Reaction of One-Sided Sterically Congested Cyclic Diynes with Organometallic Fragments

Rolf Gleiter,*,† Helmut Stahr,† and Bernhard Nuber‡

Organisch-Chemisches Institut der Universität Heidelberg and Anorganisch-Chemisches Institut der Universität Heidelberg, Im Neuenheimer Feld 270, D-69120 Heidelberg, Germany

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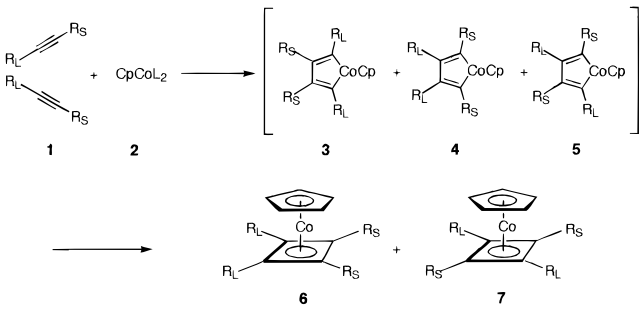
The new medium sized ring compounds 1,1,4,4-tetramethyl-1,4-disilacycloundeca-5,10-diyne **(14)**, 1,1,4,4-tetramethyl-1,4-disilacyclododeca-5,11-diyne **(15)**, 1,1,4,4-tetramethyl-1,4-disilacyclotrideca-5,12-diyne **(16)**, 1,1,4,4-tetramethyl-1,4-disilacyclotetradeca-5,13-diyne **(17)**, 1,1,2,2,3,3-hexamethyl-1,2,3-trisilacyclodeca-4,9-diyne **(18)**, 1,1,2,2,3,3-hexamethyl-1,2,3-trisilacycloundeca-4,10-diyne **(19)**, and 1,1,2,2,3,3-hexamethyl-1,2,3-trisilacyclododeca-4,11-diyne **(20)**, have been prepared. Starting materials were the terminal diynes 1,6-heptadiyne **(21)**, 1,7-octadiyne (**22**), 1,8-nona-diyne (**23**), and 1,9-decadiyne (**24**) as well as 1,4-dichloro-1,1,4,4-tetramethyl-1,4-disilane **(25)** and 1,3-dichloro-1,1,2,2,3,3-hexamethyltrisilane **(26)**. Compounds **18**−**20** were reacted with trimethylamine oxide, which led to the corresponding 2,4-dioxa compounds **27**−**29**. The reaction of **14**−**18** with (η^5-cyclopentadienyl)(η^2-cyclooctadiene)cobalt gave the corresponding intramolecular cyclobutadiene complexes **30**−**34** in good yields. The reaction of **29** with $Fe_2(CO)_9$ afforded the corresponding intramolecular (cyclobutadiene)$Fe(CO)_3$ complex **35** in poor yield. In the case of **30**, **34**, and **35** an X-ray analysis on single crystals revealed large bond length differences in the cyclobutadiene rings. The lengths of the C−C bonds between the bulky silyl groups were found to be 1.50−1.52 Å.

The cobalt-mediated cycloaddition of acetylenes proceeds either in a [2+2] fashion to yield cyclobutadienes or in a [2+2+2] fashion to give aromatic systems. The latter reaction has been used to construct new benzenoid π-systems, natural products, and heterocycles.[1−4] Despite the importance of these reactions not much is known about the mechanism. According to the work of Wakatsuki and Yamazaki steric effects play an important role.[5] In Scheme 1 we show the expected isomers if acetylenes with one large (R_L) and one small (R_S) substituent react with $CpCoL_2$ to yield a cyclobutadiene complex. There are three possible isomers (**3**−**5**) of the cobaltacycle intermediate, which can give rise to two products **6** and **7**.

From the observation that **6** is the major product it was concluded that **3** is the preferred intermediate. In **3** the large substituents are far removed from each other, while the small ones are close together. The opposite is the case in **4**.

We next examined the behavior of cyclic diynes, sterically congested about one triple bond, upon reaction with CpCo complexes. For bulky substituents on the cyclic diynes, we chose dimethylsilyl groups. In a previous paper we reported that the reaction of CpCo complexes with the cyclic diynes **8**−**10** yields via an intermolecular [2+2] cyclodimerization the corresponding superphanes **11**−**13** (Scheme 2).[6] This result was

Scheme 1



of interest as the products contained no isomers of C_{2h} symmetry and no tricyclic systems from an intramolecular pathway. To rationalize solely the formation of the C_{2v} symmetric structure we advanced the same steric arguments[6] as discussed above in connection with Scheme 1. To rationalize the absence of any intramolecular tricyclic products we argued that the CpCo-stabilized tricyclic cyclobutadiene complexes expected from an intramolecular [2+2] cyclodimerization of **8**−**10** would be much more strained than **11**−**13**. To further examine how steric factors and strain affect the competition between intermolecular and intramolecular reaction pathways, we have synthesized several new cyclic diynes **14**−**20** (Scheme 3) sterically congested at one triple bond and with ring sizes larger than those in **8**−**10**.

Preparation and Reactions of the One-Sided Sterically Congested Cyclic Diynes 14−20

The preparation of **14**−**20** was straightforward and is shown in Scheme 3. Starting materials were the

† Organisch-Chemisches Institut.
‡ Anorganisch-Chemisches Institut.
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(1) (a) Efraty, A. *Chem. Rev.* **1977**, *77*, 691. (b) Gleiter, R. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 27.
(2) Shore, N. E. *Chem. Rev.* **1988**, *88*, 1081.
(3) (a) Vollhardt, K. P. C. *Acc. Chem. Res.* **1977**, *10*, 1. (b) Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 539.
(4) Bönnemann, H. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 284.
(5) Wakatsuki, Y.; Nomura, O.; Kitaura, K.; Morokuma, K.; Yamazaki, H. *J. Am. Chem. Soc.* **1983**, *105*, 1907.
(6) Gleiter, R.; Stahr, H.; Nuber, B. *Tetrahedron Lett.* **1995**, *36*, 4607.

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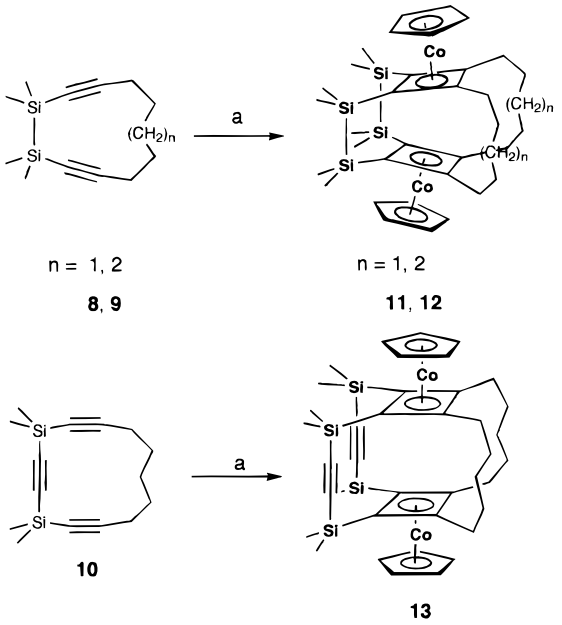
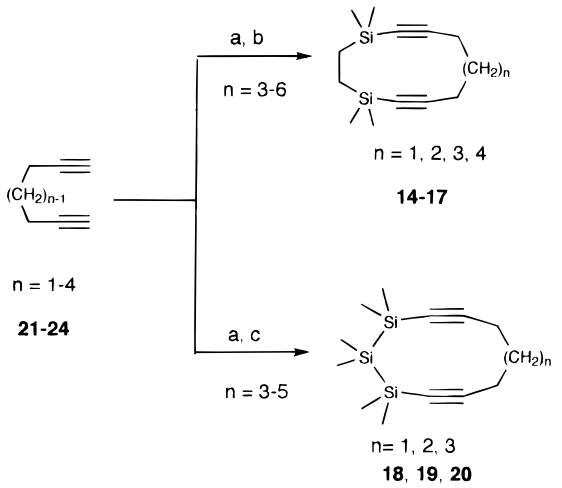
Scheme 2[a]



[a] Key: (a) CpCo(COD)/cyclooctane, reflux.

Scheme 3[a]

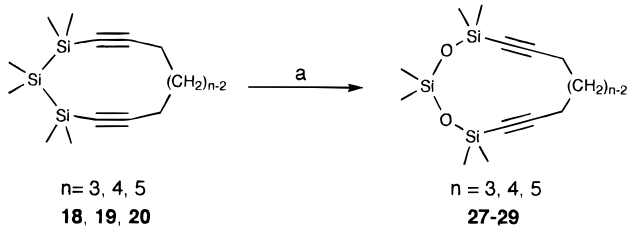


[a] Key: (a) MeMgBr/Et_2O; (b) $ClMe_2Si(C_2H_4)SiMe_2Cl$ (**25**)/THF, rt; (c) $Cl(Me_2Si)_3Cl$ (**26**)/THF, rt.

terminal diynes 1,6-heptadiyne (**21**), 1,7-octadiyne (**22**), 1,8-nonadiyne (**23**), and 1,9-decadiyne (**24**). These alkynes were transformed into the corresponding Grignard derivatives by allowing them to react with methylmagnesium bromide (MeMgBr). Subsequent treatment with either 1,4-dichloro-1,1,4,4-tetramethyl-1,4-disilane (**25**) or with 1,3-dichloro-1,1,2,2,3,3-hexamethyltrisilane (**26**)[7] afforded **14**−**20**. These diynes contain rings of medium size; therefore, yields were only in the range of 4−10%.

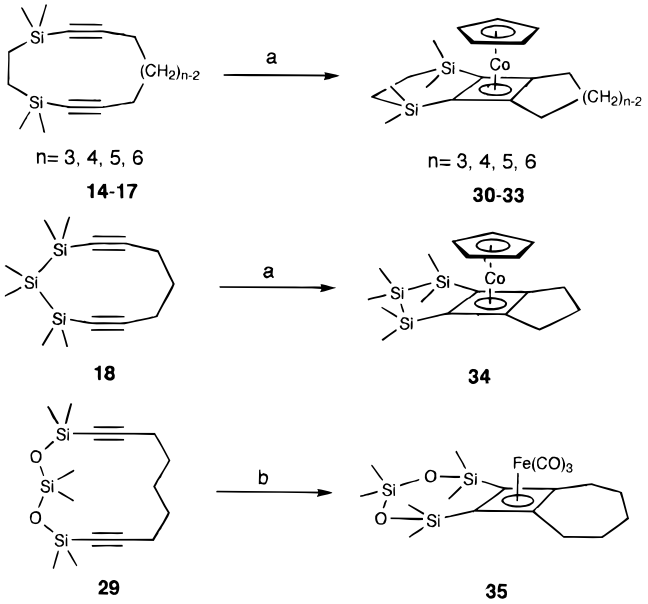
According to Sakurai et al. it is possible to enlarge cycles containing Si−Si bonds by selective oxidation.[8] By reaction of **18**−**20** with trimethylamine oxide, **27**−**29** were obtained in 45−80% yield (Scheme 4).

Scheme 4[a]



[a] Key: (a) Me_3NO/benzene, reflux.

Scheme 5[a]



[a] Key: (a) CpCo(COD)/cyclooctane, reflux; (b) $Fe_2(CO)_9$/benzene, reflux.

Reaction of **14**−**18** with (η^5-cyclopentadienyl)(η^4-cyclooctadiene)cobalt gave the corresponding tricyclic systems **30**−**34**. In all cases the yields were good (40−70%). The reaction of **29** with $Fe(CO)_5$ gave in low yield the tricyclic complex **35**. The latter reaction was carried out to investigate the effect of having a longer chain on the side of the sterically demanding group.

In the case of **30**, **34**, and **35** we were able to grow single crystals and to carry out X-ray analyses of these complexes. The structures of all three complexes are shown in Figure 1.

Common to all of them are large differences between the bond lengths in the four-membered ring. At the C−C bond between the bulky groups we find a long C−C distance in the order of 1.50−1.52 Å no matter what is the length of the bridge (see Table 1). In the structure of **34** the position of the Cp unit is not parallel to the cyclobutadiene ring. The Co atom is centered above the cyclobutadiene ring with nearly equal Co−C bond lengths, Co1−C6 (1.986(5) Å) and Co1−C8 (1.997(5) Å). However the bond distances between the Co atom and the Cp ring carbons are Co1−C9 (1.974(35) Å), Co1−C10 (2.010(34) Å), and Co1−C11 (2.065(35) Å). It seems likely that the Cp ring in **34** is forced away from its normal geometry by steric interactions with the *syn*-methyl groups on the silicons.

Discussion and Conclusion

The comparison between the reactions of **14**−**18** and the analogous carbocyclic diynes with CpCo complexes

(7) (a) Fritz, G.; Grunert, B. *Z. Anorg. Allg. Chem.* **1981**, *473*, 59. (b) Sakurai, H.; Tominaga, K.; Watanabe, T.; Kumada, M. *Tetrahedron Lett.* **1966**, *45*, 5493. (c) Ishikawa, M.; Kumada, M.; Sakurai, H. *J. Organomet. Chem.* **1970**, *23*, 63.

(8) (a) Sakurai, H.; Kira, M.; Kumada, M. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 1167. (b) Sakurai, H.; Hirama, K.; Nakadaira, Y.; Kabuto, C. *J. Am. Chem. Soc.* **1987**, *109*, 6880.

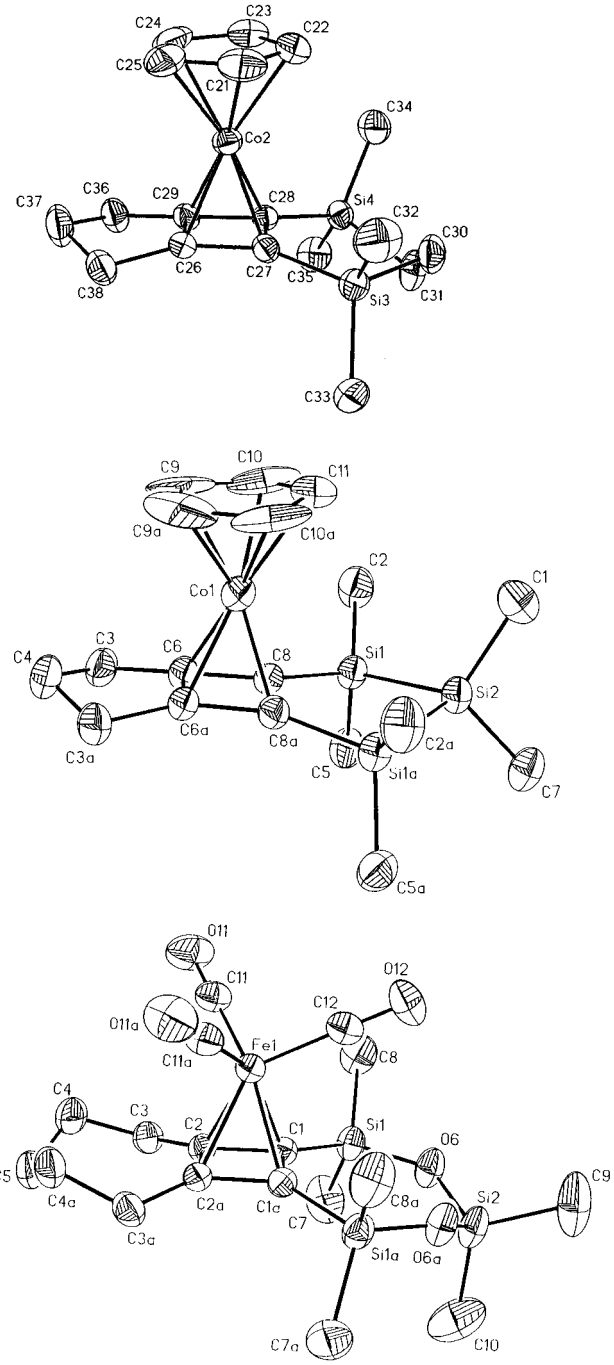


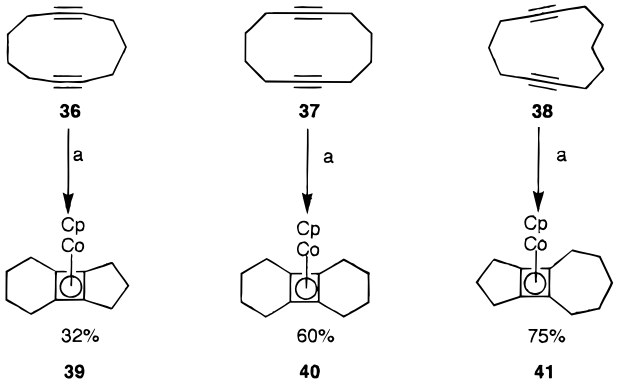
Figure 1. Molecular structures of **30** (top), **34** (middle), and **35** (bottom) in the solid state as determined by X-ray investigations.

Table 1. Selected Bond Lengths (Å) for 30, 34, and 35

	Compound **30**		
C28−C29	1.461(9)	C26−C27	1.470(9)
C29−C26	1.409(11)	C27−C28	1.516(11)
	Compound **34**		
C6−C6a	1.401(9)	C6−C8	1.462(6)
C6a−C8a	1.462(6)	C8−C8a	1.503(9)
	Compound **35**		
C1−C2	1.461(9)	C1a−C2a	1.461(3)
C2−C2a	1.430(5)	C1−C1a	1.501(5)

(Scheme 6)[9,10] does not show significant differences in yields and type of products formed. However the comparison between the products formed from diynes **8**−**10** and **14**−**18** toward $CpCoL_2$ shows a considerable difference. The cyclic diynes **8**−**10** prefer an intermolecular [2+2] pathway, affording superphanes **11**−**13**. In contrast, cyclic diynes **14**−**18** give only the intramolecular [2+2] cycloaddition products **30**−**34**. This difference is probably due to the fact that in the case of **8**−**10** intramolecular [2+2] cycloaddition would give highly strained cyclobutadiene complexes, making an intermolecular pathway considerably lower in energy. In **14**−**18**, where the bridge with the dimethylsilyl groups is larger and/or less rigid than in **8**−**10**, an intramolecular reaction path is chosen.

Scheme 6[a]



[a] Key: (a) $CpCo(CO)_2$/cyclooctane, reflux.

Experimental Section

All reactions were carried out under an atmosphere of argon. The solvents were dried over sodium metal under reflux and distilled just before use. Dichlorohexamethyltrisilane was synthesized according to the literature.[7] Dichlorotetramethyldisilabutane was purchased from ABCR and used without further purification. MeMgBr was purchased from Aldrich as a 3 M solution in ether. The diynes **21**−**24** were synthesized according to the literature.[11] Solvents of reagent grade were used for chromatography without further purification.

General Procedure for the Preparation of the Cyclic Dialkynes 14−20. To a solution of MeMgBr (3 M etheric solution) in 40 mL of THF was added a solution of the diyne in 20 mL of THF at 50 °C over a period of 20 min. A white precipitate was observed. After the solution was stirred for 1 h, 1 L of THF was added followed by the dichlorosilane (10 mmol). The resulting reaction mixture was stirred at 50 °C until the gas chromatographic analysis showed that no starting material was left. The solution was poured into a saturated solution of NH_4Cl in ice water. The organic layer was separated, and the aqueous layer was extracted with *n*-hexane (3 × 100 mL). The combined organic layers were neutralized with a saturated solution of $NaHCO_3$, dried over $MgSO_4$, and concentrated in vacuo. The crude products were chromatographed (SiO_2/CCl_4) to separate the material of high and low molecular weight. The latter fractions were concentrated in vacuo and Kugelrohr distilled. No attempts were made to investigate the composition of the residues with high molecular weight which corresponds to 90−96% of the products.

Preparation of 1,1,4,4-Tetramethyl-1,4-disilacycloundeca-5,10-diyne (14). Starting from 2 g (22 mmol) of **21**, 7 g (22 mmol) of dichlorodisilane **25**, and 14.7 mL (44 mmol) of methylmagnesium bromide solution in diethyl ether yielded

(9) King, R. B.; Efraty, A. *J. Am. Chem. Soc.* **1970**, *92*, 6071. King, R. B.; Efraty, A. *J. Am. Chem. Soc.* **1972**, *94*, 3021.
(10) Gleiter, R.; Kratz, D.; Ziegler, M. L.; Nuber, B. *Tetrahedron Lett.* **1990**, *31*, 6175.
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259 mg (5%) of **14** as colorless crystals melting at room temperature: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.1 (s, 12 H), 0.6 (s, 4 H), 1.7 (m, 2 H), 2.4 (t, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 106.6 (s), 85.7 (s), 25.9 (t), 20.4 (t), 7.7 (t), −2.0 (q); IR (KBr) 2957, 2931, 2899, 2178, 1247, 1050; UV/vis (*n*-pentane) (λ_{max}, nm (log ϵ)) 192 (3.2), 194 (3.2), 208 (2.9); HRMS (EI) (*m*/*e*) calcd for $C_{13}H_{22}Si_2$ 234.1260, found 234.1250. Anal. Calcd for $C_{13}H_{22}Si_2$ (234.13): C, 66.59; H, 9.46. Found: C, 66.39; H, 9.27.

Preparation of 1,1,4,4-Tetramethyl-1,4-disilacyclododeca-5,11-diyne (15). Starting from 1.3 g (12 mmol) of **22**, 2.6 g (12 mmol) of dichlorodisilane **25**, and 8 mL (24 mmol) of methylmagnesium bromide solution in diethyl ether yielded 225 mg (8%) of **14** as colorless crystals, mp 69 °C: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.1 (s, 12 H), 0.7 (s, 4 H), 1.7 (m, 4 H), 2.2 (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 108.0 (s), 84.5 (s), 27.4 (t), 19.7 (t), 9.0 (t), −2.3 (q); IR (KBr) 2956, 2933, 2907, 2170, 1248, 1139, 1058, 980; UV/vis (*n*-pentane) (λ_{max}, nm (log ϵ)) 194 (3.1), 198 (3.3); HRMS (EI) (*m*/*e*) calcd for $C_{14}H_{24}Si_2$ 248.1417, found 248.1415. Anal. Calcd for $C_{14}H_{24}Si_2$ (248.14): C, 67.66; H, 9.73. Found: C, 67.64; H, 9.79.

Preparation of 1,1,4,4-Tetramethyl-1,4-disilacyclotrideca-5,12-diyne (16). Starting from 2 g (17 mmol) of **23**, 3.6 g (17 mmol) of dichlorodisilane **25**, and 11.3 mL (34 mmol) of methylmagnesium bromide solution in diethyl ether yielded 617 mg (14%) of **14** as colorless crystals, mp 41 °C: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.1 (s, 12 H), 0.6 (s, 4H), 1.5 (m, 4 H), 1.7 (m, 2 H), 2.3 (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 106.9 (s), 85.0 (s), 27.4 (t), 26.1 (t), 19.6 (t), 9.3 (t), −2.2 (q); IR (KBr) 2946, 2925, 2909, 2172, 1248, 1138, 1057; UV/vis (*n*-pentane) (λ_{max}, nm (log ϵ)) 194 (3.2), 198 (3.2), 206 (3.0); HRMS (EI) (*m*/*e*) calcd for $C_{15}H_{26}Si_2$ 262.1573, found 262.1566. Anal. Calcd for $C_{15}H_{26}Si_2$ (262.16): C, 68.62; H, 9.98. Found: C, 68.92; H, 10.00.

Preparation of 1,1,4,4-Tetramethyl-1,4-disilacyclotetradeca-5,13-diyne (17). Starting from 2 g (15 mmol) of **23**, 3.2 g (15 mmol) of dichlorodisilane **25**, and 10 mL (30 mmol) of methylmagnesium bromide solution in diethyl ether yielded 264 mg (6%) of **17** as colorless crystals, mp 6 °C: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.1 (s, 12 H), 0.6 (s, 4 H), 1.5 (s, br, 8 H), 2.3 (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 107.4 (s), 84.2 (s), 27.8 (t), 27.5 (t), 19.2 (t), 9.3 (t), −2.1 (q); IR (KBr) 2931, 2908, 2878, 2858, 2173, 1250, 1134, 1054; UV/vis (*n*-pentane) (λ_{max}, nm (log ϵ)) 192 (3.3), 194 (3.3), 206 (3.0); HRMS (EI) (*m*/*e*) calcd for $C_{16}H_{28}Si_2$ 276.1730, found 276.1736. Anal. Calcd for $C_{16}H_{28}Si_2$ (276.17): C, 69.49; H, 10.20. Found: C, 69.55; H, 10.01.

Preparation of 1,1,2,2,3,3-Hexamethyl-1,2,3-trisilacyclodeca-4,9-diyne (18). Starting from 2 g (22 mmol) of **21**, 5.4 g (22 mmol) of dichlorotrisilane **26**, and 14.7 mL (44 mmol) of methylmagnesium bromide solution in diethyl ether yielded 388 mg (7%) of **18** as colorless crystals, mp 74 °C: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.2 (s, 6 H), 0.2 (s, 12 H), 1.7 (m, 2 H), 2.4 (t, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 109.8 (s), 85.0 (s), 25.9 (t),20.8 (t), −2.4 (q), −7.9 (q); IR (KBr) 2951, 2933, 2893, 2172, 1242, 1050; UV/vis (*n*-pentane) (λ_{max}, nm (log ϵ)) 192 (4.4), 210 (4.1), 230 (3.8); HRMS (EI) (*m*/*e*) calcd for $C_{13}H_{24}Si_3$ 264.1186, found 264.1219. Anal. Calcd for $C_{13}H_{24}Si_3$ (264.12): C, 59.02; H, 9.14. Found: C, 58.78; H, 9.08.

Preparation of 1,1,2,2,3,3-Hexamethyl-1,2,3-trisilacycloundeca-4,10-diyne (19). Starting from 2.2 g (21 mmol) of **22**, 5.1 g (21 mmol) dichlortrisilane **26**, and 14.3 mL (43 mmol) of methylmagnesium bromide solution in diethyl ether yielded 800 mg (14%) of **19** as colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.15 (s, 6 H), 0.21 (s, 12 H), 1.7 (m, 4 H), 2.3 (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 110.6 (s), 83.8 (s), 26.9 (t), 19.8 (t), −2.3 (q), −7.2 (q); IR (film) 2949, 2169, 1246; UV/vis (*n*-pentane) (λ_{max}, nm (log ϵ)) 192 (3.4), 210 (3.1), 230 (2.8); HRMS (EI) (*m*/*e*) calcd for $C_{14}H_{26}Si_3$ 278.1342, found 278.1312. Anal. Calcd for $C_{14}H_{26}Si_3$ (278.13): C, 60.35; H, 9.41. Found: C, 60.30; H, 9.56.

Preparation of 1,1,2,2,3,3-Hexamethyl-1,2,3-trisilacyclododeca-4,11-diyne (20). Starting from 2 g (18 mmol) of **22**, 4.4 g (18 mmol) of dichlorotrisilane **26**, and 12 mL (36 mmol) of methylmagnesium bromide solution in diethyl ether yielded 200 mg (4%) of **20** as colorless crystals, mp 40 °C: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.16 (s, 6 H), 0.22 (s, 12 H), 1.5 (m, 4 H), 1.8 (m, 2 H), 2.3 (t, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 109.3 (s), 83.9 (s), 26.1 (t), 25.1 (t), 19.3 (t), −2.0 (q), −7.1 (q); IR (KBr) 2951, 2860, 2169, 1243; UV/vis (*n*-pentane) (λ_{max}, nm (log ϵ)) 192 (4.5), 308 (4.1), 224 (3.9); HRMS (EI) (*m*/*e*) calcd for $C_{15}H_{28}Si_3$ 292.1499, found 292.1566. Anal. Calcd for $C_{15}H_{28}Si_3$ (292.15): C, 61.56; H, 9.64. Found: C, 61.42; H, 9.39.

General Procedure for the Synthesis of 27−29. A solution of the cyclic diyne (0.15 mmol) and trimethlylaminoxide (0.4 mmol) in benzene was refluxed until the diyne disappeared, as determined by GLC analysis. The solvent was removed in vacuo, and the crude product was purified by column chromatography (silica gel/CCl_4).

Preparation of 1,1,3,3,5,5-Hexamethyl-2,4-dioxa-1,3,5-trisilacyclododeca-6,11-diyne (27). Starting from 20 mg (0.08 mmol) of **18** and 22 mg (0.2 mmol) of trimethylamine oxide yielded 16 mg (71%) of **27** as colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.1 (s, 6 H), 0.3 (s, 12 H), 1.7−1.8 (m, 2 H), 2.4 (t, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 0.9 (q), 2.19 (q), 20.2 (t), 25.4 (t), 85.7 (s), 105.7 (s); IR (film) 2960, 2935, 2902, 2181, 1256, 1052; UV/vis (*n*-pentane) (λ_{max}, nm (log ϵ)) 200 (2.9); HRMS (EI) (*m*/*e*) calcd for $C_{13}H_{24}O_2Si_3$ 296.1084, found 296.1049.

Preparation of 1,1,3,3,5,5-Hexamethyl-2,4-dioxa-1,3,5-trisilacyclotrideca-6,12-diyne (28). Starting from 38 mg (0.14 mmol) of **19** and 46 mg (0.41 mmol) of trimethylamine oxide yielded 19 mg (45%) of **28** as colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.1 (s, 6 H), 0.3 (s, 12 H), 1.7 (m, 4 H), 2.4 (t, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 1.0 (q), 2.16 (q), 19.2 (t), 26.9 (t), 85.2 (s), 106.9 (s); IR (KBr) 2961, 2864, 2177, 1257, 1044; UV/vis (*n*-pentane) (λ_{max}, nm (log ϵ)) 200 (2.8); HRMS (EI) (*m*/*e*) calcd for $C_{14}H_{26}O_2Si_3$ 310.1241, found 310.1271. Anal. Calcd for $C_{14}H_{26}O_2Si_3$ (310.12): C, 54.14; H, 8.44. Found C, 54.32; H, 8.54.

Preparation of 1,1,3,3,5,5-Hexamethyl-2,4-dioxa-1,3,5-trisilacyclotetradeca-6,13-diyne (29). Starting from 50 mg (0.17 mmol) of **20** and 57 mg (0.51 mmol) of trimethylamine oxide yielded 45 mg (82%) of **29** as colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.1 (s, 6 H), 0.3 (s, 12 H), 1.5 (m, 4H), 1.8 (quintet, 2H), 2.3 (t, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 1.0 (q), 2.3 (q), 19.4 (t), 26.3 (t), 27.1 (t), 85.2 (s), 106.0 (s); IR (KBr) 2961, 2864, 2177, 1258, 1045; UV/vis (*n*-pentane) (λ_{max}, nm (log ϵ)) 208 (2.9); HRMS (EI) (*m*/*e*) calcd for $C_{15}H_{28}O_2Si_3$ 324.1397, found 324.1407.

General Procedure for the Preparation of the Tricyclic Cyclobutadiene Complexes 30−33. A solution of the diyne (0.2 mmol) and of CpCo(COD) (0.3 mmol) in degassed cyclooctane (7 mL) was refluxed for 18 h. After cooling, the solvent was removed in vacuo, the residue was dissolved in a small amount of *n*-hexane, and the solution was purified by column chromatography (alumina (grade III)/*n*-hexane). After removal of the solvent, the crude product was purified by Kugelrohr distillation.

Preparation of {(1,2,7,8-η)-3,3,6,6-Tetramethyl-3,6-disilatricyclo[4.3.0.0^{2,7}]undeca-1,7-diene}(η^5-cyclopentadienyl)cobalt (30). Starting from 32 mg (0.14 mmol) of **14** and 67 mg (0.29 mmol) of CpCo(COD) yielded 28 mg (56%) of **30** as orange crystals, mp 83 °C: ^{1}H NMR (300 MHz, C_6D_6) δ 0.2 (s, 6 H), 0.3 (s, 6 H), 0.8 (m, 4H), 1.7−1.9 (m, 4 H), 2.0 (m, 2 H), 4.7 (s, 5 H); ^{13}C NMR (75 MHz, C_6D_6) δ 94.9 (s), 79.8 (d), 57.4 (s), 28.9 (t), 28.5 (t), 9.4 (t), 0.7 (q), −1.1 (q); IR (KBr) 2955, 2889, 2842, 1447, 1314, 1239, 855, 830, 812, 770; UV/vis (*n*-pentane) (λ_{max}, nm (log ϵ)) 210 (4.3), 276 (4.1), 310 (2.8); HRMS (EI) (*m*/*e*) calcd for $C_{18}H_{27}CoSi_2$ 358.0983, found 358.0996. Anal. Calcd for $C_{18}H_{27}CoSi_2$ (358.10): C, 60.30; H, 7.59. Found: C, 60.52; H, 7.49.

Preparation of {(1,2,7,8-η)-3,3,6,6-Tetramethyl-3,6-disilatricyclo[4.4.0.0^{2,7}]dodeca-1,7-diene}(η^5-cyclopentadienyl)cobalt (31). Starting from 50 mg (0.2 mmol) of **15**

Table 2. Crystallographic Data for 30, 34 and 35

	30	34	35
formula	$C_{18}H_{27}Si_2Co$	$C_{18}H_{29}Si_3Co$	$C_{18}H_{28}O_5Si_3Fe$
fw	358.5	388.6	464.5
size, mm	0.20 × 0.25 × 0.70	0.6 × 0.75 × 1.0	0.55 × 0.55 × 0.75
cryst system	monoclinic	orthorhombic	monoclinic
space group	$P2_1/c$	$Pnma$	$P2_1/m$
a, Å	15.663(9)	23.27(1)	7.113(2)
b, Å	13.262(4)	11.849(5)	14.197(6)
c, Å	19.35(1)	7.374(2)	11.624(4)
β, deg	112.99(4)		93.13(3)
V, Å^3	3700(3)	2033.3	1172.1
Z	8	4	2
T, K	293	293	293
D_{calcd}, g/cm^3	1.29	1.27	1.32
μ, cm^{-1}	10.5	10.1	8.1
F(000)	1520	824	488
λ, Å	0.710 73	0.710 73	0.710 73
scan type	ω	ω	ω
rflns meased	7067	3032	3804
rflns obs ($I > 2.5\sigma(I)$)	3829	1731	2747
θ range, deg	1.5−25	1.5−28.75	1.5−30.5
abs corr	empirical, 6 rflns	empirical, 7 rflns	empirical, 8 rflns
range of transm, %	87−100	86−100	93−100
no. of params (NV)	358	134	134
$R(F)$,	0.062	0.062	0.047
$R_w(F)$	0.049	0.052	0.043
GOF	1.99	2.83	2.68
ρ, e Å^{-3} (max/min)	0.62/−0.40	0.51/−0.59	0.64/−0.49

and 60 mg (0.26 mmol) of CpCo(COD) yielded 46 mg (62%) of **31** as orange crystals, mp 59 °C: ^{1}H NMR (200 MHz, C_6D_6) δ 0.2 (s, 6 H), 0.3 (s, 6 H), 0.8 (m, 4 H), 1.5−2.0 (m, 8 H), 4.7 (s, 5 H); ^{13}C NMR (50 MHz, C_6D_6) δ 88.6 (s), 79.9 (d), 61.7 (s), 24.9 (t), 23.1 (t), 8.8 (t), 0.8 (q), −1.6 (q); IR (KBr) 2947, 2921, 2878, 2827, 1482, 1436, 1402, 1240, 847, 830, 812, 770, 684; UV/vis (*n*-pentane) (λ_{max}, nm (log ϵ)) 210 (4.6), 278 (4.5), 306 (3.3), 404 (2.8); HRMS (EI) (*m*/*e*) calcd for $C_{19}H_{29}CoSi_2$ 372.1140, found 372.1121. Anal. Calcd for $C_{19}H_{29}CoSi_2$ (372.11): C, 61.26; H, 7.85. Found: C, 61.46; H, 7.79.

Preparation of {(1,2,7,8-η)-3,3,6,6-Tetramethyl-3,6-disilatricyclo-[5.4.0.0^{2,7}]trideca-1,7-diene}(η^5-cyclopentadienyl)cobalt (32). Starting from 50 mg (0.19 mmol) of **16**, 60 mg (0.26 mmol) of CpCo(COD), yielded 49 mg (70%) of **32** as orange crystals, mp 103 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.04 (s,6 H), 0.20 (s, 6H), 0.70 (m, 4H), 1.58−1.96 (m, 10 H), 4.86 (s, 5 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 92.33 (s), 78.75 (d), 61.61 (s), 30.80 (t), 30.64 (t), 30.53 (t), 8.77 (t), 0.54 (q), −1.58 (q); IR (KBr) 2949, 2929, 2913, 2899, 2867, 1424, 1334, 1216, 845, 830, 811, 765; UV/vis (*n*-pentane) (λ_{max}, nm (log ϵ)) 208 (4.3), 276 (4.2), 306 (3.1), 400 (2.6); HRMS (EI) (*m*/*e*) calcd for $C_{20}H_{31}CoSi_2$ 386.1296, found 386.1327. Anal. Calcd for $C_{20}H_{31}CoSi_2$ (386.13): C, 62.14; H, 8.08. Found: C, 61.31; H, 7.84.

Preparation of {(1,2,7,8-η)-3,3,6,6-Tetramethyl-3,6-disilatricyclo[6.4.0.0^{2,7}]tetradeca-1,7-diene}(η^5-cyclopentadienyl)cobalt (33). Starting from 20 mg (0.07 mmol) of **17** and 24 mg (0.14 mmol) of CpCo(COD) yielded 49 mg (70%) of **33** as orange crystals, mp 68 °C: ^{1}H NMR (300 MHz, C_6D_6) δ 0.1 (s, 6 H), 0.2 (s, 6 H), 0.8 (m, 4 H), 1.5 (m, 8 H), 1.9 (m, 4 H), 4.7 (s, 5 H); ^{13}C NMR (75 MHz, C_6D_6) δ −1.3 (q), 0.9 (q), 9.1 (t), 26.2 (t), 27.7 (t), 29.0 (t), 63.5 (s), 79.6 (d), 90.0 (s); IR (KBr) 2926, 2865, 1635, 1242, 832, 807, 769; UV/vis (*n*-pentane) (λ_{max}, nm (log ϵ)) 208 (4.4), 276 (4.3), 310 (3.1); HRMS (EI) (*m*/*e*) calcd for $C_{21}H_{33}CoSi_2$ 400.1453, found 400.1461; Anal. Calcd for $C_{21}H_{33}CoSi_2$ (400.15): C, 62.96; H, 8.30. Found: C, 62.89; H, 8.21.

Preparation of {(1,2,6,7-η)-3,3,4,4,5,5-Hexamethyl-3,4,5,-trisilatricyclo[3.3.0.0^{2,6}]deca-1,6-diene}(η^5-cyclopentadienyl)cobalt (34). Starting from 30 mg (0.14 mmol) of **18** and 50 mg (0.27 mmol) of CpCo(COD) yielded 25 mg (46%) of **34** as orange crystals, mp 178 °C: ^{1}H NMR (200 MHz, C_6D_6) δ 0.2 (s, 3H), 0.3 (s, 6 H), 0.4 (s, 3 H), 0.5 (s, 6 H), 1.8−2.0 (m, 6 H), 4.7 (s, 5 H); ^{13}C NMR (50 MHz, C_6D_6) δ −6.2 (q), −5.9 (q), −1.1 (q), 0.01 (q), 28.5 (t), 29.1 (t), 64.6 (s), 79.6 (d), 94.3 (s); IR (KBr) 2954, 2937, 2907, 2839, 2360, 1633, 1453, 1235, 835; UV/vis (*n*-pentane) (λ_{max}, nm (log ϵ)) 196 (4.3), 280 (4.0), 312 (2.9), 400 (2.5); HRMS (EI) (*m*/*e*) calcd for $C_{18}H_{29}CoSi_3$ 388.0909, found 388.0909. Anal. Calcd for $C_{18}H_{29}CoSi_3$ (388.09): C, 55.64; H, 7.52. Found: C, 56.13; H, 7.50.

Preparation of {(1,2,8,9-η)-3,3,5,5,7,7-Hexamethyl-3,5,7-trisila-4,6-dioxotricyclo[5.5.0.0^{2,8}]tetradeca-1,8-diene}-tricarbonyliron (35). A solution of **29** (45 mg, 0.14 mmol) and $Fe_2(CO)_9$ (76 mg, 0.21 mmol) in benzene (5 mL) was refluxed under Ar atmosphere until **29** had disappeared. The solvent was removed in vacuo, and the residue was suspended in *n*-hexane and chromatographed (silica gel/*n*-hexane). The product-containing fractions were concentrated and cooled to −20 °C. The product crystallized at this temperature yielding 3 mg (5%) of **35** as slightly brown cubes: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.1 (s, 3 H), 0.3 (s, 3 H), 0.3 (s, 12 H), 1.1−1.9 (m, 10 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ −1.4 (q), −0.3 (q), 1.2 (q), 1.8 (q), 27.5 (t), 28.3 (t), 28.7 (t), 64.2 (s), 85.8 (s), 213.8 (s); IR (KBr) 2931, 2851, 2021, 1958, 1935, 1632, 1256, 1073, 1028; UV/vis (*n*-pentane) (λ_{max}, nm (log ϵ)) 200 (4.2), 238 (3.8), 304 (2.5); HRMS (EI) (*m*/*e*) calcd for $C_{18}H_{28}FeO_5Si_3$ 464.0594, found 464.0594.

X-ray Crystallography and Structure Solution. Data were collected on a SYNTEX R3 diffractometer using graphite-monochromated Mo Kα radiation. The crystallographic data are given in Table 2. Single crystals of **30** and **34** were obtained by vacuum sublimation, while crystals of **35** were obtained from hexane solution (−20 °C). Cell parameters were obtained from 26 reflections with $4.0 < 2\theta < 26.0°$ for **30**, from 25 reflections with $3.5 < 2\theta < 27.0°$ for **34**, and from 25 reflections with $3.8 < 2\theta < 29.0°$ for **35**. The structures were solved by direct methods and Patterson methods; structural refinement was carried out by least-squares techniques (*F*). The parameters of the hydrogen atoms were calculated and not refined. The calculations for **30**, **34**, and **35** were performed with the SHELXTL PLUS program.[12]

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Supporting Information Available: Tables listing positional and thermal parameters, complete bond distances and angles, and torsion angles of **30**, **34**, and **35** (16 pages). Ordering information is given on any current masthead page.

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