Towards 2-Silaallenes: Synthesis of Spirocyclic Precursors**

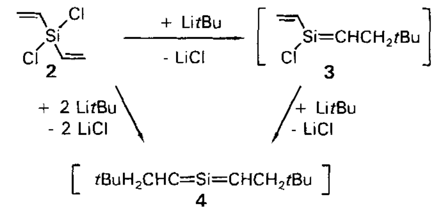
Brigitte Goetze, Bernhard Herrschaft and Norbert Auner*

Abstract: Reactions of dichlorodivinylsilane (**2**) and Li*t*Bu in a molar ratio 1/1 and 1/2 lead to highly reactive intermediates, which can be trapped by suitable reagents. In the presence of trimethylmethoxysilane, norbornadiene, anthracene and diphenylacetylene, products are formed that provide evidence for the intermediate formation of both the neopentylsilene $H_2C{=}CH(Cl)Si{=}CHCH_2tBu$ (**3**) and the 2-silaallene $tBuCH_2CH{=}Si{=}CHCH_2tBu$ (**4**). The formation of double cycloadducts from **4** is particularly interesting as a preparatively facile route for the synthesis of silaspirocycles such as **13**, **16** and **17**, which have been characterized by single-crystal X-ray structure analysis.

Keywords
cycloadditions · silaallenes · silicon · small ring systems · spiro compounds

Introduction

The reaction of chlorovinylsilanes $R^1R^2Si(Cl)CH{=}CH_2$ with Li*t*Bu leads to lithiated intermediates $R^1R^2Si(Cl)CH(Li)CH_2$-*t*Bu and, by 1,2-LiCl elimination, to highly reactive neopentylsilenes $R^1R^2Si{=}CHCH_2tBu$.[1-4] The only stable neopentylsilene to have been isolated is for $R^1 = R^2 =$ Mesityl.[5] Our experimental investigations during recent years indicate that especially dichloroneopentylsilene ($R^1 = R^2 = Cl$, **1**) shows an extraordinary activity in cycloaddition reactions, even with dienes of only low reactivity (e.g., naphthalene and furans).[6, 7] Furthermore **1** is characterized by its ability to react with butadienes and diorgano-substituted acetylenes to give monosilacyclobutanes and -butenes.[8-10] The $H_2C{=}CHSiCl_3$/Li*t*Bu system is thus an excellent reagent for the facile preparative synthesis of heterocycles containing the dichlorosilyl functional group.[4, 11] Although we have no spectroscopic proof for the existence of silene **1** and although the generation of cycloadducts might be explained by alternative reaction pathways (e.g. starting from the lithiated species $Cl_3SiCH(Li)CH_2tBu$), our experimental investigations indicate that a strongly polar Si–C double bonded species must be formed as an intermediate. Based on these experiments we now use this general principle of silene generation for the preparation of a 2-silaallene building block. Starting from a mixture of dichlorodivinylsilane (**2**) and Li*t*Bu in the molar ratio 1/2, the 2-silaallene intermediate **4** should be generated, possibly via the 1-chloro-1-vinylsilene (**3**) (Scheme 1).[12]



Scheme 1. Reactions of dichlorodivinylsilane with one or two equivalents of Li*t*Bu.

It is well known from the literature that silaspirocycles are suitable precursors for the pyrolytic generation of 2-silaallenes.[13, 14] Thus, the double cycloadducts of **4** might be possible starting materials for the retrosynthetic generation of 2-silaallenes, allowing trapping experiments and spectroscopic analyses in low-temperature matrices or in the gas phase.[15, 16] This paper reports the preparation of such precursors.

Results and Discussion

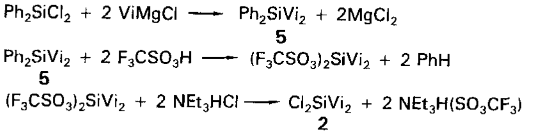
Synthesis of dichlorodivinylsilane (2): For investigations into the generation of a synthetic equivalent to 2-silaallene **4**, dichlorodivinylsilane (**2**) is required in high purity and on a preparative scale. Although there are several synthetic routes in the literature,[12, 17-21] none of these is useful for our purposes, because of their low selectivities and yields. Therefore, a new highly selective method for the generation of **2** was developed. Starting from dichlorodiphenylsilane diphenyldivinylsilane (**5**) was prepared by Grignard reaction.[22] In a one-pot procedure **5** was then treated with triflic acid to give $(CF_3SO_3)_2SiVi_2$ and refunctionalized with $HNEt_3Cl$ to yield an 82% yield of pure **2** after distillation (Scheme 2).

---

[*] Prof. Dr. N. Auner, Dipl.-Chem. B. Goetze, Dr. B. Herrschaft
Institut für Anorganische und Allgemeine Chemie
Humboldt-Universität zu Berlin, Hessische Strasse 1-2
D-10115 Berlin (Germany)
Fax: Int. code +(30)2093-6966
e-mail: norbert=auner@chemie.hu-berlin.de

[**] Silaheterocycles Part 34. For Part 33, see N. Auner, C. R. Heikenwälder, *Z. Naturforsch.*, in press.

0947-6539/97/0306-0948 $ 17.50+.50/0



$$Ph_2SiCl_2 + 2\,ViMgCl \longrightarrow \underset{\mathbf{5}}{Ph_2SiVi_2} + 2MgCl_2$$

$$\underset{\mathbf{5}}{Ph_2SiVi_2} + 2\,F_3CSO_3H \longrightarrow (F_3CSO_3)_2SiVi_2 + 2\,PhH$$

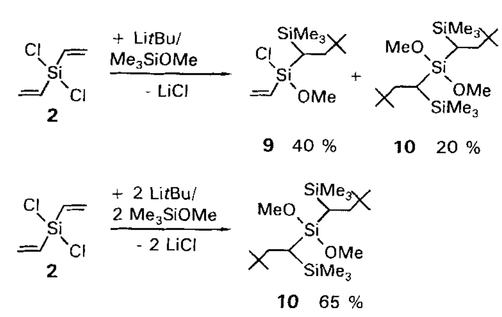
$$(F_3CSO_3)_2SiVi_2 + 2\,NEt_3HCl \longrightarrow \underset{\mathbf{2}}{Cl_2SiVi_2} + 2\,NEt_3H(SO_3CF_3)$$

Scheme 2. Synthesis of dichlorodivinylsilane from dichlorodiphenylsilane (Vi = vinyl).

Reactions of 2 with Li*t*Bu and attempts to trap the intermediates: According to the literature Li*t*Bu adds to the vinyl group of chlorovinylsilanes due to the silicon α-effect,[23, 24] giving an organolithiated species, which can be trapped by $Me_3SiOSO_2CF_3$.[6, 25–27] Intramolecular 1,2-LiCl elimination gives neopentylsilenes, which react with Me_3SiOMe, acting as a polar trapping agent.[6, 25–27] Depending on the degree of Si=C polarity and, thus, on the influence of substituents at the Si=C moiety, the intermediate silenes react with unsaturated compounds to yield cycloaddition products ([2+2] and/or [4+2] addition).[4, 11] Without trapping agents neopentylsilenes dimerize to yield 2,4-dineopentyl-1,3-disilacyclobutanes as stable products.[28]

Analogously dichlorodivinylsilane (**2**) was treated with one and two equivalents of Li*t*Bu and then with an excess of $Me_3SiOSO_2CF_3$. Although $LiCF_3SO_3$ was formed during both reactions, none of the expected products $Cl_2(H_2C{=}HC)Si[CH(Si(CH_3)_3)CH_2t\text{Bu}]$ (**6**) and $Cl_2Si[CH(Si(CH_3)_3)CH_2t\text{Bu}]_2$ (**7**) could be isolated from the reaction mixture. Instead, 1,3-dichloro-2,4-dineopentyl-1,3-divinyl-1,3-disilacyclobutane (**8**, Scheme 5), a formal head-to-tail dimerization product of silene **3**, and small amounts of higher spirocycles were formed. The preliminary lithiated intermediates that formed—$t\text{BuCH}_2\text{CH(Li)ClSi(Cl)CH{=}CH}_2$ and $[t\text{BuCH}_2\text{CH(Li)}]_2\text{SiCl}_2$—seemed to preferentially eliminate LiCl, and silene dimerization was strongly preferred over the substitution reaction with $Me_3SiOSO_2CF_3$. Not surprisingly the reaction of **2** with *one* equivalent of Li*t*Bu and Me_3SiOMe afforded the silene addition products **9** and **10** in 40 and 20% yields, respectively. From the reaction of **2** with *two* equivalents of Li*t*Bu and Me_3SiOMe only the double addition product **10** was obtained (yield: 65%) (Scheme 3).

The silicon-substituted dimethoxy compound **10** was analysed by standard methods (see Experimental Section). It crystallized at 4 °C and could be characterized by single-crystal X-ray structure analysis (Figure 1). Compound **10** was found to be thermally very stable: in the gas phase it required 980 °C to eliminate *two* equivalents of Me_3SiOMe. Thus, **10** might be a potential precursor for the gas-phase formation of silaallene **4**.[15, 16]



Scheme 3. Trapping reactions of dichlorodivinylsilane with Li*t*Bu and Me_3SiOMe.

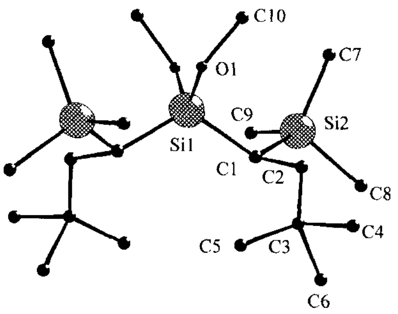
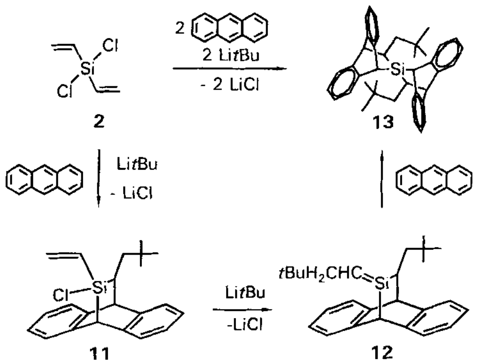


Figure 1. DIAMOND plot of the molecular structure of **10**.

Abstract in German: *Die Reaktionen von Dichlordivinylsilan (2) und tBuLi im Molverhältnis 1/1 und 1/2 führen zu hochreaktiven Verbindungen, die mit geeigneten Abfangreagentien, wie Trimethylmethoxysilan, Norbornadien und Anthracen, sowie mit Diphenylacetylen Additionsprodukte bilden. Daraus leiten sich experimentelle Hinweise auf die kurzzeitige Entstehung des Neopentylsilaethens* $H_2C{=}CH(Cl)Si{=}CHCH_2t\text{Bu}$ *(3), aber auch des 2-Silaallens* $t\text{BuCH}_2\text{CH{=}Si{=}CHCH}_2t\text{Bu}$ *(4) ab. Vor allem die einstufige Synthese doppelter Cycloaddukte aus 4 ist ein präparativ einfacher Zugang zu Silaspirocyclen, wie 13, 16 und 17, die röntgenstrukturanalytisch charakterisiert wurden.*

In earlier work we showed anthracene to be a very efficient dienophile for neopentylsilenes:[29] from the mixture of **2**/Li*t*Bu/anthracene the [4+2] cycloadduct **11** was isolated.[12] The latter obviously serves as a precursor for a sterically protected silene **12** with an exocyclic Si=C bond, because further reaction of **11** with Li*t*Bu and anthracene yielded the double cycloadduct **13**. Alternatively, **13** could be synthesized in a one-step reaction from **2** with two equivalents of Li*t*Bu and anthracene (Scheme 4).



Scheme 4. Reactions of dichlorodivinylsilane with Li*t*Bu and anthracene.

Both reactions yielded the crystalline product **13**, which was recrystallized from toluene/EtOH for X-ray structure analysis (Figure 2). Although the formation of **13** does not necessarily indicate that a silaallene intermediate is formed during the course of reaction, first pyrolysis experiments show that **13** eliminates *two* equivalents of anthracene at about 950 °C giving an identical product to that isolated in a matrix from the pyrolysis of **10**; the nature of this compound is not yet known.

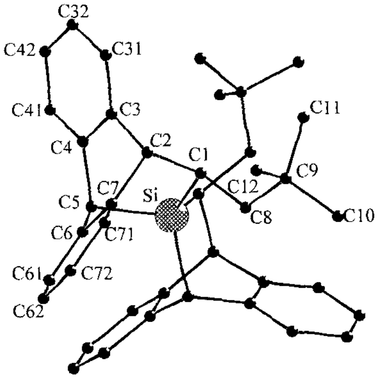
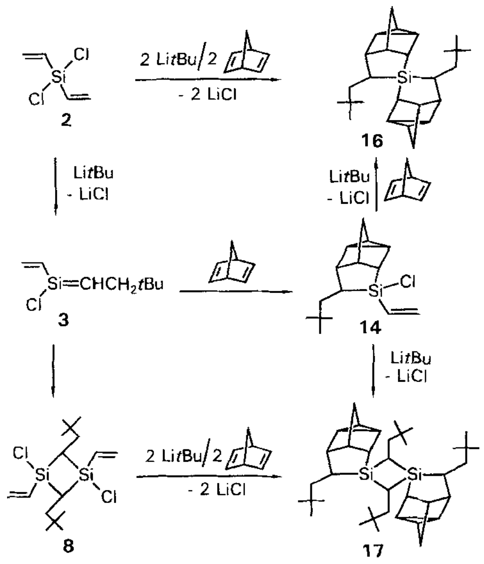


Figure 2. DIAMOND plot of the molecular structure of **13** in polymorph B.

Reaction of equimolar amounts of **2**/Li*t*Bu and norbornadiene, as a nonclassical dienophile,[26,27,30-32] clearly proved that **3** had been formed, since it was trapped in a [2+2+2] cycloaddition reaction to give **14** (Scheme 5). In a very similar reaction to that discussed for adduct **11**, **14** may serve as a precursor for the generation of a silene **15** (Scheme 6) with a sterically shielded silicon centre. Thus, **14**/Li*t*Bu was able to react slowly with a second equivalent of norbornadiene to give the double [2+2+2] adduct **16**. Alternatively **16** was isolated from the reaction mixture of **2** with two equivalents of Li*t*Bu and norbornadiene in a one-step procedure (Figure 3, Scheme 5). In strong contrast to the stepwise synthesis via **14**, the latter reaction is very fast. When the monoadduct **14** was treated with Li*t*Bu, the 1,3-disilacyclobutane **17** was obtained from a very slow reaction at room temperature. It crystallized readily and gave very hard, almost insoluble crystals, which were characterized by X-ray structure analysis (Figure 4). These findings were confirmed by the reaction of the 1,3-disilacyclobutane **8** with two equivalents of Li*t*Bu in the presence of excess norbornadiene. According to GCMS analysis of the reaction mixture only traces of a monoadduct were generated and could not be isolated. The main product **17** was obtained after distillation (Scheme 5).



Scheme 5. Reactions of dichlorodivinylsilane with Li*t*Bu and norbornadiene.

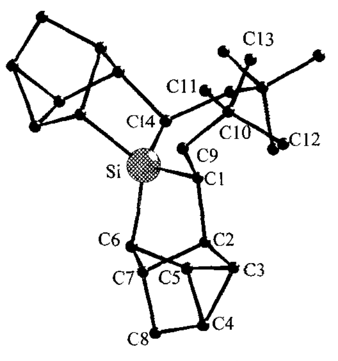


Figure 3. DIAMOND plot of the molecular structure of **16**.

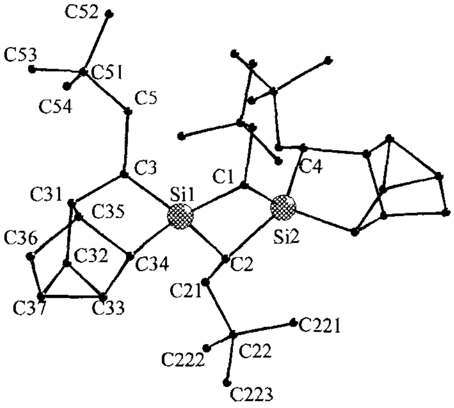
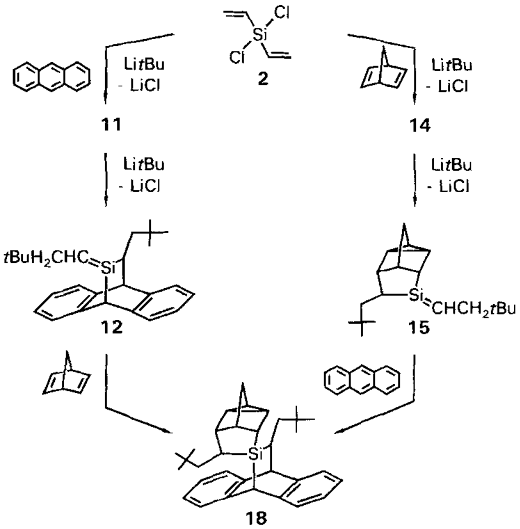


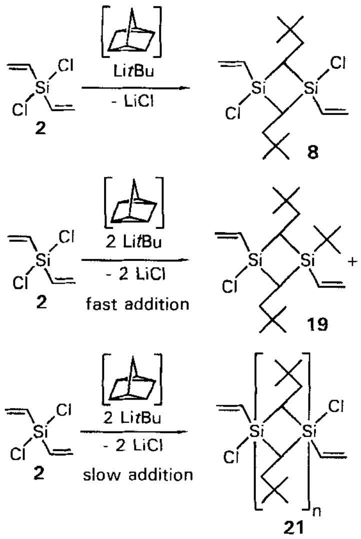
Figure 4. DIAMOND plot of the molecular structure of **17**.

The synthesis of a *mixed* double cycloadduct **18** could be achieved either by reaction of **11** with Li*t*Bu in the presence of norbornadiene or by reaction of **14** with Li*t*Bu and anthracene (Scheme 6). In the latter reaction the formation of the disilacyclobutane **17** competes with the trapping reaction. Both products were clearly identified, but not separated from each other. Thus, starting from **11** is by far the more efficient route to **18**. A dimerization product resulting from the corresponding silene precursor **11** could never be observed,[12] and **18** was isolated by distillation.



Scheme 6. Reactions of dichlorodivinylsilane with Li*t*Bu, anthracene and norbornadiene.

While dichloroneopentylsilene (**1**) is trapped by quadricyclane forming a stereoisomeric pair of silacyclobutanes, diorgano-substituted neopentylsilenes do not react with this reagent.[25–27,30,31,33] When one equivalent of Li*t*Bu was added slowly to a solution of **2** and quadricyclane in *n*-pentane, the only products to be formed were dimer **8** and oligomer **21** (Scheme 7), from 1-chloro-1-vinyl-2-neopentylsilene (**3**) or 1,3-dineopentyl-2-silaallene (**4**). These products are the same as those reported for the reaction of **2** with Li*t*Bu in the absence of a trapping agent.[28]

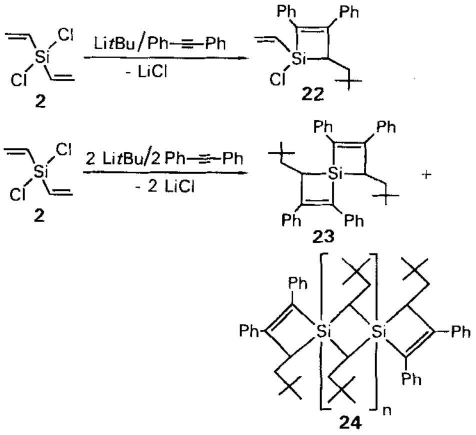


Scheme 7. Reaction of dichlorodivinylsilane with one and two equivalents of Li*t*Bu.

The product formation strongly depends on the conditions used. As can be seen from Scheme 7, the reactions in the presence of two equivalents of Li*t*Bu are much more complex: the faster Li*t*Bu was added to the solution, the higher was the yield of silicon *tert*-butyl substituted 1,3-disilacyclobutanes **19** and **20**. Evidently the substitution reaction Si–Cl to Si–*t*Bu is favoured over silene formation when the local concentration of Li*t*Bu is comparably high. In contrast, the slow reactions of the chlorovinylsilane/quadricyclane mixture with two equivalents of Li*t*Bu led to oligomers containing disilacyclobutane spirochains **21**, and some by-products that could not be identified.[34] This result was confirmed by treating **2** with two equivalents of Li*t*Bu in the absence of quadricyclane: **21** was formed in high yield.

The reaction of silene **1** with diphenylacetylene is reported to be an attractive high-yield synthesis of a dichloro-functionalized silacyclobutene. In contrast, diorgano-substituted neopentylsilenes do not react.[3,9] From the reaction of silene **3** and diphenylacetylene, the (*E*/*Z*) isomeric silacyclobutenes **22** were obtained as a viscous liquid in about 10% yield. The NMR spectroscopic data were in very good agreement with those reported for other derivatives.[3,9] However, when **2** was treated with *two* equivalents of Li*t*Bu and diphenylacetylene only traces of the spirocyclic compound **23** could be identified by NMR spectroscopic and mass spectrometric methods (yield < 5%). The main product to be isolated was the oligomer **24**, a white powder which is soluble in common nonpolar organic solvents.

The basic structural features of **24** could be determined by NMR spectroscopy, mass spectrometry and GPC methods (Scheme 8). In addition its spectroscopic and chemical properties show a strong resemblance to those of **21**.[34]



Scheme 8. Reactions of dichlorodivinylsilane with Li*t*Bu and diphenylacetylene.

Conclusions and Outlook

In this paper a facile one-pot synthesis of spirocyclic silaheterocycles is described. Starting from mixtures of dichlorodivinylsilane and Li*t*Bu (molar ratio 1/2), with or without trapping agents, either the silene **3** and/or the 2-silaallene **4** might be involved in the product-forming process. Although experimental results confirm a participation of the silaallene unit, the corresponding organolithium species must also be considered as possible product-forming equivalents. Ab initio calculations on the competitive reactions of neopentyl silenes $R^1R^2Si{=}CHCH_2$-*t*Bu and silaallene **4** and/or their lithiated analogues $R^1R^2Si(Cl)CH(Li)CH_2$*t*Bu and *t*BuCH_2CH(Li)ClSiClCH(Li)CH_2*t*Bu are currently in progress. Discounting the fact that there is currently no spectroscopic proof for the existence of silene **3** or silaallene **4**, there is no doubt that the whole series of spirocycles and addition product **10** are promising precursors for the formation of **4** in the gas phase. First investigations show that **10** and **13** eliminate two equivalents of Me_3SiOMe or anthracene, respectively, to give identical products, which can be frozen in an inert low-temperature matrix.[15] Consistent results were obtained by photoelectron spectroscopic studies *in the gas* phase.[16] The product characterization is part of our future work.

Experimental Section

X-ray structure analysis:
(4*R*,6*R*)-5,5-Dimethoxy-2,2,8,8-tetramethyl-4,6-bis(trimethylsilyl)-5-silanonane (10): Compound **10** crystallizes to give orthorhombic crystals. Crystallographic and experimental data are given in Table 1. The molecular structure of **10** (Figure 1) is characterized by a twofold symmetry in the solid state. The central silicon atom Si 1 is pseudotetrahedrally surrounded by two methoxy and two $[CH(SiMe_3)CH_2CMe_3]$ groups; the bond angles around Si 1 lie between 104.04 and 117.3(2)°. Owing to its inherent symmetry, only one independent Si 1–C (187.7(3) pm) and one Si 1–O (164.4(3) pm) distance are found. The C1–C2 bond length (138.8(7) pm) is exceptionally short.[35] The conformation of the molecule is influenced by a weak intramolecular electro-

Table 1. Experimental details of the single-crystal structure determination of **10**.

unit cell contents, mass	$C_{80}H_{192}O_8Si_{12}$, 1619.42
molecular formula, mass, Z	$C_{20}H_{48}O_2Si_3$, 404.86. 4
crystal system, Laue class	orthorhombic, *mmm*
spacegroup	*Pcan*, unconventional setting of *Pbcn* (no. 60)
unit cell dimensions [pm]	$a = 886.7(2)$, $b = 1515.9(3)$, $c = 2004.8(4)$
unit cell volume [10^6 pm^3]	2695(1)
measurement device	imaging plate diffractometer (STOE)
radiation, monochromator	$Mo_{K\alpha}$ (71.073 pm), graphite
temperature [K]	200(2)
crystal colour and size [mm]	colourless, $0.30 \times 0.48 \times 0.70$
scan range [°]	$4.88 < 2\theta < 52.70$ $h = 0/11$, $k = 0/18$, $l = 0/24$
structure solution program	direct methods, SHELXS86 for Si and O
structure refinement program	difference fourier syntheses, SHELXL93 for C
hydrogen atoms	calculated, included in F_c^2 syntheses, not refined
no. of independant reflns	2702
no. of observed reflns	2465
F_{000}	904
no. of parameters	126
refinement	full-matrix least-squares based on F^2
minimized function	$\sum w(F_o^2 - F_c^2)$
weighting function	$w^{-1} = [2(F_o^2) + (0.1703P)^2 + 0.8732P]$; $P = 1/3(F_o^2 + 2F_c^2)$
max. resid. electron density [10^{-6} pm^{-3}] R factors	0.892
conventional (observed/all)	0.0820/0.1093
$wR2$ (observed/all)	0.2479/0.2813
GoF	1.112

static interaction between O1 and one H at C2 (253 pm, O1-H-C2 121.8°). The packing of the molecules in the unit cell is also determined by weak electrostatic O···H interactions, so that the molecules form rods along the x axis.

16,16′-*meso*-15,15′-Spirobi{16-neopentyl-15-silatetracyclo[6.6.2.0^{2,7}.0^{9,14}]-hexadeca-2,4,6,9(14),10,12-hexaene} (**13**) crystallizes to give monoclinic crystals in two polymorphs, which are both found in the same sample. Crystallographic and experimental data are given in Table 2.

Polymorph A crystallizes in monoclinic form ($P2_1/n$, no. 14) with four molecules in the unit cell. The central silicon atom is situated in the spiro position of two corner sharing bicyclic systems of 1-silaethanoanthracene-type topology and is surrounded pseudotetrahedrally by four carbon atoms, the C-Si-C angles show distortion of the tetrahedral geometry: 99.6–117.8(2)° (mean: 109.6°).

Polymorph B (Figure 2) crystallizes in monoclinic form ($P2_1/c$, no. 14). The molecular geometry does not differ significantly from that of polymorph A, except in the arrangement of the neopentyl groups, as reflected by the torsion angles C9-C8-C1-Si/C9-C8-C1-C2 (A: 143.35/92.56°; B: 165.61/71.28°) and C9A-C8A-C1A-Si/ C9A-C8A-C1A-C2A (A refers to the second neopentyl group; same numbering) (A: 134.59/102.94°; B: 114.26/124.52°). To confirm these findings X-ray diffraction experiments were perfomed to prove that the bulk material is a single phase. Indexing a powder diffractogram with the lattice constants of polymorph A failed. The lattice constants of polymorph B were successfully used in the indexing procedure, but two reflections were left unindexed. These reflections could not be indexed by assuming anthracene, bisanthracene or anthraquinone to be a by-product. Thus, some by-product of unknown constitution is still present in the bulk material.

***exo*-(9*R*,9′*R*,9*S*,9′*S*)- and 9,9′-*meso*-8,8′-Spirobi{9-neopentyl-8-silatetracyclo[4.3.0.0^{2,4}.0^{3,7}]nonane}** (**16**): Compound **16** crystallizes in triclinic form. The central Si atom is placed in the spiro position of two corner-sharing sila-δ-cyclane units (Figure 3). Crystallographic and experimental data are given in Table 3. The carbon atoms C1 and C14 are chiral centres ((*S*)-C1, (*R*)-C14; numbering scheme see Figure 3). The tetrahedral silicon centre is strongly distorted, with the C-Si-C bond angles lying between 91.6(5) and 120.8(6)°. After the first cycles of the structural refinement the calculations converged at a conventional $R = 0.20$ relating to a strong peak as near as

Table 2. Experimental details of the single-crystal structure determination of **13**.

	polymorph A	polymorph B
unit cell contents, mass	$C_{160}H_{176}Si_4$, 2111.36	$C_{160}H_{176}Si_4$, 2111.36
molecular formula, mass, Z	$C_{40}H_{44}Si$, 552.84, 4	$C_{40}H_{44}Si$, 552.84, 4
crystal system, Laue class	monoclinic, 2/m	monoclinic, 2/m
spacegroup	$P2_1/n$ (no. 14)	$P2_1/c$ (no. 14)
unit cell dimensions [pm, °]	$a = 1039.3(8)$ $b = 1773(1)$ $c = 1771.6(9)$ $\beta = 90.26(5)$	949.1(2) 1788.4(2) 1890.2(3) 99.49(2)
unit cell volume [10^6 pm^3]	3264(4)	3164.5(9)
measurement device	four-circle AED with Eulerian cradle: STADI4 (Stoe)	four-circle AED with Eulerian cradle: STADI4 (Stoe)
radiation, monochromator	$Mo_{K\alpha}$ (71.073 pm), graphite	$Mo_{K\alpha}$ (71.073 pm), graphite
temperature [K]	293(2)	293(2)
crystal colour and size [mm]	colourless $0.9 \times 0.7 \times 0.7$	colourless $1.2 \times 1.2 \times 1.0$
scan type	$\omega/2\theta$	$\omega/2\theta$
scan range [°]	$3.24 < 2\theta < 45.00$ $h = -11/11$ $k = 0/19$ $l = 0/19$	$3.16 < 2\theta < 50.00$ $h = -11/11$ $k = 0/21$ $l = -20/22$
hydrogen atoms	calculated, included in F_c^2 syntheses, not refined	difference fourier syntheses, isotropically refined; H atoms on C14 calculated
no. of independent reflns	4256	6763
no. of observed reflns	4256	5563
R_{int}		0.0637
F_{000}	1192	1192
no. of parameters	341	535
refinement	full-matrix least-squares based on F^2	full-matrix least-squares based on F^2
minimized function	$\sum w(F_o^2 - F_c^2)$	$\sum w(F_o^2 - F_c^2)$
weighting function	$w^{-1} = [2(F_o^2) + (0.0720P)^2 + 4.3891P]$; $P = 1/3(F_o^2 + 2F_c^2)$	$w^{-1} = [2(F_o^2) + (0.1703P)^2 + 0.8732P]$; $P = 1/3(F_o^2 + 2F_c^2)$
extinction coefficient	0.0021(6)	0.0019(7)
max. resid. electron density [10^{-6} pm^{-3}]	0.479	0.281
R factors		
conventional (observed/all)	0.0660/0.1490	0.0469/0.0787
$wR2$ (observed/all)	0.1300/0.1862	0.1176/0.1389
GoF	1.021	0.988

0947-6539/97/0306-0952 $ 17.50+.50/0

Table 3. Experimental details of the single-crystal structure determination of **16**.

unit cell contents, mass	$C_{52}H_{40}Si_2$, 721.02
molecular formula, mass, Z	$C_{26}H_{20}Si$, 360.51, 2
crystal system, Laue class	triclinic
spacegroup	$P\bar{1}$ (no. 2)
unit cell dimensions [pm, °]	$a = 976.9(2)$, $b = 1094.0(2)$, $c = 1241.3(2)$ $\alpha = 66.95(3)$, $\beta = 87.05(3)$, $\gamma = 70.64(3)$
unit cell volume [10^6 pm^3]	1147.0(4)
measurement device	imaging plate diffractometer (STOE)
radiation, monochromator	$Mo_{K\alpha}$ (71.073 pm), graphite
temperature [K]	180(2)
crystal colour and size [mm]	colourless, 0.50 × 0.70 × 1.10
scan range [°]	$6.74 < 2\theta < 56.56$ $h = -12/12$, $k = -13/14$, $l = 0/16$
structure solution program	direct methods, SHELXS 86 for Si
structure refinement program	difference fourier syntheses, SHELXL 93 for C
hydrogen atoms	calculated, included in F_c^2 syntheses, not refined
no. of independant reflns	5193
no. of observed reflns	5193
F_{000}	380
no. of parameters	492
refinement	full-matrix least-squares based on F^2
minimized function	$\sum w(F_o^2 - F_c^2)$
weighting function	$w^{-1} = [2(F_o^2) + (0.3022P)^2 + 1.0002P]$; $P = 1/3(F_o^2 + 2F_c^2)$
max. resid. electron density	0.557
[10^{-6} pm^{-3}] R factors	
conventional (observed/all)	0.0928/0.1122
$wR2$ (observed/all)	0.2651/0.3022
GoF	0.688

Table 4. Experimental details of the single-crystal structure determination of **17**.

unit cell contents, mass	$C_{152}H_{256}Si_8$, 2308.28
molecular formula, mass, Z	$C_{38}H_{64}Si_2$, 577.07, 4
crystal system, Laue class	monoclinic, $2/m$
space group	$P2_1/n$ (no. 14)
unit cell dimensions [pm]	$a = 1192.5(2)$, $b = 1732.0(3)$, $c = 1746.9(2)$ $\beta = 99.70(2)$
unit cell volume [10^6 pm^3]	3556.5(9)
measurement device	four-circle AED with Eulerian cradle (STOE)
radiation, monochromator	$Mo_{K\alpha}$ (71.073 pm), graphite
temperature [K]	190(2)
crystal colour and size [mm]	colourless, 0.80 × 0.76 × 0.56
scan range [°]	$3.34 < 2\theta < 59.98$ $h = -16/16$, $k = 0/24$, $l = 0/24$
structure solution program	direct methods, SHELXS 86 for Si
structure refinement program	difference fourier syntheses, SHELXL 93 for C
hydrogen atoms	difference fourier syntheses, SHELXL 93
no. of independant reflns	10380
no. of observed reflns	10379
F_{000}	1280
no. of parameters	617
refinement	full-matrix least-squares based on F^2
minimized function	$\sum w(F_o^2 - F_c^2)$
weighting function	$w^{-1} = [2(F_o^2) + (0.0623P)^2 + 1.261P]$; $P = 1/3(F_o^2 + 2F_c^2)$
max. resid. electron density	0.440
[10^{-6} pm^{-3}] R factors	
conventional (observed/all)	0.0587/0.1311
$wR2$ (observed/all)	0.1217/0.1547
GoF	1.007

150 pm to the Si atom as a Si split atom position. Assuming split positions for all carbons improved the refinement and led to an occupation factor of 0.7 for the initially found molecule. The second molecule emerged in parts from the Fourier map, but was not completed in the course of subsequent difference Fourier calculations. The number of free parameters increased drastically, but the structure model did not further improve. This is partly due to the fact that many of the carbon split positions were not well resolved. Although the calculations converged at ca. $R = 0.08$, only the configuration of the molecule is confirmed. A more detailed discussion in terms of geometrical parameters is not justified. A total of five specimens were investigated in order to find a more suitable crystal, but all showed the same type of "disorder". Spectroscopic evidence suggests that all specimens under investigation are possibly mixed crystals of molecules with configurations (R/S) and (R/R).

***exo*-(9*R*,9″*R*)-Dispiro-[2′,4′-dineopentyl-1′,3′-disilacyclobutane-1′,8;3′,8″-bis-{9-neopentyl-8-silatetracyclo[4.3.0.0^{2,4}.0^{3,7}]nonane}]** (**17**): The 1,3-disilacyclobutane **17** crystallizes in monoclinic form; crystallographic and experimental data are given in Table 4. The silicon atoms of the 1,3-disilacyclobutane ring moiety are placed at the apex of a sila-δ-cyclane unit each. The neopentyl substituents attached to the 2,4-positions at the slightly folded ring (at C1 and C2) adopt a (Z) configuration with respect to its least-squares plane. The C-Si-C bond angles deviate significantly from tetrahedral symmetry (88.48(9)–124.3(1)°). The short transannular Si···Si distance within the disilacyclobutane subunit of 264.68(9) pm is even shorter than the Si–Si bond length in sterically overcrowded disilanes.[36–38] Ab initio calculations on 1,3-disilacyclobutanes show no residual electron density inside the ring, that is, no attractive interaction between the silicon atoms.[39]

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100142. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB21EZ, UK (Fax: Int. code +(1223)336-033; e-mail: deposit@chemcrys.cam.ac.uk).

General: All reactions were performed under an atmosphere of dry nitrogen. THF was distilled from Na/K alloy and benzophenone. MeOH and EtOH were distilled from magnesium turnings. *n*-Pentane and *n*-hexane were distilled from $LiAlH_4$. Toluene was distilled from sodium, and $CHCl_3$ and CH_2Cl_2 from calcium hydride. The dried solvents were stored over molecular sieves. All glassware was heated to 100 °C, evacuated and filled with dry nitrogen several times. Elemental analyses were performed on a Leco CHNS-932. GC analyses were performed on Varian Chromstar 3400 (15 m × 0.32 mm, 1 µ film, Fisons J & W scientific DB 1 column), and GCMS analyses on Chrompack CP 9000 (12.5 m × 0.25 mm, CP-SIL/5CB-MS column) and a Finnigan Mat ITD 800 as mass-selective detector. For HPLC and GPC a Varian system was used with a Varian pump 9012, a Varian autosampler 9050 and a Varian 9050 UV/VIS detector or a Varian RI-4 refractive index detector. NMR spectra were recorded with Bruker AM 300 and DPX 300 spectrometers at 20 °C. Chemical shifts were determined with the solvent resonance as standard. ^{29}Si NMR spectra were measured using either the INEPT pulse sequence or the inversed gated decoupling technique (TMS as external standard). The X-ray structures were measured on a STADI4 four-circle diffractometer with Eulerian cradle and an imaging plate diffractometer IPDS25 (STOE & CIE GmbH, Darmstadt, Germany). Crystal structure analyses were performed with SHELXS 86[40] and SHELXL 93[41]. Molecular diagrams were produced with the plot program DIAMOND.[42]

Diphenyldivinylsilane (5): In a 4 L flask with gas inlet, dry-ice condenser and a mechanical stirrer, magnesium turnings (48.62 g, 2.0 mol) were suspended in THF (1.5 L). After the addition of 1,2-dibromoethane (3 mL), vinyl chloride was passed slowly into the mixture over 3 h. The mixture was stirred for another 4 h until the magnesium had reacted completely. Then dichlorodiphenylsilane (228.16 g, 0.9 mol) was added dropwise within 0.5 h. A voluminous precipitate of $MgCl_2$ formed. The remaining Grignard reagent was hydrolysed with water. HCl (0.5 M) was added to dissolve all magnesium salts. The THF layer was washed with HCl (0.5 M) and water, and then dried over $MgSO_4$. After THF was removed, the viscous product was purified by distillation. GC analysis showed one product (**5**). Yield: 124.8 g (59%). B.p. 97–99 °C/10^{-2} mbar, ^1H NMR ($CDCl_3$): $\delta = 6.46$ (dd, $^2J_{gem} = 3.8$ Hz, $^3J_{trans} = 20.2$ Hz, 2H; CH=CH*H*), 6.82 (dd, $^2J_{gem} = 3.8$ Hz, $^3J_{cis} = 14.5$ Hz, 2H; CH=C*H*H), 7.13 (dd, $^3J_{cis} = 14.5$ Hz, $^3J_{trans} = 20.2$ Hz, 2H; C*H*=CH_2), 7.87–7.90 (m, 6H; *m,p*-H), 8.19–8.22 (m, 4H; *o*-H); ^{13}C NMR ($CDCl_3$): $\delta = 129.97$, 131.59, 135.99, 137.41 (CH, C_6H_5; *C*H=CH_2), 135.99 (C_q), 138.50 (CH=*C*H_2); ^{29}Si NMR ($CDCl_3$): $\delta = -20.53$; MS (70 eV, EI): *m/z* (%): 236 (12) [M^+], 208 (20) [$M^+ - Vi$], 182 (12) [$M^+ - 2Vi$], 158 (50) [$M^+ - Ph$], 131 (52) [$M^+ - Vi - Ph$], 105 (100) [$M^+ - 2Vi - Ph$], 77 (24) [Ph^+], 53 (50), [$M^+ - Vi - 2Ph$], 27 (23) [Vi^+]; $C_{16}H_{16}Si$ (236.39): calcd C 81.30, H 6.82; found C 81.18, H 6.99.

Dichlorodivinylsilane (2): Compound **5** (40.0 g, 169.2 mmol) was dissolved in 150 mL of *n*-pentane at 0 °C. Under strict exclusion of moisture, trifluoromethane sulfonic acid (30.0 mL, 340.0 mmol) was added within 10 min to the solution. For completion the reaction mixture was stirred at RT for an additional 60 min. $(CF_3SO_3)_2SiVi_2$ was not usually isolated, but refunctionalized in a one-pot reaction by adding freshly dried triethylamine hydrochloride (46.8 g, 340.0 mmol). After the mixture had been stirred for 15 min, the white ammonium salt disappeared, and two separate phases (a heavier brown oil and a clear solution) were obtained. The solution was separated from the oil with a cannula, and the oil was extracted twice with *n*-pentane. The combined organic solutions were distilled very slowly over a vigreux column. After *n*-pentane and benzene had been removed, **2** was obtained as a colourless liquid product. Yield: 21.2 g (82%). B.p. 114 °C; ^{1}H NMR ($CDCl_3$): $\delta = 6.1-6.3$ (m, 6*H*; $CH=CH_2$); ^{13}C NMR ($CDCl_3$): $\delta = 131.7$ ($CH=CH_2$), 138.1 ($CH=CH_2$); ^{29}Si NMR ($CDCl_3$): $\delta = 1.5$. $(CF_3SO_3)_2SiVi_2$ was characterized by NMR: ^{1}H NMR (C_6D_6): $\delta = 5.9-6.3$ (m, 6H; $CH=CH_2$); ^{13}C NMR (C_6D_6): $\delta = 118.4$ (q, $J(^{13}C,^{19}F) = 4.2$ Hz; CF_3), 128.0 ($CH=CH_2$), 145.2 ($CH=CH_2$); ^{29}Si NMR (C_6D_6): $\delta = -27.0$.

Attempted preparation of 3,3-dichloro-6,6-dimethyl-4-trimethylsilyl-3-sila-1-heptene (6): Silane **2** (1.5 g, 10.0 mmol) was dissolved in 80 mL of *n*-pentane at −78 °C, and *tert*-butyllithium (5.9 mL, 10.0 mmol, 1.7 M in *n*-pentane) was added. The solution was allowed to warm up to 5 °C until LiCl started to precipitate. Then $CF_3SO_3SiMe_3$ (2.22 g, 10.0 mmol) in 3 mL of *n*-pentane was added, and the solution was warmed up to RT. After 1 d of stirring some white LiCl and $LiCF_3SO_3$ gel were separated from the solution by filtration, and *n*-pentane was removed by distillation. Although $LiCF_3SO_3$ was formed, no substitution product could be isolated. A colourless oil resulted. GCMS analysis only showed that 1,3-dichloro-2,4-dineopentyl-1,3-divinyl-1,3-disilacyclobutane (**8**) and trimer and tetramer products had been formed.

Attempted preparation of 5,5-dichloro-2,2,8,8-tetramethyl-4,6-bis(trimethylsilyl)-5-silanonane (7): The reaction was performed as described for **6** (**2** (1.5 g, 10.0 mmol) and *t*BuLi (11.8 mL, 20.0 mmol, 1.7 M in *n*-pentane) and $CF_3SO_3SiMe_3$ (4.44 g, 20.0 mmol) in 3 mL of *n*-pentane). There were no changes in workup. Disilacyclobutane **8** and trimer and tetramer products could be detected by GCMS analysis.

(3*R*,4*R*)-, (3*S*,4*S*)-, (3*R*,4*S*)- and (3*S*,4*R*)-3-Chloro-3-methoxy-6,6-dimethyl-4-trimethylsilyl-3-sila-1-heptene (9): Silane **2** (1.5 g, 10.0 mmol) and Me_3SiOMe (1.04 g, 10.0 mmol) were dissolved in 70 mL of *n*-pentane and cooled to 0 °C. *tert*-Butyllithium (5.9 mL, 10.0 mmol, 1.7 M in *n*-pentane) was added dropwise to the solution over 10 min. A white precipitate formed. The mixture was stirred for an additional hour and then allowed to warm up to RT. After 24 h of stirring LiCl was separated from the solution by filtration and *n*-pentane was removed by distillation. GC analysis of the colourless residue showed that three compounds had formed. They were separated by distillation.

Fraction 1: Yield: 1.1 g (39%). B.p. 38 °C/10^{-2} mbar (GC: one peak (**9**)); ^{1}H NMR ($CDCl_3$): $\delta = 0.09$ (s, 9H; $Si(CH_3)_3$), 0.84, 0.85 (2s, 9H; $C(CH_3)_3$), 1.35–1.71 (m, 3H; $CHSi(CH_3)_3CH_2$), 3.46 (s, 3H; OCH_3), 5.99–6.15 (m, 3H; $CH=CH_2$); 1st diastereomer (70%): ^{13}C NMR ($CDCl_3$): $\delta = 0.01$ ($SiC(CH_3)_3$), 10.15 (CH), 29.57 ($C(CH_3)_3$), 31.56 ($C(CH_3)_3$), 36.28 (CH_2), 50.65 (OCH_3), 133.77 ($CH=CH_2$), 135.96 ($CH=CH_2$); 2nd diastereomer (30%): ^{13}C NMR ($CDCl_3$): $\delta = 0.57$ ($SiC(CH_3)_3$), 10.97 (CH), 29.52 ($C(CH_3)_3$), 31.64 ($C(CH_3)_3$), 36.34 (CH_2), 50.65 (OCH_3), 133.38 ($CH=CH_2$), 136.13 ($CH=CH_2$); ^{29}Si NMR ($CDCl_3$): $\delta = 4.32$, 4.66; MS (70 eV, EI): *m*/*z* (%): 263 (19) [$M^+ - Me$], 247 (3) [$M^+ - OMe$], 243 (2) [$M^+ - Cl$], 221 (11) [$M^+ - t$Bu], 155 (9) [$M^+ - OMe - Cl - t$Bu], 113 (100) [$M^+ - OMe - Cl - t$Bu − Vi − Me], 73 (39) [$SiMe_3^+$]; $C_{12}H_{27}Si_2Cl$ (279.0): calcd C 51.67, H 9.75, Cl 12.71; found C 51.98, H 9.87, Cl 12.63.
Fraction 2: Yield: 0.8 g (20%). B.p. 74 °C/10^{-2} mbar. GC: two peaks (**10**).

(4*R*,6*R*)-, (4*S*,6*S*)-, and 4,6-*meso*-5,5-Dimethoxy-2,2,8,8-tetramethyl-4,6-bis(trimethylsilyl)-5-silanonane (10): The synthesis was performed as described for **9** (**2** (1.5 g, 10.0 mmol) and Me_3SiOMe (2.08 g, 20.0 mmol) in 10 mL of *n*-pentane; *tert*-butyllithium (11.8 mL, 20.0 mmol, 1.7 M in *n*-pentane)). GC: two peaks (**11**). The oil was purified by distillation. Yield: 1.7 g (42%). B.p. 74 °C/10^{-2} mbar; 1st diastereomer (53%): ^{1}H NMR ($CDCl_3$): $\delta = 0.61$ (s, 9H; $Si(CH_3)_3$), 0.87 (s, 9H; $C(CH_3)_3$), 1.27–1.73 (m, 3H; $CHSi(CH_3)_3CH_2$), 3.52 (s, 3H; OCH_3); ^{13}C NMR ($CDCl_3$): $\delta = 0.61$ ($Si(CH_3)_3$), 8.81 (CH), 29.91 ($C(CH_3)_3$), 32.10 ($C(CH_3)_3$), 37.10 (CH_2), 50.87 (OCH_3); ^{29}Si NMR ($CDCl_3$): $\delta = -5.63$ ($Si(CH_3)_3$), 3.65 (Si); 2nd diastereomer (47%): ^{1}H NMR ($CDCl_3$): $\delta = 0.07$ (s, 9H; $Si(CH_3)_3$), 0.87 (s, 9H; $C(CH_3)_3$), 1.27–1.73 (m, 3H; $CHSi(CH_3)_3CH_2$), 3.50 (s, 3H; OCH_3); ^{13}C NMR ($CDCl_3$): $\delta = 0.61$ ($Si(CH_3)_3$), 9.47 (CH), 29.91 ($C(CH_3)_3$), 31.87 ($C(CH_3)_3$), 37.05 (CH_2), 50.66 (OCH_3); ^{29}Si NMR ($CDCl_3$): $\delta = -5.63$ ($Si(CH_3)_3$), 3.56 (Si); MS (70 eV, EI): *m*/*z* (%): 389 (4) [$M^+ - Me$], 247 (45) [$M^+ - CHSiMe_3CH_2CMe_3$], 157 (20) [$CHSiMe_3CH_2CMe_3^+$], 73 (100) [$SiMe_3^+$]; $C_{20}H_{48}O_2Si_3$ (404.9): calcd C 59.33, H 11.95; found C 59.68, H 12.09.

(15*R*,16*R*)-, (15*S*,16*S*)-, (15*R*,16*S*)-, and (15*S*,16*R*)-15-Chloro-16-neopentyl-15-sila-15-vinyltetracyclo[6.6.2.0^{2,7}.0^{9,14}]hexadeca-2,4,6,9(14),10,12-hexaene (11): Silane **2** (1.5 g, 10.0 mmol) and anthracene (2.4 g, 1.35 mmol) were dissolved in 100 mL of boiling toluene, and *tert*-butyllithium (5.9 mL, 10.0mmol, 1.7 M in *n*-pentane) was added dropwise to the solution within 15 min. The yellow solution quickly changed to orange and some white precipitate formed. After 1 h the mixture was cooled to RT and stirred for another 10 h. The toluene was removed by distillation, and the oily yellow-white residue was dissolved in *n*-pentane. LiCl was separated from the yellow solution by filtration. *n*-Pentane was removed by distillation and anthracene by sublimation. The residue was purified by distillation. GC analysis of the colourless oil showed two peaks. Yield: 1.3 g (14%). B.p. 125 °C/10^{-2} mbar; ^{1}H NMR ($CDCl_3$): $\delta = 1.18$ (s, 9H; $C(CH_3)_3$), 0.99–1.61 (m, 3H; $SiCHCH_2$), 4.34–4.50 (m, 2H; CH), 5.78–6.38 (m, 3H; $CH=CH_2$), 7.38–7.57 (m, 8H; 2 C_6H_4); 1st diastereomer: (11*R*,12*R*; 11*S*,12*S*) (70%): ^{13}C NMR ($CDCl_3$): $\delta = 24.29$ (CH), 29.97 ($C(CH_3)_3$), 31.59 ($C(CH_3)_3$), 42.09 (CH), 43.77 (CH_2), 54.03 (CH), 124.84–128.50 (CH; C_6H_4), 132.21 ($CH=CH_2$), 137.31 ($CH=CH_2$), 139.18, 142.39 (C; C_6H_4); ^{29}Si NMR ($CDCl_3$): $\delta = 8.85$; 2nd diastereomer: (11*R*,12*S*; 11*S*,12*R*) (30%): ^{13}C NMR ($CDCl_3$): $\delta = 27.45$ (CH), 29.91 ($C(CH_3)_3$), 31.94 ($C(CH_3)_3$), 42.17 (CH), 44.27 (CH_2), 54.03 (CH), 124.84–128.50 (CH; C_6H_4), 131.06 ($CH=CH_2$), 138.42 ($CH=CH_2$), 140.82, 141.76 (C; C_6H_4); ^{29}Si NMR ($CDCl_3$): $\delta = 8.15$; MS (70 eV, EI): *m*/*z* (%): 352 (2) [M^+], 295 (2) [$M^+ - t$Bu], 178 (100) [$C_{14}H_{10}$], 174 (1) [$M^+ - C_{14}H_{10}$], 139 (5) [$M^+ - Cl - C_{14}H_{10}$], 117 (36) [$M^+ - t$Bu $- C_{14}H_{10}$], 90 (17) [$M^+ - t$Bu $- C_{14}H_{10}$ − Vi], 57 (32) [tBu$^+$]; $C_{20}H_{25}SiCl$ (353.0): calcd C 74.86, H 7.14, Cl 10.04; found C 74.54, H 7.34, Cl 9.69.

(16*R*,16′*R*)-, (16*S*,16′*S*)- and 16,16′-*meso*-15,15′-Spirobi{16-neopentyl-15-silatetracyclo[6.6.2.0^{2,7}.0^{9,14}]hexadeca-2,4,6,9(14),10,12-hexaene} (13):

Method A: Silane **2** (1.5 g, 10.0 mmol) and anthracene (4.5 g, 25.2 mmol) were dissolved in 100 mL of boiling toluene, and *tert*-butyllithium (11.8 mL, 20.0 mmol, 1.7 M in *n*-pentane) was added dropwise to the solution over 30 min. The yellow solution changed to red and finally to almost black. After 1 h the mixture was cooled to RT and stirred for another 10 h, during which time it gradually turned colourless. Toluene was removed by distillation, and the orange residue was dissolved in CH_2Cl_2. LiCl was separated from the orange solution by filtration. CH_2Cl_2 was removed by distillation. The solid product was purified by LC (silica gel (0.063–0.200 mm, 70–230 mesh ASTM), CH_2Cl_2/*n*-pentane: 1/9, detection: TLC, CH_2Cl_2/*n*-pentane: 1/9, UV, R_f(**13**) = 0.22, R_f(anthracene) = 0.44). The yellow product was dissolved in EtOH/toluene, and colourless rhombic crystals were obtained from the solution. HPLC: two peaks (**13**). Yield: 0.6 g (10%).

Method B: Compound **11** (0.6 g, 1.70 mmol) and anthracene (0.9 g, 5.0 mmol) were dissolved in 50 mL of boiling toluene, and *tert*-butyllithium (1.08 mL, 1.7 mmol, 1.7 M in *n*-pentane) was added to the solution. The yellow solution changed to orange and finally to dark brown. After 1 h the mixture was cooled to RT and stirred for another 10 h. Toluene was removed by distillation and the orange residue was dissolved in CH_2Cl_2. LiCl was separated from the orange solution by filtration. CH_2Cl_2 was removed by distillation. The solid product was purified as described above. The yellow product was dissolved in EtOH/toluene and colourless rhombic crystals were obtained from the solution. HPLC: two peaks (**13**). Yield: 0.2 g (21%).

13: M.p. 254–256 °C; ^{1}H NMR ($CDCl_3$): $\delta = 0.44-1.22$ (m, 6H; $SiCHCH_2$), 0.65 (s, 18H; $C(CH_3)_3$), 2.90, 3.25 (2s, 1H; CH), 4.18, 4.36 (2d, 1H; CH), 6.92–7.33 (m, 16H; C_6H_4); ^{13}C NMR ($CDCl_3$): $\delta = 21.04$, 24.37 (CH), 29.19, 29.90 ($C(CH_3)_3$), 32.18, 32.56 ($C(CH_3)_3$), 37.21, 39.40 (CH), 40.58, 42.71 (CH_2), 51.29, 52.48 (SiCH), 124.24–127.23 (CH, C_6H_4), 138.89, 139.13, 140.05, 140.10, 140.29, 141.50, 142.35, 142.56 (C, C_6H_4); ^{29}Si NMR ($CDCl_3$): $\delta = -8.67$; MS (70 eV, EI): *m*/*z* (%): 552 (7) [M^+], 374 (7) [$M^+ - C_{14}H_{10}$], 317 (32) [$M^+ - C_{14}H_{10} - t$Bu], 196 (6) [$M^+ - 2C_{14}H_{10}$], 178 (83) [$C_{14}H_{10}^+$], 139 (100) [$M^+ - 2C_{14}H_{10} - t$Bu], 71 (23) [Np$^+$], 57 (32) [tBu$^+$]; $C_{40}H_{44}Si$ (552.9): calcd C 86.90, H 8.02; found C 86.50, H 8.36.

***exo*-(8*R*,9*R*)- and (8*S*,9*S*)- or (8*S*,9*R*)- and (8*R*,9*S*)-8-Chloro-9-neopentyl-8-sila-8-vinyltetracyclo$[4.3.0.0^{2,4}.0^{3,7}]$nonane (14)**: Silane **2** (1.5 g, 10.0 mmol) and norbornadiene (5.0 mL, 50.0 mmol) were dissolved in 70 mL of *n*-pentane at RT, and *tert*-butyllithium (5.9 mL, 10.0 mmol, 1.7 M in *n*-pentane) was added dropwise to the solution within 15 min. After 10 h of stirring LiCl was filtered off, and *n*-pentane and norbornadiene were removed. The residue was purified by distillation to give a colourless liquid product. GC analysis: one peak (**14**). Yield: 1.5 g (56 %). B.p. 60–62 °C/10^{-2} mbar; ^{1}H NMR ($CDCl_3$): δ = 0.87–1.19 (m, 3H, cyclo C_3H_3), 0.92 (m, 9H; $C(CH_3)_3$), 1.16 (m, 2H; $CH_2C(CH_3)_3$), 1.20 (m, 1H, CH), 1.21 (m, 1H, SiCHC*H*CH$_2$), 1.39–1.45 (m, 2H, CH_2), 1.69 (m, 1H, SiC*H*CHCH$_2$), 2.14 (m, 1H, CH), 5.97–6.32 (m, 3H; $CH{=}CH_2$); ^{13}C NMR ($CDCl_3$): δ = 10.20, 13.79, 16.52 (cyclo C_3H_3), 24.79 (CH), 29.64, 29.79 (C(*C*H$_3$)$_3$), 31.23 (*C*(CH$_3$)$_3$), 31.66 (SiCH*C*HCH$_2$), 33.18 (CH_2), 38.74 (CH), 44.20 (*C*H$_2$C(CH$_3$)$_3$), 51.68 (Si*C*HCHCH$_2$), 133.49 (*C*H=CH$_2$), 135.89 (CH=*C*H$_2$) (correlation of signals by ^{1}H^{1}H COSY and ^{13}C^{1}H HSQC NMR and ^{13}C DEPT methods); ^{29}Si NMR ($CDCl_3$): δ = 29.98. According to the X-ray single-crystal structure determination of **16** and **17** it is obvious that the neopentyl group is in an *exo* position relative to the ring system; from NMR spectra the position of the vinyl group (*exo* or *endo* to the five-membered ring) cannot be determined. MS (70 eV, EI): *m*/*z* (%): 266 (3) [M^+], 231 (28) [M^+ – Cl], 209 (24) [M^+ – *t*Bu], 181 (23) [M^+ – *t*Bu – Vi – 1], 173 (9) [$M^+ - C_7H_8 - 1$], 117 (36) [M^+ – *t*Bu – C_7H_8], 91 (64) [$C_7H_8^+ - 1$], 57 (100) [*t*Bu$^+$]; $C_{15}H_{23}SiCl$ (266.8): calcd C 67.51, H 8.69, Cl 13.28; found C 67.17, H 8.45, Cl 12.94.

***exo*-(9*R*,9′*R*)-,(9*S*,9′*S*)- and 9,9′*meso*-8,8′-Spirobi{9-neopentyl-8-silatetracyclo$[4.3.0.0^{2,4}.0^{3,7}]$nonane} (16)**:

Method A: Silane **2** (1.5 g, 10.0 mmol) and norbornadiene (10.1 mL, 100.0 mmol) were dissolved in 100 mL of *n*-pentane at RT, and *tert*-butyllithium (11.8 mL, 20.0 mmol, 1.7 M in *n*-pentane) was added dropwise over 15 min. The solution warmed slightly, and after about 10 min a white precipitate formed. After 10 h of stirring the precipitate was separated from the solution by filtration, and *n*-pentane and excess norbornadiene were removed by distillation. The oily residue was purified by distillation. GC: one peak (**16**). From an EtOH/toluene mixture colourless rhombic crystals were obtained. Yield: 0.9 g (24 %).

Method B: Compound **14** (1.0 g, 3.75 mmol) and norbornadiene (1.5 mL, 15.0 mmol) were dissolved in 50 mL of *n*-pentane, and *tert*-butyllithium (2.5 mL, 3.75 mmol, 1.7 M in *n*-pentane) was added dropwise to the solution during 5 min. LiCl precipitated only slowly. After 24 h of stirring the lithium salt was removed by filtration, and the product purified as described above. GC: one peak (**16**). Identical crystals were obtained. Yield: 0.5 g (35 %).

16: M.p. 129–131 °C, B.p. 153–155 °C/10^{-2} mbar; ^{1}H NMR ($CDCl_3$): δ = 0.67–1.91 (m, 22H; C$_7$*H*$_8$, SiC*HCH*$_2$), 0.86, 0.88 (s, 18H; $C(CH_3)_3$); ^{13}C NMR ($CDCl_3$): δ = 11.54, 11.61, 12.76, 13.07, 15.86, 16.11 (cyclo C_3H_3), 19.75, 22.13 (CH), 25.87, 27.20 (CH), 29.59, 29.65 (C(*C*H)$_3$)$_3$), 32.33, 32.36 (*C*(CH$_3$)$_3$), 33.04, 33.56 (CH_2; C_7H_8), 39.24, 39.37 (CH), 44.43, 45.47 (*C*H$_2$C(CH$_3$)$_3$), 50.45, 50.88 (SiCH) (interpretation of the ^{13}C NMR data according to **14**); ^{29}Si NMR ($CDCl_3$): δ = 45.44; MS (70 eV, EI): *m*/*z* (%): 380 (7) [M^+], 323 (100) [M^+ – *t*Bu], 231 (10) [M^+ – *t*Bu – C_7H_8], 197 (2) [$M^+ - 2C_7H_8 + 1$], 71 (13) [Np$^+$], 57 (75) [*t*Bu$^+$]; $C_{26}H_{40}Si$ (380.7): calcd C 82.03, H 10.59; found C 82.23, H 10.76.

***exo*-(9*R*,9″*R*)-Dispiro[2′,4′-dineopentyl-1′,3′-disilacyclobutane-1′,8;3′,8″-bis-{9-neopentyl-8-silatetracyclo$[4.3.0.0^{2,4}.0^{3,7}]$nonane}] (17)**:

Method A: Compound **14** (1.45 g, 5.4 mmol) was dissolved in *n*-pentane (50 mL) at RT, and *tert*-butyllithium (3.2 mL, 5.4 mmol, 1.7 M in *n*-pentane) was added dropwise within 15 min. After 24 h of stirring the solution had become slightly yellow with very little LiCl precipitate. GCMS monitoring of the solution proved that the reaction was only complete after 20 d.[43] LiCl was removed by filtration and *n*-pentane by distillation. The residue was distilled for purification. GC: two major peaks. Crystallization from CH_2Cl_2 gave very hard colourless crystals that were hardly soluble in all common solvents. GC: one peak (**17**). Yield: 0.1 g (3.2 %).

Method B: Disilacyclobutane **8** (1.3 g, 3.6 mmol) and norbornadiene (3.7 mL, 36.4 mmol) were dissolved in *n*-pentane (50 mL) at RT, and *tert*-butyllithium (4.3 mL, 7.3 mmol, 1.7 M in *n*-pentane) was added dropwise within 5 min. The solution immediately turned yellow, it warmed slightly and some white precipitate formed. After the mixture had been stirred at RT for an additional 10 h, it was separated by filtration. *n*-Pentane and norbornadiene were removed by distillation. The oily orange residue was purified by distillation.

17: M.p. 239–241 °C; B.p. 170–175 °C/10^{-2} mbar; ^{1}H NMR (CD_2Cl_2): δ = 0.70–2.14, 3.63, 5.35, 5.36 (m, 32H), 0.91 (s, 18H, $C(CH_3)_3$), 0.99 (s, 18H, $C(CH_3)_3$); ^{13}C NMR (CD_2Cl_2): δ = 11.93, 13.89, 16.42 (cyclo C_3H_3), 12.80 (Si*C*HSi*CH*), 24.71 (CH), 29.54, 30.71 (C(*C*H$_3$)$_3$), 31.88 (*C*(CH$_3$)$_3$), 32.77 (CH_2), 32.86 (*C*(CH$_3$)$_3$), 33.78 (CH), 39.25 (CH), 39.66 (CH_2), 44.41 (CH_2), 48.62 (CH), 70.85 (CH_2) (interpretation of ^{13}C NMR data according to **14**); ^{29}Si NMR (CD_2Cl_2): δ = 21.06; MS (70 eV, EI): *m*/*z* (%): 576 (4) [M^+], 519 (15) [M^+ – *t*Bu], 287 (3) [$M^+/2 - 1$], 71 (12) [Np$^+$], 57 (100) [*t*Bu$^+$]; $C_{38}H_{64}Si_2$ (577.1): calcd C 79.09, H 11.18; found C 78.70, H 11.34.

9′,15-Spiro{16-neopentyl-15-silatetracyclo$[6.6.2.0^{2,7}.0^{9,14}]$hexadeca-2,4,6,9-(14),10,12-hexaene}{9′-neopentyl-8′-silatetracyclo$[4.3.0.0^{2,4}.0^{3,7}]$nonane} (18):

Method A: Compound **14** (2.6, 10.0 mmol) and anthracene (2.0 g, 11.0 mmol) were dissolved in 100 mL of boiling toluene, and *tert*-butyllithium (5.9 mL, 10.0 mmol, 1.7 M in *n*-pentane) was added dropwise over 10 min. The yellow solution turned to orange and almost to black after 10 min. After an additional 5 min it began to become brighter and turn red. After 10 h of stirring GCMS monitoring proved that **14** had reacted completely. When the red solution was cooled to RT it turned yellow. Toluene was removed by distillation and *n*- pentane was added. LiCl was filtered off. GCMS: a mixture of anthracene, **17** and **18** was detected. It was inseparable by sublimation or crystallization. According to GCMS analysis LC (silica gel/*n*-hexane/$CHCl_3$) destroyed **18**.

Method B: Compound **11** (0.6 g, 1.7 mmol) and norbornadiene (0.92 g, 10.0 mmol) were dissolved in 50 mL of boiling toluene. When *tert*-butyllithium (5.9 mL, 10.0 mmol, 1.7 M in *n*-pentane) was added, the solution turned orange. After 6 h of stirring, toluene and norbornadiene were removed by distillation, and *n*-pentane was added to extract the residue. LiCl was filtered off, and *n*-pentane removed by distillation. The residue was a white solid. GC: two peaks (**18**). Yield: 0.4 g (50 %). M.p. 56–57 °C, B.p. 188–194 °C/10^{-2} mbar; ^{1}H NMR (C_6D_6): δ = 0.44–2.00 (m, 14H, C_7H_8, 2 × SiC*HCH*$_2$), 0.65 (s, 9H; $C(CH_3)_3$ anthracenyl side), 0.96 (s, 9H; $C(CH_3)_3$ norbornadienyl side), 3.79 (s, 1H, CH), 4.39 (d, 1H, CH), 6.91–7.15 (m, 8H, C_6H_4); ^{13}C NMR (C_6D_6): δ = 10.30, 12.02, 14.06 (cyclo C_3H_3), 19.61 (CH norbornadienyl side), 22.17 (CH anthracenyl side), 26.63 (CH norbornadienyl side), 27.72 (C(*C*H$_3$)$_3$), 29.10 (C(*C*H$_3$)$_3$), 31.05 (CH_2; C_7H_8), 31.56, 31.64 (*C*(CH$_3$)$_3$), 37.82, 38.23 (CH), 41.67, 42.04 (*C*H$_2$C(CH$_3$)$_3$), 50.78, 50.91 (SiCH), 123.36, 123.50, 123.61, 124.14, 124.33, 124.96, 125.20, 126.18 (CH; C_6H_4),138.92, 139.85, 140.60, 141.71 (C; C_6H_4) (interpretation of the ^{1}H and ^{13}C NMR data according to **13** and **16**); ^{29}Si NMR (C_6D_6): δ = 22.21; MS (70 eV, EI): *m*/*z* (%): 466 (4) [M^+], 288 (4) [$M^+ - C_{14}H_{10}$], 231 (22) [$M^+ - C_{14}H_{10}$ – *t*Bu], 178 (26) [$C_{14}H_{10}^+$], 57 (100) [*t*Bu$^+$]; $C_{33}H_{42}Si$ (466.78): calcd C 84.91, H 9.07; found C 84.59, H 9.51.

Attempted reaction of 2 with 1 equiv of Li*t*Bu in the presence of quadricyclane:

Method A: Silane **2** (1.5 g, 10.0 mmol) and quadricyclane (1.8 g, 20 mmol) were dissolved in 80 mL of *n*-pentane, and *tert*-butyllithium (5.9 mL, 10.0 mmol, 1.7 M in *n*-pentane) was added dropwise within 10 min at RT.

Method B: Silane **2** (1.5 g, 10.0 mmol) and quadricyclane (3.7 g, 40 mmol) were dissolved in 80 mL of *n*-pentane, and *tert*-butyllithium (5.9 mL, 10.0 mmol, 1.7 M in *n*-pentane) was added dropwise over 40 min at RT.

In both experiments LiCl precipitated quickly. After 1 d of stirring at RT, LiCl was filtered off, and *n*-pentane and quadricyclane were removed by distillation to give a colourless oily residue. Yield: 0.5 g. By GCMS analysis no cycloadduct could be detected; disilacyclobutane **8** was formed during the reaction.

Attempted reaction of 2 with 2 equiv of Li*t*Bu in the presence of quadricyclane:

Method A: Silane **2** (1.5 g, 10.0 mmol) and quadricyclane (3.7 g, 40 mmol) were dissolved in 80 mL of *n*-pentane, and *tert*-butyllithium (11.8 mL, 20.0 mmol, 1.7 M in *n*-pentane) was added dropwise within 15 min at RT. The solution warmed up and turned slightly yellow; LiCl precipitated very slowly. After 1 d of stirring the salt was filtered off, and *n*-pentane and quadricyclane were removed by distillation. The residue was purified by distillation. A yellow oil and some colourless crystalline material was obtained. Yield: 0.5 g. GCMS analysis proved the formation of a complex product mixture consisting mainly of 1,3-disilacyclobutane **8** and of oligomers **21**. These compounds could not be separated by either crystallization, distillation or sublimation.

Method B: **2** (1.5 g, 10.0 mmol) and quadricyclane (3.7 g, 40 mmol) were dissolved in *n*-pentane (80 mL), and *tert*-butyllithium (11.8 mL, 20.0 mmol, 1.7 M in *n*-pentane) was added quickly at RT. The solution warmed up, turned yellow and LiCl precipitated within 1 h. After 1 d this was filtered off with *n*-pentane and quadricyclane then removed by distillation. The residue was purified by distillation, and a yellow oil containing a small amount of crystalline material was obtained. Yield: 0.6 g. GCMS analysis showed that a complex mixture of products had been formed, which could not be separated by crystallization, distillation or sublimation, and consisted mainly of 3-*tert*-butyl-1-chloro-2,4-dineopentyl-1,3-divinyl-1,3-disilacyclobutanes (**19**) and of 1,3-di-*tert*-butyl-1-chloro-2,4-dineopentyl-1,3-divinyl-1,3-disilacyclobutanes (**20**) (for characterization see refs. [12] and [28]).

(1*R*,4*R*)-, (1*S*,4*S*)-, (1*R*,4*S*)-, and (1*S*,4*R*)-1-Chloro-4-neopentyl-2,3-diphenyl-1-sila-1-vinyl-2-cyclobutene (22): Silane **2** (1.5 g, 10.0 mmol) and diphenylacetylene (1.8 g, 10.0 mmol) were dissolved in 60 mL of *n*-pentane at RT, and *tert*-butyllithium (5.9 mL, 10.0 mmol, 1.7 M in *n*-pentane) was added dropwise within 5 min. After 15 min the solution had warmed slightly and LiCl precipitated. The mixture was stirred overnight. LiCl was separated by filtration, and *n*-pentane and diphenylacetylene (1.6 g, 9.2 mmol) were removed by distillation. The oily residue was purified by distillation. GC analysis: two peaks. Yield: 0.3 g (8%). B.p. 145 °C/10^{-2} mbar; ^{1}H NMR ($CDCl_3$): $\delta = 0.85$, 0.94–1.81 (m, 12 H; SiCH, $CH_2C(CH_3)_3$), 6.20–6.48 (m, 3 H; $CH{=}CH_2$), 7.26–7.42 (m, 10 H; C_6H_5); 1st diastereomer (57%): ^{13}C NMR ($CDCl_3$): $\delta = 29.59$ ($C(CH_3)_3$), 30.82 ($C(CH_3)_3$), 34.27 (SiCH), 40.34 ($CH_2C(CH_3)_3$), 127.15–128.62 (CH; C_6H_5), 131.72 ($CH{=}CH_2$), 135.82, 135.94 (C), 137.87 ($CH{=}CH_2$), 143.08, 158.78 (C); ^{29}Si NMR ($CDCl_3$): $\delta = -5.97$; 2nd diastereomer (43%): ^{13}C NMR ($CDCl_3$): $\delta = 29.30$, 29.41 ($C(CH_3)_3$), 30.73 ($C(CH_3)_3$), 36.70 (SiCH), 40.80 ($CH_2C(CH_3)_3$), 127.15–128.62 (CH; C_6H_5), 132.80 ($CH{=}CH_2$), 135.60, 136.27 (C), 138.84 ($CH{=}CH_2$), 142.80, 158.21 (C); ^{29}Si NMR ($CDCl_3$): $\delta = 0.58$; MS (70 eV, EI): *m*/*z* (%): 352 (100) [M^+], 317 (37) [$M^+ - Cl$], 295 (88) [$M^+ - t$Bu], 290 (10) [$M^+ - Cl - Vi$], 267 (27) [$M^+ - t$Bu $-$ Vi $- 1$], 259 (30) [$M^+ - t$Bu $-$ Cl $- 1$], 179 (10) [PhC≡CPh + 1], 117 (23) [$M^+ - t$Bu $-$ PhC≡CPh]; $C_{22}H_{25}SiCl$ (353.0): calcd C 74.86, H 7.14, Cl 10.04; found C 74.73, H 7.32, Cl 9.79.

(4*R*,4′*R*)- and (4*S*,4′*S*)- or 4,4′-*meso*-1,1′-Spirobi{4-neopentyl-2,3-diphenyl-1-sila-2-cyclobutene} (23) and silaspirochains (24): Silane **2** (1.5 g, 10.0 mmol) and diphenylacetylene (3.6 g, 20.0 mmol) were dissolved in 60 mL of *n*-pentane, and *tert*-butyllithium (11.8 mL, 20.0 mmol; 1.7 M in *n*-pentane) was added within 5 min at RT. After 15 min the solution was heated to reflux and a white precipitate formed. Within 2 h the solution turned red. After stirring for 12 h toluene was added to the orange mixture, and LiCl was removed by washing twice with water. The combined organic phases were dried over Na_2SO_4, and the solvents and remaining diphenylacetylene (2.2 g, 12.3 mmol) were removed by distillation. Impurities were extracted from the oily green residue with MeOH. The product was dried in vacuo to give a white solid (**24**). HPLC and GPC showed at least four different products. Yield: 1.9 g. M.p. 123–130 °C; ^{1}H NMR ($CDCl_3$): $\delta = 0.35$–2.23 ($CH_2C(CH_3)_3$, SiCH), 6.85–7.32 (C_6H_5), ^{13}C NMR ($CDCl_3$): $\delta = 26.61$–35.0 (SiCH, $C(CH_3)_3$, $C(CH_3)_3$), 36.8–40.3 ($CH_2C(CH_3)_3$), 123.2–127.5 (C_6H_5, 2C-Ph); ^{29}Si NMR ($CDCl_3$): $\delta = 3.38$, 6.68; MS (70 eV, EI): The repetition unit $\Delta M = 196$ was found. Elemental analysis found C 73.87, H 10.94.[34]

Traces of **23** (< 5%) were detected in the crude product and in the methanolic solution, but could not be separated: ^{1}H NMR ($CDCl_3$): $\delta = 0.92$–1.64, 2.42 (m, 24 H; $CH_2C(CH_3)_3$, SiCH), 7.20–7.41 (m, 20 H; C_6H_5); ^{13}C NMR ($CDCl_3$): $\delta = 21.29$, 21.63 (SiCH), 29.25, 29.91 ($C(CH_3)_3$), 35.55, 36.00 ($C(CH_3)_3$), 39.25, 41.26 ($CH_2C(CH_3)_3$), 125.44–129.13 (C_6H_5), 137.80, 161.82 (2C-Ph); ^{29}Si NMR ($CDCl_3$): $\delta = 4.48$; MS (70 eV, EI): *m*/*z* (%): 552 (1) [M^+], 495 (1) [$M^+ - t$Bu], 475 (1) [$M^+ - Ph$], 374 (1) [$M^+ -$ PhC≡CPh], 317 (1) [$M^+ -$ PhC≡CPh $- t$Bu], 195 (9) [$M^+ - 2$PhC≡CPh $- 1$], 178 (8) [PhC≡CPh$^+$], 139 (6) [$M^+ - 2$PhC≡CPh $- t$Bu], 77 (5) [Ph$^+$], 71 (10) [Np$^+$], 57 (100) [tBu$^+$]; $C_{40}H_{44}Si$ (552.9).

Preparation of silaspirochains (21): Silane **2** (3.0 g, 20.0 mmol) was dissolved in *n*-pentane (100 mL), and *tert*-butyllithium (23.6 mL, 40.0 mmol; 1.7 M in *n*-pentane) was added within 5 min at 0 °C. When the solution had warmed to 10 °C a white precipitate formed. After 2 h this was filtered off, and the solvent was removed by distillation to give a yellow solid, which was purified by extraction with MeOH and dried in vacuo to give a white powder (**21**). HPLC and GPC showed at least three different products. Yield: 3.3 g. M.p. 130–132 °C; ^{1}H NMR ($CDCl_3$): $\delta = 0.81$–2.22 ($CH_2C(CH_3)_3$, SiCH), 5.51–6.40 ($CHCH_2$); ^{13}C NMR ($CDCl_3$): $\delta = 0.38$–1.49 (SiCH, $C(CH_3)_3$, $C(CH_3)_3$), 1.49–2.35 ($CH_2C(CH_3)_3$); ^{29}Si NMR ($CDCl_3$): $\delta = 2.92$, 6.37; MS (70 eV, EI): the repetition unit $\Delta M = 196$ was found. Elemental analysis found C 68.77, H 12.75.[34]

Acknowledgements: We thank Dow Corning, the Stiftung Volkswagenwerk and the German Israel Foundation for financial support, Wacker-Chemie and Chemetall for gifts of chlorosilanes and lithium alkyls.

Received: December 16, 1996 [F 547]

---

[1] P. R. Jones, T. F. O Lim, *J. Am. Chem. Soc.* **1977**, *99*, 2013.
[2] P. R. Jones, T. F. O. Lim, *J. Am. Chem. Soc.* **1977**, *99*, 8447.
[3] P. R. Jones, M. E. Lee, L. T. Lin, *Organometallics*, **1983**, *2*, 1039.
[4] Review: N. Auner, *J. prakt. Chem.* **1995**, *337*, 79; and references therein.
[5] G. Delpon-Lacaze, C. Couret, *J. Organomet. Chem.* **1994**, *480*, C14.
[6] N. Auner, C. Seidenschwarz, N. Sewald, E. Herdtweck, *Angew. Chem.* **1991**, *103*, 425; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 444.
[7] N. Auner, A. Wolff, *Chem. Ber.* **1993**, *126*, 575.
[8] N. Sewald, W. Ziche, A. Wolff, N. Auner, *Organometallics*, **1993**, *12*, 4123.
[9] N. Auner, C. Seidenschwarz, E. Herdtweck, *Angew. Chem.* **1991**, *103*, 1172; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1151.
[10] N. Auner, C.-R. Heikenwälder, C. Wagner, *Organometallics*, **1993**, *12*, 4135.
[11] N. Auner in *Neopentylsilenes: Laboratory Curiosities or Useful Building Blocks for the Synthesis of Silaheterocycles* (Eds.: N. Auner, J. Weis), 1st ed., VCH, Weinheim, **1994**, 103.
[12] N. Auner, *J. Organomet. Chem.* **1989**, *377*, 175.
[13] G. Bertrand, G. Manuel, P. Mazerolles, *Tetrahedron* **1978**, *34*, 1951.
[14] M. Urbanová, E. A. Volnina, L. E. Gusel'nikov, Z. Bastl, J. Pola, *J. Organomet. Chem.* **1996**, *509*, 73.
[15] IR spectroscopic studies on the pyrolysis products at 10 K are currently under investigation: W. Sander, Ruhr Universität Bochum, **1996**.
[16] PE spectroscopic studies of the pyrolysis products in the gas phase are currently under investigation: H. Bock, B. Solouki, Johann Wolfgang von Goethe Universität Frankfurt, **1996**.
[17] Hurd (Gen. Electric Co.), US 2420912, **1945**; [*J. Am. Chem. Soc.* **1945**, *67*, 1813].
[18] Bartocha (Bartocha), US 3100217, **1959** [*Chem. Abstr.* **1964**, *60*, 551h].
[19] V. F. Mironov, *Bull. Acad. Sci. USSR Div. Chem. Sci (Engl. Transl.)*, **1962**, 1797.
[20] V. I. Zhun', O. L. Ustinova, V. D. Sheludyakov, G. N. Turkel'taub, T. F. Slyusarenko, *J. Gen. Chem. USSR (Engl. Transl.)*, **1990**, *60(5)*, 986.
[21] V. D. Sheludyakov, V. I. Zhun', G. N. Turkel'taub, M. V. Polyakova, M. G. Kutsnetsova, V. F. Mironov, *J. Gen. Chem. USSR (Engl. Transl.)*, **1980**, *50(4)*, 700.
[22] D. Rosenberg, J. J. Walburn, T. D. Stankovich, A. E. Balint, H. E. Ramsden, *J. Org. Chem.* **1957**, *22*, 1200.
[23] M. A. Brook, A. Neuy, *J. Org. Chem.* **1990**, *55*, 3609.
[24] A. R. Bassindale, P. G. Taylor in *Activating and directive effects of silicon* (Eds.: S. Patai, Z. Rappoport), Wiley & Sons, Chichester, UK, **1989**.
[25] N. Auner, W. Ziche, E. Herdtweck, *J. Organomet. Chem.* **1992**, *426*, 1.
[26] W. Ziche, N. Auner, J. Behm, *Organometallics*, **1992**, *11*, 2494.
[27] N. Auner, C. Wagner, W. Ziche, *Z. Naturforsch.* **1994**, *49b*, 831.
[28] N. Auner, R. Gleixner, *J. Organomet. Chem.* **1990**, *393*, 33.
[29] N. Auner, *J. Organomet. Chem.* **1988**, *353*, 275.
[30] A. Wolff, *Dissertation: 1,1-Dichlor-2-neopentylsilaethen, ein Baustein zur Synthese neuartiger Silaheterocyclen*, TU München, **1991**.
[31] N. Auner, C.-R. Heikenwälder, W. Ziche, *Chem. Ber.* **1993**, *126*, 2177.
[32] W. Ziche, N. Auner, P. Kiprof, *J. Am. Chem. Soc.* **1992**, *114*, 4910.
[33] P. R. Jones, T. F. O. Lim, R. A. Pierce, *J. Am. Chem. Soc.* **1980**, *102*, 4970.
[34] The oligomer silaspirochains described in this paper are characterized by GPC, HPLC, ^{1}H NMR, ^{13}C NMR and ^{29}Si NMR spectroscopy and elemental analysis. The repetition unit ($\Delta M = 196$) is verified by mass spectrometric methods. Possible reaction pathways, determination of the chain length and the polymer properties is currently under investigation and will be published elsewhere.
[35] The C1–C2 bond length (138.8(7) pm) seems to be unusually short for a C–C single bond compared to the average of 154.6 pm in the molecule. This "shortening" is an artefact which arose in the course of the refinement procedure. The initial bond length of 145.6 pm where only C2 is refined isotropically drops to 138.8(7) pm when C2 is also refined anisotropically. All attempts to find a suitable split atom model that describes the geometry more accurately failed. The resolution in the range 80 to 83 pm is low due to the poor quality of the crystal. Therefore the "short" distance is a consequence of the inferior quality of the data set and should not be interpreted in terms of the electronic situation in the bonding system of the molecule.

[36] N. Wiberg, H. Schuster, A. Simon, K. Peters, *Angew. Chem.* **1986**, *98*, 100; *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 79.

[37] A. Schäfer, M. Weidenbruch, K. Peters, H. G. von Schnering, *Angew. Chem.* **1984**, *96*, 311; *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 302.

[38] M. Weidenbruch, B. Flintjer, K. Peters, H. G. von Schnering, *Angew. Chem.* **1986**, *98*, 1090; *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 1129.

[39] A. Savin, H.-J. Flad, H. Preuß, H. G. v. Schnering, *Angew. Chem.* **1992**, *104*, 185; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 185.

[40] G. M. Sheldrick in Crystallographic Computing 3, G. M. Sheldrick, C. Krüger, R. Goddard, Oxford University Press, *175*, **1985**.

[41] G. M. Sheldrick, *Acta Crystallogr.* A46, *467*, **1990**.

[42] DIAMOND—Visuelles Informationssystem für Kristallstrukturen, Prof. Dr. G. Bergerhoff, Gerhard-Domagk-Str. 1, 53121 Bonn.

[43] GCMS monitoring of the reaction mixture proves that **14** continuously disappeared. Simultaneously **15** could be detected over weeks, and product **17** was formed very slowly. That means that either silene **15** forms or that the lithiated precursor that eliminates LiCl in the hot GCMS injector is relatively stable and may be detected in future experiments (e.g. NMR-monitored reactions).