

Cyclic Diynes with Dimethylsilyl and Dimethylgermyl Groups in the Bridges. Syntheses and Properties

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The syntheses of the cyclic diynes **8–20** could be achieved. Common to all of them are one dimethylsilyl group (**8, 9, 11, 13**), one dimethylgermyl group (**10, 12, 14**), two dimethylsilyl groups (**15, 17**), two dimethylgermyl groups (**16**), or three dimethylsilyl groups (**18–20**) in the bridges between the triple bonds. X-ray investigations on the single crystals of **8, 9**, and **11** reveal twisted chairlike conformations in the solid state. The He I PE spectra show a very strong splitting of 0.9–1.2 eV between the bands assigned to the removal of electrons from the π_i^- and π_i^+ orbitals of the 10-membered ring (**9, 10, 15, 16, 19**, and **21**). The first ionization energy varies between 8 and 9 eV.

Introduction

It has been shown that steric effects play an important role in the reaction of η^5 -(cyclopentadienyl)cobalt (CpCo) species with cyclic diynes.¹ As an example, we show in Scheme 1 the reactions of 1,6-cyclodecadiyne (**1**) and its derivative **2** with cyclopropano groups in the propargylic positions of the 10-membered rings with CpCo(CO)₂. These reactions yield in the case of **1** the inter- and intramolecular reaction products **5** and **6**.² The reaction of **2** with CpCo(CO)₂ gave neither the inter- nor the intramolecular product. Only when it was reacted with bis(ethylene)(η^5 -pentamethylcyclopentadienyl)cobalt (Cp*Co(C₂H₄)₂) could the intermolecular product **7** be isolated.³ To rationalize this different behavior, we invoked steric effects and argued that in the corresponding intermediates **3** and **4** large groups in the propargylic positions may prevent a second intramolecular ring closure to a second cyclobutadiene ring. The larger Cp* cap instead of the smaller Cp cap may help to force the triple bonds together in **4**.⁴

To find out more about the role of steric effects, especially in the propargylic positions, we synthesized a number of cyclic diynes and studied their structures, bonding properties, and reactions with various CpCoL₂ reagents. In this paper we report the syntheses as well as the structural and bonding properties of **8–20** (Chart 1).

Syntheses

Common to the diynes **8–16** and **18–20** is at least one dimethylsilyl or dimethylgermyl unit in the prop-

argylic position of the ring. To synthesize such species, one can think of several routes. Three of them are outlined in Scheme 2. In one case (route **A**) the ring system is constructed first and the triple bonds are introduced later via the functional groups *F*. In the other three ways shown in Scheme 2, the triple bonds are present already in the building blocks.

Route **A** is usually avoided, because it comprises several steps to introduce the triple bond and therefore a long and tedious synthesis results. It has been applied successfully to synthesize carbocyclic rings such as **1** and 1,5-cyclononadiyne.^{5,6} For larger hydrocarbon rings the route **B1** has been applied at several occasions for pure hydrocarbons.^{7–9} However, the application of this route to silicon-containing diynes has been restricted to the preparation of 6-isopropylidene-1,1-dimethyl-1-silacyclodeca-3,8-diyne only.¹⁰ We ascribe this limitation to the fact that the dimethylsilyl group stabilizes carbanion formation in the α -position.¹¹ This in turn favors side reactions via allenyl intermediates. Therefore, this route is limited to only very reactive dihalides.

More promising for silicon-containing species was route **B2**, which served already in the preparation of **9** and **15**.¹² As an example, we show in Scheme 3 the preparation of **9**. According to this procedure, 1,9-dibromononane-2,7-diyne (**22**) was reacted with dichlorodimethylsilane (**23**) in the presence of magnesium and

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(2) Gleiter, R.; Karcher, M.; Ziegler, M. L.; Nuber, B. *Tetrahedron Lett.* **1987**, *28*, 195.

(3) Gleiter, R.; Merger, R.; Irngartinger, H.; Nuber, B. *J. Org. Chem.* **1993**, *58*, 2025.

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Scheme 1

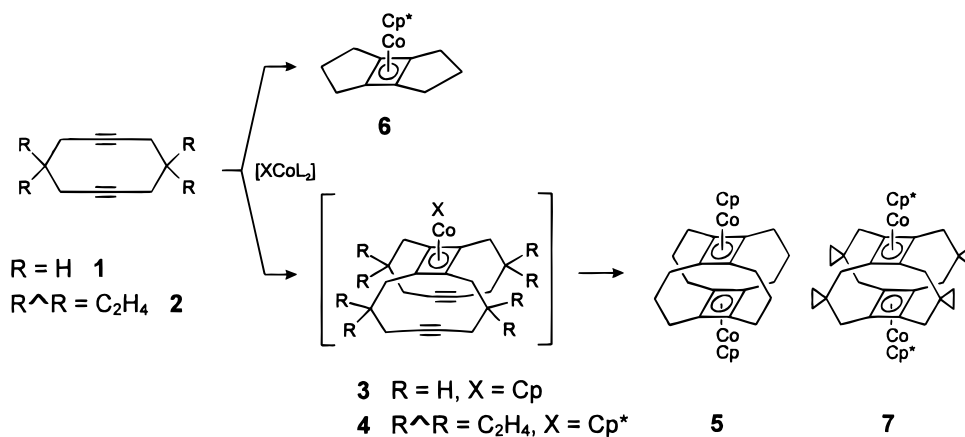
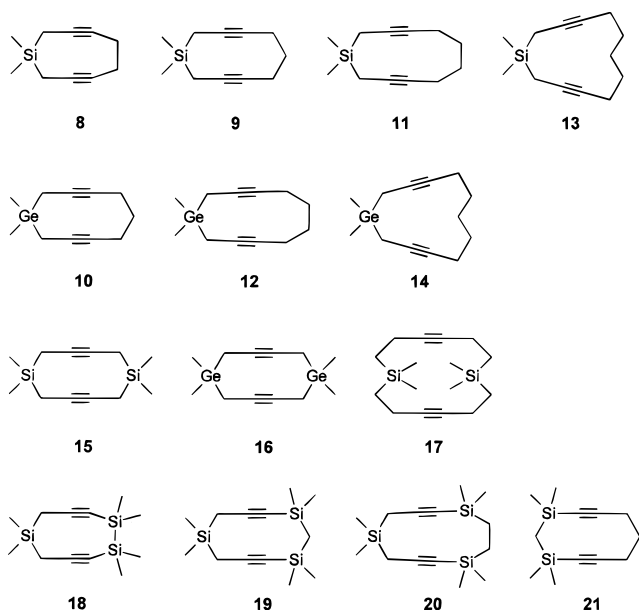
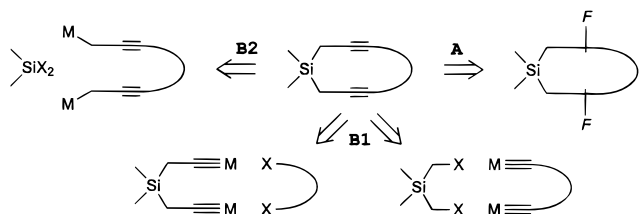


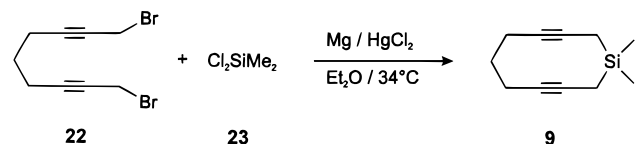
Chart 1



Scheme 2



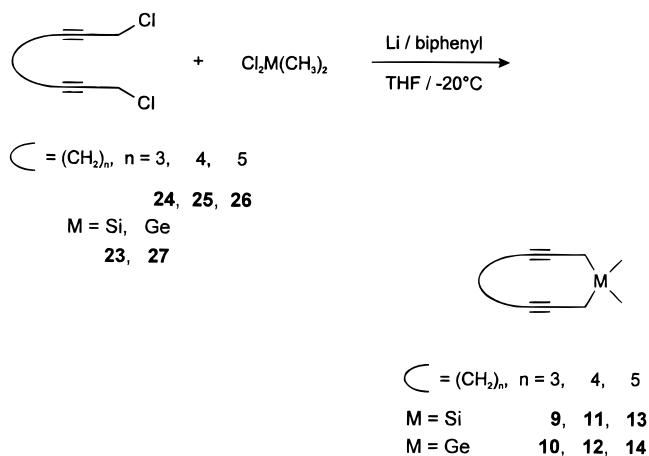
Scheme 3



mercuric chloride. The advantage of this procedure is its simplicity and the availability of the starting materials. However, the yields leave much to be desired. In the case of the example shown in Scheme 3, the yield of **9** was only 5%.

To improve the yield in this reaction, we replaced magnesium by another metal, assuming that the intermediately formed Grignard compounds might give rise to allenic species in a SE_2' reaction. This assumption

Scheme 4

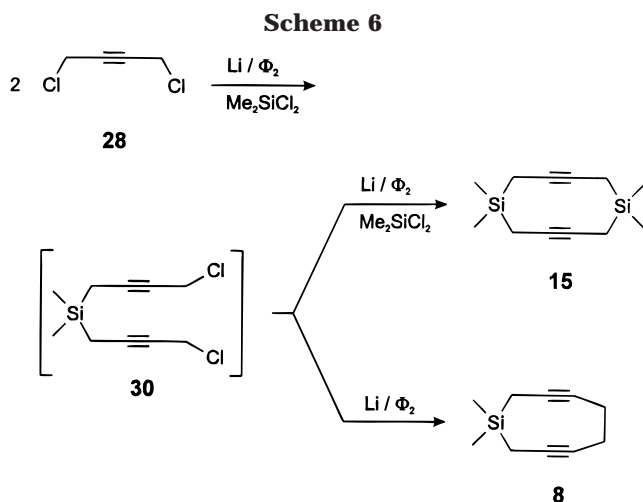
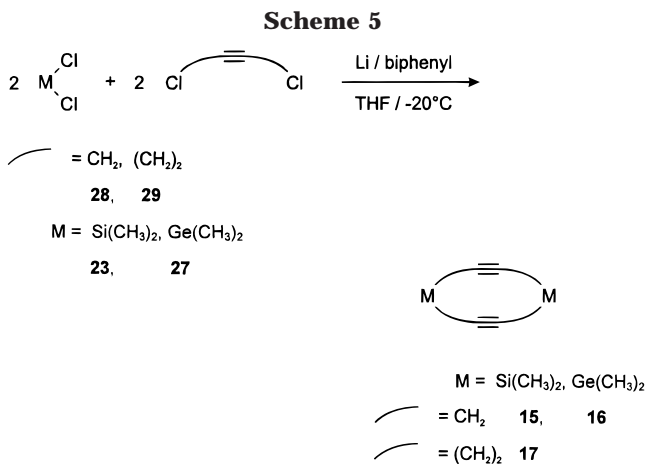


was confirmed by the observation that replacement of diethyl ether by the more basic tetrahydrofuran in the reaction shown in Scheme 3, yielded no **9** at all. To circumvent the assumed side reactions, we applied lithium, because primary propargylic lithium compounds are known to react only according to an SE_2 mechanism.^{13,14}

Indeed, when we carried out the reaction shown in Scheme 3 with lithium in the presence of catalytic amounts of biphenyl, the yield of **9** was increased to 10%. Additionally, we found that a large number of systems related to **9** are accessible by this protocol (Scheme 4). Starting with 1,9-dichloronona-2,7-diyne (**24**), 1,10-dichlorodeca-2,8-diyne (**25**), 1,11-dichloroundeca-2,9-diyne (**26**), and dichlorodimethylsilane (**23**) and -germane (**27**) we prepared the cyclic dienes **9–14** in 10–22% yield. The protocol described in Scheme 4 can be carried over to the synthesis of the cycles with two dimethylsilyl and two dimethylgermyl groups, such as **15–17** via a four-component cyclization reaction (Scheme 5). As starting materials we used as alkyne components 1,4-dichloro-2-butyne (**28**) and 1,6-dichloro-3-hexyne (**29**). The other components were either **23** or **27**. With these starting materials 1,1,6,6-tetramethyl-1,6-disilacyclodeca-3,8-diyne (**15**) could be isolated in 20% yield.

(13) Yamagisawa, A.; Habane, S.; Yamamoto, H. *J. Am. Chem. Soc.* **1991**, *113*, 8593. Yamagisawa, A.; Yamamoto, H. In *Active Metals*; Furstner, A., Ed.; VCH: Weinheim, Germany, 1996; p 62, and references therein.

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Similarly, 1,1,8,8-tetramethyl-1,8-disilacyclotetradeca-4,11-diyne (**17**; 11% yield) and 1,1,6,6-tetramethyl-1,6-digermacyclodeca-3,8-diyne (**16**; 17% yield) could be obtained.

To get some insight into the mechanism of this reaction, we varied the ratio of 1,4-dichloro-2-butyne (**28**) and dichlorodimethylsilane (**23**) (see Scheme 6). If the ratio of **23** and **28** was 1:2, we obtained 1,1-dimethylcyclonona-3,7-diyne (**8**) in 15% yield, while **15** was present only in traces. This result could be reversed by using **23** and **28** in a ratio of 1:1. In this case **15** was formed and not **8**. We rationalize this change in the products by assuming that **30** was formed as an intermediate, as shown in Scheme 6.

The procedures summarized in Scheme 3 could be extended to 1,8-dichloro-4,4,5,5-tetramethyl-4,5-disilaoccta-2,6-diyne (**31**), 1,9-dichloro-4,4,6,6-tetramethyl-4,6-disilano-2,7-diyne (**32**), and 1,10-dichloro-4,4,7,7-tetramethyl-4,7-disiladeca-2,8-diyne (**33**) to yield the cycles **18–20** in 17–32% yield (Scheme 7).

Structural Investigations

Single crystals of **8**, **9**, and **11** could be obtained by crystallization from pentane at -20°C . In the solid state of **8** and **11** we observed a twisted chairlike conformation. Due to a disorder in the propano bridge we observe for **9** the chair as well as the boat conformation in the crystal. As examples we have shown the molecular structures of **8**, **9** (chair conformation), and **11** in Figure

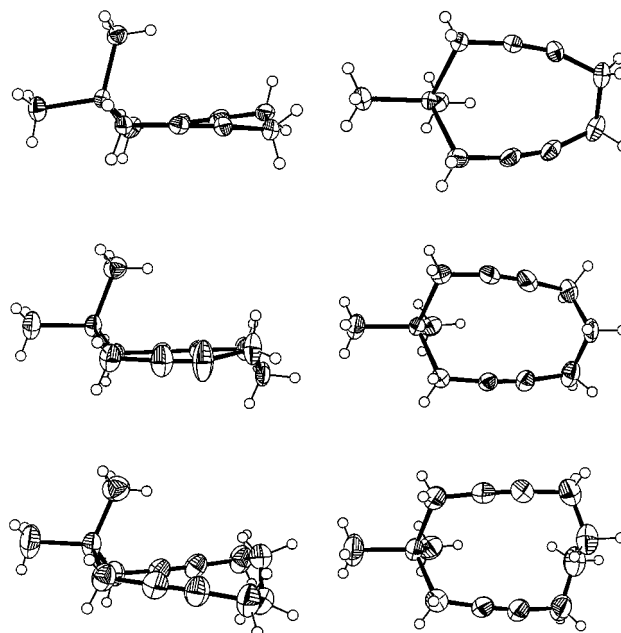


Figure 1. ORTEP plots of the molecular structures of **8** (top), **9** (center), and **11**: (right) top view; (left) side view. The plots are presented at 50% probability of the thermal ellipsoids.

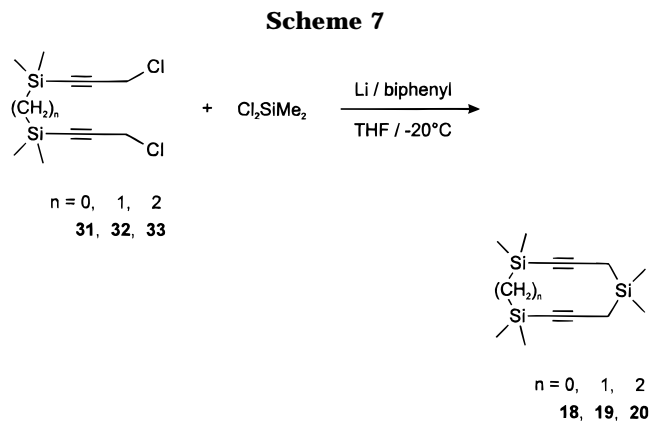


Table 1. Comparison of Selected Bond Lengths (Å), Bond Angles (deg), and Torsion Angles (deg) in **8**, **9**, and **11**^a

transannular dist		deformation from 180° at the sp centers		torsion	
a	b	a	b	C _{sp} -C _{sp} ...C _{sp} -C _{sp}	
8	3.104(2)	2.734(2)	8.8	16.0	9.9
9	3.232(2)	3.053(2)	7.4	10.5	3.8
11	3.500(2)	3.730(3)	3.3	6.4	13.9

^a Bond and torsion angles are average values.

1. In Table 1 we have compared the transannular distances between the two termini of the triple bonds (**a**, **b**), the deformation from 180° at the sp centers, and the torsion angles between the triple bonds. As anticipated, the distances between the sp centers **a** and **b** increase from **8** to **11**; also the deviation from linearity is largest in the case of the 9-membered ring of **8** (9, 16°) and smallest in the 11-membered ring of **11** (3, 6°).

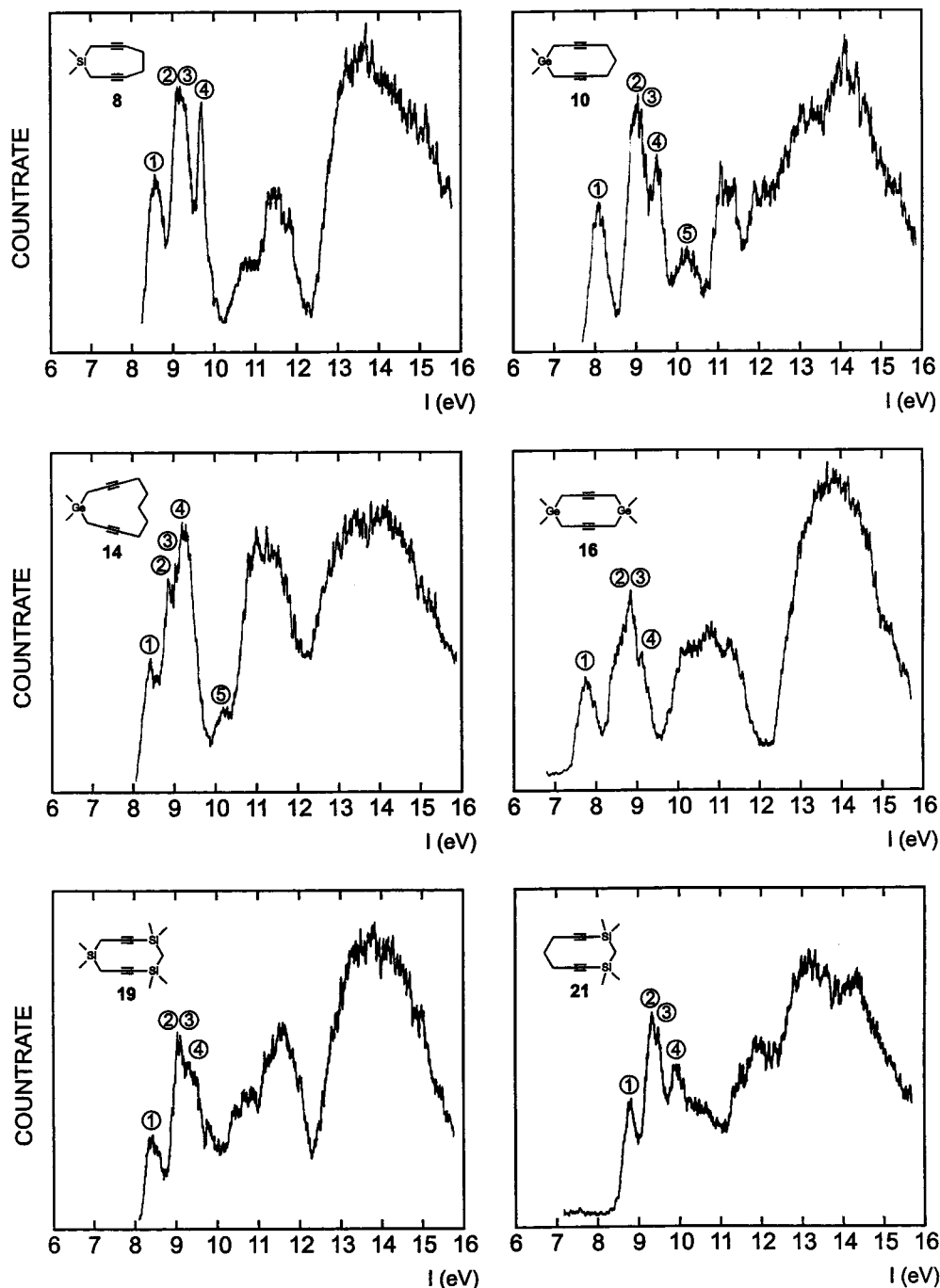


Figure 2. He I photoelectron spectra of **8**, **10**, **14**, **16**, **19**, and **21**.

Photoelectron Spectroscopic Investigations

He I photoelectron spectroscopy is a good means to study interactions of nonconjugated π -systems. Therefore, we have investigated the He I photoelectron (PE) spectra of **8**, **10**–**14**, **16**, **17**, **19**, and **21**.¹⁵ The PE spectra of **9** and **15** have been reported earlier.¹⁰ To analyze the interactions in these species, we subdivide them in two groups, such as **8**–**14** and **15**–**17**, **19**, and **21**. Common to all spectra are a series of bands between 8 and 10 eV, followed by close-lying transitions at higher energies. As examples we have shown in Figure 2 the PE spectra of **8**, **10**, **14**, **16**, **19**, and **21**.

The ionization energies of **8**, **10**–**14**, **16**, **17**, **19**, and **21** are collected in Table 2. To interpret the first bands of the PE spectra, we compare them with those of related species. We also correlated the individual bands with values from calculated orbital energies, assuming the validity of Koopmans' theorem.¹⁶ The calculations were performed by ab initio methods (RHF/3-21G* basis).¹⁷ The orbital energies are based on the optimized geometries.

In Figure 3 we have compared the first four bands of the PE spectra of **8**–**14** with each other. For the sake of clarity we have subdivided the π -molecular orbitals into those which are mainly localized in the plane (π_i) spanned by the four sp centers and those which are

(15) The synthesis of **21** will be published in a forthcoming paper by the same authors.

(16) Koopmans, T. *Physica* **1934**, *1*, 104.

localized perpendicularly (π_0) to this plane. From each set we can construct two linear combinations, a bonding one (π^+) and an antibonding one (π^-). It is seen that with the exception of **8** the splitting of π_0^+ and π_0^- remains essentially constant (0.2–0.4 eV). Only when both triple bonds are relatively close together, as in the case of **8**, does the splitting between π_0^+ and π_0^- increase to 0.6 eV. The splitting of the π_i bands is largest in the cases of **9** and **10**. This is anticipated, because the through-bond interaction is largest in the case of propeno groups, as demonstrated by the PE spectrum of **1**.⁶ We also notice slightly lower ionization energies for the germanium compounds **10**, **12**, and **14** as compared to the corresponding silicon rings **9**, **11**, and **13**. We ascribe this to the lower basis orbital energy of a Ge–C bond as compared to a Si–C bond. This assumption is supported by the first ionization energies of tetramethylsilane (10.57 eV)¹⁸ and tetramethylgermane (10.23 eV).¹⁸ The lower ionization energy of a Ge–C σ -orbital as compared to the Si–C σ -orbital is also the reason for the band at 10 eV in the PE spectra of **10**, **12**, and **14**. This band we can assign to the ionization from the antibonding linear combination of the σ -orbital localized at the Ge(CH₃)₂ group. The corresponding band in the PE spectra of the silicon congeners **9**, **11**, and **13** is expected at higher energies.

In Figure 4 we have correlated the first bands of the PE spectra of **15**–**17**, **19**, and **21** with that of **1**.⁶ With the exception of **17**, we are dealing here with 10-membered rings in which the triple bonds are tethered by chains composed of 3-membered bridges. Due to the aforementioned optimal through-bond interaction between three-membered bridges and π -systems we expect and find a large splitting between the peaks assigned to the in plane π MOs π_i^- and π_i^+ . The energy difference between π_i^- and π_i^+ is largest in the PE spectrum of **1** (1.6 eV) and decreases to 1.1–1.2 eV in the PE spectra of the 2-fold substitution (**15**, **16**, and **21**) and is smallest in the PE spectrum of the trisubstituted ring system **19** (0.9 eV). We also find that the interaction between the π_i linear combination and the Si–C σ -bonds is larger when the Si(CH₃)₂ group is placed in a propargylic position (**15**) as compared to the α -positions of the triple bonds (**21**). This observation can be rationalized on the basis of second-order perturbation theory.¹⁹ Accordingly, the interaction between the carbon–silicon σ -bond and the π_i orbital depends on the basis orbital energies and the overlap integral of the interacting fragments. Due to the fact that the AO coefficients of a Si–C σ -orbital are larger at carbon than at silicon, the overlap integral between the C–Si bond and π_i is larger in **15** than in **21**. As a result, the π_i bands in **1** and **21** are very similar

(17) We used the Gaussian 94 program: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanyakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. Gaussian94, Revision B1; Gaussian, Inc., Pittsburgh, PA, 1995.

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Table 2. Comparison between the Recorded Vertical Ionization Energies ($I_{v,j}$) and the Calculated Orbital Energies ($-\epsilon_j$) of **8, **10**–**14**, **16**, **17**, **19**, and **21**^a**

compd	band	$I_{v,j}$	assignt		$-\epsilon_j(3-21G^*)$
8	1	8.5	44a	π_i^-	8.95
	2	9.0	43a	π_0^-	9.50
	3	9.1	42a	π_i^+	9.71
	4	9.6	41a	π_0^+	10.11
10	1	8.0	21a''	π_i^-	8.47
	2	9.0	36a'	π_0^+	9.49
	3	9.1	20a''	π_0^-	9.57
	4	9.4	35a'	π_i^+	10.03
	5	10.2	34a'	$\sigma_{\text{Ge-Me}}$	11.15
11	1	8.4	52a	π_i^-	8.99
	2	9.1	51a	π_i^+	9.54
	3	9.1	50a	π_0^-	9.64
	4	9.4	49a	π_0^+	8.89
12	1	8.2	61a	π_i^-	8.84
	2	9.0	60a	π_i^+	9.35
	3	9.1	59a	π_0^-	9.64
	4	9.3	58a	π_0^+	9.86
	5	10.2	57a	$\sigma_{\text{Ge-Me}}$	11.17
13	1	8.6	22a''	π_i^-	8.86
	2	9.0	34a'	π_i^+	9.58
	3	9.1	21a''	π_0^-	9.61
	4	9.3	33a'	π_0^+	9.92
14	1	8.4	25a''	π_i^-	8.71
	2	8.9	40a'	π_i^+	9.41
	3	9.0	24a''	π_0^-	9.61
	4	9.2	39a'	π_0^+	9.86
	5	10.2	38a'	$\sigma_{\text{Ge-Me}}$	11.16
16	1	7.8	14a _u	π_i^-	8.34
	2	8.9	13b _g	π_0^-	9.29
	3	8.9	26a _g	π_i^+	9.36
	4	9.1	25b _u	π_0^+	9.41
17	1	8.8	76a	π_i^-	9.46
	2	9.0	75a	π_0^+	9.72
	3	9.0	74a	π_0^-	9.74
	4	9.2	73a	π_i^+	9.96
19	1	8.4	30a''	π_i^-	9.06
	2	9.0	42a'	π_0^+	9.80
	3	9.1	29a''	π_0^-	9.82
	4	9.3	41a'	π_i^+	10.19
21	1	8.9	27a''	π_i^-	9.26
	2	9.4	26a''	π_0^-	9.89
	3	9.5	33a'	π_0^+	10.00
	4	10.0	32a'	π_i^+	10.61

^a The orbital energies are based on HF-SCF calculations using a 3-21G* basis set. All values in eV.

in energy, while those of **15** are strongly destabilized. In the PE spectrum of **16** the destabilization of π_i^+ is even so high that its ionization energy is lower than the corresponding π_0^+ band.

Conclusion

We have presented a synthetic protocol which allows the synthesis of 10-membered cyclic diynes with at least one dimethylsilyl or one dimethylgermyl group in the propargylic position. The investigations of the structures of **8**, **9**, and **11** reveal very similar molecular conformations. The PE spectra show an especially strong splitting between the first and fourth band for the 10-membered rings (**9**, **10**, **15**, **16**, **19**, and **21**). This can be ascribed to a strong interaction between the in-plane π -linear combinations of the triple bonds and the bridges.

Experimental Section

General Methods. All reactions were carried out under an argon atmosphere with magnetic stirring. The solvents were purified and dried using standard procedures. The ¹H and ¹³C

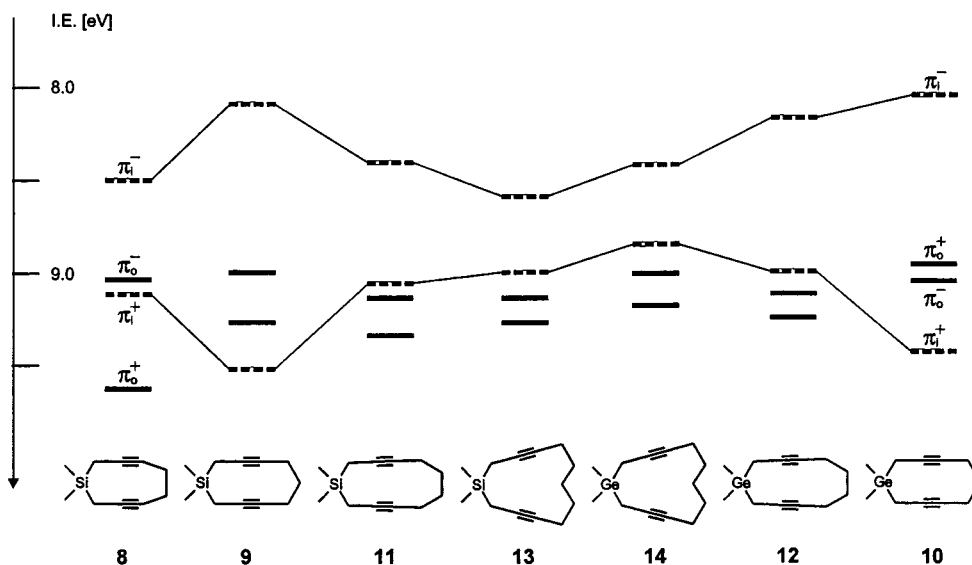


Figure 3. Correlation between the first bands of the PE spectra of **8–14**.

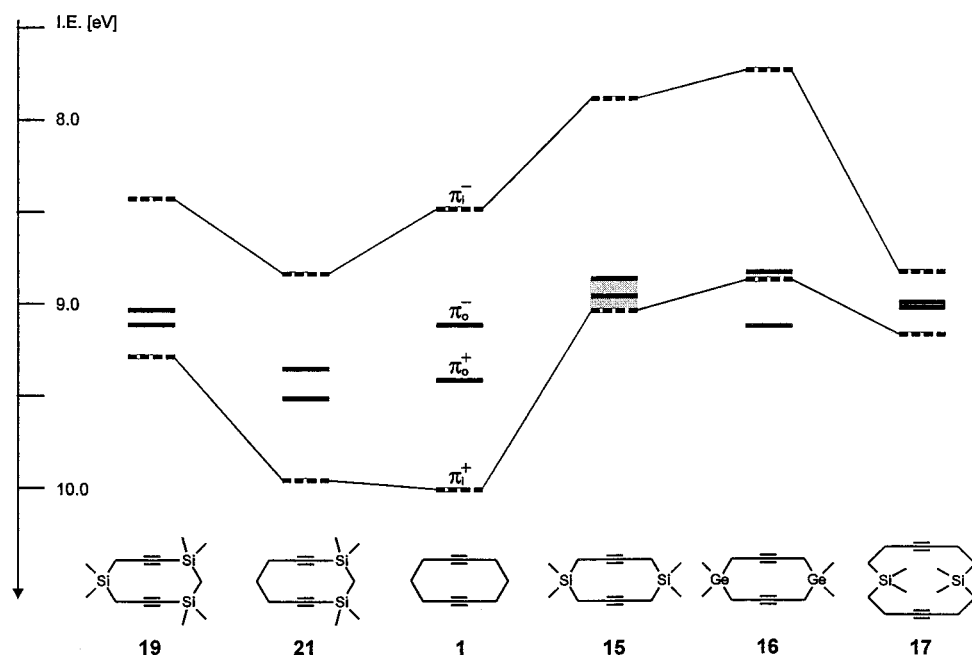


Figure 4. Correlation between the first bands of the PE spectra of **1, 15–17, 19, and 21**.

NMR spectra were recorded at 300 and 75 MHz, respectively, in CDCl_3 if not otherwise noted. Elemental analyses were performed at the Mikroanalytisches Laboratorium der Universität Heidelberg, Germany.

General Procedure. To 2.4 g (0.35 mol) of lithium powder and 0.3 g (82 mmol) of diphenyl was added at -75°C 350 mL of dry THF in such a way that the solution remained deep green. Subsequently, the solution was warmed to -20°C and a solution of 25 mmol of the propargylic chloride and 25 mmol of either **23** or **27** in 75 mL of THF was added within 20–30 min. This was accompanied by a discharge of the color. After the color (red to green) appeared again (usually 30 min after the addition was completed), the lithium was filtered in the presence of air to destroy the radical anion of diphenyl (green). The solvent was removed and the crude material purified by chromatography on silica gel with CCl_4 (except **9**, for which we used Alox III with petroleum ether). Further purification was achieved by Kugelrohr distillation to yield colorless crystals.

1,1-Dimethyl-1-silacyclonona-3,7-diyne (8). Starting materials: 12.3 g (100 mmol) of **28**, 6.5 g (50 mmol) of **23**, 4.9 g

(0.7 mol) of lithium powder, and 0.9 g (6 mmol) of diphenyl. Yield: 1.23 g (15%) of **8**. Colorless crystals (mp 60°C) were obtained by Kugelrohr distillation ($110^\circ\text{C}/1.2\text{ mbar}$). ^1H NMR: δ 2.3 (m, 4H), 1.6 (m, 4H), 0.2 (s, 6H). ^{13}C NMR: δ 86.6 (s), 81.4 (s), 20.2 (t), 7.6 (t), -2.6 (q). IR (KBr, cm^{-1}): 2958, 2919, 2884, 2848, 2203, 1731, 1651, 1440, 1403. HRMS (EI): m/e calcd for $\text{C}_{10}\text{H}_{14}\text{Si}$, 162.0865; found, 162.0859. Anal. Calcd for $\text{C}_{10}\text{H}_{14}\text{Si}$: C, 74.00; H, 8.69. Found: C, 74.21; H, 8.88.

1,1-Dimethyl-1-silacyclodeca-3,8-diyne (9).¹² Starting materials: 7.6 g (40 mmol) of **24**, 5.2 g (40 mmol) of **23**, 3.5 g (0.5 mol) of lithium powder, and 0.6 g (4 mmol) of diphenyl. Yield: 0.94 g (13%) of **9**.

1,1-Dimethyl-1-germacyclodeca-3,8-diyne (10). Starting materials: 2.3 g (12 mmol) of **24**, 2.1 g (12 mmol) of **27**, 0.8 g (0.12 mol) of lithium powder, 0.2 g (1 mmol) of diphenyl, and 85 mL of THF. Yield: 0.26 g (10%) of **10**. Colorless crystals (mp 61°C) were obtained by Kugelrohr distillation ($140^\circ\text{C}/0.3\text{ mbar}$). ^1H NMR: δ 2.2 (m, 4H), 1.7 (t, 4H), 1.6 (m, 2H), 0.3 (s, 6H). ^{13}C NMR: δ 79.6 (s), 79.4 (s), 26.2 (t), 19.7 (t), 5.9 (t), -4.0 (q). IR (KBr, cm^{-1}): 2953, 2932, 2902, 2835, 2219, 1700, 1651, 1434. HRMS (EI): m/e calcd for $\text{C}_{11}\text{H}_{16}^{74}\text{Ge}$,

Table 3. Crystal Data and Structure Refinement for **8**, **9**, and **11**

	8	9	11
empirical formula	C ₁₀ H ₁₄ Si	C ₁₁ H ₁₆ Si	C ₁₂ H ₁₈ Si
fw	162.3	176.3	190.4
cryst color	colorless	colorless	colorless
cryst size (mm)	0.38 × 0.36 × 0.12	0.50 × 0.50 × 0.30	0.40 × 0.30 × 0.20
temp (K)	200(2)	223(2)	268(2)
wavelength (Å)	0.71073	0.71073	0.71073
cryst syst	monoclinic	monoclinic	monoclinic
space group	<i>P2</i> ₁ / <i>n</i>	<i>P2</i> ₁ / <i>n</i>	<i>P2</i> ₁ / <i>n</i>
<i>Z</i>	4	4	4
<i>a</i> (Å)	8.4899(4)	10.794(2)	10.736(1)
<i>b</i> (Å)	7.3559(4)	9.411(1)	10.125(1)
<i>c</i> (Å)	15.4305(8)	10.810(1)	11.307(2)
β (deg)	97.780(1)	99.73(1)	102.52(1)
<i>V</i> (Å ³)	954.76(8)	1082.3(3)	1199.9(3)
<i>D</i> _{calcd} (Mg/m ³)	1.13	1.08	1.05
abs coeff, μ (mm ⁻¹)	0.18	0.17	0.15
θ range for data collection (deg)	2.6–25.4	2.5–28.0	2.4–28
index ranges	–8 ≤ <i>h</i> ≤ 9, –8 ≤ <i>k</i> ≤ 8, –18 ≤ <i>l</i> ≤ 18	0 ≤ <i>h</i> ≤ 14, 0 ≤ <i>k</i> ≤ 12, –14 ≤ <i>l</i> ≤ 14	0 ≤ <i>h</i> ≤ 14, 0 ≤ <i>k</i> ≤ 13, –14 ≤ <i>l</i> ≤ 14
no. of rflns collected	6692	2729	3022
no. of indep rflns	1652 (<i>R</i> (int) = 0.020)	2598 (<i>R</i> (int) = 0.009)	2876 (<i>R</i> (int) = 0.008)
max, min transmissn	0.979, 0.771	0.955, 0.929	0.972, 0.958
no. of obsd data/params	1435/156	2164/153	1870/184
goodness of fit on <i>F</i> ²	1.04	1.06	1.04
<i>R</i> , <i>R</i> _w	0.027, 0.072	0.039, 0.106	0.042, 0.102
($\Delta\rho$) _{max} , ($\Delta\rho$) _{min} (e Å ⁻³)	0.23, –0.15	0.31, –0.31	0.29, –0.17

222.0464; found, 222.0465. Anal. Calcd for C₁₁H₁₆Ge: C, 59.83; H, 7.30. Found: C, 59.66; H, 7.29.

1,1-Dimethyl-1-silacycloundeca-3,9-diyne (11). Starting materials: 8.1 g (40 mmol) of **25**, 5.2 g (40 mmol) of **23**, 3.5 g (0.5 mol) of lithium powder, and 0.6 g (4 mmol) of diphenyl. Yield: 1.21 g (16%) of **11**. Colorless crystals (mp 66 °C) were obtained by Kugelrohr distillation (120 °C/0.3 mbar). ¹H NMR (CDCl₃, 200 MHz): δ 1.9 (m, 4H), 1.5 (m, 4H), 1.4 (t, 4H), 0.0 (s, 6H). ¹³C NMR (CDCl₃, 50 MHz): δ 79.9 (s), 77.1 (s), 27.6 (t), 19.8 (t), 6.4 (t), –3.5 (q). IR (KBr, cm⁻¹): 2952, 2842, 2213, 1436. HRMS (EI): *m/e* calcd for C₁₂H₁₈Si, 190.1178; found, 190.1178. Anal. Calcd for C₁₂H₁₈Si: C, 75.72; H, 9.53. Found: C, 76.00; H, 9.73.

1,1-Dimethyl-1-germacycloundeca-3,9-diyne (12). Starting materials: 2.4 g (12 mmol) of **25**, 2.1 g (12 mmol) of **27**, 0.8 g (0.12 mol) of lithium powder, 0.2 g (1 mmol) of diphenyl, and 85 mL of THF. Yield: 0.62 g (22%) of **12**. Colorless crystals (mp 63 °C) were obtained by Kugelrohr distillation (140 °C/0.3 mbar). ¹H NMR: δ 2.1 (m, 4H), 1.7 (t, 4H), 1.6 (m, 4H), 0.3 (s, 6H). ¹³C NMR: δ 79.7 (s), 78.1 (s), 27.6 (t), 19.6 (t), 5.7 (t), –3.6 (q). IR (KBr, cm⁻¹): 2951, 2932, 2899, 2863, 2842, 2214, 1700, 1651, 1449, 1436. HRMS (EI): *m/e* calcd for C₁₂H₁₈⁷⁴Ge, 236.0620; found, 236.0606. Anal. Calcd for C₁₂H₁₈Ge: C, 61.37; H, 7.72. Found: C, 61.46; H, 7.70.

1,1-Dimethyl-1-silacyclododeca-3,10-diyne (13). Starting materials: 8.7 g (40 mmol) of **26**, 5.2 g (40 mmol) of **23**, 3.5 g (0.5 mol) of lithium powder, and 0.6 g (4 mmol) of diphenyl. Yield: 1.02 g (12%) of **13**. Colorless crystals (mp 53 °C) were obtained by Kugelrohr distillation (120 °C/0.2 mbar). ¹H NMR: δ 2.2 (m, 4H), 1.8 (m, 2H), 1.5 (t, 4H), 1.4 (m, 4H), 0.1 (s, 6H). ¹³C NMR: δ 78.3 (s), 77.9 (s), 25.3 (t), 24.6 (t), 17.9 (t), 6.5 (t), –3.4 (q). IR (KBr, cm⁻¹): 2934, 2856, 2216, 1631, 1457, 1437. HRMS (EI): *m/e* calcd for C₁₃H₂₀Si, 204.1334; found, 204.1367. Anal. Calcd for C₁₃H₂₀Si: C, 76.40; H, 9.86. Found: C, 76.11; H, 9.89.

1,1-Dimethyl-1-germacyclododeca-3,10-diyne (14). Starting materials: 2.6 g (12 mmol) of **26**, 2.1 g (12 mmol) of **27**, 0.8 g (0.12 mol) of lithium powder, 0.2 g (1 mmol) of diphenyl, and 85 mL of THF. Yield: 0.29 g (10%) of **14**. Colorless crystals (mp 52 °C) were obtained by Kugelrohr distillation (140 °C/0.3 mbar). ¹H NMR: δ 2.2 (m, 4H), 1.8 (m, 2H), 1.7 (t, 4H), 1.4 (m, 4H), 0.3 (s, 6H). ¹³C NMR: δ 78.9 (s), 78.4 (s), 25.6 (t), 24.8 (t), 18.0 (t), 5.8 (t), –3.6 (q). IR (KBr, cm⁻¹): 2978, 2930, 2857, 2322, 2216, 2172, 1453, 1436. HRMS (EI): *m/e* calcd for

C₁₃H₂₀⁷⁴Ge, 250.0777; found, 250.0772. Anal. Calcd for C₁₃H₂₀Ge: C, 62.74; H, 8.10. Found: C, 62.73; H, 7.98.

1,1,6,6-Tetramethyl-1,6-disilacyclododeca-3,8-diyne (15).¹² Starting materials: 4.9 g (40 mmol) of **28**, 5.2 g (40 mmol) of **23**, 2.4 g (0.35 mol) of lithium powder, and 0.6 g (4 mmol) of diphenyl. Yield: 0.88 g (20%) of **15**.

1,1,6,6-Tetramethyl-1,6-digermacyclododeca-3,8-diyne (16). Starting materials: 2.2 g (18 mmol) of **28**, 3.1 g (18 mmol) of **27**, 1.3 g (0.18 mol) of lithium powder, 0.3 g (2 mmol) of diphenyl, and 85 mL of THF. Yield: 0.48 g (17%) of **16**. Colorless crystals (mp 139 °C) were obtained by Kugelrohr distillation (140 °C/0.3 mbar). ¹H NMR (CDCl₃, 200 MHz): δ 1.7 (s, 8H), 0.3 (s, 12H). ¹³C NMR (CDCl₃, 50 MHz): δ 77.3 (s), 6.8 (t), –2.9 (q). IR (KBr, cm⁻¹): 2975, 2896, 2210, 1651, 1412. HRMS (EI): *m/e* calcd for C₁₂H₂₀⁷⁴Ge₂, 311.9989; found, 311.9980. Anal. Calcd for C₁₂H₂₀Ge₂: C, 46.57; H, 6.51. Found: C, 46.62; H, 6.36.

1,1,8,8-Tetramethyl-1,8-disilacyclotetradeca-4,11-diyne (17). Starting materials: 1.6 g (7 mmol) of **29**, 0.9 g (7 mmol) of **23**, 0.5 g (0.07 mol) of lithium powder, 0.1 g (0.5 mmol) of diphenyl, and 85 mL of THF. Yield: 0.11 g (11%) of **17**. Colorless crystals (mp 45 °C) were obtained by Kugelrohr distillation (160 °C/0.2 mbar). ¹H NMR: δ 2.2 (m, 8H), 0.9 (m, 8H), 0.0 (s, 12H). ¹³C NMR: δ 81.8 (s), 15.0 (t), 13.4 (t), –3.6 (q). IR (KBr, cm⁻¹): 2952, 2901, 2842, 1700, 1632, 1437, 1408. HRMS (EI): *m/e* calcd for C₁₆H₂₈Si₂, 276.1730; found, 276.1693. Anal. Calcd for C₁₆H₂₈Si₂: C, 69.49; H, 10.20. Found: C, 69.28; H, 10.26.

1,1,2,2,6,6-Hexamethyl-1,2,6-trisilacyclonona-3,8-diyne (18). Starting materials: 6.6 g (25 mmol) of **31**, 3.2 g (25 mmol) of **23**, 2.4 g (0.35 mol) of lithium powder, and 0.3 g (2 mmol) of diphenyl. Yield: 1.05 g (17%) of **18**. Colorless crystals (mp 76 °C) were obtained by Kugelrohr distillation (125 °C/0.3 mbar). ¹H NMR: δ 1.7 (s, 4H), 0.18 (s, 6H), 0.17 (s, 12H). ¹³C NMR: δ 109.9 (s), 84.2 (s), 8.5 (t), –3.0 (q), –3.7 (q). IR (KBr, cm⁻¹): 2956, 2895, 2147, 2053, 1405. HRMS (EI): *m/e* calcd for C₁₂H₂₂Si₃, 250.1029; found, 250.1014. Anal. Calcd for C₁₂H₂₂Si₃: C, 57.52; H, 8.85. Found: C, 57.62; H, 8.71.

1,1,3,3,7,7-Hexamethyl-1,3,7-trisilacyclododeca-4,9-diyne (19). Starting materials: 6.9 g (25 mmol) of **32**, 3.2 g (25 mmol) of **23**, 2.4 g (0.35 mol) of lithium powder, and 0.3 g (2 mmol) of diphenyl. Yield: 2.09 g (32%) of **19**. Colorless crystals (mp 43 °C) were obtained by Kugelrohr distillation (130 °C/0.3 mbar). ¹H NMR: δ 1.7 (s, 4H), 0.2 (s, 6H), 0.1 (s,

12H), -0.2 (s, 2H). ^{13}C NMR: δ 105.7 (s), 84.3 (s), 8.4 (t), 2.9 (t), 1.4 (q), -3.7 (q). IR (KBr, cm^{-1}): 2960, 2899, 2163, 1406. HRMS (EI): m/e calcd for $\text{C}_{13}\text{H}_{24}\text{Si}_3$, 264.1186; found, 264.1185. Anal. Calcd for $\text{C}_{13}\text{H}_{24}\text{Si}_3$: C, 59.01; H, 9.14. Found: C, 59.09; H, 9.18.

1,1,4,4,8,8-Hexamethyl-1,4,8-trisilacycloundeca-5,10-diyne (20). Starting materials: 7.3 g (25 mmol) of **33**, 3.2 g (25 mmol) of **23**, 2.4 g (0.35 mol) of lithium powder, and 0.3 g (2 mmol) of diphenyl. Yield: 1.24 g (18%) of **20**. Colorless crystals (mp 59 °C) were obtained by Kugelrohr distillation (130 °C/0.2 mbar). ^1H NMR: δ 1.7 (s, 4H), 0.6 (s, 4H), 0.2 (s, 6H), 0.1 (s, 12H). ^{13}C NMR: δ 103.7 (s), 83.3 (s), 7.9 (t), 7.8 (t), -2.1 (q), -3.6 (q). IR (KBr, cm^{-1}): 2958, 2899, 2871, 2159, 1409. HRMS (EI): m/e calcd for $\text{C}_{14}\text{H}_{26}\text{Si}_3$, 278.1342; found, 278.1373. Anal. Calcd for $\text{C}_{13}\text{H}_{24}\text{Si}_3$: C, 60.35; H, 9.41. Found: C, 60.53; H, 9.44.

X-ray Structural Analysis of 8, 9, and 11. The crystallographic data were collected with a Bruker Smart CCD diffractometer (**8**) and with an Enraf-Nonius CAD4 diffractometer (**9**, **11**). Intensities were corrected for Lorentz and polarization effects. A semiempirical absorption correction (multiscan method) was applied to **8**, while a numerical method was used in the case of **9** and **11**. The structures were solved by direct methods. The structural parameters of the non-hydrogen atoms were refined anisotropically (F^2) according to full-matrix least-squares methods (**8**, SHELXTL-PLUS;²⁰ **9** and **11**, SHELX-97²¹). Disorder effects occurred at the atoms

C6 and C7, each with two positions with 50% probability in compound **9**. Hydrogen atoms were refined isotropically for **8** but not for compounds **9** and **11**. The hydrogen positions of the methyl groups and at the disordered atoms were calculated in **9**, while the hydrogens of the methyl groups of **11** were refined with fixed thermal parameters. The crystallographic data are listed in Table 3.

Photoelectron Spectra. The photoelectron spectra were recorded with a PS18 spectrometer (Perkin-Elmer) and calibrated using Ar and Xe. A resolution of 20 meV was obtained for the $^2\text{P}_{3/2}$ line of Ar.

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Supporting Information Available: Tables giving positional and thermal parameters and bond distances and angles for **8**, **9**, and **11**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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