Synthesis of Linear Oligomers of [1,3-Diethynyl-2,4-bis(trimethylsilyl)cyclobutadiene]-cyclopentadienylcobalt: Dimer to Nonamer

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Coupling of [1,3-diethynyl-2,4-bis(trimethylsilyl)cyclobutadiene]cyclopentadienylcobalt (**1**) under Hay conditions in boiling butanone gives rise to the isolation of the oligomers (dimer **2** to nonamer **9**) after column chromatography (**2**−**4**) and preparative HPLC over a cyanophenyl phase (**5**−**9**) in moderate yields. Depending on the reaction time either favorably **2** (45 min), a mixture of **2**−**4** (90 min), or higher oligomers **3**−**9** (3 h) are formed. Quite interesting are the UV−vis spectra. They show from **3** up to **9** the occurrence of a band at $\lambda = 312-348$ nm which intensifies during the series. The highest wavelength absorption at $\lambda = 435$ nm is almost independent of the oligomer length. An X-ray crystal structure analysis of **2** was undertaken. Deprotection of **2** and **3** with tetramethylammonium fluoride in DMSO yielded the parent dimer **11** and the trimer **12** in almost quantitative yield. Attempts to determine the rotation barrier around the butadiyne units in **2**, **3**, **10**, and **11** showed that the complexes are torsionally mobile on the NMR time scale down to −100 °C and no rotational barrier could be determined.

Introduction

The chemistry of tricarbonyliron-complexed cyclobutadiene was established by Pettit and Crigee 3 decades ago.[1] As a consequence, a good deal of knowledge had been piled up concerning the reactivity of the organic ligand and many different substituents were introduced into the four-membered ring[2] during the 1960s and early 1970s. Surprisingly no alkynyl-substituted cyclobutadiene complexes are reported from that period. In our laboratories we have developed syntheses of mono-, di-, and tetraalkynyl-substituted tricarbonyl(cyclobutadiene)irons by manipulation of the parent complex.[3] In 1978 Vollhardt[4a] discovered that the dimerization of bis(trimethylsilyl)butadiyne over $CpCo(CO)_2$ gave rise to the formation of **1** (Chart 1) in preparative useful yields. Quantities of up to 5−10 g of **1** can be obtained in a single pot. However, the synthetic potential of the *p*-diethynyl **1** was never investigated in depth.[4b]

Organometallic polymers[5] have a considerable potential as electroactive, NLO-active, or liquid crystalline materials, but comparatively few have been synthesized. In an earlier communication we showed that **1** gives a polymer[6] (**10**) under relatively drastic copper-catalyzed Hay-coupling conditions. It was particularly interesting to note that in the UV−vis spectrum of **10** a considerable bathochromic shift of the recorded bands occurred, as compared to the monomer **1**. In addition an increase in the ϵ value of the absorptions was observed.

Studies of oligomeric model compounds are an essential requisite for establishing structure−property relationships in conjugated polymers.[7] The usefulness of such series of oligomers has been demonstrated in the case of poly(*p*-phenylene)s,[7] poly(*p*-phenylenevinylene)s,[8] and polythiophenes.[8] The convergence of optical and electronic parameters such as absorption or redox potential with increasing chain length of the conjugated π-system defines the value of the so-called “effective conjugation length”.[8] This value describes the size of the π-system which is necessary to reach size-independent optical and electronic properties of the macromolecule. The desire to understand the optical properties of **10** led in our case to the synthesis of a series of oligomers **2**−**9**. A second reason for our interest in oligomers of **1** was the expectation that these

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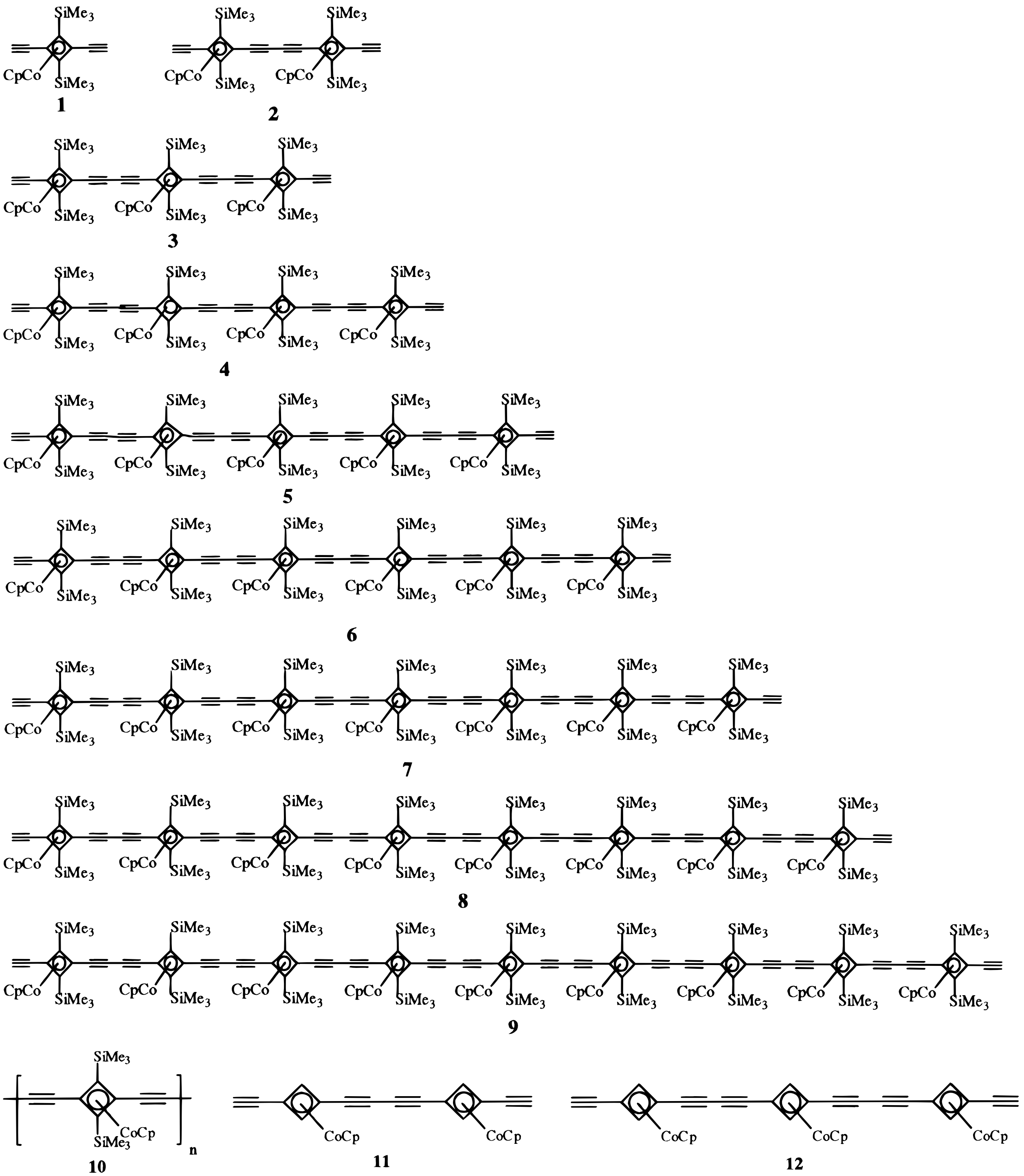
Chart 1



could be used themselves as building blocks or telecheles for the construction of molecular objects of larger dimensions and novel (co)polymers, utilizing the fact that these oligomers still possess terminal alkynes and therefore would be reactive. Herein we wish to report the synthesis of a homologous series of oligomers **2**–**9** starting from **1**.

Results and Discussion

Synthesis of the Oligomers 2–9. Attempts to couple **1** under Hay conditions[9] with an equimolar amount of copper(I) chloride/TMEDA/O_2 in acetone at room temperature for 6 h just allowed the isolation of a 3% yield of the dimer **2**. Changing the solvent to butanone and raising the reaction temperature to 80 °C, after 45 min of reaction and aqueous workup, gave a product mixture containing 27% **2**, 6% **3**, and 2% **4** besides 53% of recovered monomer **1**. The oligomers were isolated by repeated chromatography of the raw product over aluminum oxide. If the reaction time was prolonged to 1.5 h, the obtained yields were 31% (**2**), 10% (**3**), and 4% (**4**) besides 29% reisolated monomer **1**. The formation of higher oligomers was not observed under the employed conditions.

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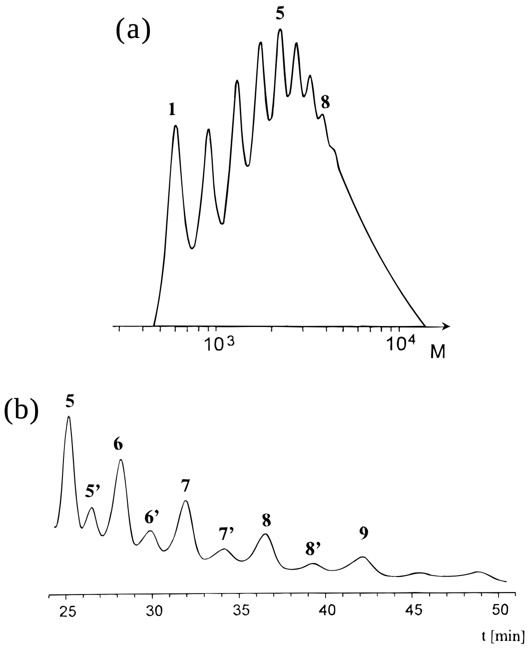

Figure 1. (a) GPC trace of the raw oligomer mixture. (b) HPLC trace of the higher oligomers (heptane/acetone, 19:1). The peaks marked with **5′**−**8′** belong to side products of unknown constitution which have been isolated.

In a third experiment the reaction time was extended to 3 h in refluxing butanone and the isolated residue was enriched in the higher oligomers **4**−**9** as could be seen by FD mass spectroscopy and analytical gel permeation chromatography (GPC). A typical GPC trace is shown in Figure 1a. Attempts to separate the mixture by column chromatography or preparative GPC was not particularly successful insofar as the higher oligomers **5**−**9** were not separable from each other. In order to achieve separation, we used preparative HPLC with heptane/acetone (95:5) as eluent. From the first HPLC fraction we obtained **2**−**4** which were isolated by column chromatography (*vide supra*). The following five fractions contained the pentamer **5** up to the nonamer **9** (**5**, 6.1%, **6**, 5.3%, **7**, 4.1%, **8**, 3.3%, **9**, 2.1%). The lower oligomers **2**−**4** are crystalline yellow-tan solids, while the higher oligomers (**5**−**9**) solidify as tan-colored glassy or microcrystalline materials. All oligomers are stable under ordinary laboratory conditions for extended periods of time (>2 months) in solution as well as in the solid state. The observed stability is in marked contrast to the observed sensitivity of the butadiyne-bridged *o*-cymantrenylenes,[3d] which we have prepared recently by a similar route. The high stabilitiy in **2**−**9** is accorded to the presence of the shielding Cp ligand, rendering **2**−**9** almost ferrocene-like stable.

A second set of compounds giving much smaller peaks in the HPLC were separated as well. These minor fractions (see Figure 1b), at best 15 mg per peak, were located in between the main fractions. Proton and carbon NMR and mass spectroscopy strongly suggest that they also contain the monomer subunit in their molecular structure: particularly mass spectroscopy shows that the molecular weight difference between two minor fractions is 366 amu which corresponds to the molecular weight of [**1** − H_2]. The first minor fraction of isolated **5′** is the one after the pentamer but shows a molecular weight of 2639 amu which would formally correspond to a mono addition product of butanone to **7**.

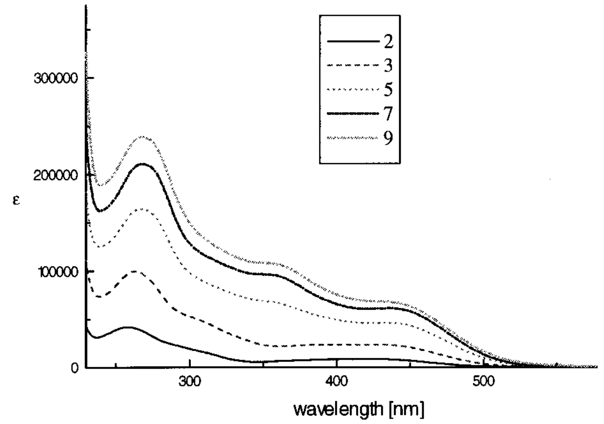

Figure 2. UV−vis spectra of selected oligomers in dichloromethane at 21 °C.

The elution behavior of **5′**−**8′** is not understood, and we have not been able to assign definitive structures to the intermediate fractions. We assume, however, that they are half-substituted oligomers of **1**. The quest for the constitution of these compounds cannot be solved with certainty unless an X-ray crystal structure is at hand.

Deprotection of 2 and 3. In order to obtain the parent systems **11** and **12** we undertook a protodesilylation reaction of **2** and **3** with tetramethylammonium fluoride in DMSO. In order to achieve complete deprotection it was necessary though to dissolve the fluoride prior to the reaction in warm (100 °C) DMSO and add **2** or **3** after cooling (21 °C) to the reagent mixture. This protocol led in 16 h to the almost quantitative formation of the desired compounds. They were obtained in 92% (**11**) and 90% (**12**) after chromatography over flash silica gel.

Spectroscopic Properties of 1−**9.** Since the investigation of Gleiter *et al.*,[10a] it is known that the parent (cyclobutadiene)cyclopentadienylcobalt has a HOMO of 7.3 eV and a set of sub-HOMOs at an energy of ca. 9.4 eV. These sub-HOMOs (15a′ and 9a″) have electron density at the two diagonally opposite corners of the cyclobutadiene ligands. The HOMO of butadiyne[10b] on the other hand was measured to be 10.2 eV by photoelectron spectroscopy. An interaction between the energetically similar orbitals of the cyclobutadiene ligand and the butadiyne units should result in a considerable split. Conjugation and in consequence a bathochromic shift in the UV−vis spectra of our complexes should occur. In Figure 2 the UV−vis spectra of selected oligomers are shown. While the most dramatic changes in the spectra occur among the **1**−**3**, the spectra of the higher oligomers > **7** strongly resemble the UV−vis spectrum of the polymer **10**. In the monomer two bands are observed at $\lambda = 247$ and 298 nm. The dimer **2** again shows two bands ($\lambda = 258$ and 431 nm). *While these two bands appear in all oligomers at roughly the*

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Table 1. Important Bond Distances (Å) and Bond Angles (deg) for Dimer 2

Co1−C3	1.95(1)	C5−C6	1.44(1)
Co1−C4	2.00(1)	C5−C7	1.46(2)
Co1−C5	1.95(1)	C7−C8	1.20(1)
Co1−C6	2.00(1)	C8−C9	1.34(2)
C29−C30	1.37(2)	C9−C10	1.20(1)
C29−C33	1.37(2)	C10−C11	1.43(2)
C30−C31	1.38(2)	C11−C12	1.46(2)
C31−C32	1.39(2)	C11−C14	1.49(2)
C32−C33	1.41(2)	C12−C13	1.46(2)
C2−C3	1.43(2)	C13−C14	1.50(2)
C2−C1	1.15(1)	C13−C15	1.42(2)
C3−C4	1.50(2)	C15−C16	1.12(1)
C3−C6	1.47(2)	C33−C29−C30	109.9(14)
C4−C5	1.46(2)		

C31−C30−C29	107.0(15)	C7−C5−C6	133.9(12)
C32−C31−C30	109.5(14)	C5−C6−C3	85.7(9)
C33−C32−C31	105.7(14)	C8−C7−C5	175.7(12)
C32−C33−C29	107.9(15)	C9−C8−C7	177.3(13)
C1−C2−C3	179.2(16)	C10−C9−C8	179.6(13)
C4−C3−C2	133.9(13)	C11−C10−C9	179.0(16)
C6−C3−C2	131.7(13)	C14−C11−C12	93.2(9)
C6−C3−C4	93.7(9)	C13−C12−C11	88.2(10)
C5−C4−C3	84.0(10)	C14−C13−C12	92.9(10)
C6−C5−C4	96.6(9)	C13−C14−C11	85.7(10)
C7−C5−C4	129.3(12)		

*same energy, in the trimer **3** up to the polymer **10** the appearance of a new band at 350 nm is observed.*[10c] This absorption gains considerable intensity up to the heptamer **7**. In **7** the effective conjugation length seems to be reached because the UV−vis spectrum of **7** is almost superimposable with that of the polymer **10**. Consequently the band at 348 nm is attributed to the interaction of the diyne units with the π-complexed cyclobutadiene ring. This behavior, i.e. the saturation observed for the heptamer (6.1 nm, 0.87 nm per unit), is in good agreement with values found for organic molecules such as oligomeric ethynylenephenylenes.[8d]

Similarly to the UV-spectra, the ^{13}C NMR spectra of the oligomers converge at the stage of the pentamer **5** while the IR spectra from **2** to **9** are almost superimposable with the exception that the absorption for the terminal alkyne C−H vibration at 3305 cm^{-1} monotonically decreases in intensity.

One important measure for the conformational properties of rigid rod polymers such as **10** is the quest for the unhindered rotation of the organometallic moieties around the C−C bonds of the butadiyne linkage. While there should be no reason for an *electronically* imposed rotational barrier, it still might be possibly that the steric interaction of two bulky organometallic ligands leads to the occurrence of such a hindered rotation. To this end the compounds **2**, **3**, **11**, and **12** were examined by variable-temperature ^{1}H NMR spectroscopy in THF-d_8, but even at −100 °C coalescence of the signals assigned to the cyclopentadienyl or trimethylsilyl groups did not occur. Only a slight broadening of the bands accorded to the cyclopentadienyl and/or the cyclobutadiene protons (increase of viscosity) and a considerable shift of the signal of the alkyne protons toward lower field (0.4−0.5 ppm) was observed.

Structure of 2. In order to corroborate the structural assessments of the low-temperature proton NMR studies for the solid state, we undertook an X-ray crystal structure analysis of **2**. The hydrocarbon ligand in **2** as a whole is slightly bent upward (dihedral angle between the cyclobutadiene rings is 10.5°). The π-ligands of each cobalt atom are all parallel, with bond lengths in good agreement with the expected values (see Table 1 and Figure 3, an ORTEP plot of **2**) with exception of the four-membered rings. These are distorted (instead of 90°, the angles are in the range between 84 and 97°). The distortion is such that the square is deformed to a rhombus, with the shorter diagonal linking the two alkynyl-substituted carbons. Additionally the bond lengths are slightly different in the four-membered ring (1.44−1.50 Å, 0.04 Å = 2 σ). It is to date not clear which factor governs the observed asymmetry in the cyclobutadiene ligand, if it is an electronic or a crystal packing effect. The most eye-catching feature of the structure is that the two cyclopentadienyl rings of **2** are *cis*-oriented to each other in the solid state, indicating that the butadiyne bridge separates the two organometallic fragments from each other to such an extent that no appreciable *van der Waals* interaction between the two bulky organometallic moieties exists. This is in good agreement with the observations obtained by the variable-temperature NMR study.

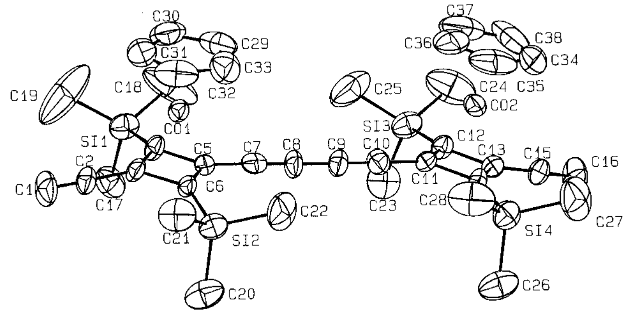

Figure 3. ORTEP plot and numbering scheme of **2**.

Conclusions

In conclusion we have been able to show that the Hay coupling of **1** in refluxing butanone gave rise to the isolation of a series of oligomers **2**−**9**. Depending upon the reaction time, it is (to a certain extent) possible to direct the formation of either the lower oligomers **2**−**4** or the higher ones (**3**−**9**). The oligomers are all completely stable under laboratory conditions for at least several months. Their two reactive terminal alkyne protons make them valuable building blocks for the synthesis of larger organometallic species and/or novel copolymers containing the *oligo*-**1** motif. The UV−vis spectra of **2**−**9** indicate that a considerable amount of conjugation is transmitted through the hydrocarbon ligand, similar to that observed in Tour's phenylene-ethynylenes.[8d]

Experimental Section

General Methods. Cyclobutadiene complex **1** was synthesized according to ref 4b and purified by flash chromatography over silica gel with pentane as eluent; copper(I) chloride and tetramethylethylenediamine (TMEDA) were purchased from Aldrich and used without further purification. The instrumentation (IR, NMR, gel permeation chromatography) used is described elsewhere.[3c,6,12] For preparative HPLC a Gilson Abimed 305 with a Merck LiCroSorb CN (10 μm) column (21 cm × 5 cm) was used with a 95:5 mixture of heptane (Merck, pa quality) and acetone (Riedel de Haen, pa quality) as eluent (flow rate 20 mL/min).

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Oligomerization Experiment 1. The amounts of 987 mg (2.68 mmol) of **1**, 529 mg (5.36 mmol) of copper(I) chloride, and 623 mg (5.34 mmol) of tetramethylethylenediamine (TMEDA) are dissolved in ca. 300 mL of butanone in a 500 mL three-necked flask, equipped with a stir bar, reflux condenser, and oxygen inlet. The mixture is heated to reflux (80 °C), and during 30 min a slow stream of pure oxygen is admitted to the reaction mixture. To isolate the product, the butanone is removed under vacuum, dissolved in dichloromethane, and washed several times with water. Chromatography over aluminum oxide with first pentane and then pentane/dichloromethane (95:5) first gives **α-ethynyl-*ω*-[(3-ethynyl-2,4-bis(trimethylsilyl)cyclobutadien-1-yl)cyclopentadienylcobalt]**{**[(1,3-(2-bis(trimethylsilyl)cyclobutadienylene))cyclopentadienylcobalt](1,4-butadiynediyl)**} (**2**): 262 mg (27%); mp 145 °C; IR (KBr) ν (cm^{-1}) 3305, 3282, 3106, 2956, 2897, 2127, 2095, 1261, 1247, 844, 812; ^{1}H-NMR (CD_2Cl_2) δ 0.26 (s, 36 H), 3.04 (s, 2 H), 4.95 (s, 10 H); ^{13}C-NMR (CD_2Cl_2) δ −0.48 (q, 12 C), 63.46, 65.09, 77.30 (3 s, 8 C), 81.88 (d, 10 C), 76.82, 81.72 (2 s, 4 C), 78.90 (d, 2 C) 82.30 (s, 2 C); UV/vis (CH_2Cl_2) λ_{max} (nm) 258 (ϵ 42 110), 421 (ϵ 8300); MS (FD) *m/z* 734. Anal. Calcd for $C_{38}H_{48}Si_4Co_2$ (734.99): C, 62.10; H, 6.58. Found: C, 62.04; H, 6.59. The next fraction isolated is **α-ethynyl-*ω*-[(3-ethynyl-2,4-bis-(trimethylsilyl)cyclobutadien-1-yl)cyclopentadienylcobalt]bis**{**[(1,3-(2,4-bis(trimethylsilyl)cyclobutadienylene)-(cyclopentadienylcobalt](1,4-butadiynediyl)**} (**3**): 59 mg (6.0%); mp > 210 °C dec; IR (KBr) ν (cm^{-1}) 3308, 3287, 3106, 2956, 2898, 2124, 2096, 1261, 1247, 845, 812; ^{1}H-NMR (CD_2Cl_2) δ 0.26 (s, 36 H), 0.27 (s, 18 H), 3.04 (s, 2 H), 4.95 (s, 10 H), 4.97 (s, 5 H); ^{13}C-NMR (CD_2Cl_2) δ −0.51 (2 q, 18 C), 63.31, 64.71, 65.10, 76.96, 77.30 (5 s, 12 C), 81.81, 81.85 (2 d, 15 C), 76.76, 78.12, 81.41 (3 s, 8 C), 78.90 (d, 2 C) 82.24 (s, 2 C); UV/vis (CH_2Cl_2) λ_{max} (nm) 263 (ϵ 99 860), 393 (ϵ 23 730), 428 (ϵ 23 400); MS (FD) *m/z* 1100. Anal. Calcd for $C_{57}H_{71}Si_6Co_3$ (1101.47): C, 62.16; H, 6.50. Found: C, 61.81; H, 5.72. As the last fraction isolated is **α-ethynyl-*ω*-[(3-ethynyl-2,4-bis-(trimethylsilyl)cyclobutadien-1-yl)cyclopentadienylcobalt]tris**{**[(1,3-(2,4-trimethylsilylcyclobutadienylene))-cyclopentadienylcobalt](1,4-butadiynediyl)**} (**4**): 20 mg (2.0%); mp > 210 °C dec; IR (KBr) ν (cm^{-1}) 3308, 3286, 3107, 2959, 2900, 2127, 2098, 1260, 1247, 845, 812; ^{1}H-NMR (CD_2Cl_2) δ 0.26 (s, 36 H), 0.27 (s, 36 H), 3.04 (s, 2 H), 4.95 (s, 10 H), 4.97 (s, 10 H); ^{13}C-NMR (CD_2Cl_2) δ −0.53, −0.50 (2 q, 24 C), 64.61, 65.12, 76.96, 77.32 (4 s, 16 C), 81.81, 81.86 (2 d, 20 C), 76.68, 76.88, 78.17, 81.39, 81.63 (5 s, 12 C), 78.90 (d, 2 C) 82.25 (s, 2 C); UV/vis (CH_2Cl_2) λ_{max} (nm) 264 (ϵ 104 060), 377 (ϵ 28 980), 433 (ϵ 25 110); MS (FD) *m/z* 1467. Anal. Calcd for $C_{76}H_{94}Si_8Co_4$ (1467.96): C, 62.18; H, 6.45. Found: C, 61.79; H, 6.49.

Oligomerization Experiment 2. The amounts of 249 mg (0.676 mmol) of **1**, 134 mg (1.354 mmol) of copper(I) chloride, and 158 mg (1.36 mmol) of TMEDA are dissolved in ca. 300 mL of butanone. The mixture is treated for 1.5 h as described (*vide supra*). Chromatography yielded the oligomers **2**−**4**: **2**, 77.2 mg (31%); **3**, 27.4 mg (11%); **4**, 9.9 mg (4%).

Oligomerization Experiment 3. The amounts of 1.24 g (3.37 mmol) of **1**, 67.2 mg (0.678 mmol) of copper(I) chloride, and 77.1 mg (0.664 mmol) of TMEDA in 400 mL of butanone are treated for 3 h as described *(vide supra*) and worked up accordingly. Purification of the material is ensued by filtration over aluminum oxide with a mixture of pentane/dichloromethane (75:25) to yield 67% (833 mg) of oligomeric material. Separation of the higher oligomers was ensued by preparative HPLC: **2**, 43 mg (3.6%); **3**, 57 mg (4.6%); **4**, 76 mg (6.1%); **5**, 76 mg (6.1%); **6**, 66 mg (5.3%); **7**, 51 mg (4.1%); **8**, 41 mg (3.3%); **9**, 26 mg (2.1%).

α-Ethynyl-*ω*-[(3-ethynyl-2,4-bis(trimethylsilyl)cyclobutadien-1-yl)cyclopentadienylcobalt]tetrakis{**[(1,3-(2,4-bis(trimethylsilyl)cyclobutadienylene))cyclopentadienylcobalt](1,4-butadiynediyl)**} **(5):** mp > 210 °C dec; IR (KBr) ν (cm^{-1}) 3309, 3288, 3108, 2956, 2900, 2127, 2096, 1260, 1247, 843, 812; ^{1}H-NMR (CD_2Cl_2) δ 0.26 (s, 36 H), 0.28 (s, 54 H), 3.04 (s, 2 H), 4.95 (s, 10 H), 4.98 (s, 15 H); ^{13}C-NMR (CD_2Cl_2): δ −0.52, −0.49 (2 q, 30 C), 63.30, 64.65, 64.76, 65.11, 76.97, 77.32 (6 s, 20 C), 81.81, 81.85 (2 d, 25 C), 76.71, 76.87, 78.17, 81.37, 81.64, 81.70 (6 s, 16 C), 78.90 (d, 2 C) 82.23 (s, 2 C); UV/vis (CH_2Cl_2) λ_{max} (nm) 267 (ϵ 164 260), 347 (ϵ 69 700), 434 (ϵ 46 380); MS (FD) *m/z* 1834. Anal. Calcd for $C_{95}H_{117}Si_{10}Co_5$ (1834.456): C, 62.20; H, 6.43. Found: C, 61.50; H, 6.84.

α-Ethynyl-*ω*-[(3-ethynyl-2,4-bis(trimethylsilyl)cyclobutadien-1-yl)cyclopentadienylcobalt]pentakis{**[(1,3-(2,4-bis(trimethylsilyl)cyclobutadienylene))cyclopentadienylcobalt](1,4-butadiynediyl)**} **(6):** mp > 210 °C dec; IR (KBr) ν (cm^{-1}) 3309, 3289, 3108, 2956, 2898, 2127, 2096, 1260, 1247, 844, 813; ^{1}H-NMR (CD_2Cl_2) δ 0.26 (s, 36 H), 0.27 (s, 72 H), 3.04 (s, 2 H), 4.95 (s, 10 H), 4.98 (s, 20 H); ^{13}C-NMR (CD_2Cl_2) δ −0.54, −0.49 (2 q, 36 C), 64.64, 64.76, 76.97, 77.31 (4 s, 24 C), 81.81, 81.85 (2 d, 30 C), 76.86, 78.17, 78.21, 81.60, 81.70 (5 s, 20 C), 78.90 (d, 2 C) 82.23 (s, 2 C); UV/vis (CH_2Cl_2) λ_{max} (nm) 267 (ϵ 174 170), 352 (ϵ 77 100), 435 (ϵ 51 600); MS (FD) *m/z* 2201. Anal. Calcd for $C_{114}H_{140}Si_{12}Co_6$ (2200.94): C, 62.21; H, 6.41. Found: C, 62.38; H, 6.45.

α-Ethynyl-*ω*-[(3-ethynyl-2,4-bis(trimethylsilyl)cyclobutadien-1-yl)cyclopentadienylcobalt]hexakis{**[(1,3-(2,4-bis(trimethylsilyl)cyclobutadienylene))cyclopentadienylcobalt](1,4-butadiynediyl)**} **(7):** mp > 210 °C dec; IR (KBr) ν (cm^{-1}) 3310, 3106, 2956, 2898, 2124, 2096, 1260, 1247, 843, 812; ^{1}H-NMR (CD_2Cl_2) δ 0.26 (s, 36 H), 0.27 (s, 90 H), 3.04 (s, 2 H), 4.95 (s, 10 H), 4.98 (s, 25 H); ^{13}C-NMR (CD_2Cl_2) δ −0.51 (q, 42 C), 64.69, 76.92 (2 s, 28 C), 81.84 (d, 35 C), 78.26, 81.66 (2 s, 24 C), 78.92 (d, 2 C) 82.22 (s, 2 C); UV/vis (CH_2Cl_2) λ_{max} (nm) 268 (ϵ 210 950), 348 (ϵ 96 620), 435 (ϵ 61 210); MS (FD) *m/z* 2568. Anal. Calcd for $C_{133}H_{163}Si_{14}Co_7$ (2567.43): C, 62.22; H, 6.40. Found: C, 61.98; H, 6.42.

α-Ethynyl-*ω*-[(3-ethynyl-2,4-bis(trimethylsilyl)cyclobutadien-1-yl)cyclopentadienylcobalt]heptakis{**[(1,3-(2,4-bis(trimethylsilyl)cyclobutadienylene))cyclopentadienylcobalt](1,4-butadiynediyl)**} **(8):** mp > 210 °C dec; IR (KBr) ν (cm^{-1}) 3309, 3107, 2956, 2900, 2125, 2097, 1260, 1247, 844, 812; ^{1}H-NMR (CD_2Cl_2) δ 0.26 (s, 36 H), 0.27 (s, 108 H), 3.04 (s, 2 H), 4.95 (s, 10 H), 4.98 (s, 30 H); ^{13}C-NMR (CD_2Cl_2) δ −0.54 (q, 48 C), 64.64, 76.97, 77.31 (3 s, 32 C), 81.81 (d, 40 C), 76.86, 78.21 (s, 28 C), 78.90, (d, 2 C), 82.24 (s, 2 C); UV/vis (CH_2Cl_2) λ_{max} (nm) 268 (ϵ 272 500), 348 (ϵ 129 960), 435 (ϵ 80 530); MS (FD) *m/z* 2929.

α-Ethynyl-*ω*-[(3-ethynyl-2,4-bis(trimethylsilyl)cyclobutadien-1-yl)cyclopentadienylcobalt]octakis{**[(1,3-(2,4-bis(trimethylsilyl)cyclobutadienylene))cyclopentadienylcobalt](1,4-butadiynediyl)**} **(9):** mp > 210 °C dec; IR (KBr) ν (cm^{-1}) 3310, 3108, 2956, 2899, 2126, 2098, 1260, 1247, 844, 812; ^{1}H-NMR (CD_2Cl_2) δ 0.26 (s, 36 H), 0.27 (s, 126 H), 3.04 (s, 2 H), 4.95 (s, 10 H), 4.98 (s, 35 H); ^{13}C-NMR (CD_2Cl_2) δ −0.54 (q, 54 C), 64.64, 76.87, 77.30 (3 s, 36 C), 81.81 (d, 45 C), 78.21, 81.60 (2 s, 32 C), 78.89 (d, 2 C); UV/vis (CH_2Cl_2) λ_{max} (nm) 268 (ϵ 238 810), 348 (ϵ 168 800), 434 (ϵ 68 120); MS (FD) *m/z* 3302.

Deprotection of 2 and 3. A solution of 26 mg (0.035 mmol) of **2** dissolved in 5 mL of diethyl ether was added to a stirred suspension of finely divided tetramethylammonium fluoride (6.6 mg, 0.071 mmol) in 5 mL of DMSO. The resulting mixture was stirred at 21 °C under nitrogen for 16 h. Aqueous workup and extraction with dichloromethane followed by flash chromatography over silica gel (4:1 pentane/dichloromethane) yielded 14.4 mg (92%) of **11** as an ochre powder. The same experiment was conducted with **3** (29 mg, 0.026 mmol) with 4.9 mg (0.053 mmol) of tetramethtylammonium fluoride to yield 15.7 mg (90%) of **12**.

α-Ethynyl-*ω*-[(3-ethynylcyclobutadien-1-yl)cyclopentadienylcobalt]{**[(1,3-cyclobutadienylene)cyclopentadienylcobalt](1,4-butadiynediyl)**} **(11):** mp > 166 °C, dec; IR (KBr) ν (cm^{-1}) 3293, 3108, 2135, 2105, 1378, 813; ^{1}H-NMR (CD_2Cl_2) δ 2.89 (s, 2 H), 4.59 (s, 4 H), 5.03 (s, 10 H); ^{13}C-NMR ($CDCl_3$) δ 52.80, 54.48 (2 s, 4 C), 65.22 (d, 4 C), 79.03, 80.04 (2 s, 4 C), 77.78 (d, 2 C), 75.08 (s, 2 C), 81.54 (d, 10 C); UV/vis (CH_2Cl_2) λ_{max} (nm) 255 (ϵ 60 370), 402 (ϵ 11 980); MS (FD) *m/z* 446. Anal. Calcd for $C_{26}H_{16}Co_2$ (446.27): C, 69.98; H, 3.61. Found: C, 69.83; H, 3.71.

α-Ethynyl-ω-[(3-ethynylcyclobutadien-1-yl)cyclopentadienylcobalt]bis{[(1,3-cyclobutadienylene)cyclopentadienylcobalt](1,4-butadiynediyl)} (12): mp > 158 °C, dec; IR (KBr) ν (cm^{-1}) 3287, 3108, 2137, 2108, 1460, 1377, 815; ^{1}H-NMR (CD_2Cl_2) δ 2.98 (s, 2 H), 4.60 (s, 4 H), 4.66 (s, 2 H), 5.03 (s, 10 H), 5.05 (s, 5 H); ^{13}C-NMR ($CDCl_3$) δ 52.69, 54.12, 54.54 (3 s, 6 C), 65.25, 65.80 (2 d, 6 C), 75.28, 78.72, 79.23, 80.01 (4 s, 8 C), 77.79 (d, 2 C), 74.99 (s, 2 C), 81.55 (d, 15 C); UV/vis (CH_2Cl_2) λ_{max} (nm) 260 (ϵ 80 290), 392 (ϵ 19 800); MS (FD) *m/z* 666.

Crystallographic Data for 2. $C_{38}H_{48}Si_4Co_2$ (**2**): M = 735.0, light yellow, air-stable blocks (0.20 × 0.25 × 0.50 mm^3), space group $P2_1/n$, a = 14.719(2) Å, b = 15.091(2) Å, c = 20.642(1) Å, $\alpha = 90°$, $\beta = 108.970(7)°$, $\gamma = 90°$, V = 4335.9(8) Å^3, Z = 4, 6409 reflections with 2603 ($F > 3\sigma(F)$), R = 0.046, R_w = 0.051, D_x = 1.199 g cm^{-3}, μ = 75.62 cm^{-1}. Data collection was carried out at 298 K with an Enraf-Nonius CAD4 automatic diffractometer (Cu Kα radiation, λ = 1.5405 Å). The structures were solved by the heavy-atom method (Patterson), and the non-hydrogen atoms were refined anisotropically. Programs used were CRYSTALS and MOLEN. An empirical absorption correction was applied. Refinement was done by full-matrix least-squares analyses with anisotropic temperature factors for all non-hydrogen atoms. The hydrogen atoms were refined with fixed isotropic temperature factors in the riding mode.

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Supporting Information Available: Tables of positional and thermal parameters and bond distances and angles and text describing X-ray procedures (7 pages). Ordering information is given on any current masthead page.

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