Cyclic diynes with tetramethyldisilyl groups in the bridges. Syntheses and properties

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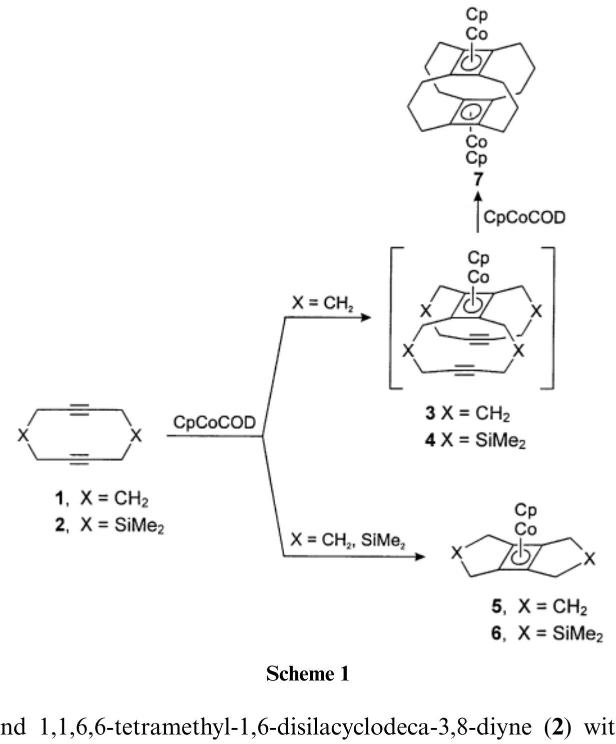
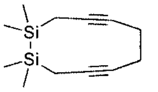
A series of cyclic diynes (**8**–**15**) with tetramethyldisilyl groups as bridging units have been synthesized from α,ω-bis(chloromethyl)diynes and 1,2-dichloro-1,1,2,2-tetramethyldisilane with lithium in the presence of catalytic amounts of biphenyl. X-Ray investigations of single crystals of **8**–**14** reveal a twisted-chair conformation for **9**–**11** and **14**, and a twisted half-chair conformation for **8** and **12**, whereas **13** adopts a twisted-boat conformation in the solid state. The He(I) photoelectron spectra of **8**–**14** reveal ionization energies between 8.5–10 eV for the ionization processes from the π-orbitals.

Our investigations of the reactivity of cyclic diynes with organometallic cobalt compounds such as (η^4-cycloocta-1,5-diene)(cyclopentadienyl)cobalt (CpCoCOD) reveal that the chain length and steric effects of the bridges of cyclic diynes play an important role.[1,2] As an example for the latter case we show in Scheme 1 the reaction of cyclodeca-1,6-diyne (**1**) and 1,1,6,6-tetramethyl-1,6-disilacyclodeca-3,8-diyne (**2**) with CpCoCOD. In the case of the reaction of **1** with CpCoCOD the intramolecular (**5**) and intermolecular (**7**) products were formed.[3] In the case of **2** only the intramolecular product **6** could be isolated.[4] This difference was ascribed to steric effects. The intermediately formed tricyclic diyne **3** will give rise to **7**. In the case of the tricyclic diyne **4** the large dimethylsilyl groups may prevent the second [2+2]cycloaddition and thus only **6** could be isolated.



Scheme 1

To learn more about the role of steric effects, especially in the propargylic (prop-2-ynylic) positions, we synthesized a series of cyclic diynes with tetramethyldisilyl groups, studied their structure, electronic properties and their reactions with $CpCoL_2$ reagents. In this paper we report on the syntheses and properties of **8**–**15**. Common to the cyclic diynes **8**–**15** is at least one tetramethyldisilyl unit in one of the bridges. Therefore it seems reasonable to use pathways with 1,2-dichloro-1,1,2,2-tetramethyldisilane (**16**),[5] as the building block. As the metal we applied lithium in the presence of catalytic amounts of biphenyl.[6] This protocol was used successfully to prepare related cyclic systems.[7] Scheme 2 summarizes our one pot synthesis of **9**–**14**. This protocol has the advantage that the starting materials are not expensive and are easily available. The yields vary between 10% and 30%.



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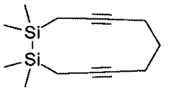

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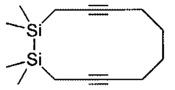

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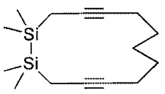

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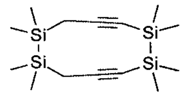

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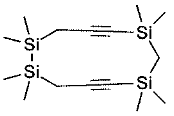

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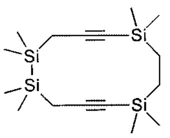

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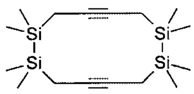

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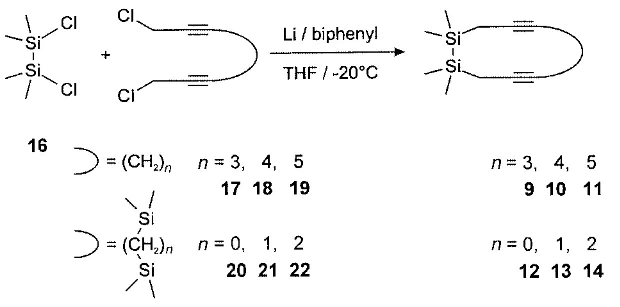
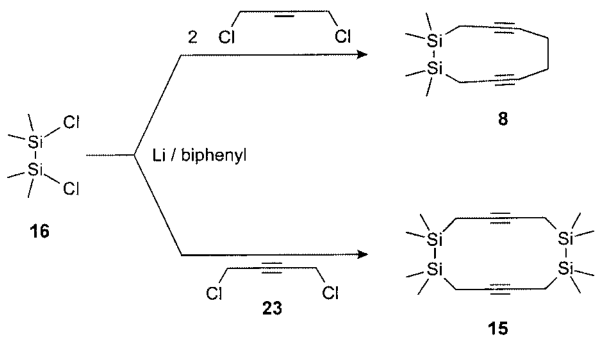
To prepare **8** and **15** we used a slight variation of the procedure discussed above (Scheme 3). Reaction of **16** with 1,4-dichlorobut-2-yne (**23**) in a ratio of 1 : 2 in the presence of lithium and catalytic amounts of biphenyl affords **8** in 10% yield. If the components **16** and **23** are reacted in a ratio of 1 : 1 in the presence of lithium and catalytic amounts of biphenyl the twelve-membered ring system **15** was isolated in 9% yield. In these two cases a three- and four-component cyclization, respectively, were achieved.

Table 1 Selected distances (Å) and angles (°) of **8**–**14**. The standard deviations of the angles are in order 0.1°

Compound	Transannular distances *a*	Transannular distances *b*	*cisoid* Deformation at the sp centers		Torsion angles C_{ring}–Si–Si–C_{ring}	Torsion angles C_{sp}–$C_{sp}\cdots C_{sp}$–C_{sp}
8	3.721(2)	2.830(2)	6.1	7.9	98.1	16.0
9	4.006(3)	3.306(3)	5.3	2.8	113.3	0.4
10	4.484(2)	4.228(2)	1.3	4.2	123.2	32.4
11	5.014(3)	5.031(3)	2.1	3.8	134.8	10.6
12	4.057(2)	3.511(2)	3.2	8.6	98.3	23.8
13	3.723(2)	3.545(2)	4.7	5.8	36.2	28.3
14	5.021(2)	4.944(2)	4.7	7.5	148.6	27.8



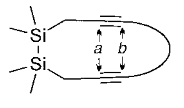
Scheme 2



Scheme 3

Structural investigations

Single crystals of **8**–**14** could be obtained by recrystallization of samples from pentane and CCl_4 (**11**, **13**) at −20 °C. Crystals of **9**, **10**, **11**, and **14** adopt a twisted chair conformation, **8** and **12** show a twisted half-chair conformation, and **13** adopts a twisted boat conformation. As examples we show in Fig. 1 the structures of **8**, **11**, and **13**. The disilabutane bridges, together with the adjacent triple bonds adopt a twisted conformation in all seven structures. As a measure for the twist we can use the torsion angle C_{ring}–Si–Si–C_{ring} (Table 1). This angle is larger than 90° for all compounds except **13** for which an angle of 36.2° was encountered. In Table 1 we also list the torsion angle between opposite triple bonds (last column). This angle is a function of the length of the second bridge. In molecules with an odd number of atoms in the bridge (**9**, **11**) the torsion angle is smaller (0.4°, 10.6° respectively) than in rings with an even number of atoms in the bridge (**8**: 16°, **10**: 34.4°, **12**: 23.8°, and **14**: 27.8°). This tendency is also encountered in the carbocyclic cases. In the case of cyclododeca-1,7-diyne,[8] the torsion angle amounts to 24° while for cyclodeca-1,6-diyne[8] the two triple bonds are oriented parallel to each other. For the pentamethylene bridge of **11** we find a disorder in the solid state. This disorder could be rationalized by assuming for 75% of the molecules a zig-zag and for 25% a gauche arrangement for the pentamethylene chain.[9]



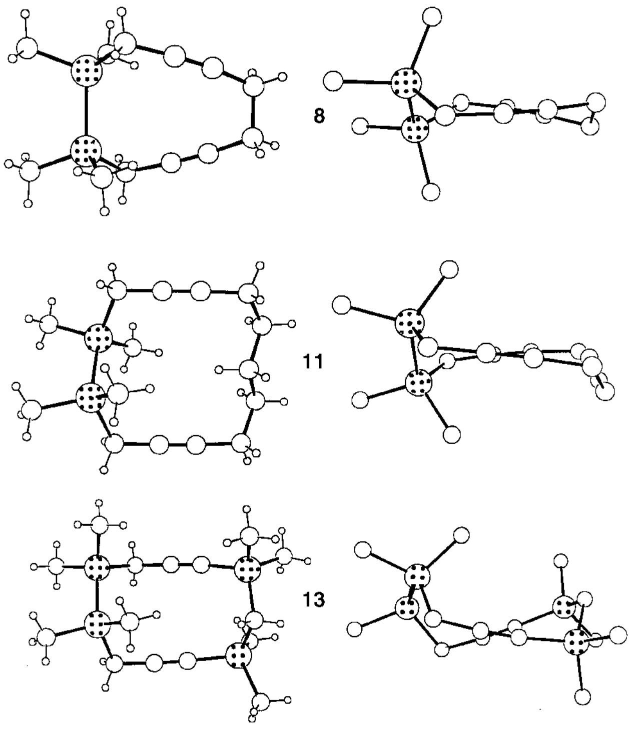


Fig. 1 Molecular structures of **8**, **11** and **13**. The silicon atoms are indicated by dotted circles.

The transannular distances between the sp-centers (*a*, *b*) depend on the lengths of the bridges. The distance *b* increases from **8** to **11** from 2.83 Å to 5.03 Å with an increasing number of methylene groups. The same trend is anticipated in the series **12**, **13**, and **14**. Due to the twisted boat conformation of **13** the value for *b* is smaller than that of **12**. A comparison of the transannular distances *a* and *b* for **8**–**14** yields very similar values for **11** and **14** as well as **9** and **12**. This leads to the outcome that the replacement of three methylene by two dimethylsilyl groups yields very similar transannular distances. This result is based on the larger covalent atomic radii of silicon (1.17 Å)[10] as compared to carbon (0.77 Å).[10] In Table 1 we also list the *cisoid* deformation of the triple bonds. It is largest in the case of the ten-membered rings **8** (6.1° and 7.9°) and **12** (3.2° and 8.6°).

Photoelectron spectroscopic investigations

The He(I) photoelectron (PE) spectra of **8**–**15** have been recorded. Common to all of them is a weakly structured broad peak centered around 9 eV as seen in the PE spectra of **8**, **10**, and **15** (Fig. 2). To assign this peak to individual transitions we make use of Koopmans' theorem,[11] which allows us to correlate the ionization energies with calculated values of orbital energies. The orbital energies (ε_j) for **8**–**15** are compared with

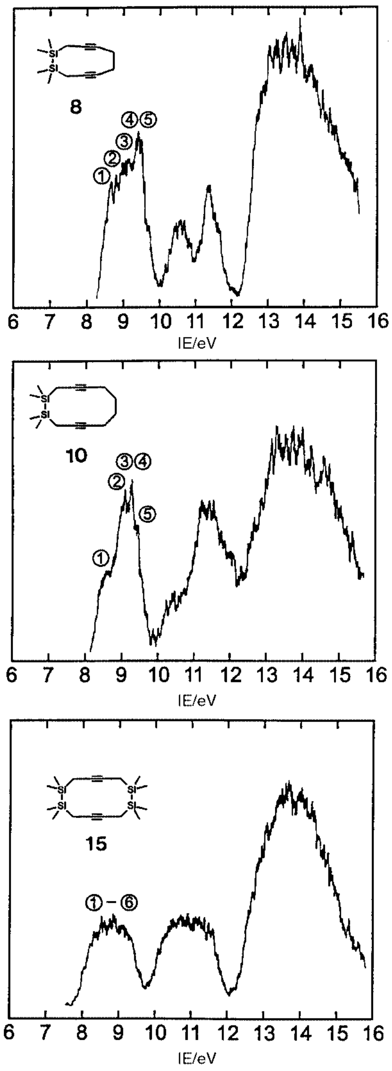


Fig. 2 He(I) photoelectron spectra of **8**, **10** and **15**.

the vertical ionization energies ($IE_{v,j}$) in Table 2. The orbital energies are based on the optimized structures of **8**–**15** using the HF-SCF procedure applying a 3-21G* basis.[12] In the case of **8**, **10**, **12**, **14** and **15** C_2 symmetry was assumed.

The four π molecular orbitals of the two triple bonds can be subdivided into those which are mainly localized in the plane of the molecule (π_i^+ and π_i^-) and the out of plane linear combinations (π_o^+ and π_o^-).

The energy difference of the out of plane linear combination depends mainly on the distance between the two triple bonds. It should be largest for **8** and **13**. As shown on several other occasions,[8,13] the energy difference of the in plane linear combination depends on the interactions with the σ-frame. In the case of even bridges such as in **8** and **10** we expect that the π^+–σ linear combination is on top of the π_i^- linear combination. Due to the large distance between the triple bonds and the relatively long chains all the π-bands are predicted to be close in energy, this leads to the broad peak in the PE spectra for all eight compounds.

Experimental

General

All reactions were carried out under an argon atmosphere with magnetic stirring. The solvents were purified and dried using standard procedures. The ^1H and ^{13}C NMR spectra were recorded at 300 and 75 MHz in $CDCl_3$ if not otherwise noted. Elemental analyses were performed at the Mikroanalytisches Laboratorium der Universität Heidelberg, Germany.

Table 2 Comparison between the measured vertical ionization energies ($IE_{v,j}$) of **8**–**15** and calculated orbital energies (ε_j). All values in eV

Compound	Band	$IE_{v,j}$	Assignment		$-\varepsilon$ (3-21G*)
8	1	8.6	29b	π_i^-	9.20
	2	8.8	31a	$\pi_i^+ - \sigma_{Si–Si}$	9.34
	3	9.0	30a	π_o^-	9.60
	4	9.3–	29a	$\pi_i^+ + \sigma_{Si–Si}$	9.93
	5	9.5	28b	π_o^+	10.06
9	1	8.5	64a	π_i^-	8.91
	2	8.7	63a	$\pi_i^+ - \sigma_{Si–Si}$	9.35
	3	9.0	62a	π_o^-	9.67
	4	—	61a	π_o^+	9.74
	5	9.3	60a	$\pi_i^+ + \sigma_{Si–Si}$	10.05
10	1	8.6	35a	$\pi_i^+ - \sigma_{Si–Si}$	9.18
	2	9.1	33b	π_i^-	9.37
	3	9.2–	34a	π_o^-	9.69
	4	9.3	32b	π_o^+	9.81
	5	9.4	33a	$\pi_i^+ + \sigma_{Si–Si}$	9.96
11	1	8.7	72a	$\pi_i^+ - \sigma_{Si–Si}$	9.12
	2	8.9	71a	π_i^-	9.34
	3	—	70a	π_o^-	9.73
	4	—	69a	π_o^+	9.78
	5	9.3	68a	$\pi_i^+ + \sigma_{Si–Si}$	10.10
12	1	8.0	43a	$\pi_i^+ - \sigma_{Si–Si}$	8.77
	2	8.9	41b	π_i^-	9.49
	3	—	42a	$\sigma_{CH_2Si–SiCH_2}$	9.75
	4	—	40b	π_o^+	10.00
	5	9.3	41a	π_o^-	10.05
	6	10.4	40a	$\pi_i^+ + \sigma_{Si–Si}$	10.83
13	1	8.7	88a	π_i^-	9.31
	2	9.0	87a	$\pi_i^+ - \sigma_{Si–Si}$	9.31
	3	—	86a	π_o^-	9.89
	4	—	95a	π_o^+	9.93
	5	9.5	84a	$\pi_i^+ + \sigma_{Si–Si}$	10.12
14	1	8.6	47a	π_i^+	9.25
	2	9.0	45b	π_i^-	9.59
	3	—	46a	$\pi_o^- - \sigma_{Si–Si}$	9.87
	4	—	44b	π_o^+	9.96
	5	9.4	45a	$\pi_o^- + \sigma_{Si–Si}$	10.04
15	1	8.3	47a	π_i^+	8.80
	2		45b	π_i^-	9.13
	3	to	46a	π_o^-	9.51
	4		44b	π_o^+	9.52
	5		45a	σ	9.69
	6	9.2	44a	σ	10.01

General procedure

To 2.4 g (0.35 mol) of lithium powder and 0.3 g (82 mmol) of biphenyl were added at −75 °C 350 ml of dry THF in such a way that the solution remained at a deep green color. Subsequently the solution was warmed to −20 °C and a solution of 25 mmol of the propargylic chloride and 25 mmol of **16** in 75 ml THF was added within 20–30 min. This was accompanied by a decolorization of the solution. After the color (red to green) appeared again (usually 30 min after the addition was completed) the lithium was filtered off in the presence of air to destroy the radical anion of biphenyl (green color). The solvent was removed and the raw material purified by chromatography on silica gel with CCl_4. Further purification was achieved by Kugelrohr distillation to yield colorless crystals.

1,1,2,2-Tetramethyl-1,2-disilacyclodeca-4,8-diyne 8

Starting materials: 4.2 g (34 mmol) of **23**, 3.2 g (17 mmol) of **16**, 2.4 g (0.34 mol) of lithium powder and 0.3 g (2 mmol) of biphenyl. Yield: 0.4 g (10%) of **8**. Colorless crystals (mp 42 °C) were obtained by Kugelrohr distillation (110 °C/0.3 mbar); $\tilde{\nu}$ (KBr)/cm^{-1} 2947, 2926, 2882, 2846, 2219, 1634, 1434; λ_{max} (CH_2Cl_2)/nm 230, 260; δ_H (200 MHz) 2.3 (m, 4H), 1.5 (m, 4H), 0.2 (s, 12H); δ_C (50 MHz) 81.4 (s), 78.6 (s), 19.4 (t), 5.7 (t), −3.4 (q); HRMS (EI) 220.1104, calc. for $C_{12}H_{20}Si_2$: 220.1104 (Found: C 64.99, H 9.54. Calc. for $C_{12}H_{20}Si_2$: C 65.38, H 9.14).

Table 3 Crystal data and structure refinement for **8**, **9**, **10**, and **11**

	Compound			
	8	**9**	**10**	**11**
Empirical formula	$C_{12}H_{20}Si_2$	$C_{13}H_{22}Si_2$	$C_{14}H_{24}Si_2$	$C_{15}H_{26}Si_2$
Formula weight	220.5	234.5	248.5	262.5
T/K	200(2)	223(2)	200(2)	253(2)
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Triclinic
Space group	$C222_1$	$C2/c$	$P2_1/c$	$P\bar{1}$
Z	4	4	4	2
a/Å	10.1723(8)	13.363(5)	10.4260(2)	10.268(2)
b/Å	10.5020(8)	10.520(2)	12.3151(1)	11.346(2)
c/Å	12.964(1)	11.258(5)	13.0649(2)	8.679(2)
α/°	90	90	90	111.72(3)
β/°	90	111.82(3)	110.448(1)	113.95(3)
γ/°	90	90	90	70.04(3)
V/Å^3	1384.9(2)	1469.2(9)	1571.80(4)	836.4(3)
Absorption coefficient, μ/mm^{-1}	0.223	0.21	0.203	0.19
Reflection collected	3206	1838	7035	4290
Independent reflections	1181 (R(int) = 0.014)	1768 (R(int) = 0.013)	2680 (R(int) = 0.017)	4028 (R(int) = 0.017
R,R_w ($I > 2\sigma(I)$)	0.023, 0.061	0.039, 0.109	0.030, 0.076	0.037, 0.100

1,1,2,2-Tetramethyl-1,2-disilacycloundeca-4,9-diyne 9

Starting materials: 5.7 g (30 mmol) of **17**, 5.6 g (30 mmol) of **16**, 2.4 g (0.34 mol) of lithium powder and 0.5 g (3 mmol) of biphenyl. Yield: 0.9 g (12%) of **9**. Colorless crystals (mp 53 °C) were obtained by Kugelrohr distillation (140 °C/0.3 mbar); $\tilde{\nu}$ (KBr)/cm^{-1} 2951, 2899, 2875, 2223, 1438; λ_{max} (CH_2Cl_2)/nm 230, 256; δ_H 2.3 (m, 4H), 1.6 (m, 2H), 1.5 (t, 4H), 0.2 (s, 12H); δ_C 78.8 (s), 78.0 (s), 27.1 (t), 19.5 (t), 5.4 (t), −3.6 (q); HRMS (EI) 234.1283, calc. for $C_{13}H_{22}Si_2$: 234.1260 (Found: C 66.70, H 9.74. Calc. for $C_{13}H_{22}Si_2$: C 66.59, H 9.46).

1,1,2,2-Tetramethyl-1,2-disilacyclododeca-4,10-diyne 10

Starting materials: 8.1 g (40 mmol) of **18**, 7.5 g (40 mmol) of **16**, 3.5 g (0.5 mol) of lithium powder and 0.6 g (4 mmol) of biphenyl. Yield: 1.9 g (19%) of **10**. Colorless crystals (mp 53 °C) were obtained by Kugelrohr distillation (140 °C/0.3 mbar); $\tilde{\nu}$ (KBr)/cm^{-1} 2938, 2894, 2861, 2219, 1433; λ_{max} (CH_2Cl_2)/nm 230, 256; δ_H 2.2 (m, 4H), 1.6 (m, 4H), 1.5 (m, 4H), 0.2 (s, 12H); δ_C 79.1 (s), 77.9 (s), 27.2 (t), 18.3 (t), 5.6 (t), −3.2 (q); HRMS (EI) 248.1455, calc. for $C_{14}H_{24}Si_2$: 248.1417 (Found: C 67.61, H 10.01. Calc.for $C_{14}H_{24}Si_2$: C 67.66, H 9.73).

1,1,2,2-Tetramethyl-1,2-disilacyclotrideca-4,11-diyne 11

Starting materials: 6.5 g (30 mmol) of **19**, 5.6 g (30 mmol) of **16**, 2.8 g (0.4 mol) of lithium powder and 0.5 g (3 mmol) of biphenyl. Yield: 1.5 g (19%) of **11**. Colorless crystals (mp 64 °C) were obtained by Kugelrohr distillation (150 °C/0.3 mbar); $\tilde{\nu}$ (KBr)/cm^{-1} 2927, 2860, 2217, 1461; λ_{max} (CH_2Cl_2)/nm 230, 256; δ_H 2.2 (m, 4H), 1.7 (m, 2H), 1.5 (t, 4H), 1.4 (m, 4H), 0.2 (s, 12H); δ_C 78.6 (s), 78.0 (s), 27.5 (t), 26.1 (t), 18.5 (t), 5.3 (t), −3.3 (q); HRMS (EI) 262.1599, calc. for $C_{15}H_{26}Si_2$: 262.1573 (Found: C 68.53, H 10.15. Calc, for $C_{15}H_{26}Si_2$: C 68.62, H 9.98).

1,1,2,2,6,6,7,7-Octamethyl-1,2,6,7-tetrasilacyclodeca-4,8-diyne 12

Starting materials: 6.6 g (25 mmol) of **20**, 4.7 g (25 mmol) of **16**, 2.4 g (0.35 mol) of lithium powder and 0.3 g (2 mmol) of biphenyl. Yield: 2.1 g (27%) of **12**. Colorless crystals (mp 78 °C) were obtained by Kugelrohr distillation (150 °C/0.2 mbar); $\tilde{\nu}$ (KBr)/cm^{-1} 2953, 2892, 2184, 2150, 2063, 1404; δ_H 1.7 (s, 4H), 0.19 (s, 12H), 0.17 (s, 12H); δ_C 108.2 (s), 81.8 (s), 7.6 (t), −3.2 (q), −3.4 (q); HRMS (EI) 308.1279, calc. for $C_{14}H_{28}Si_4$: 308.1268 (Found: C 54.71, H 9.20. Calc. for $C_{14}H_{28}Si_4$: C 54.47, H 9.14).

1,1,2,2,6,6,8,8-Octamethyl-1,2,6,8-tetrasilacycloundeca-4,9-diyne 13

Starting materials: 6.9 g (25 mmol) of **21**, 4.7 g (25 mmol) of **16**, 2.4 g (0.35 mol) of lithium powder and 0.3 g (2 mmol) of biphenyl. Yield: 1.4 g (18%) of **13**. Colorless crystals (mp 37 °C) were obtained by Kugelrohr distillation (150 °C/0.2 mbar); $\tilde{\nu}$ (KBr)/cm^{-1} 2955, 2896, 2190, 2158, 1403; δ_H 1.7 (s, 4H), 0.2 (s, 12H), 0.1 (s, 12H), −0.2 (s, 2H); δ_C 106.1 (s), 83.5 (s), 7.4 (t), 3.4 (t), 1.6 (q), −3.2 (q); HRMS (EI) 322.1436, calc. for $C_{15}H_{30}Si_4$: 322.1425 (Found: C 55.88, H 9.50. Calc. for $C_{15}H_{30}Si_4$: C 55.82, H 9.37).

1,1,2,2,6,6,9,9-Octamethyl-1,2,6,9-tetrasilacyclododeca-4,10-diyne 14

Starting materials: 7.3 g (25 mmol) of **22**, 4.7 g (25 mmol) of **16**, 2.4 g (0.35 mol) of lithium powder and 0.3 g (2 mmol) of biphenyl. Yield: 1.2 g (15%) of **14**. Colorless crystals (mp 84 °C) were obtained by Kugelrohr distillation (150 °C/0.2 mbar); $\tilde{\nu}$ (KBr)/cm^{-1} 2957, 2911, 2175, 2148, 1631, 1407; δ_H 1.7 (s, 4H), 0.6 (s, 4H), 0.2 (s, 12H), 0.1 (s, 12H); δ_C 105.3 (s), 82.7 (s), 8.8 (t), 7.2 (t), −2.0 (q), −3.3 (q); HRMS (EI) 336.1583, calc. for $C_{16}H_{32}Si_4$: 336.1581 (Found: C 57.00, H 9.58. Calc. for $C_{16}H_{32}Si_4$: C 57.06, H 9.58).

1,1,2,2,7,7,8,8-Octamethyl-1,2,7,8-tetrasilacyclododeca-4,10-diyne 15

Starting materials: 4.3 g (35 mmol) of **23**, 8.4 g (45 mmol) of **16**, 2.4 g (0.35 mol) of lithium powder and 0.3 g (2 mmol) of biphenyl. Yield: 0.5 g (9%) of **15**. Colorless crystals (mp 91 °C) were obtained by Kugelrohr distillation (170 °C/0.2 mbar); $\tilde{\nu}$ (KBr)/cm^{-1} 2951, 2873, 2187, 1655, 1400; λ_{max} (CH_2Cl_2)/nm 228, 254; δ_H ($CDCl_3$) 1.4 (s, 8H), 0.0 (s, 24H); δ_C ($CDCl_3$) 77.1 (s), 6.5 (t), −2.6 (q); HRMS (EI) 336.1576, calc. for $C_{16}H_{32}Si_4$: 336.1581 (Found: C 57.23, H 9.61. Calc. for $C_{16}H_{32}Si_4$: C 57.06, H 9.58).

X-Ray structural analysis of 8–14

The crystallographic data were collected with a Bruker Smart CCD diffractometer (**8**, **10**) and with an Enraf-Nonius CAD4 diffractometer (**9**, **11**–**14**). Intensities were corrected for Lorentz and polarization effects. An empirical absorption correction was applied to **8** and to **10**–**14**, a numerical method to **9**. The structures were solved by direct methods. The structural parameters of the non-hydrogen atoms were refined anisotropically against F^2 according to a full-matrix least-squares

Table 4 Crystal data and structure refinement for **12**, **13** and **14**

	Compound		
	12	**13**	**14**
Empirical formula	$C_{14}H_{28}Si_4$	$C_{15}H_{30}Si_4$	$C_{16}H_{32}Si_4$
Formula weight	308.7	322.8	336.8
T/K	223(2)	223(2)	223(2)
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/c$	$P\bar{1}$	$P2_1/c$
Z	4	2	4
a/Å	11.139(2)	11.725(2)	8.331(1)
b/Å	14.468(1)	12.678(1)	21.336(5)
c/Å	12.472(2)	8.391(1)	12.510(2)
α/°	90	92.44(1)	90
β/°	97.34(2)	110.73(1)	100.58(1)
γ/°	90	65.26(1)	90
V/Å^3	1993.5(5)	1051.3(2)	2185.9(7)
Absorption coefficient, μ/mm^{-1}	0.29	0.27	0.26
Reflection collected	5018	5268	5593
Independent reflections	4782 (R(int) = 0.027)	5042 (R(int) = 0.011)	5249 (R(int) = 0.024)
R,R_w ($I > 2\sigma(I)$)	0.032, 0.086	0.029, 0.080	0.029, 0.074

technique (**8** and **10**: SHELXTL-PLUS;[14] **9** and **11**–**14**: SHELX-97[15]). Hydrogen atoms were refined isotropically (**8**, **10**) or calculated at fixed positions (H's at the methyl groups of **12**−**14** and all H atoms of **9** and **11**). Disorder effects occurred in the compounds **9** (central atom C5 of the trimethylene bridge with 50:50%) and **11** (C7, C8 of the pentamethylene bridge with 75:25%). The crystallographic data are listed in Tables 3 and 4.†

Photoelectron spectra

The photoelectron spectra of **8**–**15** were recorded with a PS18 spectrometer (Perkin-Elmer) at room temperature. The calibration was performed with Ar (15.76 and 15.94 eV) and Xe (12.13 and 13.44 eV). A resolution of 20 meV was obtained for the $^2P_{3/2}$ line of Ar.

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