

## Highly unsaturated macrocyclic silicohydrocarbons

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### Abstract

Nineteen 12-, 15-, 18-, 24- and 30-membered, highly unsaturated macrocyclic silicohydrocarbons containing  $-\text{SiC}\equiv\text{CSi}-$ , (*E*)- $\text{SiCH}=\text{CHSi}-$  and  $-\text{SiCH}_2\text{CH}_2\text{Si}-$  fragments in the ring were synthesized by the reaction of  $\text{Me}_2\text{Si}(\text{C}\equiv\text{CMgBr})_2$  or  $\text{BrMgC}\equiv\text{CMe}_2\text{SiC}\equiv\text{CSiMe}_2\text{C}\equiv\text{CMgBr}$  with  $\text{FMe}_2\text{SiCH}_2\text{CH}_2\text{SiMe}_2\text{F}$ ; (*E*)- $\text{FMe}_2\text{SiCH}=\text{CHSiMe}_2\text{F}$  or (*E, E*)- $(\text{ClMe}_2\text{SiCH}=\text{CH})_2\text{SiMe}_2$ ; (*E*)- $\text{BrMgC}\equiv\text{CMe}_2\text{SiCH}=\text{CHSiMe}_2\text{C}\equiv\text{CMgBr}$  or  $\text{Me}_2\text{Si}(\text{C}\equiv\text{CSiMe}_2\text{C}\equiv\text{CMgBr})_2$  with (*E, E*)- $(\text{ClMe}_2\text{SiCH}=\text{CH})_2\text{SiMe}_2$ ; and  $\text{Me}_2\text{Si}(\text{C}\equiv\text{CSiMe}_2\text{C}\equiv\text{CMgBr})_2$ ,  $\text{BrMgC}\equiv\text{CMe}_2\text{SiC}\equiv\text{CSiMe}_2\text{C}\equiv\text{CSiMe}_2\text{C}\equiv\text{CMgBr}$  or  $\text{BrMgC}\equiv\text{CMgBr}$  with (*E*)- $\text{FMe}_2\text{SiCH}=\text{CHSiMe}_2\text{F}$  under conditions of high dilution.

Two 20-membered and one 26-membered macrocyclic silicohydrocarbons containing 6 or 8 silicon atoms bonded by 6 or 8  $\text{C}\equiv\text{C}$  bonds and an endocyclic  $\text{CH}_2\text{CH}_2$  or  $\text{CH}=\text{CH}$  bridge were obtained for the first time by treating  $\text{BrMgC}\equiv\text{CMe}_2\text{SiC}\equiv\text{CSiMe}_2\text{C}\equiv\text{CMgBr}$  with  $\text{Cl}_2\text{MeSiCH}_2\text{CH}_2\text{SiMeCl}_2$  or (*E*)- $\text{F}_2\text{MeSiCH}=\text{CHSiMeF}_2$ , as well as  $\text{Me}_2\text{Si}(\text{C}\equiv\text{CSiMe}_2\text{C}\equiv\text{CMgBr})_2$  with (*E*)- $\text{F}_2\text{MeSiCH}=\text{CHSiMeF}_2$ .

### Introduction

In 1970, Fritz and Schober synthesized a cyclic silicohydrocarbon, 1,1,4,4,6,6,9,9-octamethyl-1,4,6,9-tetrasilacyclodeca-2,7-diene [1], containing four silicon atoms and two triple bonds in a 10-membered ring. Three years later, the first highly unsaturated macrocyclic silicohydrocarbon, 1,1,4,4,7,7,10,10-octamethyl-1,4,7,10-tetrasilacyclododeca-2,5,8,11-tetraene, whose macrocycle was made of four silicon atoms and four  $\text{C}\equiv\text{C}$  groups, was obtained by one of us [2] through the reaction of calcium carbide with dimethyldichlorosilane in a molten eutectic  $\text{LiCl}-\text{KCl}$  mixture at  $400^\circ\text{C}$ . Recently, 8–24-membered organosilicon macroheterocycles including endocyclic  $\text{SiC}\equiv\text{CSi}$  and  $\text{Si}(\text{CH}_2)_n\text{Si}$  fragments ( $n = 0-4$ ) have been synthesized [3] and the molecular and crystalline structures of four of them have

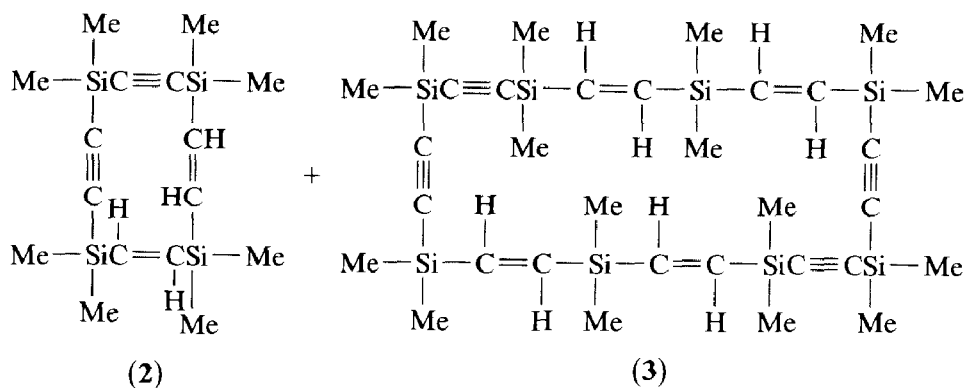
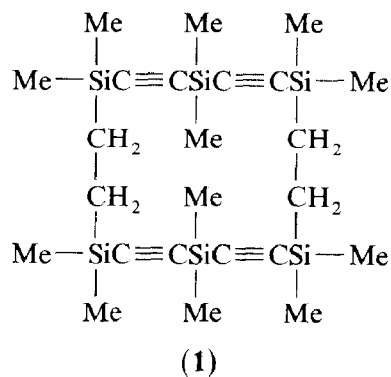
been studied [4]. Macrocyclic systems containing Si-Si and C≡C groups have been prepared from BrMgC≡CMe<sub>2</sub>SiSiMe<sub>2</sub>C≡CMgBr and Cl(Me<sub>2</sub>Si)<sub>3</sub>Cl [5], as well as from BrMgC≡CMe<sub>2</sub>SiSiMe<sub>2</sub>C≡CMe<sub>2</sub>SiSiMe<sub>2</sub>C≡CMgBr and Cl(Me<sub>2</sub>Si)<sub>2</sub>Cl [6].

## Results and discussion

Extending the research in the field of highly unsaturated macrocyclic silicohydrocarbons, we have synthesized a series of new 12-, 15-, 18-, 24- and 30-membered representatives of this interesting class of organosilicon compounds containing SiC≡CSi, (*E*)-SiCH=CHSi and SiCH<sub>2</sub>CH<sub>2</sub>Si fragments in the ring.

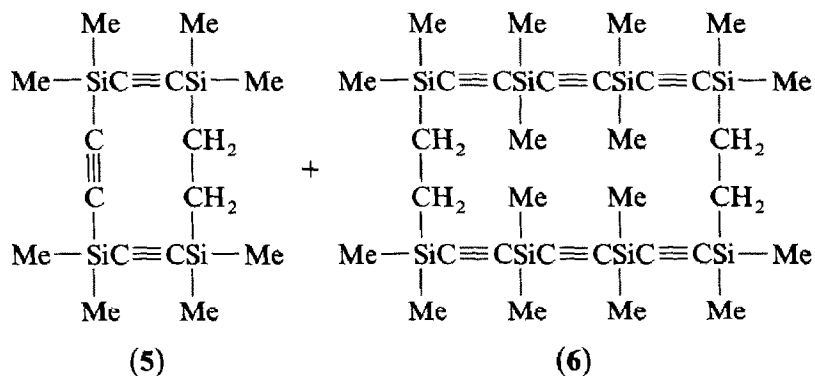
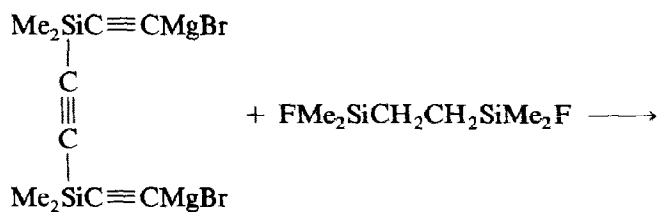
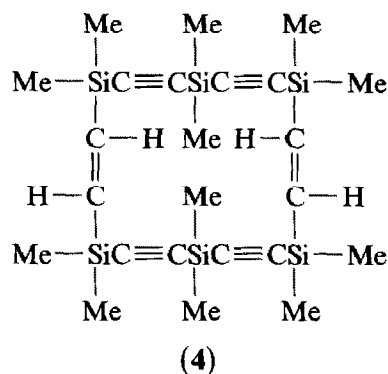
1,1,4,4,7,7,10,10,13,13,16,16-Dodecamethyl-1,4,7,10,13,16-hexasilacyclooctadene-2,5,11,14-tetraene (**1**) was obtained by treating bis(bromomagnesiumethynyl)dimethylsilane with 1,2-bis(dimethylfluorosilyl)ethane in THF [7,8].

Analogously, by the reaction of bis(bromomagnesiumethynyl)dimethylsilane with (*E,E*)-bis(2-dimethylchlorosilylvinyl)dimethylsilane, 1,1,4,4,7,7,10,10-octamethyl-1,4,7,10-tetrasilacyclododeca-2,5-diene-8,11-diene (**2**) and 1,1,4,4,7,7,10,10,13,13,16,16,19,19,22,22-hexadecamethyl-1,4,7,10,13,16,19,22-octasilacyclotetracos-2,5,14,17-tetraene-8,11,20,23-tetraene (**3**) were prepared.

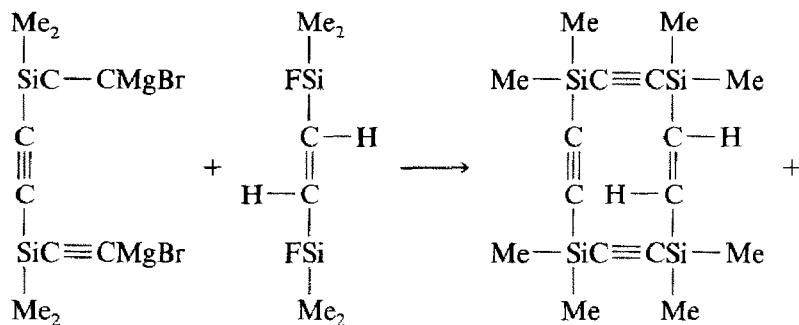


The reaction of bis(bromomagnesiumethynyl)dimethylsilane with (*E*)-1,2-bis(dimethylfluorosilyl)ethylene leads to 1,1,4,4,7,7,10,10,13,13,16,16-dodecamethyl-1,4,7,10,13,16-hexasilacyclooctadeca-2,11-diene-5,8,14,17-tetraene (4).

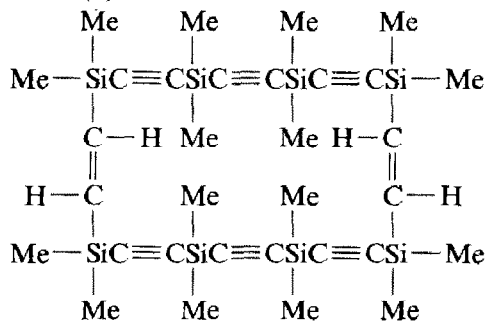
1,1,4,4,7,7,10,10-Octamethyl-1,4,7,10-tetrasilacyclododeca-2,5,8-triene (5) and 1,1,4,4,7,7,10,10,13,13,16,16,19,19,22,22-hexadecamethyl-1,4,7,10,13,16,19,22-octasilacyclotetracos-2,5,8,14,17,23-hexaene (6) turned out to be the products of the reaction of bis(dimethylbromomagnesiummethylsilyl)acetylene with 1,2-bis(dimethylfluorosilyl)ethane.



By treating bis(dimethylbromomagnesiummethylsilyl)acetylene with (*E*)-1,2-bis(dimethylfluorosilyl)ethylene, it was possible to synthesize 1,1,4,4,7,7,10,10-octamethyl-1,4,7,10-tetrasilacyclododeca-2-ene-5,8,11-triene (7) and 1,1,4,4,7,7,10,10,13,13,16,16,19,19,22,22-hexadecamethyl-1,4,7,10,13,16,19,22-octasilacyclotetracos-2,14-diene-5,8,11,17,20,23-hexaene (8).



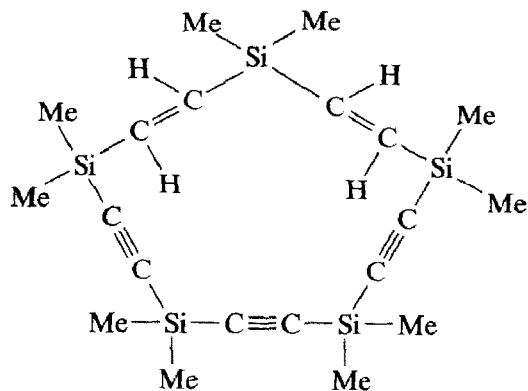
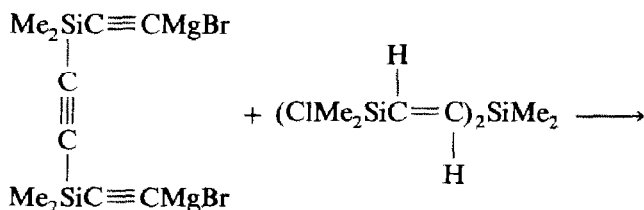
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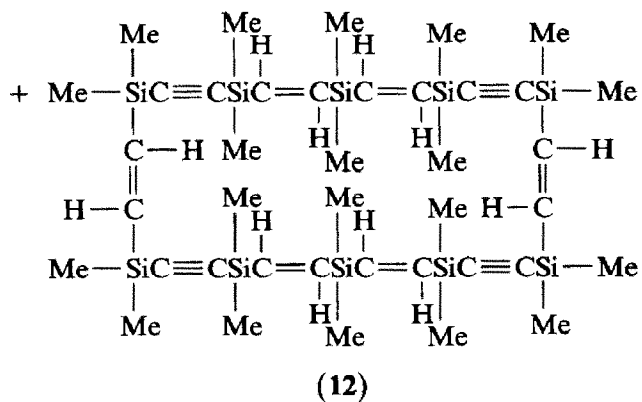
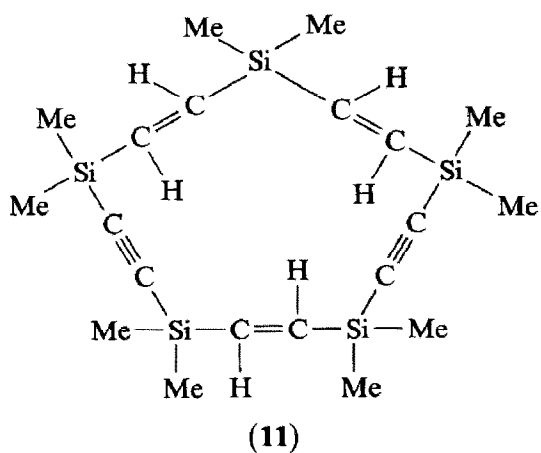
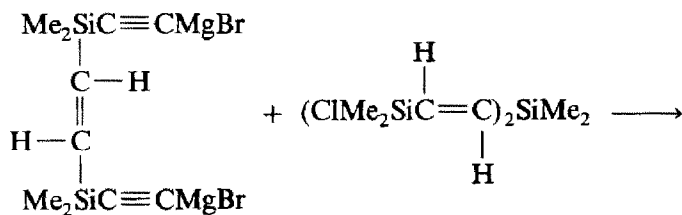
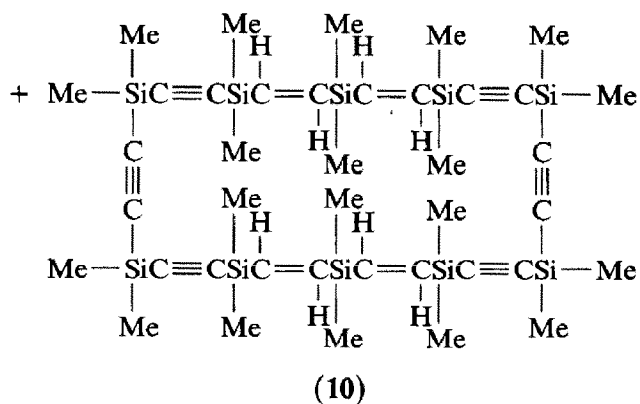
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1,1,4,4,7,7,10,10,13,13-Decamethyl-1,4,7,10,13-pentasilacyclopentadeca-2,5-diene-8,11,14-triene (9) and 1,1,4,4,7,7,10,10,13,13,16,16,19,19,22,22,25,25,28,28-eicosamethyl-1,4,7,10,13,16,19,22,25,28-decasilacyclotriaconta-2,5,17,20-tetraene-8,11,14,26,29-hexaene (10) were prepared by the reaction of bis(dimethylbromomagnesiumethynylsilyl)acetylene with (*E,E*)-bis(2-dimethylchlorosilylvinyl)dimethylsilane.

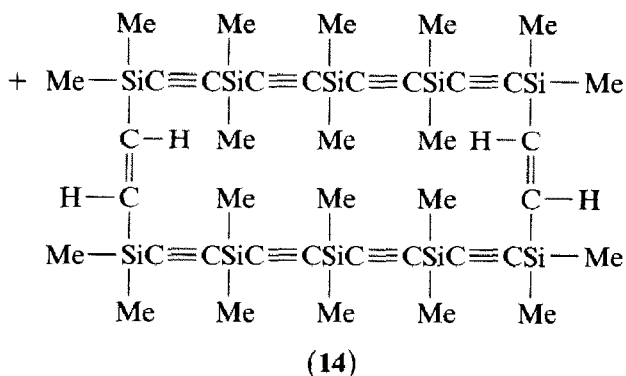
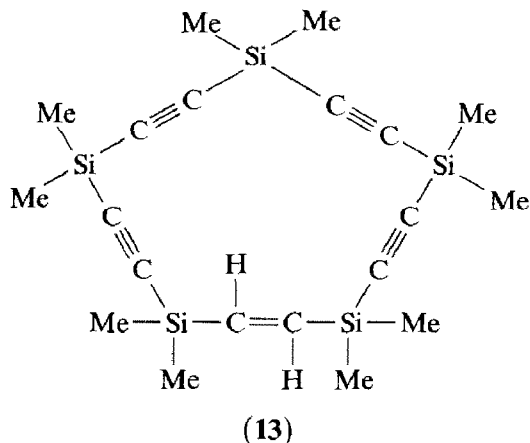
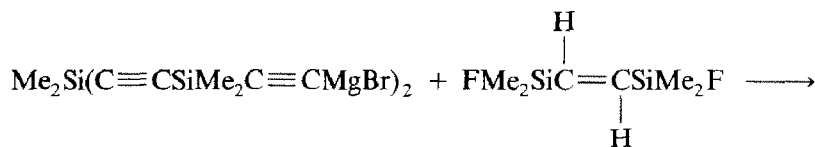
The reaction of (*E*)-1,2-bis(dimethylbromomagnesiumethynylsilyl)ethylene with (*E,E*)-bis(2-dimethylchlorosilylvinyl)dimethylsilane gave 1,1,4,4,7,7,10,10,13,13-decamethyl-1,4,7,10,13-pentasilacyclopentadeca-2,5,11-triene-8,14-diene (11) and 1,1,4,4,7,7,10,10,13,13,16,16,19,19,22,22,25,25,28,28-eicosamethyl-1,4,7,10,13,16,19,22,25,28-decasilacyclotriaconta-2,5,11,17,20,26-hexaene-8,14,23,29-tetraene (12).



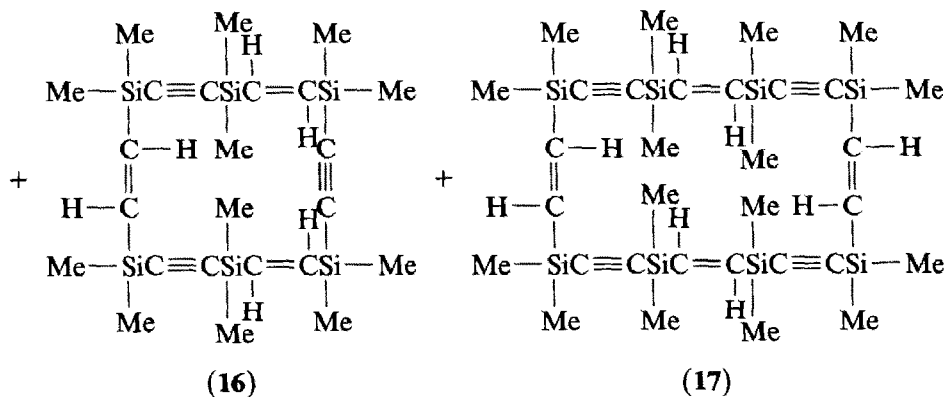
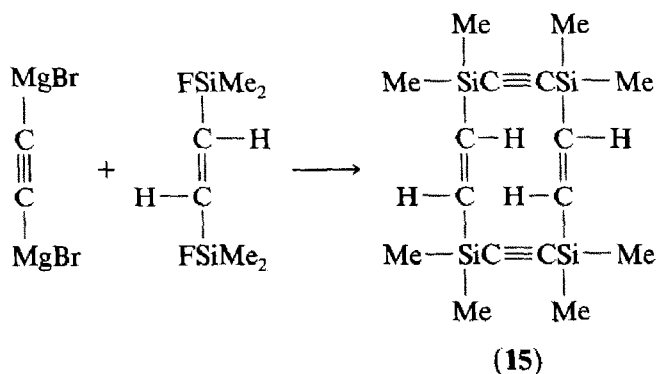
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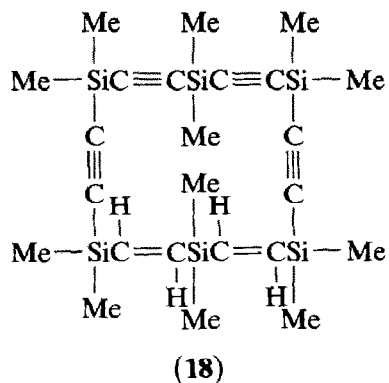
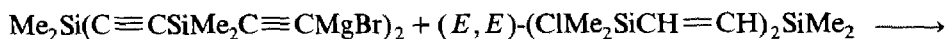
The reaction of bis[(dimethylbromomagnesiumethynyl)silyl]dimethylsilane with (*E*)-1,2-bis(dimethylfluorosilyl)ethylene afforded 1,1,4,4,7,7,10,10,13,13-decamethyl-1,4,7,10,13-pentasilacyclopentadeca-2-ene-5,8,11,14-tetraene (**13**) and 1,1,4,4,7,7,10,10,13,13,16,16,19,19,22,22,25,25,28,28-eicosamethyl-1,4,7,10,13,16,19,22,25,28-decasilacyclotriaconta-2,17-diene-5,8,11,14,20,23,26,29-octaine (**14**).



1,1,4,4,7,7,10,10,-Octamethyl-1,4,7,10-tetrasilacyclododeca-2,8-diene-5,11-diene (**15**), 1,1,4,4,7,7,10,10,13,13,16,16-dodecamethyl-1,4,7,10,13,16-hexasilacyclooctadeca-2,8,14-triene-5,11,17-triene (**16**) and 1,1,4,4,7,7,10,10,13,13,16,16,19,19,22,22-hexadecamethyl-1,4,7,10,13,16,19,22-octasilacyclotetracos-2,8,14,20-tetraene-5,11,17,23-tetraene (**17**) were the products of the reaction of di(bromomagnesium)acetylene with (*E*)-1,2-bis(dimethylfluorosilyl)ethylene.

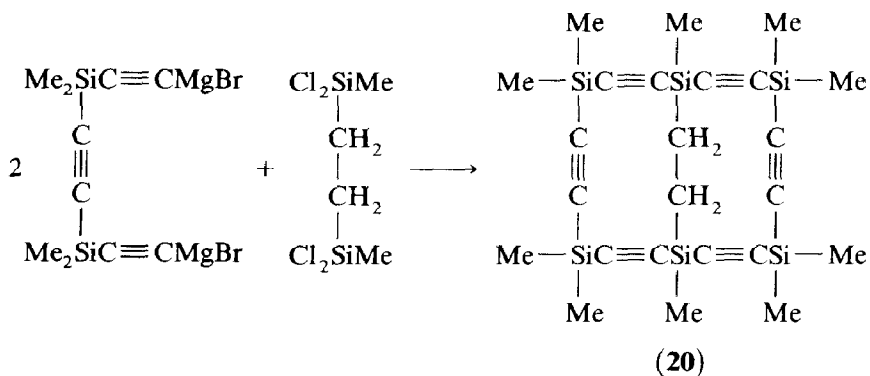
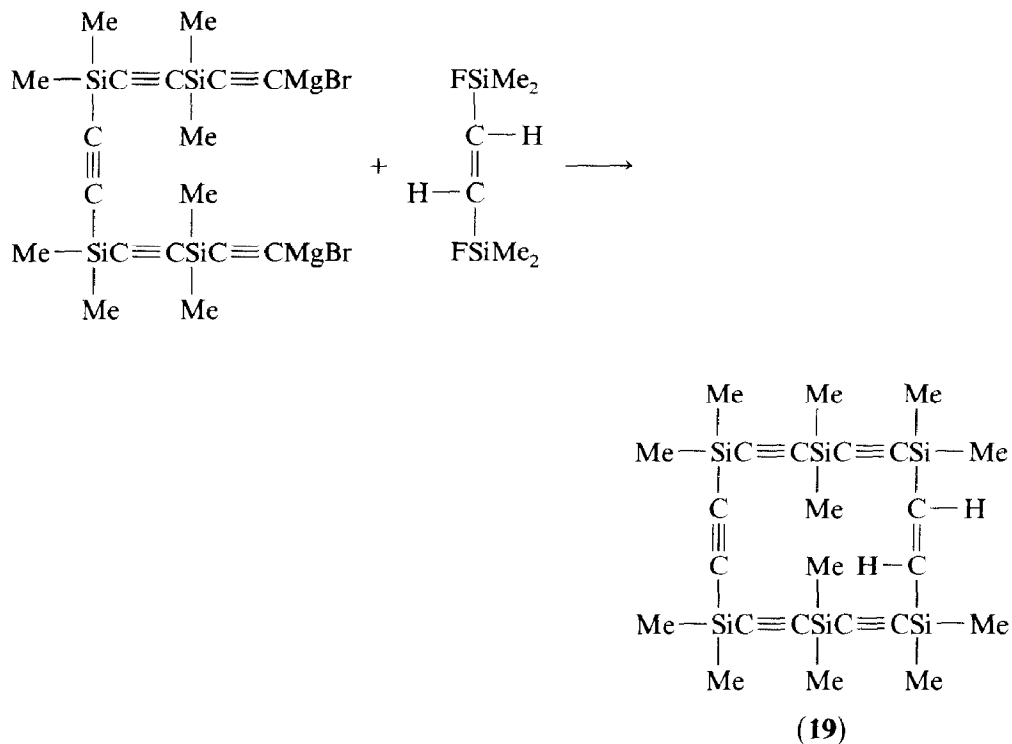


By the reaction of bis[(dimethylbromomagnesiumethynyl)silyl]ethynyl]dimethylsilane with (*E,E*)-bis(2-dimethylchlorosilylvinyl)dimethylsilane, 1,1,4,4,7,7,10,10,13,13,16,16-dodecamethyl-1,4,7,10,13,16-hexasilacyclooctadeca-2,5-diene-8,11,14,17-tetraene (18) was synthesized.



The reaction of bis[(dimethylbromomagnesiumethynyl)silyl]ethynyl]dimethylsilyl]acetylene with (*E*)-1,2-bis(dimethylfluorosilyl)ethylene led to 1,1,4,4,7,7,10,10,13,13,16,16-dodecamethyl-1,4,7,10,13,16-hexasilacyclooctadeca-2-ene-5,8,11,14,17-pentaine (19).

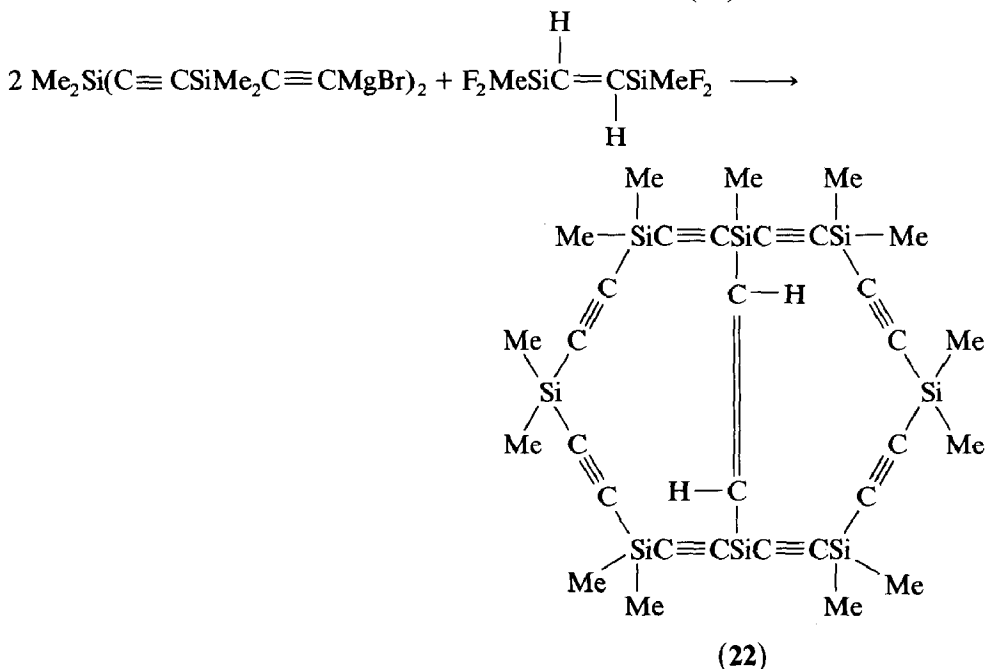
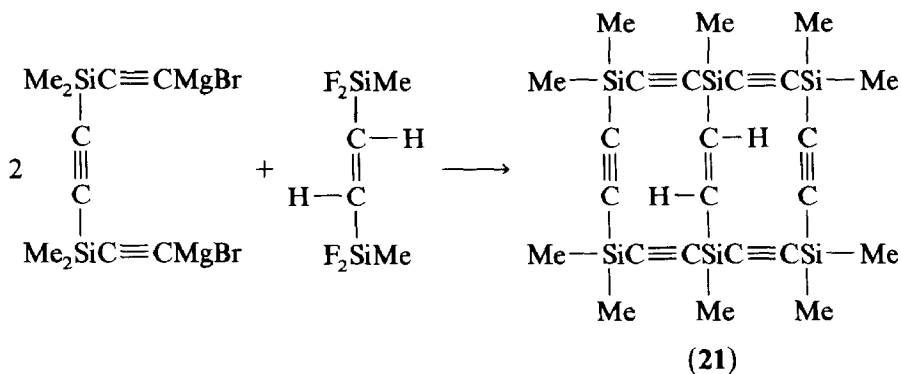
We have also synthesized for the first time highly unsaturated macrobicyclic silicohydrocarbons containing an *endo*-cyclic  $\text{CH}_2\text{CH}_2$  or (*E*)- $\text{CH}=\text{CH}$  bridge. Thus, the reaction of bis(dimethylbromomagnesiumethynyl)silyl acetylene with 1,2-bis(methyldichlorosilyl)ethane gave 1,4,4,7,7,10,13,13,16,16-decamethyl-1,4,7,10,13,16-hexasilabicyclo[8',8',2']eicosa-2,5,8,11,14,17-hexaine (**20**).



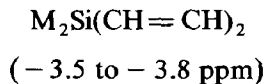
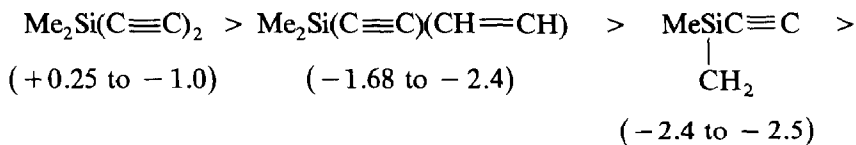
An analogous reaction of bis(dimethylbromomagnesiumethynyl)silyl acetylene with (*E*)-1,2-bis(methyldifluorosilyl)ethylene gave 1,4,4,7,7,10,13,13,16,16-decamethyl-1,4,7,10,13,16-hexasilabicyclo[8',8',2']eicosa-19-ene-2,5,8,11,14,17-hexaine (**21**).

Finally, by treating bis[(dimethylbromomagnesiumethynyl)silyl]dimethylsilane with (*E*)-1,2-bis(methyldifluorosilyl)ethylene, 1,4,4,7,7,10,10,13,16,16,19,19,22,22-tetradecamethyl-1,4,7,10,13,16,19,22-octasilabicyclo[11',11',2']-hexacos-25-en-2,5,8,11,14,17,20,23-octaine (**22**) was synthesized.





Melting points, yields, and analytical and mass spectral data of the compounds obtained are given in Table 1. Macrocyclic silicohydrocarbons are colourless, crystalline substances with high melting points, the latter rising with increasing unsaturation. Among compounds of similar unsaturation, the highest melting points are displayed by 18-membered silicohydrocarbons and the lowest ones by 15-membered.  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{29}\text{Si}$  NMR data are presented in Table 2. The methyl group carbon atoms in  $\text{C}\equiv\text{CSiMe}_2\text{C}\equiv\text{C}$  are more deshielded owing to the presence of two electronegative ethynyl groups at the silicon atom. Thus, deshielding of the methyl group carbons at the silicon atom will increase as the electronegativity of the remaining substituents decreases:



(continued on p. 20)

Table 1  
 Polyunsaturated macrocyclic silicohydrocarbons

Compound	Yield, (%)	M.p., (°C)	Found (calcd.) (%)			Mass spectrum ( <i>m/z</i> )	General formula
			C	H	Si		
<b>1</b>	2.0	188	57.24 (57.52)	8.87 (8.85)	34.00 (33.63)	500(8),485(6),472(3),457(6),427(3),399(6), 207(4),183(3),155(7),141(4),140(4),125(8), 99(4),97(8),85(4),83(8),73(100)	C <sub>24</sub> H <sub>44</sub> Si <sub>6</sub>
<b>2</b>	4.5	190	56.85 (57.83)	8.21 (8.43)	32.65 (33.73)	332(16),317(33),291(3),289(6),273(6),259 (15),207(5),175(5),165(9),155(8),125(4), 97(14),83(27),73(100)	C <sub>16</sub> H <sub>28</sub> Si <sub>4</sub>
<b>3</b>	3.2	183	56.71 (57.83)	8.24 (8.43)	33.09 (33.73)	664(2),649(3),591(9),561(3),517(2),503(3), 493(2),317(3),259(2),251(3),209(2),207(2), 168(5),165(5),155(11),141(4),129(4),127(10), 125(4),97(4),83(11),73(100)	C <sub>32</sub> H <sub>56</sub> Si <sub>8</sub>
<b>4</b>	7.5	246	57.91 (57.98)	8.34 (8.11)	33.04 (33.93)	496(2),481(5),423(9),394(4),165(6),155(7), 125(4),97(8),83(27),73(100)	C <sub>24</sub> H <sub>40</sub> Si <sub>6</sub>
<b>5</b>	13.2	172	57.80 (57.83)	8.43 (8.43)	33.48 (33.73)	332(100),317(72),304(50),289(39),273(4), 259(6),247(2),245(3),231(11),152(12),144(18), 97(6),85(5),83(8),73(60)	C <sub>16</sub> H <sub>28</sub> Si <sub>4</sub>
<b>6</b>	3.8	160	58.19 (57.83)	8.54 (8.43)	33.00 (33.73)	664(7),649(4),636(1),621(2),591(6),563(4), 561(2),409(6),317(5),289(5),207(4),155(9), 125(6),97(7),85(9),83(5),73(100)	C <sub>32</sub> H <sub>56</sub> Si <sub>8</sub>
<b>7</b>	7.0	228	58.00 (58.18)	8.23 (7.88)	3.80 (33.93)	330(44),315(100),257(10),232(11),97(11), 83(24),73(100)	C <sub>16</sub> H <sub>26</sub> Si <sub>4</sub>
<b>8</b>	0.6	207	58.97 (58.18)	7.94 (7.88)	33.65 (33.93)	660(10),645(9),602(1),587(9),315(3),231(3), 165(3),155(10),97(6),83(11),73(100)	C <sub>32</sub> H <sub>52</sub> Si <sub>8</sub>
<b>9</b>	17.0	172	57.97 (57.89)	8.30 (8.26)	33.50 (33.85)	414(20),399(47),341(19),311(9),168(14), 97(9),83(19),73(100)	C <sub>20</sub> H <sub>34</sub> Si <sub>5</sub>
<b>10</b>	0.7	186	58.19 (57.89)	8.11 (8.26)	33.12 (33.85)	828(2),813(1),755(2),725(1),667(1),399(2), 317(2),232(2),168(5),155(9),153(3),97(3) 83(1),73(100)	C <sub>40</sub> H <sub>68</sub> Si <sub>10</sub>

11	25.0	140	57.87 (57.61)	8.73 (8.70)	32.36 (33.69)	416(12),401(35),343(31),314(14),304(9), 97(9),83(17),73(100)	C <sub>20</sub> H <sub>36</sub> Si <sub>5</sub>
12	0.5	172	58.84 (57.61)	8.52 (8.70)	33.82 (33.69)	832(3),817(1),759(2),155(16),83(13),73(100)	C <sub>40</sub> H <sub>72</sub> Si <sub>10</sub>
13	11.0	198	58.19 (58.17)	7.95 (7.81)	33.62 (34.01)	412(30),397(100),353(6),339(12),323(6), 313(8),299(3),231(5),165(4),155(4),125(4), 97(10),83(12),73(100)	C <sub>20</sub> H <sub>32</sub> Si <sub>5</sub>
14	0.4	191	58.08 (58.17)	7.73 (7.81)	34.20 (34.01)	824(2),809(1),751(2),232(2),165(3),145(11), 131(2),125(3),97(7),83(9),73(100)	C <sub>40</sub> H <sub>64</sub> Si <sub>10</sub>
15	9.1	185	57.84 (57.83)	8.43 (8.43)	33.83 (33.73)	332(17),317(42),259(20),245(8),97(13),83(25), 73(100)	C <sub>16</sub> H <sub>28</sub> Si <sub>4</sub>
16	4.4	238	56.55 (57.83)	8.24 (8.43)	33.71 (33.73)	498(3),483(7),425(13),396(5),165(6),155(7), 97(7),83(16),73(100)	C <sub>24</sub> H <sub>42</sub> Si <sub>6</sub>
17	3.3	171	58.05 (57.83)	8.10 (8.43)	32.91 (33.73)	664(18),649(5),691(12),560(3),516(4),502(5), 313(5),236(4),165(7),155(4),97(6),83(11), 73(100)	C <sub>32</sub> H <sub>58</sub> Si <sub>8</sub>
18	11.0	255	58.64 (57.98)	8.62 (8.11)	33.59 (33.93)	496(36),481(50),437(5),423(24),408(5),407(5), 393(8),383(4),365(4),250(7),235(4),231(4), 168(16),165(6),155(10),97(8),83(13),73(100)	C <sub>24</sub> H <sub>40</sub> Si <sub>6</sub>
19	14.0	257	58.64 (58.22)	7.76 (7.74)	34.19 (34.04)	494(51),435(6),421(22),407(5),406(5),405(5), 391(8),339(10),248(4),231(4),165(6),155(7), 97(12),83(25),73(100)	C <sub>24</sub> H <sub>38</sub> Si <sub>6</sub>
20	1.0	277	58.67 (58.69)	6.98 (6.97)	34.33 (34.32)	490(33),475(17),462(12),457(9),417(3),359(3), 97(5),83(7),73(100)	C <sub>24</sub> H <sub>34</sub> Si <sub>6</sub>
21	0.5	305				488(25),473(30),415(6),401(16),343(16), 329(4),327(7),313(8),175(7),165(5),155(8), 97(12),83(18),73(100)	C <sub>24</sub> H <sub>32</sub> Si <sub>6</sub>
22	1.0	280	59.67 (58.81)	7.25 (6.79)	34.18 (34.40)	652(58),637(67),626(6),543(5),579(13),550(7), 155(7),110(4),97(7),83(17),73(100)	C <sub>32</sub> H <sub>44</sub> Si <sub>8</sub>





(0.36)<sub>a</sub>  
(0.24)<sub>b</sub>

6.71

(0.33)<sub>a</sub>  
(-1.67)<sub>b</sub>

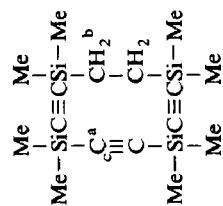
9.21

148.44

(111.17)<sub>a</sub>  
(112.74)<sub>b</sub>

(-41.5)<sub>a</sub>  
(-25.7)<sub>b</sub>

(4)



(0.30)<sub>a</sub>  
(0.16)<sub>b</sub>

0.77

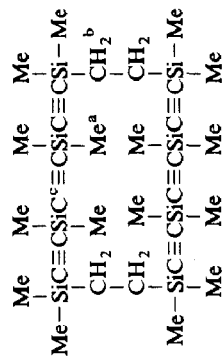
(-0.54)<sub>a</sub>  
(-2.43)<sub>b</sub>

9.21

(113.58)<sub>a</sub>  
(111.31)<sub>c</sub>

(-41.5)<sub>a</sub>  
(-14.0)<sub>b</sub>

(5)



(0.33)<sub>a</sub>  
(0.15)<sub>b</sub>

0.61

(0.17)<sub>a</sub>  
(-2.56)<sub>b</sub>

8.04

(110.98)<sub>a</sub>  
(110.00)<sub>c</sub>  
(114.55)<sub>b</sub>

(-42.1)<sub>a</sub>  
(-14.3)<sub>b</sub>

(6)



(-41.8)<sup>a</sup>  
(-26.2)<sup>b</sup>  
(-14.6)<sup>c</sup>

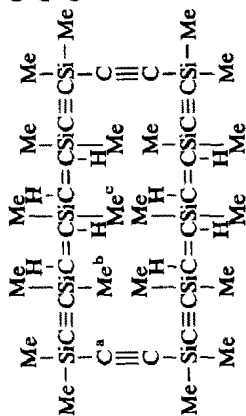
(111.06)<sup>a</sup>  
(110.73)<sup>b</sup>  
(113.71)<sup>c</sup>

(147.41)<sup>b</sup>  
(151.15)<sup>c</sup>

(-0.27)<sup>a</sup>  
(-1.63)<sup>b</sup>  
(-3.41)<sup>c</sup>

6.78,6.57  
<sup>3</sup>J(t)22.0

(0.34)<sup>a</sup>  
(0.24)  
(0.16)<sup>c</sup>



(-26.0)<sup>a</sup>  
(-14.9)<sup>b</sup>

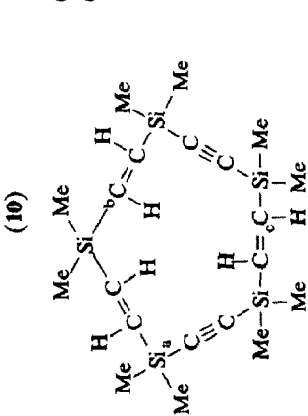
112.57  
113.17

(147.60)<sup>a</sup>  
(148.60)<sup>c</sup>  
(150.93)<sup>b</sup>

(-1.68)<sup>a</sup>  
(-3.41)<sup>b</sup>

6.78,6.59  
<sup>3</sup>J(t)22.2

(0.22)<sup>a</sup>  
(0.16)<sup>b</sup>



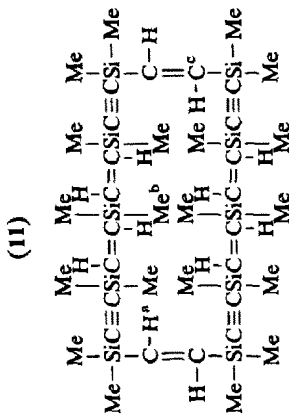
112.90  
113.12

(148.71)<sup>c</sup>  
(147.74)<sup>a</sup>  
(150.93)<sup>b</sup>

(-1.52)<sup>a</sup>  
(-3.41)<sup>b</sup>

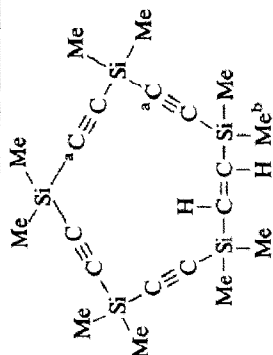
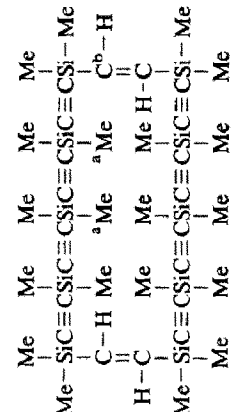
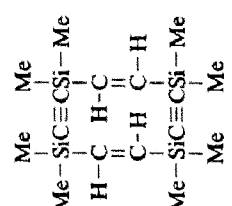
6.78,6.59  
<sup>3</sup>J(t)22.2

(0.22)<sup>a</sup>  
(0.16)<sup>b</sup>



(12)

Table 2 (continued)

Compound	$^1\text{H}$		$^{13}\text{C}$			$^{29}\text{Si}$		
	$\text{CH}_3\text{Si}$	$\text{CH}_2\text{Si}$	$=\text{CHSi}$	$\text{CH}_3\text{Si}$	$\text{CH}_2\text{Si}$	$=\text{CHSi}$	$\equiv\text{CSi}$	
 <p>(13)</p>	(0.32) <sup>a</sup> (0.23) <sup>b</sup>		6.73	(-0.16) <sup>a</sup> (-1.68) <sup>b</sup>	148.49	110.79 110.52 110.19 (112.68) <sup>b</sup>	(-41.7) <sup>a</sup> (-25.6) <sup>b</sup>	
 <p>(14)</p>	(0.35) <sup>a</sup> (0.26) <sup>b</sup>		6.72	(-0.22) <sup>a</sup> (-1.95) <sup>b</sup>	148.38	111.00 110.68 110.52 (113.12) <sup>b</sup>	(-41.3) <sup>a</sup> (-41.7) <sup>a</sup> (-25.8) <sup>b</sup>	
 <p>(15)</p>	0.23		6.93	-2.21	150.68	116.47	-26.5	



$  \begin{array}{c}  \text{Me} \quad \text{Me} \\    \quad   \\  \text{Me}-\text{SiC}\equiv\text{CSi}-\text{Me} \\    \quad   \\  \text{C}-\text{H} \quad \text{Me} \\     \quad   \\  \text{H}-\text{C} \quad \text{Me} \\    \quad   \\  \text{Me}-\text{SiC}\equiv\text{CSi}-\text{Me} \\    \quad   \\  \text{Me} \quad \text{Me}  \end{array}  $	0.25	6.71	-1.57	148.60	113.06	-26.1
$  \begin{array}{c}  \text{Me} \quad \text{Me} \\    \quad   \\  \text{Me}-\text{SiC}\equiv\text{CSi}-\text{Me} \\    \quad   \\  \text{C}-\text{H} \quad \text{Me} \\     \quad   \\  \text{H}-\text{C} \quad \text{Me} \\    \quad   \\  \text{Me}-\text{SiC}\equiv\text{CSi}-\text{Me} \\    \quad   \\  \text{Me} \quad \text{Me}  \end{array}  $	0.25	6.72	-1.57	148.71	113.22	-26.2
$  \begin{array}{c}  \text{Me} \quad \text{Me} \\    \quad   \\  \text{Me}-\text{SiC}\equiv\text{CSi}-\text{Me} \\    \quad   \\  \text{C}-\text{H} \quad \text{Me} \\     \quad   \\  \text{H}-\text{C} \quad \text{Me} \\    \quad   \\  \text{Me}-\text{SiC}\equiv\text{CSi}-\text{Me} \\    \quad   \\  \text{Me} \quad \text{Me}  \end{array}  $	(0.33) <sup>a</sup> (0.23) <sup>b</sup> (0.16) <sup>c</sup>	6.80 6.55 <i>J</i> (H-H,t) 22.5	(0.26) <sup>a</sup> (-1.56) <sup>b</sup> (-3.45) <sup>c</sup>	(147.30) <sup>b</sup> (151.13) <sup>c</sup>	110.66 110.81 111.33 113.54	(-41.3) <sup>a</sup> (-41.8) <sup>a</sup> (-25.8) <sup>b</sup> (-14.5) <sup>c</sup>
$  \begin{array}{c}  \text{Me} \quad \text{Me} \\    \quad   \\  \text{Me}-\text{SiC}\equiv\text{CSi}-\text{Me} \\    \quad   \\  \text{C}-\text{H} \quad \text{Me} \\     \quad   \\  \text{H}-\text{C} \quad \text{Me} \\    \quad   \\  \text{Me}-\text{SiC}\equiv\text{CSi}-\text{Me} \\    \quad   \\  \text{Me} \quad \text{Me}  \end{array}  $	(17)					
$  \begin{array}{c}  \text{Me} \quad \text{Me} \\    \quad   \\  \text{Me}-\text{SiC}\equiv\text{CSi}-\text{Me} \\    \quad   \\  \text{C}^a \quad \text{Me}^a \\     \quad   \\  \text{C}^b \quad \text{Me}^b \\    \quad   \\  \text{Me}-\text{SiC}\equiv\text{CSi}-\text{Me} \\    \quad   \\  \text{Me} \quad \text{Me}  \end{array}  $	(18)					

Table 2 (continued)

Compound	<sup>1</sup> H			<sup>13</sup> C			<sup>29</sup> Si		
	CH <sub>3</sub> Si	CH <sub>2</sub> Si	=CHSi	CH <sub>3</sub> Si	CH <sub>2</sub> Si	=CHSi	CH <sub>2</sub> Si	=CHSi	=CSi
$  \begin{array}{c}  \text{Me} \quad \text{Me} \quad \text{Me} \\    \quad   \quad   \\  \text{Me}-\text{SiC}\equiv\text{CSiC}\equiv\text{CSi}-\text{Me} \\    \quad   \quad   \\  \text{C}^a \quad \text{C}^b-\text{H} \\     \quad    \\  \text{C} \quad \text{C} \\    \quad   \\  \text{Me} \quad \text{H}-\text{C} \\    \\  \text{Me}-\text{SiC}\equiv\text{CSiC}\equiv\text{CSi}-\text{Me} \\    \quad   \quad   \\  \text{Me} \quad \text{Me} \quad \text{Me}  \end{array}  $	(0.35) <sub>a</sub> (0.25) <sub>b</sub>		6.70	(-0.27) <sub>a</sub> (-1.79) <sub>b</sub>		148.28		110.35 110.62 111.11 112.73 113.06	(-41.6) <sub>a</sub> (-41.9) <sub>a</sub> (-25.9) <sub>b</sub>
$  \begin{array}{c}  \text{Me} \quad \text{Me} \\    \quad   \\  \text{Me}-\text{SiC}\equiv\text{CSiC}\equiv\text{CSi}-\text{Me} \\    \quad   \\  \text{C}^a \quad \text{C}^b \\    \quad   \\  \text{C} \quad \text{C} \\    \quad   \\  \text{Me} \quad \text{C}^c \\    \\  \text{Me}-\text{SiC}\equiv\text{CSiC}\equiv\text{CSi}-\text{Me} \\    \quad   \quad   \\  \text{Me} \quad \text{Me} \quad \text{Me}  \end{array}  $	(0.31) <sub>a</sub> (0.35) <sub>b</sub>	1.23		(-1.00) <sub>a</sub> (-3.14) <sub>b</sub>	10.38		(122.22) <sub>c</sub> (112.48) <sub>a</sub> (144.49) <sub>b</sub>	(-33.9) <sub>a</sub> (-24.30) <sub>b</sub>	



(0.35)<sup>a</sup>  
(0.31)<sup>b</sup>

(-0.92)<sup>a</sup>  
(-2.55)<sup>b</sup>

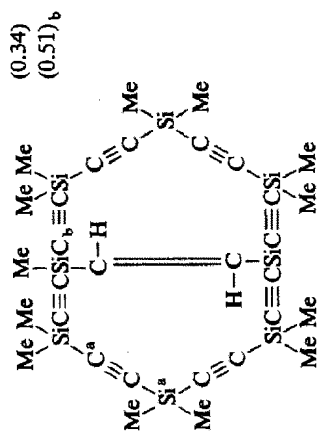
7.43

151.42

(112.03)<sup>c</sup>  
(113.55)<sup>a</sup>  
(116.48)<sup>b</sup>

(-40.9)<sup>a</sup>  
(-42.6)<sup>b</sup>

(21)



(0.34)  
(0.51)<sup>b</sup>

(-0.27)<sup>a</sup>  
(-2.55)<sup>b</sup>

6.96

146.70

110.52  
113.87

(-41.32)<sup>a</sup>  
(-41.4)<sup>b</sup>

(22)



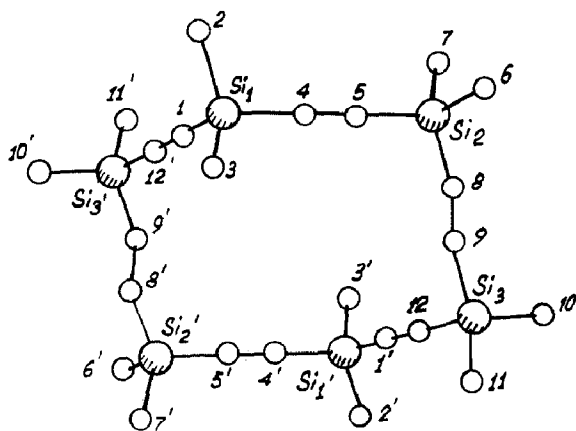


Fig. 1. The structure and labelling scheme of **1**.

The structure of compound **1** (Fig. 1) was proved by X-ray diffraction (bond lengths and valence angles are given in Table 3). The molecular structure of **1** in crystal form shows crystallographic symmetry  $C_i$ , although its intrinsic symmetry is higher,  $C_{2h}$ ; the double axis lies through the middle of the C(8)–C(9) and C(8')–C(9') bonds, the mirror line lying normally through the Si(1) and Si(1') atoms. The 18-membered macroheterocycle exhibits the boat conformation, the almost flat “backs” of which (Si(2) ··· Si(1) ··· Si(3) and Si(2') ··· Si(1') ··· Si(3')) fragments) form dihedral angles of  $109.9^\circ$  with the “chair-bottom” plane, the Si(1) and Si(1') atoms being  $+2.61\text{\AA}$  displaced out of the latter. In general, the 18-membered macrocycle of **1** is rigid and a change in its conformation leads to considerable distortion of either normal tetrahedral or linear coordination of the Si and C atoms, or makes the SiCH<sub>2</sub>CH<sub>2</sub>Si bridges adopt a disadvantageous *cis*-conformation.

The average Si–C( $sp^3$ ) distance is  $1.840\text{\AA}$ , evidently because no correction for thermal motion of the atoms (especially that of methyl groups) was taken into consideration. The C≡C bond lengths are  $1.202$  and  $1.207(8)\text{\AA}$ , which are normal for this class of compound. Figure 2 shows that there is a cavity  $3\text{\AA}$  in diameter inside molecule **1** restricted by the Van der Waals surface. However, the reciprocal

Table 3

Main bond lengths,  $d$  (Å) and valence angles ( $^\circ$ ) in molecules **1**

Bond	$d$	Angle	
Si(1)–C(1)	1.842(6)	C(1)Si(1)C(4)	106.6(3)
Si(1)–C(4)	1.842(6)	C(5)Si(2)C(8)	109.3(3)
Si(2)–C(5)	1.848(6)	C(9)Si(3)C(12)	109.8(3)
Si(2)–C(8)	1.854(7)	Si(1)C(1)C(12)	177.1(6)
Si(3)–C(9)	1.875(7)	Si(1)C(4)C(5)	176.7(5)
Si(3)–C(12)	1.838(6)	Si(2)C(5)C(4)	177.6(6)
C(1)–C(12)	1.207(8)	Si(2)C(8)C(9)	155.8(4)
C(4)–C(5)	1.201(8)	Si(3)C(9)C(8)	115.2(4)
C(8)–C(9)	1.522(9)	Si(3)C(12)C(1)	178.6(6)

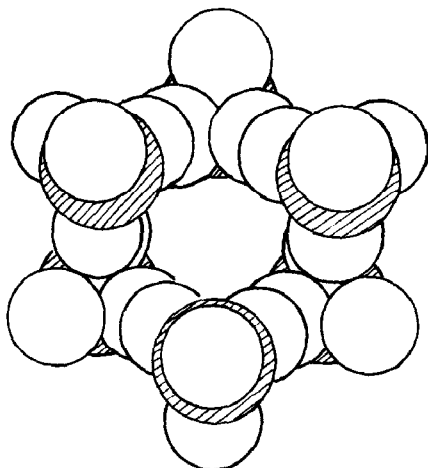


Fig. 2. Space filling model of **1**, with Van der Waals radii, showing the 3 Å cavity.

orientation of molecules in the crystal allows no through channels to be present in the crystalline structure. The molecules form layers, with the outer surface consisting of SiC≡CSi fragments with C(3), C(6), and C(11) methyl substituents.

X-Ray diffraction analysis: crystals of **1**, triclinic,  $a$  5.873,  $b$  10.735(7), 13.970(3) Å;  $\alpha$  105.55(4),  $\beta$  102.03(1),  $\gamma$  92.35(4)°;  $V$  823.7(5) Å<sup>3</sup>,  $d_{\text{calc.}}$  = 1.01 g/cm<sup>3</sup>,  $\mu$  = 2.59 cm<sup>-1</sup>,  $Z$  = 1; C<sub>24</sub>H<sub>44</sub>Si<sub>6</sub>, space group  $P\bar{1}$ . The intensities of 2028 reflections were measured at 300 K with a Hilger–Watts automatic diffractometer ( $\lambda(\text{Mo-}K_{\alpha})$  radiation  $\theta/2\theta$  scan,  $2\theta_{\text{max}}$  61°). The structure was solved by using the direct method (MULTAN program) and refined by the block-diagonal least-squares technique to an anisotropic approximation for non-hydrogen atoms and to an isotropic approximation for hydrogen atoms (located in the difference Fourier synthesis) to  $R$  = 0.056 ( $R_w$  = 0.063) for 1228 reflections with  $I \geq 2\sigma(I)$ . All calculations were carried out with an Eclipse S/200 computer using the INTEXTL program package [10].

## Experimental

Mass spectra were recorded on an MAT-212 (Varian) chromatomass-spectrometer (ionizing voltage 70 eV). NMR spectra were recorded on a JEOL FX 90Q instrument (15% solution in CDCl<sub>3</sub>, TMS).

*1,1,4,4,7,7,10,10,13,13-Decamethyl-1,4,7,10,13-pentasilacyclopentadeca-2-ene-5,8,11,14-tetraene (13)* and *1,1,4,4,7,7,10,10,13,13,16,16,19,19,22,22,25,25,28,28-eicosamethyl-1,4,7,10,13,16,19,22,25,28-decasilacyclotriaconta-2,17-diene-5,8,11,14,20,23,26,29-octaine (14)*

Me<sub>2</sub>Si(C≡CSiMe<sub>2</sub>C≡CMgBr)<sub>2</sub> (obtained from 2.43 g of Mg, 10.9 g of EtBr and 13.63 g of Me<sub>2</sub>Si(C≡CSiMe<sub>2</sub>C≡CH)<sub>2</sub> in 100 ml of THF) and 9.17 g of (*E*)-FMe<sub>2</sub>SiCH=CHSiMe<sub>2</sub>F also in 100 ml of THF) were added dropwise under stirring from two dropping funnels to 100 ml of dry THF. A refluxer was replaced by a descending cooler and the major portion of THF was distilled off. After cooling, the mixture was diluted with ether and decomposed by a saturated NH<sub>4</sub>Cl solution.

After convenient treatment and drying over  $\text{CaCl}_2$ , the solvents were distilled off; from the residue 2.31 g (11.2%) of compound **13** was isolated by distillation in vacuum (1 Torr) and then 0.082 g (0.4%) of compound **14** by distillation in high vacuum ( $1 \times 10^{-5}$  Torr) (Table 1). The compounds obtained were recrystallized from hexane.

Compounds **1–12** and **14–22** were obtained in a similar manner (see Table 1).

### Acknowledgements

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