)–Si(7)–C(14)	106.0 (5)	C–Si–C(avg)	107.2
Si–Si–C			
Si(1)–Si(2)–C(3)	111.7 (3)	Si(7)–Si(6)–C(11)	111.4 (3)
Si(1)–Si(2)–C(4)	106.4 (3)	Si(7)–Si(6)–C(12)	107.7 (4)
Si(1)–Si(13)–C(25)	104.0 (3)	Si(8)–Si(9)–C(17)	111.1 (3)
Si(1)–Si(13)–C(26)	115.3 (3)	Si(8)–Si(9)–C(18)	102.1 (4)
Si(2)–Si(3)–C(5)	109.3 (3)	Si(8)–Si(7)–C(13)	108.7 (3)
Si(2)–Si(3)–C(6)	106.4 (4)	Si(8)–Si(7)–C(14)	102.6 (3)
Si(2)–Si(1)–C(1)	107.3 (3)	Si(9)–Si(10)–C(19)	115.5 (3)
Si(2)–Si(1)–C(2)	108.3 (3)	Si(9)–Si(10)–C(20)	105.6 (3)
Si(3)–Si(4)–C(7)	106.6 (3)	Si(9)–Si(8)–C(15)	105.4 (4)
Si(3)–Si(4)–C(8)	110.1 (3)	Si(9)–Si(8)–C(16)	107.5 (3)
Si(3)–Si(2)–C(3)	109.1 (3)	Si(10)–Si(11)–C(21)	112.2 (3)
Si(3)–Si(2)–C(4)	105.5 (3)	Si(10)–Si(11)–C(22)	106.5 (3)
Si(4)–Si(5)–C(9)	109.3 (4)	Si(10)–Si(9)–C(17)	115.5 (3)
Si(4)–Si(5)–C(10)	112.0 (3)	Si(10)–Si(9)–C(18)	103.9 (3)
Si(4)–Si(3)–C(5)	109.4 (3)	Si(11)–Si(12)–C(23)	109.8 (3)
Si(4)–Si(3)–C(6)	109.6 (4)	Si(11)–Si(12)–C(24)	103.3 (3)
Si(5)–Si(6)–C(11)	110.9 (4)	Si(11)–Si(10)–C(19)	110.3 (3)
Si(5)–Si(6)–C(12)	105.7 (4)	Si(11)–Si(10)–C(20)	106.5 (3)
Si(5)–Si(4)–C(7)	107.1 (3)	Si(12)–Si(13)–C(25)	106.5 (3)
Si(5)–Si(4)–C(8)	107.5 (3)	Si(12)–Si(13)–C(26)	109.3 (3)
Si(6)–Si(7)–C(13)	114.9 (3)	Si(12)–Si(11)–C(21)	108.2 (3)
Si(6)–Si(7)–C(14)	105.4 (3)	Si(12)–Si(11)–C(22)	105.5 (3)
Si(6)–Si(5)–C(9)	107.7 (3)	Si(13)–Si(12)–C(23)	112.4 (3)
Si(6)–Si(5)–C(10)	108.9 (4)	Si(13)–Si(12)–C(24)	105.7 (3)
Si(7)–Si(8)–C(15)	105.7 (3)	Si(13)–Si(1)–C(1)	104.3 (3)
Si(7)–Si(8)–C(16)	103.8 (3)	Si(13)–Si(1)–C(2)	115.8 (3)
Si–Si–C(av) 108.3			

Odd-numbered macrocycle rings cannot fit the diamond-lattice model and consequently must be distorted with respect to bond lengths, bond angles, torsional angles, or combinations of these. For cyclotridecanes calculations[19] indicate that the [346] three-cornered and [13333] five-cornered conformations have the lowest energy. The structure of cyclotridecane is unknown, but of the few X-ray crystal structures known for 13-membered rings, all show one of these two conformations.[20,21]

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(18) Hummel, J. P.; Stackhouse, J.; Mislow, K. *Tetrahedron* **1977**, *33*, 1925.

(19) (a) Anet, F. A. L.; Rawdah, T. N. *J. Am. Chem. Soc.* **1978**, *100*, 7810. (b) Dale, J. *Top. Stereochem.* **1976**, *9*, 199. (c) Casanova, J.; Zahra, J.-P.; Waegll, B. *Org. Mag. Reson.* **1980**, *13*, 29 and references cited therein.

Table II. Selected Bonding Parameters for **2**

		Bond Lengths, pm			
Si(1)–Si(2)	235.1 (2)	Si(1)–C(1)	189.6 (4)	Si(5)–C(10)	189.1 (4)
Si(2)–Si(3)	235.7 (2)	Si(1)–C(2)	189.0 (4)	Si(6)–C(11)	188.8 (4)
Si(3)–Si(4)	235.6 (1)	Si(2)–C(3)	188.9 (5)	Si(6)–C(12)	189.3 (4)
Si(4)–Si(5)	236.0 (2)	Si(2)–C(4)	188.5 (5)	Si(7)–C(13)	188.2 (4)
Si(5)–Si(6)	234.9 (1)	Si(3)–C(5)	188.7 (4)	Si(7)–C(14)	188.2 (4)
Si(6)–Si(7)	235.6 (2)	Si(3)–C(6)	189.2 (4)	Si(8)–C(15)	188.5 (4)
Si(7)–Si(8)	236.0 (2)	Si(4)–C(7)	188.6 (4)	Si(8)–C(16)	189.1 (4)
Si(8)–Si(1)	234.8 (1)	Si(4)–C(8)	189.5 (4)	Si–C(avg)	188.9
Si–Si(avg)	235.5	Si(5)–C(9)	188.6 (4)		
		Bond Angles, deg			
Si(2)–Si(1)–Si(8)	114.2 (1)	Si(8)–Si(1)–C(1)	112.5 (1)	Si(2)–Si(3)–C(6)	108.2 (2)
Si(1)–Si(2)–Si(3)	112.2 (1)	Si(8)–Si(1)–C(2)	106.6 (1)	Si(4)–Si(3)–C(5)	113.3 (1)
Si(2)–Si(3)–Si(4)	113.0 (1)	Si(2)–Si(1)–C(1)	108.2 (1)	Si(4)–Si(3)–C(6)	106.5 (1)
Si(3)–Si(4)–Si(5)	111.9 (1)	Si(2)–Si(1)C(2)	107.4 (2)	Si(3)–Si(4)–C(7)	113.4 (1)
Si(4)–Si(5)–Si(6)	110.2 (1)	Si(1)–Si(2)–C(3)	107.9 (2)	Si(3)–Si(4)–C(8)	106.5 (2)
Si(5)–Si(6)–Si(7)	114.1 (1)	Si(1)–Si(2)–C(4)	110.6 (2)	Si(5)–Si(4)–C(7)	110.2 (2)
Si(6)–Si(7)–Si(8)	109.4 (1)	Si(3)–Si(2)–C(3)	111.6 (2)	Si(5)–Si(4)–C(8)	107.9 (2)
Si(7)–Si(8)–Si(1)	110.1 (1)	Si(3)–Si(2)–C(4)	107.9 (2)	Si(4)–Si(5)–C(9)	109.6 (1)
Si–Si–Si(avg)	111.9	Si(2)–Si(3)–C(5)	108.9 (1)	Si(4)–Si(5)–C(10)	108.3 (1)
Si(6)–Si(5)–C(9)	112.1 (1)	Si(8)–Si(7)–C(14)	108.1 (2)	C(1)–Si(1)–C(2)	107.5 (2)
Si(6)–Si(5)–C(10)	107.8 (1)	Si(7)–Si(8)–C(15)	110.4 (1)	C(3)–Si(2)–C(4)	106.5 (2)
Si(5)–Si(6)–C(11)	109.9 (1)	Si(7)–Si(8)–C(16)	108.4 (2)	C(5)–Si(3)–C(6)	106.6 (2)
Si(5)–Si(6)–C(12)	106.7 (1)	Si(1)–Si(8)–C(15)	114.0 (1)	C(7)–Si(4)–C(8)	106.5 (2)
Si(7)–Si(6)–C(11)	110.5 (1)	Si(1)–Si(8)–C(16)	107.3 (1)	C(9)–Si(5)–C(10)	108.8 (2)
Si(7)–Si(6)–C(12)	107.0 (1)	Si–Si–C(avg)	109.4	C(11)–Si(6)–C(12)	108.5 (2)
Si(6)–Si(7)–C(13)	113.4 (2)			C(13)–Si(7)–C(14)	106.7 (2)
Si(6)–Si(7)–C(14)	109.0 (2)			C(15)–Si(8)–C(16)	106.4 (2)
Si(8)–Si(7)–C(13)	110.2 (1)			C–Si–C(avg)	107.2

Table III. Torsion Angles in **1** and **2** Compared with Those in Corresponding Cycloalkanes[a]

	2	**3**[b]	**1**	**4** [13333][c]	**4** [346][c]
w_1	89.3	54.5	96.5	-55.7	-55.9
w_2	91.4	58.6	-60.5	-50.8	-49.7
w_3	-158.0	-177.6	-178.7	173.9	177.7
w_4	93.9	179.0	-170.8	-169.3	-169.7
w_5	-169.5	-58.1	76.3	72.4	21.4
w_6	168.4	-59.3	-120.6	-101.3	82.9
w_7	-93.1	-177.4	60.7	160.4	-163.4
w_8	163.5	-178.1	79.9	-75.2	110.2
w_9	-89.3	54.6	-177.5	-73.8	-113.0
w_{10}	91.4	55.1	118.5	170.8	168.0
w_{11}	158.0	-175.6	-69.5	-77.9	-77.5[d]
w_{12}	-93.9	-179.9	121.3	-72.3	-72.9
w_{13}	169.5	-58.8	-163.4	164.6	165.0
w_{14}	-168.4	-50.3			
w_{15}	93.1	179.0			
w_{16}	-163.5	177.8			

[a] In degrees. [b] Values from ref 14. [c] Values from ref 21. [d] The sign has been changed to correct a misprint in ref 27.

Table IV. Carbon–Carbon Distances Less than 400 pm for **2**

	Intramolecular		
C(1)–C(11)	374.0	C(5)–C(9)	384.7
C(1)–C(5)	391.6	C(5)–C(15)	386.7
C(1)–C(7)	393.6	C(5)–C(11)	392.7
C(1)–C(13)	393.9	C(7)–C(12)	385.2
C(2)–C(3)	361.6	C(8)–C(10)	367.0
C(2)–C(16)	366.3	C(9)–C(13)	386.0
C(2)–C(13)	397.8	C(10)–C(12)	373.8
C(3)–C(7)	393.1	C(11)–C(14)	376.7
C(4)–C(6)	363.8	C(12)–C(15)	387.2
C(6)–C(8)	359.4	C(14)–C(16)	367.0
	Intermolecular		
C(1)–C(14)′	386.6		
C(3)–C(16)′	393.3		
C(4)–C(4)′	381.6		
C(4)–C(15)′	390.3		
C(4)–C(16)′	397.1		
C(10)–C(13)′	399.7		

Table V. Carbon–Carbon Distances Less Than 400 pm for **1**

		Intramolecular			
C(1)–C(4)	359.7	C(7)–C(19)	358.7	C(15)–C(18)	352.8
C(1)–C(25)	348.9	C(7)–C(26)	380.0	C(16)–C(18)	389.8
C(2)–C(5)	390.6	C(8)–C(9)	358.6	C(16)–C(20)	388.0
C(2)–C(7)	396.6	C(8)–C(11)	358.9	C(17)–C(21)	387.6
C(2)–C(23)	383.8	C(8)–C(26)	390.9	C(17)–C(26)	397.0
C(3)–C(6)	384.2	C(9)–C(12)	372.4	C(18)–C(20)	358.8
C(4)–C(5)	387.6	C(10)–C(13)	372.3	C(20)–C(22)	343.0
C(4)–C(6)	385.2	C(11)–C(17)	391.4	C(21)–C(24)	382.6
C(5)–C(7)	393.5	C(12)–C(14)	346.3	C(21)–C(26)	394.5
C(5)–C(10)	393.8	C(13)–C(16)	376.2	C(22)–C(23)	392.1
C(7)–C(13)	388.4	C(14)–C(15)	367.5	C(22)–C(24)	375.7
C(7)–C(17)	398.5	C(14)–C(16)	371.8	C(24)–C(25)	343.7
		Intermolecular			
C(2)–C(14)′	395.0	C(13)–C(16)′	392.0		
C(3)–C(21)′	382.7	C(14)–C(22)′	396.5		
C(5)–C(15)′	386.3	C(17)–C(25)′	392.2		
C(10)–C(24)	398.7	C(26)–C(26)′	367.7		
C(12)–C(21)′	384.2				

Torsional angles for **1** and for the two conformations of **4** are shown in Table III. The angles deviate somewhat more from ideal values for **4** than for **3**, reflecting the greater transannular strain in the 13-membered ring. For the [13333] form of **4**, seven of the torsional angles are gauche (50–78°), five are trans (>160°), and one is intermediate (101.3°). The structure of **1** is unusual in having *four* intermediate torsional angles, three having values very close to 120° and so leading to eclipsing of methyl groups. The results for this structure, as for **2**, are consistent with great torsional flexibility at the Si–Si bonds.

Intramolecular methyl–methyl distances in **1** are listed in Table V; 36 of these are between 343 and 400 pm. Again, the structure can be interpreted in terms of a balance between attractive and repulsive CH_3–CH_3 van der Waals' interactions. As for **2**, there are a few short intermolecular methyl–methyl contacts also, which may also affect the solid-state conformation.

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(20) Samuel, G.; Weiss, R. *Tetrahedron Lett.* **1969**, *33*, 2803.

(21) An example is α,ω-bis(methyldodeca-1,12-diylammonio)hexane dibromide (**4**) which exists as two independent types of molecules in the unit cell, one in which both 13-membered rings have the [13333] conformation, and one in which both rings have the [346] conformation. See: Rubin, B. H.; Williamson, M.; Takeshita, M.; Menger, F. M.; Anet, F. A. L.; Bacon, B.; Allinger, N. L. *J. Am. Chem. Soc.* **1984**, *106*, 2088.

Table VI. Summary of Crystal Data and Intensity Collection

parameter	2	1
empirical formula	$Si_{16}C_{32}H_{96}$	$Si_{13}C_{26}H_{78}{\cdot}H_2O$
cryst dimensions (mm)	0.28 × 0.28 × 0.75	0.25 × 0.31 × 0.72
temp (°C)	−75 ± 5	−80 ± 5
cell parameters		
a (Å)	15.338 (2)	16.656 (2)
b (Å)	13.946 (2)	13.278 (2)
c (Å)	15.451 (2)	24.044 (3)
β (deg)	110.58 (2)	103.82 (1)
v (Å^3)	3094.1	5163.6
space group	$P2_1/c$	$P2_1/n$
Z	2	4
density, calcd (g/cm^3)	1.002^a	1.014
radiation Mo Kα	graphite monochromtd	Mo Kα (λ = 0.71073 Å)
abs coeff, μ (cm^{-1})	3.08	3.01
scan range		
(deg below $2\theta_{K\alpha 1}$)	0.8	0.65
(deg above $2\theta_{K\alpha 2}$)	0.9	0.65
scan rate (deg/min)	2.0–24.0	3.0–24.0
2θ limits (deg)	3.5–54.9	3.5–48.3
$\sin\theta/\lambda_{max}$ (Å^{-1})	0.649	0.576
unique data		
theor	7065	8266
obsd, $F_o > 3\sigma(F_o)$	4175	4535
discrepancy indices		
R_1	0.051	0.069
R_2	0.059	0.073

^{a}The measured density of **1** of 0.958 g/cm^3 was determined by flotation at room temperature. The compound undergoes a phase transition between −70 °C and room temperature.

Table VII. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (pm^2 × 10^{-1}) for $(Me_2Si)_{13}$ (**1**)

	x	y	z	U^a
O(1)	900 (3)	−58 (5)	146 (3)	45 (2)
Si(1)	3591 (1)	1748 (2)	497 (1)	28 (1)
Si(2)	4981 (1)	1391 (2)	953 (1)	29 (1)
Si(3)	5456 (1)	1993 (2)	1898 (1)	31 (1)
Si(4)	5389 (1)	3745 (2)	1982 (1)	30 (1)
Si(5)	5884 (1)	4348 (2)	2910 (1)	34 (1)
Si(6)	5584 (1)	6065 (2)	2958 (1)	36 (1)
Si(7)	4182 (2)	6404 (2)	2954 (1)	36 (1)
Si(8)	3412 (2)	7416 (2)	2210 (1)	38 (1)
Si(9)	3137 (1)	7040 (2)	1231 (1)	33 (1)
Si(10)	2052 (1)	5888 (2)	895 (1)	31 (1)
Si(11)	1874 (1)	5516 (2)	−92 (1)	31 (1)
Si(12)	2058 (1)	3834 (2)	−350 (1)	32 (1)
Si(13)	3417 (1)	3185 (2)	−98 (1)	31 (1)
C(1)	3197 (6)	666 (7)	−13 (4)	44 (3)
C(2)	2956 (5)	1726 (7)	1062 (4)	41 (3)
C(3)	5712 (5)	1823 (7)	510 (4)	45 (3)
C(4)	5069 (6)	−30 (6)	1008 (4)	47 (3)
C(5)	4843 (6)	1381 (7)	2373 (4)	47 (4)
C(6)	6557 (6)	1567 (9)	2146 (5)	63 (4)
C(7)	4266 (5)	4097 (7)	1753 (4)	39 (3)
C(8)	6007 (6)	4372 (7)	1514 (4)	47 (4)
C(9)	7041 (6)	4201 (8)	3124 (5)	61 (4)
C(10)	5429 (7)	3645 (8)	3444 (4)	66 (5)
C(11)	5913 (6)	6777 (8)	2389 (5)	58 (4)
C(12)	6250 (6)	6525 (9)	3670 (4)	64 (4)
C(13)	3548 (6)	5262 (7)	3035 (4)	51 (4)
C(14)	4222 (6)	7205 (8)	3612 (4)	51 (4)
C(15)	3947 (6)	8679 (7)	2290 (5)	57 (4)
C(16)	2387 (6)	7581 (7)	2403 (4)	50 (4)
C(17)	4114 (5)	6785 (8)	1001 (4)	45 (3)
C(18)	2724 (7)	8251 (8)	900 (5)	64 (4)
C(19)	2103 (6)	4695 (7)	1319 (4)	52 (4)
C(20)	1078 (5)	6554 (8)	967 (4)	57 (4)
C(21)	2531 (5)	6350 (7)	−443 (4)	46 (4)
C(22)	758 (5)	5837 (7)	−452 (4)	47 (3)
C(23)	1295 (5)	2995 (7)	−106 (4)	45 (3)
C(24)	1756 (6)	3869 (7)	−1177 (4)	52 (4)
C(25)	3656 (6)	2717 (8)	−786 (4)	54 (4)
C(26)	4164 (5)	4241 (7)	160 (4)	51 (4)

^{a}Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

To see what would happen if **1** was forced into a hydrocarbon-like conformation, a hypothetical structure was calculated by taking the [13333] structure for **4** and multiplying the unit cell constants by r_{Si-Si}/r_{C-C}, the ratio of the average Si–Si to C–C bond lengths in the actual molecules. Methyl groups were then added at the appropriate distances in place of the hydrogens or methylene groups of **4**. Finally, the intramolecular C–C distances between methyl groups on different silicon atoms in the hypothetical structure were calculated. They are extremely short, with nine having values from 290 to 340 pm, clearly in the strongly repulsive region. A similar calculation was carried out for a hypothetical [4444] conformation of **2**, beginning with the structure of **3**. Again, very short intramolecular C–C distances would be found, eight lying between 310 and 340 pm. These calculations show that hydrocarbon-like structures are highly unfavorable for **1** and **2**.

In cyclosilanes, the Si–Si–Si bond angles are slightly greater than tetrahedral, even for "strain-free" molecules such as $(Me_2Si)_6$, leading to a slight flattening of these rings.[22] In **2** the average Si–Si–Si angle has a value normal for cyclosilanes, 111.9°. But in **1** the average angle is significantly larger, 115.7°. In this feature **1** resembles $(Me_2Si)_7$, which has Si–Si–Si = 116.2°. The ring flattening in these compounds probably reduces transannular methyl–methyl repulsions, as discussed above.

The large Si–Si–Si bond angles in **1** do not lead to a decrease in the average C–Si–C angle, which is normal for cyclosilanes at 107.2°. Instead, the Si–Si–C angles are slightly smaller than normal, averaging 108.3°. The average Si–Si and Si–C bond lengths in **1**, 235.5 and 188.8 pm, and in **2**, 235.5 and 188.9, respectively, are all in the normal range for unstrained cyclopolysilanes.[22]

X-ray Crystallography

Compounds **1** and **2** were prepared and purified by previously known procedures.[2b,c] Single crystals of **1** were obtained by vapor diffusion of methanol into a dichloromethane solution of **1** at −80 °C. Because a phase transition occurs for each of these compounds below room temperature, crystals of both compounds were mounted on the diffractometer directly into a cold nitrogen stream with care being taken to prevent the crystals from warming during the mounting process. Since preliminary data collection on **2** at room temperature showed that the crystal decomposes in the X-ray beam, data were taken at −80 ± 5 °C for **1** and −75 ± 5 °C for **2**.

Data were collected on a Syntex-Nicolet P$_{\bar{1}}$ four-circle diffractometer equipped with a modified LT-1 low-temperature device. Crystals of **1** and **2** are both monoclinic, space group $P2_1/n$ and $P2_1/c$, respectively. Unit cell parameters were obtained from least-squares refinements based on the setting angle of 60 reflections collected at $\pm 2\theta$ ($2\theta \sim 35°$) at the same temperature as the data collection. The crystal dimensions, the unit cell parameters, and other crystal data are given in Table VI.

Intensity data were collected by using a fresh crystal of **1** which was grown as mentioned earlier, and the data were collected with the crystal used for preliminary examinations for **2**. Details of intensity measurements are given in Table VI. Four standard reflections from diverse regions of reciprocal space were measured every 50 reflections throughout data collection to monitor the long term stability. No significant trend was observed for **1** or **2**. Structure amplitudes and their standard deviations were calculated from the intensity data by procedures similar to those described previously.[23]

The structures were solved by direct methods using the MULTAN package.[24] The positions of the silicon atoms were revealed by

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(22) To compare the bond lengths and bond angles in **1** and **2** with those in other cyclopolysilanes, see the complete listing of average values for organosilicon rings in ref 8, Table V.

(23) Haller, K. J.; Enemark, J. H. *Inorg. Chem.* **1978**, *17*, 3552.

Table VIII. Fractional Monoclinic Coordinates for $(Me_2Si)_{16}$ (**2**)[a]

atom	*X*	*Y*	*Z*
Si(1)	0.18807 (8)	−0.09623 (7)	0.35493 (7)
Si(2)	0.11039 (8)	0.05189 (8)	0.33627 (8)
Si(3)	0.21333 (7)	0.17970 (8)	0.40059 (7)
Si(4)	0.27068 (8)	0.25270 (8)	0.29383 (7)
Si(5)	0.41154 (7)	0.33530 (7)	0.36814 (7)
Si(6)	0.53896 (7)	0.23555 (7)	0.38121 (7)
Si(7)	0.68359 (7)	0.29745 (7)	0.47716 (7)
Si(8)	0.79799 (7)	0.17644 (7)	0.50724 (6)
C(1)	0.3048 (3)	−0.0759 (3)	0.34139 (27)
C(2)	0.1172 (3)	−0.1767 (3)	0.25706 (27)
C(3)	0.0450 (4)	0.0704 (4)	0.2087 (3)
C(4)	0.0203 (3)	0.0497 (3)	0.3936 (4)
C(5)	0.30821 (28)	0.13631 (28)	0.50857 (25)
C(6)	0.1470 (3)	0.2756 (3)	0.4383 (3)
C(7)	0.2847 (3)	0.1666 (3)	0.20548 (26)
C(8)	0.1801 (3)	0.3438 (4)	0.2276 (3)
C(9)	0.4142 (3)	0.38040 (28)	0.48412 (27)
C(10)	0.4167 (3)	0.44150 (28)	0.29405 (28)
C(11)	0.51916 (27)	0.11251 (28)	0.42184 (28)
C(12)	0.5443 (3)	0.2242 (3)	0.26108 (27)
C(13)	0.6809 (3)	0.3487 (3)	0.58890 (28)
C(14)	0.7183 (3)	0.3982 (3)	0.4148 (3)
C(15)	0.77303 (27)	0.09489 (28)	0.40403 (25)
C(16)	0.91396 (28)	0.2352 (3)	0.5245 (3)

[a] The numbers given in parentheses are the estimated standard deviations of the least significant digits.

the E maps, and the carbon atoms were located by subsequent electron density difference maps. The full-matrix least-squares refinements of the structures were based on F_o and by using the relections with $F_o > 3\sigma(F_o)$. Atomic form factors were taken from Cromer and Waber[25] and that for hydrogen was taken from Stewart, Davidson, and Simpson.[26] The structures were refined to convergence by using isotropic thermal parameters for the non-hydrogen atoms, and electron density difference maps were used to locate positions for the hydrogen atoms. It also became apparent at this point that there was one molecule of water of crystallization in the lattice of **1**.

The final cycles of refinement of **1** and **2** assumed that the non-hydrogen atoms vibrate anisotropically and included the hydrogen atoms as idealized isotropic fixed contributors. The water of crystallization in **1** was treated as an idealized group with anisotropic oxygen and isotropic hydrogen atoms. The final values of the discrepancy indices $R_1 = \Sigma\, ||F_o| - |F_c||/\Sigma|F_o|$ and $R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o)^2]^{1/2}$ are given in Table VI. The final difference electron density maps were featureless. Final atomic parameters are reported in Tables VII and VIII for **1** and **2**, respectively.

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Supplementary Material Available: Tables of anisotropic thermal parameters and hydrogen atom positions as for **1** and **2** (5 pages); a listing of observed and calculated structure factors (×10) (45 pages). Ordering information is available on any current masthead page.

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(24) Germain, G.; Main, P.; Woolfson, M. M. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1971**, *27*, 368.

(25) Cromer, D. T.; Waber, J. T. *International Tables for X-ray* crystallogrphy; Kynoch Press: Birmingham, England, 1974; Vol. 4, pp 99–101, Table 2.2B.

(26) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

Synthesis and Reactivity of a Dimeric Molybdenum(III) Complex with a Bridging Hydrosulfido Ligand

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Abstract: A (cyclopentadienyl)molybdenum(III) dimer with a bridging hydrosulfido ligand $(MeCpMo)_2(S_2CH_2)(\mu\text{-}SCH_3)(\mu\text{-}SH)$ (**3**) ($MeCp = CH_3C_5H_4$) has been synthesized by an unusual reaction of molecular hydrogen with the paramagnetic species $(MeCpMo)_2(S_2CH_2)(\mu\text{-}SCH_3)(\mu\text{-}S)$ (**5**). Mechanistic features of this reaction are discussed. Complex **3** has been characterized by spectral methods, and the reactivity of the hydrosulfido ligand has been investigated. The ligand is deprotonated by methoxide ion and alkylated by alkyl halides in the absence of base. Activated alkenes and alkynes insert into the S–H bond of the ligand in the absence of base to form new dimers with alkyl or alkenyl thiolate ligands. The regio- and stereochemistries of the products of these reactions have been characterized and compared to those of reactions of the conjugate base of **3**, which has been synthesized independently. Complex **3** also serves as a hydrogen atom transfer agent to certain unsaturated molecules. The relevance of these systems as models for the hydrodesulfurization catalysts is discussed.

The hydrodesulfurization (HDS) of organosulfur compounds is an important industrial process used in the purification of petroleum feedstocks. The most common catalysts are derived from sulfided molybdenum and cobalt ions supported on alumina.[1] In addition to the hydrogenolysis of carbon–sulfur bonds, hydrogenation of unsaturated compounds and isomerization of olefins also occur over this heterogeneous catalyst.[2] The mechanisms of the reactions are not well understood, although it is generally thought that a MoS_2 phase is the catalytic site for the HDS reaction. Mechanistic proposals for HDS have suggested that

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(1) (a) Schuman, S. C.; Shalit, H. *Catal. Rev.* **1970**, *4*, 245. (b) Massoth, F. E. *Adv. Catal.* **1978**, *27*, 265. (c) Grange, P. *Catal. Rev.—Sci. Eng.* **1980**, *21*, 135.

(2) Mitchell, C. P. H. In *Catalysis*; Kemball, C., Ed.; The Chemical Society: London, 1977; Vol. 1, p 223; Vol. 4, p 203 (Special Periodical Report).

0002-7863/86/1508-5482$01.50/0