Organometallics **2007,** *26,* 644−650

Transannular Interactions in Mixed Superphanes with One Thiophene and One CpCo-Stabilized Cyclobutadiene Ring: Syntheses, Structures, and Electrochemistry

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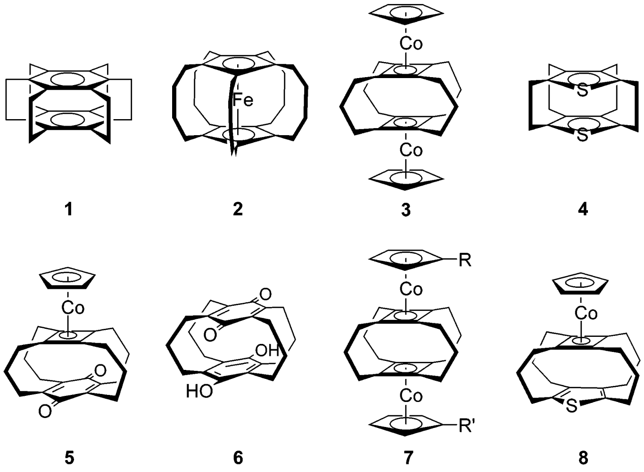
Received September 8, 2006

Superphanes consisting of one thiophene ring and various substituted RCo-stabilized cyclobutadiene (CBD) rings (R = Cp, $C_5H_4(CH_3)$, $C_5(CH_3)_5$, $C_5H_4(Si(CH_3)_3)$, $C_5H_4(COCH_3)$, **8**−**12**) and one superphane with one thiophene ring and one CpCo-stabilized cyclopentadienone ring (**13**) were synthesized. The starting point was a tricyclic diyne with a central thiophene ring and two condensed 4-cyclodecynes, **19**. Heating of **19** with RCo(COD) yielded **8**−**12**, whereas the heating of **19** with $CpCo(CO)_2$ gave **13**. X-ray structural investigation of **8**−**13** afforded the geometrical parameters in the solid state. Cyclic voltammetry showed a strong interaction between the thiophene ring and the CpCo-stabilized cyclobutadiene part. This interaction was substantiated by comparison between the CV data of **8**−**12** and model systems containing only the CpCo(CBD) part.

Introduction

The term “phane” is commonly used when two cyclic conjugated π-systems are fixed on top of each other by alkane bridges.[1] When all hydrogens of both conjugated π-systems are replaced by bridges between the π-units, the term “superphane” is used. This definition is best illustrated by looking at the first superphane (**1**), which was reported by Boekelheide et al. in 1979.[2] It consists of two benzene rings that are tied on top of each other by six ethandiyl bridges. The superphane terminology can easily be extended to other cyclic conjugated π-systems such as **2**−**4**[3−5] to name only a few.[1] The term “mixed superphane” is commonly used when two different conjugated π-systems are “supertied” to each other. We became interested in such species when we studied the electrochemical oxidation of **3** by cyclic voltammetry (CV).[6] In the case when the electron hole is localized in one part of the superphane, we are dealing with a donor−acceptor species. Such species can also be generated by discriminating the sides of the superphanes structurally as shown in **5**−**7**.[7−9] For studying the electronic interaction prevailing in a mixed superphane we developed a route to synthesize various derivatives of **7**.[9] Recently, we reported briefly the synthesis of **8**,[10] which can be looked at as a mixed superphane between **3** and **4**. In this paper we describe in detail the synthesis of the superphanes **8**−**13** and their structural and electrochemical properties.

Chart 1. Examples for Superphanes 1−4 and Mixed Superphanes



Results and Discussion

Syntheses. Our previous studies showed that the best way to synthesize **8**−**13** is by starting with the tricyclic diyne **19**.[10] This system is readily available from 5-cyclodecynol (**14**) in eight steps.[10]

In Scheme 1 we summarize the synthesis of **19**. The key step in our strategy was the reaction of **15** to **16** in a one-pot

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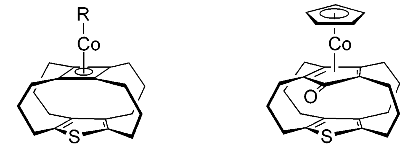
10.1021/om0608206 CCC: \$37.00

Chart 2. Superphanes 9−13



R = $C_5H_4(CH_3)$ **9**
$C_5(CH_3)_5$ **10**
$C_5H_4(Si(CH_3)_3)$ **11**
$C_5H_4(COCH_3)$ **12**

13

procedure using in situ-prepared zirconocene ("Cp_2Zr") and S_2Cl_2 following protocols published by Negishi et al.[11] and Nugent et al.[12] The resulting tricyclic thiophene derivative **16** was transferred to the isomeric mixture of **17** by removing the protecting groups with aqueous HF and subsequent oxidation of the mixture of isomeric alcohols with pyridinium chlorochromate. For the transformation of **17** to **19** we followed a protocol first published by Lalezari et al.[13]

By heating **19** in mesitylene at 165 °C with various Cp-substituted (η^4-cyclooctadiene)(η^5-cyclopentadienyl)cobalt species (RCo(COD)) we obtained our target molecules **8**−**12** (Scheme 2). By heating **19** in decalin at 190 °C in the presence of dicarbonyl(η^5-cyclopentadienyl)cobalt [$CpCo(CO)_2$] we isolated in 50% yield the superphane **13** (Scheme 2).

To estimate the contribution of the thiophene moiety in **8**−**13** upon the electrochemical oxidation of the cyclopentadienyl−cobalt−cyclobutadiene (CpCo(CBD)) unit, we prepared model systems in which the thiophene ring was absent. We chose the systems **22**−**28**. In **22**−**24** and **28** the effect of the bridges was approximately taken care of by the ethanyl substituents. When we planned our synthesis, we assumed that the ethanyl groups were oriented away from the cyclobutadiene unit for sterical reasons. In **25**−**27** we have CpCo(CBD) units with pentamethylene bridges that are oriented more or less in the plane of the four-membered π-system.

The synthesis of **22**−**28** was straightforward, as summarized in Scheme 3. The tetraethyl derivatives **22**−**24** were obtained by heating 3-hexyne (**20**) at 170 °C with RCo(COD). The samples were red-colored, air-sensitive oils that solidified at low temperatures. Similarly, **25**−**27** were synthesized by heating 1,8-cyclotetradecadiyne (**21**)[14,15] with RCo(COD) at 170 °C in decalin. The cyclopentadienone derivative **28** was prepared by heating 3-hexyne with $CpCo(CO)_2$ in decalin at 170−180 °C.[9] In the case of **24** we were able to confirm our assumption that the four ethyl groups are bent away from the CpCo fragment by X-ray studies on single crystals (Figure 1). The X-ray investigations on **27** revealed that the methylene groups bound to the cyclobutadiene ring are bent away from the metal (see below).

Structural Investigations. In the cases of **8**−**13** we were able to grow single crystals, which provided their molecular structures in the solid state. In Figures 2 and 3 we show as an example the molecular structures of **11** and **13**. The structure of **8** was previously reported.[10] In the molecular structures of **8**−**12** the propandiyl bridges at the positions α to the sulfur atom adopt a conformation in which the central CH_2 groups of the chains point away from the heteroatom (see Figure 2). The X-ray data for **13** show a *syn*-configuration of the thiophene and cyclopentadienone rings (Figure 3). In this case the central CH_2 groups of the propandiyl bridges in the α-positions to the heteroatoms point toward those, and the chains in the β-positions show a mixture of two conformations in the ratio of 60:40. Both are shown in Figure 3b.

To describe the geometric relationship between the thiophene ring and the RCo-complexed diene ring, we use the orthogonal distances of the latter four carbon atoms from a plane spanned by the four carbon atoms of the thiophene ring (Chart 3). For **8** to **12** it is found that the RCo-complexed cyclobutadiene ring is almost perfectly parallel to the plane through the four carbon atoms of the thiophene ring. The distance between the two planes amounts to 289 ± 2 pm (Table 1). In the cyclopentadienone complex **13** however, the two planes of the aromatic superphane rings are no longer parallel; they incline by about 5°, presumably due to the steric demand of the carbonyl group opposite the sulfur atom. In all cases the sulfur atom is slightly bent out of the thiophene ring by about 8 pm away from the opposite diene ring. It is interesting to note that the bridges in the α-positions in **13** adopt a conformation in which the central methylene group points toward the S atom, unlike the α-bridges in **8**−**12** (e.g., Figure 2).

To describe the bending of the carbon atoms bound to the aromatic rings out of the planes of the ring, we defined the angles α, β, α', and β' (Table 1) calculated from the arithmetic means of the corresponding angles as defined in Chart 3. For **8**−**13** the angles α are larger than β, whereas α' and β' are about equal. Presumably the enlargement of α is caused by the same steric reason as the out-of-plane bending of the sulfur atom.

The bending of the substituents away from the CpCo moiety in **24** and **27** (definition analogous) is very similar to that found for the superphanes **8**−**12**; thus we can assume that the bending indicated by α' and β' is not due to strain in the superphane.

Cyclic Voltammetric Studies. Cyclic voltammetry (CV) is suitable to study the effects of intramolecular redox processes. Several studies on cyclophanes revealed that those molecules that were substituted by thiophenes or that incorporated thiophene or tetrathiafulvalene (TTF) rings into the cyclophane scaffold or that were complexed by metal fragments show reversible oxidation processes.[16] Therefore, we also expected for our mixed superphanes useful results in terms of reversible redox processes. In Table 2 we list the recorded oxidation potentials of **8**−**13** as well as **22**−**28** relative to that of ferrocene/ferrocenium (Fc/Fc^+). The latter value was determined to be 500 ± 10 mV vs Ag/AgCl at room temperature. A comparison of our oxidation studies with those of several CpCo-stabilized superphanes[6,7,9] shows that the electron is removed from the cobalt center. The comparison between the data of the superphanes **8**−**12** reveals that methyl groups at the Cp ring lower the oxidation potential considerably (**9**, **10** in Table 2) as compared to the parent system **8**. The trimethylsilyl (**11**) and the acetyl (**12**) substituent increase the oxidation potential. For **13** the oxidation potential is irreversible, as found for other CpCo-substituted cyclopentadienone complexes.[9]

To elucidate the effect of stabilizing the positive charge at the CpCo(CBD) fragment in **8**−**12** by the thiophene ring, we have compared in Figure 4 the differences of the oxidation

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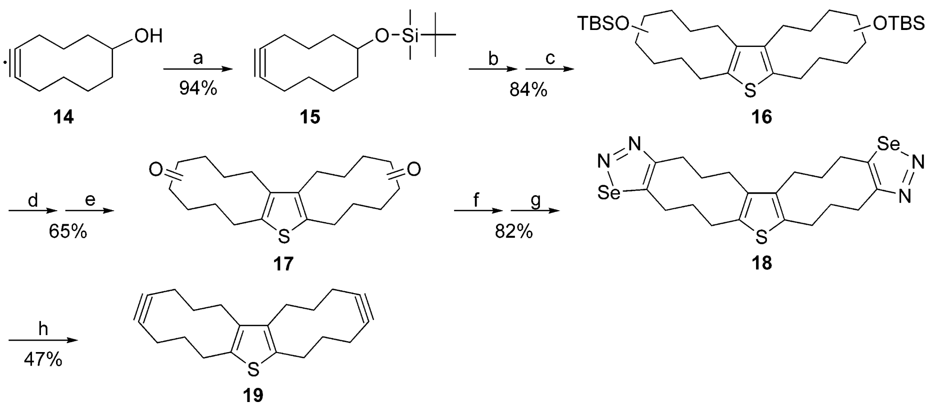
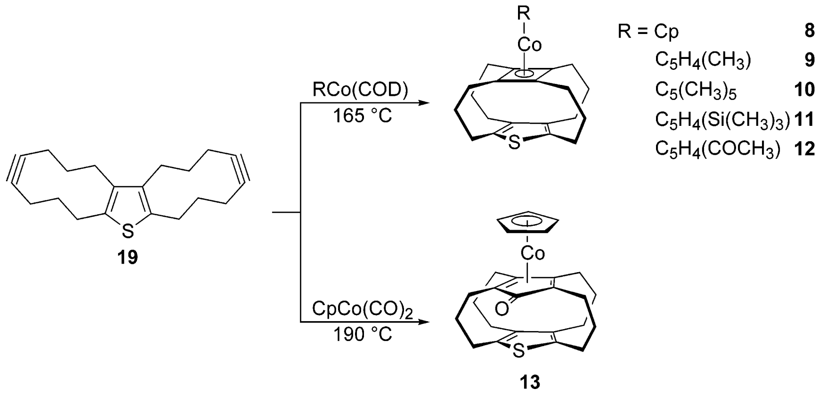
Scheme 1[a]

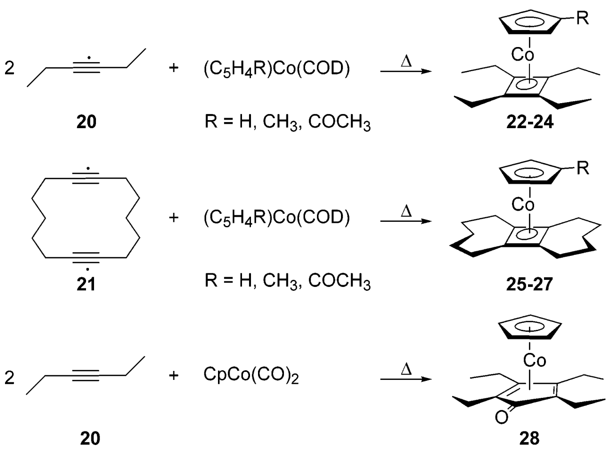


[a] Conditions:[10] (a) (TBDMS)Cl/imidazole/CH_2Cl_2; (b) Cp_2ZrCl_2/*n*-BuLi/THF, −78 °C; (c) S_2Cl_2; (d) HF(aq)/CH_3CN; (e) PCC/CH_2Cl_2; (f) $H_3N_2CONH_2$·HCl/NaOAc/EtOH; (g) SeO_2/CH_3CO_2H; (h) 180−200 °C/Cu.

Scheme 2



Scheme 3



potentials (OP) of **8**, **9**, and **12** with the model systems **22**−**24** on one side and **25**−**27** on the other. The comparison shows a strong shift of the oxidation potential toward higher values when the thiophene ring was removed. Depending on the model system (**22**−**24** or **25**−**27**), the stabilization is on the order of 121−132 or 87−94 mV, respectively. Both values argue for a strong charge transfer during the oxidation process.

A slight substituent effect can also be seen in the ground-state properties of **8**−**12** by comparing the chemical shift of the ^{13}C NMR spectra of **9**−**12** with those of **8** (Table 3). We find a low-field shift for the ^{13}C signals at the cyclobutadiene rings of **9** and **10** with the donor ligands. A high-field shift of the respective signals was encountered in the case of **12** (Table 3). A comparison between the ^{13}C NMR signals at the cyclobutadiene rings of **8**−**12** with the model systems **22**−**27** reveals a low-field shift of the signals in the latter species, indicating that in the superphanes **8**, **9**, and **12** the thiophene

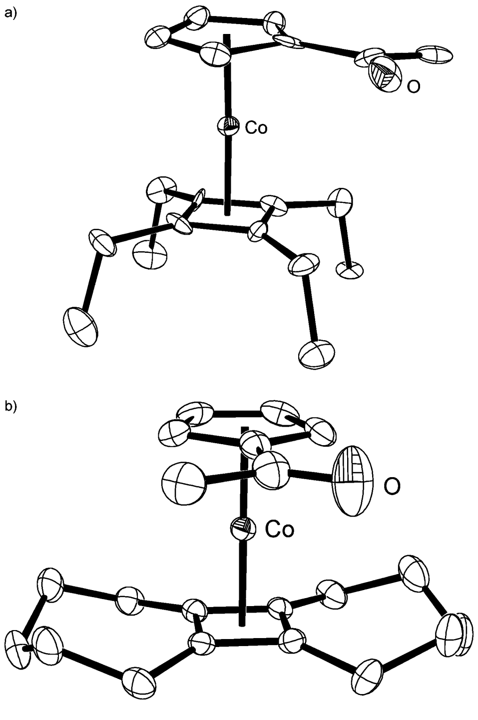


Figure 1. Molecular structures of **24** and **27**. The hydrogen atoms are omitted for the sake of clarity. The thermal ellipsoids are drawn at the 50% probability level.

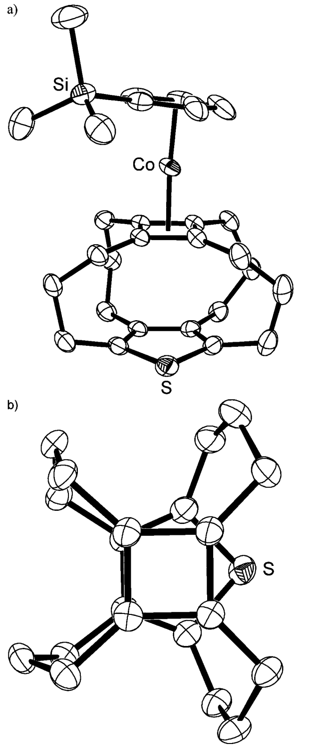


Figure 2. (a) Molecular stucture of **11**. The hydrogen atoms are omitted for the sake of clarity. The thermal ellipsoids are drawn at the 50% probability level. (b) Conformation of the propandiyl bridges in **11**. For the sake of clarity we have omitted the C_5H_4-TMSCo fragment and the hydrogen atoms.

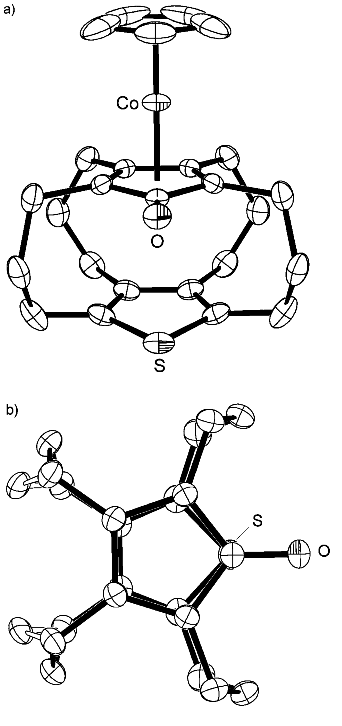


Figure 3. (a) Molecular structure of **13**. The hydrogen atoms are omitted for the sake of clarity. The thermal ellipsoids are drawn at the 50% probability level. (b) The conformations of the propandiyl bridges give rise to two conformers per bridge in the ratio 60:40. For the sake of clarity we have omitted the CpCo fragment and the hydrogen atoms.

ring causes a slight charge transfer as compared to the CpCo(CBD) models (Table 4).

Chart 3. Definition of Selected Geometrical Parameters of 8−13

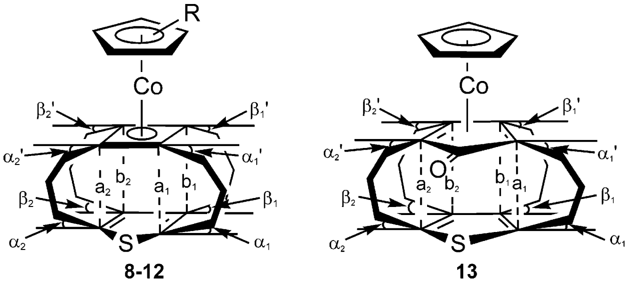


Table 1. Orthogonal Distances (*a*, *b*) and Bonding Angles (α, *β*, α′, *β*′) of 8−13, 24, and 27

	α [deg][a]	*β* [deg][a]	α′ [deg][b]	*β*′ [deg][b]	*a* [Å][c]	*b* [Å][c]
8	11.2	2.4	6.9	7.4	2.91	2.89
9	11.2	2.0	5.7	8.3	2.89	2.89
	11.2	2.7	6.6	8.0	2.89	2.89
	11.5	2.3	6.4	7.7	2.90	2.89
10	11.5	2.2	7.1	7.4	2.91	2.89
11	11.5	1.7	6.8	8.0	2.90	2.88
12	10.6	2.9	6.0	7.4	2.87	2.88
13	9.3	3.2	4.3	3.8	2.99	2.87
24			4.8	7.3		
27			6.5	8.2		

[a] α and *β* are the arithmetic means of α_1, α_2 and β_1, β_2, respectively. [b] α′ and *β*′ are the arithmetic means of α_1', α_2' and β_1', β_2', respectively. [c] *a* and *b* are the arithmetic means of a_1, a_2 and b_1, b_2, respectively. For the definition of the used abbreviations see Chart 3.

Table 2. Oxidation Potentials (mV) of 8−13 and 22−28 Relative to That of Fc/Fc$^+$

8	−77[10]	**12**	+158	**24**	+290	**28**	+677[a]
9	−109	**13**	+501[a]	**25**	+10		
10	−257	**22**	+46	**26**	−21		
11	−8	**23**	+12	**27**	+252		

[a] Irreversible

To interpret the observed shifts of the oxidation potentials between superphanes and the models, we have carried out single-point calculations on **8**, adopting the geometrical parameters found by X-ray investigations. The calculations were performed using the Gaussian 03 program package.[17] We used the RHF-SCF method applying the 6-311G* basis set for S, C, and H.[18] For Co we have chosen Wachters' (14s, 9p, 5d) basis set augmented with a 4f polarization function.[19] For the sake of a clear representation we show in Figure 5 a schematic drawing instead of the isosurface of the HOMO. The wave function clearly shows strong *π*-character on the cyclobutadiene *and* thiophene part. This explains the strong effect of the thiophene ring encountered in our electrochemical experiments.

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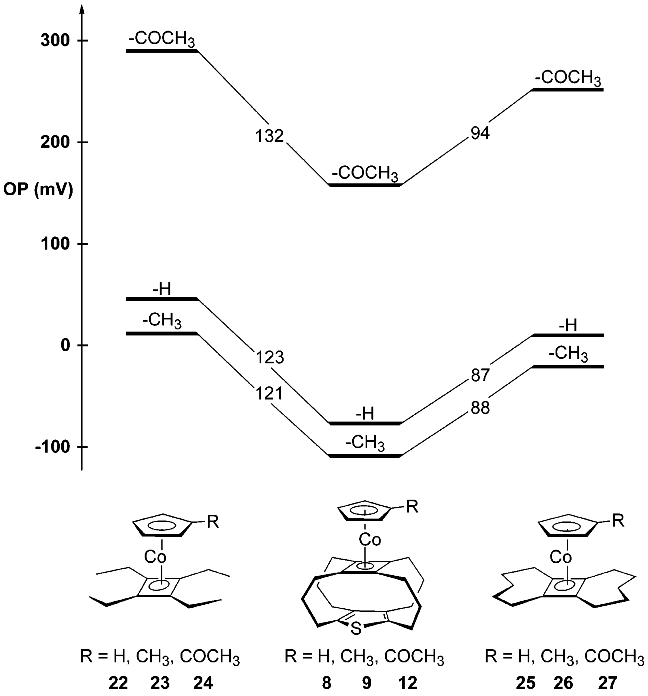

Figure 4. Comparison between the oxidation potentials (OP) of **8**, **9**, and **12** (center), **22**−**24** (left), and **25**−**27** (right).

Table 3. Comparison between the ^{13}C Chemical Shift Data at the Cyclobutadiene (CBD) Carbon Atoms of 9−12 Relative to 8, Showing the Electronic Effects of the Cp Substituents

	δ_{CBD}	$\Delta\delta$
8	78.5	0
	75.9	0
9	77.7	−0.8
	75.2	−0.7
10	73.9	−4.6
	72.1	−3.8
11	78.5	0.0
	75.8	−0.1
12	80.6	+2.1
	78.0	+2.1

Table 4. Comparison between the ^{13}C Chemical Shift Data at the Cyclobutadiene (CBD) Carbon Atoms of 8, 9, and 12 with Those of 22−27, Showing the Electronic Effect of the Thiophene Ring

	δ_{CBD}		δ_{CBD}	$\Delta\delta$		δ_{CBD}	$\Delta\delta$
8	78.5	**22**	79.8	−1.3	**25**	79.5	−1.0
	75.9			−3.9			−3.6
9	77.7	**23**	78.9	−1.2	**26**	78.5	−0.8
	75.2			−3.7			−3.3
12	80.6	**24**	81.7	−1.0	**27**	81.5	−0.8
	78.0			−3.6			−3.4

Experimental Section

General Methods. All reactions were conducted with oven-dried glassware under argon atmosphere with magnetic stirring. Decalin and mesitylene were dried with sodium and distilled under argon. Decalin was degassed prior to using. Melting points are uncorrected. Material for column chromatography: silica gel 60 (Machery-Nagel), Alox III (VWR). NMR spectra were recorded at 300 or 500 MHz (^{1}H) and 75.5 or 125.8 MHz (^{13}C), respectively, using the solvent as internal standard. The IR spectra were recorded with a Bruker Vector 22 FT-IR instrument. The UV/vis absorption spectra were recorded using a Hewlett-Packard 8452 A spectrometer. The high-resolution mass spectra (HRMS) were recorded in the FAB+ or EI (70 eV) mode. Elemental analyses were carried out by the Mikroanalytisches Laboratorium der Universität Heidelberg.

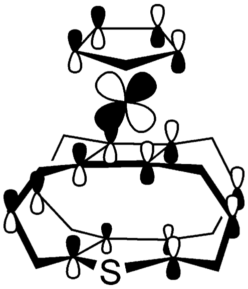

Figure 5. Schematic drawing of the highest occupied MO of **8** according to a HF-SCF calculation.

The electrochemical experiments were carried out using the traditional three-electrode, three-compartment cell geometry with a Metrohm PGStat 20 potentiostat using a glassy carbon disk working electrode, a Pt wire counter electrode, and a Ag/AgCl reference electrode. The measurements were carried out in CH_2Cl_2 solution containing 0.1 M n-Bu_4NPF_6 as a supporting electrolyte with scan rates of 50−900 mV/s at room temperature. An internal standard of ferrocene was added near the end of each experiment to calibrate the potentials. The cyclic voltammograms were measured between −2.5 and +2.5 V. The concentration of the measured compounds was 10^{-3} mol/L. The interpretation of the cyclic voltammograms was carried out graphically following the diagnostic criteria proposed by Nicholson and Shain.[20]

1,2,3,6,7,8,9,10,11,14,15,16-Dodecahydro-4,5,12,13-tetradehydro-1*H*,9*H*-dicyclodeca[*b*,*d*] thiophene (**19**) and the superphane **8** were prepared according to literature methods.[10,11]

Preparation of Superphanes 9−12. To a heated (165 °C) solution of 1.25 mmol of RCo(COD), with R = $C_5H_4(CH_3)$, $C_5(CH_3)_5$, $C_5H_4(Si(CH_3)_3)$, and $C_5H_4(COCH_3)$, in 50 mL of mesitylene was added a solution of 150 mg (0.50 mmol) of **19** in 100 mL of mesitylene within 2 h. The progress of the reaction was controlled by TLC. After all of **19** had disappeared (12 h), the solvent was removed under vacuum. The residue was dissolved in petroleum ether and purified on basic Alox III. After removal of the solvent, the corresponding products were obtained.

Complex 9. Starting material: 308 mg $(C_5H_4(CH_3))Co(COD)$, yield: 52 mg (24%) of yellow crystals, mp: 143 °C. ^{1}H NMR (300 MHz, C_6D_6): δ 4.35 (ps, 2H, Cp), 4.26 (ps, 2H, Cp), 2.92−2.79 (m, 2H, CH_2), 2.58−2.40 (m, 6H, CH_2), 2.40−2.27 (m, 2H, CH_2), 2.17−1.93 (m, 6H, CH_2), 1.92 (s, 3H, CH_3), 1.86−1.69 (m, 6H, CH_2), 1.62−1.47 (m, 2H, CH_2). ^{13}C NMR (75 MHz, C_6D_6): δ 137.9 (Th), 131.8 (Th), 91.6 (C, Cp), 81.2 (CH, Cp), 80.1 (CH, Cp), 77.7 (CBD), 75.2 (CBD), 26.6 (CH_2), 26.5 (CH_2), 26.4 (CH_2), 25.8 (CH_2), 25.6 (CH_2), 23.8 (CH_2), 13.0 (CH_3). IR (KBr): 3085 (w), 2957−2851 (s), 1718 (m), 1636 (s), 1458 (m), 1431 (s). CV: −109 mV (referenced to the ferrocene/ferrocenium couple). UV/vis (CH_2Cl_2, $\lambda_{\max}$, nm, log ϵ): 238 (4.20), 284 (4.55), 310 (3.30). Anal. Calcd for $C_{26}H_{31}CoS$ (434.53): C, 71.87; H, 7.19; S, 7.38. Found: C, 71.65; H, 7.11; S, 7.38.

Complex 10. Starting material: 378 mg $(C_5(CH_3)_5)Co(COD)$, yield: 42 mg (17%) of bright orange crystals, mp: >280 °C dec. ^{1}H NMR (500 MHz, C_6D_6): δ 2.98−2.85 (m, 2H, CH_2), 2.62−2.50 (m, 4H, CH_2), 2.50−2.32 (m, 2H, CH_2), 2.07−1.92 (m, 2H, CH_2), 1.89−1.75 (m, 12H, CH_2), 1.74 (s, 15H, CH_3), 1.67−1.55 (m, 2H, CH_2). ^{13}C NMR (125 MHz, C_6D_6): δ 137.8 (Th), 131.8 (Th), 86.9 (Cp), 73.9 (CBD), 72.1 (CBD), 26.8 (CH_2), 26.6 (CH_2), 26.5 (CH_2), 26.0 (CH_2), 24.4 (CH_2), 22.4 (CH_2), 9.5 (CH_3). IR (KBr): 2956−2851 (s), 1628 (br), 1459 (m), 1430 (s), 1378 (s),

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1313 (m), 1028 (s). CV: −257 mV (referenced to the ferrocene/ferrocenium couple). UV/vis (CH_2Cl_2, λ_{max}, nm, log ϵ): 244 (4.23), 292 (4.58), 328 (3.55), 370 (2.94). Anal. Calcd for $C_{30}H_{39}CoS$ (490.64): C, 73.44; H, 8.01; S, 6.54. Found: C, 73.34; H, 8.04; S, 6.61.

Complex 11. Starting material: 380 mg of $(C_5H_4(Si(CH_3)_3))Co(COD)$, yield: 145 mg (59%) of bright orange crystals, mp: 103 °C. ^{1}H NMR (300 MHz, C_6D_6): δ 4.54−4.49 (m, 2H, Cp), 4.49−4.44 (m, 2H, Cp), 2.90−2.79 (m, 2H, CH_2), 2.59−2.53 (m, 1H, CH_2), 2.53−2.42 (m, 5H, CH_2), 2.41−2.25 (m, 2H, CH_2), 2.25−1.90 (m, 6H, CH_2), 1.90−1.67 (m, 6H, CH_2), 1.61−1.46 (m, 2H, CH_2), 0.28 (s, 9H, CH_3). ^{13}C NMR (125 MHz, C_6D_6): δ 137.8 (Th), 131.7 (Th), 84.9 (CH, Cp), 84.7 (CH, Cp), 83.9 (C, Cp), 78.6 (CBD), 75.8 (CBD), 26.6 (CH_2), 26.4 (CH_2), 26.3 (CH_2), 26.2 (CH_2), 25.7 (CH_2), 24.5 (CH_2), 0.6 (CH_3). IR (KBr): 3083 (w), 2943−2852 (s), 1638 (br), 1426 (m), 1246 (m), 1164 (m), 1031 (m), 833 (s). CV: −8 mV (referenced to the ferrocene/ferrocenium couple). UV/vis (CH_2Cl_2, $\lambda_{max,}$ nm, log ϵ): 256 (3.68), 286 (3.81), 326 (3.26). Anal. Calcd for $C_{28}H_{37}CoSSi$ (492.69): C, 68.26; H, 7.57; S, 6.51. Found: C, 68.52; H, 7.58; S, 6.63.

Complex 12. Starting material: 343 mg of $(C_5H_4(COCH_3))Co(COD)$, yield: 65 mg (28%) of orange crystals, mp: 157 °C. ^{1}H NMR (300 MHz, C_6D_6): δ 4.92 (ps, 2H, Cp), 4.45 (ps, 2H, Cp), 2.85−2.73 (m, 2H, CH_2), 2.50−2.36 (m, 4H, CH_2), 2.34−2.20 (m, 4H, CH_2), 2.15 (s, 3H, CH_3), 2.01−1.80 (m, 6H, CH_2), 1.79−1.60 (m, 6H, CH_2), 1.58−1.43 (m, 2H, CH_2). ^{13}C NMR (125 MHz, C_6D_6): δ 194.7 (CO), 137.9 (Th), 132.4 (Th), 93.4 (C, Cp), 85.2 (CH, Cp), 81.1 (CH, Cp), 80.7 (CBD), 78.1 (CBD), 26.8 (CH_3), 26.5 (CH_2), 26.2 (CH_2), 26.1 (CH_2), 25.5 (CH_2), 25.1 (CH_2), 23.4 (CH_2). IR (KBr): 3090 (w), 2954−2852 (s), 1649 (s), 1454 (s), 1363 (m), 1283 (s). CV: +158 mV (referenced to the ferrocene/ferrocenium couple). UV/vis (CH_2Cl_2, λ_{max}, nm, log ϵ): 280 (4.39), 332 (3.66), 398 (3.00). Anal. Calcd for $C_{27}H_{31}OSCo$ (462.54): C, 70.11; H, 6.76; S, 6.93. Found: C, 70.04; H, 6.70; S, 6.92.

Preparation of Superphane 13. To a heated (190 °C) solution of 405 mg (2.25 mmol) of $CpCo(CO)_2$ in 60 mL of decalin was added a solution of 150 mg (0.50 mmol) of **19** in 110 mL of decalin within 5 h. The progress of the reaction was controlled by TLC. After all **19** had disappeared (8 days), the solvent was removed under vacuum. The residue was dissolved in dichloromethane and purified on basic Alox III. After removal of the solvent, 116 mg (52%) of dark orange crystals was obtained, mp 240 °C dec. ^{1}H NMR (500 MHz, C_6D_6): δ 4.17 (s, 5H, Cp), 3.04−2.94 (m, 2H, CH_2), 2.85−2.79 (m, 2H, CH_2), 2.72−2.57 (m, 4H, CH_2), 2.54−2.47 (m, 2H, CH_2), 2.35−2.28 (m, 2H, CH_2), 2.22−2.14 (m, 2H, CH_2), 2.13−2.07 (m, 2H, CH_2), 1.91−1.68 (m, 8H, CH_2). ^{13}C NMR (125 MHz, C_6D_6): δ 151.2 (CO), 140.0 (Th), 134.9 (Th), 88.7 (Cpd) 85.2 (Cpd), 82.0 (Cp), 27.9 (CH_2), 27.7 (CH_2), 26.1 (CH_2), 25.3 (CH_2), 24.6 (CH_2), 24.4 (CH_2). IR (KBr): 3093 (w), 2954−2849 (s), 1639 (s), 1544 (s), 1453 (s), 1157 (m), 1107 (m) 1078 (m), 1006 (m). CV: +501 mV (referenced to the ferrocene/ferrocenium couple). UV/vis (CH_2Cl_2, $\lambda_{max,}$ nm, log ϵ): 280 (4.04), 330 (4.22). HRMS (FAB+): calcd for $C_{26}H_{30}OCoS$ (448.51) 449.1349, found 449.1398. Anal. Calcd for $C_{26}H_{29}OSCo{\cdot}0.15CH_2Cl_2$ (461.25): C, 68.09; H, 6.40; S, 6.95. Found: C, 68.12; H, 6.65; S, 6.73.

Preparation of (η^4-1,2,3,4-Tetraethylcyclobutadiene)(η^5-cyclopentadienyl)cobalt (22), (η^4-1,2,3,4-Tetraethylcyclobutadiene)(1-methyl-η^5-cyclopentadienyl)cobalt (23), and (η^4-1,2,3,4-Tetraethylcyclobutadiene)(1-carboxymethyl-η^5-cyclopentadienyl)cobalt (24). To a heated (190 °C) solution of 4 mmol of RCo(COD), with R = Cp, $C_5H_4(CH_3)$, and $C_5H_4(COCH_3)$, in 300 mL of decalin was added a solution of 0.98 g (12 mmol) of 3-hexyne (**20**) in 300 mL of decalin within 24 h. The temperature was lowered to 150 °C for another 24 h. After the solvent was removed under vacuum, the residue was dissolved in petroleum ether and purified on basic Alox III. After removal of the solvent, the corresponding products were obtained.

Complex 22. Starting material: 0.93 g of CpCo(COD), yield: 0.43 g (37%) of a dark orange liquid. ^{1}H NMR (500 MHz, C_6D_6): δ 4.65 (s, 5H, Cp), 2.06−1.80 (m, 8H, CH_2), 1.14−0.97 (m, 12H, CH_3). ^{13}C NMR (125 MHz, C_6D_6): δ 79.8 (CBD), 79.7 (Cp), 20.5 (CH_2), 14.8 (CH_3). IR (KBr): 2866 (s), 1757 (w), 1684 (w), 1608 (w), 1460 (s), 1368 (s), 819 (s). CV: +46 mV (referenced to the ferrocene/ferrocenium couple). UV/vis (CH_2Cl_2, λ_{max}, nm, log ϵ): 234 (3.08), 264 (3.24), 298 (2.03), 380 (1.53). Anal. Calcd for $C_{17}H_{25}Co$ (288.15): C, 71.51; H, 9.00. Found: C, 71.59; H, 8.91.

Complex 23. Starting material: 0.98 g $(C_5H_4(CH_3))Co(COD)$, yield: 0.67 g (55%) of a dark red liquid. ^{1}H NMR (500 MHz, C_6D_6): δ 4.56 (m, 2H, Cp), 4.49 (m, 2H, Cp), 2.11−1.78 (m, 11H, CH_2, CpCH_3), 1.37−0.71 (m, 12H, CH_2-CH_3). ^{13}C NMR (125 MHz, C_6D_6): δ 92.4 (C, Cp), 80.7 (CH, Cp), 79.0 (CH, Cp), 78.9 (CBD), 20.3 (CH_2), 14.8 (CH_2-CH_3), 13.2 (CpCH_3). IR (KBr): 3088 (w), 2962−2870 (s), 1458 (m), 1371 (br), 1313 (w), 1052 (m), 1038 (m), 1021 (m), 821 (m), 799 (s). CV: +12 mV (referenced to the ferrocene/ferrocenium couple). UV/vis (CH_2Cl_2, λ_{max}, nm, log ϵ): 268 (4.34), 302 (3.16), 378 (2.81). Anal. Calcd for $C_{18}H_{27}Co$ (302.34): C, 70.82; H, 8.74. Found: C, 70.82; H, 8.73.

Complex 24. Starting material: 1.10 g of $(C_5H_4(COCH_3))Co(COD)$, yield: 0.90 g (68%) of a red liquid. ^{1}H NMR (500 MHz, C_6D_6): δ 5.15 (t, 2H, Cp), 4.65 (t, 2H, Cp), 2.10 (s, 3H, (CO)-CH_3), 1.78 (q, 8H, CH_2), 0.95 (t, 12 H, CH_2-CH_3). ^{13}C NMR (125 MHz, C_6D_6): δ 195.2 (CO), 94.0 (C, Cp), 83.8 (CH, Cp), 81.7 (CBD), 81.0 (CH, Cp), 27.1 ((CO)CH_3), 19.9 (CH_2), 14.2 (CH_2-CH_3). IR (KBr): 2964−2873 (s), 1670 (s), 1455 (m), 1413 (w), 1372 (w), 1262 (s), 1097 (br), 1019 (br), 864 (m), 801 (br). CV: +290 mV (referenced to the ferrocene/ferrocenium couple). UV/vis (CH_2Cl_2, λ_{max}, nm, log ϵ): 260 (4.20), 284 (3.94), 328 (3.48), 384 (3.05). Anal. Calcd for $C_{19}H_{27}OCo$ (330.35): C, 69.08; H, 8.24. Found: C, 68.75; H, 8.27.

Preparation of (1,2:8,9-η^4-Tricyclo[7.5.0.0^{2,8}]tetradeca-1,8-diene)(η^5-cyclopentadienyl)cobalt (25), (1,2:8,9-η^4-Tricyclo[7.5.0.0^{2,8}]tetradeca-1,8-diene)(1-methyl-η^5-cyclopentadienyl)cobalt (26), and (1,2:8,9-η^4-Tricyclo[7.5.0.0^{2,8}]tetradeca-1,8-diene)(1-carboxymethyl-η^5-cyclopentadienyl)cobalt (27). A solution of 0.94 g (5 mmol) of freshly sublimed 1,8-cyclotetradecadiyne (**21**) and 5 mmol of RCo(COD), whereas R = Cp, $C_5H_4(CH_3)$, and $C_5H_4(COCH_3)$, in 150 mL of decalin was heated to 170 °C for 4 days. After the solvent was removed under vacuum, the residue was dissolved in petroleum ether and purified on basic Alox III. After removal of the solvent, the corresponding products were obtained.

Complex 25. Starting material: 1.16 g of CpCo(COD), yield: 0.58 g (37%) of red crystals, mp: 96 °C. ^{1}H NMR (500 MHz, C_6D_6): δ 4.76 (s, 5H, Cp), 2.03−1.75 (m, 10H, CH_2), 1.75−1.42 (m, 8H, CH_2), 0.91−0.74 (m, 2H, CH_2). ^{13}C NMR (125 MHz, C_6D_6): δ 79.5 (CBD), 79.2 (Cp), 31.1 (CH_2), 30.8 (CH_2), 28.2 (CH_2). IR (KBr): 3083 (w), 2911 (s), 2847 (m), 2814 (s), 1628 (br), 1442 (s), 1429 (m), 1326 (m), 1226 (m), 1106 (m), 996 (m), 801 (s). CV: +10 mV (referenced to the ferrocene/ferrocenium couple). UV/vis (CH_2Cl_2, λ_{max}, nm, log ϵ): 266 (4.30), 302 (3.09), 378 (2.49). Anal. Calcd for $C_{19}H_{25}Co$ (312.34): C, 73.06; H, 8.07. Found: C, 73.04; H, 7.89.

Complex 26. Starting material: 1.23 g of $(C_5H_4(CH_3))Co(COD)$, yield: 0.46 g (28%) of red-brown crystals, mp 90 °C. ^{1}H NMR (500 MHz, C_6D_6): δ 4.70 (ps, 2H, Cp), 4.64 (ps, 2H, Cp), 2.01−1.73 (m, 13H, CH_3 and CH_2), 1.73−1.42 (m, 8H, CH_2), 0.95−0.78 (m, 2H, CH_2). ^{13}C NMR (125 MHz, C_6D_6): δ 92.1 (C, Cp), 80.5 (CH, Cp), 78.2 (CH, Cp), 78.5 (CBD), 31.0 (CH_2), 30.7 (CH_2), 27.9 (CH_2), 13.6 (CH_3). IR (KBr): 3075 (w), 2957−2843 (s), 2815 (m), 1637 (br), 1440 (s), 1326 (m), 1220 (s), 1023 (m), 838 (m), 795 (s). CV: −21 mV (referenced to the ferrocene/ferrocenium couple). UV/vis (CH_2Cl_2, λ_{max}, nm, log ϵ): 270 (4.42), 300 (3.50), 368 (3.11). Anal. Calcd for $C_{20}H_{27}Co$ (326.37): C, 73.60; H, 8.34. Found: C, 73.39; H, 8.26.

Complex 27. Starting material: 1.37 g ($(C_5H_4(COCH_3))Co(COD)$), yield: 1.12 g (63%) of red-brown crystals, mp: 131 °C. ^{1}H NMR (500 MHz, C_6D_6): δ 5.38 (ps, 2H, Cp), 4.69 (ps, 2H, Cp), 2.10 (s, 3H, CH_3), 1.89−1.74 (m, 10H, CH_2), 1.56−1.45 (m, 4H, CH_2), 1.45−1.35 (m, 4H, CH_2), 0.80−0.71 (m, 2H, CH_2). ^{13}C NMR (125 MHz, C_6D_6): δ 195.6 (CO), 93.4 (C, Cp), 83.4 (CH, Cp), 81.5 (CBD), 80.8 (CH, Cp), 30.7 (CH_2), 30.2 (CH_2), 27.5 (CH_2), 26.8 (CH_3). IR (KBr): 3093 (w), 2922−2820 (s), 1666 (s), 1453 (s), 1421 (m), 1373 (s), 1326 (m), 1282 (s), 1223 (m), 1034 (m), 1016 (m), 892 (m), 815 (s), 620 (s). CV: +252 mV (referenced to the ferrocene/ferrocenium couple). UV/vis (CH_2Cl_2, λ_{max}, nm, log ϵ): 262 (4.33), 288 (4.03), 322 (3.59), 388 (2.89), 312 (4.42). Anal. Calcd for $C_{20}H_{27}Co$ (326.37): C, 71.18; H, 7.68. Found: C, 71.22; H, 7.55.

Preparation of (η^4-2,3,4,5-Tetraethylcyclopentadienone)(η^5-cyclopentadienyl)cobalt (28). To a heated (190 °C) solution of 540 mg (3 mmol) of $CpCo(CO)_2$ in 50 mL of decalin was added a solution of 740 mg (9 mmol) of 3-hexyne (**20**) in 100 mL of decalin within 24 h. The temperature was lowered to 170 °C, and the mixture was stirred for another 5 days. After the solvent was removed under vacuum, the residue was dissolved in dichloromethane and purified on basic Alox III. After removal of the solvent, 655 mg (69%) of red crystals was obtained, mp 67 °C. ^{1}H NMR (500 MHz, C_6D_6): δ 4.29 (s, 5H, Cp), 3.13−2.86 (m, 6H, CH_2), 2.71−2.60 (m, 2H, CH_2), 1.63−1.57 (m, 12H, CH_3). ^{13}C NMR (125 MHz, C_6D_6): δ 157.6 (CO), 100.4 (Cpd), 91.8 (Cpd), 89.5 (Cp), 24.5 (CH_2), 24.0 (CH_2), 21.0 (CH_3), 19.4 (CH_3). IR (KBr): 3092 (w), 2968−2873 (s), 1572 (s), 1468 (m), 1451 (m), 1056 (m), 872 (s), 840 (br). CV: +677 mV (referenced to the ferrocene/ferrocenium couple). UV/vis (CH_2Cl_2, λ_{max}, nm, log ϵ): 286 (4.50), 360 (3.56), 420 (3.17). HRMS (FAB+): Calcd for $C_{18}H_{25}OCo$ [M + H$^+$] 317.1309; found 317.1303. Anal. Calcd for $C_{18}H_{25}OCo$ (316.33): C, 68.35; H, 7.97. Found: C, 68.85; H, 8.04.

X-ray Diffraction Analysis. The reflection data for the structure analyses of **9**, **10**, **12**, and **24** were taken with a Bruker APEX diffractometer and for **11**, **13**, and **27** with a Bruker Smart diffractometer at 200 K in all cases except for **24** (100 K). Mo Kα radiation was used to take sets of 0.3 deg ω-scans, covering a whole sphere in reciprocal space in all cases. Intensities were corrected for Lorentz and polarization effects, and empirical absorption corrections were applied using SADABS[21] based on the Laue symmetry of the reciprocal space. Structures were solved by direct methods and refined against F^2 with a full-matrix least-squares algorithm using the SHELXTL-PLUS (5.10) software package.[22] Hydrogen atoms were treated using appropriate riding models (**11**, **13**, **24**, **27**) or refined isotropically (**9**, **10**, **12**).

CCDC 615102−615108 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Complex 9: colorless crystal (irregular), dimensions 0.32 × 0.18 × 0.12 mm^3, crystal system monoclinic, space group $P2_1/c$, Z = 12, a = 16.403(1) Å, b = 8.4564(7) Å, c = 44.008(4) Å, β = 93.849(2)°, V = 6090.4(8) Å^3, ρ = 1.422 g/cm^3, T = 200(2) K, θ_{max}= 28.36°, 60 862 reflections measured, 15 067 unique (R(int) = 0.0420), 12 761 observed ($I > 2\sigma(I)$), μ = 0.96 mm^{-1}, T_{min} = 0.75, T_{max} = 0.89, 1124 parameters refined, goodness of fit 1.09 for observed reflections, final residual values R1(F) = 0.044, wR(F^2) = 0.099 for observed reflections, residual electron density −0.36 to 0.85 e Å^{-3}. CCDC 615102.

Complex 10: orange crystal (irregular), dimensions 0.15 × 0.08 × 0.04 mm^3, crystal system monoclinic, space group $P2_1/n$, Z = 4, a = 11.108(1) Å, b = 13.813(2) Å, c = 15.658(2) Å, β = 90.244(3)°, V = 2402.4(6) Å^3, ρ = 1.356 g/cm^3, T = 200(2) K, θ_{max}= 23.26°, 15 826 reflections measured, 3426 unique (R(int) = 0.0614), 2693 observed ($I > 2\sigma(I)$), μ = 0.82 mm^{-1}, T_{min} = 0.89, T_{max} = 0.97, 445 parameters refined, goodness of fit 1.01 for observed reflections, final residual values R1(F) = 0.035, wR(F^2) = 0.070 for observed reflections, residual electron density −0.26 to 0.25 e Å^{-3}. CCDC 615103.

Complex 11: orange crystal (polyhedron), dimensions 0.22 × 0.20 × 0.12 mm^3, crystal system monoclinic, space group $P2_1/c$, Z = 4, a = 13.9656(1) Å, b = 11.7519(2) Å, c = 15.0065(2) Å, β = 94.1660(10)°, V = 2456.39(6) Å^3, ρ = 1.332 g/cm^3, T = 200(2) K, θ_{max}= 27.48°, 25 191 reflections measured, 5641 unique (R(int) = 0.0468), 4159 observed ($I > 2\sigma(I)$), μ = 0.85 mm^{-1}, T_{min} = 0.84, T_{max} = 0.91, 283 parameters refined, goodness of fit 1.01 for observed reflections, final residual values R1(F) = 0.035, wR(F^2) = 0.078 for observed reflections, residual electron density −0.64 to 0.40 e Å^{-3}. CCDC 615104.

Complex 12: orange crystal (irregular), dimensions 0.25 × 0.06 × 0.05 mm^3, crystal system orthorhombic, space group $P2_12_12_1$, Z = 4, a = 8.5043(9) Å, b = 15.731(2) Å, c = 15.953(2) Å, V = 2134.3(4) Å^3, ρ = 1.439 g/cm^3, T = 200(2) K, θ_{max}= 24.71°, 16 872 reflections measured, 3617 unique (R(int) = 0.0483), 3300 observed ($I > 2\sigma(I)$), μ = 0.92 mm^{-1}, T_{min} = 0.80, T_{max} = 0.96, 395 parameters refined, Flack absolute structure parameter 0.008(12), goodness of fit 1.00 for observed reflections, final residual values R1(F) = 0.028, wR(F^2) = 0.057 for observed reflections, residual electron density −0.17 to 0.22 e Å^{-3}. CCDC 615105.

Complex 13: red crystal (polyhedron), dimensions 0.32 × 0.12 × 0.10 mm^3, crystal system monoclinic, space group $P2_1/m$, Z = 2, a = 8.2687(2) Å, b = 16.1624(4) Å, c = 10.3270(2) Å, β =103.4230(10)°, V = 1342.42(5) Å^3, ρ = 1.530 g/cm^3, T = 200(2) K, θ_{max}= 27.48°, 13 946 reflections measured, 3176 unique (R(int) = 0.0290), 2706 observed ($I > 2\sigma(I)$), μ = 1.14 mm^{-1}, T_{min} = 0.71, T_{max} = 0.89, 211 parameters refined, goodness of fit 1.07 for observed reflections, final residual values R1(F) = 0.028, wR(F^2) = 0.067 for observed reflections, residual electron density −0.40 to 0.39 e Å^{-3}. Two molecules of CH_2Cl_2 per Co complex were found in the solid state. CCDC 615106.

Complex 24: red crystal (irregular), dimensions 0.29 × 0.23 × 0.12 mm^3, crystal system triclinic, space group $P\bar{1}$, Z = 4, a = 8.042(1) Å, b = 13.583(2) Å, c = 16.189(2) Å, α = 84.765(3)°, β = 89.333(3)°, γ = 82.326(2)°, V = 1745.3(4) Å^3, ρ = 1.257 g/cm^3, T = 100(2) K, θ_{max} = 23.26°, 12 183 reflections measured, 4981 unique (R(int) = 0.0290), 2261 observed ($I > 2\sigma(I)$), μ = 0.98 mm^{-1}, T_{min} = 0.76, T_{max} = 0.89, 389 parameters refined, goodness of fit 0.91 for observed reflections, final residual values R1(F) = 0.028, wR(F^2) = 0.065 for observed reflections, residual electron density −0.21 to 0.31 e Å^{-3}. CCDC 615107

Complex 27: orange crystal (polyhedron), dimensions 0.20 × 0.12 × 0.10 mm^3, crystal system triclinic, space group $P\bar{1}$, Z = 2, a = 7.7263(4) Å, b = 9.6435(5) Å, c = 12.9682(7) Å, α = 75.4550(10)°, β = 84.6800(10)°, γ = 67.9290(10)°, V = 866.74(8) Å^3, ρ = 1.358 g/cm^3, T = 200(2) K, θ_{max} = 27.47°, 9026 reflections measured, 3926 unique (R(int) = 0.0543), 3228 observed ($I > 2\sigma(I)$), μ = 0.99 mm^{-1}, T_{min} = 0.83, T_{max} = 0.91, 209 parameters refined, goodness of fit 1.05 for observed reflections, final residual values R1(F) = 0.036, wR(F^2) = 0.082 for observed reflections, residual electron density −0.29 to 0.35 e Å^{-3}. CCDC 615108.

Acknowledgment. Dedicated to Professor Peter Hofmann on occasion of his 60th birthday. We are grateful to the Deutsche Forschungsgemeinschaft for financial support. We thank Mrs. P. Krämer for her help in preparing the manuscript.

Supporting Information Available: CIF files for all crystal structures. This information is available free of charge via the Internet at http://pubs.acs.org.

OM0608206

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