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Superphanes with CpCo-Stabilized Cyclopentadienone Units. Synthesis and Properties

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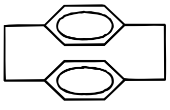
The cyclic alkynes 5-cyclononynone (**23**) and 5-cyclodecynone (**24**) were dimerized by heating with $CpCo(CO)_2$ to form the tricyclic CpCo-stabilized cyclopentadienone derivatives **25** and **26**, respectively. These diketones were transformed to the tricyclic diynes **30**, **31**, and **33**, via the corresponding bis(selenadiazoles). Whereas the diynes **30** and **31** did not yield the desired bis(cyclopentadienono)phanes, we were successful with **33**. Heating of **33** in the presence of $CpCo(CO)_2$ at 150 °C yielded the intramolecular cycloaddition product **34** and the mixed superphane **35**. Irradiation of **33** in the presence of $CpCo(CO)_2$ at 5 °C yielded the 2-fold CpCo-capped bis(cyclopentadieno)superphane **44**. The key compounds of this reaction sequence, **26a**, **31**, **33**, **34**, and **44**, have been characterized by X-ray structural analysis.

Introduction

When D. J. Cram and H. Steinberg published a rational synthesis of [2.2]cyclophane (**1**) in 1951, they started the chemistry of phanes.[1] Phanes[2] were used in the following years as model compounds to test to what extent aromatic rings—mostly six-membered—can be bent and molded together. Furthermore, they were used to test transannular effects of two aromatic units. Examples of these efforts were next to **1**, the [*n*]cyclophanes such as **2**,[3] Staab's donor−acceptor phanes, e.g. **3**,[4] or Boekelheide's superphane **4**,[5] to name only a few.



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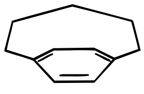

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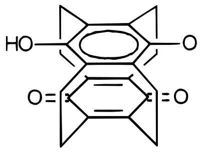

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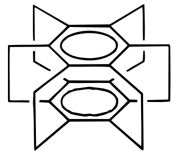

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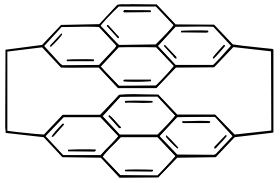
While the six-membered rings adopted boat shapes in **1** and **2**, they were planar in **4** due to the six bridges. In most cases, six-membered rings were used. Others such as the five-membered heteroaromatics or the cyclopentadiene rings were the exceptions. Later on, larger systems such as the pyrenophane **5**,[6] azulenophane **6**,[7] and even multilayered systems such as **7**[8] were also added to the family of phanes.



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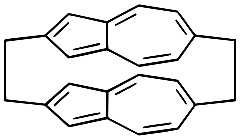

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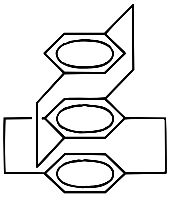

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We contributed to the large family of phanes at the "lower end", i.e., to the 2π- and 4π-systems, such as [3.3]-cyclopropenyliophane (**9**)[9,10] and the superphane **10**.[11,12] In both cases we started with 1,6-cyclodecadiyne (**8**).[13]

[†] Organisch-Chemisches Institut der Universität Heidelberg.

[‡] Anorganisch-Chemisches Institut der Universität Heidelberg.

(1) Cram, D. J.; Steinberg, H. *J. Am. Chem. Soc.* **1951**, *73*, 5691.

(2) Vögtle, F. *Cyclophan-Chemie*; Teubner: Stuttgart, 1990. Keehn, P. M.; Rosenfeld, S. M. *Cyclophanes*; Academic Press: New York, 1983. Diederich, F. *Cylophanes*; The Royal Society of Chemistry: Cambridge, 1991. Schulz, J.; Vögtle, F. *Topics Curr. Chem.* **1994**, *172*, 41, and references therein.

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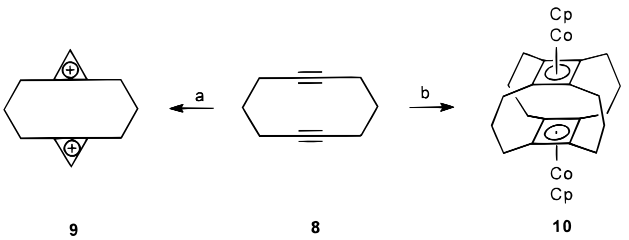
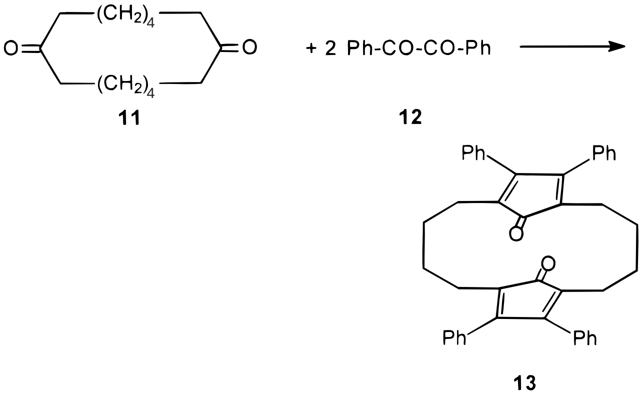
10.1021/om991000e CCC: $19.00

Scheme 1[a]



[a] Key: (a) CX_2, (b) $CpCoL_2$.

Scheme 2



The triple bonds were used to build up the final π-systems, and the propano bridges provided the tethers (Scheme 1). In connection with these latter studies we embarked on the synthesis of phanes with metal-stabilized cyclopentadienone rings.[14] The first and only member of the phanes with cyclopentadienone rings, **13**, was reported by Jutzi et al.[15] (Scheme 2). In **13** the two cyclopentadienone units were achieved by the condensation of tetradeca-1,8-dione (**11**) with benzil (**12**).[15]

Results and Discussion

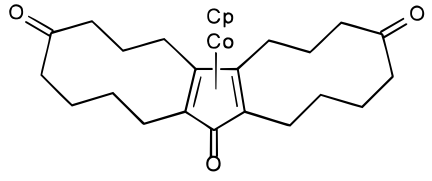
A. Formation of Tricyclic CpCo-Capped Cyclopentadienones. In our alternative route we made use of the metal-supported [2+2+1] cycloaddition of two alkynes and one CO group to cyclopentadienone.[16-21] In our synthesis we adopt an approach similar to that previously used by preparing superphanes[12] in a stepwise fashion.[22] Our proceedings are outlined in Scheme 3.

It starts with a cyclic alkyne **A** bearing a functional group *F*. In the first step, the cyclopentadienone unit, **B**, is built up, followed by a sequence of steps that transform the functional group *F* into triple bonds. The resulting tricyclic diyne, **C**, can be transformed to a cyclophane, **D**, in an intramolecular cyclization process.

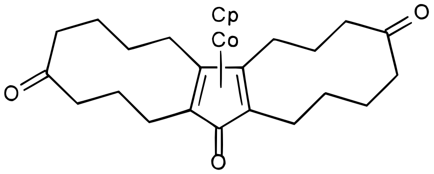
The generation of cyclopentadienone from two alkyne units and carbon monoxide has been known for more than 40 years.[16] Several metal carbonyls have been used as catalysts, such as $Fe(CO)_5$[16-18] and $CpCo(CO)_2$.[16,19-21] The resulting cyclopentadienone was generated either by heating[16-19] or by irradiation[20,21] of the carbonyl complex and the alkyne units.

Crucial for our endeavors were good yields for preparing the tricyclic cyclopentadienone of type **B** (Scheme 3). To achieve this goal, we optimized the yield by using medium-sized cyclic alkynes and $CpCo(CO)_2$. When we irradiated cyclooctyne[23] or 5-cyclononynone[24] in the presence of $CpCo(CO)_2$ in THF, we obtained the trimer of the alkyne as the main product (40%) and the desired CpCo-stabilized cyclopentadienone only in 4% yield. After this failure we changed to thermal conditions. For the cyclic alkynes we found satisfactory yields when we added the alkyne dissolved in decalin to a 190 °C heated solution of $CpCo(CO)_2$ in decalin for 5 days. The yields of the resulting tricyclic cyclopentadienone complexes **17**−**19** and the trimerization products are given in Scheme 4.

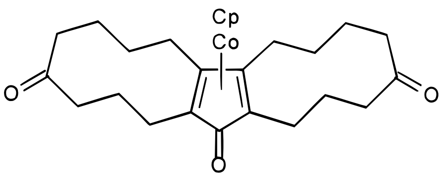
Having achieved satisfactory yields with cyclic alkynes, we investigated cyclic alkynones. The reactions of 5-cyclononynone (**23**)[24] and 5-cyclodecynone (**24**)[25] afforded satisfactory yields by using the same protocol as applied for cyclic alkynes. The results obtained for **23** and **24** are summarized in Scheme 5. In the case of **25** only one regioisomer is formed, while for the reaction of **24** with $CpCo(CO)_2$ three regioisomers, **26a**, **26b**, and **26c**, are possible. Our procedure afforded **26a**−**c** in a total yield



26a



26b



26c

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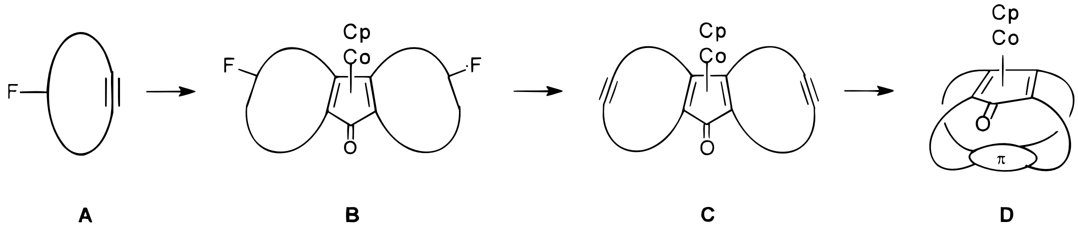
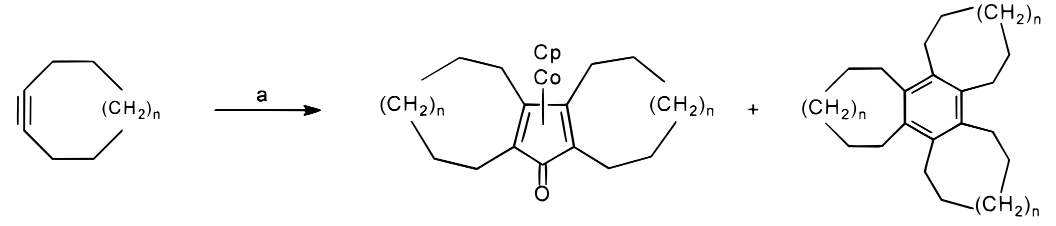
Scheme 3



Scheme 4[a]



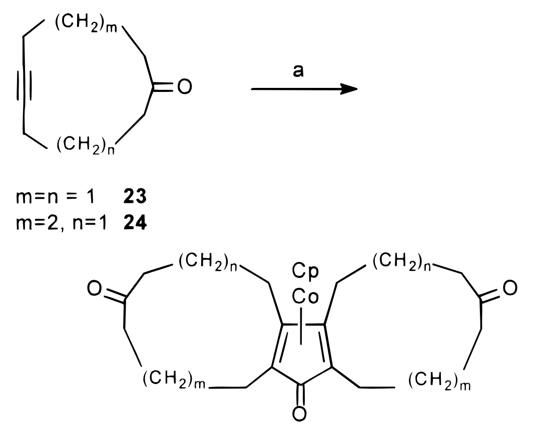
n = 2 **14**
n = 3 **15**
n = 6 **16**

17 (66 %)
18 (52 %)
19 (29 %)

20 (17 %)
21 (2 %)
22 (< 1%)

[a] Key: (a) $CpCo(CO)_2$, decalin, 190 °C, 5 days.

Scheme 5[a]



m=n = 1 **23**
m=2, n=1 **24**

m=n = 1 **25** (52 %)
m=2, n=1 **26** (66 %)

[a] Key: (a) $CpCo(CO)_2$, decalin, 190 °C, 5 days.

of 66%. As it is shown below, the diketones **26a**−**c** yield in high regioselectivity the tricyclic diyne **33**. To rationalize this observation, we show in Figure 1 the carbon skeleton of **26a** as obtained from X-ray diffraction studies. The conformations of the 10-membered rings are close to the calculated conformation of 1,6-cyclodecadiene. Under the assumption that the regioselectivity of the selenadiazole formation is controlled thermodynamically, one can expect from the similarity of both structures that those regioisomers are preferred in which the 1,6-cyclodecadiene ring system of lowest energy is formed. This should lead to **32a** (see Scheme 7).

The diketone **25** was transformed into the bissemicarbazone **27**. Treatment of the latter with SeO_2 yields four regioisomeric bisselenadiazoles. Two of them, **28a** and **29a**, are shown in Scheme 6. This reaction is based on a procedure first suggested by Lalezari[26] and later applied by Maier.[27] The different isomers **28a**,**b** and **29a**,**b** could not be separated. By heating the mixture with copper powder under high vacuum at 195 °C for 10 min, we obtained a 3:1 mixture of two isomers, which

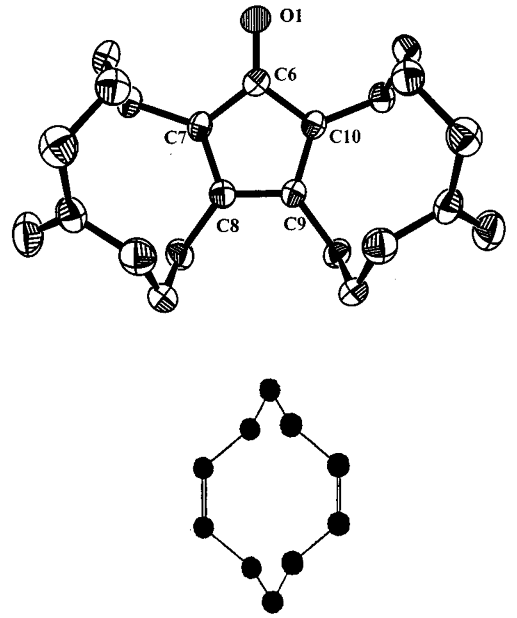


Figure 1. Comparison between the conformation of the carbon skeleton of **26a** (top) as determined by X-ray investigations and the calculated conformation of 1,6-cyclodecadiene. The CpCo fragment of **26a** was omitted for the sake of clarity. Selected bond length [Å] of the cyclopentadienone fragment: C(6)O(1), 1.272(3); C(6)C(7), 1.458(4); C(7)C(8), 1.437(4); C(8)C(9), 1.456; C(9)C(10), 1.437(4); C(6)C(10), 1.458(4).

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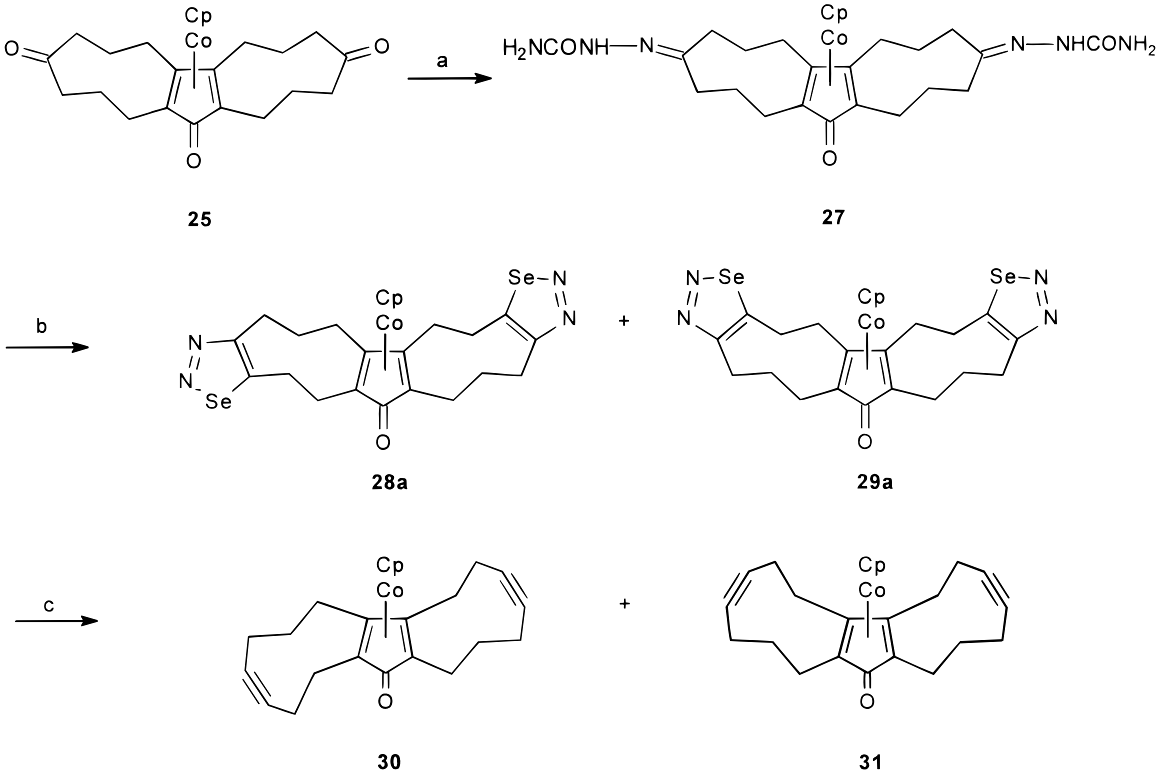
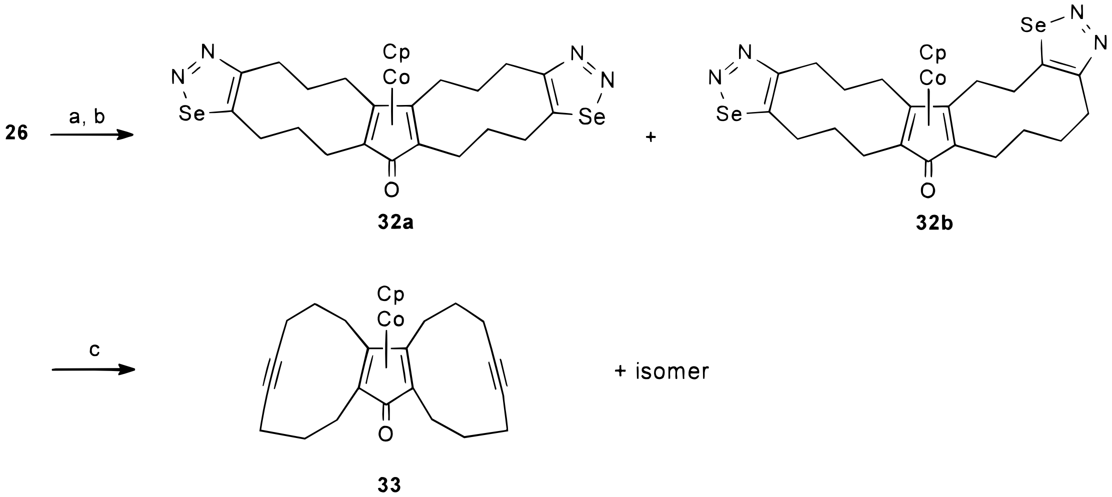
Scheme 6[a]



[a] Key: (a) semicarbazide acetate, (b) SeO_2/HOAc, (c) Cu, 0.1 mbar, 190 °C, 10 min.

Scheme 7[a]



[a] Key: (a) semicarbazide acetate, (b) SeO_2/HOAc, (c) Cu, 0.1 mbar, 190 °C, 15 min.

were separated by HPLC. The structures were assigned to **30** and **31** on the basis of their NMR spectra. The structure of **31** could be further confirmed by X-ray investigations on single crystals (Figure 2, top). It is found that the centers of gravity between both triple bonds are 5.3 Å apart. Both are arranged approximately parallel to the double bonds of the cyclopentadienone ring. Heating the mixture of **30** and **31** at 190 °C in decalin yields only very small amounts of low molecular weight, so that we refrained from further investigations.

Starting from the mixture of isomeric ketones **26a**−**c** by applying the same procedure as shown in Scheme 6, we obtained in 60% yield a mixture of regioisomeric selenadiazoles, **32**, which could not be separated and were characterized by a high-resolution mass spectrum (Scheme 7).

Pyrolysis of the regioisomers **32** with copper powder at 195 °C for 12−15 min at 0.1 mbar yielded a 4:1 mixture of two isomers in 55% yield. By means of HPLC the main component **33** was identified on the basis of its NMR spectra. In the ^{13}C spectrum of **33** we found six signals between $\delta = 15$ and $\delta = 35$ for the sp^3 carbons. Between $\delta = 80$ and $\delta = 100$ we found next to the intensive signals for the Cp carbons four weaker signals resulting from the cyclopentadiene carbons and the sp-centers. The signal for the carbon at the CO group was found at $\delta = 157.7$. A further confirmation of the structure of **33** was obtained by X-ray investiga-

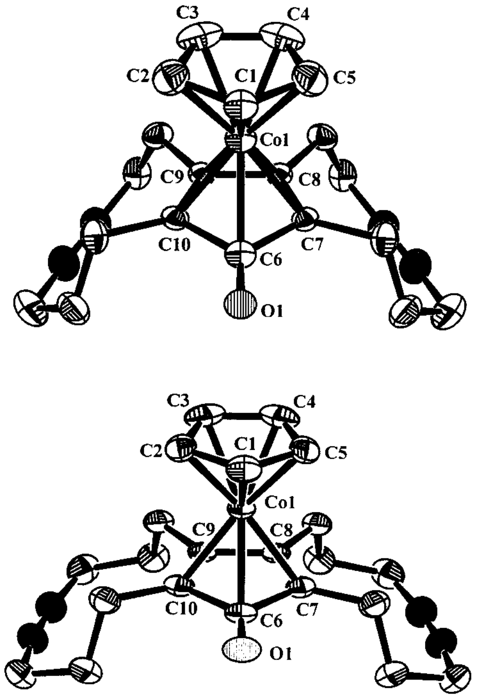
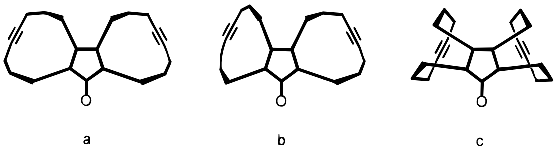


Figure 2. ORTEP plot of the molecular structures of **31** (top) and **33**. The plots are presented at 50% probability of the thermal ellipsoids. The oxygen atom is hatched, and the sp centers are represented as full circles. Selected bond lengths [Å] of **31**: CpCp (average), 1.399(6), CoC(6), 2.219(5); CoC(7), 2.053(4); CoC(8), 1.995(3); C(6)O(1), 1.247(7); C(6)C(7), 1.460(5); C(7)C(8), 1.434(5); C(8)C(9), 1.445(7). Selected bond lengths [Å] of **33**: CoCp (average), 2.061(3), CoC(6), 2.185(4); CoC(7), 2.057(3); CoC(8), 2.015(3); C(6)O(1), 1.276 (5); C(6)C(7), 1.460(4); C(7)C(8), 1.444(4); C(8)C(9), 1.446 (6).

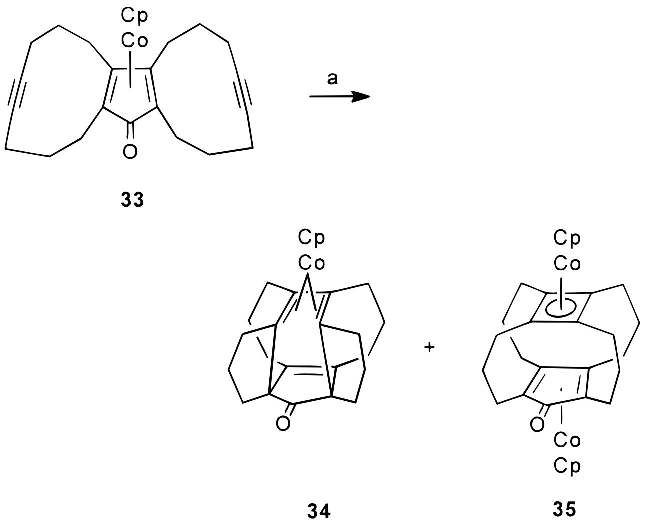


	a	b	c
d [Å]	7.6	6.5	4.4
rel. Energy [kcal/mol]	0	-3.0	-1.1

Figure 3. Calculated (MMX) energy minima for the carbon skeleton of **33**. Minimum **a** corresponds to the conformation adopted in the solid state.

tions (Figure 2). The molecular structure of **33** found in the solid state reveals a distance of 8 Å between the centers of gravity of the triple bonds. To find out if there are further minima available between 0 and 200 °C, we carried out force field calculations[28] on the tricyclic cyclopentadienone skeleton. The result is pictured in Figure 3. It shows two further minima (**b**, **c**) about the same energy as the X-ray conformer (**a**), in which the distance between the triple bonds varies between 4.4 and 6.5 Å. These distances between the triple bond make a metal-supported [2+2] or [2+2+1] cycloaddition more likely than the conformation found in the solid state.

Scheme 8[a]



[a] Key: (a) CpCo(CO)$_2$, cyclooctane, 150 °C, 3 h.

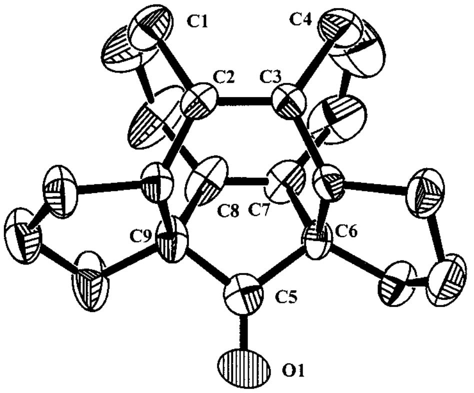


Figure 4. X-ray structure of **34**. The CpCo fragment was omitted for the sake of clarity. Selected bond lengths [Å] of **34**: C(1)C(2), 1.441(6); C(2)C(3), 1.421(6); C(3)C(4), 1.452(6); C(5)O(1), 1.212(5); C(5)O(6), 1.500(6), C(6)C(7), 1.520(6); C(7)C(8), 1.334(6); C(8)C(9), 1.520(6); C(5)C(9), 1.499(6).

B. Reactions of 33 with CpCo(CO)$_2$. The reactions of **33** described in this section were carried out with the crude product obtained according to Scheme 7. A solution of **33** in cyclooctane was added to a boiling solution of CpCo(CO)$_2$ in cyclooctane within 45 min. After the solution had boiled for another 3 h, the purification and separation yielded two yellow-colored products, **34** and **35**, in 25% and 5% yield, respectively (Scheme 8). The structural assignment of **34** is based on its NMR data, especially on a HMQC correlation. A further confirmation is given by the X-ray investigation of single crystals. It reveals a 4-fold-bridged bicyclo[4.2.1]nona-2,4,7-triene-4-one unit complexed with a CpCo fragment. In Figure 4 we show the carbon skeleton of this species as obtained from X-ray investigations on single crystals of **34**. The minor product was **35**, a mixed superphane.[12] It was identified by comparison with an independently synthesized sample (see below).

The genesis of **34** deserves special interest because it gives some insight in the superphane formation. It can be assumed that during reaction the CpCo unit that stabilizes the cyclopentadienone unit was removed. To learn more about the mechanism that leads to the

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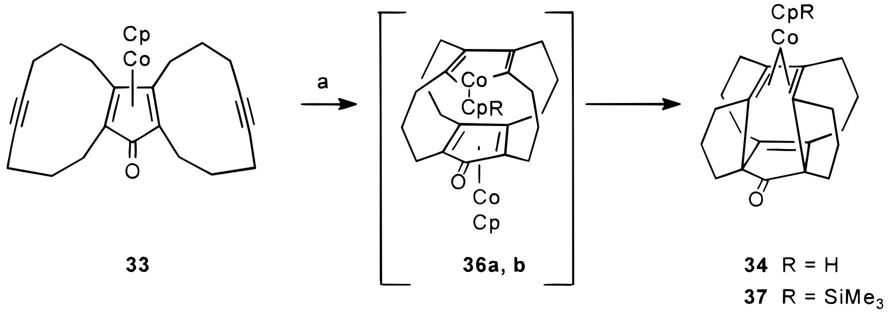
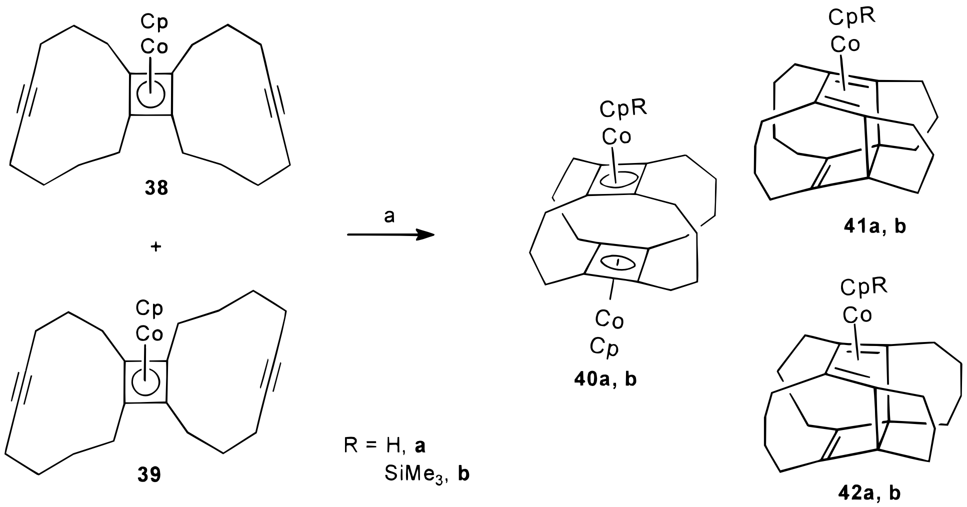
Scheme 9[a]



[a] Key: (a) $RCpCo(CO)_2$ (R = H, $SiMe_3$), cyclooctane, 150 °C, 3 h.

Scheme 10[a]



[a] Key: (a) $RCpCo(CO)_2$ (R = H, $SiMe_3$), cyclooctane, 150 °C.

formation of **34**, we reacted **33** with $RCpCo(CO)_2$(R= CH_3, $SiMe_3$), as shown in Scheme 9. In the case of R= $SiMe_3$, we were able to isolate 27% of **37**. However, we only found traces of the product when we used the methyl derivative $CH_3C_5H_4Co(CO)_2$. We assume that a metallacycle (**36a**,**b**) is formed first from $RCpCo(CO)_2$ and the two diyne units. In a second step the metallacycle reacts with the CpCo-stabilized cyclopentadienone ring to form **37**. A similar reaction was observed when the mixture **38** and **39** was heated with $RCpCo(CO)_2$ (Scheme 10).[29]

After this intermezzo at 150 °C we raised the temperature of the reaction of **33** with $CpCo(CO)_2$ to 190 °C and used decalin as solvent. This change increased the yield of the mixed superphane, **35**, to 20% and reduced that of **34** to 5%. As a further side product (ca. 2% yield) we isolated **44**, a new type of superphane[12] (see Scheme 12). The reasonable yield of **35** allowed its separation and identification. To further ensure the structure of **35**, we synthesized this species independently from the cyclobutadiene complex **43**. Irradiation of **43** with $CpCo(CO)_2$ in THF at room temperature yielded 60% of the superphane **10** and only traces of the mixed superphane **35**. Lowering the temperature to −10 °C (see Scheme 11) increased the yield of **35** up to 18%.

The light-induced [2+2+1] cycloaddition applied for the synthesis of **35** was also applied to synthesize the desired superphane with two CpCo-capped cyclopentadienone rings as building blocks (Scheme 12). Irradiation of **33** at 5 °C in THF in the presence of $CpCo(CO)_2$ yielded as main product the superphane **44**. As minor products ca. 1−2% yield of the superphanes **45** and **35** were found. The superphane **44** adopts the *syn*-configuration of both cyclopentadienone rings. The structure of **44** is based on its spectral properties and on X-ray investigations[14] of single crystals. The two cyclopentadienone moieties are relatively close together. The *inter-ring* distances between carbon atoms 8 and 8′ of the cyclopentadienone rings amount to 2.803 Å, and those between carbon atoms 7 and 7′ to 2.969 Å (Figure 5). The oxygen atoms of the cyclopentadiene rings of **44** are slightly bent away from each other. The distances between carbon atoms 6 and 6′ of both rings amount to 3.046 Å, while the distance between the oxygens were found to be 3.312 Å.

We ascribe the fact that only the *syn*-isomer of **44** was generated to steric effects. We assume that the triple bonds in **33** are oriented parallel to the double bonds in the cyclopentadienone unit. Thus, in an intermediate cobaltacyclopentadiene the metal should be located close to the CO group of the neighboring ring. Treatment of the isomeric mixture of **30** and **31** (3:1) with $CpCo(CO)_2$ at 190 °C in decalin yielded only traces of a product of low molecular weight.

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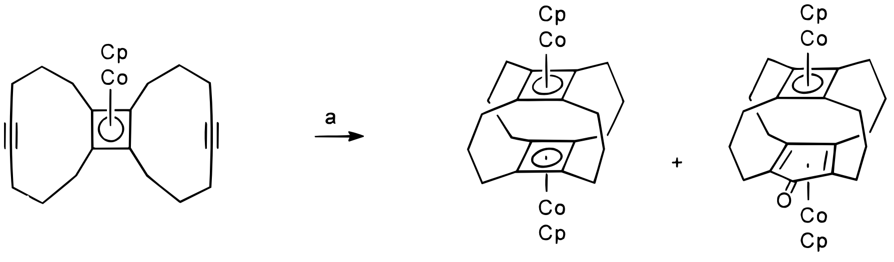
[29] Gleiter, R.; Langer, H.; Nuber, B. *Angew. Chem.* **1994**, *106*, 1350; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1272.

Scheme 11[a]

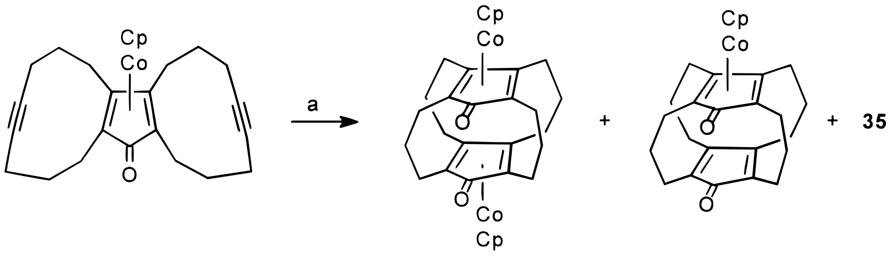


43 **10** **35**

T [°C]	% (**10**)	% (**35**)
25	60	<1
10	35	4
0	23	11
-10	11	18

[a] Key: (a) $CpCo(CO)_2$, *hν*.

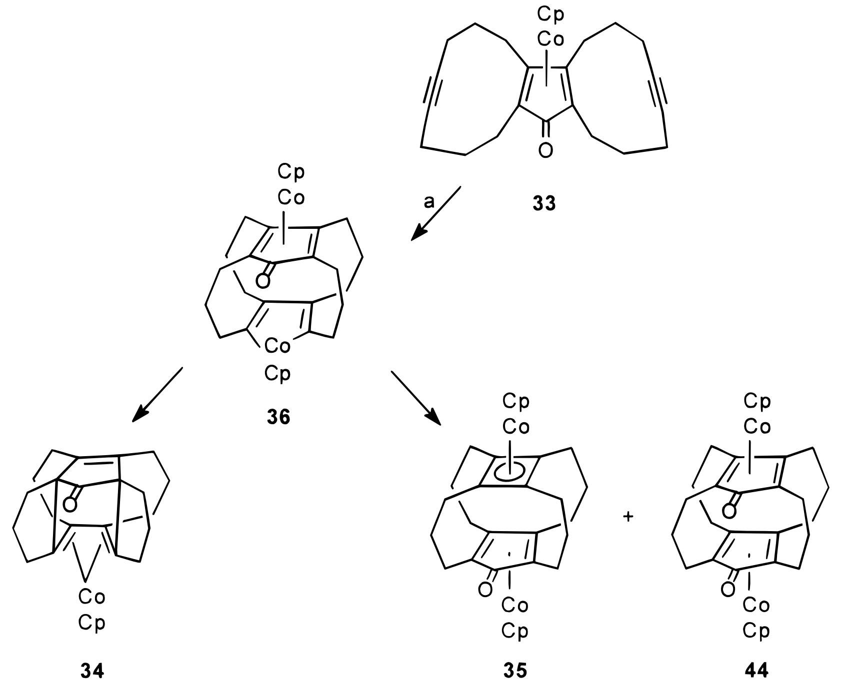
Scheme 12[a]



33 **44** **45**

[a] Key: (a) $CpCo(CO)_2$, *hν*, 5 °C, 6 h.

Scheme 13[a]



33 **36** **34** **35** **44**

[a] Key: (a) $CpCo(CO)_2$, *hν*, 5 °C, 6 h.

Conclusion

The key compound in our synthesis was the tricyclic cyclopentadienone complex **33**. Its availability was made possible by the thermal reaction of $CpCo(CO)_2$ with the alkynone **24**. The chemoselectivity of **33** was controlled by the reaction conditions: At 150 °C we isolated the cage compound **34**. Its occurrence was rationalized by

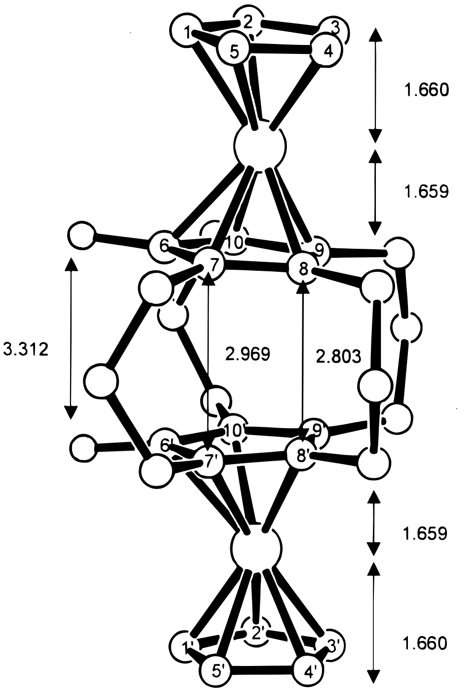


Figure 5. Side view of the molecular structure of **44**.

assuming the metallacycle **36** as an intermediate. At 150 °C this intermediate reacts faster with the cyclopentadienone unit to achieve **34**. At higher temperatures (190 °C) the stabilization of the metallacycles occurs to yield the mixed superphane **35**. The irradiation of **33** at 5 °C in the presence of $CpCo(CO)_2$ leads to the CpCo-capped bis(cyclopentadienone)superphane **44**. We ascribe the fact that only the *syn*-isomer of **44** was observed to steric effects. It remains to be seen if the occurrence of **44** can also be rationalized by the intermediacy of a metallacycle related to that of **36**.

Experimental Section

General Comments. All melting points are 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 were performed at Microanalytisches Labor der Universität Heidelberg. All reactions were carried out in an argon atmosphere using dried and oxygen-free solvents.

General Procedure for the Synthesis of Tricyclic (η^4-Cyclopentadienone)(η^5-cyclopentadienyl)cobalt Complexes 17, 18, and 19. A solution of 1.8 g (10 mmol) of $CpCo(CO)_2$ in 50 mL of decalin was heated at 190 °C. During 24 h 6 mmol of the corresponding cyclic alkyne dissolved in 50 mL of decalin was added. When the addition was completed, the heating was continued for 4 more days. The reaction mixture was allowed to cool to room temperature and then filtered through alumina (neutral, grade III). With pentane as eluent unreacted $CpCo(CO)_2$ and the benzoic byproducts could be extracted, while the cyclopentadienones remained as a solid at the top of the column. It could be dissolved with some CH_2Cl_2 and was extracted with 20:1 CH_2Cl_2/methanol as a broad red-orange band. After removal of the solvent the crude product was purified by column chromatography (silica gel/methylenechloride/methanol).

{(1,3,10,11-η)-Tricyclo[9.6.0.0^{3,10}]heptadeca-1(11),3(10)-diene-2-one}-(η^5-cyclopentadienyl)cobalt (17) and Tetracyclo[16.6.0.0^{2,9}.0^{10,17}]quatrocosa-1,9,17-triene (**20**). **17**: yield 66% (0.66 g); red solid, mp = 163 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.60 (s, 5H, Cp), 3.01−2.94 (m, 2H, CH_2), 2.69−2.62 (m, 2H, CH_2), 2.47−2.37 (m, 2H, CH_2), 2.01−1.91 (m, 2H, CH_2), 1.79−1.59 (m, 2H, CH_2), 1.46−1.27 (m, 2H, CH_2); ^{13}C NMR (50 MHz, $CDCl_3$) δ 157.9 (s, C=O), 92.7 (s, C), 82.7 (d, Cp), 82.6 (s, C), 31.3 (t, CH_2), 29.4 (t, CH_2), 26.9 (t, CH_2), 26.3 (t, CH_2), 24.6 (t, CH_2), 24.3 (t, CH_2); HRMS (FAB) calcd for $C_{22}H_{29}CoO$, 368.1552; found, 368.1572; IR (KBr) [cm^{-1}] 2924, 2852, 1641, 1562, 1535, 1456, 1275; UV/vis (CH_2Cl_2) (λ_{max}, nm (log ϵ)) 222 (3.90), 286 (4.17), 358 (3.28), 364 (3.28), 412 (2.94). Anal. Calcd for $C_{22}H_{29}CoO$: C, 71.71; H, 7.94. Found: C, 71.46; H, 8.01. **20**: yield: 17% (0.10 g); white solid, mp = 195 °C, more analytical data in ref 30. Anal. Calcd for $C_{24}H_{36}$: C, 88.81; H: 11.19. Found: C, 88.58; H, 11.11.

{(1,3,11,12-η)-Tricyclo[10.7.0.0^{3,11}]nonadeca-1(12),3(11)-diene-2-one}-(η^5-cyclopentadienyl)cobalt (18) and Tetracyclo[18.7.0.0^{2,10}.0^{11,19}]heptacosa-1,10,19-triene (21). 18: yield 52% (0.58 g); red solid, mp = 135 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.55 (s, 5H, Cp), 3.00−2.93 (m, CH_2), 2.73−2.66 (m, CH_2), 2.46−2.37 (m, CH_2), 2.07−1.97 (m, CH_2), 1.81−1.61 (m, CH_2), 1.45−1.34 (m, CH_2), together 28H; ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.4 (s, C=O), 92.9 (s, C), 83.0 (s, C), 82.4 (d, CH), 27.3 (t, CH_2), 25.8 (t, CH_2), 25.5 (t, CH_2), 24.4 (t, CH_2), 24.1 (t, CH_2), 23.9 (t, CH_2); HRMS (FAB) calcd for $C_{24}H_{34}CoO$ (M + H), 397.1943; found, 397.1956; IR (KBr) [cm^{-1}] 2922, 2849, 1570, 1539, 1261, 1125, 1031; UV/vis (CH_2Cl_2) (λ_{max}, nm (log ϵ)) 222 (4.04), 288 (4.38), 358 (3.46), 364 (3.46). Anal. Calcd for $C_{24}H_{34}CoO$: C, 72.71; H, 8.39. Found: C, 72.65; H, 8.45. **21**: yield 2% (14 mg); white solid, mp = 182 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.85−2.81 (m, 12H, CH_2), 1.68 (m, CH_2), 1.49−1.35 (m, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.5 (s, C=C), 29.0 (t, CH_2), 28.4 (t, CH_2), 28.2 (t, CH_2), 24.4 (t, CH_2); HRMS (EI) calcd for $C_{27}H_{43}$ (M + H), 367.3366; found 367.3367; IR (KBr) [cm^{-1}] 3002, 2920, 2843, 2674, 1700, 1489, 1446, 1346; UV/vis (CH_2Cl_2) (λ_{max}, nm (log ϵ)) 196 (3.58), 222 (4.50). Anal. Calcd for $C_{27}H_{42}$: C, 88.45; H, 11.55. Found: C, 88.23; H, 11.56.

{(1,3,14,15-η)-Tricyclo[13.10.0.0^{3,14}]pentacosa-1(15),3-(14)-diene-2-one}-(η^5-cyclopentadienyl)cobalt (19): yield 29% (0.42 g); red solid, mp = 151 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 4.55 (s, 5H, Cp), 2.56−1.38 (m, 40H, CH_2); ^{13}C NMR (50 MHz, $CDCl_3$) δ 157.5 (s, C=O), 92.9 (s, C), 82.6 (d, CH), 82.4 (s, C), 29.0 (t, CH_2), 27.6 (t, CH_2), 27.2 (t, CH_2), 26.7 (t, CH_2), 26.6 (t, CH_2), 26.5 (t, CH_2), 24.2 (t, CH_2), 23.6 (t, CH_2), 22.4 (t, CH_2), 22.2 (t, CH_2); HRMS (FAB) calcd for $C_{30}H_{45}CoO$, 480.2805; found, 480.2804; IR (KBr) [cm^{-1}] 2927, 2854, 1633, 1577, 1542, 1417; UV/vis (CH_2Cl_2) (λ_{max}, nm (log ϵ)) 220 (4.11), 286 (4.43), 360 (3.52). Anal. Calcd for $C_{30}H_{45}CoO$: C, 74.97; H, 9.44. Found: C, 74.95; H, 9.57.

General Procedure for the Synthesis of Tricyclic (η^4-Cyclopentadienonedione)(η^5-cyclopentadienyl)cobalt Complexes 25 and 26a−c. A solution of 6.1 g (34 mmol) of $CpCo(CO)_2$ in 150 mL of decalin was heated at 190 °C. During 24 h 30 mmol of the corresponding cyclic alkynone dissolved in 150 mL of decalin was added. When the addition was completed, the heating was continued for 4 more days. The reaction mixture was allowed to cool to room temperature and then filtered through alumina (neutral, grade III). With pentane as eluent the unreacted $CpCo(CO)_2$ could be extracted, while the product remains as a solid at the top of the column. It could be dissolved with some CH_2Cl_2 and was extracted with 10:1 CH_2Cl_2/methanol as a broad red-orange band. After

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(30) Wittig, G.; Krebs, A. *Chem. Ber.* **1961**, *94*, 3260. Parlier, A.; Rudler, H.; Platzer, N.; Fontanille, M.; Soum, A. *J. Chem. Soc., Dalton Trans.* **1987**, 1041.

(31) Sheldrick, G. M. *SHELX97*; University of Göttingen, Göttingen, Germany, 1997.

removal of the solvent the crude products were purified by column chromatography (silica gel/methylenechloride/methanol).

{(1,3,11,12-η)-Tricyclo[10.7.0.0^{3,11}]nonadeca-1(12),3(11)-diene-2,7,16-trione}(η^5-cyclopentadienyl)cobalt (25): yield 52% (3.3 g); red solid, mp >250 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.54 (s, 5H, Cp), 2.98−2.90 (m, CH_2), 2.77−2.69 (m, CH_2), 2.55−2.46 (m, CH_2), 2.36−2.11 (m, CH_2), 1.92−1.79 (m, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 214.5 ($C{=}O$), 157.8 (s, $C{=}O$), 91.8 (s, C), 82.7 (d, CH), 82.2 (s, C), 40.5 (t, CH_2), 40.1 (t, CH_2), 25.2 (t, CH_2), 23.3 (t, CH_2), 22.9 (t, CH_2), 22.3 (t, CH_2); HRMS (FAB) calcd for $C_{24}H_{29}CoO_3$ 424.1449; found 424.1405; IR (KBr) [cm^{-1}] 2954, 1699, 1594, 1450, 1415; UV/vis (CH_2Cl_2) (λ_{max}, nm (log ϵ)) 222 (4.30), 288 (4.62), 362 (3.56), 418 (2.94). Anal. Calcd for $C_{24}H_{29}CoO_3$: C, 67.92; H, 6.89. Found: C, 67.63; H, 6.78.

{(1,3,12,13-η)-Tricyclo[11.8.0.0^{3,12}]heneicosa-1(13),3(12)-diene-2,8,17-trione}(η^5-cyclopentadienyl)cobalt (26a) and Isomers b,c: yield 66% (4.5 g); red solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.51 (s, 5H, Cp), 4.50 (s, 5H, Cp), 2.88−2.57 (m, CH_2), 2.53−2.34 (m, CH_2), 2.27−2.14 (m, CH_2), 2.10−1.55 (m, CH_2), together 56H; ^{13}C NMR (50 MHz, $CDCl_3$) δ 213.6 (s, $C{=}O$), 213.5 (s, $C{=}O$), 157.3 ($C{=}O$), 93.1 (s, C), 92.8 (s, C), 91.6 (s, C), 91.4 (s, C), 83.8 (d, CH), 83.7 (d, CH), 83.4 (s, C), 82.8 (s, C), 81.9 (s, C), 81.1 (s, C), 45.0 (t, CH_2), 44.6 (t, CH_2), 44.5 (t, CH_2), 43.8 (t, CH_2), 39.3 (t, CH_2), 37.8 (t, CH_2), 37.3 (t, CH_2), 28.8 (t, CH_2), 28.5 (t, CH_2), 26.0 (t, CH_2), 25.6 (t, CH_2), 24.7 (t, CH_2), 24.6 (t, CH_2), 24.5 (t, CH_2), 24.3 (t, CH_2), 24.2 (t, CH_2), 24.1 (t, CH_2), 23.1 (t, CH_2), 22.7 (t, CH_2), 22.5 (t, CH_2), 22.4 (t, CH_2), 22.0 (t, CH_2), 20.3 (t, CH_2), 19.6 (t, CH_2); HRMS (FAB) calcd for $C_{26}H_{33}CoO_3$ 452.1762; found 452.1745; IR (KBr) [cm^{-1}] 3435, 2921, 1702, 1569, 1449, 1406, 1369; UV/vis (CH_2Cl_2) (λ_{max}, nm (log ϵ)) 224 (4.33), 292 (4.54), 362 (3.86), 410 (3.68). Anal. Calcd for $C_{26}H_{33}CoO$: C, 69.02; H, 7.35. Found: C, 68.91; H, 7.35.

Synthesis of {(1,3,11,12-η)-Tricyclo[10.7.0.0^{3,11}]nonadeca-1(12),3(11)-diene-2-one-7,16-bissemicarbazone}(η^5-cyclopentadienyl)cobalt (27). A solution of 24.0 g (0.22 mol) of semicarbazide hydrochloride and 15.7 g (0.19 mol) of NaOAc in 140 mL of methanol was refluxed and filtered. A 4.8 g amount (11 mmol) of **25** was added to the filtrate, and the solution was refluxed for 5 days. The reaction was controlled by TLC. When the starting material had disappeared, the solvent was removed in vacuo. The crude product was filtered through silica gel (methylenechloride/methanol) and used for the following reaction without any further purification. Yield: 90% (5.5 g); red-orange solid; HRMS (FAB) calcd for $C_{26}H_{36}CoO_3N_6$ (M + H), 539.2182; found, 539.2204.

The synthesis of the bissemicarbazones of **26a**−**c** was performed in an analogous way.

Bisselenadiazoles 28a/29a. A solution of 6.2 g (11.5 mmol) of **27** and 4.4 g (40 mmol) of SeO_2 was dissolved in 250 mL of concentrated acetic acid. The mixture was heated for 3 h to 45 °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 (300 mL) was added to the residue, and it was neutralized with aqueous Na_2CO_3 (5%) solution. The aqueous layer was extracted again with chloroform. The combined organic layers were washed with water, dried ($MgSO_4$), and concentrated in vacuo. The mixture of **28a** and **29b** 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 purifications. Yield: 58% (4.0 g); orange-red solid; HRMS (FAB) calcd for $C_{24}H_{26}CoON_{4}78Se_{2}$ (M + H) 600.9786; found, 600.9762.

The synthesis of the bisselenadiazoles **32a**,**b** was performed in an analogous way. **32a,b**: yield 60% (1.02 g); red-orange solid; HRMS (FAB) calcd for $C_{26}H_{30}CoON_{4}78Se_{2}$ (M + H), 629.0099; found, 629.0064.

General Procedure for the Synthesis of Tricyclic Cyclopentadienonediynes 30/31 and 33. In a 100 mL flask 150 mg of the corresponding mixed bisselenadiazoles was adsorbed on 1.5 g of copper powder by using $CHCl_3$ as solvent. The flask was evacuated and heated to 200 °C for 10 min. The orange-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).

{(1,3,11,12-η)-Tricyclo[10.7.0.0^{3,11}]nonadeca-1(12),3(11)-diene-2-one-6,15-diyne}(η^5-cyclopentadienyl)cobalt (30) and {(1,3,11,12-η)-Tricyclo[10.7.0.0^{3,11}]-nonadeca-1(12),3-(11)-diene-2-one-7,15-diyne}(η^5-cyclopentadienyl)cobalt (31). Mixture of **30**/**31**: yield: 41% (1.0 g) (25 reactions); red solid; HRMS (FAB) calcd for $C_{24}H_{25}CoO$, 388.1238; found, 388.1231. Anal. Calcd for $C_{24}H_{25}CoO$: C, 74.20; H, 6.49. Found: C, 74.01; H, 6.52. The separation of **30**/**31** on an analytical scale was achieved by HPLC; the ratio of **30** to **31** proved to be 3:1.

30: red solid, mp = 173 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.57 (s, 5H, Cp), 3.02−2.93 (m, CH_2), 2.90−2.73 (m, CH_2), 2.52−2.39 (m, CH_2), 2.29−1.97 (m, CH_2), 1.63−1.58 (m, CH_2), together 20H; ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.4 ($C{=}O$), 97.2 (s, C), 91.2 (s, C), 89.3 (s, C), 89.1 (s, C), 87.2 (s, C), 87.0 (s, C), 85.7 (s, C), 83.4 (d, CH), 80.7 (s, C), 32.5 (t, CH_2), 28.9 (t, CH_2), 28.8 (t, CH_2), 28.4 (t, CH_2), 25.2 (t, CH_2), 24.9 (t, CH_2), 20.3 (t, CH_2), 19.6 (t, CH_2), 19.0 (t, CH_2), 18.8 (t, CH_2); IR (KBr) [cm^{-1}] 2931, 2847, 2225, 1633, 1570, 1437, 1324; UV/vis (CH_2Cl_2) (λ_{max}, nm (log ϵ)) 230 (3.90), 288 (4.34), 364 (3.44), 414 (3.10).

31: red solid, mp = 190 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.60 (s, 5H, Cp), 3.06−2.99 (m, CH_2), 2.91−2.84 (m, CH_2), 2.73−2.67 (m, CH_2), 2.64−2.63 (m, CH_2), 2.44−2.39 (m, CH_2), 2.18−1.87 (m, CH_2), together 20H; ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.3 ($C{=}O$), 90.4 (s, C), 89.6 (s, C), 88.0 (s, C), 85.7 (s, C), 83.5 (d, CH), 28.7 (t, CH_2), 28.4 (t, CH_2), 25.0 (t, CH_2), 21.3 (t, CH_2), 18.8 (t, CH_2); IR (KBr) [cm^{-1}] 2944, 2920, 2847, 1633, 1568, 1435, 1321; UV/vis (CH_2Cl_2) (λ_{max}, nm (log ϵ)) 230 (3.70), 290 (4.20), 366 (3.22), 422 (2.91).

{(1,3,12,13-η)-Tricyclo[11.8.0.0^{3,12}]heneicosa-1(13),3(12)-dien-7,17-diyne-2-on)(η^5-cyclopentadienyl)cobalt 33 (+ isomer): mixture of **33** + isomer, yield 55% (0.5 g); HRMS (FAB) calcd for $C_{26}H_{29}CoO$, 416.1552; found, 416.1525. Anal. Calcd C, 74.99; H, 7.02. Found: C, 74.85; H, 7.09.

The separation of **33** and its isomer on an analytical scale was achieved by HPLC; the ratio of **33** to its isomer proved to be 4:1. **33**: red solid, mp = 167 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.55 (s, 5H, Cp), 2.99−2.88 (m, CH_2), 2.72−2.66 (m, CH_2), 2.44−2.37 (m, CH_2), 2.15−2.05 (m, CH_2), 1.86−1.77 (m, CH_2), 1.52−1.50 (m, CH_2), together 24H; ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.7 (s, $C{=}O$), 94.1 (s, C), 84.1 (s, C), 84.0 (s, C), 83.3 (d, CH), 82.7 (s, C), 29.9 (t, CH_2), 26.6 (t, CH_2), 24.6 (t, CH_2), 24.1 (t, CH_2), 19.8 (t, CH_2), 19.0 (t, CH_2); IR (KBr) [cm^{-1}] 3065, 2929, 1571, 1436, 818; UV/vis (CH_2Cl_2) (λ_{max}, nm (log ϵ)) 224 (4.16), 292 (4.37), 358 (3.64), 364 (3.65), 418 (3.44).

General Procedure for the Reaction of 33 with RCpCo(CO)$_2$ at 150 °C to 34 and 37. A solution of 1.4 mmol of RCpCo(CO)$_2$ (R = H (**34**/**35**) or $SiMe_3$ (**37**)) in 15 mL of cyclooctane was heated at 150 °C. Within 1.5 h a solution of 0.14 g (0.3 mmol) of **33** (+ isomer) was dropped into the mixture and stirred for a further 30 min. The mixture was allowed to cool to ambient temperature, concentrated in vacuo, adsorbed on silica gel, and chromatographed (alumina neutral, grade III). The nonatrienones were extracted with pentane. For further purification the crude products were chromatographed again (alumina neutral, grade III).

34 and {η^4:η^4-[3$_4$]Cyclobutadienocyclopentadienonophane}bis(η^5-cyclopentadienyl)cobalt (35). 34: yield 25% (35 mg); yellow solid, mp >250 °C; ^{1}H NMR (500 MHz, C_6D_6) δ 4.42 (s, 5H, Cp), 2.70−2.56 (m, CH_2), 2.18−2.11 (m, CH_2), 1.79−1.62 (m, CH_2), 1.57−1.54 (m, CH_2), 1.48−1.33 (m, CH_2), together 24H; ^{13}C NMR (125 MHz, C_6D_6) δ 214.6 (s, $C{=}O$),

Table 1. Crystal Data and Structure Refinement for 26a, 31, 33, and 34

	26a	**31**	**33**	**34**
empirical formula	$C_{26}H_{37}CoO_5$	$C_{24}H_{25}CoO$	$C_{29}H_{32}Cl_9CoO$	$C_{26}H_{29}CoO$
fw	488.5	388.4	747.6	416.4
cryst color	orange	red-brown	orange	red-brown
cryst shape	plate	plate	irregular	irregular
cryst size [mm]	0.40 × 0.23 × 0.11	0.05 × 0.30 × 0.85	0.48 × 0.38 × 0.28	0.36 × 0.22 × 0.10
temp [K]	233	273	200	200
wavelength [Å]	0.71073	0.71073	0.71073	0.71073
cryst syst	monoclinic	orthorhombic	monoclinic	monoclinic
space group	$P2_1/n$	*Pnma*	$P2_1/m$	$P2_1/n$
Z	4	4	2	8
a [Å]	9.5620(3)	13.455(4)	8.7271(2)	9.3903(2)
b [Å]	17.5799(5)	17.303(5)	17.2411(3)	29.3719(6)
c [Å]	14.3062(3)	7.853(3)	11.3050(2)	14.0811(4)
β [deg]	94.012(1)		95.111(1)	90.995(1)
V [Å^3]	2399(1)	1828(1)	1694(1)	3883(1)
D_{calcd} [g/cm^3]	1.353	1.41	1.52	1.425
abs coeff, μ [mm^{-1}]	0.749	0.95	1.239	0.898
θ range for data collection [deg]	1.84−25.41	3.0−60.0	1.81−25.51	1.60−25.58
index ranges	$-10 < h < 10$, $-10 < k < 20$, $-16 < l < 16$	$0 < h < 19$, $-18 < k < 25$, $0 < l < 12$	$-9 < h < 9$, $-19 < k < 20$, $-12 < l < 11$	$-11 < h < 7$, $-33 < k < 29$, $-16 < l < 15$
no. of reflns collected	10 662	5618	7808	17 850
no. of ind reflns	3975	2737	2927	6485
max. and min. transmission	0.80 and 0.69	1.0 and 0.87	0.80 and 0.61	0.93 and 0.81
no. of obs data/params	3958/302		2927/268	6470/505
goodness-of-fit on F^2	1.109	1.63	1.047	1.08
$R(F)$	0.0415	0.061	0.043	0.052
$R_w(F^2)$	0.0867	0.047	0.105	0.107
$(\Delta\rho)$max, $(\Delta\rho)$min [e Å^{-3}]	0.397, −0.388	1.35, −0.49	0.895, −0.744	0.38, −0.36

146.2 (s, C), 89.6 (s, C), 83.5 (d, CH), 58.9 (s, C), 47.6 (s, C), 42.0 (t, CH_2), 27.7 (t, CH_2), 27.2 (t, CH_2), 25.3 (t, CH_2), 24.7 (t, CH_2), 24.4 (t, CH_2); HRMS (FAB) calcd for $C_{26}H_{30}CoO$ (M + H), 417.1628; found, 417.1611; IR (KBr) [cm^{-1}] 3088, 2923, 2852, 1733, 1620, 1460; UV/vis (CH_2Cl_2) (λ_{max}, nm (log ϵ)) 232 (4.63), 260 (4.46), 302 (4.17), 426 (3.05).

35: yield 2% (5 mg); red solid, mp = 195 °C; for analytical data see below.

37: yield 27% (39 mg); yellow solid, mp = 136 °C; ^{1}H NMR (500 MHz, C_6D_6) δ 5.18 (pt, 2H, Cp), 3.72 (pt, 2H, Cp), 2.72−2.63 (m, 2H, CH_2), 2.52−2.44 (m, 2H, CH_2), 2.15−1.93 (m, 6H, CH_2), 1.79−1.50 (m, 10H, CH_2), 1.44−1.31 (m, 4H, CH_2), 0.15 (s, 9H, CH_3); ^{13}C NMR (125 MHz, C_6D_6) δ 214.5 (C═O), 146.2 (s, C), 96.1 (s, C), 89.7 (s, C, Cp), 86.8 (d, CH, Cp), 85.8 (d, CH, Cp), 58.9 (s, C═C), 47.5 (s) 42.0 (t, CH_2), 27.7 (t, CH_2), 27.2 (t, CH_2), 25.2 (t, CH_2), 24.3 (t, CH_2), −0.1 (q, CH_3); HRMS (FAB) calcd for $C_{29}H_{37}CoOSi$, 488.1948; found, 488.1948; IR (KBr) [cm^{-1}] 2950, 2855, 1736, 1623, 1455; UV/vis (CH_2Cl_2) (λ_{max}, nm (log ϵ)) 238 (4.31), 266 (4.13), 306 (3.94), 432 (3.16).

Photochemical Reaction of 43 with $CpCo(CO)_2$. A solution of 0.13 g (0.7 mmol) of $CpCo(CO)_2$ in 110 mL of THF was cooled in a photoreactor to −10 °C and irradiated with a high-pressure mercury lamp. A solution of 50 mg (0.1 mmol) of **43** dissolved in 10 mL of THF was added in four portions within 2 h. The irradiation was continued for 24 h. The mixture was concentrated in vacuo, adsorbed on silica gel, and chromatographed (alumina neutral, grade III). Unreacted $CpCo(CO)_2$ and **10** were extracted with pentane. By using methylenechloride/methanol (10:1) **35** was extracted. For further purification the crude products were chromatographed again on alumina (neutral, grade III) using pentane (**10**) and 20:1 methylenechloride/methanol (**35**).

{η^4:η^4-[3$_4$]Cyclobutadienophane}bis(η^5-cyclopentadienyl)cobalt (10): yield 11% (7 mg); yellow solid, mp > 300 °C; for analytical data see ref 11.

{η^4:η^4-[3$_4$]Cyclobutadienocyclopentadienonophane}bis(η^5-cyclopentadienyl)cobalt (35): yield 18% (10 mg); red solid, mp = 195 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.49 (s, 5H, Cp), 4.34 (s, 5H, Cp), 2.95−2.84 (m, CH_2), 2.78−2.68 (m, CH_2), 2.58−2.49 (m, CH_2), 2.34−2.24 (m, CH_2), 2.13−1.79 (m, CH_2), together 24H; ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.4 (s, C═O), 90.8 (s, C), 84.3 (s, C), 82.1 (s, C), 81.6 (d, Cp), 80.2 (d, Cp), 76.8 (s; C), 26.3 (t, CH_2), 26.0 (t, CH_2), 25.4 (t, CH_2), 24.8 (t, CH_2), 23.0 (t, CH_2), 20.5 (t, CH_2) HRMS (FAB) calcd for $C_{31}H_{35}Co_2O$ (M + H), 541.1351; found, 541.1365; IR (KBr) [cm^{-1}] 2919, 1631, 1705, 1632, 1522, 1453; UV/vis (CH_2Cl_2) (λ_{max}, nm (log ϵ)) 232 (4.32), 290 (4.30), 358 (4.30).

Synthesis of {η^4:η^4-[3$_4$]Cyclopentadienonophane}bis(η^5-cyclopentadienyl)cobalt (44) and {[3$_4$]Cyclopentadienonophane}mono(η^5-cyclopentadienyl)cobalt (45) via Photochemical Reaction of 33 with $CpCo(CO)_2$. A solution of 0.36 g (2.0 mmol) of $CpCo(CO)_2$ in 110 mL of THF was cooled in a photoreactor to 5 °C and irradiated with a high-pressure mercury lamp. A solution of 0.1 g (0.2 mmol) of **33** dissolved in 10 mL of THF was added in four portions within 2 h. The irradiation was continued for 4 h. The mixture was concentrated in vacuo, adsorbed on silica gel, and chromatographed (alumina neutral, grade III). Unreacted $CpCo(CO)_2$ was extracted with methylene chloride. By using methylenechloride/methanol (50:1) **35** was extracted first, followed by **45** (20:1) and **44** (10:1). For further purification the crude products were chromatographed again on alumina (neutral, grade III, methylene chloride/methanol).

{η^4:η^4-[3$_4$]Cyclobutadienocyclopentadienonophane}bis(η^5-cyclopentadienyl)cobalt (35): yield <1% (10 mg); red solid, mp = 195 °C; for analytical data see above.

{[3$_4$]Cyclopentadienonophane}mono(η^5-cyclopentadienyl)cobalt (45): yield 2% (2 mg) dark red solid, mp = 205−210 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.57 (s, 5H, Cp), 2.88−2.84 (m, CH_2), 2.73−2.72 (m, CH_2), 2.63−2.52 (m, CH_2), 2.37−2.12 (m, CH_2), 1.66 (m, CH_2); ^{13}C NMR (125 MHz, $CDCl_3$) δ 201.2 (C═O), 152.2 (C═C), 130.4 (C═C), 90.7 (C═C), 89.8 (C═C), 83.1 (d, CH), 26.8 (t, CH_2), 25.0 (t, CH_2), 24.9 (t, CH_2), 24.4 (t, CH_2), 23.3 (t, CH_2), 22.8 (t, CH_2); HRMS (FAB) calcd for $C_{27}H_{30}CoO_2$ (M + H) 445.1579; found 445.1576; IR (KBr) [cm^{-1}] 2923, 1696, 1634, 1526, 1450, 1346; UV/vis (CH_2Cl_2) (λ_{max}, nm (log ϵ)) 230 (3.80), 296 (3.60), 282 (3.83).

{η^4:η^4-[3$_4$]Cyclopentadienonophane}bis(η^5-cyclopentadienyl)cobalt (44): yield 38% (52 mg) dark red solid, mp = 180 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.52 (s, 10H, Cp), 3.14−3.10 (m, CH_2), 2.81−2.63 (m, CH_2), 2.29−2.14 (m, CH_2), 1.72−

1.67 (m, CH_2); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.1 (C=O), 89.7 (s, C), 87.4 (C), 82.3 (d, CH), 25.3 (t, CH_2), 24.1 (t, CH_2), 23.1 (t, CH_2), 20.6 (t, CH_2); HRMS (FAB) calcd for $C_{32}H_{35}Co_2O_2$ (M + H) 569.1301; found, 569.1326; IR (KBr) [cm^{-1}] 2921, 1634, 1525, 1452, 1257, 1106, 1082, 1007, 812, 526, 422; UV/vis (CH_2Cl_2) (λ_{max}, nm (log ϵ)) 222 (4.39), 262 (4.26), 328 (4.54), 410 (3.55).

X-ray Crystallography and Structure Solution. Data were collected on a Syntex-R3-diffractometer (**31**) at 293 K or Siemens SMART CCD (**26a**, **33**, **34**) at 200 K. Relevant crystal and data collection parameters are given in Table 1. The structures were solved by using direct methods, least-squares refinement, and Fourier techniques. Structure solution and refinement were performed with SHELX-97.[31]

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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 **26a**, **31**, **33**, and **34**. This material is available free of charge via the Internet at http://pubs.acs.org.

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