Sterically Hindered Cyclic Diynes − Syntheses and Structures

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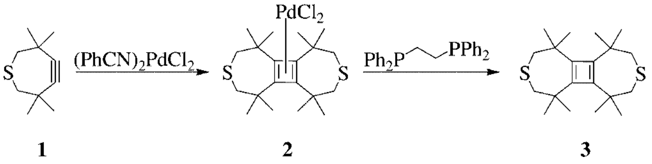
The synthesis of three 14-membered ring systems **8a**–**8c** with the 1,3,8,10-tetraoxa-2,9-disilacyclotetradeca-5,12-diyne skeleton is described. In all three ring systems the α-positions are substituted with *gem*-dimethyl and/or *gem*-diphenyl groups. Structural investigations on **8a** and **8c** reveal a chair like conformation of the central ring with parallel alkyne units. For **8b** the voluminous phenyl groups cause a twist-chair and a twist-boat conformation. Columnar structures were encountered for **8a** in the solid state. Reactions with octacarbonyldicobalt yield for **8a** mono- and biscomplexation (**12**, **13**). For **8b** only the mono complexation product **14** was isolated. For **8c** the bis(hexacarbonyldicobalt) complex **15** was obtained. X-ray investigations revealed columnar structures in the solid state for **12**, **13**, and **15**.

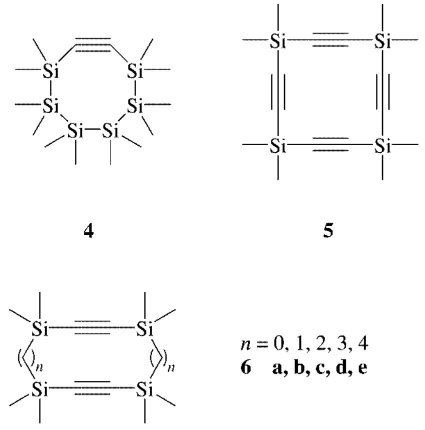
Introduction

Cyclic alkynes with methyl groups in the positions adjacent to the triple bonds are rare but not unknown.[1−6] One of the most prominent members of the family of cyclic monoalkynes is 1-thia-3,3,6,6-tetramethyl-4-cycloheptyne (**1**) and those congeners in which the sulfur atom is replaced by a CH_2, a SO_2, or a $SiMe_2$ group.[7] For **1** a rich and partly unexpected chemistry has been unravelled (Scheme 1) which was ascribed to steric effects and the bent triple bond.[8,9] As an example Scheme 1 shows the generation of the first stable cyclobutadiene derivative, **3**, resulting from **1**.



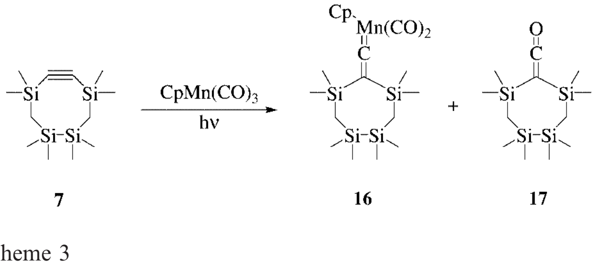
Scheme 1

The results reported for **1** encouraged us to look for ways to prepare cyclic diynes with bulky substituents in positions adjacent to the triple bonds. Most candidates known so far which fulfil the steric requirements are those with dimethylsilyl groups next to the triple bonds such as **4**−**6**[1−6] depicted in Scheme 2.



Scheme 2

The weaker C−Si bond as compared to a C−C bond often causes quite unexpected chemistry, as shown in Scheme 3. Irradiation of **7** in the presence of $CpMn(CO)_3$ yielded the species **16** and **17** which demonstrate a skeletal rearrangement.[10] A related rearrangement was also reported when **7** was heated with $Fe(CO)_5$ or $Fe_2(CO)_9$.[11] These differences prompted us to synthesise cyclic diynes with bulky CR_2 groups adjacent to the triple bonds such as **8a**−**c** (Scheme 4).



Scheme 3

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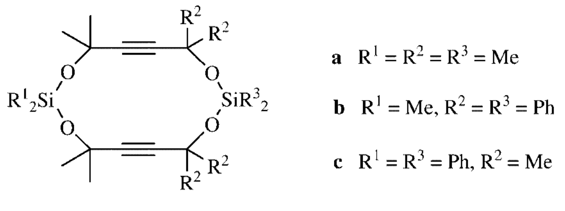


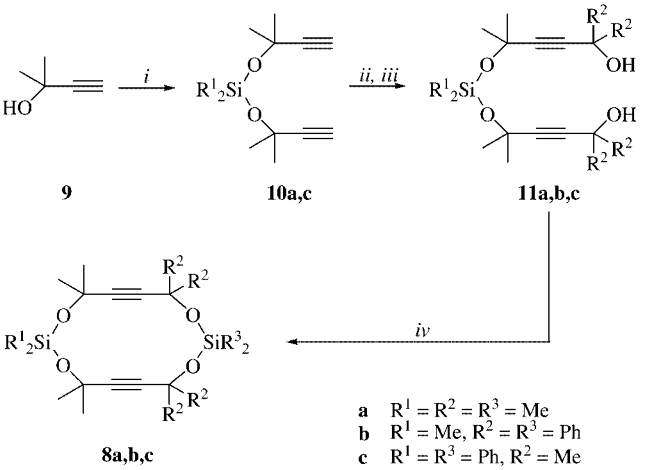
8

Scheme 4

Results and Discussion

Synthesis

The synthesis of **8** is straightforward and is summarised in Scheme 5. It commences with the reaction of 2-methyl-3-butyn-2-ol (**9**) with either dimethyldichlorosilane (R^1 = CH_3) or diphenyldichlorosilane (R^1 = C_6H_5) to yield the dialkynes **10a** and **10c** respectively. The bis(lithium) salt of **10a** and **10c** can be converted into the bis(alcohols) **11a−c** by reaction with acetone or benzophenone.

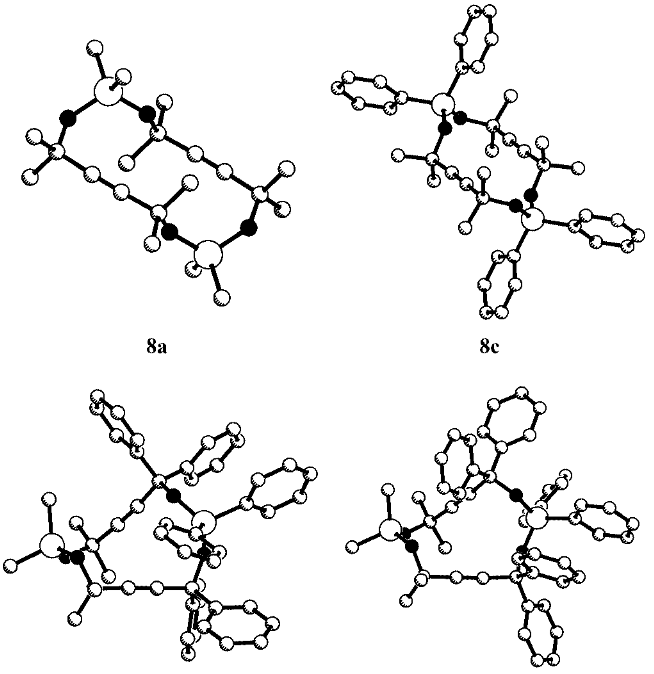


Scheme 5. Reagents: (i) $R^1{}_2SiCl_2$, DMAP, CH_2Cl_2; (ii) *n*BuLi, THF; (iii) $R^2{}_2CO$; (iv) $R^3{}_2SiCl_2$, DMAP, CH_2Cl_2

Further condensation of **11a−c** with $R^3{}_2SiCl_2$ afforded the final products **8a−c**. The yields for the various steps vary strongly. The overall yield is 25% for **8a** and decreases to 4% (**8b**) and 19% (**8c**) when the substituents change to C_6H_5.

Structural Investigations

All three final products of the reaction sequence in Scheme 5 were colourless solids from which crystals were obtained. In Figure 1 the molecular structures of **8a−c** are shown.



8a **8c**

8b (twisted boat) **8b** (twisted chair)

Figure 1. Molecular structures of **8a**, **8c** and the two independent molecules of **8b**; the hydrogen atoms have been omitted for clarity. The oxygen atoms are represented by full circles

In all three cyclic diynes the geometry of the 14-membered ring is determined by the rigid and linear 1,1,4,4-tetrasubstituted 2-butyne units. These parts are bridged at both ends by a bent O−Si−O bridge. For **8a** and **8c** a chair like conformation results with parallel alkyne units, similar to several cyclotetradeca-4,11-diyne derivatives reported in the literature.[12] The actual ring conformation of **8a** and **8c** is compared to the chair conformation in Figure 2. The substituents at the silicon evade the substituents at the α-position to the triple bonds so that the bridge deviates strongly from the ideal zigzag arrangement. This brings the butyne-units closer together in a parallelogram like arrangement. In Table 1 the most relevant structural parameters of **8a−c** are listed. A comparison with the transannular distances of cyclotetradeca-4,11-diyne (464 pm), cyclotetradeca-4,11-diyne-1,8-dione (520 pm), and 1,8-dioxacyclotetradeca-4,11-diyne (471 pm)[12] shows that the transannular distances in all three cyclic diynes **8a−c** are shorter.

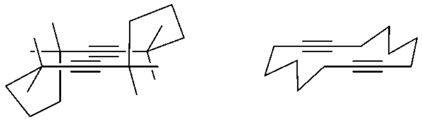


Figure 2. Ring conformation of **8a** and **8c** in the solid state (left; substituents at the silicon are omitted) and chair conformation for cyclotetradeca-1,8-diyne (right)

Table 1. Transannular distances between the triple bonds, torsion angles between the triple bonds and bond angles at the sp-centres of **8a−8c**

Compound	Distance *d* [a]/pm	Torsion γ[a] /°	C−C≡C angles /°
8a	450.1	0	176.7−177.0
8b	364.5/384.8	59.4/61.8	174.3−179.5
8c	419.3	0	175.1−177.5

[a] See Figure 7 for illustration of distance *d* and torsion angle γ.

For **8b** we found two independent molecules in the unit cell. One molecule adopts a twisted boat-like conformation while the other molecule adopts a twisted chair-like conformation as can be seen in Figure 3. These structures are mainly due to a minimisation of steric interactions between the two pairs of bulky diphenylmethano and the diphenylsilano units. In the resulting conformations the torsional angles between the opposite triple bonds are found to be 61.5° and 64.8° respectively. The torsional angle γ is illustrated in Figure 7.

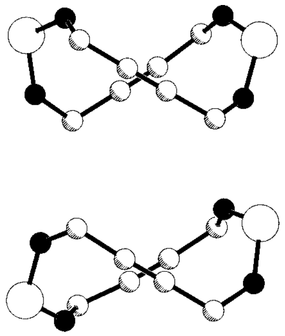


Figure 3. Different ring conformations of **8b** in the unit cell: Twisted boat-like conformation (top), twisted chair-like conformation (bottom); all substituents have been omitted for clarity. The oxygen atoms are represented by full circles

For **8a** we noticed in the solid state the appearance of a columnar structure. This structure arises by stacking the rings on top of each other (see Figure 4). In the solid state of **8a** we find interactions between the C−H bonds of the methyl groups of one entity and the oxygen atoms of the other (Figure 5). The H···O intermolecular distance amounts to 2.703 Å (C···O distance 3.603 Å). This value is similar to that found for weak H···O bonds.[13−15]

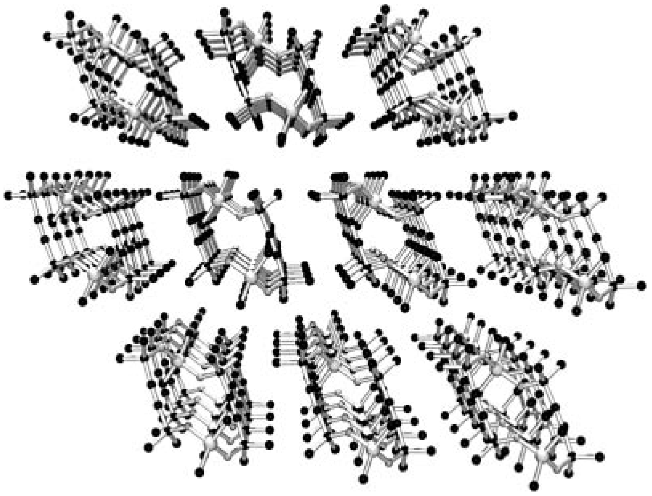


Figure 4. Columnar structure of **8a** in the solid state (view along *a* axis of the unit cell)

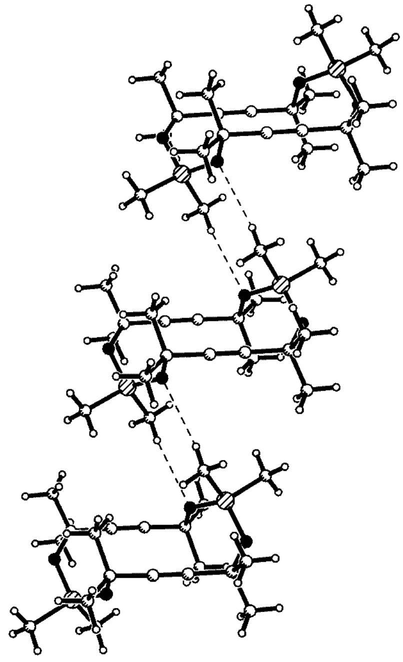
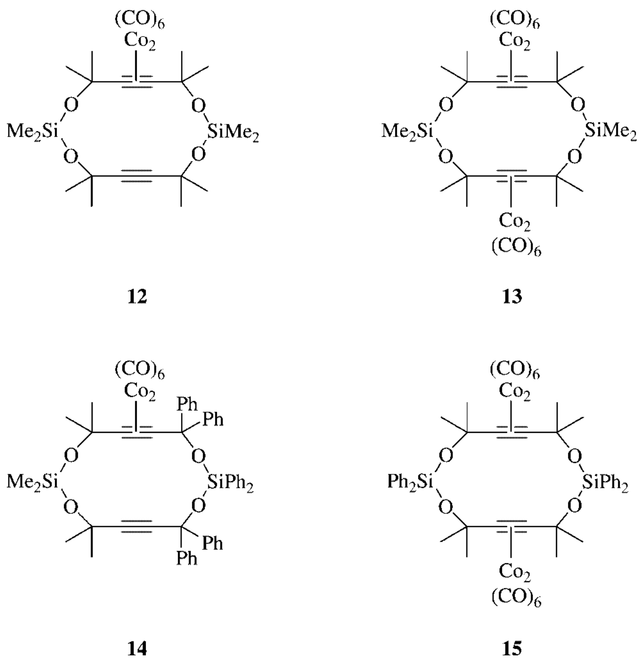


Figure 5. C−H···O interactions within the columnar structure of **8a**. The silicon centres are hatched, the oxygen atoms are represented by full circles

Reactions with Octacarbonyldicobalt

The formation of hexacarbonyldicobalt complexed alkynes by the reaction of alkynes with octacarbonyldicobalt is a well established method in organometallic chemistry.[16] We used this reaction to investigate whether the sterically hindered alkynes were still able to be attacked at the triple bonds. Recently, unsubstituted cyclic diynes were investigated regarding their reactivity towards octacarbonyldicobalt and it was shown that these diynes afford the twofold complexes in good yields.[17] To test the reactions with cobaltcarbonyls we treated **8a−c** with an excess of octacarbonyldicobalt in dichloromethane at room temperature



Scheme 6

(Scheme 6). In the case of **8a** the use of 4 equivalents of octacarbonyldicobalt afforded the mono complexed product **12** in 30% yield. We ascribe this result to the bulky methyl groups which make the attack at the triple bonds difficult. By the use of 8 equivalents of octacarbonyldicobalt the twofold complexed product **13** could be isolated in 45% yield. When reacting the cyclic diyne **8b** with octacarbonyldicobalt, even 10 equivalents of octacarbonyldicobalt lead only to the formation of the mono complexed product **14** in 25% yield. This decrease in reactivity can be attributed to the extreme shielding of the triple bond by the phenyl groups. In the case of **8c** the reaction with 10 equivalents of octacarbonyldicobalt afforded the twofold complexed product in 79% yield. All yields are lower than for the analogous unsubstituted all-carbon ring, 1,8-cyclotetradecadiyne, which affords the twofold complexed product in 90% yield.[17,18]

Table 2. Transannular distances between the (former) triple bonds, torsion angles between the (former) triple bonds, and bond angles at the (former) sp centres of **12−15**

Compound	Distance *d* [a]/pm	Torsion γ[a] /°	C−C≡C angles /°
12	519.5	5.3	141.4/172.8−172.9
13	632.2	70.3	141.1−143.3
14	534.6	17.9	143.9−144.8/ 169.4−175.8
15	648.3	0	144.4−145.6

[a] See Figure 7 for illustration of distance *d* and torsion angle γ.

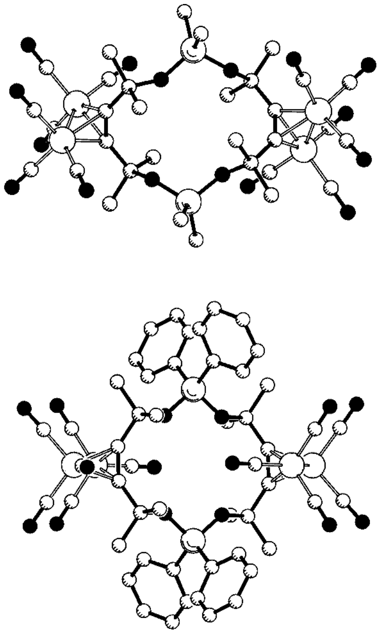


Figure 6. Molecular structures of **13** and **15**; the hydrogen atoms have been omitted for clarity. The oxygen atoms are represented by full circles

For all isolated complexes, single crystals were obtained from a mixture of ethanol and diethyl ether at 4 °C. As an example, the molecular structures of **13** and **15** are shown in Figure 6. The most relevant distances and angles of **12−15** are compiled in Table 2. The transannular distance *d* and the torsion angle γ is illustrated in Figure 7.

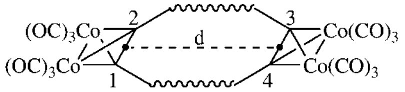


Figure 7. Illustration of the triple bond length *d* (the transannular distance between the triple bond centres or former triple bond centres, respectively) and the torsion angle γ (the torsion angle 1 − centre 1,2 − centre 3,4−4)

The distances between the metal atoms, between Co and CO, as well as the C−C distances for the former triple bond compare well with those reported for $Co_2(CO)_6$ complexes of cyclic diynes.[17] As anticipated, the distance between one complexed triple bond and one uncomplexed (**12**, **14**) is considerably shorter than between two complexed triple bonds.

It is also noteworthy that **12**, **13**, and **15** (Figure 8) form columnar structures in the solid state. In the case of **15** the dipolar interactions between CO groups of neighbouring molecules are found within the column (Figure 9). The

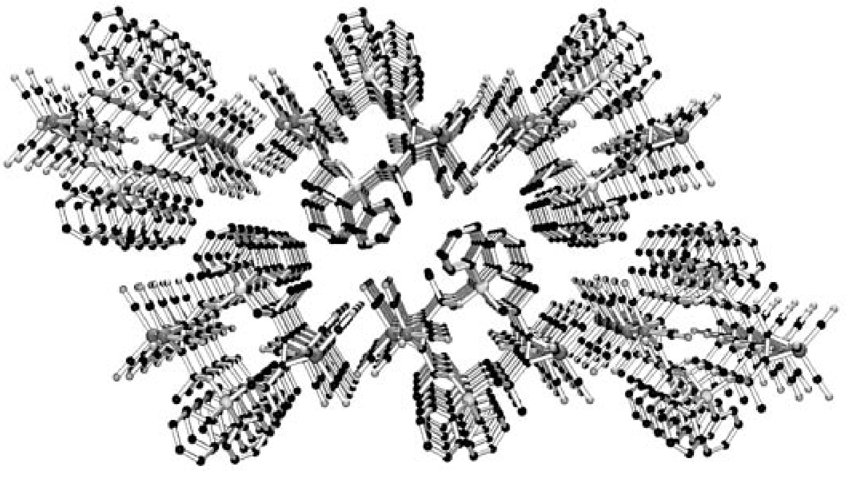


Figure 8. Columnar structure of **15** in the solid state (view along *a* axis of the unit cell)

O···CO contacts (3.056 and 3.161 Å) are shorter than the sum of the van der Waals radii.[15] Between the columns there are C−H···O interactions (2.584 Å, C···O distance 3.499 Å) between phenyl groups and CO units (Figure 10). These intermolecular interactions seem to be partially responsible for the columnar arrangement in the solid state. The distances found are in the same order of those reported in the literature.[13]

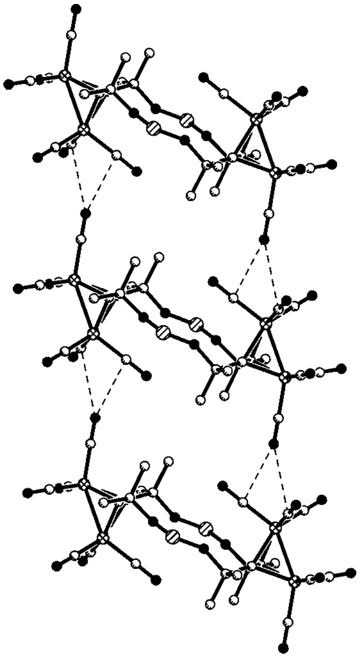


Figure 9. O···CO interactions within the columnar structure of **15** (phenyl substituents are omitted for clarity). The silicon centres are hatched, the oxygen atoms are represented by full circles

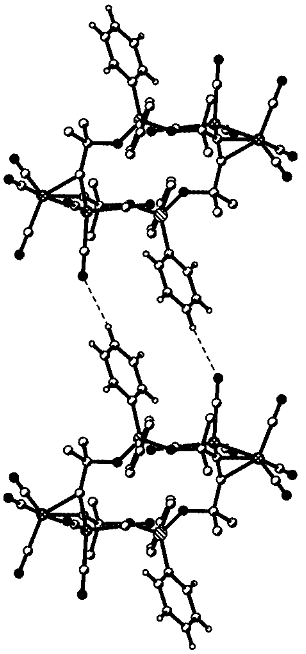


Figure 10. C−H···O interactions between the columns of **15**. The silicon centres are hatched, the oxygen atoms are represented by full circles

In the case of **12** and **13** the interactions within the crystal are less clear cut and more difficult to visualise than for **15**. Therefore we summarise the observed intermolecular short contacts. In the crystal structure of **12** we find dipolar interactions between CO groups within the columns (3.194 Å) and C−H···O interactions between the columns (2.685 Å, C···O distance 3.706 Å). In the crystal structure of **13** there are again dipolar interactions between CO groups within the columns (3.184 Å) and also between the columns (3.162 Å) as well as C−H···O interactions between the columns (2.686 Å, C···O distance 3.432 Å).

Conclusion

Starting from 2-methyl-3-butyn-2-ol we were able to design a simple and short route to prepare sterically hindered cyclic diynes with the 1,3,8,10-tetraoxa-2,9-disilacyclotetradeca-5,12-diyne skeleton. The *gem*-dimethyl and *gem*-diphenyl groups in the α-position of the triple bonds and at the silicon atoms influence the conformation of the 14-membered ring in so far as the expected zigzag arrangement of the $CR_2-O-SiR_2-O-CR_2$ chain is not adopted in the solid state. For **8b** the expected chair like conformation is not possible. A boat like twisted and chair like twisted conformation is preferred instead. The steric hindrance of the triple bonds also shows up in the reactivity with $Co_2(CO)_8$. To get the bis complexation, an eightfold excess had to be used and in the case of **8b** even a tenfold excess yielded only the mono complexed species **14**. It is interesting to note that the rings of **8a**, **12**, **13**, and **15** show columnar stacking in the solid state. In the case of **8a** this observation could partially be traced back to weak C−H···O interactions. For **12**, **13**, and **15** we assume that the columnar stacking is a result of dipolar interactions between the CO groups and weak C−H···O bonds between the oxygen centres of the CO groups and the C−H groups of the phenyl ring.

Experimental Section

General Remarks: All melting points are uncorrected. The NMR spectra were measured with a Bruker WH 300 or Avance 500 spectrometer (^1H NMR at 300 or 500 MHz and ^{13}C NMR at 75 or 125 MHz) using the solvent as internal standard (δ). The mass spectra refer to data from a JEOL JMS-700 instrument. IR spectra were recorded with a Bruker Vector 22 FT-IR spectrometer. UV/Vis absorption data were recorded using a Hewlett Packard HP 8452A Diode Array-spectrometer. Elemental Analysis: Microanalytical laboratory of the University of Heidelberg. All reactions were carried out under an argon atmosphere using dried and oxygen-free solvents.

X-ray Crystallographic Study: Data were collected on a Bruker Smart CCD-diffractometer at 200 K. Relevant crystal and data collection parameters are given in Tables 3 and 4. The structures were solved by direct methods and refined against F^2 with a full-matrix least-square algorithm by using SHELXTL-97[19] software. In all cases an empirical absorption correction was applied by using SADABS,[20] based on the Laue symmetry of the reciprocal space.

Table 3. Crystal data and structural refinement for **8a**, **8b**, and **8c**

	8a	**8b**	**8c**
Empirical formula	$C_{20}H_{36}O_4Si_2$	$C_{50}H_{48}O_4Si_2$	$C_{40}H_{44}O_4Si_2$
Molecular mass	396.67	769.06	644.93
Wavelength [Å]	0.71073	0.71073	0.71073
Crystal system	triclinic	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
Temp. [K]	200(2)	200(2)	200(2)
Z	1	4	1
a	7.6905(1)	11.2936(3)	9.8850(1)
b	8.8782(2)	19.5588(5)	9.8861(1)
c	9.2541(1)	20.0941(5)	11.4361(1)
α	103.407(1)	80.151(1)	69.514(1)
β	107.154(1)	89.200(1)	75.144(1)
γ	91.458(1)	80.780(1)	61.628(1)
V [Å^3]	584.3	4316.2	915.6
$D_{calcd.}$ [g/cm^3]	1.13	1.18	1.17
Abs. coeff. μ [mm^{-1}]	0.17	0.13	0.14
Max./min. transmission	0.82/0.98	0.49/0.98	0.73/0.97
Crystal shape	polyhedron	polyhedron	polyhedron
Crystal size [mm^3]	0.39 × 0.20 × 0.14	0.36 × 0.36 × 0.14	0.44 × 0.34 × 0.22
θ range for data coll. [deg]	2.4 to 27.5	1.0 to 24.1	1.9 to 27.5
Index ranges	$-9 \le h \le 9$	$-12 \le h \le 12$	$-12 \le h \le 12$
	$-11 \le k \le 11$	$-22 \le k \le 22$	$-12 \le k \le 12$
	$-12 \le l \le 12$	$-23 \le l \le 23$	$-14 \le l \le 14$
Reflns. collected	6102	34568	9426
Indep. reflns. [R(int)]	2660 (0.0297)	13670 (0.0432)	4143 (0.0238)
Observed reflns.	2308 [$I > 2\sigma(I)$]	9719 [$I > 2\sigma(I)$]	3554 [$I > 2\sigma(I)$]
Data/restraints/params.	2660/0/190	13670/0/1021	4143/0/212
Goodness-of-fit on F^2	1.06	1.03	1.04
$R(F)$	0.035	0.042	0.037
$R_W(F^2)$	0.095	0.101	0.097
(Δp)max, (Δp)min [e·Å^{-3}]	0.42 and −0.31	0.28 and −0.34	0.38 and −0.31

CCDC-205108 (**8a**), -205109 (**8b**), -205110 (**8c**), -205111 (**12**), -205112 (**13**), -205113 (**14**), and -205114 (**15**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44−1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

General Procedure for the Synthesis of the Terminal Diynes 10a and 10c: A solution of 2-methyl-3-butyn-2-ol in dichloromethane was cooled to 0 °C. Then DMAP and triethylamine were added. To this mixture the dichlorosilane was added slowly. After warming up to room temperature the mixture was hydrolysed. The organic phase was separated, dried and the solvent was removed. Column chromatography (SiO_2, diethyl ether/petroleum ether, 1:2) yielded the pure compounds.

3,3,5,5,7,7-Hexamethyl-4,6-dioxa-5-silanona-1,8-diyne (10a): Reaction mixture: 2-methyl-3-butyn-2-ol (2.00 g, 23.8 mmol), dichloromethane (100 mL), DMAP (22 mg, 0.20 mmol), triethylamine (3.13 mL, 29.0 mmol), dimethyldichlorosilane (1.54 g, 11.9 mmol). Yield 1.67 g (63%). Colourless liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.28 (s, 6 H, CH_3), 1.55 (s, 12 H, CH_3), 2.40 (s, 2 H, CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 1.7 (CH_3), 32.9 (CH_3), 66.8 (C), 70.7 (CH), 89.0 (C) ppm. HRMS (positive EI) calcd. for $C_{12}H_{19}O_2Si$ ([M − H]$^+$), 223.1155; found, 223.1176 (+2.1 mmu). IR (film): $\tilde{\nu}$ = 3307, 2986, 2936, 1464, 1379, 1361, 1258, 1224 cm^{-1}.

3,3,7,7-Tetramethyl-5,5-diphenyl-4,6-dioxa-5-silanona-1,8-diyne (10c): Reaction mixture: 2-methyl-3-butyn-2-ol (2.00 g, 23.8 mmol), dichloromethane (100 mL), DMAP (22 mg, 0.20 mmol), triethylamine (3.13 mL, 29.0 mmol), diphenyldichlorosilane (3.01 g, 11.9 mmol). Yield 3.86 g (93%). White solid, m.p. 39 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.55 (s, 12 H, CH_3), 2.28 (s, 2 H, CH), 7.30−7.34 (m, 6 H, CH), 7.68−7.70 (m, 4 H, CH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 32.7 (CH_3), 68.1 (C), 70.8 (CH), 88.6 (C), 127.4 (CH), 129.8 (CH), 135.6 (C) ppm. HRMS (positive EI) calcd. for $C_{22}H_{24}O_2Si$ ([M]$^+$), 348.1546; found, 348.1541 (−0.5 mmu). IR (KBr): $\tilde{\nu}$ = 3284, 3070, 2985, 1428, 1382, 1363, 1226 cm^{-1}. UV/Vis (CH_2Cl_2) (logε) λ_{max} = 254 (2.81), 260 (2.88), 266 (2.92), 272 (2.81), 286 (2.20) nm. $C_{22}H_{24}O_2Si$ (348.52): calcd. C 75.82, H 6.94; found C 75.42, H 6.92.

General Procedure for the Synthesis of the Terminal Diols 11a−c: A solution of the respective diyne in THF was cooled to −40 °C and *n*-butyllithium was added. After warming up to room temperature the ketone was added. Aqueous workup and extraction of the aqueous phase with dichloromethane yielded after further purification by column chromatography (SiO_2, diethyl ether/petroleum ether, 1:1) the pure diols.

2,12-Dihydroxy-2,5,5,7,7,9,9,12-octamethyl-6,8-dioxa-7-silatrideca-3,10-diyne (11a): Reaction mixture: **10a** (6.93 g, 31.2 mmol), THF (1 L), *n*-butyllithium (1.6 M in hexane, 39.2 mL, 62.7 mmol), acetone (2.0 g, 34.4 mmol). Yield 8.50 g (80%). Colourless oil. ^{1}H

Table 4. Crystal data and structural refinement for **12**, **13**, **14**, and **15**

	12	**13**	**14**	**15**
Empirical formula	$C_{28}H_{41}Co_2O_{10.50}Si_2$	$C_{32}H_{36}Co_4O_{16}Si_2$	$C_{60}H_{58}Co_2O_{11}Si_2$	$C_{52}H_{44}Co_4O_{16}Si_2$
Molecular mass	719.65	968.51	1129.10	1216.77
Wavelength [Å]	0.71073	0.71073	0.71073	0.71073
Crystal system	monoclinic	triclinic	triclinic	triclinic
Space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
Temp. [K]	200(2)	200(2)	200(2)	200(2)
Z	4	2	2	1
a	8.1528(1)	8.1680(1)	10.8861(2)	8.8530(2)
b	22.6349(2)	15.1054(2)	13.5324(2)	13.0117(3)
c	19.3840(3)	16.9358(1)	21.4017(4)	13.4693(3)
α	90	86.054(1)	72.516(1)	117.287(1)
β	93.171(1)	89.442(1)	78.186(1)	97.246(1)
γ	90	83.581(1)	69.516(1)	98.947(1)
V [Å^3]	3571.6	2071.5	2799.4	1327.2
$D_{\text{calcd.}}$ [g/cm^3]	1.34	1.55	1.34	1.52
Abs. coeff. μ [mm^{-1}]	1.04	1.70	0.69	1.34
Max./min. transm.	0.85/0.75	0.95/0.66	1.00/0.93	0.95/0.58
Crystal shape	polyhedron	polyhedron	polyhedron	polyhedron
Crystal size [mm^3]	0.49 × 0.21 × 0.19	0.31 × 0.09 × 0.04	0.50 × 0.24 × 0.17	0.46 × 0.14 × 0.05
θ range for data coll. [deg]	1.4 to 27.5	1.2 to 27.5	1.0 to 25.7	1.8 to 27.5
Index ranges	$-10\le h\le 10$ $-29\le k\le 29$ $-24\le l\le 25$	$-10\le h\le 10$ $-19\le k\le 19$ $-21\le l\le 21$	$-13\le h\le 13$ $-16\le k\le 16$ $-26\le l\le 26$	$-11\le h\le 11$ $-16\le k\le 16$ $-17\le l\le 17$
Reflns. collected	36769	21671	25591	13726
Indep. reflns. [R(int)]	8193 (0.0387)	9444 (0.0575)	10613 (0.0237)	6026 (0.0322)
Observed reflns.	6469 [$I > 2\sigma(I)$]	5572 [$I > 2\sigma(I)$]	8753 [$I > 2\sigma(I)$]	4482 [$I > 2\sigma(I)$]
Data/restraints/params.	8193/10/418	9444/0/499	10613/0/682	6026/0/338
Goodness-of-fit on F^2	1.03	0.96	1.07	0.97
$R(F)$	0.030	0.044	0.030	0.031
$R_W(F^2)$	0.068	0.081	0.075	0.068
(Δp)max, (Δp)min [e·Å^{-3}]	0.30 and −0.33	0.40 and −0.42	0.34 and −0.34	0.48 and −0.37

NMR (300 MHz, $CDCl_3$): δ = 0.27 (s, 6 H, CH_3), 1.49 (s, 12 H, CH_3), 1.52 (s, 12 H, CH_3), 2.45 (s, 2 H, OH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 1.8 (CH_3), 31.5 (CH_3), 33.0 (CH_3), 65.1 (C), 66.9 (C), 87.2 (C), 87.2 (C) ppm. HRMS (positive FAB) calcd. for $C_{18}H_{32}O_4SiNa$ ($[M + Na]^+$), 363.1967; found, 363.1956 (−0.4 mmu). IR (film): ṽ = 3359, 2983, 2934, 1456, 1369, 1256 cm^{-1}. $C_{18}H_{32}O_4Si$ (340.53): calcd. C 63.49, H 9.47; found C 63.20, H 9.50.

1,11-Dihydroxy-4,4,6,6,8,8-hexamethyl-1,1,11,11-tetraphenyl-5,7-dioxa-6-silaundeca-2,9-diyne (11b): Reaction mixture: **10a** (6.93 g, 31.2 mmol), THF (1 L), *n*-butyllithium (1.6 м in hexane, 39.2 mL, 62.7 mmol), benzophenone (5.83 g, 32.0 mmol). Yield 14.3 g (78%). Colourless oil. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.15 (s, 6 H, CH_3), 1.57 (s, 12 H, CH_3), 3.13 (br., OH), 7.08−7.17 (m, 12 H, CH), 7.31−7.45 (m, 8 H, CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 1.4 (CH_3), 32.7 (CH_3), 67.1 (C), 74.2 (C), 85.2 (C), 92.1 (C), 126.1 (CH), 127.5 (CH), 128.1 (CH), 145.0 (C) ppm. HRMS (positive EI) calcd. for $C_{38}H_{40}O_4Si$ ($[M]^+$), 588.2768; found, 588.2732 (+3.6 mmu). IR (KBr): ṽ = 3060, 2983, 1658, 1598, 1490, 1448, 1318, 1279, 1244 cm^{-1}. UV/Vis (CH_2Cl_2) (logε) λ_{max} = 254 (4.38), 332 (2.60) nm.

2,12-Dihydroxy-2,5,5,9,9,12-hexamethyl-7,7-diphenyl-6,8-dioxa-7-silatrideca-3,10-diyne (11c): Reaction mixture: **10c** (10.9 g, 31.2 mmol), THF (1 L), *n*-butyllithium (1.6 м in hexane, 39.2 mL, 62.7 mmol), acetone (2.0 g). Yield 11.5 g (79%). White solid, m.p. 75 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.30 (s, 12 H, CH_3), 1.59 (s, 12 H, CH_3), 1.80 (br., OH), 7.34−7.40 (m, 6 H, CH), 7.71−7.74 (m, 4 H, CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 31.1 (CH_3), 33.1 (CH_3), 64.8 (C), 68.0 (C), 86.7 (C), 87.6 (C), 127.6 (CH), 129.9 (CH), 135.4 (CH), 136.5 (C). HRMS (positive FAB) calcd. for $C_{28}H_{36}NaO_4Si$ ($[M + Na]^+$), 487.2281; found, 487.2258 (−2.3 mmu). IR (KBr): ṽ = 3357, 3296, 2983, 2933, 1429, 1398, 1377, 1362, 1263 cm^{-1}. UV/Vis (CH_2Cl_2) (logε) λ_{max} = 230 (3.66), 260 (2.92), 266 (2.96), 272 (2.83) nm. $C_{28}H_{36}O_4Si$ (464.68): calcd. C 72.37, H 7.81; found C 72.08, H 7.78.

General Procedure for the Synthesis of the Cyclic Diynes 8a−c: A solution of the diol and a solution of the respective dichlorosilane, both in dichloromethane, were added synchronously to a solution of triethylamine and DMPA in dichloromethane over a period of one hour at 0 °C. The mixture was warmed to room temperature and after aqueous workup and purification by column chromatography (SiO_2, diethyl ether/petroleum ether, 5:1) the cyclic diynes were obtained.

2,2,4,4,7,7,9,9,11,11,14,14-Dodecamethyl-1,3,8,10-tetraoxa-2,9-disilacyclotetradeca-5,12-diyne (8a): Reaction mixture: **11a** (8.10 g, 23.8 mmol) in dichloromethane (50 mL), dimethyldichlorosilane (3.07 g, 23.8 mmol) in dichloromethane (50 mL), DMAP (42.7 mg, 0.35 mmol) and triethylamine (6.22 mL, 57.9 mmol) in dichloromethane (150 mL). Yield 4.72 g (50%). White solid, m.p. 71 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.23 (s, 12 H, CH_3), 1.53 (s, 24 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 2.0 (CH_3), 32.6 (CH_3), 67.1 (C), 87.0 (C) ppm. HRMS (positive EI) calcd. for $C_{20}H_{36}O_4Si_2$ ($[M]^+$), 396.2152; found, 396.2169 (+1.7 mmu). IR (film): ṽ = 3310, 2984, 2935, 2868, 2362, 1908, 1729, 1459, 1407, 1367, 1257 cm^{-1}. UV/Vis (CH_2Cl_2) ($\log\varepsilon$) $\lambda_{max} = 252$ (2.56) nm. $C_{20}H_{36}O_4Si_2$ (396.67): calcd. C 60.56, H 9.15. found: calcd. C 60.46, H 9.10.

2,2,4,4,14,14-Hexamethyl-7,7,9,9,11,11-hexaphenyl-1,3,8,10-tetraoxa-2,9-disilacyclotetradeca-5,12-diyne (8b): Reaction mixture: **11b** (14.0 g, 23.8 mmol) in dichloromethane (50 mL), diphenyldichlorosilane (6.03 g, 23.8 mmol) in dichloromethane (50 mL), DMAP (42.7 mg, 0.35 mmol), and triethylamine (6.22 mL, 57.9 mmol) in dichloromethane (150 mL). Yield 1.46 g (8%). White solid, m.p. 139 °C. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = -0.02$ (s, 6 H, CH_3), 1.41 (s, 12 H, CH_3), 7.03−7.11, 7.17−7.25, 7.39−7.42 (m, 30 H, CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 1.5$ (CH_3), 32.4 (CH_3), 67.1 (C), 76.8 (C), 84.5 (C), 92.8 (C), 126.8 (CH), 126.9 (CH), 127.0 (CH), 127.5 (CH), 129.0 (CH), 134.6 (C), 135.2 (CH), 145.6 (C) ppm. MS (positive FAB): *m/z* = 691 ($[M - Ph]^+$). IR (KBr): $\tilde{\nu} = 3059$, 2980, 1489, 1448, 1430, 1378, 1245 cm^{-1}. UV/Vis (CH_2Cl_2) ($\log\varepsilon$) $\lambda_{max} = 254$ (3.63), 286 (2.71) nm. $C_{50}H_{48}O_4Si_2$ (769.10): calcd. C 78.08, H 6.29. found C 77.83, H, 6.27.

4,4,7,7,11,11,14,14-Octamethyl-2,2,9,9-tetraphenyl-1,3,8,10-tetraoxa-2,9-disilacyclotetradeca-5,12-diyne (8c): Reaction mixture: **11c** (11.1 g, 23.8 mmol) in dichloromethane (50 mL), diphenyldichlorosilane (6.03 g, 23.8 mmol) in dichloromethane (50 mL), DMAP (42.7 mg, 0.35 mmol) and triethylamine (6.22 mL, 57.9 mmol) in dichloromethane (150 mL). Yield 3.99 g (26%). White solid, m.p. 186 °C. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.48$ (s, 24 H, CH_3), 7.27−7.38 (m, 6 H, CH), 7.68−7.71 (m, 4 H, CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 32.3$ (CH_3), 68.0 (C), 86.4 (C), 127.1 (CH), 129.2 (CH), 134.8 (CH), 136.7 (C) ppm. HRMS (positive EI) calcd. for $C_{40}H_{44}O_4Si_2$ ($[M]^+$), 644.2778; found, 644.2768 (−1.0 mmu). IR (KBr): $\tilde{\nu} = 3068$, 2985, 1628, 1429, 1378, 1361, 1271 cm^{-1}. UV/Vis (CH_2Cl_2) ($\log\varepsilon$) $\lambda_{max} = 256$ (3.00), 262 (3.11), 266 (3.13), 272 (2.96) nm. $C_{40}H_{44}O_4Si_2$ (644.96): calcd. C 74.49, H 6.88, found C 74.31, H 7.14.

General Procedure for the Synthesis of the $Co_2(CO)_6$ Complexed Diynes: To the solution of the diyne in dichloromethane dicobaltoctacarbonyl was added and stirred overnight. The solvent was evaporated and the residue purified by column chromatography on Al_2O_3/6%H_2O with petroleum ether as mobile phase.

(μ:μ-2,2,4,4,7,7,9,9,11,11,14,14-Dodecamethyl-1,3,8,10-tetraoxa-2,9-disilacyclotetradeca-5,12-diyne)mono(hexacarbonyldicobalt) (12): Reaction mixture: **8a** (100 mg, 0.252 mmol), $Co_2(CO)_8$ (345 mg, 1.01 mmol), dichloromethane (10 mL). Yield 52 mg (30%). Dark red solid, m.p. 71 °C. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.21$ (s, 12 H, CH_3), 1.49 (s, 12 H, CH_3), 1.75 (s, 12 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 2.0$ (CH_3), 32.8 (CH_3), 33.3 (CH_3), 66.8 (C), 79.3 (C), 87.5 (C), 109.3 (C), 208.8 (CO) ppm. MS (positive FD): *m/z* = 682 ($[M]^+$). IR (KBr): $\tilde{\nu} = 2985$, 2088, 2048, 2020, 1628, 1459, 1378, 1360, 1258 cm^{-1}. UV/Vis (CH_2Cl_2) ($\log\varepsilon$) $\lambda_{max} = 254$ (4.27), 312 (3.78), 350 (3.80) nm. $C_{26}H_{36}Co_2O_{10}Si_2$ (682.60): calcd. C 45.75, H 5.32, found C 45.72, H 5.35.

(μ:μ-2,2,4,4,7,7,9,9,11,11,14,14-Dodecamethyl-1,3,8,10-tetraoxa-2,9-disilacyclotetradeca-5,12-diyne)bis(hexacarbonyldicobalt) (13): Reaction mixture: **8a** (100 mg, 0.252 mmol), $Co_2(CO)_8$ (690 mg, 2.016 mmol), dichloromethane (10 mL). Yield 110 mg (45%). Dark red solid, m.p. 60 °C (dec.). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.27$ (s, 12 H, CH_3), 1.73 (s, 24 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 3.5$ (CH_3), 33.1 (CH_3), 76.2 (C), 108.4 (C), 200.5 (CO) ppm. MS (positive FD): *m/z* = 968 ($[M]^+$). IR (KBr): $\tilde{\nu} = 2934$, 2088, 2050, 2017, 1632, 1378, 1261 cm^{-1}. UV/Vis (CH_2Cl_2) ($\log\varepsilon$) $\lambda_{max} = 252$ (4.62), 316 (4.05), 350 (4.09), 406 (3.74) nm. $C_{32}H_{36}Co_4O_{16}Si_2$ (968.53): calcd. C 39.68, H 3.75, found C 39.78, H 3.73.

(μ:μ-2,2,4,4,14,14-Hexamethyl-7,7,9,9,11,11-hexaphenyl-1,3,8,10-tetraoxa-2,9-disilacyclotetradeca-5,12-diyne)mono(hexacarbonyldicobalt) (14): Reaction mixture: **8b** (500 mg, 0.650 mmol), $Co_2(CO)_8$ (500 mg, 6.50 mmol), dichloromethane (40 mL). Yield 144 mg (25%). Brownish red solid, m.p. 124 °C (dec.). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.23$ (s, 6 H, CH_3), 1.55 (s, 6 H, CH_3), 2.23 (s, 6 H, CH_3), 6.96 (m, 14 H, CH), 7.26 (m, 10 H, CH), 7.53 (m, 4 H, CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 2.0$ (CH_3), 32.9 (CH_3), 34.4 (CH_3), 67.0 (C), 77.4 (C), 86.5 (C), 88.5 (C), 92.9 (C), 109.9 (C), 111.3 (C), 126.5 (CH), 127.0 (CH), 127.0 (CH), 127.2 (CH), 127.3 (CH), 127.6 (CH), 129.2 (CH), 130.6 (CH), 133.5 (C), 136.3 (CH) 145.3 (C), 146.1 (C), 199.9 (CO) ppm. HRMS (positive FAB) calcd. for $C_{50}H_{48}Co_2O_4Si_2$ ($[M^+ - 6\,CO]$) 886.1755; found, 886.1777 (+2.2 mmu). IR (KBr): $\tilde{\nu} = 2087$, 2049, 2020, 1627, 1448, 1258 cm^{-1}. UV/Vis (CH_2Cl_2) ($\log\varepsilon$) $\lambda_{max} = 264$ (4.17), 318 (3.16), 348 (3.47), 418 (2.77), 426 (2.77), 432 (2.76) nm.

(μ:μ-4,4,7,7,11,11,14,14-Octamethyl-2,2,9,9-tetraphenyl-1,3,8,10-tetraoxa-2,9-disilacyclotetradeca-5,12-diyne)bis(hexacarbonyldicobalt) (15): Reaction mixture: **8c** (94 mg, 0.146 mmol), $Co_2(CO)_8$ (499 mg, 1.46 mmol), dichloromethane (10 mL). Yield 140 mg (79%). Dark red solid, m.p. 110 °C (dec.). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.62$ (s, 24 H, CH_3), 7.14−31, 7.65 (m, 20 H, CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 34.1$ (CH_3), 78.1 (C), 127.5 (CH), 130.3 (CH), 136.0 (C), 136.7 (CH) ppm. MS (positive FD): *m/z* = 1216 ($[M]^+$). IR (KBr): $\tilde{\nu} = 2990$, 2088, 2051, 2020, 1632, 1460, 1430, 1380, 1221 cm^{-1}. UV/Vis (CH_2Cl_2) ($\log\varepsilon$) $\lambda_{max} = 260$ (4.57), 324 (4.02), 350 (4.11), 422 (3.57) nm.

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[1] E. Kloster-Jensen, G. A. Eliassen, *Angew. Chem.* **1985**, *97*, 587−588; *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 565−566.

[2] H. Sakurai, Y. Nakadaira, A. Hosomi, Y. Eriyama, C. Kabuto, *J. Am. Chem. Soc.* **1983**, *105*, 3359−3360.

[3] L. T. Scott, M. J. Cooney, in: *Modern Acetylene Chemistry* (Ed.: P. J. Stang, F. Diederich), VCH, Weinheim, **1995**, p. 321−351.

[4] H. Sakurai, in: *Recent Advances in Silicon-Containing Cyclic Polyacetylenes* (Ed.: E. Block), John Wiley & Sons, **1989**, p. 323−333.

[5] W. Ando, N. Nakayama, Y. Kabe, T. Shimizu, *Tetrahedron Lett.* **1990**, *31*, 3597−3598; W. Ando, F. Hojo, S. Sekigawa, N. Nakayama, T. Shimizu, *Organometallics* **1992**, *11*, 1009−1011; F. Hojo, S. Sekigawa, N. Nakayama, T. Shimizu, W. Ando, *Organometallics* **1993**, *12*, 803−810.

[6] E. Hengge, A. Baumegger, *J. Organomet. Chem.* **1989**, *369*, C39−C42; A. Baumegger, E. Hengge, S. Gamper, E. Hardtweck, R. Janoschek, *Monatshefte für Chemie* **1991**, *122*, 661−671.

[7] H. Kimling, A. Krebs, *Angew. Chem.* **1972**, *84*, 952−953; *Angew. Chem. Int. Ed. Engl.* **1972**, *11*, 932−933.

[8] A. Krebs, J. Wilke, *Top. Curr. Chem.* **1983**, *109*, 189−233.

[9] B. Jessel, Dissertation, University of Hamburg, **1984**.

[10] H. Sakurai, T. Fujii, K. Sakamoto, *Chem. Lett.* **1992**, 339−342.

[11] H. Sakurai, K. Hirama, Y. Nakadaira, C. Kabuto, *Chem. Lett.* **1988**, 485−486.

[12] R. Gleiter, M. Ramming, H. Weigl, V. Wolfart, H. Irngartinger, T. Oeser, *Liebigs Ann./Recueil* **1997**, 1545−1550.

[13] T. Steiner, *Angew. Chem.* **2002**, *114*, 50−80; *Angew. Chem. Int. Ed.* **2002**, *41*, 48−76; G. R. Desiraju, T. Steiner in *The Weak Hydrogen Bond: Applications to Structural Chemistry and Biology*, Oxford University Press, Oxford **1999**.

[14] R. Taylor, O. Kennard, *J. Am. Chem. Soc.* **1982**, *104*, 5063−5070.

[15] A. Bondi, *J. Phys. Chem.* **1964**, *68*, 441−451.

[16] R. S. Dickson, P. J. Fraser, *Adv. Organomet. Chem.* **1974**, *12*, 323−377; J. P. Collman, L. S. Hegedus, J. R. Norton, R. G. Finke, in: *Principles and Applications of Organotransition Metal Chemistry*, Univ. Science Books, Mill Valley, Calif. **1987**, 861−864.

[17] B. J. Rausch, R. Gleiter, F. Rominger, *J. Chem. Soc., Dalton Trans.* **2002**, 2219−2226.

[18] R. B. King, I. Haiduc, A. Efraty, *J. Organomet. Chem.* **1973**, *47*, 145−151.

[19] *SHELXTL V5.10 G*, M. Sheldrick, Bruker Analytical X-ray-Division, Madison, Wisconsin **1997**.

[20] G. Sheldrick, **1996**, unpublished work based on the method described in: R. H. Blessing, *Acta Crystallogr., Sect. A* **1995**, S1−S33.

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