

Synthesis and Structural Characterization of Novel Organometallic Dehydroannulenes with Fused CpCo-Cyclobutadiene and Ferrocene Units Including a Cyclic Fullerenyne Segment

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Abstract: The synthesis of fused organometallic dehydroannulenes containing cyclobutadiene(cyclopentadienyl)-cobalt or ferrocene units separated by butadiyne linkers is presented. Starting from the corresponding 1,2-diethynylated sandwich complexes, either Eglinton, Hay, or Vögtle-type coupling furnishes the desired dehydroannulenes. The choice of the coupling variant is critical for the success of this reaction. It was found that for diethynylferrocene a variant of the classic Eglinton system utilizing a Cu₂Cl₂/CuCl₂ mixture in pyridine works successfully, while for the case of the cyclobutadiene(cyclopentadienyl)cobalt complexes the Vögtle coupling utilizing Cu(OAc)₂ in acetonitrile gave the most impressive results, leading to a 87% yield of cyclized material. To obtain perethynylated organometallic dehydroannulenes, a novel synthesis of tetraethynylated cyclobutadiene complexes was developed. Flash vacuum pyrolysis of a bisbutadiynylated CpCo-ligated cyclobutadiene furnishes the desired tetraethynylated cyclobutadiene complex via a Bergman-type rearrangement. The two TMS and two TIPS substituents of the cyclobutadiene complex are oriented pairwise *ortho* with respect to each other. Removal of the TMS groups accesses a monomer, which under the conditions of the Vögtle coupling cyclizes to novel trimeric and tetrameric, perethynylated, cyclobutadiene fused, organometallic dehydroannulenes.

Introduction

Fused dehydroannulenes have attracted the attention of chemists for almost half a century. One of the first reported examples was the cyclic dimer¹ of 1,2-diethynylbenzene,^{1a,2} and cyclooligomerization of terminal diynes by copper salts^{3,4} remains the preferred tool for the synthesis of dehydroannulenes.⁵

Dehydroannulenes are fascinating due to their structural relationship to graphite and its segments,⁶ fullerenes,⁷ fullerenynes,⁸ fullerene fragments,⁹ and other proposed allotropes of carbon.¹⁰ Recently, Rubín¹¹ and Tobe¹² have made cage-like

dehydroannulenes forming C₆₀-ions under mass spectrometric conditions. Both, novel carbon allotropes and their smaller segments, come with the promise of exciting optical, electronic, conducting, and supramolecular properties.

While the field of organic dehydroannulenes is flourishing, less is known about the organometallic "arm" of this enterprise. Diederich¹³ accomplished the preparation of a dicobalt complex of C₁₈. More recently, Youngs^{14a,b} reported titanium- or platinum-containing cyclines,^{14c} while Tilley¹⁵ accessed large-ring zirconacyclopentadienes. However, organometallic derivatives of dehydroannulenes in which a π -sandwich, such as ferrocene or cyclobutadiene Cp-cobalt, is fused to the dehydroannulene part are not described. This class of compounds

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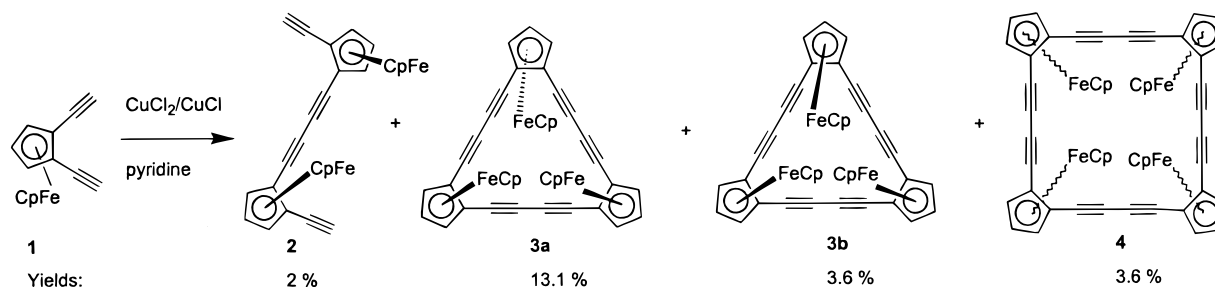
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Scheme 1



would be the organometallic equivalent of dehydrobenzannulenes. Vollhardt and Youngs^{14d-f} demonstrated that dehydrobenzannulenes are precursors for carbon-anions and novel conjugated polymers. Extrapolation suggests that organometallic dehydrobenzannulenes could show similar properties. They are structures of intrinsic beauty and important in a fundamental way for the study of through-bond vs through-space interactions in intramolecular electron transfer.^{14d,e}

We are interested in multiply ethynylated π -complexes of iron, manganese, and cobalt¹⁶ as modules for larger organometallic targets. Linear,¹⁷ star,⁸ and dumbbell shaped¹⁸ representatives have been reported. Here we present the synthesis and structure of a cyclic organometallic fullerene segment and of novel CpCo-cyclobutadiene-fused dehydroannulenes.¹⁹

Results and Discussion

Ferrocene-Fused Dehydroannulenes. Treatment of 1,2-diethynylferrocene **1**²⁰ under Hay conditions (Cu_2Cl_2 , acetone, 25 °C, O_2 ; Scheme 1) furnished large amounts of polymeric material which showed extremely broad lines in both its ^1H and ^{13}C NMR spectra. However, traces of a single compound, **3a**, could be isolated. Attempts to use $\text{Cu}(\text{OAc})_2$ in acetonitrile at 60 °C led to decomposition of **1**. A mixture of Cu_2Cl_2 and CuCl_2 in pyridine provided the cycles **3** in yields of 13.1% (**3a**) and 3.6% (**3b**). In addition to **3**, **1**, a small amount of the open dimer **2**, and a mixture of higher cycles, predominantly tetramer **4**, were isolated. To obtain **3** it was necessary to add the solution of **1** in pyridine over of 14 h via syringe pump to the suspension of $\text{Cu}_2\text{Cl}_2/\text{CuCl}_2$. After complete product analysis the fate of 25% of **1** could be detected. The first assumption was that large

amounts of poly-**1** may have formed, but we were never able to detect any. This is in contrast to the case of 1,2-diethynylcymantrene, where oxidative coupling gave a well-defined and fully characterized polymer.^{8a} As for **1**, the formation of a dark and insoluble material is attributed to partial oxidation/degradation of the ferrocene nucleus. Oxidative degradation is probable, if it is taken into account that even the dimerization of ethynylferrocene to 1,4-diferrocenylbutadiyne proceeds only in modest yield (36%).²¹ Obviously the ferrocene nucleus is not particularly stable toward the conditions of the copper-catalyzed couplings. The two trimers **3a** and **3b** were identified according to their ^{13}C NMR spectra. While the highly symmetric *syn*-cycle **3b** displays only six signals, in *anti*-**3a** the signals are split due to the loss of the 3-fold axis.

How much does the positional isomerism of the CpFe residues in **3a** and **3b** influence their electronic and electroactive²² properties? The UV/vis spectra of **3a/b** are virtually superimposable. This suggests that the electronic ground state in the neutral molecules **3a,b** is quite similar. We investigated the electrochemistry of the two cycles **3** and here we *do* find a difference in their respective cyclic voltammograms. While *anti*-**3a** gives rise to three oxidation waves at 0.61, 0.74, and 0.83 V, *syn*-**3b** displays only two waves at 0.61 and 0.78 V. For comparison, monomer **1** oxidizes at a potential of 0.60 V. The observed splits in **3** are relatively small, which suggests that *both* through-bond and through-space interactions are weak in these cycles.

Structural proof for **3a** was obtained by a single-crystal X-ray structure analysis of a very small specimen grown from dichloromethane. The data set was recorded on a CCD instrument, due to the insufficient number of reflections acquired on a conventional single-crystal diffractometer. The molecular structure of **3a** is shown in Figure 1. The bond lengths and angles of **3a** are in excellent agreement with reported values for similar ethynylated cyclobutadiene complexes and cymantrenes.^{7,16-18} The hydrocarbon ligand in **3a** is flat; the butadiyne bridges are close to linear and appear almost unstrained. The larger bond angles (72°; the optimum would be 60°) are easily accommodated by the three butadiyne bridges.

CpCo(cyclobutadiene)-Fused Dehydroannulenes. In the first experiment we subjected **5**^{24b} to the conditions of the Hay coupling reaction at a temperature of 40 °C. After 2 h, all of **5**

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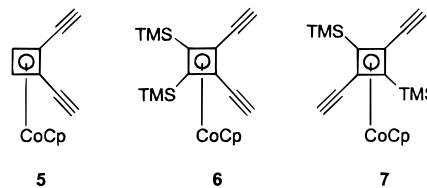
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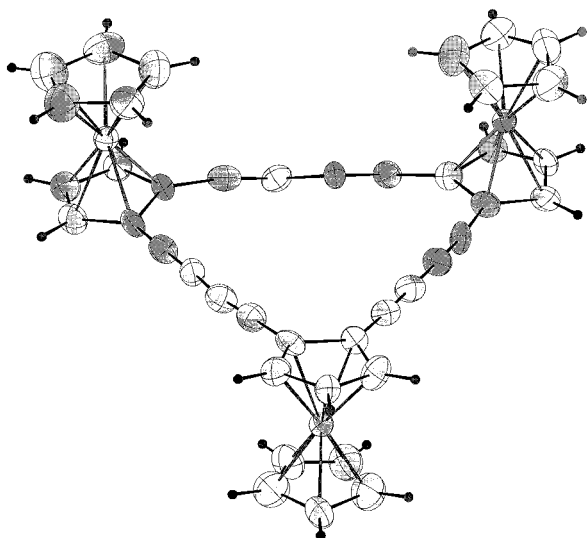


Figure 1. ORTEP plot of **3a**.

was consumed, but no defined compound could be isolated, suggesting that ring formation is not efficient. The propensity toward ring formation in aliphatic systems can be enhanced by the introduction of geminal dimethyl substituents, described as the Thorpe–Ingold effect.²³ It is entropic in nature. Introduction of large substituents seems to favor conformations in open oligomers, which are prone to ring closure. A transfer of this concept to **5** suggested that the bulky complex **6** might be a better choice as monomer than **5**. Hay reaction of **6**²⁴ (boiling TMEDA, 1 h reaction time, introduction of O₂) under conditions developed for the oligomerization of **7**^{17,25} led to a mixture of products. Column chromatography combined with preparative gel permeation chromatography separated the cyclotrimers (**8**) from the cyclotetramers (**9**) and the cyclopentamers (**10**) (Scheme 2). The crude yield of all cyclized material was 63%.

The two trimers **8a/8b** were obtained in 10.1% (*anti*) and 4.4% (*syn*) yield after repeated column chromatography. The crude mixture of the tetramers **9a–d** was separated by preparative HPLC. A yield of 4.0% of **9a**, 17.8% of a mixture of **9b,c**, and 4.7% of **9d** was isolated. While the stereoisomers **9b,c** were not completely separable, single fractions enriched in either **9b** or **9c** were obtained by repeated HPLC. This protocol allowed spectroscopic identification of **9b** and **9c**. Subjecting **6** to the conditions of the Vögtle⁴-type coupling (Cu(OAc)₂, boiling acetonitrile) leads to a crude yield of 87% of cycles **8–10**. Chromatography furnished 16.6% **8a**, 7.9% **8b**, 6.6% **9a**, 26.8% **9b,c**, 7.5% **9d**, and 13% of the mixture of the four pentamers **10**. Analytical HPLC of the diastereomeric mixture of **10** showed that three diastereomers form in a ratio of approximately 1:1:1.

Using a simple model, the statistic stereoisomer distribution for all cycles can be calculated. For the trimer **8** two isomers, *syn* and *anti* in a ratio of 1:2, are expected. The tetramer **9** should form four stereoisomers with a distribution of 1:4:2:1, and the pentamer **10** should likewise form four diastereomers but in a ratio of 3:3:3:1. If the yields of the respective stereoisomers are compared to the statistical model, a good agreement is reached (see Figure 2). In the case of the pentamer **10** one diastereomer (the minor one) is missing. It likely co-elutes with one of the three major diastereomers.

The statistical distribution of diastereomers can be interpreted by the fact that the monomer units in the cycles do not interact with each other, despite the considerable bulk of both the CpCo as well as the SiMe₃ groups. Butadiynes are sufficiently long spacers to separate the monomer units so that free rotation is possible in the open oligomeric precursors.

How are the diastereomers of **8** and **9** discerned? The ¹H NMR spectra of all of the cycles show one signal for the TMS groups and, depending upon symmetry, up to three signals for the Cp ring (**9b**). Diastereomer **9b** has three different Cp rings, thus three different Cp signals are recorded. The Cp signals all fall in the range of 4.99–5.06 ppm, and it is possible to develop an increment system: If the Cp ring under consideration has two adjacent Cp rings oriented *syn*, its signal is shifted downfield to 5.06 ppm. This holds for all Cp signals in **8b**, one Cp signal in **9b**, and all of the Cp signals in **9d**. If the Cp ring under consideration has two neighboring *anti* Cp rings, its signal is recorded at 4.99 ppm (**8a** and **9a,c**). If the Cp ring under consideration has one *syn* and one *anti* positioned Cp ring as neighbor, its shift is observed in the range of 5.02–5.04 ppm (**8a**, 5.03; **9b**, 5.04; **9c**, 5.02). This assignment is supported by the correct values obtained for the integration of the corresponding Cp signals. Likewise, the ¹³C NMR spectroscopic data uphold this assignment. The reason for the small but distinct downfield shift in the presence of a *syn*-oriented Cp-ring lies in its aromaticity. A proton in the vicinity and in the same plane as the Cp ring experiences deshielding, resulting in a downfield shift of its ¹H NMR signal.

Treatment of **8a** by Me₄N⁺F⁻^{24b} leads to the deprotected cycle **8c** in almost quantitative yield (mp 156). The unsatisfying cyclization of **5**, as a consequence, can *not* be attributed to the instability of the formed products. Trimer **8c** is stable, further supporting the notion that the steric environment (i.e., bulky TMS groups), may exert a similar effect toward ring closure of **6** to **8–10**, as the *gem*-dimethyl groups do in the Thorpe–Ingold case.²³

A cyclic voltammogram of **8c** shows one irreversible oxidation wave at 0.91 V suggesting that the CpCo fragments do not interact. To get more information on the electronic structure of **8–10**, UV/vis spectra of **8a,b**, **9d**, and the isomeric mixture of **10** were recorded. Both **8a** and **8b** show superimposable UV/vis spectra, suggesting analogy to the ferrocene case. The relationship (*syn/anti*) of the organometallic fragments with respect to each other does not play a role for the *electronic* structure of the complexes in their ground state. With this proviso we are confident that **9d** appropriately represents the UV/vis spectra of all of the tetramers. The UV/vis spectra of the pentamers **10** were obtained from the diastereomeric mixture. The absorption spectra of **9** and **10** resemble each other (Figure 3). They are similar to the ones obtained for the linear oligomers and polymers of **7**.¹⁷ However, the trimer **8a** reveals an additional band at 390 nm that is absent in the larger cycles. The presence of this additional transition in the trimer is not too surprising. We expect **8** to be strained with a slightly altered hybridization and concomitantly a changed electronic environment. However, there is no conclusive evidence for enhanced conjugation or specific aromatic stabilization/destabilization in these cycles. It seems much more that **8** or **9** are similar to Mitchell's ferrocene-fused dihydropyrenes.²⁶ In these, ferrocenes or Cr(CO)₃-ligated benzenes strongly *localize* the aromatic units and diminish the aromaticity of the large perimeter. The cyclobutadiene complexes in **8–10** and the ferrocene units in **3** appear to have the same effect on their dehydroannulenic cores.

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Scheme 2

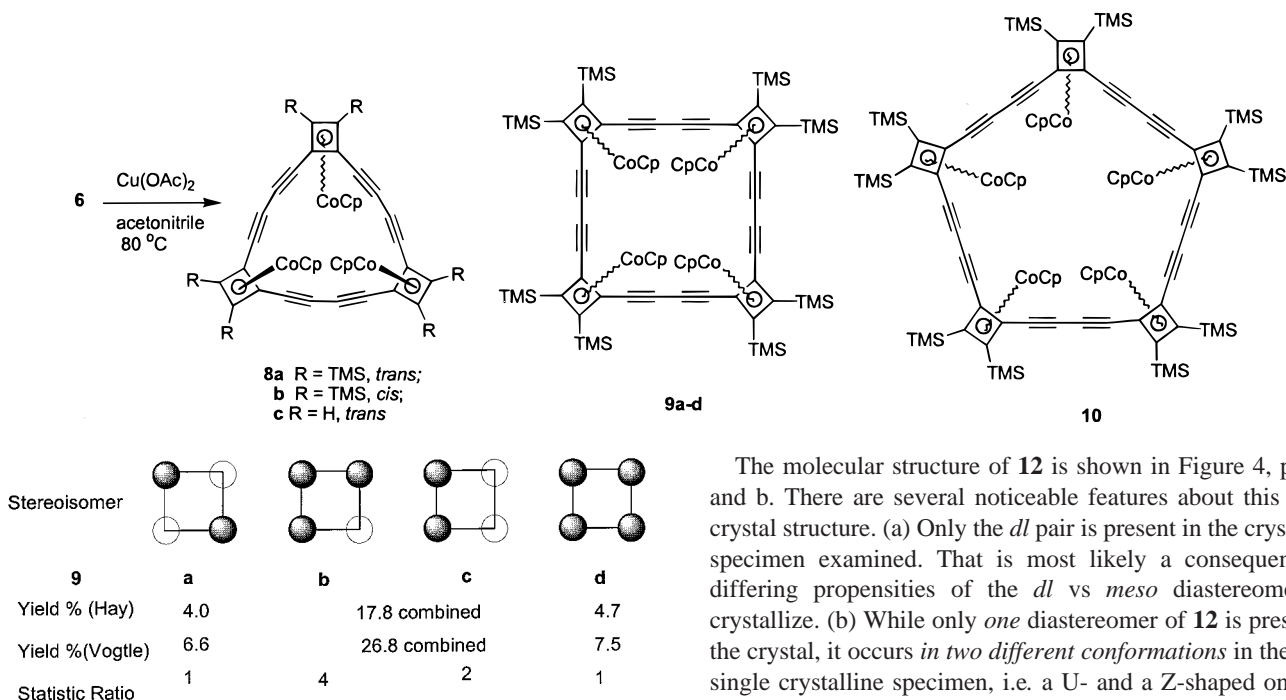


Figure 2. Distribution of diastereomers for **9**. Data for the Hay type and the Vögtle type coupling are compared to the statistic ratio.

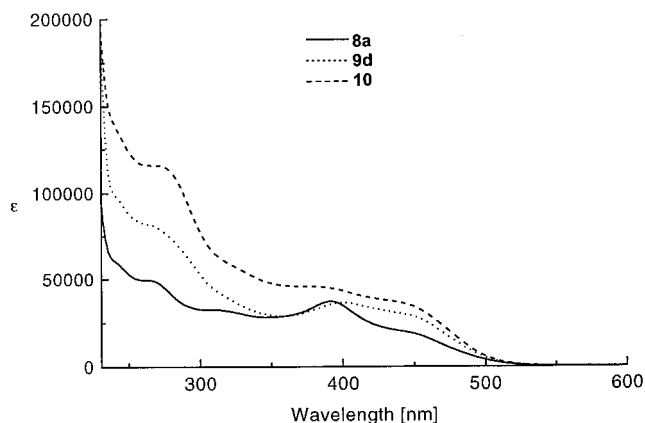


Figure 3. UV/vis spectra of **8a**, **9d**, and **10** overlaid (chloroform).

Extended Monomers. A possible extension of this chemistry would involve the synthesis of dehydroannulenes with octatetrayne bridges. To that end, the monomers **11** would have to be accessed. Scott^{14c} has recently described a method for directed alkyne–alkyne cross coupling utilizing a preformed copper acetylide. Treatment of **6** with BuLi in THF and addition of CuI, propylamine, and TIPS–C≡C–Br furnishes **11b** in a 53% yield (Scheme 3). A second product **12** is formed in this reaction. Only one set of signals is found in the ¹³C NMR spectrum of **12**. We assume that the dimer exists as a mixture of diastereomers with accidentally unresolved NMR shifts. The alternative, involving the diastereoselective coupling of the monomers, seems less probable. To obtain proof of topology and stereochemistry of **12**, a single-crystal X-ray structure was obtained.

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The molecular structure of **12** is shown in Figure 4, parts a and b. There are several noticeable features about this X-ray crystal structure. (a) Only the *dl* pair is present in the crystalline specimen examined. That is most likely a consequence of differing propensities of the *dl* vs *meso* diastereomers to crystallize. (b) While only *one* diastereomer of **12** is present in the crystal, it occurs in *two different conformations* in the same single crystalline specimen, i.e. a U- and a Z-shaped one.

To access **11** via an alternative route, **6** can be reacted with 1-bromopropyn-3-ol under the conditions of the Cadiot–Chodkiewicz coupling. The bisdiyne **11a** is isolated in 83% yield.²⁸ The hydroxymethyl group in **11a** is removed by a mixture of MnO₂/KOH in benzene to furnish a solution of **11c**. Attempts to sequester **11c** led to immediate polymerization under formation of a dark tarry residue. A similar observation was made upon removal of the TIPS groups in **11b**. The solution of **11c** was added to a mixture of Cu(OAc)₂ in acetonitrile and stirred for 24 h at ambient temperature. Aqueous workup led to the isolation of the orange polymer **13** (87%) (Scheme 4), only partially soluble in dichloromethane or chloroform. The polymeric nature of **13** was evidenced by GPC of the soluble extract. Cycles could not be detected.

Perethynylated Cyclobutadiene-Fused Dehydroannulenes.

An important class of compounds for organometallic all-carbon networks would be derivatives of **8–9** in which the trimethylsilyl groups were replaced by alkynyl substituents. These would be the cycles **15** and **16**. To access them, a route to a partially deprotected, tetraethynylated cyclobutadiene complexes, viz. **14c**, was necessary. A Stille-type route to tetraethynylated cyclobutadiene complexes has been developed for Fe(CO)₃-stabilized representatives,¹⁸ but these do not form cycles upon oxidative couplings.^{18a} The unavailability of iodinated CpCo-(cyclobutadiene) complexes renders the Stille reaction useless for the synthesis of **14c**.

Vollhardt^{24b,29} discovered that silyl-transposition in **6** is possible by flash vacuum pyrolysis, furnishing **5b** (Scheme 5). This rearrangement probably proceeds by a Bergman-type³⁰ reaction. Its preparative value would be limited, if only TMS

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Scheme 3

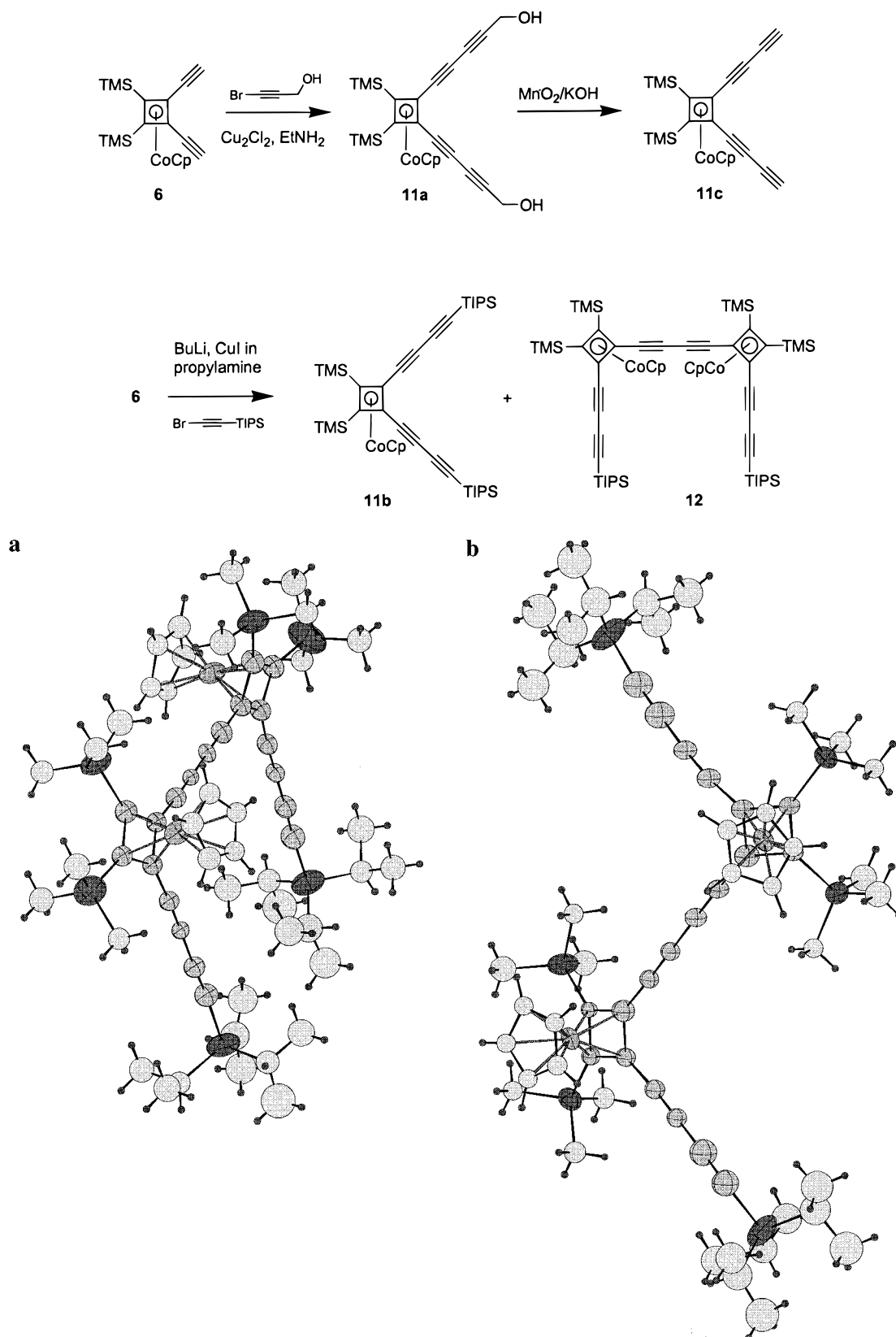


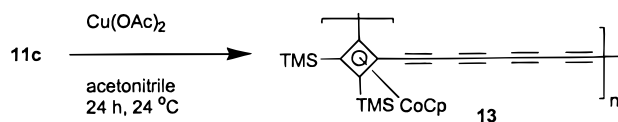
Figure 4. (a) ORTEP plot of **12**, U-shaped conformation. (b) ORTEP plot of **12**, Z-shaped conformation.

groups were to be transposed. If this rearrangement could be extended to other substituents, the transposition of alkyne groups might likewise be feasible. Retrosynthetic analysis suggested **11b** as potential precursor to **14c**. Indeed, flash vacuum pyrolysis

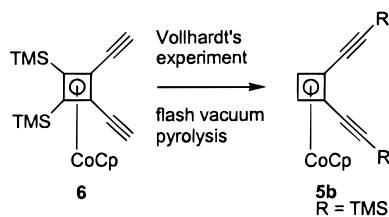
of **11b** furnishes **14a** (Scheme 6). After optimization with regard to temperature and rate of sublimation an 87% yield of **14a** was obtained.^{19b} The star is the only isolable compound of this reaction, besides unconverted **11b**. Attempts to extend this rearrangement by utilizing a phenyl instead of the triisopropyl-

(30) Bergman, R. G. *Acc. Chem. Res.* **1973**, *6*, 25.

Scheme 4



Scheme 5



silyl substituent in **11b** were unsuccessful and led to the isolation of a ceramic-graphitic material of unknown structure.

It suffices to use a high-temperature heat gun to sublime **11b** in substance into the heated quartz spiral; **11b** is stable in the solid state at high temperatures, obviously due to its bulky substituents. Approximately 50 mg of **11b** can be pyrolyzed in several hours. The reaction is not particularly sensitive to moderate pressures in the pyrolysis spiral, and it was sufficient to employ a vacuum of 0.01 mmHg.

In **14a** both the TMS and the TIPS groups are *ortho* to each other. Potassium carbonate in methanol removes only the TMS groups. The semi-deprotected **14b** is stable to ambient conditions and can be stored for extended periods of time. Complete deprotection of **14a** occurred (89%) when it was treated with tetramethylammonium fluoride in DMSO for 1 h. Chromatography (flash silica gel/pentane) furnished **14c**, which displayed only four signals (δ 59.9, 77.1, s; 82.3, 84.5, d) in its ^{13}C NMR spectrum and two singlets (δ 3.33, 4.97; ratio 4:5) in its ^1H NMR spectrum. The bright yellow **14c** is stable in the crystalline state for a couple of hours at ambient temperature and can be stored at $0\text{ }^\circ\text{C}$ for several days. The sterically demanding CpCo group is responsible for the substantially enhanced stability when **14c** is compared to its $\text{Fe}(\text{CO})_3$ -stabilized cousin.¹⁸ A single-crystal X-ray structure of **14c** has been obtained and discussed.^{19b}

Treatment of **14b** with $\text{Cu}(\text{OAc})_2$ in acetonitrile⁴ furnishes a mixture of the trimers **15** and the tetramers **16** in a combined yield of 76% (Scheme 7). The residual 24% of the starting material must be incorporated into higher oligomers and polymers that were not mobile under the chromatographic conditions employed. Repeated flash chromatography and preparative TLC enabled the separation of the two diastereomers of **15** and the isolation of one diastereomer (all *anti*) of **16**. The three remaining diastereomers of **16** were inseparable from each other but one fraction was sufficiently enriched (*all-syn-16d*) to obtain its ^1H NMR spectrum. All of the diastereomers are yellow crystalline powders stable under ambient conditions. The dehydroannulenes decompose above $245\text{ }^\circ\text{C}$ (observed under a polarizing microscope) without melting. As expected, the two diastereomers of **15** show different ^{13}C NMR spectra. The C_s -symmetrical **15a** displays six signals for the three cyclobutadiene carbons, six signals for the butadiyne bridges, three signals for the alkyne substituents (unresolved), and two signals for the Cp rings in a ratio of 2:1.

The *syn*-isomer **15b** is C_{3h} -symmetric and six resonances are expected in its ^{13}C NMR spectrum (hydrocarbon ligand). Five are observed and we conclude from the position of the signals that two singlets for the cyclobutadiene ring are unresolved. One signal for the cyclopentadienyl rings is observed. The molecular weights for the cycles **15** and **16** were determined

by mass spectroscopy and are in accord with our assessment. **15** as well as **16** gave the expected molecular ions (+2 mass units, EI mode) with the correct isotopic distribution.

Conclusion

The synthesis of dehydroannulenes fused to an organometallic sandwich can be performed by cyclization of diethynylated π -complexes. The key to obtain the organometallic dehydroannulenes **3**, **8–10**, and **15–16** was the careful selection of the coupling reaction, dependent upon the organometallic precursor. The separation of different diastereomers presented a challenge. The diastereomers arise from the orientation of the organometallic fragments with respect to each other and the plane of the polycyclic hydrocarbon ligand. These diastereomers allow, at least in principle, through-bond versus through-space interactions to be separated in intramolecular electron transfer of sandwich complexes. Surprisingly, the absorption spectra are dominated by the transitions of the organometallic fragments and their respective relationship (*syn/anti*) seems to be of minute influence on the electronic structure of these complexes. The UV/vis spectra of different diastereomers of the same ring size are superimposable in all of the examined cases.

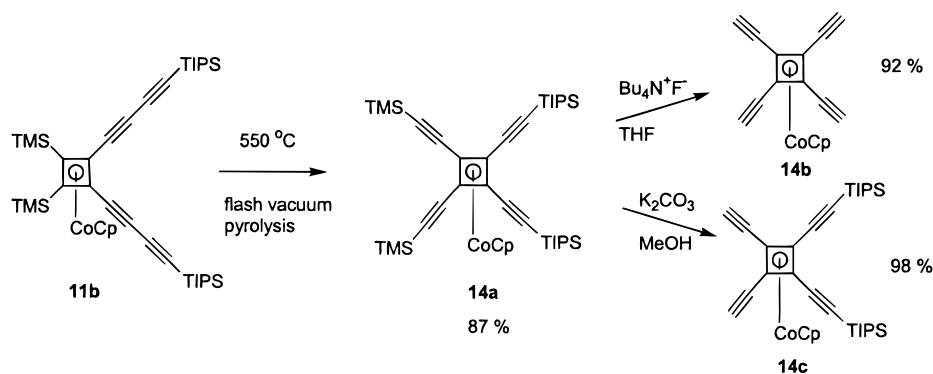
The presented results depict a major step in the direction toward larger and closed segments of organometallic all-carbon networks. The use of the stable ferrocenes and CpCo-ligated cyclobutadienes (in comparison to cymantrenes and tricarbonyl iron cyclobutadiene complexes) has rewarded our efforts to make these novel rings. With the synthesis of compound **14b**, access to the structurally spectacular cycles **15** and **16** has been achieved. In the future, we will exploit the chemistry of the star-shaped tetraethynylcyclobutadiene **14**.

Experimental Section

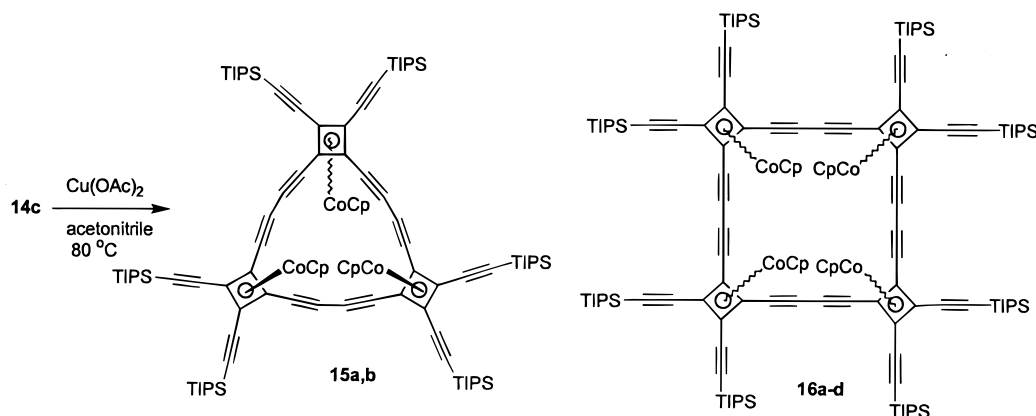
Oxidative Coupling of 1. A mixture of Cu_2Cl_2 (5.41 g, 60.8 mmol) and CuCl_2 (10.1 g, 81.0 mmol) in 100 mL of pyridine was prepared in a 250 mL flask under nitrogen. Compound **1** (948 mg, 4.05 mmol, in 30 mL of pentane) was added over 14 h using a syringe pump. Aqueous workup (dichloromethane) followed by chromatography over flash silica gel (pentane/dichloromethane, 80:20) gave **1** (26 mg, 2.7%), dimer **2** (19 mg, 2.0%), **3a**, **3b**, and higher cycles **4** (34 mg, 3.6%). **3a** (124 mg, 13.1%): Mp $165\text{ }^\circ\text{C}$ dec. IR (KBr): ν 3097, 2925, 2215, 2152, 1413, 1108, 1003, 825 cm^{-1} . ^1H NMR (CDCl_3): δ 4.34 (bs, 3 H), 4.35, 4.40 (2 s, 15 H), 4.60 (bs, 6 H). ^{13}C NMR (CD_2Cl_2): δ 68.63, 68.68, 68.83, 69.37, 71.64, 71.70, 72.26, 72.37, 74.15, 74.20, 77.86, 78.03, 78.07. UV/vis (CH_2Cl_2): λ_{max} (ϵ) 296 (449370), 319 (494230), 383 (103620), 464 (61910). MS (FD) m/z 696.1. $\text{C}_{42}\text{H}_{24}\text{Fe}_3$ (696.2). Calcd C 72.47, H 3.48; found C 72.38, H 3.54. **3b** (31 mg, 3.3%): Mp $176\text{ }^\circ\text{C}$ dec. IR (KBr): ν 3099, 2925, 2212, 2150, 1106, 1001, 825 cm^{-1} . ^1H NMR (CDCl_3): δ 4.30 (t, $^3J_{\text{HH}} = 2.70\text{ Hz}$, 3 H), 4.41 (s, 15 H), 4.56 (d, $^2J_{\text{HH}} = 2.70\text{ Hz}$, 6 H). ^{13}C NMR (CD_2Cl_2): δ 69.71, 70.22, 72.37, 72.72, 74.93, 78.53. UV/vis (CH_2Cl_2): λ_{max} (ϵ) 272 (382210), 296 (420510), 319 (475080), 382 (103620), 465 (61910). MS (FD): m/z 696.1. $\text{C}_{42}\text{H}_{24}\text{Fe}_3$ (696.2). Calcd C 72.47, H 3.48; found C 72.18, H 3.65.

Hay Coupling of 6. A solution of **6** (1.08 g, 2.93 mmol) and Cu_2Cl_2 (0.594 g, 6.00 mmol) in 200 mL of TMEDA was heated to reflux ($122\text{ }^\circ\text{C}$). For 1 h, O_2 was bubbled through the solution. The TMEDA was removed at 0.1 Torr/ $40\text{ }^\circ\text{C}$, the residue was hydrolyzed (ammonia solution) and extracted with dichloromethane. Filtration over aluminum oxide (pentane/dichloromethane, 80:20) furnished crude product (683 mg, 63%). The separation of **8a,b** was achieved by repetitive chromatography of the residue over aluminum oxide with pentane as eluent to give **8a** (109 mg, 10.1%) as a first fraction followed by **8b** (48 mg, 4.4%). Compounds **9** and **10** were isolated as last fraction. They were pre-separated by preparative gel permeation chromatography (GPC) into a fraction containing only **9** and one containing only **10**. The single fractions were separated into their diastereomers by preparative HPLC.

Scheme 6



Scheme 7



The following yields were obtained: **9a** (43 mg, 4.0%), a mixture of **9b,c** (192 mg, 17.8%) and **9d** (51 mg, 4.7%). The pentamers **10** were isolated as a mixture of diastereomers (130 mg, 12.0%) but not separated on a preparative scale.

Vögtle Coupling of 6. A solution of **6** (470 mg, 1.28 mmol) and $\text{Cu}(\text{OAc})_2$ (3.10 g, 17.0 mmol) in 300 mL of acetonitrile was heated under nitrogen to reflux (80 °C) for 3 h. The acetonitrile was removed under reduced pressure. Aqueous workup with dichloromethane followed by filtration over aluminum oxide (pentane/dichloromethane, 80:20) furnished crude product (409 mg, 87%). The separation of the cycles was performed by a combination of preparative GPC and HPLC. **8a** (78 mg, 16.6%): Mp >230 °C dec. IR (KBr): ν 3107, 2956, 2900, 2178, 2120, 1259, 1247, 841, 811 cm^{-1} . ^1H NMR (CD_2Cl_2): δ 0.20 (s, 18 H), 0.21 (s, 36 H), 4.99 (s, 5 H), 5.03 (s, 10 H). ^{13}C NMR (CD_2Cl_2): δ 0.14, 0.17, 68.70, 68.87, 69.03, 73.68, 73.72, 74.04, 78.57, 78.70, 78.87, 80.91, 81.18, 81.26, 81.68, 81.79. UV/vis (CH_2Cl_2): λ_{max} (ϵ) 264 (45050), 308 (29470), 391 (33280). MS (FD): m/z 1099.1. $\text{C}_{57}\text{H}_{69}\text{Si}_6\text{Co}_3$ (1099.5). Calcd C 62.27, H 6.33; found C 61.93, H 6.46. **8b** (37 mg, 7.9%): Mp >230 °C dec. IR (KBr): ν 3107, 2955, 2900, 2176, 2126, 1259, 1247, 841, 812 cm^{-1} . ^1H NMR (CD_2Cl_2): δ 0.22 (s, 54 H), 5.06 (s, 15 H). ^{13}C NMR (CD_2Cl_2): δ 1.56, 70.38, 75.17, 80.31, 82.54, 83.01. UV/vis (CH_2Cl_2): λ_{max} (ϵ) 264 (49560), 392 (29890). MS (FD): m/z 1099.1. $\text{C}_{57}\text{H}_{69}\text{Si}_6\text{Co}_3$ (1099.5). Calcd C 62.27, H 6.33; found C 62.56, H 5.90. **9a** (31 mg, 6.6%): Mp >240 °C dec. IR (KBr): ν 3108, 2954, 2925, 2904, 2366, 2179, 2124, 1259, 1247, 841, 812 cm^{-1} . ^1H NMR (CD_2Cl_2): δ 0.21 (s, 72 H), 5.01 (s, 20 H). ^{13}C NMR (CD_2Cl_2): δ 0.19, 67.51, 75.24, 81.95, 77.91, 80.07. UV/vis (CH_2Cl_2): λ_{max} (ϵ) 266 (75400), 360 (45750). MS (FD) m/z 1465.1. $\text{C}_{76}\text{H}_{92}\text{Si}_8\text{Co}_4$ (1466.1). Calcd C 62.27, H 6.33; found C 61.99 H 6.34. Mixture of **9b** and **9c** (126 mg, 26.6%). **9b**: IR (KBr): ν 3107, 2955, 2925, 2898, 2364, 2178, 2129, 2125, 2050, 1259, 1247, 842, 812 cm^{-1} . ^1H NMR (CD_2Cl_2): δ 0.21 (s, 54 H), 0.22 (s, 18 H), 4.99 (s, 5 H), 5.04 (s, 10 H), 5.06 (s, 5 H). ^{13}C NMR (CD_2Cl_2): δ 0.27, 67.68, 67.83, 75.05, 75.16, 75.28, 78.02, 78.17, 80.10, 80.20, 81.84, 81.94, 82.00. MS (FD): m/z 1465.1. $\text{C}_{76}\text{H}_{92}\text{Si}_8\text{Co}_4$ (1466.1). **9c**: ^1H NMR (CD_2Cl_2): δ 0.21 (s, 72 H), 5.02 (s, 20 H). **9d** (35 mg, 7.5%): Mp >240 °C dec. IR (KBr): ν 3106, 2955, 2924, 2367, 2180, 2127, 1260, 1247, 842,

811 cm^{-1} . ^1H NMR (CD_2Cl_2): δ 0.20 (s, 72 H), 5.06 (s, 20 H). ^{13}C NMR (CD_2Cl_2): δ 0.20, 67.69, 75.08, 78.08, 80.16, 81.81. UV/vis (CH_2Cl_2): λ_{max} (ϵ) 266 (81480), 401 (36470). MS (FD): m/z 1465.1. $\text{C}_{76}\text{H}_{92}\text{Si}_8\text{Co}_4$ (1466.1). Calcd C 62.27, H 6.33; found C 61.91 H 6.50. **10** (61 mg, 13.0%), mixture of diastereomers.

Desilylation of 8a. To a suspension of $\text{Me}_4\text{N}^+\text{F}^-$ (3.8 mg, 41 μmol) in 5 mL of DMSO, was added **8a** (22 mg, 20 μmol) in 5 mL of ethyl ether under N_2 . The reaction mixture was stirred for 16 h at 21 °C. Aqueous workup and chromatography (silica gel, pentane/dichloromethane, 80:20) affords **8c** (12 mg, 90%): Mp 156 °C. IR (KBr): ν 3104, 2178, 2117, 1004, 816 cm^{-1} . ^1H NMR (CD_2Cl_2): δ 4.19 (s, 6 H), 5.05 (s, 5 H), 5.09 (s, 10 H). ^{13}C NMR (CD_2Cl_2): δ 59.46, 59.73, 59.93, 61.77, 61.82, 62.05, 78.36, 78.47, 78.52, 80.23, 80.54, 80.59, 81.64, 81.70. UV/vis (CH_2Cl_2): λ_{max} (ϵ) 261 (39570), 315 (30400), 383 (41210). MS (FD): m/z 666.3. $\text{C}_{39}\text{H}_{21}\text{Co}_3$ (666.5). Calcd C 70.28, H 3.16; found C 70.17, H 3.75.

Synthesis of 11a. At 0 °C a 100 mL Schlenk flask was charged under N_2 with Cu_2Cl_2 (109 mg, 1.00 mmol), hydroxylamine hydrochloride (150 mg, 2.16 mmol), aqueous ethylamine solution (5 mL, 70% in H_2O), methanol, and a solution of **6** (403 mg, 1.09 mmol). Subsequently 1-bromopropyn-3-ol (386 mg, 2.86 mmol) was added at 0 °C. The mixture was stirred for 1 h at ambient temperature, hydrolyzed with dilute HCl, and extracted with ether. Chromatography of the crude product (silica gel/dichloromethane) furnishes **11a** (431 mg, 83%): Mp 98 °C. IR (KBr): ν 3285, 3102, 2958, 2932, 1462, 1245, 847 cm^{-1} . ^1H NMR (CDCl_3): δ 0.20 (s, 18 H), 4.26, 4.28 (2 s, 4 H), 5.05 (s, 5 H). ^{13}C NMR (CD_2Cl_2): δ 0.31, 51.25, 67.26, 70.33, 75.16, 75.66, 76.61, 82.40, 84.12. $\text{C}_{24}\text{H}_{27}\text{Si}_2\text{CoO}_2$ (462.1). Calcd C 62.32, H 6.13; found C 62.48, H 6.53.

Synthesis of 11c via MnO_2/KOH . Powdered KOH (560 mg, 10.0 mmol), activated MnO_2 (1.74 g, 20.0 mmol), and **11a** (431 mg, 904 μmol) in 20 mL of benzene were stirred for 1 h at ambient temperature. The resulting suspension was filtered over silica gel and eluted with pentane. According to TLC control, the material was homogeneous. Attempts to isolate **11c** were unsuccessful, due to its spontaneous polymerization upon concentration of the pentane/benzene solutions. ^1H NMR (CDCl_3): δ 0.15 (s, 18 H), 2.63 (s, 2 H), 4.94 (s, 5 H).

Polymerization of 11c to 13. A solution of **11c** in pentane/benzene, Cu(OAc)₂ (3.63 g, 20.0 mmol), and 200 mL of acetonitrile were combined. The mixture was stirred for 24 h at ambient temperature, filtered, and concentrated under reduced pressure. Precipitation into methanol furnished **13** as an insoluble orange material (350 mg, 87% with respect to **11a**). ¹H NMR of soluble fraction (CD₂Cl₂): δ 0.20 (s, 18 H), 5.02 (s, 5 H). End groups can be seen as a weak signal at δ 2.73.

Synthesis of 11b. A flame-dried Schlenk flask was charged with **6** (398 mg, 1.08 mmol) and 50 mL of THF and cooled to -78 °C. BuLi (1.38 mL, 2.20 mmol, hexanes) was added and the reaction mixture warmed to 0 °C. CuI (419 mg, 2.20 mmol) was introduced. After 15 min the mixture was recooled to -78 °C and 10 mL of dry propylamine and bromo(triisopropylsilyl)acetylene (577 mg, 2.21 mmol) were injected by syringe. After warming to 21 °C, aqueous workup, and chromatography (flash silica gel/pentane) **11b** and as a second band **12** were isolated. **11b** (421 mg, 53%): Mp 103 °C. IR (KBr): ν 3105, 2955, 2938, 2180, 1247, 846 cm⁻¹. ¹H NMR (CD₂Cl₂): δ 0.17 (s, 18 H), 1.09 (s, 42 H), 4.98 (s, 5 H). ¹³C NMR (CD₂Cl₂): δ 0.00, 11.49, 18.51, 66.69, 73.32, 75.39, 81.69, 88.62, 90.75. C₄₁H₆₅Si₄Co (729.2). Calcd C 67.53, H 8.98; found C 67.68, H 8.31. **12** (125 mg, 22%): Mp 119 °C. IR (KBr): ν 3107, 2955, 2939, 2182, 1248, 848 cm⁻¹. ¹H NMR (CD₂Cl₂): δ 0.21 (s, 36 H), 1.10, 1.11 (2 s, 42 H), 5.02 (s, 10 H). ¹³C NMR (CD₂Cl₂): δ 0.27, 11.76, 18.77, 66.55, 67.76, 73.75, 75.55, 75.77, 77.36, 77.95, 80.17, 81.95, 88.82, 91.08.

Pyrolysis of 11b. A coiled quartz tube (1 m × 8 mm) was held at 550 °C under 1.5 × 10⁻¹ to 10⁻⁴ mmHg (dynamic) while **11b** (50 mg, 68.6 μmol) was sublimed/distilled with a heating gun at 170–250 °C through the quartz tube. The product was collected in a U-tube held at ambient temperature. Chromatography (flash silica gel/pentane) furnished back **11b** (12 mg, 24%) and as a second band **14a** (33 mg, 66%; 87% with respect to consumed starting material). **14a**: Mp 88 °C. IR (KBr): ν 3104, 2955, 2948, 1450, 847 cm⁻¹. ¹H NMR (CDCl₃): δ 0.21 (s, 18 H), 1.11 (s, 42 H), 4.89 (s, 5 H). ¹³C NMR (CDCl₃): δ -0.10, 11.51, 18.86, 60.61, 61.80, 84.37, 97.49, 98.75, 100.68, 100.70. UV/vis (CH₂Cl₂): λ_{max} (ε) 275 (23220), 335 (4120). MS (FD): *m/z* 728.2. C₄₁H₆₅Si₄Co (729.2). Calcd. C 67.53, H 8.98; found C 68.49, H 8.75.

Deprotection of 14a to 14b or 14c. (a) **14a** (20.0 mg, 27.4 μmol) was dissolved in 10 mL of dichloromethane. A suspension of potassium carbonate (500 mg, 3.67 mmol) in 3 mL of methanol was added and the reaction mixture stirred for 10 min. Aqueous workup and chromatography (flash silica gel, pentane) furnished **14b** (15.6 mg, 98%): Mp 53 °C. IR (KBr): ν 3301, 3102, 2956, 1456, 1248, 848 cm⁻¹. ¹H NMR (CDCl₃): δ 1.12 (s, 42 H), 3.33 (s, 2 H), 4.97 (s, 5 H). ¹³C NMR (CDCl₃): δ 11.51, 18.86, 59.87, 61.61, 77.69, 81.90, 84.33, 97.73, 100.17. MS (FD): *m/z* 584.1. C₃₅H₄₉Si₂Co (584.9). (b) Tetramethylammonium fluoride (300 mg, 3.22 mmol) was dissolved in 15 mL of DMSO at 140 °C. After the mixture was cooled to 21 °C, **14a** (45.0 mg, 61.7 μmol) in 10 mL of ethyl ether was added and the mixture was stirred for 2 h at 21 °C. Aqueous workup and chromatography (flash silica gel/pentane) gave **14c** (15.0 mg, 89%): Mp 105 °C dec. IR (KBr): ν 3302, 3103, 1245 cm⁻¹. ¹H NMR (CDCl₃): δ 3.33 (s, 4

H), 4.97 (s, 5 H). ¹³C NMR (CDCl₃): δ 59.86, 77.05, 82.30, 84.52. UV/vis (CH₂Cl₂): λ_{max} (ε) 268 (24290), 324 (8200). MS (FD): *m/z* 272.26. C₁₇H₉Co (272.2). Calcd. C 75.02, H 3.33; found C 75.20, H 4.21.

Synthesis of 15 and 16. A mixture of Cu(OAc)₂ (1.00 g, 5.51 mmol), **14b** (100 mg, 0.171 mmol) in 50 mL of acetonitrile was heated to reflux for 8 h. Aqueous workup and column filtration (1:4 dichloromethane/hexane) led to the isolation of 76 mg (76%) of cycles. The mixture was subjected to column chromatography (Merck silicagel 60, pure hexane, gradually increasing to a 1:49 mixture of dichloromethane/hexane) to furnish 39 mg of the trimers **15** and 37 mg of the tetramers **16**. Repeated thick-layer chromatography of the isomeric mixtures of **15** (Merck thick-layer plates, 1:49 dichloromethane/hexane) furnishes **15a** and **15b**. The same procedure was applied for the tetramers **16** (1:19 dichloromethane/hexane) to furnish **16a**, a mixture of **16b,c**, in which two isomers were identified by their ¹H and ¹³C NMR spectra, and as a last fraction **16d**. All of the obtained cycles decompose above 245 °C without melting. **15a** (15 mg, 15%): IR (KBr): ν 3078, 2958, 2925, 2866, 2140, 1261, 1020, 801 cm⁻¹. ¹H NMR (CD₂Cl₂): δ 5.05 (s, 10 H), 5.02 (s, 5 H), 1.26 (s, 18 H), 1.12 (s, 108 H). ¹³C NMR (CD₂Cl₂): δ 12.21, 14.76, 61.82, 62.08, 62.34, 62.57, 79.92, 80.12, 80.24, 80.83, 80.91, 81.00, 84.81, 84.87, 98.85, 98.91, 98.94, 100.34. UV/vis (CH₂Cl₂): λ_{max} 278, 333, 412. MS (FD): *m/z* 1748.2. C₁₀₅H₁₄₁-Co₃Si₆ (1747.8). **15b** (11 mg, 11%): IR (KBr): ν 2924, 2864, 2136, 1463, 996, 884. ¹H NMR (CDCl₃): δ 5.03 (s, 15 H), 1.24 (s, 18 H), 1.09 (s, 108 H). ¹³C NMR (CDCl₃): δ 12.21, 19.79, 62.58, 62.60, 80.37, 81.49, 84.78, 98.76, 100.57. UV/vis (CH₂Cl₂): λ_{max} 281, 333, 408. MS (FD): *m/z* 1748.2. C₁₀₅H₁₄₁Co₃Si₆ (1747.8). **16a** (13 mg, 13%): ¹H NMR (CDCl₃): δ 4.99, 4.96 (2 s, 20 H), 1.24 (s, 24 H), 1.09 (s, 144 H). ¹³C NMR (CDCl₃): δ 11.20, 18.77, 60.05, 62.81, 77.80, 79.45, 83.87, 83.98, 97.76, 99.67. MS (FD): *m/z* 2330.3. C₁₄₀H₁₈₈Co₄Si₈ (2331.02). **16b** and **16c** (24 mg, 24%): ¹H NMR (CDCl₃): δ 5.08, 5.06, 5.05, 5.02 (4 s, 20 H), 1.27 (s, 24 H), 1.13 (s, 144 H). ¹³C NMR (CDCl₃): δ 12.25, 19.72, 61.40, 61.49, 61.66, 63.64, 78.86, 81.01, 84.60, 84.72, 84.75, 84.93, 98.51, 101.42. **16d** (7 mg, 7%): ¹H NMR (CDCl₃): δ 5.04 (s, 20 H), 1.24 (s, 24 H), 1.09 (s, 144 H).

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Supporting Information Available: Details and tables for X-ray crystal structures of **3a**, **8a**, and **12** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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