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Synthesis of some Di- and Tricyclic Silaalkanes[a]

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Abstract: The mono-, di- and spirocyclic silaalkanes **5**, **6** and **9/10** are readily prepared from the di- and tetraallylsilanes **4** and **8** respectively by Cp_2Zr induced ring forming reactions. The diallylsilole **16** reacts at 0°C and in presence of an excess of Cp_2Zr to the tricyclic compound **19** whereas the sila-spiro[4.4]nonadienes **21** and **22** are formed at room temperature. High stereoselectivity is observed in all of these Cp_2Zr induced cyclization reactions. © 1997 Elsevier Science Ltd.

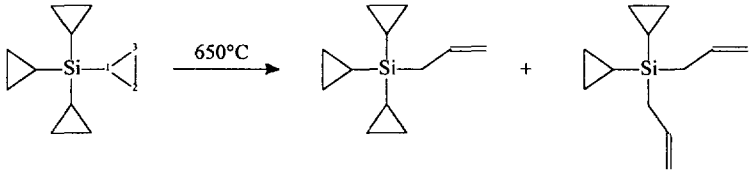
INTRODUCTION

The chemical, structural and electronic properties make Si an important element. Organic chemistry considers Si an important 'helper' group for protection of functionalities and for control of chemo-, regio- and stereoselective reactions.[1,2,3] Very often the desired Si-containing compounds are prepared by hydrosilylation of alkynes, alkenes and carbonyl compounds.[4,5] In catalysis dendrimeric silane catalysts are useful for reactions under homogeneous conditions allowing their ready separation from the reaction mixture.[6,7,8] The discovery of silatranes and their strong biological activity, some of which are much more toxic than strychnine, led to the development of Si-containing bioactive compounds.[9,10] Also, the important applications of Si-containing compounds in macromolecular chemistry and material science as conducting organic polymers might be mentioned here.[11,12] Si as a group IV element shares with carbon the strong structural propensity for a predominant tetrahedral geometry in tetracoordination. However quite different from C, Si can adopt penta- or hexa-coordination with a dramatic change of the structural and chemical properties.[13] As part of our interest in planarizing distortions in compounds of group IV elements, we explored the deformation space of tetracoordinated $Si(C)_4$ and $Si(N)_4$ and concluded, that strong planarizing distortions or even planar structures are possible and compounds with these structural elements are therefore attractive target molecules.[14,15] The high reactivity of $SiCl_4$ and SiH_4 as well as of all oxidation states in between provide easy access to intermediates which could be cyclized thermally or by transition metal induced reactions. With this aim we prepared a variety of bicyclic, tricyclic and spiro Si-containing compounds and report here our results.

RESULTS AND DISCUSSION

In a first attempt to prepare sila-cycloalkanes we investigated the pyrolysis of tetracyclopropylsilane **1**. This compound is remarkably stable and is pyrolyzed only at temperatures above 550°C (Scheme 1). At 550-650°C **1** rearranges to a mixture of **2** and **3** by breaking of the C_1-C_2 bond rather than of the C_2-C_3 bond.[16] Higher temperature decreases the amount of recovered starting material. The use of the Pd-$BaSO_4$ catalyst allows the same transformation at lower temperatures, whereas the Pt-Alox catalyst is rather 'non-productive' (Table).

Scheme 1



1 **2** **3**

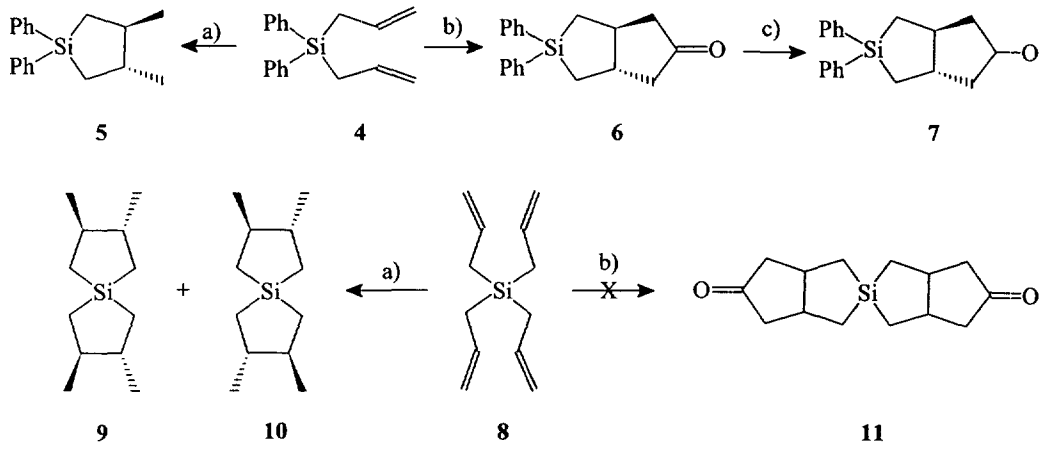
Table: Pyrolysis of tetracyclopropylsilane **1**; ratios determined by GC analysis

Temp. (°C)	catalyst	ratio **1** : **2** : **3**	mass balance (%)
400	no	1 : 0 : 0	90
500	no	1 : 0 : 0	88
550	no	8 : 0 : 1	85
650	no	2 : 2 : 3	79
600	Pd-$BaSO_4$	2 : 2 : 3	82
600	Pt-Alox	10 : 1 : 4	81
700	Pt-Alox	0 : 1 : 0	20

In a further approach we investigated the Cp_2Zr induced cyclizations[17,18,19] of the diallyl- and tetraallylsilane **4**[20] and **8**.[21] The reaction of the diallylsilane **4** with Cp_2Zr gave trans-3,4-dimethyl-1,1-diphenyl-1-sila-cyclopentane **5** as described by Koenig.[20] The tetraallylsilane **8** led under the same conditions to an unseparated 3:2 mixture of two stereosisomeric 3,4,7,8-tetramethyl-5-sila-spiro[4.4]nonanes in a yield of 62%. Based on the ^{13}C NMR spectrum which displays only 6 signals with the expected multiplicity and the preferential formation of trans-1,2-disubstituted cyclopentanes in the Cp_2Zr induced cyclization reactions the stereoisomers most likely have the trans-structures **9** and **10** to which the configuration has yet to be assigned. Applying Negishi's cyclization-carbonylation protocol for the preparation of ketones[19] to the diallylsilane **4**

gave the bicyclic ketone **6** rather than the expected hydroxy compound **7**.[18] Surprisingly, when the cyclization-carbonylation of **4** was terminated by the usual oxidative work up with I_2 no characterizable products could be isolated. Application of the same reaction conditions to the tetraallylsilane **8** afforded neither the tetracyclic sila-spiro diketone **11** nor the corresponding diol.

Scheme 2

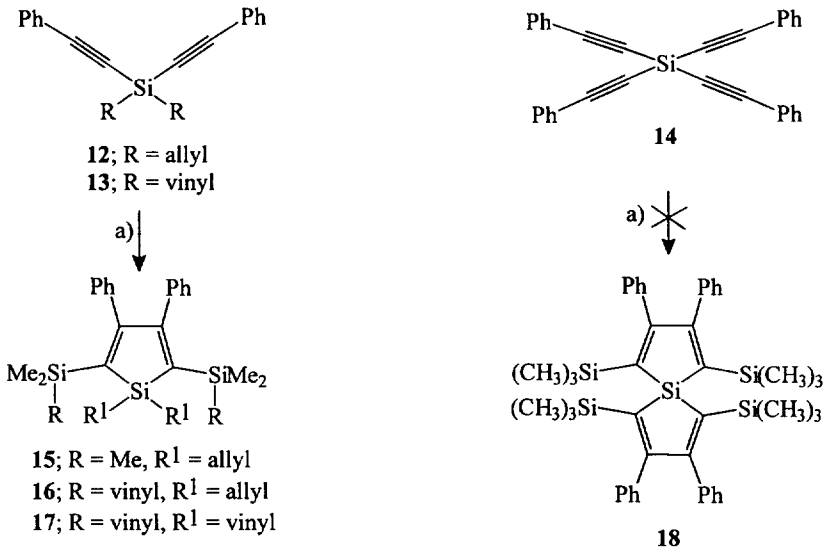


a) Cp_2ZrCl_2, 2 n-BuLi, -78°C, 1h; **4** or **8**, r.t., 12h; 3M HCl. b) Cp_2ZrCl_2, 2 n-BuLi, -78°C, 1h; **4** or **8**, r.t., 12h; CO (1 atm), 5h, 0°C; 3M HCl. c) $NaBH_4$, $CeCl_3$, CH_3OH, r.t., 15min.

According to GC analysis and ^{13}C NMR spectra **6** is formed as a single isomer. Proof for the *trans* configuration of the product **6** comes from the GC analysis with a chiral stationary phase which revealed 2 peaks with almost equal size. In addition, the ipso C-atoms of the 2 phenyl substituents appear as one singlet in the ^{13}C NMR spectrum. The observed *trans* stereoselectivity in the formation of **6** as well as that of **5** is in good accordance with analogous cyclizations described for hepta-1,6-dienes[17,18,19] and diallylamines.[22,23] Nevertheless, the exclusive formation of the *trans* diastereomers in these Si-containing compounds is remarkable. The carbinol **7**, obtained by reduction of the bicyclic ketone **6** with $NaBH_4$ / $CeCl_3$ gave ^{13}C-signals for most of the C-atoms, including 2 signals for the ipso C-atoms of the 2 phenyl groups bonded to Si. Only C(3) (δ= 75.66, d) and the para C-atoms (δ= 129.34, d) appear as single signals. This again confirms that **6** had been formed as the trans-isomer.

Based on *Tamao's* observation, that bis(phenylethynyl)-silanes can be cyclized to siloles by reaction with Li-naphthalene and trapping of the dianions with chlorosilanes,[11] we prepared the tetrafunctionalized silanes **12**, **13** and **14**. The intermediate silole-dianions obtained from **12** and **13** could be trapped with a variety of functionalized dimethylchlorosilanes to give **15-17** in good yields whereas the double reductive cyclization of the tetra-(phenylethynyl)-silane **14** to give the spiro-compound **18** has failed so far. All attempts to generate **18** gave polymeric products.

Scheme 3



a) $LiC_{10}H_8$, THF, r.t., 3h; **12**, **13** or **14**, -70°, 15min; Me_2RSiCl (R = Me or vinyl).

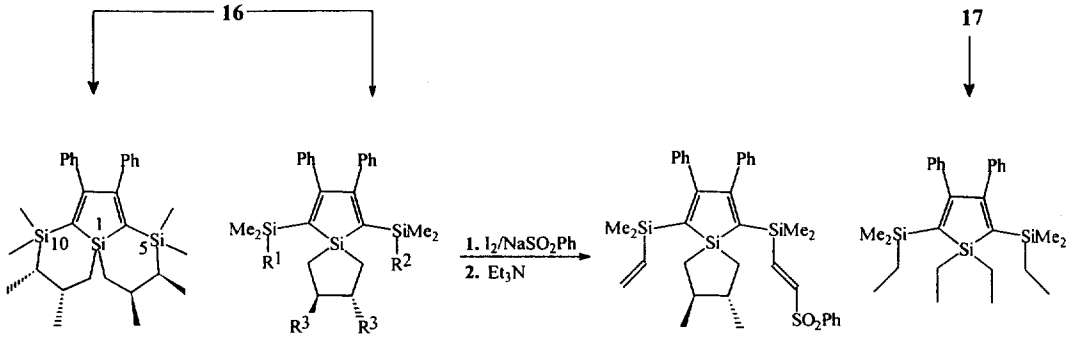
The silole **16**, bearing 2 allyl substituents at the central Si and 2 vinyl groups at the peripheral Si atoms was used for further investigations of the Cp_2Zr induced cyclization reaction.

When the reaction of **16** is performed with a 3 fold excess of Cp_2ZrCl_2 / n-BuLi at a temperature below 0°C, the tricyclic compound **19** is obtained in 45% yield. Apparently high concentration of the active Cp_2Zr species favours the reaction between the allylic and the vinylic double bonds leading to 2 six-membered rings instead of a silapentane. The C_2 symmetry of this compound is apparent from the ^{13}C NMR spectra which shows only signals of the expected multiplicity. According to ^1H-^1H-COSY- and ^1H-^{13}C-correlation-NMR spectra the methyl groups are cis to each other indicating that the tricyclic compound **19** is formed with exclusive *cis* stereoselectivity. This is in accordance to literature examples for the formation of six-membered rings in Cp_2Zr-catalyzed reactions.[19]

When **16** was treated with the Cp_2Zr-catalyst under *Negishi's* conditions followed **23** by hydrolytic work up with 1M HCl, the bicyclic spiro compounds **20** was obtained in a yield of 42%.[16,17,18] With I_2 instead of 1M HCl **21** bearing 2 iodomethyl substituents in position 7 and 8 was obtained in 13% yield (Scheme 4).

The *trans* relationship of the 2 methyl groups in position 7 and 8 in **20** has been deduced from the ^{13}C NMR spectrum of compound **22,** which was obtained from **20** by reaction with 1 molequiv. of $I_2/NaSO_2Ph$ in

Scheme 4



19 **20**: $R^1 = R^2$ = vinyl, R^3 = Me; **21**: $R^1 = R^2$ = vinyl, $R^3 = CH_2I$ **22** **23**

Cp_2ZrCl_2 (1 or 3 eq.), n-BuLi (2 or 6 eq.), -70°C, 1h; 16 or 17, 0°C or r.t. or reflux, 2-20h; 1M HCl or I_2/H_2SO_4

the presence of triethylamine.[24] The 2 CH_3 groups display separate doublets at δ = 1.13 and 1.15 ppm and the H-atoms of the adjacent CH_2 groups show each a doublet of doublets with coupling constants in the range expected for an ABC-system.

If the concentration of the Zr catalyst is reduced to 1 equivalent in the same reaction as described for the synthesis of **19**, the cyclization becomes very slow and the bicyclo[4.3.0]nona-3,4-diene derivative, resulting from a mono cyclization, was the only product detected after 8 hours in very low yield. These results clearly indicate that 2 different reaction pathways are possible for the cyclization of **16**. Depending on the concentration of the Zr catalyst and the reaction temperature either 2 six-membered or 1 five-membered ring is formed. Thus the chemoselectivity of the reaction can be controlled by the applied reaction conditions.

When the tetra-vinyl substituted compound **17** was treated with a 3 fold excess of Cp_2ZrCl_2 / n-BuLi at 0°C for 20 hours followed by hydrolytic work up, no characterizable products could be isolated. Under reflux the double bonds are reduced, giving the silole **23** instead of the desired tricyclic product containing 3 five-membered rings. These results clearly show the different behaviour of sila-allylic and sila-vinylic double bonds in the Zr-promoted cyclizations. Allylic double bonds readily react under *Negishi's* conditions to form cyclic products. Vinylic double bonds only react under special conditions with allylic double bonds to form cyclic products (e.g. **19**) but the coupling of the 2 sila-vinylic double bonds in **17** to form either five- (exo-exo-cyclization) or six-membered (exo-endo-cyclization) rings could not be effected.

So far attempts to form 2 additional rings in **21** by radical induced (Bu_3SnH / AIBN) reactions have remained unsuccessful. The isolation of **20** shows that reduction of **21** is favoured over radical addition reactions at the vinylic double bond.

CONCLUSIONS

A variety of dicyclo-, tricylo- and spiro-silaalkanes are readily accessible from di- and tetraallylsilanes by Cp_2Zr induced ring forming reactions. These cyclizations proceed with high stereoselectivity and give *trans*-1,2-disubstituted silapentane structures. The cyclization-carbonylation protocol was successful only with compound **4** containing two phenyl-substitutents at the Si-center, and leads upon treatment with HCl in contrast to literature examples to the bicyclic ketone rather than to the hydroxy derivative. The formation of the dimethyl substituted six-membered rings of the tricyclic compound **19** proceeds with high *cis* selectivity. The diallyl-silanes investigated show higher stereoselectivity in the Cp_2Zr promoted cyclizations than their all-carbon counterparts or the diallylic amines.

EXPERIMENTAL

General: Reactions were normally performed under an Ar or N_2 atmosphere. Chemicals were purchased from commercial suppliers and used without further purification. Butyllithium (*Fluka pract.*) was used as a 1.6M solution in hexane. Vinyl-MgCl (*Aldrich*) was used as a 1M solution in THF. After work up by pouring the reaction mixture onto ice and extraction with ether the solutions were dried over $MgSO_4$. Melting points were determined on a *Büchi 510* melting point apparatus and are uncorrected. Thin layer chromatography was performed on silicagel plates SIL G/UV_{254} (*Macherey & Nagel*). GC analyses were performed on a *Hewlett Packard HP-5890* instrument with a HP-5 Ultra capillary column (length 10m, i.d. 0.2mm) with a temperature program 40-220°C (3°/min), t_r in min.. Chiral analyses: *Hewlett Packard HP-5890* instrument with modified cyclodextrins as chiral stationary phases and variable temperature programs; column *A*: 10m, 30% oktakis-{2,3-di-O-acetoxy-6-O-[(tert-butyl)-dimethylsilyl]}-γ-cyclodextrin in OV 1701, He, 20kPa, 40°C (isothermic); column *B*: 10m, 100% heptakis-{2,3-di-O-acetoxy-6-O-[(tert-butyl)-dimethylsilyl]}-γ-cyclodextrin in OV 1701, He, 100kPa, 180°C (isothermic). Preparative HPLC was performed with a 715004 ET, 250/10, Nuc. 50-7 column (*Macherey & Nagel*), flow: 12ml/min. IR (recorded on a *Perkin-Elmer-782* IR-spectro photometer) and NMR spectra (recorded on *Bruker AC 300* spectrometer [^1H, 300 MHz; ^{13}C, 75 MHz] and a *Bruker DRX 500* spectrometer [^{29}Si, 99.325MHz]) were measured in $CHCl_3$ and $CDCl_3$ respectively. Chemical shifts are given in (δ)ppm relative to internal $CHCl_3$ δ(7.27 ppm) for ^1H NMR, $CDCl_3$ δ(77.0ppm) for ^{13}C NMR and $Si(CH_3)_4$ δ(0.0ppm) for ^{29}Si NMR. Multiplicities are indicated as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet and st = stack. Mass spectra (MS) were determined on a *Varian MAT CH7A* (70eV, EI) and a *Fisons Autospec Q* spectrometer and are reported in units of *m/z* and in relative intensities to the base peak. GC-MS were performed on a *VG Autospec* spectrometer.

Tetracyclopropylsilane (**1**): After addition of 3.0 g (17.5 mmol) $SiCl_4$ to 100 ml cyclopropylmagnesium bromide in THF, prepared from 12.1 g (100 mmol) bromocyclopropane and 2.4 g (100 mmol) Mg in THF at

r.t., stirring for 3 h and reflux for 12 h, work up with sat. NH_4Cl soln., extraction with hexane and distillation (72°C / 1.5 mm Hg) gave **1** (2.09 g, 42%) as a colourless liquid. R_f (hexane): 0.77. GC: t_R 18.33. IR: 3073, 3000, 2929, 1719, 1288, 1057, 1034, 900. ^1H NMR: -0.72 to -0.61(m, 4H); 0.35-0.39(m, 8H); 0.48-0.53(m, 8H). ^{13}C NMR: -9.76 (d), 0.28 (t). MS: 192(M^+, 1), 164(2), 151(100), 136(10), 123(41), 109(79), 95(97), 83(45), 69(71), 55(34), 43(80).

Pyrolysis of **1** was performed on a 181-4/20g SPEZ instrument, fitted with a quartz tube (20 cm x 1 cm). The whole system was kept at a pressure of 0.5 mm Hg and the collecting flask was cooled to -196°. The quartz tube was loaded with different catalysts and heated to the desired temperature. The reaction mixture was analyzed by GC, and around 95% products were obtained by preparative GC.

Allyltricyclopropylsilane (**2**): GC: t_R 16.67. IR: 3029; 3000; 1525; 1424; 1259; 1034; 928; 900. ^1H NMR: -0.63 -0.54(m, 3H); 0.30-0.37(m, 6H); 0.50-0.56(m, 6H); 1.48(dd, J=1.47Hz; J=1.1Hz, 1H); 1.50(dd, J01.47Hz; J=1.1Hz, 1H); 4.79-4.95(m, 2H); 5.85-5.99(m, 1H). ^{13}C NMR: -9.23(d); 0.54(t); 19.81(t); 112.65(t); 135.47(d); GC-MS: 192(M^+,1); 164(2);151(90); 123(23); 109(74); 95(100); 83(45); 69(75); 55(33); 43(79).

Diallyldicyclopropylsilane (**3**): GC: t_R 15.32. IR: 3028; 3015; 2960; 1525; 1474,1424; 1097; 928. ^1H NMR: -0.54- -0.43 (m, 2H); 0.29-0.34(m, 4H); 0.52-0.59(m, 4H); 1.49(dd, J=1.47Hz; J=1.1Hz, 2H); 1.52(dd, J=1.47Hz; J=1.1Hz,2H); 4.82-4.94(m, 4H); 5.79-5.93(m, 2H). ^{13}C NMR: -8.38(d); 0.82(t); 19.27(t); 113.14(t); 134.91(d). GC-MS: 192(M^+,2); 164(1); 151(99); 123(44); 109(100); 95(95); 83(46); 69(78); 55(34); 43(84).

Diphenyldiallylsilane (**4**)[20]: $(C_6H_5)_2SiCl_2$ [6.33 g (25 mmol)] was added to 100 ml of an ethereal soln. of allyl-MgBr, obtained by slow addition of 7.26 g (60 mmol) allyl bromide to 1.58 g (65 mmol) Mg in ether. The reaction mixture was vigorously stirred at r.t. for 6 h. After cooling to 0° and addition of sat. NH_4Cl soln. followed by extraction with pentane and chromatography (silicagel, pentane), **4** (4.54 g, 69%) was obtained as a colourless liquid. R_f (pentane): 0.26. GC: t_R 25.84. IR: 3072; 2964; 1628; 1426; 1392; 1156; 1110; 994; 902. ^1H NMR: 2.21(d, 4H); 4.96(t, 4H); 5.85(m, 2H); 7.42(m, 6H); 7.59(m, 4H). ^{13}C NMR: 19.99(t); 114.69(t); 127.77(d); 129.43(d); 133.68(d); 134.97(d). MS: 265([M+1]$^+$, 2); 264(M^+, 9); 224(20); 223(88); 222(100); 183(22); 145(42); 105(50).

trans-3,4-Dimethyl-1,1-diphenyl-1-sila-cyclopentane (**5**)[20]: To a suspension of 800 mg (2.73 mmol) Cp_2ZrCl_2 in 15 ml THF was added 3.64 ml (5.46 mmol) n-BuLi at -78°. After stirring for 1 h 687.5 mg (2.60 mmol) **4** in 2 ml THF was added. After 2 h at -78°, the reaction mixture was slowly warmed to r.t. and stirred for 12 h, hydrolyzed at 0° with 15 ml 3M HCl and extracted with pentane. Chromatography (silicagel, pentane) gave **5** (419 mg, 59%) as a colourless liquid. R_f (pentane): 0.32. GC: t_R 26.9. IR: 3070; 3030; 2990; 2870; 1480; 1420; 1380; 1100; 1020. ^1H NMR: 0.78-0.99(st, 2H); 1.14(d, 6H); 1.51(m, 4H); 7.39(m, 6H); 7.58(m, 4H). ^{13}C NMR: 21.88(q); 22.60(t); 42.41(d); 127.89(d); 129.14(d); 134.71(d); 137.13(s). MS: 267([M+1]$^+$, 266(M^+, 81); 224(75); 223(100); 188(62); 183(38); 182(82); 181(82); 179(24); 147(17); 105(54). HR-MS: 266.1491 (calc. $C_{18}H_{22}Si^+$ 266.1491).

trans-7,7-Diphenyl-7-sila-bicyclo[3.3.0]octan-3-one **(6)**: To a suspension of Cp_2ZrCl_2 (400 mg, 1.37 mmol) in 15 ml THF was added 1.82 ml (2.73 mmol) n-BuLi at -78°. After 1 h 344 mg (1.30 mmol) **4** in 2 ml THF was added and stirring continued for 2 h at -78°. The reaction mixture was slowly warmed to r.t., stirred for 12 h, cooled to 0° and put under 1 atm of CO for 5 h. After work up by pouring the reaction mixture onto 20 ml ice cold 3M HCl, extraction with ether and chromatography (silicagel, hexane/ether 1:1), **6** (268 mg, 35%) was isolated as a slightly yellow solid. M.p.: 72-73°. R_f (hexane/ether 1:1): 0.45. GC: t_R 34.05; column *B*: t_R 127.41 and 129.57 (1:1). IR: 3070; 3000; 2960; 2900; 1740; 1425; 1410; 1345; 1155; 1110; 1045. ^{1}H NMR: 0.95(m, 2H); 1.69(dd, 2H); 1.90-2.10(st, 4H); 2.59(d, 2H); 7.37-7.44(st, 6H); 7.56-7.62(st, 4H). ^{13}C NMR: 16.92(t); 47.26(t); 47.34(d); 128.03(d); 129.60(d); 134.58(d); 135.75(s); 219.20(s). MS: 293([M+1]$^+$, 37); 292(M$^+$, 100); 251(24); 238(81); 214(62); 199(50); 181(33); 150(38); 105(26); 83(25); 56(25). HR-MS: 292.12834 (calc. $C_{19}H_{20}SiO^+$ 292.12845).

trans-7,7-Diphenyl-7-sila-bicyclo[3.3.0]octan-3-ol **(7)**: $CeCl_3$ x $7H_2O$ [273 mg (0.74 mmol)] and 210 mg (0.72 mmol) **6** were dissolved in 10ml MeOH. $NaBH_4$ (32 mg , 0.84 mmol) was added and stirring continued for 15 min.. After addition of 1 ml H_2O and extraction with ether, the yellowish crude product was crystallized from hexane / ether 2:1 to give **7** (152.6 mg, 72%) as a white powder. M.p.: 77-79°. R_f (ether/hexane 2:1) 0.32. GC: t_R 34.11. IR: 3600; 3430; 3070; 2950; 2860; 1425; 1155; 1110; 1010. ^{1}H NMR: 0.80(m, 2H); 1.24(m, 1H); 1.40-1.59(st, 4H); 1.63(s, 1H); 1.86(dd, 1H); 2.02(m, 1H); 2.45(dt, 1H); 4.58(q, 1H); 7.39(m, 6H); 7.57(m, 4H). ^{13}C NMR: 16.12(t); 16.39(t); 42.95(t); 43.05(t); 48.65(d); 50.42(d); 75.66(d); 127.89(d); 127.93(d); 129.34(d); 134.57(d); 134.58(d); 136.72(s); 136.78(s). MS: 295([M+1]$^+$, 11); 294(M$^+$, 42); 216(83); 212(50); 200(76); 199(100); 183(38); 181(53); 138(23); 123(18); 105(35).

Tetraallylsilane **(8)**[21]: $SiCl_4$ (4.25 g, 25 mmol) was added to 135 ml of an ethereal soln. of allyl-MgCl, obtained by slow addition of 10.3 g (135 mmol) allyl chloride to 3.4 g (140 mmol) Mg in ether. The reaction mixture was vigorously stirred at 35° for 4 h. After cooling to 0° and addition of sat. NH_4Cl soln. followed by extraction with pentane and chromatography (silicagel, pentane) **8** (3.46 g, 72%) was isolated as a colourless liquid. R_f (pentane): 0.44. GC: t_R 12.79. IR: 3070; 3000; 2980; 2880; 1630; 1420; 1390; 1190; 1160; 1040; 990. ^{1}H NMR: 1.65(dt, 8H); 4.93(tm, 8H); 5.84(m, 4H). ^{13}C NMR: 19.16(t); 113.85(t); 133.98(d). MS: 192(M$^+$, 10); 164(27); 152(57); 151(100); 150(41); 124(35); 123(95); 109(75); 95(66); 81(26); 69(31).

2,3,7,8-Tetramethyl-5-sila-spiro[4.4]nonane **(9)** and **(10)**: As described for **5**, 500 mg (2.6 mmol) **8** gave compounds **9** and **10** (316 mg, 62%) as a mixture of two stereoisomers which could not be separated by HPLC. M.p.: 33-34°C. R_f (pentane): 0.72. GC: t_R 13.70 and 13.85 (3:2); column *A*: t_R 22.27 and 22.88 (3:2). IR: 2960; 2920; 2880; 1510; 1450; 1090. ^{1}H NMR: 0.35(m, 4H); 0.94(dd, 4H); 0.98(d, 6H); 1.02(d, 6H); 1.20-1.41(st, 4H). ^{13}C NMR: 22.03(q); 22.08(q); 22.11(t); 22.37(t); 41.74(d); 41.86(d). MS: 197([M+1]$^+$, 7); 196(M$^+$, 36); 195(18); 155(100); 154(87); 113(22); 112(40); 111(23); 97(14). HR-MS: 196.1647 (calc. $C_{12}H_{24}Si^+$ 196.1647).

General procedure for the synthesis of the dialkyl-di-(phenylethynyl)-silanes **(12)** and **(13)**: Phenylacetylene (2.04 g , 20 mmol), dissolved in 10 ml THF was slowly added to 12.5 ml (20 mmol) n-BuLi in 20 ml

THF at -70°. The reaction mixture was warmed to r.t., stirred for 30 min. and cooled again to -70°C. Slow addition of 1.70 g (10 mmol) $SiCl_4$ in 5 ml THF and warming to -15°C followed by the addition of either 20 ml (20 mmol) of a freshly prepared soln. of allyl-MgCl, obtained by the addition of 1.91 g (25 mmol) allyl chloride to 656 mg (27 mmol) Mg in 25 ml THF, and stirring for 2 h, or 20 ml (20 mmol) of a 1M soln. of vinyl-MgCl in THF, warming to r.t., stirring for 1 h and refluxing for an additional hour, work up with sat. NH_4Cl soln., extraction with ether and chromatography (silicagel, hexane/ether 20:1) gave the pure products in 41% (**12**) and 46% (**13**) yield, respectively.

Di-phenylethynyl-diallylsilane (**12**): R_f (hexane/ether 20:1): 0.54. IR: 3070; 2160; 1635; 1490; 1220; 1030; 900. ^1H NMR: 1.92(dt, J=8.1Hz; 1.1Hz, 4H); 5.02-5.12(m, 4H); 5.91-5.99(m, 2H); 7.28-7.40(m, 6H); 7.49-7.57(m, 4H). ^{13}C NMR: 21.83(t); 87.69(s); 107.54(s); 115.39(t); 122.43(s); 128.19(d); 129.01(d); 132.21(d); 132.46(d). ^{29}Si NMR: -40.14. MS: 313([M+1]$^+$,18); 285(24); 271(100); 245(15); 231(35); 169(59); 153(29); 129(90); 105(23). HR-MS: 312.1329 (calc. $C_{22}H_{20}Si^+$ 312.1334).

Di-phenylethynyl-divinylsilane (**13**): R_f (hexane/ether 20:1): 0.50. IR: 3060; 2160; 1595; 1490; 1220; 1000; 965. ^1H NMR: 6.29-6.30(m, 6H); 7.36-7.39(m, 6H); 7.58-7.61(m, 4H). ^{13}C NMR: 87.01(s); 108.09(s); 122.46(s); 128.31(d); 129.19(d); 132.08(d); 132.29(d); 136.48(t). ^{29}Si NMR: -52.91. MS: 284(M$^+$,30); 257(55); 231(57); 206(15); 181(27); 155(16); 153(16); 129(100); 103(92). HR-MS: 284.1016 (calc. $C_{20}H_{16}Si^+$ 284.1021).

Tetra-phenylethynl-silane (**14**): Phenylacetylene (4.08 g, 40 mmol) was slowly added to 25 ml (40 mmol) n-BuLi in 40 ml THF at -70°, followed by warming to 0° and stirring for 1 h. After cooling to -70° 1.48 g (9.0 mmol) $SiCl_4$ was added. The reaction mixture was slowly warmed to r.t., stirred for 12 h and refluxed for 2 h. Work up with sat. NH_4Cl soln., extraction with ether and recrystallization from toluene gave **14** (2.25 g, 58%) as white crystals. M.p.: 191-192°. R_f (toluene/hexane 1:1): 0.55. IR: 3062; 3014; 2158; 1596; 1489; 1442; 1239; 1069; 1026; 919. ^1H NMR: 7.37-7.42(m, 12H); 7.63-7.66(m, 8H). ^{13}C NMR: 85.98(s); 106.61(s); 121.91(s); 128.24(d); 129.49(d); 132.45(d). MS: 432(M$^+$,100); 355(28); 329(16); 260(18); 245(60); 229(30); 202(45); 153(58); 129(48); 102(36); 91(36). Anal. calc. for $C_{32}H_{20}Si$: C 88.85, H 4.66; found: C 88.77, H 4.57.

1,1-Diallyl-3,4-diphenyl-2,5-bis(trimethylsilyl)-silole (**15**): To a soln. of 256 mg (2 mmol) naphthalene and 30 mg (4.28 mmol) Li, dissolved in 10 ml THF and stirred at r.t. until the soln. was dark green (3 h) was added -70°C 312 mg (1 mmol) di-(phenylethynyl)-diallyl-silane (**12**). After 15 min the reaction was quenched by addition of 434 mg (4 mmol) trimethylchlorosilane and warmed to r.t.. Work up and chromatography (silicagel, hexane) gave **15** (370 mg, 79%) as a colourless oil. R_f (hexane): 0.25. IR: 2960; 2940; 1635; 1470; 1250; 1010; 835. ^1H NMR: -0.09(s, 18H); 2.04(dt, J=8.1Hz; J=1.1Hz, 4H); 4.93-5.03(m, 4H); 5.81-5.89(m, 2H); 6.82-6.85(m, 4H); 7.03-7.06(m, 6H). ^{13}C NMR: 0.82(q); 20.42(t); 113.75(t); 126.10(d); 126.85(d); 128.84(d); 133.49(d); 140.67(s); 142.63(s); 171.60(s). ^{29}Si NMR: -9.93; 19.74.

1,1-Diallyl-3,4-diphenyl-2,5-bis(dimethylvinylsilyl)-silole (**16**): As described for **15**, 312 mg (1 mmol) di-(phenylethynyl)-diallyl-silane (**12**) was transformed to **16** by quenching the reaction mixture with 483 mg (4 mmol) dimethylvinylchlorosilane in 74% yield. R_f (hexane): 0.11. IR: 2960; 2920; 1630; 1470; 1245; 1230;

1010; 830; 815. ^{1}H NMR: -0.09(s, 12H); 1.99(dt, J=7.7Hz; J=1.1Hz, 4H); 4.88-5.00(m, 4H); 5.55(dd, J=19.8Hz; J=4.0Hz, 2H); 5.74-5.89(m, 4H); 6.06(dd, J=19.8Hz; J=14.7Hz, 2H); 6.80-6.84(m, 4H); 7.00-7.05(m, 6H). ^{13}C NMR: -1.42(q); 20.26(t); 113.67(t); 126.22(d); 126.84(d); 128.88(d); 130.68(t); 133.50(d); 139.50(s); 140.03(d); 142.49(s); 172.00(s). ^{29}Si NMR: -16.98; 19.65. MS: 482(M^+, 85); 441(71); 413(34); 399(74); 271(22); 213(29); 195(23); 159(51); 145(70); 129(57); 105(89); 85(80); 59(100). HR-MS: 482.2291 (calc. $C_{30}H_{38}Si_3^+$ 482.2281).

1,1-Divinyl-3,4-diphenyl-2,5-bis(dimethylvinylsilyl)-silole (**17**): As described for **15**, 284 mg (1 mmol) di-(phenylethynyl)-divinyl-silane (**13**) was transfromed to **17** by quenching the reaction mixture with 483 mg (4 mmol) dimethylvinylchlorosilane in 70% yield. R_f (hexane): 0.22. IR: 2980; 2920; 1600; 1550; 1475; 1450; 1410; 1255; 1040; 1010; 960. ^{1}H NMR: -0.12(s, 12H); 5.48(dd, J=19.83Hz; J=4.4Hz, 2H); 5.77(dd, J=14.24Hz; J=4.1Hz, 2H); ,5.94(dd, J=19.83Hz; J=14.7Hz, 2H); 5.08(dd, J=19.47Hz; J=4.05, 2H); 6.20(dd, J=14.7Hz; J= 6.86-6.89(m, 4H); 7.03-7.06(m, 6H). ^{13}C NMR: -1.25(q); 126.30(d); 126.91(d); 128.75(d); 130.39(t); 132.94(d); 135.35(t); 140.04(d); 140.90(s); 142.45(s); 171.74(s). ^{29}Si NMR: -16.38; 2.79. MS: 454(M^+,100); 426(23); 268(91); 256(62); 240(40); 225(26); 195(35); 183(28); 159(33);145(48); 131(26); 85(54). HR-MS: 454.1962 (calc. $C_{28}H_{34}Si_3^+$ 454.1968).

rel-(3S, 4S, 11S, 12S)-7,8-Diphenyl-3,4,5,5,10,10,11,12-octamethyl-1,5,10-trisila-tricyclo[7.4.0.0^{1,6}]trideca-6,8-diene (**19**): As described for **5**, 0.9 g (3 mmol) Cp_2ZrCl_2 / 2n-BuLi were treated with 480 mg (1 mmol) **16**. The reaction mixture was warmed to 0° and stirred for 20 h. Work up by pouring the reaction mixture onto 60 ml icecold 1M HCl, extraction with ether and chromatography (silicagel, hexane), gave 220 mg (45%) **19** as a colourless oil.- R_f (hexane): 0.19. IR: 2920; 2900; 2885; 1600; 1545; 1505; 1470; 1440; 1400; 1375; 1250; 1100; 1080; 1030; 1010. ^{1}H NMR: -0.60(s, 6H); 0.11(s, 6H); 0.17(dq, J = 11Hz, 7.4Hz, 2H); 0.50(dd, J = 13.7Hz, 13.0Hz, 2H); 0.94(d, J = 7.4Hz, 6H); 1.13(d, J = 6.4Hz, 6H); 1.18(dd, J = 14.3Hz, 1.9Hz, 2H); 1.76(qdd, J = 6.2Hz, 11.5Hz, 1.7Hz, 2H); 6.84-7.08(m, 10H). ^{13}C NMR: -4.17(q); -4.07(q); 14.17(q); 23.40(t); 26.08(q); 29.82(d); 32.07(d); 126.03(d); 126.93(d); 128.79(d); 142.52(s); 145.15(s); 165.92(s). ^{29}Si NMR: -5.32; 17.34. MS: 486(M^+, 8); 445(4); 301(6); 260(30); 245(100); 205(6); 178(35); 159(18); 129(20); 105(74); 77(36); 57(87). HR-MS: 486.2588 (calc. $C_{30}H_{42}Si_3^+$ 486.2594).

trans-7,8-Dimethyl-1,4-di-(vinyldimethylsilyl)-2,3-diphenyl-5-sila-spiro[4.4]nona-1,3-diene (**20**): As described for **5**, 600 mg (2 mmol) Cp_2ZrCl_2 / 2n-BuLi was reacted with 480 mg (1 mmol) **16** for 12 h at r.t.. After work up by pouring the reaction mixture onto 50 ml icecold 1M HCl and extraction with ether, **20** (200mg, 42%) was obtained by chromatography (silicagel, hexane) as a colourless oil.- **20**: R_f (hexane): 0.24. IR: 3027; 3011; 2956; 1600; 1467; 1248; 1003. ^{1}H NMR: -0.14(s, 6H); -0.12(s, 6H); 0.85(dd, J=15.06Hz; J=11.76Hz, 2H); 1.16(d, J=5.9Hz, 6H); 1.25(dd, J= 15.08Hz; J=5.9Hz, 2H); 1.58-1.69(m, 2H); 5.55(dd, J=19.8Hz; J=4.1Hz, 2H); 5.82(dd, J=14.3Hz; J=4.1Hz, 2H); 6.00(dd, J=19.9Hz; J=14.7Hz, 2H); 6.83-6.85(m, 4H); 7.02-7.04(m, 6H). ^{13}C NMR: -1.20(q); -1.17(q); 20.61(t); 22.20(q); 42.40(d); 126.14(d); 126.87(d); 128.83(d);

130.46(t); 140.26(d); 140.65(s); 142.72(s); 170.28(s). ^{29}Si NMR: -16.06; 29.67. MS: 484(M^+,10); 250(15); 206(50); 178(58); 149(28); 120(60); 105(100); 77(91). HR-MS: 484.2455 (calc. $C_{30}H_{40}Si_3^+$ 484.2439).

trans-7,8-Di-(iodomethyl)-1,4-di-(vinyldimethylsilyl)-2,3-diphenyl-5-sila-spiro[4.4]nona-1,3-diene (**21**): As described for **20**, compound **21** was prepared from 480 mg (1 mmol) **16** by addition of 1.27 g (5 mmol) I_2 in 6 ml THF at -70° and 10% H_2SO_4 and extraction with ether. Chromatography (silicagel, hexane) gave **21** (94 mg, 13%) as a colorless oil. R_f (hexane): 0.14. IR: 3019; 2960; 1256; 1043; 841; 796. ^{1}H NMR: -0.13(s, 6H); -0.09(s, 6H); 1.22(m, 4H); 1.49-1.56(m, 2H); 3.41(dd, J=10.3Hz; J=4.4Hz, 2H); 3.54(dd, J=10.3Hz; J=1.9Hz, 2H); 5.62(dd, J=19.9Hz; J=4.1Hz, 2H); 5.88(dd, J=14.3Hz; 4.1Hz, 2H); 6.06(dd, J=20.3Hz; J=14.7Hz, 2H); 6.94-7.12(m, 10H). ^{13}C NMR: -1.21(q); -1.20(q); 17.23(t); 17.25(t); 44.67(d); 126.37(d); 127.05(d); 128.79(d); 131.20(t); 139.42(s); 139.89(d); 142.31(s); 171.27(s). ^{29}Si NMR: -16.01; 26.24. MS: 736([M+1]$^+$, 21); 654(100); 527(38); 399(22); 368(28); 341(18); 269(19); 256(21); 185(30); 171(19); 159(31); 145(22); 135(16); 85(32). HR-MS: 736.0351 (calc. $C_{30}H_{38}Si_3I_2^+$ 736.0371).

trans-7,8-Dimethyl-1-(dimethylvinylsilyl)-4-[dimethyl(2'-Benzenesulfonyl)vinylsilyl]-2,3-diphenyl-5-sila-spiro[4.4]nona-1,3-diene (**22**): To 50 mg (0.1mmol) **20** and 20 mg (0.12mmol) sodium benzenesulfinate in 10ml THF-methanol (1:10) was added slowly 31 mg (0.12mmol) I_2 at 0^{0}C. The solution was warmed to room temperature over 5h. Afterwards 0.03ml (0.2mmol) triethylamine was added and stirring continued for 2h. The solvent was evaporated under reduced pressure, the residue dissolved in diethyl ether, washed with 1N HCl and 1M sodium thiosulfate. The organic phase was dried over anhydrous $MgSO_4$, evaporated and the vinylsulfone **22** (30mg, 51%) purified by flash chromatography. R_f (n-hexane: Et_2O= 2:1): 0.5. IR: 3035; 2960; 2880; 1620; 1605; 1545; 1470; 1310; 1250; 1150; 1090; 1005; 975. ^{1}H NMR: -0.15(s, 3H); -0.13(s, 3H); -0.073(s, 3H); -0.069(s, 3H); 0.73(dd, J=15.06Hz; J=11.76Hz, 1H); 0.85(dd, J=15.42Hz; J=11.73Hz, 1H); 1.13(d, J=3.33Hz, 3H); 1.15(d, J=2.94Hz, 3H); 1.20(dd, J=15.09Hz; 5.88Hz, 1H); 1.25(dd, J=15.08Hz; J=5.52Hz, 1H); 1.46-1.67(m, 2H); 5.54(dd, J=19.83Hz; J=4.05Hz, 1H); 5.82(dd, J=14.34Hz; J=4.05Hz, 1H); 5.98(dd, J=19.86Hz; 14.07Hz, 1H); 6.41(d, J=18.0Hz, 1H); 6.69-6.83(m, 4H); 6.92-7.04(m, 7H); 7.54-7.67(m, 3H); 7.84-8.87(m, 2H). ^{13}CNMR: -1.29(q); -1.27(q); -1.25(q); -1.22(q); 20.37(t); 20.61(t); 22.09(q); 22.12(q); 42.36(d); 42.62(d); 126.36(d); 126.69(d); 126.97(d); 127.14(d); 127.96(d); 128.35(d); 128.42(d); 128.71(d); 128.78(d); 129.21(d); 130.78(t); 133.30(d); 137.30(s); 139.88(d); 140.08(s); 140.67(d); 142.02(s); 142.06(s); 142.19(s); 145:79(d); 169.94(s); 172.37(s). MS: 624(M^+, 100); 595(23); 540(11); 499(16); 399(27); 253(17); 225(12); 199(21); 159(20); 135(19). HR-MS: 624.23699 (calc. $C_{36}H_{44}O_2SSi_3^+$ 624.23676).

1,1-Diethyl-3,4-diphenyl-2,5-bis(dimethylethyl)-silole (**23**): As described for **5**, 900 mg (3 mmol) Cp_2ZrCl_2 / 2n-BuLi was treated with 450 mg (1 mmol) **17** for 30 min. at r.t., followed by reflux for 2 h. After work up by pouring the reaction mixture onto 60 ml ice cold 1M HCl, extraction with ether and chromatography (silicagel, hexane), **23** (278 mg, 60%) was obtained as a white solid. R_f (hexane): 0.27. IR: 2950, 2880, 1465, 1420, 1240, 1005; 955. ^{1}H NMR: -0.12(s, 12H); 0.25(q, J=8.1Hz, 4H); 0.81(t, J=8.1Hz, 6H); 0.99-1.01(m, 10H); 6.85-

6.89(m, 4H); 7.01-7.06(m, 6H). ^{13}C NMR: -1.92(q); 5.27(t); 7.28(q); 7.58(q); 8.20(t); 125.96(d); 126.81(d); 128.84(d); 141.11(s); 143.19(s); 171.32(s). ^{29}Si NMR: -7.005; 29.927. MS: 462(M^+, 50); 433(100); 132(16); 112(21); 97(28); 71(38); 57(42). HR-MS: 462.2588 (calc. $C_{28}H_{42}Si_3^+$ 462.2594).

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