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Macromolecular and macrocyclic polyunsaturated silicohydrocarbons

O G Yarosh, M G Voronkov, E I Brodskaya

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Abstract. **The results of studies on polyunsaturated macromolecular and macrocyclic silicohydrocarbons, the skeleton of which is made up of silicon atoms and the $-C\equiv C-$ or $-CH=CH-$ groups or of a combination of these and certain other fragments, are surveyed and treated systematically for the first time. Attention is concentrated on studies in the field of polyunsaturated macrocyclic silicohydrocarbons. The methods of synthesis of macromolecular and macrocyclic silicohydrocarbons, their structures, and physical and chemical properties, are examined. The bibliography includes 110 references.**

I. Introduction

Macromolecular polyunsaturated hydrocarbons containing isolated or conjugated multiple bonds have been very widely investigated. They include, in particular, synthetic or natural rubbers, polyethynes, etc.[1] On the other hand, the polymers made up of the $-CR_2CH=CH-$ and $-CMe_2C\equiv C-$ units are little known and difficult to obtain. The question of the existence of organic macrocycles of similar structure was not even formulated for many years and the possibility of the incorporation of $C\equiv C$ bonds in a hydrocarbon ring was regarded at one time as extemely problematical.[2] Macrocycles synthesised by a multistage procedure and having the general formulae $(Me_2CC\equiv C)_n$, where $n = 5-8$, and $(Me_2CC\equiv CC\equiv C)_n$, where $n = 5$ or 6, have been only recently described in a series of publications by Scott and coworkers.[3–10]

The possibility of the existence of macromolecular polyunsaturated silicohydrocarbons, made up of the $-SiR_2CH=CH-$ and $-SiR_2C\equiv C-$ units, was predicted in 1952.[11] It was proposed that they be called polydialkylsilethenes and polydialkylsilethynes respectively. Polymers of this type were obtained in 1960.[12] At the present time, a large number of such polymers with a wide variety of structures have been synthesised and, apart from their theoretical importance, they have acquired a practical importance for the preparation of ceramic materials and fibres and photo- and radiation-sensitive materials. The first macrocyclic silicohydrocarbon — octamethylcyclotetrasilethyne $(Me_2SiC\equiv C)_4$ — was synthesised in 1973. Its preparation initiated fundamental studies on these lines by the authors of the present review and their foreign colleagues. The present review is in fact devoted to the synthesis and study of the macromolecular and macrocyclic silicohydrocarbons and covers the publications in the periodical and patent literature from 1960 up to 1994.

The nomenclature of the compounds considered is fairly simple for polymers and macrocycles with a regular structure. The units from which they are made up are named in accordance with the corresponding hydrocarbon fragment with the prefix sil — for example, polysilbuta-1,3-diene $H(H_2SiCH=CHCH=CH)_nSiH_3$ or permethylcyclooctasil-1,4-but-2-yne $(Me_2SiCH_2C\equiv CCH_2)_8$. The oxa-aza nomenclature is needed to name the polymers and macrocycles under consideration when these have an irregular structure.

II. Macromolecular polyunsaturated silicohydrocarbons

1. Polysilethynes

The first communication on the macromolecular polyunsaturated silicohydrocarbons of the ethyne series — perorganylpolysilethynes $(R_2SiC\equiv C)_n$ — appeared in 1960 when Jenker patented a polymer obtained by the reaction of disodioethyne with diethyldifluorosilane.[12]

Two years later, Korshak and Sladkov [13,14] synthesised analogous polymers from bis(bromomagnesio)ethyne (the lotsich reagent) and dichlorodiorganylsilanes or dichlorodiorganylgermanes.

$$BrMgC\equiv CMgBr + R_2ECl_2 \longrightarrow [-R_2EC\equiv C-]_n$$

R = Me, Ph; E = Si, Ge.

The interaction of disodioethyne with dichlorodimethylsilane in hexadecane at 250 °C led to the same polymer $[(Me_2SiC\equiv C)_n]$ in 52% yield.[15,16]

The reaction of dialkylbis(lithioethynyl)silanes with dialkyldichlorosilanes was used for the same purpose.[17,18]

$$R_2Si(C\equiv CLi)_2 + R'_2SiCl_2 \longrightarrow [-R_2SiC\equiv CSiR'_2C\equiv C-]_n$$

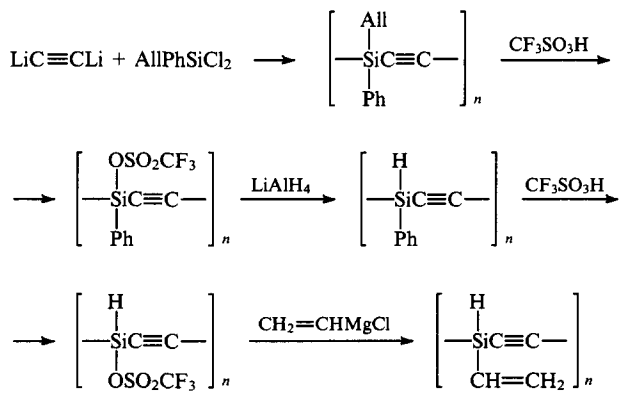
R = Me, Ph, $CH=CH_2$; R′ = H, Me, Ph.

The sequence of the monomer units in the copolymer obtained was established by ^{13}C and ^{29}Si NMR spectroscopy.[19]

O G Yarosh, M G Voronkov, E I Brodskaya Irkutsk Institute of Organic Chemistry, Siberian Division of the Russian Academy of Sciences, ul. Favorskogo 1, 664033 Irkutsk, Russian Federation. Tel. (7-395) 246 06 85 (O G Yarosh); (7-395) 246 24 00 (M G Voronkov); (7-395) 246 27 (E I Brodskaya). Fax (7-395) 246 03 31

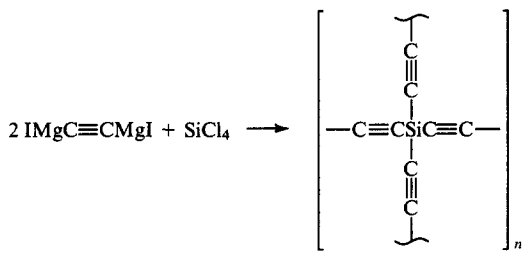
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Polyallylphenylsilethyne, synthesised by the reaction of dilithioethyne with allyldichlorophenylsilane, readily splits off the allyl group with formation of the corresponding triflate on reaction with trifluoromethanesulfonic acid. Its reduction with lithium tetrahydroaluminate leads to polyphenylhydrosilethyne. On treatment with trifluoromethanesulfonic acid, the latter splits off also the phenyl group. The resulting triflate reacts with vinylmagnesium chloride to form a polyvinylhydrosilethyne.[20]



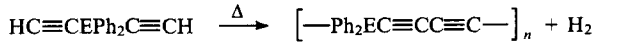
All = allyl

Bis(iodomagnesio)ethyne and tetrachlorosilane have been used to obtain materials with a ceramic coating.[21]



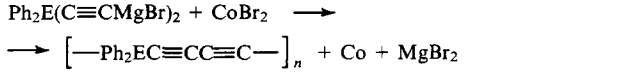
2. Polysilalkadiynes

Perorganylpolysilbutadiynes $[-R_2SiC{\equiv}CC{\equiv}C-]_n$ and their germa-analogues $[-R_2GeC{\equiv}CC{\equiv}C-]_n$ were first obtained in 1968 by the thermal polydehydrocondensation of the diethynyldiphenyl derivatives of silane or germane at 150–180 °C under a nitrogen atmosphere.[22]



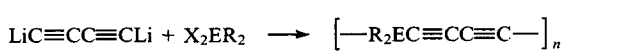
E = Si, Ge.

It proved possible to synthesise the same polymers by treating bis(bromomagnesioethynyl)dimethyl derivatives with $CoBr_2$.[22]



E = Si, Ge.

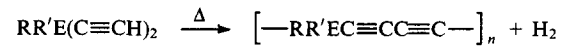
Almost a quarter of a century later, similar polymers were synthesised from dilithiodiethyne and dialkyldihalosilanes or dialkyldihalogermanes.[23–25]



E = Si, Ge; R = Me, Et, Ph, 4-MeC_6H_4; X = Cl, Br.

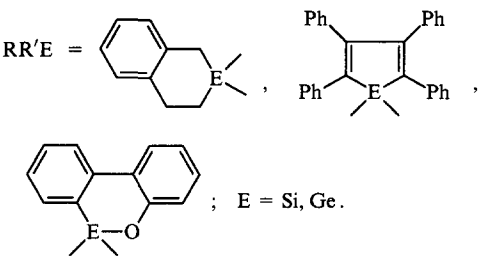
Their pyrolysis at 1400 °C leads to a mixture of silicon carbide and carbon with the ratio SiC : C = 1 : 4.[26,27]

A large series of new preorganylpolysilbutadiynes and their germanium analogues containing fairly complex substituents at the silicon or germanium atoms have been synthesised by thermal polydehydrocondensation of diethynyldiorganylsilanes and the corresponding germanes.[28,29]



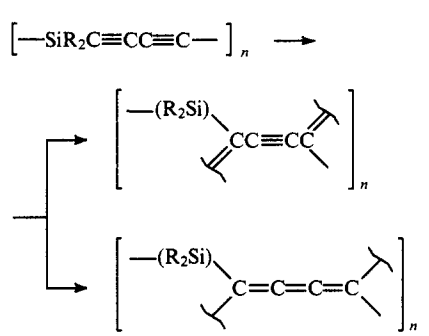
R = Ph, R′ = C_5H_5, $CH{=}CH_2$;

R = R′ = C_6H_5, 4-$MeOC_6H_4$, 4-$Me_2NC_6H_4$;

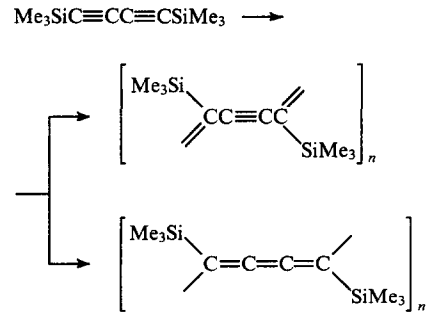


Polymers of the type $[-RR'SiC{\equiv}CC{\equiv}C-]_n$ proved to be high-resistance semiconductors at room temperature.[30]

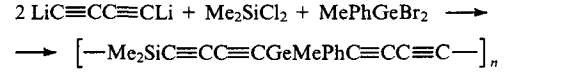
The pyrolysis of organosilicon diethyne polymers in a stream of argon at 1400 °C leads to the formation of a ceramic material containing the SiC group in a yield up to 85%. Before the mineralisation stage (~300 °C), the macrochains are cross-linked with participation of the diethyne fragments.[31]



On heating to 200 °C (for 30 days), bis(trimethylsilyl)-butadiyne gives rise to a polymer with butadienyne and butatriene fragments.[27]

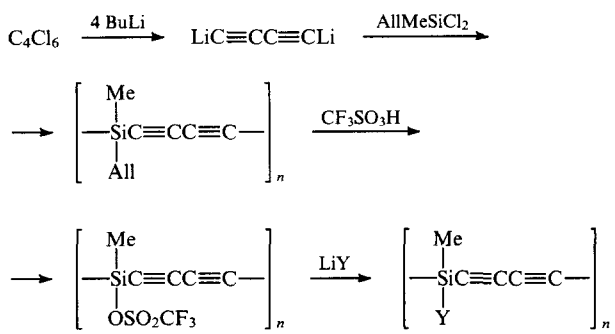


Polymers of the butadiyne series, containing simultaneously silicon and germanium atoms in the main chain, have also been synthesised.[25]



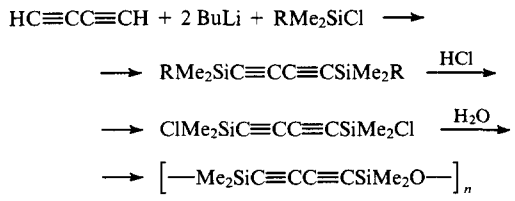
Polyallylmethylsilbutadiyne has been obtained by the reaction of dilithiodiethyne with allyldichloromethylsilane.[20]

Its interaction with trifluoromethanesulfonic acid proceeds with the elimination of the allyl group and the formation of the corresponding triflate. The latter reacts with lithioethynyltrimethylsilane to form polymethyl(trimethylsilylethynyl)silbutadiyne. The reactions with vinyllithium and triphenylsilyllithium proceed similarly.



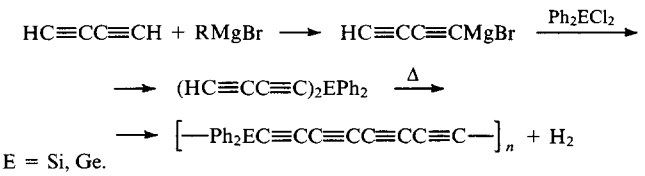
Y = CH_2=CH, $Me_3SiC{\equiv}C$, Ph_3Si.

Polymers with alternating SiC≡CC≡C and SiOSi fragments, which are stable up to 700 °C, have been synthesised by the reaction of dilithiodiethyne with chloromethoxydimethylchloro(dimethylamino)dimethyl-, and chlorohydrodimethylsilanes, the monomers obtained being subsequently treated with hydrogen chloride and water.[32]



R = H, MeO, Me_2N.

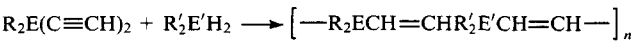
Polymers containing octatetraynyl fragments — perphenylpolysiloctatetraynes [and the corresponding germanium-containing polymers (Ed. of Translation)] — have been synthesised by the thermal polydehydrocondensation of dibutadiynyldiphenylsilane or the corresponding germane.[33]



E = Si, Ge.

3. Polysilethenes

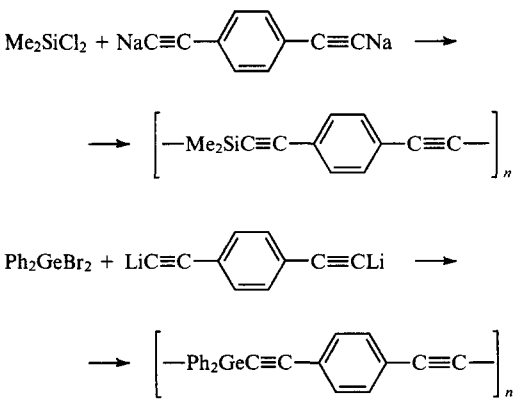
Polydiorganylsilethenes have been obtained by the hydrosilylation of diethynyldiorganylsilanes with the corresponding diorganylsilanes.[34] Their germanium and tin analogues were synthesised by a similar procedure.



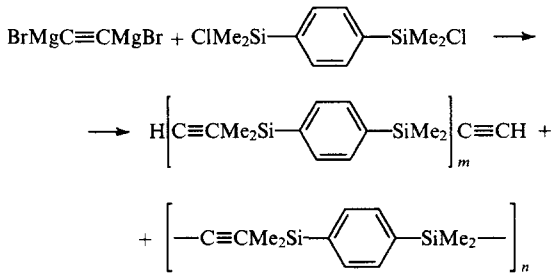
R, R′ = Me, Et, Ph; E, E′ = Si, Ge, Sn.

4. Polymers containing the C≡C and C=C multiple bonds and arylene or heteroarylene fragments

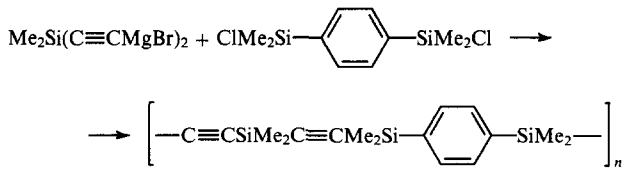
High-molecular-mass polyunsaturated silicohydrocarbons, containing simultaneously triple bonds and phenylene fragments in the macrochain, have been synthesised by the reaction of the sodium or lithium derivatives of 1,4-diethynylbenzene with dichlorodimethylsilane [35,36] or dibromodiphenylgermane.[37]



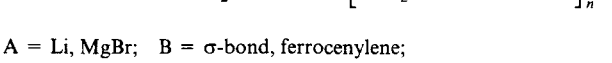
Analogous oligomers and polymers have been obtained from 1,4-bis(chlorodimethylsilyl)benzene and Iotsich reagent or bis(bromomagnesioethynyl)dimethylsilane.[38]



m = 2–6.



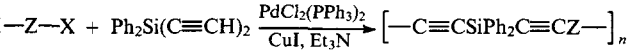
Silicoethyne polymers containing ferrocenylene nuclei in the macrochain have been synthesised from dilithio- or bis(bromomagnesioethynyl)ferrocene by reaction with dialkyldichlorosilanes.[39]



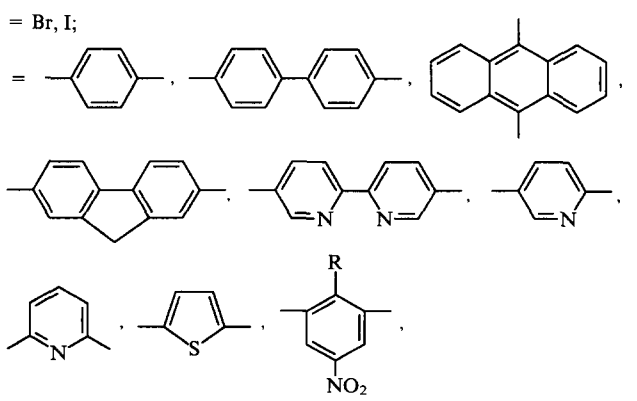
A = Li, MgBr; B = σ-bond, ferrocenylene;

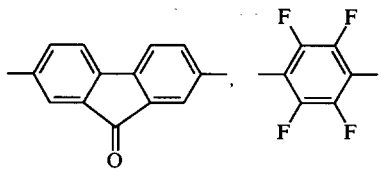
R = H, Me, CH_2=CH, Ph, ferrocenyl.

The palladium chloride-catalysed cross-polycondensation of dihaloarenes with diethynylsilanes affords a large series of silicoethyne polymers with arylene or heteroalylene fragments in the chain.[40]



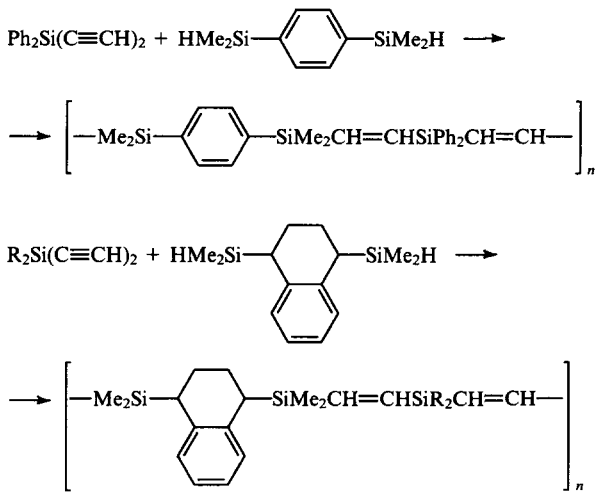
X = Br, I;

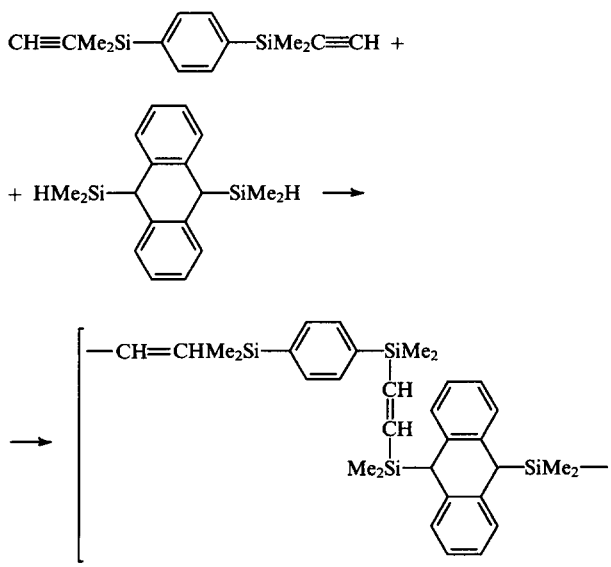
Z = 



R = NH_2, NMe_2, OH.

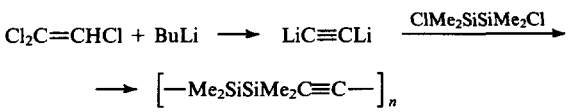
Polymers containing double bonds C=C and arylene fragments in the main chain have been obtained by hydrosilylating diethynyldiorganylsilanes with 1,4-bis-(dimethylsilyl)benzene [41] and 1,4-bis(dimethylsilyl)tetralin [42] and also by hydrosilylating 1,4-bis(ethynyldimethylsilyl)benzene with 9,10-bis(dimethylsilyl)dihydroanthracene.[43]



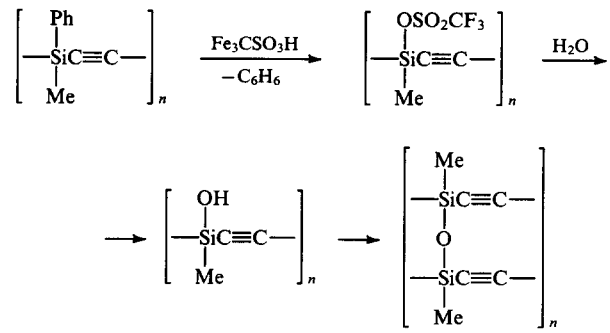


5. Polymers containing the C≡C and $(R_2Si)_n$ groups

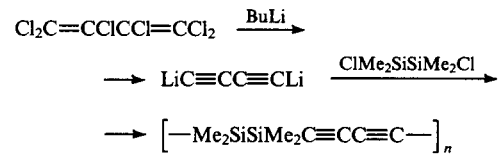
Polymers with triple bonds and disilanyl fragments in the main chain have been synthesised from dilithioethyne and 1,2-dichlorotetramethyldisilane.[44,45]



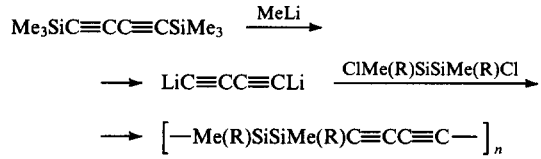
Polysilethynes have been obtained similarly.[44,45] These polymers were used to obtain fibres which were cross-linked without change in shape after treatment with F_3CSO_3H vapour and subsequent hydrolysis or UV irradiation. When they were subsequently heated to 1300 °C, silicon carbide fibres were obtained.[44,45]



Polymers of the butadiyne series have been synthesised by the same procedure from dilithiodiethyne and 1,2-dichlorotetramethyldisilane.[46,47]

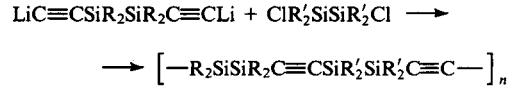


The same polymers have been obtained from bis(trimethylsilyl)butadiyne.[48]



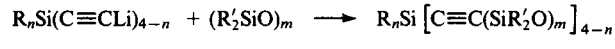
R = Et, Ph.

The reaction of tetraalkyl-1,2-bis(lithioethynyl)disilanes with tetraalkyl-1,2-dichlorodisilanes leads to polymers containing methyl and butyl groups at the silicon atom.[49]

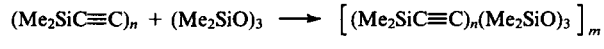


R, R′ = Me, Bu.

Finally, polymers containing the R_2SiO groups in addition to the triple bonds C≡C have been synthesised from dialkylbis(lithioethynyl)silanes and cyclodialkylsiloxanes.[50]



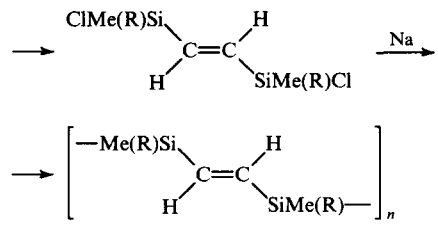
Polymers of this type are also formed from permethylcyclosilethynes $(Me_2SiC{\equiv}C)_n$, where n = 5 or 6 (see Section III), and hexamethylcyclotrisiloxane in the presence of BuLi, MeLi, $Ph_2Si(OLi)_2$, $Me_2Si(C{\equiv}CLi)_2$, and $Ph_2Si(C{\equiv}CLi)_2$ as the catalysts.[51]



The polymers obtained from 1,4-diethynylbenzene and dichloro-1,2-dimethyl-1,2-diphenyldisilane have been recommended as photo- and radiation-sensitive materials.[52]

The reaction of (*E*)-1,2-bis(chlorodiorganylsilyl)ethenes with metallic sodium in benzene leads to polymers which contain simultaneously the CH=CH and R_2SiSiR_2 fragments.[53]

$$ClMe(R)SiC{\equiv}CH + HMe(R)SiCl \longrightarrow$$



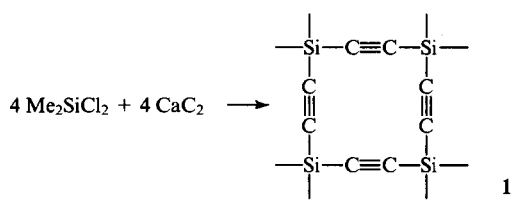
R = Me, Ph.

III. Macrocyclic polyunsaturated silicohydrocarbons

1. Cyclosilethynes

It has been suggested that the term cyclosilethynes be given to the cyclic polyethyne silicohydrocarbons made up of alternating $-R_2SiC{\equiv}C-$ groups and corresponding to the general formula $(R_2SiC{\equiv}C)_n$.[11] Compounds of this type, in which the $R_2SiC{\equiv}C$ fragments differ in the substitution at the silicon atom, have to be named in accordance with the extremely cumbersome oxa-aza nomenclature. For example, the macrocycle $(Me_2SiC{\equiv}C)_4$ is octamethylcyclotetrasilethyne, while $[Me_2SiC{\equiv}CSiMe(CH{=}CH_2)C{\equiv}C]_2$ is 1,4,4,7,7,10,10-hexamethyl-1,7-divinyl-1,4,7,10-tetrasilacyclododeca-2,5,8,11-tetrayne.

The first macrocyclic (12-membered) silicohydrocarbon made up of four alternating $Me_2SiC{\equiv}C$ fragments — 1,1,4,4,7,7,10,10-octamethyl-1,4,7,10-tetrasilacyclododeca-2,5,8,11-tetrayne or octamethylcyclotetrasilethyne **1** — was synthesised by Voronkov and Pavlov[54] in 1973 by the reaction of dichlorodimethylsilane with calcium carbide in a fused LiCl–KCl eutectic mixture at 400 °C.†



1

The great importance of this study has been noted in the literature.[55]

This silicohydrocarbon as well as decamethylcyclopentasilethyne **2** were later obtained by the reaction of the potassium–sodium alloy with ethyne and dichlorodimethylsilane in tetrahydrofuran (THF).[56,57]

$$Me_2SiCl_2 + Na/K + HC{\equiv}CH \longrightarrow (Me_2SiC{\equiv}C)_n$$

1, 2

n = 4 (**1**), 5 (**2**).

The reaction of bis(lithioethynyl)dimethylsilane with dichlorodimethylsilane affords dodecamethylcyclohexasilethyne **3**.[58]

$$Me_2Si(C{\equiv}CLi)_2 + Cl_2SiMe_2 \longrightarrow (Me_2SiC{\equiv}C)_6$$

3

Compounds belonging to the homologous series of permethylcyclosilethynes $(Me_2SiC{\equiv}C)_n$, n = 4–10, have been synthesised by Voronkov and Yarosh.[59,60] Thus octamethylcyclotetrasilethyne **1** and hexadecamethylcyclooctasilethyne **4** have been obtained by the reaction of bis(bromomagnesioethynyl)dimethylsilane (EDMS) with (chlorodimethylsilylethynyl)dimethylsilane (CDMS).[59,60]

† In this and a number of subsequent structural formulae, the methyl groups surrounding the macrocyclic silicon are not shown but are only indicated by valence bonds.

$$Me_2Si(C{\equiv}CMgBr)_2 + (ClMe_2SiC{\equiv}C)_2SiMe_2 \longrightarrow$$

$$\longrightarrow (Me_2SiC{\equiv}C)_n$$

1, 4

n = 4 (**1**), 8 (**4**).

Similarly the interaction of bis(bromomagnesioethynyldimethylsilyl)ethyne (BESA) with bis(chlorodimethylsilylethynyl)silane affords decamethylcyclopentasilethyne **2** and eicosamethylcyclodecasilethyne **5**.[59,60]

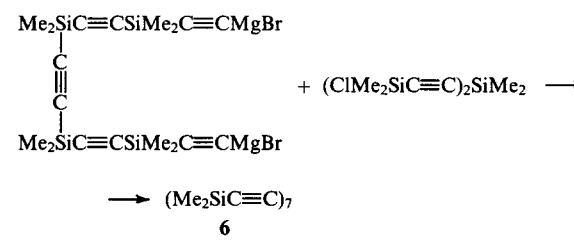
$$BrMgC{\equiv}CMe_2SiC{\equiv}CSiMe_2C{\equiv}CMgBr +$$

$$+ (ClMe_2SiC{\equiv}C)_2SiMe_2 \longrightarrow (Me_2SiC{\equiv}C)_n$$

2, 5

n = 5 (**2**), 10 (**5**).

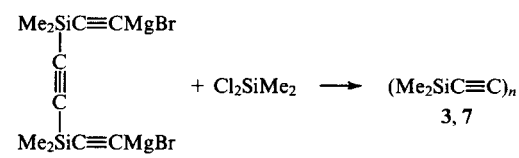
The reaction of bis(bromomagnesioethynyldimethylsilylethynyl)dimethylsilylethyne (DBES) with CDMS led to tetradecamethylcycloheptasilethyne **6**.[59,60]



$$\longrightarrow (Me_2SiC{\equiv}C)_7$$

6

Dodecamethylcyclohexasilethyne **3** and octadecamethylcyclononasilethyne **7** have been synthesised by the reaction of BESA with Me_2SiCl_2.[60]



3, 7

n = 6 (**3**), 9 (**7**).

Octamethylcyclotetrasilethyne **1**, dodecamethylcyclohexasilethyne **3**, and hexadecamethylcyclooctasilethyne **4** were isolated from the products of the reaction of EDMS with Me_2SiCl_2.[59,60]

$$Me_2Si(C{\equiv}CMgBr)_2 + Cl_2SiMe_2 \longrightarrow (Me_2SiC{\equiv}C)_n$$

1, 3, 4

n = 4 (**1**), 6 (**3**), 8 (**4**).

Voronkov and Yarosh[59,60] also synthesised cyclosilethynes containing the substituents H, $CH{=}CH_2$, (*E*)-$CH{=}CHSiMe_3$ and $C{\equiv}CSiMe_3$ at certain silicon atoms in addition to methyl groups. Thus the cyclosilethynes **8** and **9** were obtained by the reaction of EDMS with dichloromethyl(vinyl)silane.[59,60]

$$Me_2Si(C{\equiv}CMgBr)_2 + Cl_2Si(CH{=}CH_2)Me \longrightarrow$$

$$\longrightarrow [-Me_2SiC{\equiv}CSiMe(CH{=}CH_2)C{\equiv}C-]_n$$

8, 9

n = 2 (**8**), 3 (**9**).

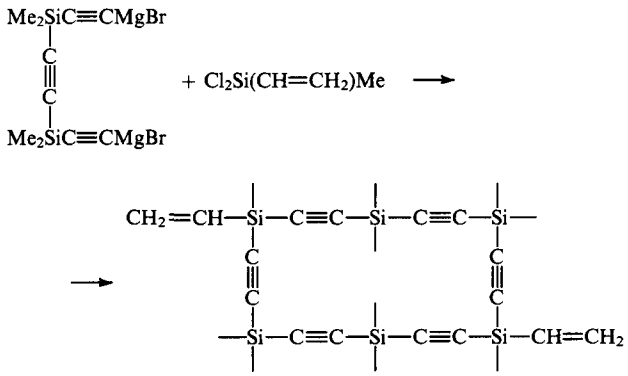
1,4,7,10-Tetramethyl-1,4,7,10-tetravinyl-1,4,7,10-tetrasilacyclododeca-2,5,8,11-tetrayne **10** has been synthesised by the reaction of bis(bromomagnesioethynyl)methyl(vinyl)silane with dichloromethyl(vinyl)silane.[59,60]

$$Me(CH_2{=}CH)Si(C{\equiv}CMgBr)_2 + Cl_2Si(CH{=}CH_2)Me \longrightarrow$$

$$\longrightarrow [Me(CH_2{=}CH)SiC{\equiv}C]_4$$

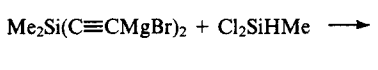
10

The interaction of BESA with dichloromethyl(vinyl)silane led to 1,4,4,7,7,10,13,13,16,16-decamethyl-1,10-divinyl-1,4,7,10,13,16-hexasilacyclooctadeca-2,5,8,11,14,17-hexayne **11**.[59,60]



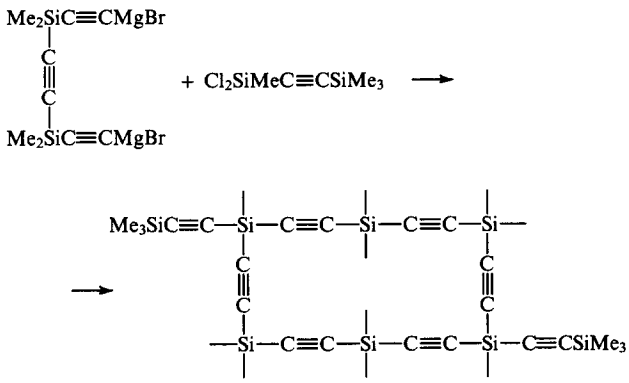
11

The reaction of EDMS with $MeHSiCl_2$ led to the isolation of 1,4,4,7,7,10,10-hexamethyl-1,7-dihydro-1,4,7,10-tetrasilacyclododeca-2,5,8,11-tetrayne **12**.[59,60]



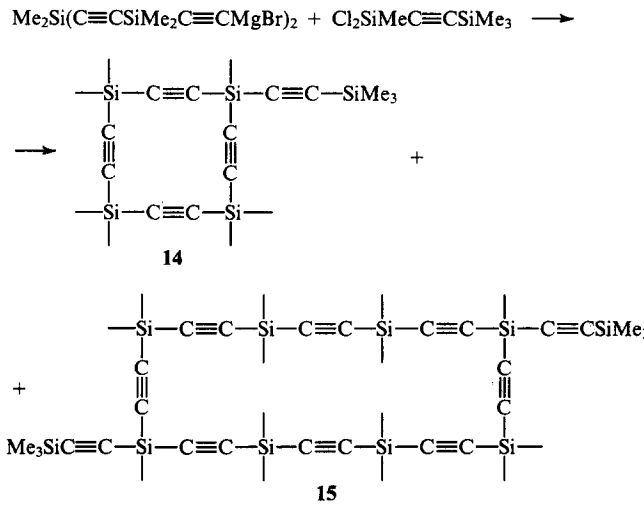
12

The interaction of BESA with dichloromethyl(trimethylsilylethynyl)silane (TMSA) affords under the same conditions with disubstituted 18-membered macrocycle **13**.[61]



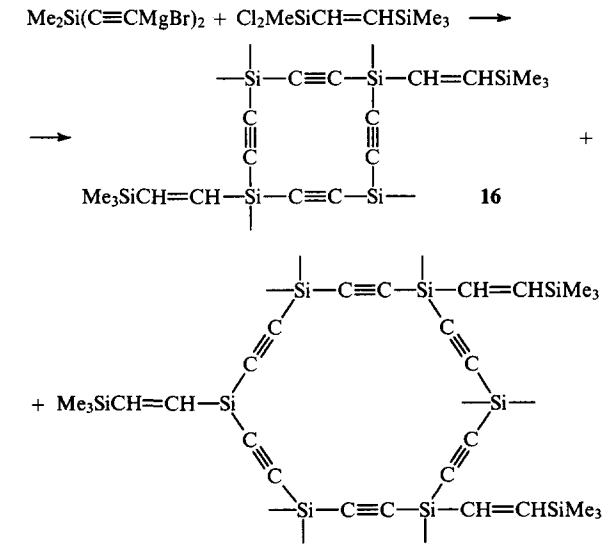
13

Bis[(bromomagnesioethynyldimethylsilyl)ethynyl]dimethylsilane (DMDS) reacts similarly with $Cl_2SiMe(C{\equiv}CSiMe_3)$ to form substituted macrocyclic ethyne silicohydrocarbons — the heptamethyl derivative **14** of 1-(trimethylsilylethynyl)-1,4,7,10-tetrasilacyclododeca-2,5,8,11-tetrayne and the tetradecamethyl derivative **15** of 1,13-bis(trimethylsilylethynyl)-1,4,7,10,13,16,19,22-octasilacyclotetracosa-2,5,8,11,14,17,20,23-octayne.[61]



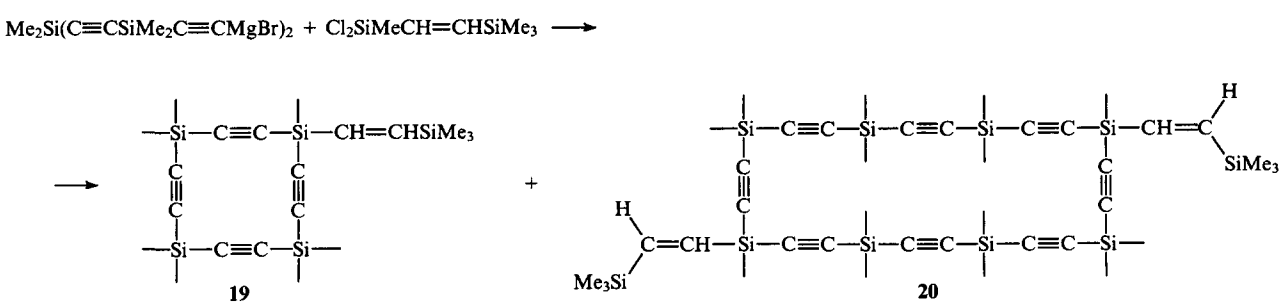
14, **15**

The interaction of EDMS with (*E*)-dichloro(methyl)-2-trimethylsilylvinylsilane (ETMS) afforded the cyclosilethynes **16** and **17**.[62]



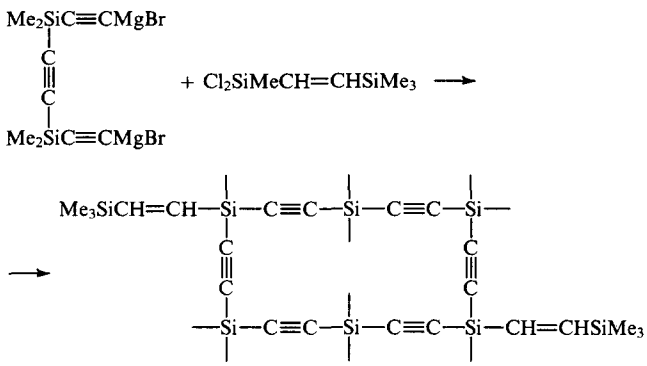
16, **17**

Scheme 1



19, **20**

Compound **18**, the product of the reaction of BESA with ETMS, is an analogue of compound **13**.[62]



18

The analogues of compounds **14** and **15** — the heptamethyl derivative **19** of 1-[(*E*)-2-trimethylsilylvinyl]-1,4,7,10-tetrasilacyclododeca-2,5,8,11-tetrayne and the tetradecamethyl derivative **20** of 1,13-bis[(*E*)-2-trimethylsilylvinyl]-1,4,7,10,13,16,19,22-octasilacyclotetracosa-2,5,8,11,14,17,20,23-octayne — were synthesised in their turn by the interaction of DMDS with ETMS (Scheme 1).[62]

Compounds **1**–**20** were obtained under the conditions of high dilution in THF and were isolated by fractional distillation or sublimation in a high vacuum (10^{-4}–10^{-5} Torr). Their yields were low and amounted to 4%–13%.

2. Macrocycles containing simultaneously triple and double bonds

Voronkov and Yarosh [63–69] synthesised by methods of fine organosilicon synthesis a series of polyunsaturated macrocyclic silicohydrocarbons containing simultaneously triple and double bonds with different numbers and orders of alternation of the latter (the silicohydrocarbons **21**–**42**). They also include compounds containing exocyclic unsaturated groups (compounds **37**–**42**).[67–69]

The reaction of the Iotsich reagent with (*E*)-1,2-bis(fluorordimethylsilyl)ethene [(*E*)-FSE] produced the 12-, 18-, and 24-membered macroheterocycles **21**–**23** with alternating double and triple bonds.[63,64]

$$BrMgC{\equiv}CMgBr + FMe_2SiCH{=}CHSiMe_2F \longrightarrow$$

$$\longrightarrow [-Me_2SiCH{=}CHSiMe_2C{\equiv}C-]_n$$

21–**23**

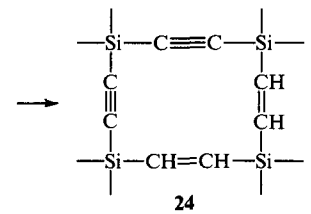
n = 2 (**21**), 3 (**22**), 4 (**23**).

The macrocyclic silicohydrocarbons **24** and **25** with alternating double and triple bonds have been synthesised by the reaction of EDMS with (*E,E*)-bis(2-chlorodimethylsilylvinyl)-dimethylsilane (BCVS).[63,64]

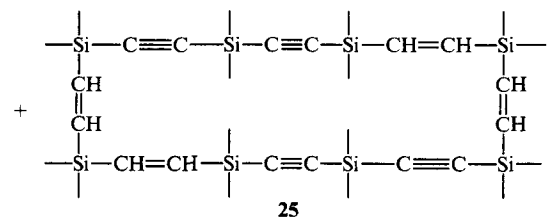
The interaction of EDMS with (*E*)-FSE led to the isolation of 1,1,4,4,7,7,10,10,13,13,16,16-dodecamethyl-1,4,7,10,13,16-hexasilacyclooctadeca-2,11-diene-5,8,14,17-tetrayne **26**.[64,65]

The polyunsaturated macrocycles **27** and **28** were synthesised similarly from bis(bromomagnesioethynyldimethylsilyl)ethyne and (*E*)-FSE.[64,65]

$$Me_2Si(C{\equiv}CMgBr)_2 + (ClMe_2SiCH{=}CH)_2SiMe_2 \longrightarrow$$

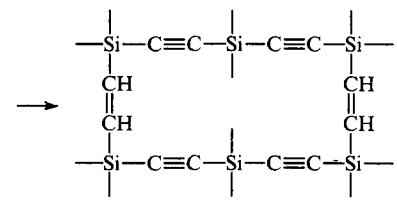


24



25

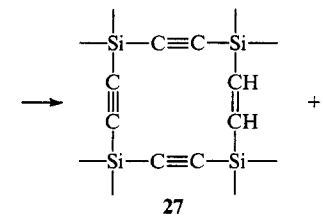
$$Me_2Si(C{\equiv}CMgBr)_2 + FMe_2SiCH{=}CHSiMe_2F \longrightarrow$$



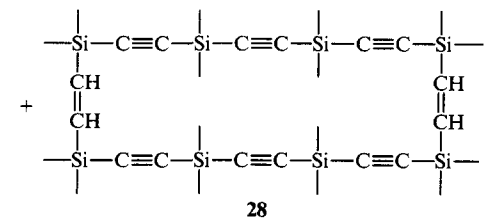
26

$$BrMgC{\equiv}CSiMe_2C{\equiv}CSiMe_2C{\equiv}CMgBr +$$

$$+ FMe_2SiCH{=}CHSiMe_2F \longrightarrow$$



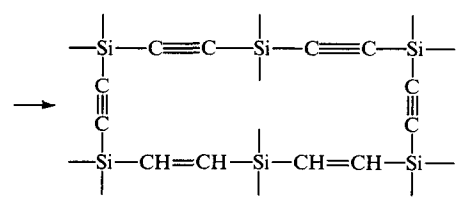
27



28

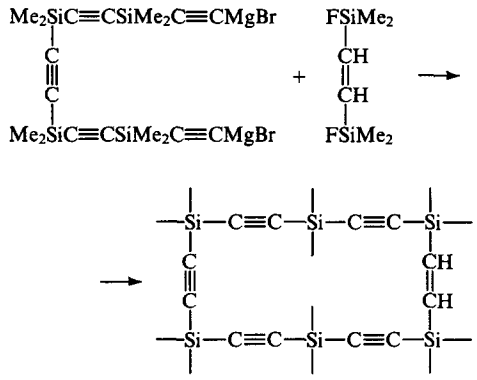
The reaction of DMDS with BCVS produced the dodecamethyl derivative **29** of 1,4,7,10,13,16-hexasilacyclooctadeca-2,5-diene-8,11,14,17-tetrayne.[64,65]

$$Me_2Si(C{\equiv}CSiMe_2C{\equiv}CMgBr)_2 + (ClMe_2SiCH{=}CH)_2SiMe_2 \longrightarrow$$



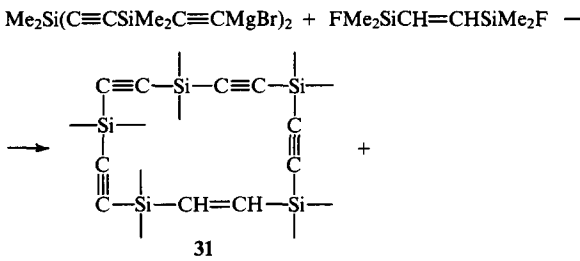
29

The product of the reaction of DBES with (*E*)-FSE is 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-pentayne **30**.[64,65]

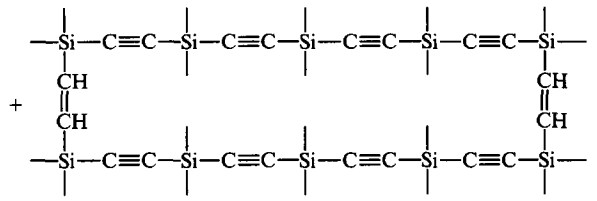


30

The interaction of DMDS with (*E*)-FSE affords the macrocycles **31** and **32**.[64,66]

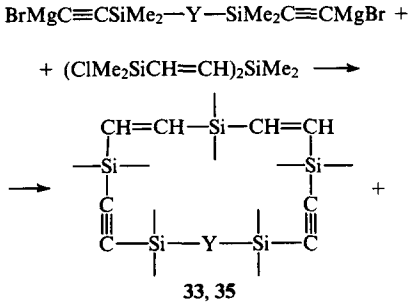


31

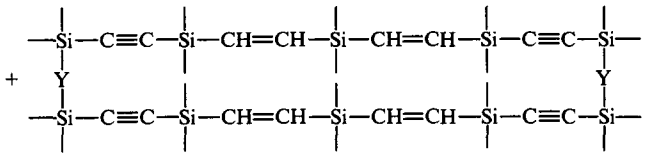


32

The highly unsaturated cyclic systems **33**–**36** were obtained similarly by the reaction of bis(bromomagnesioethynyldimethylsilyl)ethyne or (*E*)-1,2-bis(bromomagnesioethynyldimethylsilyl)ethene with BCVS.[64,66]



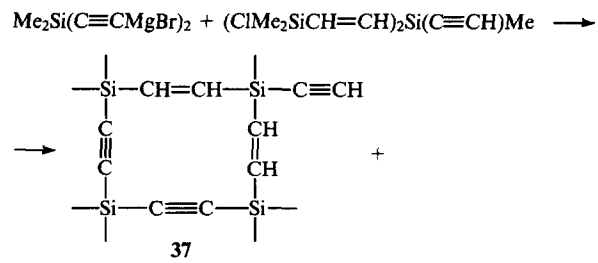
33, 35



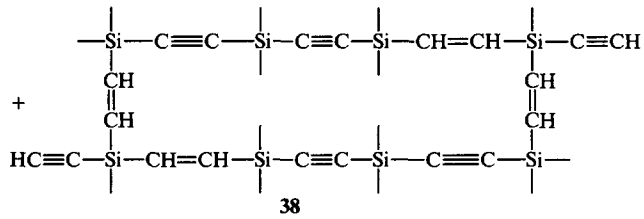
34, 36

Y = C≡C (**33**, **34**), CH=CH (**35**, **36**)

The condensation of EDMS with (*E,E*)-bis(2-chlorodimethylsilylvinyl)ethynylmethyl silane (BCVES) results in the formation of the heptamethyl derivative **37** of 1-ethynyl-1,4,7,10-tetrasilacyclododeca-2,11-diene-5,8-diyne and the tetradecamethyl derivative **38** of 1,13-diethynyl-1,4,7,10,13,16,19,22-octasilacyclotetracosa-2,11,14,23-tetraene-5,8,17,20-tetrayne containing exocyclic HC≡C groups.[67]

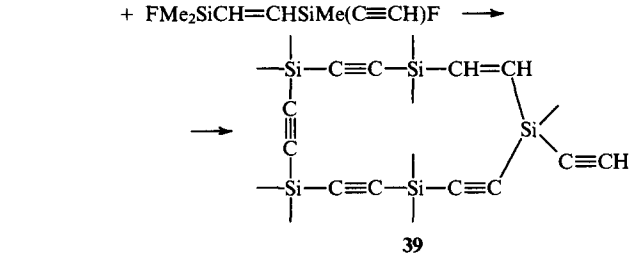


37



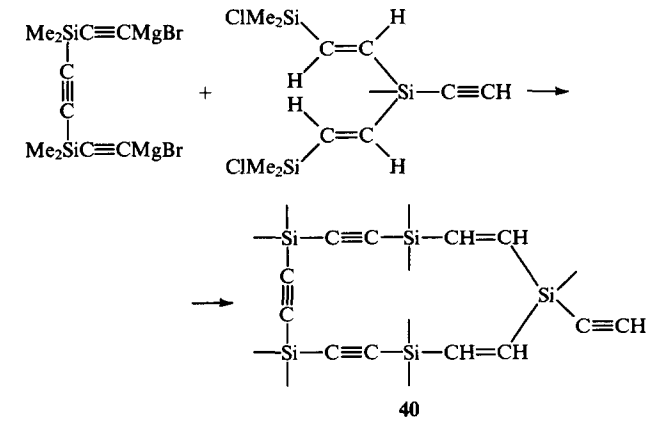
38

Similarly the reaction of DMDS with (*E*)-1-fluorodimethylsilyl-2-ethynylfluoro(methyl)silylethene produced 1-ethynyl-1,4,4,7,7,10,10,13,13-nonamethyl-1,4,7,10,13-pentasilacyclopentadeca-2-ene-5,8,11,14-tetrayne **39**.[68]



39

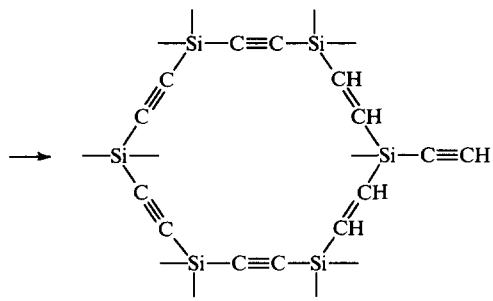
The reaction of BESA or DMDS with BCVES led to 1-ethynyl-1,4,4,7,7,10,10,13,13-nonamethyl-1,4,7,10,13-pentasilacyclopentadeca-2,14-diene-5,8,11-triyne **40** and a derivative of 1-ethynylundecamethyl-1,4,7,10,13,16-hexasilacyclooctadeca-2,17-diene-5,8,11,14-tetrayne **41**.[68]



40

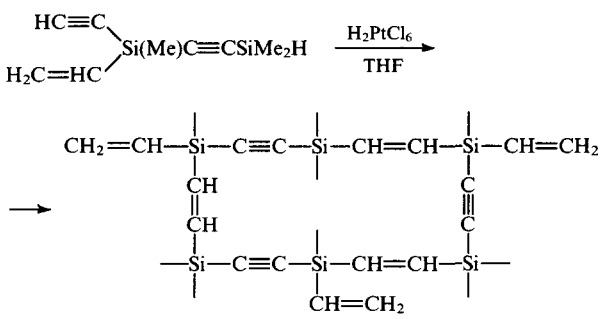
$Me_2Si(C{\equiv}CSiMe_2C{\equiv}CMgBr)_2$ +

+ $(ClMe_2SiCH{=}CH)_2Si(Me)C{\equiv}CH$ ⟶



41

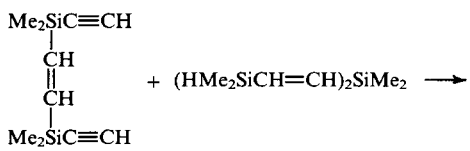
In the H_2PtCl_6-catalysed autohydrosilylation of 1-ethynyl-methylvinylsilyl-2-dimethyl silylethyne at high dilution in THF, only the ethynyl group reacts. The product of this reaction is 1,4,4,7,10,10,13,16,16-nonamethyl-1,7,13-trivinyl-1,4,7,10,13,16-hexasilacyclooctadeca-2,8,14-triene-5,11,17-triyne **42**.[69]



42

3. Cyclosilethenes

It has been suggested that the polyunsaturated macrocyclic silicohydrocarbons made up of alternating SiCH=CH fragments be called cyclosilethenes or, more precisely, cyclosil-1,2-ethenes.[11] Silicohydrocarbons of this type were first synthesised by Voronkov and Yarosh[70] by means of the autohydrosilylation reaction in the presence of H_2PtCl_6 at high dilution. The *Si*-permethylcyclosilethenes $(Me_2SiCH{=}CH)_n$ (**43**: $n = 5$; **44**: $n = 6$) were obtained in this way from ethynyldimethylsilane.[70] In addition, the specific synthesis of *Si*-decamethylcyclosilethene **43** has also been achieved by hydrosilylating (*E*)-1,2-bis-(ethynyldimethylsilyl)ethene with (*E,E*)-bis(2-dimethylsilylvinyl-dimethyl)silane.[71]



⟶ $(Me_2SiCH{=}CH)_5$

43

Si-Octamethylcyclotetrasilethene **45** was obtained in the same way — by the addition of (*E,E*)-bis(2-dimethylsilyl-vinyl)dimethylsilane to diethynyldimethyl silane.[71]

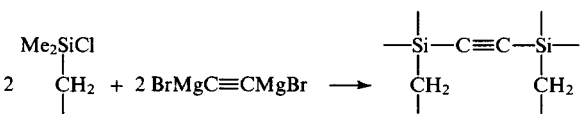
$Me_2Si(C{\equiv}CH)_2$ + $(HMe_2SiCH{=}CH)_2SiMe_2$ ⟶

⟶ $(Me_2SiCH{=}CH)_4$

45

4. Macrocycles containing endocyclic $(CH_2)_n$ ($n = 1-4$) fragments

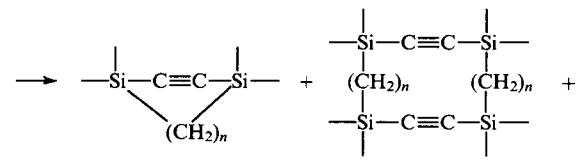
The first cyclic (10-membered) silicohydrocarbon — 1,1,4,4,6,6,9,9-octamethyl-1,4,6,9-tetrasilacyclodeca-2,7-diyne **46** — was synthesised as early as 1970 by Fritz and Schober[72] by condensing the Iotsich reagent with bis(chlorodimethyl-silyl)methane.



46

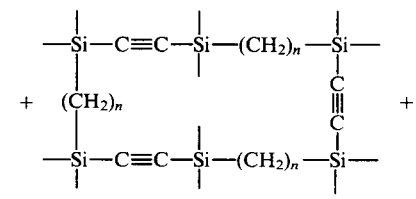
A series of cyclic and macrocyclic silicohydrocarbons (compounds **47**–**55**), containing saturated $(CH_2)_n$ ($n = 1-4$) fragments in the ring as well as the triple bonds, have been synthesised by the interaction of the Iotsich reagent with bis-(chlorodimethylsilyl)methane, 1,2-(chlorodimethylsilyl)methane, 1,3-bis(chlorodimethylsilyl)propane, or 1,4-bis(chloro-dimethyl-silyl)butane.[73]

$ClMe_2Si(CH_2)_nSiMe_2Cl$ + $BrMgC{\equiv}CMgBr$ ⟶



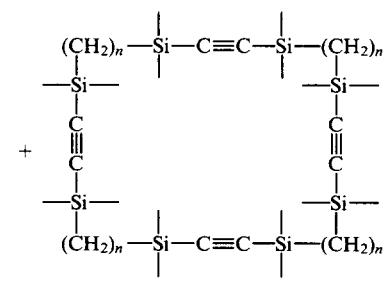
47, 48 — n = 3 (**47**), 4 (**48**)

46, 49–51 — n = 1 (**46**), 2 (**49**), 3 (**50**), 4 (**51**)



52, 53

n = 1 (**52**), 2 (**53**)

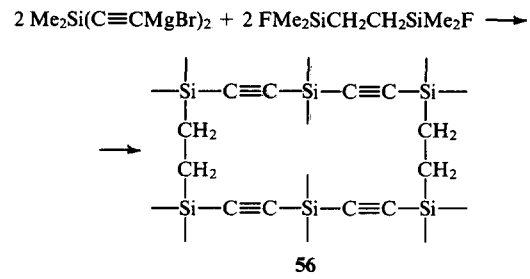


54, 55

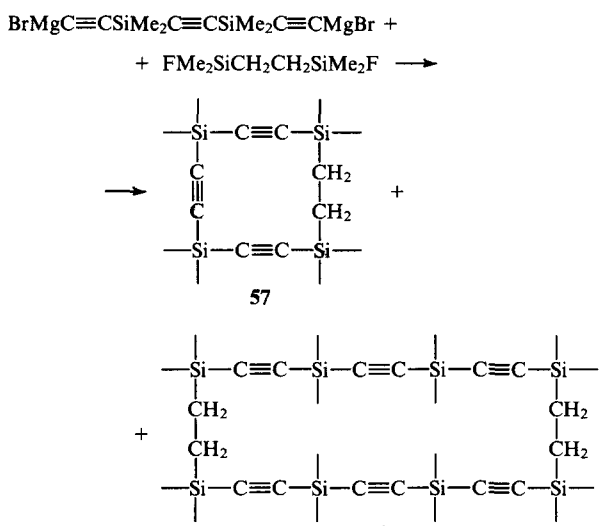
n = 1 (**54**), 2 (**55**)

On the other hand, the 18-membered 1,1,4,4,7,7,10,10,13,13,16,16-dodecamethyl-1,4,10,13,16-hexasilacycloocta-deca-2,5,11,14-tetrayne **56** has been synthesised by the reaction of EDMS with 1,2-bis(fluorodimethylsilyl)ethane[64,74,75] (see over).

Similarly the reaction of BESA with 1,2-bis-(fluorodimethylsilyl)ethane led to macrocyclic compounds — the octamethyl derivative **57** of 1,4,7,10-tetrasilacyclododeca-2,5,8-triyne and the hexadecamethyl derivative **58** of 1,4,7-10,13,16,19,22-octasilacyclotetracosa-2,5,8,14,17,20-hexayne.[63,64]



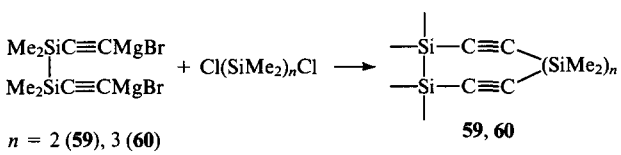
56



57, 58

5. Macrocycles containing the $(SiR_2)_n$ (n = 2, 3) fragments

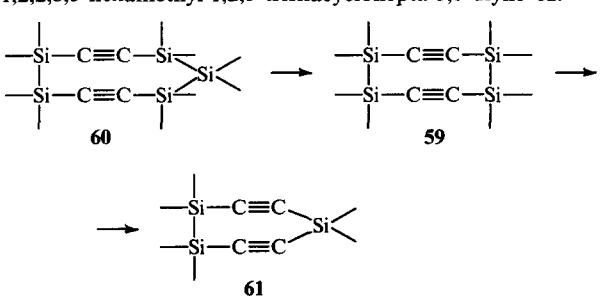
The first cyclic and macrocyclic polyunsaturated silicohydrocarbons containing simultaneously the C≡C and $(SiR_2)_n$ (n = 2, 3) groups were synthesised in 1983 by Sakurai[76-78] by means of the reaction of 1,2-bis(bromomagnesioethynyl)tetramethyldisilane with 1,2-dichlorotetramethyldisilane and 1,3-dichlorohexamethyltrisilane.



n = 2 (**59**), 3 (**60**)

59, 60

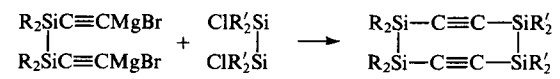
When the silicohydrocarbon **60** is heated to 680 °C under an inert atmosphere, dimethylsilylene is eliminated with formation of compound **59**, which is converted in the same way into 1,1,2,2,5,5-hexamethyl-1,2,5-trisilacycloheptа-3,6-diyne **61**.[77]



60, 59, 61

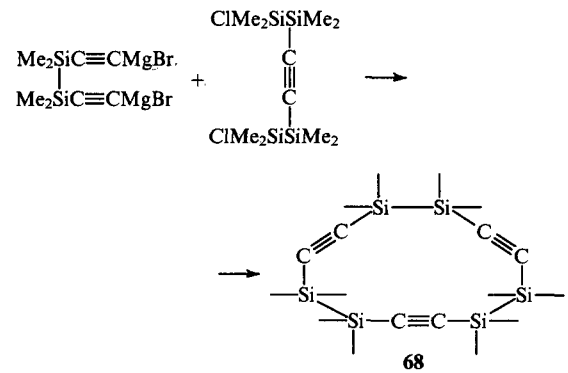
The analogous cyclic silicohydrocarbons with ethyl, butyl, hexyl, and phenyl groups were later synthesised.[78-81]

The interaction of 1,2-bis(bromomagnesioethynyl)tetramethyldisilane with bis(2-chlorotetramethyldisilanyl)ethyne led to 1,1,2,2,5,5,6,6,9,9,10,10-dodecamethyl-1,2,5,6,9,10-hexasilacyclododeca-3,7,11-triyne **68**.[82]



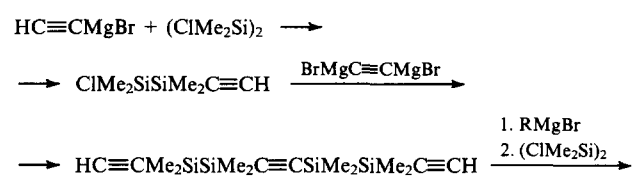
62-**67**

R = R′ = Me (**62**); R = Me, R′ = Bu (**63**); R = R′ = Bu (**64**); R = Me, R′ = Et (**65**); R = Me, R′ = C_6H_{13} (**66**); R = Me, R′ = Ph (**67**).

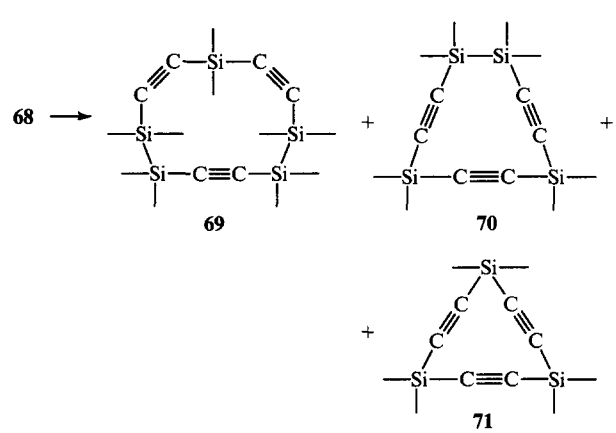


68

The same compound has been obtained in accordance with the following scheme:[83]

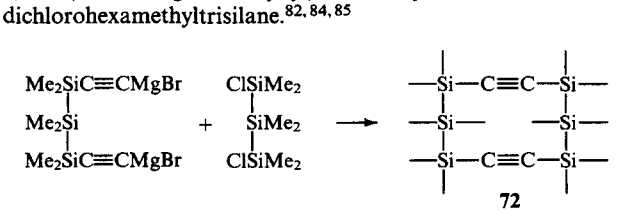


When compound **68** is heated to 540 °C, a mixture of compounds **69**-**71** is obtained in 8%, 27%, and 11% yields respectively. On the other hand, heating of compound **68** to 690 °C results in the formation of only compound **71** in 68% yield.[83]



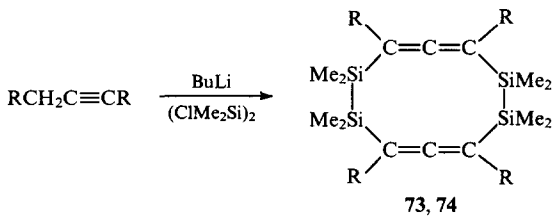
69, 70, 71

1,1,2,2,3,3,6,6,7,7,8,8-Dodecamethyl-1,2,3,6,7,8-hexasilacyclododeca-4,9-diyne **72** was obtained by the reaction of 1,3-bis(bromomagnesioethynyl)hexamethyltrisilane with 1,3-dichlorohexamethyltrisilane.[82,84,85]



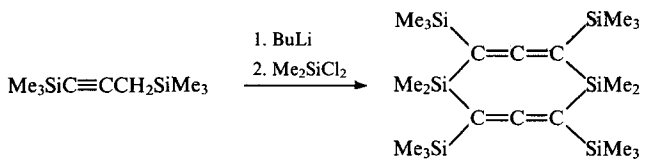
72

The reaction of 1,3-diphenylpropyne or 1,3-bis(trimethylsilyl)propyne with butyllithium and 1,2-dichlorotetramethyldisilane or dichlorodimethylsilane leads to the corresponding allene silicohydrocarbons **73**–**75**.[86,87]



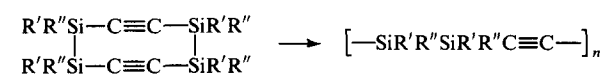
73, 74

R = Ph (**73**), Me_3Si (**74**).



75

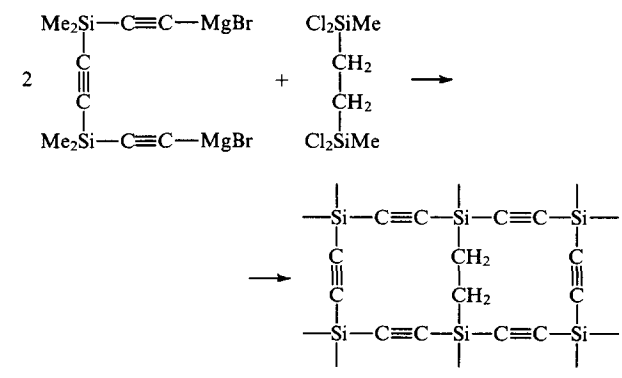
Ishikawa and coworkers[88,89] showed that, on heating to 230 °C or on treatment with a catalytic amount of butyllithium,[81,88] 1,2,5,6-tetrasilacycloocta-3,7-diynes undergo ring opening with formation of polymeric compounds:



R′ = Me, Et; R″ = Et, Ph, C_6H_{13}.

6. Bicyclic, tricyclic, and spiran systems

Bimacrocyclic trimacrocyclic and spiromacrocyclic highly unsaturated silicohydrocarbons have been obtained by methods of fine organic synthesis. Thus the first silicohydrocarbons of this type — 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-hexayne **76** — was obtained in 1988 by the interaction of BESA with 1,2-bis(chloromethylsilyl)ethane (BCSE).[64,90]

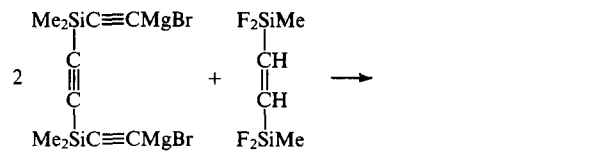


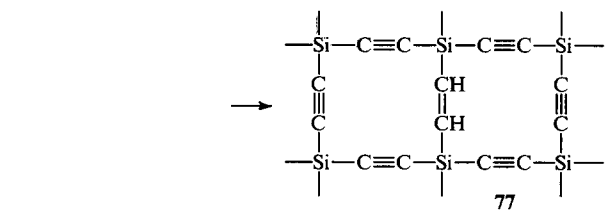
76

The bicyclic compound **77** was obtained similarly from BESA and (*E*)-1,2-bis(difluoromethylsilyl)ethene (DFSE).[64,65]

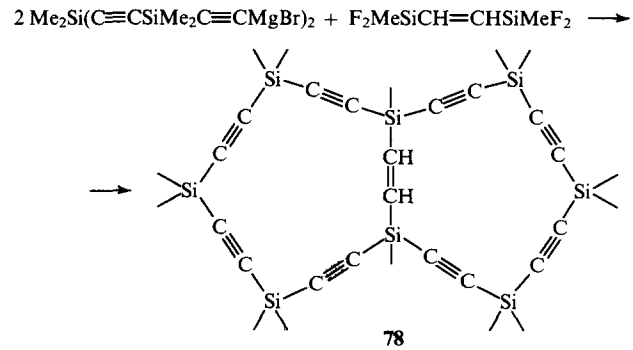
1,4,4,7,7,10,10,13,16,16,19,19,22,22-Tetradecamethyl-1,4,7,10,13,16,19,22-octasilabicyclo[11′,11′,2′]hexacosa-25-ene-2,5,8,11,14,17,20,23-octayne **78** was obtained in exactly the same way by the reaction of DMDS with DFSE.[64,65]

New highly unsaturated bicyclic silicohydrocarbons — the decamethyl derivative **79** of 1,4,7,10,13,16-hexasilabicyclo-[8′,8′,2′]eicosa-5,14-diene-2,8,11,17-tetrayne and the decamethyl derivative **80** of 1,4,7,10,13,16-hexasilabicyclo[8′,8′,2′]eicosa-5,14,19-triene-2,8,11,17-tetrayne — have been synthesised by the reaction of (*E*)-bis(bromomagnesioethynyldimethylsilyl)ethene (BESE) with BCSE and DFSE respectively.[91]

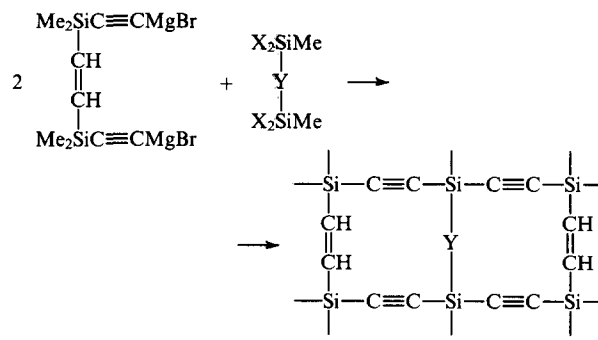




77



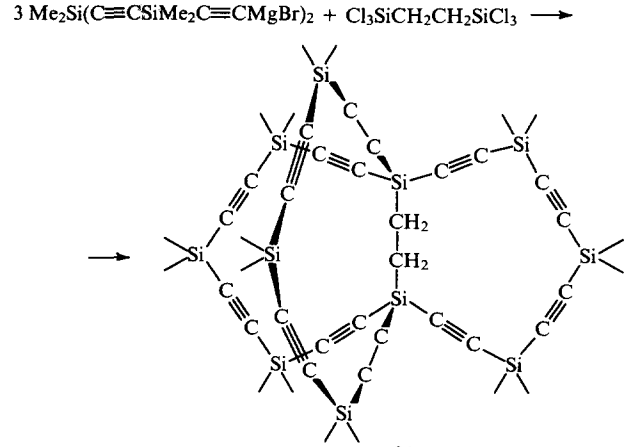
78



79, 80

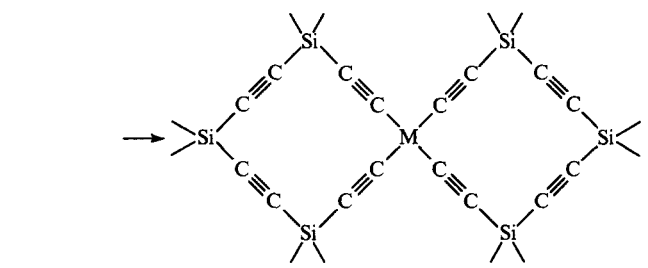
X = F, Cl; Y = CH_2CH_2 (**79**), CH=CH (**80**).

The interaction of DMDS with 1,2-bis(trichlorosilyl)ethane led to the synthesis of the first and hitherto the only trimacrocyclic silicohydrocarbon with the propellane structure — 3,3,6,6,9,9,15,15,18,18,21,21,27,27,30,30,33,33-octadecamethyl-3,6,9,12,15,18,21,24,27,30,33-undecasilatricyclo[11′,11′,11′,2′]heptatriaconta-1,4,7,10,13,16,19,22,25,28,31,34-dodecayne **81**.[92]

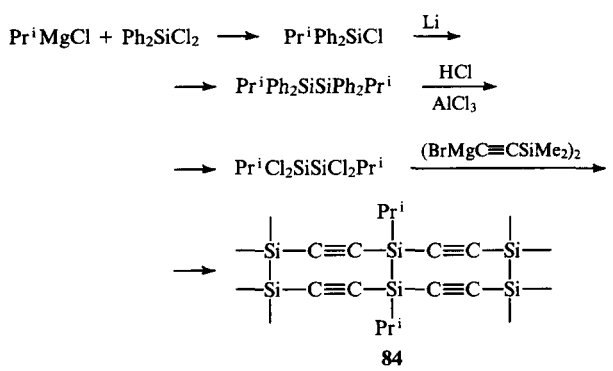


81

Finally, the first spiromacrocyclic polyethyne silicohydrocarbons — 3,3,6,6,9,9,15,15,18,18,21,21-dodecamethyl-3,6,9,12,15,18,21-heptaspiro[11′,11′]tricosa-1,4,7,10,13,16,19,22-octayne **82** and its 12-germa-analogue **83** — have been obtained by the reaction of DMDS with $SiCl_4$ and $GeCl_4$.[60,93]



M = Si (**82**), Ge (**83**).

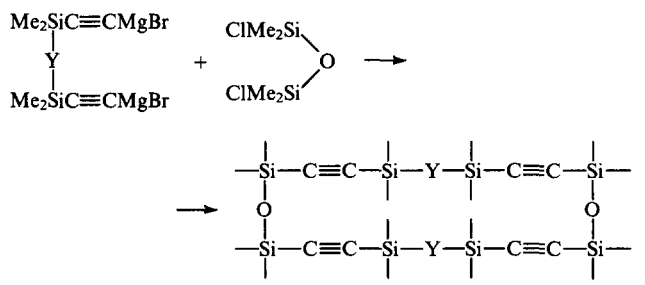


84

Compounds **5** and **15**, containing 10 triple bonds, and compound **81**, containing 12 triple bonds, are unique highly unsaturated molecular record holders. The synthesis of 1,8-diisopropyl-4,4,5,5,11,11,12,12-octamethyl-1,4,5,8,11,12-hexasilabicyclo[6′,6′,0′]tetradeca-2,6,9,13-tetrayne **84** — the only known bicyclic silicohydrocarbon containing Si–Si fragments in addition to the C≡C groups, has been achieved recently.[94]

7. Macrocycles containing endocyclic oxygen atoms

The macrocyclic polyunsaturated tetrasiloxanes **85** and **86** have been obtained by the reaction of BESA and BESE with 1,3-dichlorotetramethyldisiloxane respectively.[95,96]



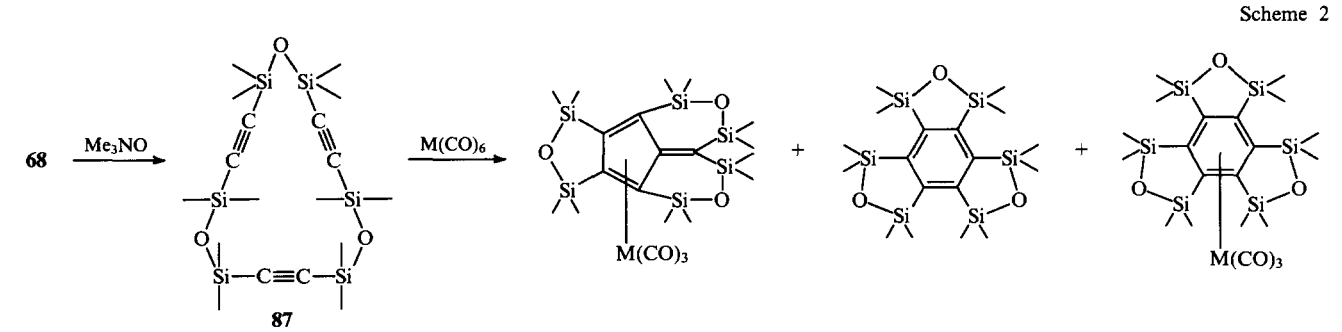
85, 86

Y = C≡C (**85**), (*E*)-CH=CH (**86**).

The oxidation of the silicohydrocarbon **68** by trimethylamine oxide leads to 1,1,4,4,6,6,9,9,11,11,14,14-dodecamethyl-1,4,6,9,11,14-hexasila-5,10,15-trioxacyclopentadeca-2,7,12-triyne **87**. The interaction of the latter with chromium molybdenum, or tungsten hexacarbonyls led to the remarkable derivatives of benzene and fulvene presented in Scheme 2.[97]

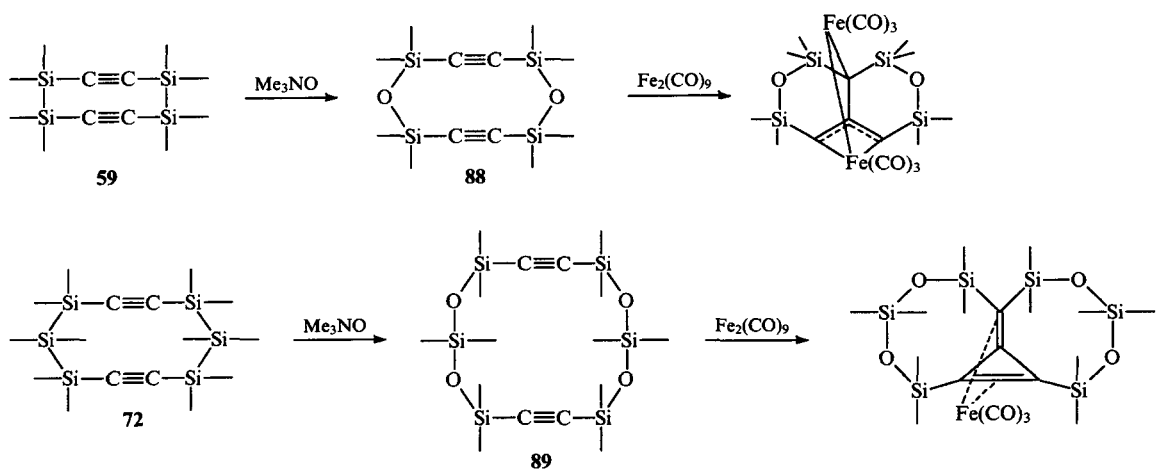
The reactions of the cyclic siloxanes **88** and **89** on treatment with $Fe_2(CO)_9$ have been investigated (Scheme 3).[84,85]

Scheme 2



M = Cr, Mo, W.

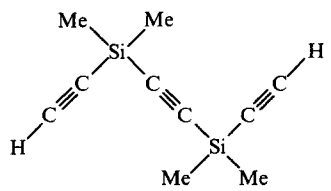
Scheme 3



IV. Physical properties

1. Molecular structure

The molecular structures of a series of polyunsaturated macrocyclic silicohydrocarbons have been established by X-ray diffraction. For a better understanding of the latter, we shall consider initially model acyclic structures:



90

and $(Me_3SiC{\equiv}C)_4Si$.

91

The molecule of compound **90** is not linear but has a zig-zag shape.[98] The Si–C(*sp*) bond lengths are 1.832 and 1.834 Å and are close to the standard Si–C(*sp*) distance of 1.837 Å.[98] The C(*sp*)–Si–C(*sp*) angles in the structure (106.6°) are smaller than the tetrahedral angle. Since there is no conformational strain in the molecule of compound **90**, the distortion of the ideal tetrahedral coordination of the silicon atoms is most probably caused by the steric interaction of the methyl substituents.

The central silicon atom in the molecule of compound **91**, surrounded by four linear $Me_3SiC{\equiv}C$ groups, has a tetrahedral configuration.[99] The C(*sp*)–C(*sp*) and Si–C(*sp*) bond lengths are respectively 1.17–1.20 and 1.840–1.871 Å, while the Si–C(*sp*)–C(*sp*) angle is close to the linear value (175–178°).[99]

The cyclic molecules of compounds **46** and **88** contain two triple bonds and have the 'chair' conformation.[100] The lengths of the bonds Si–C(*sp*) (1.839 and 1.842 Å) and C(*sp*)–C(*sp*) (1.215 and 1.216 Å) are respectively almost identical. The average Si–C(*sp*)–C(*sp*) angle is 175.5°.

The macrocyclic molecules of compounds **47**–**55** differ only in the number of methylene groups separating the $SiC{\equiv}CSi$ fragments.[101] The single unit cell of the crystal of compound **47** contains three molecules (space group *P*1), among which one is approximately at the centre of symmetry, whilst the others are in general positions and are linked by the centre of symmetry. The crystals of compound **47** contain two different conformers — the 'chair' and 'boat' conformers. The bond lengths and valence angles in compounds **46** and **49**–**51** (n = 1–4) are presented in Table 1. The rings with an even number n are more strained than those with an odd number. In all these molecules, the silicon atoms are located in one plane. The Si–C(*sp*) and C(*sp*)–C(*sp*) bond lengths in compound **62** (R = R′ = Me) are close to the standard values (1.838–1.848 and 1.182 Å respectively).[57] There are two conformers in the crystal of compound **67** (R = Me, R′ = Ph) — with the *cis,trans*- and *trans,trans*-configurations.[81] The eight-membered ring of the first conformer is planar within ±0.5 Å and has a centre of symmetry. In the first conformer, the phenyl groups are in the *trans*-positions relative to one another at each Si–Si bond and in the *cis*-positions relative to each $Si{-}C{\equiv}C{-}Si$ fragment. In the second conformer, the phenyl groups at the silicon atoms in the Si–Si and $Si{-}C{\equiv}C{-}Si$ fragments are in the *trans*-positions. Its eight-membered ring is bent (the maximum deviation from the mean square plane is 0.27 Å).[81]

The macrocyclic molecules having the general formula $(Me_2SiC{\equiv}C)_n$ (n = 4–6) (compounds **1**–**3**) have different ring conformations.[57,102] The molecule of compound **1** (n = 4) consists of a 12-membered ring with a square plane structure (D_{4h} symmetry).[57] The C(sp^3)–(Si)–C(sp^3) angles are larger than the tetrahedral angle (110.7°, 112.6°), while the C(*sp*)–(Si)–C(*sp*) angles are smaller (102.96°, 103.77°). The triple bonds are bent to the outside owing to ring strain. Compound **2** (n = 5) consists of a nonplanar ring with the envelope conformation.[57] Its triple bonds are slightly bent into the interior of the ring. As in compound **1**, the C(sp^3)–(Si)–C(sp^3) bond angles are larger than the tetrahedral value (111.4–113.5°), while the C(*sp*)–(Si)–C(*sp*) angles are smaller (104.73–106.83°). The molecule of compound **3** (n = 6) has the 'chair' conformation.[102] The C(*sp*)–C(*sp*) bond lengths in compounds **1**–**3** are 1.205–1.209, 1.210–1.220, and 1.218–1.222 Å for n = 4, 5, and 6 respectively, i.e. they increase with increase in ring size and are larger than in their C-analogues (1.18–1.19 Å), which is evidently due to their electronic interaction with the silicon atom.

The Si–C(*sp*) bond lengths (1.808–1.829 and 1.818–1.847 Å) in compound **27** are shorter[103] than in 1,1,4,4,7,7,10,10-octamethyl-1,4,7,10-tetrasilacyclododeca-2,8-diyne **47**,[101] but are approximately the same as in compound **2**.[57]

The crystal of compound **56** has C_i symmetry, although its intrinsic symmetry is C_{2h}. This 18-membered macroheterocycle has an overall 'chair' conformation and is on the whole rigid. The average Si–C(*sp*) distance (1.850 Å) differs little from the average Si–C(sp^3) distance (1.857 Å), apparently owing to failure to take into account corrections for the thermal motions of the atoms (especially the methyl groups). The length of the triple bond (1.201–1.207 Å) has the usual value. The molecules of compound **56** form stacks in the crystal, the outer surfaces of which are made up of the $Si{-}C{\equiv}C{-}Si$ fragments.[75]

A characteristic feature of the macrocyclic silicohydrocarbons with endocyclic $Si{-}C{\equiv}C{-}Si$ and Si–CH=CH–Si groups is a tendency towards disorder in the crystal structure.[95,103,104] This is frequently caused by their great flexibility combined with an appreciable looseness of the crystal structure — which is a consequence of the noninvolvement of the endocyclic $-C{\equiv}C-$ and CH=CH– bonds in the intermolecular contacts, which leads to the coexistence in the crystal of two or more conformers with different orientations.[75,95]

The molecular structure of compound **85** with endocyclic Si–O–Si (two) and $Si{-}C{\equiv}C{-}Si$ (six) groups is ordered.[95] The molecule of compound **86** differs from the structurally similar molecule of compound **85** by the presence of the CH=CH groups instead of the two $C{\equiv}C$ groups.[96] The Si–O bond lengths (1.630 Å) in compound **85** are greater than in compound **86** (1.605 Å), which is due to the greater strain in compound **85**. The latter leads in its turn to a decrease in the Si–O–Si bond angle in compound **85** (148.9°) compared with compound **86** (156.9°). The remaining bond lengths and bond angles in compound **85** are close to those observed in compound **86** [the Si–C(*sp*) bond lengths are 1.839 and 1.834 Å respectively].

The overall configuration of the bicyclic molecule of compound **78** ('butterfly'), determined primarily by the tetrahedral valence environment of the 'bridging' Si atoms, is the most compact.[104] The *trans*-structure of the Si–CH=CH–Si bridge disturbs the symmetry of this molecule. The disorder is comparatively small and is associated with the presence of

Table 1. The bond lengths (Å) and bond angles (deg) in compounds **46** and **49**–**51**.[101]

Compound	n	Si–C(*sp*)	Si–C(sp^2)	Si–C(sp^3)	C≡C	Si–C(*sp*)–C(*sp*)
46	1	1.867	1.872	1.842	1.216	176.9
49	2	1.866	1.879	1.844	1.213	173.7
50	3	1.862	1.877	1.851	1.216	179.5
51	4	1.867	1.877	1.843	1.220	178.1

two enantiomers at each crystallographic site. In the ordered fragments of the molecule of compound **78**, the bond lengths and bond angles have the usual values. Thus the average Si–C(*sp*) distance is the same as the value observed in other silicohydrocarbons.[101] A similar type of disorder has been observed also in the crystals of the macrocyclic compounds **24**, **27**, **49**, and **54** with four silicon atoms in the ring and an asymmetric distribution of the C≡C, CH=CH, and CH_2-CH_2 groups.[103]

The structure of compound **31** can be regarded as the same as one of the condensed heterocycles in the molecule of compound **78**.[103] The macrocycle **31** with five silicon atoms exists in the crystal in the form of three conformers, which is manifested by a pronounced structural disorder. All three conformers of this heterocycle have virtually the same, almost symmetrical, 'large envelope' configuration.

2. Melting points

The melting points of the cyclodimethylsilethynes $(Me_2SiC{\equiv}C)_n$ (n = 3–10) exceed 140 °C and oscillate markedly as the ring size varies. The compounds with an even number n have higher melting points (the melting point is a maximum for n = 6). Among the compounds with an odd number n, the minimum melting point is observed for n = 3 (Fig. 1).[59,60,83] A similar behaviour is manifested by the first three known analogues of these compounds containing only one double bond, namely $(Me_2SiC{\equiv}C)_{n-1}(Me_2SiCH{=}CH)$, the melting points of which are 228, 198, and 257 °C for n = 4, 5, and 6 respectively;[64–66] this also applies to cyclodimethylsilethenes $(Me_2SiCH{=}CH)_n$, the melting points of which are 158, 110, and 230 °C for n = 4, 5, and 6 respectively.[71]

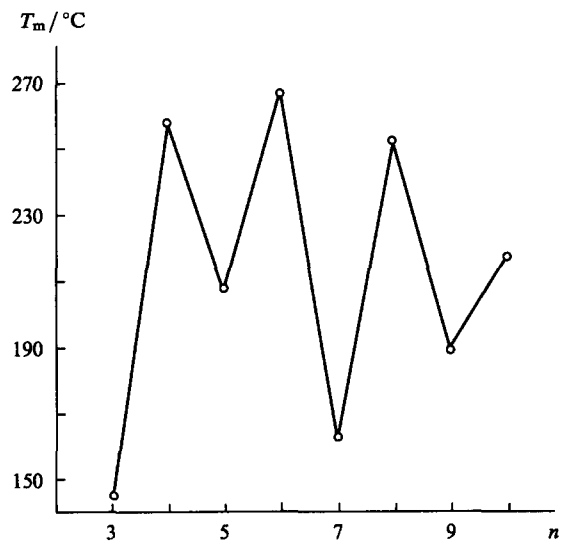


Figure 1. Melting points of the cyclodimethylsilethynes $(Me_2SiC{\equiv}C)_n$ (n = 3–10).[59,60,83]

The replacement of the methyl groups in the polyunsaturated macrocyclic silicohydrocarbons by substituents such as H, C_2H_5, $CH{=}CH_2$, C≡CH, $CH{=}CHSiMe_3$, and $C{\equiv}CSiMe_3$, leading to a decrease in ring symmetry, diminishes the melting point.[59–62] A decrease in the degree of unsaturation of the macrocycle also entails a decrease in the melting point.

The bicyclic and tricyclic as well as spirocyclic polyunsaturated silicohydrocarbons differ from the monocyclic ones by higher melting points (Table 2). A decrease in the melting point with decrease in the degree of unsaturation is also observed for these substances.

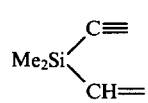
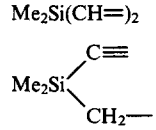
Table 2. The melting points of the bicyclic, tricyclic, and spirocyclic macrocycles.[61,65,66,90–92]

Compound	Cyclic system	T_m/°C	Compound	Cyclic system	T_m/°C
76	bicycle	277	**80**	bicycle	274
77	"	305	**81**	tricycle	269
78	"	280	**82**	spiran	293
79	"	255	**83**	"	299

3. NMR spectra

The chemical shifts of the protons in the methyl groups at the silicon atom in the polyunsaturated macrocyclic silicohydrocarbons are determined by the nature of the neighbouring endocyclic bonds and are almost independent of the size of the macroring (Table 3).

Table 3. The chemical shifts (δ) of the methyl protons in the ^{1}H NMR spectra of macrocyclic polyunsaturated silicohydrocarbons.

Fragment	δ/ppm	Ref.
$Me_2Si(C{\equiv})_2$	0.26–0.32	59–71
	0.23–0.24	74
$Me_2Si(CH{=})_2$	0.16–0.19	75
	0.15–0.16	90–93

The chemical shifts of the protons in the endocyclic CH=CH and CH_2-CH_2 groups have the usual values for the acyclic SiCH=CHSi and $SiCH_2CH_2Si$ groups (6.0–7.10 and 0.62 ppm respectively).

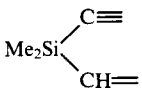
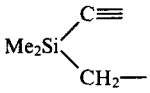
On the other hand, in the ^{13}C NMR spectra the chemical shifts of the carbon atoms of the methyl groups are determined both by the ring size and by the nature of the neighbouring bonds. With increase in the size of the macrocycle, the ^{13}C signal arising from Me_2Si undergoes a downfield shift. Thus the ^{13}C chemical shift of Me_2Si in the NMR spectra of the cyclodimethylsilethynes **1**, **2**, and **3** (n = 4–6) varies in the following sequence: −0.80 to −0.69, 0.12–0.15, and 0.62–0.87 ppm respectively.[59,60]

In the NMR spectrum of the $Me(CH_2{=}CH)Si(C{\equiv})_2$ fragment, the signal due to the methyl carbon atom undergoes an upfield shift (δ = −2.10 to −2.21 ppm).[59,60] The shift of the methyl carbon atom in the $Me(H)Si(C{\equiv})_2$ (δ = −3.89 ppm) [59,60] and $Me_2Si(CH{=})_2$ (δ = −3.37 to −3.80 ppm) fragments[63,65] is even more pronounced. The $^{13}C(sp^3)$ chemical shift is −2.43 to −2.57 ppm for the $Me_2Si(C{\equiv})(CH{=})$ fragment and −4.01 to −4.90 ppm for the $Me(HC{\equiv}C)Si(C{\equiv})(CH{=})$ fragment, depending on the ring size. The ^{13}C chemical shift of the ^{13}C atom in $-CH_2-$ in the endocyclic $Me_2Si(CH_2)(C{\equiv})$ fragment is 8.10 ppm.[63,75]

The chemical shifts of the C(sp) atoms in the endocyclic $SiC{\equiv}CSi$ fragment are in the range 105.1–117.2 ppm [$\delta(^{13}C)$ = 113.02 ppm for $Me_2SiC{\equiv}CSiMe_3$ [105]]. The ^{13}C chemical shifts for the exocyclic ethynyl groups linked to the silicon atom have the following values: 84.60–86.30 ppm (C≡) and 95.51–95.76 ppm (≡CH).

The ^{13}C signal for the endocyclic SiCH=CHSi fragment is at 146.15–150.45 ppm (for comparison, we may note that the signal for $Me_3SiCH{=}CHSiMe_3$ is at 150.0 ppm [106]). The ^{13}C chemical shifts for the exocyclic vinyl groups linked to the silicon atom are at 130.70–132.85 ppm (CH=) and 135.60–136.25 ppm ($=CH_2$).

Table 4. The chemical shifts of the silicon atoms (δ_{Si}) in the ^{29}Si NMR spectra of highly saturated macrocyclic silicohydrocarbons.

Fragment	δ_{Si}/ppm	Ref.
$Me_2Si(C\equiv)_2$	−40.1 to −42.7	59–71
	−26.1 to −27.6	74
$Me_2Si(CH=)_2$	−14.7 to −17.4	75
$Si(C\equiv)_4$	−66.9 (in spiran)	90–93
$MeSi(C\equiv)_3$	−69.0 to −70.0 (in monocycle)	
$Me(HC\equiv C)Si(CH=)_2$	−32.1	
	−14.5	
$Me(CH_2=CH)Si(C\equiv)_2$	−48.5 to −49.0	
$CH_3Si(C\equiv)_3$	−54.6 (in tricycle)	

The silicon chemical shifts in the ^{29}Si NMR spectra are independent of the size of the macrocycle and are determined exclusively by the nature of the endocyclic and exocyclic substituents (Table 4).

4. UV, Raman, and photoelectron spectra

The silicohydrocarbons containing the $SiC\equiv CSi$ fragment absorb in the near ultraviolet. A maximum at 215 nm and a shoulder at 228 nm are observed in the UV spectrum of $(Me_2SiC\equiv C)_4$ **1**, while the spectrum of $(Me_2SiC\equiv C)_5$ **2** has only a shoulder at 230 nm.[57] Quantum-chemical calculations by the semiempirical AM1 method for the molecule of compound **2** indicate a marked conjugation between the π MO of the $C(sp)-C(sp)$ bond and the π MO of the silicon atom, which leads to the splitting of the corresponding molecular orbitals to the extent of 1.73 eV. According to UV spectroscopic data, conjugation in the molecules increases from compound **24** to compound **21** and to compound **19**.[107] This is accompanied by a bathochromic shift of the bands (210, 217, and 223 nm respectively), compared with $(Me_2SiC\equiv CSiMe_2O)_2$ **88** (202, 207, and 215 nm).[101]

The linear (disilanylene)ethynylene polymers of the type $(SiR_2SiR_2C\equiv C)_n$ (R = alkyl) absorb in the range 241–244 nm with an extinction coefficient of 13 000–17 000 litre mol^{-1} cm^{-1} per unit.[49,82] An electron is transferred from the MO involving the Si–Si σ-bond. Quantum-chemical calculations (CNDO/2) show that the highest occupied and the lowest unoccupied MO are σ-type orbitals.[108] This agrees with the finding that the polymer of the type $(Et_2SiOSiEt_2C\equiv C)_n$, not containing the Si–Si group, absorbs at shorter wavelengths (at 216 nm).[82]

As a consequence of the symmetry of the triple bond in the $SiC\equiv CSi$ fragment in macrocyclic ethyne hydrocarbons, the stretching vibrations of the triple bond are inactive in the IR spectra, while the Raman spectra show an intense C≡C stretching vibration band. The ν(C≡C) band in the Raman spectra of cyclodimethylsilethynes $(Me_2SiC\equiv C)_n$ with $n = 4-6$ undergoes a slight hypsochromic shift (2132, 2134, and 2137 cm^{-1} respectively).[57] The band due to the stretching vibration of the triple bond in the Raman spectra which we obtained for crystalline cyclodimethylsilethynes ($n = 4-10$) is located in the lower-frequency range 2110–2120 cm^{-1} and decreases slightly with increase in n from 5 to 10 (Table 5). The lower ν(C≡C) frequency for $n = 4$ (2113 cm^{-1}) is apparently due to the 'rigid' molecular structure (see above). The Raman spectra of the spirocyclic compounds **82** and **83** show two lines characteristic of the triple bond vibration (2116, 2122, and 2116, 2127 cm^{-1} respectively). The doublet nature of the lines is apparently associated with the resonance of the triple bonds in the orthogonal rings. The triple bond vibration appears in the Raman spectra of the model compounds $(Me_3SiC\equiv C)_4E$ (E = Si, Ge) by a single line (2114.5 and 2118.5 cm^{-1} respectively).

Table 5. The stretching vibration frequency of the triple bond in the Raman spectra of compounds of the type $(Me_2SiC\equiv C)_n$.

Compound	n	ν(C≡C)/cm^{-1}	Compound	n	ν(C≡C)/cm^{-1}
1	4	2113	**6**	7	2115
8	4	2118	**4**	8	2112.5
2	5	2119	**7**	9	2113, 2109 sh.
3	6	2118.5	**5**	10	2113

The He(I) photoelectron spectra of compounds **59**, **68** and **71** have been obtained. The interpretation of the first bands in these spectra is based on a comparison with the orbital energies calculated by the semiempirical MINDO/3 and MNDO methods.[109,110] The Si–Si bonds have very low ionisation energies and may therefore destabilise the π orbitals of the ethyne fragments.[109] An interaction via the σ-bonds between the out-of-plane π orbitals and the Si–Si σ-bonds, leading to a marked destabilisation of the $a_g(\pi)$ orbital (8.13 eV), has been observed in compound **59**. A similar interaction via σ-bonds has also been noted for compound **68**.

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