Synthesis and Properties of Donor-Acceptor-Substituted Metal-Capped Fourfold-Bridged Cyclobutadienophanes

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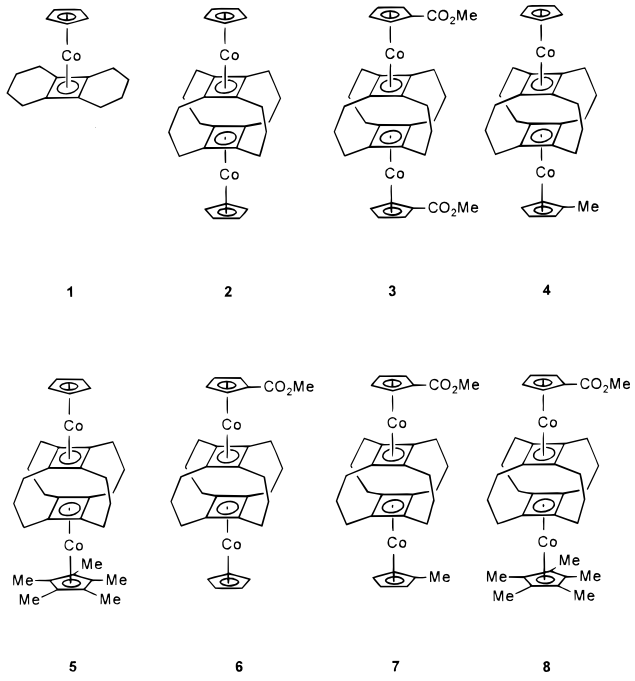
The synthesis of the superphanes **4**−**8** could be achieved from {(1,2,11,12-η^4)-tricyclo-[10.8.0.0^{2,11}]eicosa-1,11-diene-6,17-diyne}(η^5-cyclopentadienyl)cobalt (**15**) and its methoxycarbonyl congener **14** by heating with R−CpCo(CO)$_2$ (R = H, CH$_3$, (CH$_3$)$_5$). X-ray investigations on the superphanes **3**, **6**, and **8** reveal distances between the two cyclobutadiene units between 2.922 Å (**3**) and 2.941 Å (**6**). Investigations by means of cyclic voltammetry show a decrease of the first oxidation potentials with increasing number of CH$_3$ substituents at the cyclopentadienyl ligands. The comparison between the first oxidation potentials of **2**−**6**, **4**−**7**, and **5**−**8** gives evidence for a partial charge delocalization over both CpCoCb fragments of the superphanes.

Introduction

Organometallic compounds with two metal centers can often be oxidized to radical cations and dications. Well-known examples are biferrocene[1] and Boekelheide's superphane complexed with two C$_6$H$_5$Ru units.[2] In the nomenclature introduced by Robin and Day[3] for compounds having transition metals as charge-bearing units, the charge can be either localized (class I), totally delocalized over both metals (class III), or partially delocalized (class II). The latter two cases are of special interest because the delocalization promised new properties of the corresponding radical cations. Due to their rigidity, metal-complexed phanes and especially superphanes are attractive models for studying the electron delocalization of two metal centers. Recent investigations on the cyclophane **2** by means of cyclic voltammetry (CV) revealed[4] a reversible first oxidation process (E_1(**2**) = 656 mV). The comparison of this value with that obtained for **1** (801 mV) was rationalized by assuming a considerable ground-state interaction in **2**$^{\bullet+}$ insofar as the positive charge is stabilized by the second π-fragment in **2**$^{\bullet+}$. A more detailed investigation by a combined CV/IR study of **3** supported this view of a charge delocalization.[5] It was shown that electronic charge is distributed over both halves of the molecule. This finding encouraged us to probe the charge delocalization over both π-fragments by using substituent effects; therefore we have synthesized different substituted congeners of **2** and **3**, the superphanes **4**−**8**.



Synthesis of 4−**8.** To synthesize the superphanes **4**−**8**, we used a stepwise approach published earlier.[6] The two key compounds are the tricyclic diynes **14** and **15**. The starting point to prepare **14** was 6-cyclodecynol (**9**).[7] Its reaction with (η^4-cyclooctadienyl)(η^5-methoxycarbonylcyclopentadienyl)cobalt (CpECo(COD)) led to the tricyclic cyclobutadiene complexes **10**, as a mixture of regioisomers that could not be separated. The mixture

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(3) Robin, M.; Day, P. *Adv. Inorg. Radiochem.* **1967**, *10*, 247.
(4) Gleiter, R.; Röckel, H.; Pflästerer, G.; Treptow, B.; Kratz, D. *Tetrahedron Lett.* **1993**, *34*, 8075.
(5) Stoll, M. E.; Lovelace, S. R.; Geiger, W. E.; Schimanke, H.; Hyla-Kryspin, I.; Gleiter, R. *J. Am. Chem. Soc.* **1999**, *121*, 9343.
(6) Gleiter, R.; Langer, H.; Schehlmann, V.; Nuber, B. *Organometallics* **1995**, *14*, 975.
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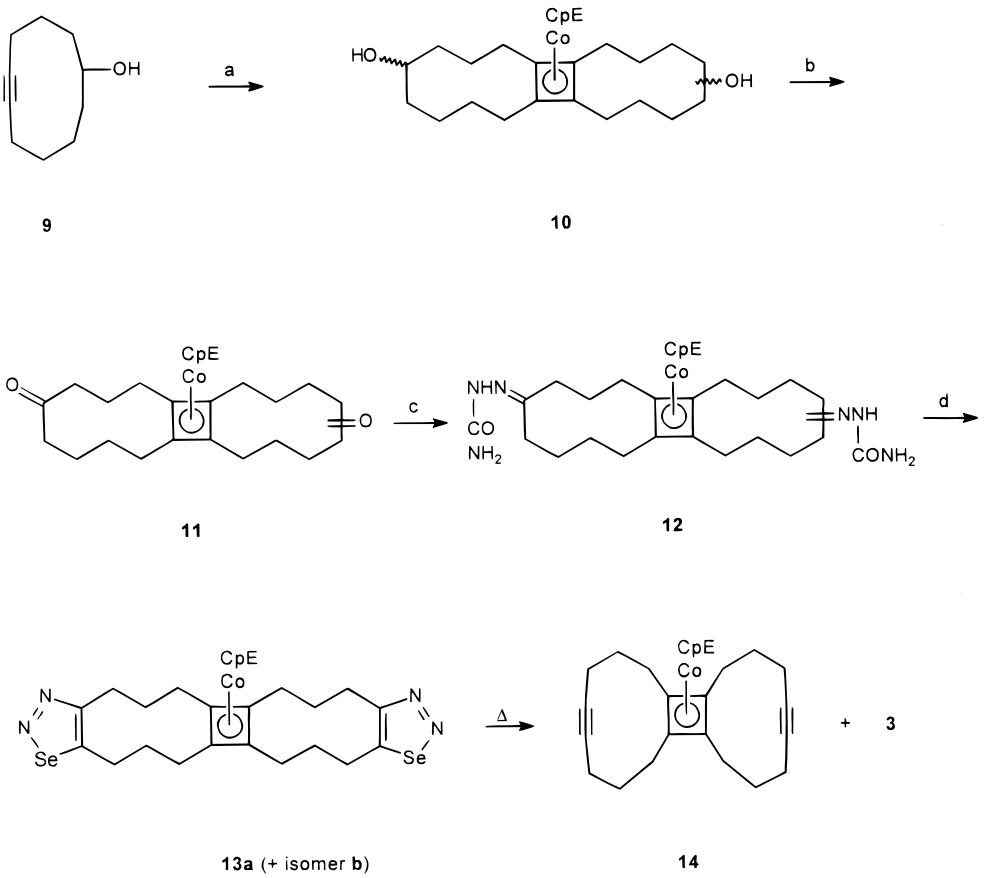
Scheme 1[a]



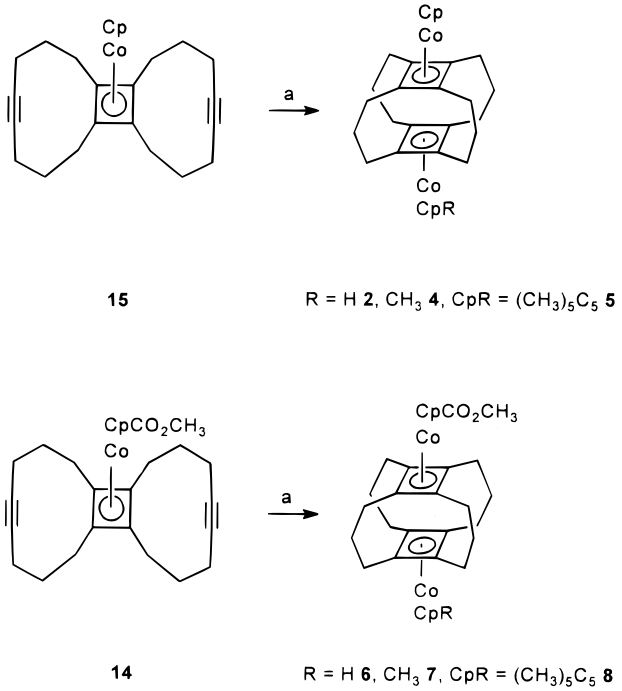
[a] Key: (a) CH_3CO_2−CpCo(COD), (b) Oppenauer oxidation; (c) semicarbazide acetate, (d) SeO_2/HOAc.

of diols **10** was oxidized to the corresponding diketones **11** by using the Oppenauer procedure, which guarantees only an oxidation of the alcohol functions. To transfer the diketones **11** into the tricyclic diyne **14**, we applied a protocol first used by Lalezari.[8] The diketones were transformed first into the bissemicarbazones **12**, which were treated with SeO_2 to yield a mixture of bisselenadiazoles **13**. This latter step represents the bottleneck of the protocol shown in Scheme 1, because the yield amounted to 15−19% only. The isomeric mixture of bisselenadiazoles was thermolyzed at 180 °C and 0.1 bar for 10 min to yield the tricyclic diyne **14** in 64% yield together with about 3% of **3**.

The transformation of the tricyclic diynes **14** and **15** into the superphanes **4**−**8** was accomplished by heating with R−CpCo$(CO)_2$ according to Scheme 2. The yields of this last step varied between 60% and 80%.

We were able to grow single crystals of **3**, **6**, and **8**, which allowed us to study the molecular structure of these molecules in more detail. X-ray structures of all three compounds reveal two nearly parallel cyclobutadiene moieties, separated by 2.922 Å (**3**), 2.941 Å (**6**), and 2.939 Å (**8**). In Figure 1a we show an ORTEP plot of **8**. The distances are very similar to the one reported for **2** (2.944 Å).[9] The propano chains in **3**, **6**, and **8** adopt a pinwheel conformation (Figure 1b) also found in **2**.[9]

Scheme 2[a]



[a] Key: (a) R−CpCo$(CO)_2$, R = H, CH_3, $(CH_3)_5$.

Cyclovoltammetric Investigations. To probe the interactions between the CpCoCb units in **4**−**8**, we have carried out studies by means of cyclovoltammetry (CV). In Figure 2 we show as an example the CV of **5**. It is seen that the first oxidation step is reversible while the

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(10) Sheldrick, G. M. *SHELX-97*; Universität Göttingen: Germany, 1997.

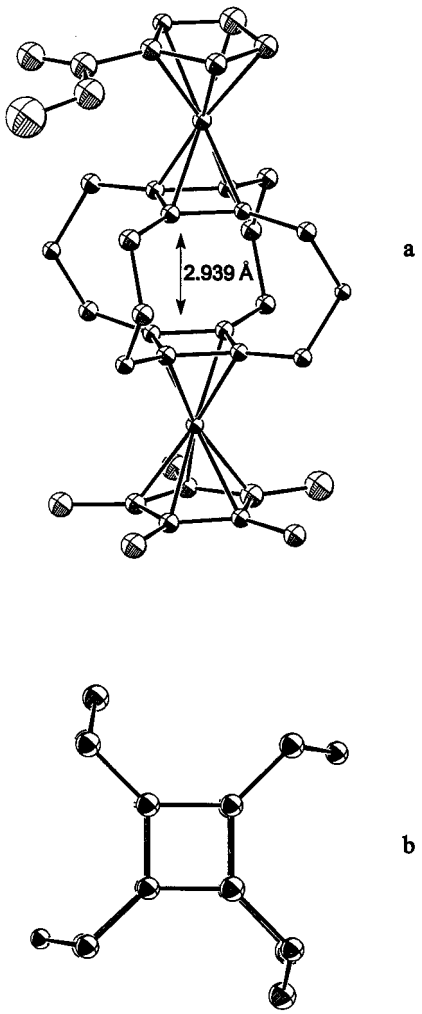

Figure 1. (a) Molecular structure of **8**. ORTEP drawing (50% probability ellipsoids). The H atoms are omitted. (b) Projection of the central skeleton of **8** along the Co−Co axis. The CpCo fragments and the hydrogens are omitted.

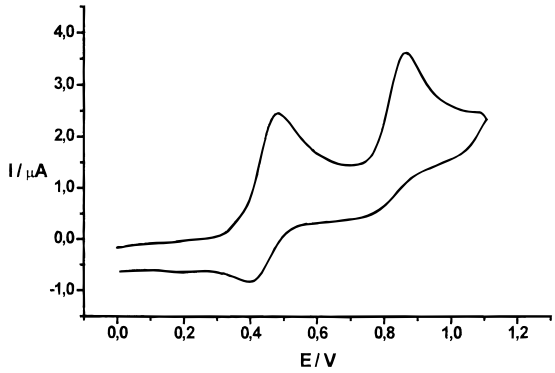

Figure 2. Cyclic voltammogram of **5**.

second is not. This holds for all five compounds as well as **2** and **3**. The recorded oxidation potentials are listed in Table 1. The comparison between the series **2**, **4**, and **5** as well as **6**, **7,** and **8** shows a decrease of the first oxidation step. This is anticipated since the number of methyl groups on one Cp ring is increased in both series. This finding suggests that the first electron is removed from the RCpCoCb fragment in which R is CH_3 or RCp is equal to Cp*. The assumption that the electrochemical oxidation removes the first electron from the alkyl-substituted R−CpCoCb fragment allows us also to probe

Table 1. Oxidation Potentials of 1, 2, 4−8

compound	E_1 (mV)	E_2 (mV)
1	801	
2	656	1101[a]
4	616	1015[a]
5	443	864[a]
6	714	1313[a]
7	644	1336[a]
8	510	1089[a]

[a] Irreversible oxidation.

the aforementioned intramolecular interaction in $\mathbf{2}^{\bullet+}$ and related species. This can be seen from the comparison of the first oxidation potentials of **2** and **6**, **4** and **7**, and **5** and **8**. This comparison shows in all three cases that the ester group causes a shift of the first oxidation potential to higher values: $E_1(\mathbf{2}) - E_1(\mathbf{6}) = -58$ mV, $E_1(\mathbf{4}) - E_1(\mathbf{7}) = -28$ mV and $E_1(\mathbf{5}) - E_1(\mathbf{8}) = -67$ mV. This increase in oxidation potential is strong evidence for the delocalization of the positive charge between the two π-fragments of the cyclophanes.

Concluding Remarks. A stepwise approach was used to generate a series of five donor−acceptor-substituted CpCo-stabilized cyclobutadienosuperphanes. The convergent synthesis is distinguished by easily accessible starting material. The structural investigations reveal that the four propano bridges guarantee a parallel arrangement of the cyclobutadiene units at 2.9 Å. The CV data show that the first oxidation process is reversible and that the first oxidation potential is influenced by the substituents at the cyclopentadienyl ligand. The comparison between the pairs **2**−**6**, **4**−**7**, and **5**−**8** shows a clear substituent effect of the far removed ester group on the positive center. This gives new evidence for a charge delocalization over both fragments in the radical cations of **2**−**8**.

Experimental Section

General Procedures. All melting points were uncorrected. The NMR spectra were measured with a Bruker WH 300 or Avance 500 spectrometer (^{1}H NMR at 300 or 500 MHz and ^{13}C NMR at 75.47 or 125.33 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. UV light absorption data were recorded using a Hewlett-Packard 8452A spectrometer. Elemental analyses: Microanalytisches Labor der Universität Heidelberg. All reactions were carried out in argon atmosphere using dried and oxygen-free solvents.

{(1,2,11,12-η^4)-Tricyclo[10.8.0.0^{2,11}]eicosa-1,11-dien-6,-16-diol}(η^5-methoxycarbonylcyclopentadienyl)cobalt and {(1,2,11,12-η^4)-Tricyclo[10.8.0.0^{2,11}]eicosa-1,11-dien-6,17-diol}(η^5-methoxycarbonylcyclopentadienyl)cobalt (10). A solution of 1.8 g (6.2 mmol) of $(CpCO_2CH_3)Co(COD)$ in 4.0 mL of decalin was heated to 150−160 °C. During 6 days 2.8 g (18 mmol) of **9**, dissolved in 140 mL of decalin, was added. While the addition of **9** was continued, a further portion of $(CpCO_2CH_3)Co(COD)$ was added after 2 days (0.7 g (2.4 mmol)) and after 4 days (0.5 g (1.7 mmol)). When the addition of **9** was completed, the heating was continued for a further day. The reaction mixture was allowed to cool to room temperature and then filtered through alumina (neutral, grade III). With *n*-pentane as eluent the unreacted $(CpCO_2CH_3)Co(COD)$ could be extracted, while the product **10** remained as a solid at the top of the column. It could be dissolved with some CH_2Cl_2 and was extracted with ether as a broad yellow band. After removal of the solvent the crude product was purified by column

chromatography (silica gel/ether). A separation of the isomers of **10** failed. The reaction yielded 1.9 g (43%) of a yellow solid which contained all isomers of **10**. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.01 (pt, 2H, Cp), 4.64 (pt, 2H, Cp), 3.77 (s, 3H, CH_3), 2.36−2.11 (m, CH_2), 2.02−1.50 (m, CH_2), 1.26−1.24 (m, CH_2). ^{13}C NMR (50 MHz, $CDCl_3$): δ 168.8 (C), 85.0 (CH), 84.9 (C), 84.8 (C), 82.9 (C), 82.8 (C) 82.6 (C), 82.5 (CH), 71.2 (CH), 70.8 (CH), 70.1 (CH), 69.9 (CH), 51.6 (CH_3), 31.9 (CH_2), 27.9 (CH_2), 27.7 (CH_2), 27.6 (CH_2), 27.3 (CH_2), 27.0 (CH_2), 25.6 (CH_2), 25.4 (CH_2), 24.9 (CH_2), 24.7 (CH_2), 24.5 (CH_2), 24.3 (CH_2), 23.9 (CH_2), 23.7 (CH_2), 23.6 (CH_2), 23.3 (CH_2), 21.3 (CH_2). IR (KBr) [cm^{-1}]: 3426, 2927, 2854, 1709, 1684, 1655, 1464, 1329, 1289, 1189, 1141, 1029, 897. UV/vis (CH_2Cl_2) (λ_{max}, nm (log e)): 220 (4.39), 268 (4.57). HRMS (FAB): Calcd for $C_{27}H_{39}CoO_4$ 486.2182. Found: 486.2198. Anal. Calcd for $C_{27}H_{39}CoO_4$: C, 66.65; H, 8.08. Found: C, 66.86; H, 7.80.

{(1,2,11,12-η^4)-Tricyclo[10.8.0.0^{2,11}]eicosa-1,11-dien-6,-16-dione}(η^5-methoxycarbonylcyclopentadienyl)cobalt and {(1,2,11,12-η^4)-Tricyclo[10.8.0.0^{2,11}]eicosa-1,11-dien-6,17-dione}(η^5-methoxycarbonylcyclopentadienyl)-cobalt (11). A solution of 1.2 g (3 mmol) of **10** and 3.2 g (16 mmol) of aluminum triisopropylate in 46 mL of toluene and 22 mL of acetone (22 mL) was heated under reflux for 14 h. By checking the reaction with TLC, we noticed in addition to the products and the starting material an intermediately formed monoketone. After the reaction mixture had cooled to room temperature 100 mL of water was added, and the solution was concentrated in vacuo. To the residue were added ether and 10% H_2SO_4. The aqueous layer was extracted with ether. The combined organic layers and extracts were washed with saturated $NaHCO_3$ solution, dried ($MgSO_4$), concentrated in vacuo, and adsorbed on silica gel. The product was purified by column chromatography (silica gel/CH_2Cl_2) and yielded 0.7 g (1.5 mmol) (60%) of a yellow solid containing both isomers of **11**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.99 (pt, 2H, CH), 4.60 (pt, 2H, CH), 3.75 (s, 3H, CH_3), 2.99−2.87 (m, CH_2), 2.51−2.47 (m, CH_2), 2.27−2.11 (m, CH_2), 1.98−1.78 (m, CH_2), 1.56−1.53 (m, CH_2). ^{13}C NMR (75 MHz, $CDCl_3$): δ 213.0 (C), 169.1 (C), 84.7, 84.6, 84.4, 82.3, 82.2, 82.1, 81.9, 81.2, 80.9, 51.2 (CH_3), 43.8 (CH_2), 43.5 (CH_2), 37.8 (CH_2), 37.2 (CH_2), 28.3 (CH_2), 27.2 (CH_2), 24.0 (CH_2), 23.9 (CH_2), 23.6 (CH_2), 23.5 (CH_2), 23.4 (CH_2), 23.2 (CH_2), 22.6 (CH_2), 21.8 (CH_2). HRMS (FAB) Calcd for $C_{27}H_{35}CoO_4$: 482.1868. Found: 482.1856. IR (KBr) [cm^{-1}]: 2934, 2852, 1703, 1654, 1641, 1461, 1401, 1367, 1323, 1284, 1129, 1034, 968. UV/vis (CH_2Cl_2) (λ_{max}, nm (log e)): 230 (3.96), 270 (4.33), 300 (3.45). Anal. Calcd for $C_{27}H_{35}CoO_4$: C, 67.19; H, 7.32. Found: C, 67.46; H, 7.46.

{(1,2,11,12-η^4)-Tricyclo[10.8.0.0^{2,11}]eicosa-1,11-dien-6,16-bissemicarbazone}(η^5-methoxycarbonylcyclopentadienyl)cobalt and {(1,2,11,12-η^4)-Tricyclo-[10.8.0.0^{2,11}]-eicosa-1,11-dien-6,17-bissemicarbazone}(η^5-methoxycarbonylcyclopentadienyl)cobalt (12). A solution of 4.6 g (41 mmol) of semicarbazide hydrochloride and 4.1 g (50 mmol) of NaOAc in 140 mL of methanol was refluxed and filtered. A 7.2 g amount (2 mmol) of the mixed ketones **11** was added to the filtrate, and the solution was refluxed for 1 h. The reaction was controlled by TLC. When the starting material had disappeared, the solvent was removed in vacuo. To the residue were added 500 mL of chloroform and 100 mL of water. The organic layer was separated, washed with saturated $NaHCO_3$ solution, and dried ($MgSO_4$). After the solvent had been removed 7.8 g of the crude product was obtained as a yellow solid, which could not be recrystallized and was used for the following reaction without any further purification.

Bisselenadiazoles 13a/b. A solution of 7.0 g (12.0 mmol) of the isomeric mixture of **12** and 5.1 g (46.0 mmol) of SeO_2 was dissolved in 330 mL of concentrated acetic acid. The mixture was heated for 5−6 h to 30−40 °C. It proved to be quite difficult to control the progress of the reaction by TLC because of the chromatographical behavior of the starting material. After the reaction was stopped the solvent was removed in vacuo. Chloroform was added to the residue, and it was neutralized with aqueous Na_2CO_3 (5%) solution. The organic layer was separated, washed with water, dried ($MgSO_4$), and concentrated in vacuo. The mixture of **13a** and **13b** was chromatographed (silica gel/CH_2Cl_2), and the product was obtained as a yellow solid (1.5 g), which was used for the following reactions without further purification.

{(1,2,11,12-η^4)-Tricyclo[10.8.0.0^{2,11}]eicosa-1,11-dien-6,-16-diyne}(η^5-methoxycarbonylcyclopentadienyl)cobalt (14) and {η^4:η^4-[3$_4$]Cyclobutadienophane}bis(η^5-methoxycarbonylcyclopentadienyl)cobalt (3). In a 100 mL flask 150 mg of the mixed bisselenadiazoles **13a** and **13b** was adsorbed on 1.5 g of copper powder by using $CHCl_3$ as solvent. The flask was evacuated and heated to 180 °C for 10 min. The yellow product sublimed to the upper region of the flask. The reaction mixture was allowed to cool to room temperature. To filter the copper powder off, the product was dissolved in CH_2Cl_2. After filtration the crude product was adsorbed on silica gel and purified by column chromatography (silica gel/CH_2Cl_2, CH_3OH, 20:1), yielding **3**[6] (3%) and **14** as a brown-yellow solid in 64% yield, mp 123 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.99 (pt, 2H, Cp), 4.61 (pt, 2H, Cp), 3.72 (s, 3H, CH_3), 2.31−2.24 (m, CH_2), 2.13−2.04 (m, CH_2), 1.75−1.73 (m, CH_2), 1.44−1.43 (m, CH_2), together 24H. ^{13}C NMR (125 MHz, $CDCl_3$): δ 168.4 (C), 93.8 (C), 84.3 (CH), 84.0 (C), 81.9 (C), 81.8 (CH), 51.0 (CH_3), 27.2 (CH_2), 24.8 (CH_2), 19.1 (CH_2). HRMS (FAB) Calcd for $C_{27}H_{31}CoO_2$: 446.1656. Found: 446.1674. IR (KBr) [cm^{-1}]: 2932, 2858, 1705, 1632, 1464, 1434, 1362, 1281, 1190, 1134, 814, 773. UV/vis (CH_2Cl_2) (λ_{max}, nm (log e)): 220 (4.32), 268 (4.44), 304 (3.79), 368 (3.37) Anal. Calcd for $C_{27}H_{31}CoO_2$: C, 72.63; H, 7.00. Found: C, 72.51; H, 6.98.

General Procedure for the Synthesis of Superphanes. A solution of 0.1 mmol of **14** or **15** and 0.4 mmol of RCpCo(CO)$_2$ (R = H, CH_3 or RCp=Cp*) in 25 mL of decalin was heated at 180 °C. The reaction was stopped after 18 h, and the mixture was allowed to cool to ambient temperature, concentrated in vacuo, adsorbed on alumina (neutral, grade III), and chromatographed (alumina neutral, grade III/pentane or pentane/ether). The column chromatography was repeated.

{η^4:η^4-[3$_4$]Cyclobutadienophane}bis(η^5-cyclopentadienyl)cobalt (2). Yield: 80% (41 mg); yellow solid, mp > 300 °C; analytical data: see ref 6.

{η^4:η^4-[3$_4$]Cyclobutadienophane}(η^5-cyclopentadienyl)-(η^5-methylcyclopentadienyl)cobalt (4). Yield: 71% (37 mg); yellow solid, mp >250 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.66 (s, 5H, Cp), 4.52 (pt, 2H, MeCp), 4.42 (pt, 2H, MeCp), 2.31−2.22 (m, CH_2), 2.06 (s, 3H, CH_3), 1.68−1.60 (m, CH_2). ^{13}C NMR (125 MHz, $CDCl_3$): δ 91.7 (C), 81.2 (CH), 80.3 (CH), 80.0 (CH), 78.6 (C), 77.8 (C), 28.0 (CH_2), 26.8 (CH_2), 26.4 (CH_2); 13.0 (CH_3). HRMS (FAB) Calcd for $C_{31}H_{36}Co_2$: 526.1483. Found: 526.1467. IR (KBr) [cm^{-1}]: 3088, 2928, 2836, 1651, 1514, 1449, 1431, 1344, 1104, 1071, 1036, 796, 561. UV/vis (CH_2Cl_2) (λ_{max}, nm (log e)): 220 (4.44), 254 (4.29), 302 (4.83). Anal. Calcd for $C_{31}H_{36}Co_2$: C, 70.70; H, 6.90. Found: C, 70.60; H, 6.90.

{η^4:η^4-[3$_4$]Cyclobutadienophane}(η^5-cyclopentadienyl)-(η^5-pentamethylcyclopentadienyl)cobalt (5). Yield: 70% (41 mg); yellow solid; mp >250 °C. ^{1}H NMR (500 MHz, C_6D_6): δ 4.56 (s, 5H, Cp), 2.26−2.23 (m, CH_2), 1.84 (m, CH_2), 1.83−1.82 (m, CH_2), 1.77 (s, 15H, CH_3), 1.58 (m, CH_2). ^{13}C NMR (125 MHz, C_6D_6): δ 87.7 (C), 81.0 (CH), 79.2 (C), 74.7 (C), 28.8 (CH_2), 27.7 (CH_2), 25.7 (CH_2), 10.2 (CH_3). HRMS (FAB) Calcd for $C_{35}H_{44}Co_2$: 582.2109. Found: 582.2124. IR (KBr) [cm^{-1}]: 2898, 2851, 1651, 1640, 1450, 1431, 1376, 1346, 795, 669, 560. UV/vis (CH_2Cl_2) (λ_{max}, nm (log e)): 210 (3.98), 222 (4.07), 308 (4.71). Anal. Calcd for $C_{35}H_{44}Co_2$: C, 72.14; H, 7.62. Found: C, 72.09; H, 7.59.

{η^4:η^4-[3$_4$]Cyclobutadienophane}(η^5-methoxycarbonylcyclopentadienyl)(η^5-cyclopentadienyl)cobalt (6). Yield: 63% (36 mg); yellow solid; mp >250 °C. ^{1}H NMR (500 MHz, C_6D_6): δ 5.23 (pt, 2H, CpE), 4.51 (pt, 2H, CpE), 4.48 (s, 5H, Cp), 3.59 (s, 3H, CH_3), 2.18−2.02 (m, CH_2), 1.51−1.45 (m,

Table 2. Crystal Data and Structure Refinement for 3, 6, and 8

	3	6	8
empirical formula	$C_{34}H_{38}Co_2O_4$	$C_{32}H_{36}Co_2O_2$	$C_{37}H_{46}Co_2O_2$
fw	628.5	570.5	640.6
cryst color	orange	orange	orange
cryst shape	plate	plate	plate
cryst size [mm]	0.3 × 0.3 × 0.1	0.2 × 0.2 × 0.1	0.2 × 0.2 × 0.05
temp [K]	293	200	200
wavelength [Å]	0.71073	0.71073	0.71073
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/c$	$P2_1/n$
Z	2	4	4
a [Å]	9.595(2)	20.022(4)	14.033(3)
b [Å]	13.832(4)	8.155(2)	15.803(3)
c [Å]	10.998(4)	16.421(3)	14.497(3)
β [deg]	107.96(2)	110.85(3)	109.59(3)
V [Å^3]	1388.5(7)	2506(1)	3029(1)
D_{calcd} [Mg/m^3]	1.50	1.51	1.41
abs coeff, μ [mm^{-1}]	1.23	1.353	1.128
θ range for data collection [deg]	2.4−28.0	2.2−26.1	2.0−26.0
index ranges	$0 < h < 12$, $0 < k < 18$, $-14 < l < 13$	$-24 < h < 24$, $-10 < k < 10$, $-20 < l < 20$	$-16 < h < 16$, $19 < k < 19$, $-17 < l < 17$
no. of reflns collected	3534	35851	26939
no. of indep reflns	3345	4946	5844
max. and min. transmn	0.808 and 0.930		
no. of obs data/params	2753/254	3568/469	4132/384
goodness-of-fit on F^2	1.04	1.03	0.97
$R(F)$	0.035	0.04	0.037
$R_w(F^2)$	0.092	0.075	0.074
$(\Delta\rho)$max, $(\Delta\rho)$min [e Å^{-3}]	0.89, −0.49	0.53, −0.41	0.55, −0.27

CH_2), together 24H. ^{13}C NMR (125 MHz, C_6D_6): δ 168.6 (C), 84.9 (CH), 82.7 (CH), 81.4 (C), 81.2 (C), 81.0 (CH), 79.5 (C), 51.4 (CH_3), 28.4 (CH_2), 27.2 (CH_2), 26.5 (CH_2). HRMS (FAB) Calcd for $C_{32}H_{36}Co_2O_2$: 570.1381. Found: 570.1375. IR (KBr) [cm^{-1}]: 3087, 2913, 2838, 1706, 1652, 1460, 1431, 1279, 1131, 796, 560. UV/vis (CH_2Cl_2) (λ_{max}, nm (log e)): 210 (4.07), 222 (4.31), 302 (4.72). Anal. Calcd for $C_{32}H_{36}Co_2O_2$: C, 67.35; H, 6.36. Found: C, 67.51; H, 6.45.

{η^4:η^4-[3$_4$]Cyclobutadienophane}(η^5-methoxycarbonylcyclopentadienyl)(η^5-methylcyclopentadienyl)cobalt (7). Yield: 64% (37 mg); yellow solid; mp >250 °C. ^{1}H NMR (500 MHz, C_6D_6): δ 5.34 (pt, 2H, CpE), 4.62 (pt, 2H, CpE), 4.48 (pt, 2H, Cp), 4.39 (pt, 2H, Cp), 3.70 (s, 3H, OCH_3), 2.21−2.16 (m, CH_2), 2.02 (s, 3H, CH_3), 1.64−1.56 (m, CH_2). ^{13}C NMR (75 MHz, C_6D_6): δ =167.9 (C), 91.7 (C), 84.3 (C), 84.2 (CH), 82.0 (CH), 81.2 (CH), 80.7 (C), 80.1 (CH), 78.0 (C), 50.7 (CH_3), 27.8 (CH_2), 26.3 (CH_2), 25.9 (CH_2), 12.9 (CH_3). HRMS (FAB) Calcd for $C_{33}H_{38}Co_2O_2$: 584.1538. Found: 584.1559. IR (KBr) [cm^{-1}]: 2914, 1708, 1652, 1461, 1432, 1359, 1280, 1130, 1033, 798, 560. UV/vis (CH_2Cl_2) (λ_{max}, nm (log e)): 210 (3.89), 220 (4.20), 306 (4.69). Anal. Calcd for $C_{33}H_{38}Co_2O_2$: C, 67.79; H, 6.56. Found: C, 67.76; H, 6.72.

{η^4:η^4-[3$_4$]Cyclobutadienophane}(η^5-methoxycarbonylcyclopentadienyl)(η^5-pentamethylcyclopentadienyl)cobalt (8). Yield: 51% (33 mg); red-brown solid; mp >250 °C. ^{1}H NMR (300 MHz, C_6D_6): δ 5.38 (pt, 2H, CpE), 4.65 (pt, 2H, CpE), 3.71 (s, 3H, OCH_3), 2.26−2.22 (m, CH_2), 2.04 (s, 3H, CH_3), 1.90−1.85 (m, CH_2), 1.83 (s, 15H, CH_3), 1.68−1.64 (m, CH_2). ^{13}C NMR (75 MHz, C_6D_6): δ 168.0 (C), 87.0 (CH), 84.3 (CH), 84.1 (C), 82.0 (C), 80.6 (C), 74.2 (C), 50.6 (CH_3), 27.8 (CH_2), 26.0 (CH_2), 24.8 (CH_2), 9.4 (CH_3). HRMS (FAB) Calcd for $C_{37}H_{46}Co_2O_2$: 640.2164. Found: 640.2140. IR (KBr) [cm^{-1}]: 2899, 2850, 1709, 1513, 1462, 1430, 1280, 1133, 1028, 805, 745. UV/vis (CH_2Cl_2) (λ_{max}, nm (log e)): 210 (4.07), 222 (4.22), 316 (4.68). Anal. Calcd for $C_{37}H_{46}Co_2O_2$: C, 69.35; H: 7.24. Found: C, 69.34; H, 7.02.

Electrochemistry. Traditional three-electrode, three-compartment cell geometry was employed for voltammetry experiments with a Ag/AgCl reference electrode in CH_2Cl_2 separated from the test solution by a Haber-Luggin capillary. The $E_{1/2}$ values reported for chemically reversible systems were an average of the observed anodic and cathodic peak potentials. A supporting electrolyte concentration of 0.1 M of [NBu_4]-[PF_6] was employed unless otherwise noted. The working electrode for cyclic voltammetry was a GC disk of 3 mm diameter.

X-ray Crystallography and Structure Solution. Data were collected on a Nonius-CAD4-diffractometer (**3**) at 293 K or Nonius Kappa CCD (**6** and **8**) at 200 K. Relevant crystal and data collection parameters are given in Table 2. The structures were solved by using direct methods, least-squares refinement, and Fourier techniques. Structure solution and refinement were performed with SHELX-97.[10]

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Supporting Information Available: Further details of the crystal structure determination including tables of atomic coordinates, bond lengths and angles, thermal parameters, and structure refinement for **3**, **6**, and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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