Reaction of 1,6-Cyclodecadiyne and 1,8-Cyclotetradecadiyne with Substituted CpCo(cod)

Rolf Gleiter* and Georg Pflästerer

Organisch-Chemisches Institut der Universität Heidelberg,
Im Neuenheimer Feld 270, D 6900 Heidelberg, Germany

Received September 16, 1992

The yields of CpCo-capped cyclobutadiene superphane from 1,6-cyclodecadiyne (1) and (R-C_5H_4)Co(cod) varies considerably with the substituents R. Electron-withdrawing substituents give yields between 35 and 45% while electron-donating substituents give very small yields. In the case of 1,8-cyclotetradecadiyne (2) such a dependence on R is much less pronounced. The reaction between 1 and 2 and the indenyl complex (η^5-C_9H_7)Co(cod) is also reported.

Introduction

Recently, we found a simple route to CpCo-capped cyclobutadiene superphanes.[1,2] This in turn provides a new method for the formation of unusual hydrocarbons.[2,3] Reaction of 1,6-cyclodecadiyne (1)[4] and 1,8-cyclotetradecadiyne (2),[5] respectively, with (η^4-cyclooctadiene)(η^5-cyclopentadienyl)cobalt (**3c**) produces the intermolecular CpCo-capped superphanes **4c** and **5c**, respectively, together with the intramolecular complex 7. (Complex 6 is only found when the reaction is carried out with CpCo-$(CO)_2$.[1,2]) Although we have also achieved a stepwise synthesis of 4,[6] it is still simpler and more economical to use the one-pot reaction outlined in Scheme I. The main goal of this project was to improve the yields of the superphane formation, since the investigation of the physical and chemical properties of the superphanes depends very much on their availability.

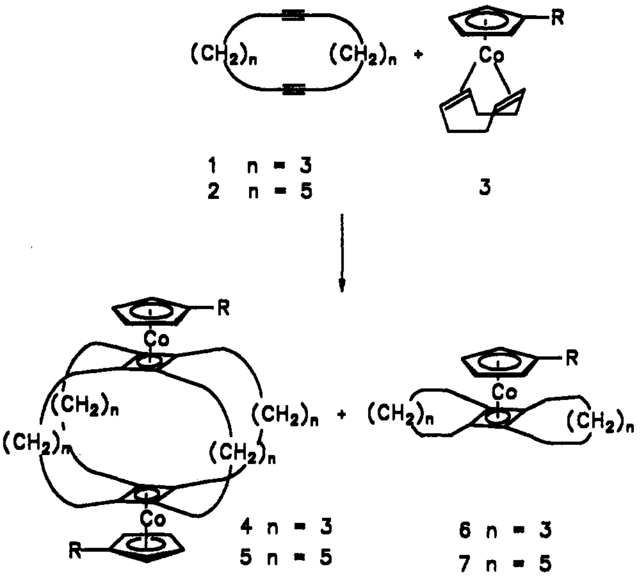
The studies of the groups of Bönnemann[7] and of Wakatsuki[8] prompted us to investigate the effect of electron-donating and -withdrawing groups on the cyclopentadienyl ring of 3. We preferred this compound instead of dicarbonyl(η^5-cyclopentadienyl)cobalt because with the latter several side products have been encountered.[9]

Results

To determine the influence of a substituent R on the cyclopentadienyl ligand of 3 and to optimize the yields of 4 and 5, respectively, we allowed 1 and 3 to react with a set of Co complexes where R is varied from a weakly electron-donating group such as CH_3 to an electron-accepting group such as the methoxycarbonyl substituent.

In Table I we show the yields for the reaction of 1 with **3a–3g**. A remarkable dependence of the yield on the substituent is found. In Table I we also list the ^{59}Co NMR shifts of **3a–3g** as determined by Bönnemann.[10]

Scheme I



a = CH_3; b = Cl; c = H; d = $SiMe_3$;
e = C_6H_6; f = COOMe; g = CHO

The structures of **4a**, **4c–4e**, and **4g** have been studied by X-ray investigations on single crystals.[1,11] It reveals in all cases distances between the cyclobutadiene moieties on the order of 2.90–2.96 Å and a pinwheel conformation for the bridges, as already found for **4c**.[1] The substituents at the Cp rings adopt a trans orientation in the crystals.[11]

The enhanced reactivity of the indenyl ligand ("the indenyl effect")[12] as compared to the cyclopentadienyl moiety prompted us to try the above reaction with (η^5-indenyl)(η^4-cyclooctadiene-1,5)cobalt (8). When the reaction between 1 and 8 is carried out, good yields (29–

---

[1] Gleiter, R.; Karcher, M.; Ziegler, M. L.; Nuber, B. *Tetrahedron Lett.* 1987, *28*, 195.

[2] Gleiter, R. *Angew. Chem.* **1992**, *104*, 29; *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 27 and references therein.

[3] Gleiter, R.; Karcher, M. *Angew Chem. 100*, 851; *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 840.

[4] Gleiter, R.; Karcher, M.; John, R.; Irngartinger, H., *Chem. Ber.* **1988**, *121*, 735.

[5] Dale, J.; Hubert, A. J.; King, G. S. D., *J. Chem. Soc.* **1963**, 73.

[6] Gleiter, R.; Schehlmann, V., Angew. *Chem.* **1990**, *102*, 1450; *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1426.

[7] Bönnemann, H.; Brijoux, W.; Brinkmann, R.; Meurers, W.; Mynott, R. *J. Organomet. Chem.* **1984**, *272*, 231. Bönnemann, H. *Angew. Chem.* **1985**, *97*, 264; *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 248.

[8] (a) Wakatsuki, Y.; Yamazaki, H. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 2715. (b) Wakatsuki, Y.; Yamazaki, H.; Kobayashi, T.; Sugawara, Y. *Organometallics* **1987**, *6*, 1191.

[9] Gleiter, R.; Kratz, D. *Tetrahedron Lett.* **1990**, *31*, 5893.

[10] Bönnemann, H. *Angew. Chem.* **1978**, *90*, 517; *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 505. Benn, R.; Cibura, K.; Hofmann, P.; Jonas, K.; Rufinska, A. *Organometallics* **1985**, *4*, 2214.

[11] Nuber, B. Unpublished results.

[12] White, C.; Mawby, R. J. *Inorg. Chim. Acta* **1970**, *4*, 261. Turaki, N. N.; Huggins, J. M.; Lebioda, L. *Inorg. Chem.* **1988**, *27*, 424. Caddy, P.; Green, M.; O'Brien, E.; Smart, L. E.; Woodward, P., *J. Chem. Soc., Dalton Trans.* **1980**, 962. Kakkar, A. K.; Taylor, N. J.; Marder, T. B. *Organometallics* **1989**, *8*, 1765. Rerek, M. E.; Basolo, F. *J. Am. Chem. Soc.* **1984**, *106*, 5908. O'Connor, J. M.; Casey, C. P. *Chem. Rev.* **1987**, *87*, 307.

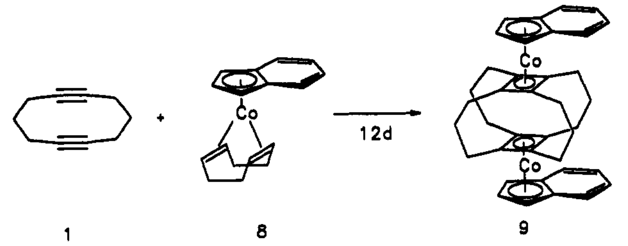
0276-7333/93/2312-1886$04.00/0

Table I. Conditions and Yields for the Reaction of (η^4-Cyclooctadiene-1,5)(η^5-R-cyclopentadienyl)cobalt with 1,6-Cyclodecadiyne in *n*-Octane (Left) and ^{59}Co Shifts and Relative Shifts of 3a–3g (Right)

	product 4				educt 3	
	R	time (days)	eluent	yield (%)[a]	$\delta(^{59}Co)$	δ_{rel}
a	CH_3	6–7	pentane	1–2	−1227	−51
b	Cl	6–7	pentane	5–7	−1199	−23
c	H	2	pentane	9–10	−1176	0
d	$SiMe_3$	4	pentane	12–14	−1149	+27
e	C_6H_5	4	pentane	19–26	−1077	+88
f	CO_2CH_3	2	pentane/ether = 1/1 → ether	39–43	−1047	+129
g	CHO	2		36–45	−1033	+143

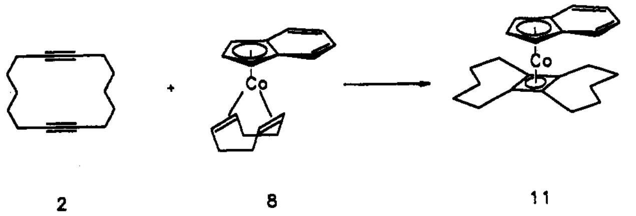
[a] The yields were determined from five runs.

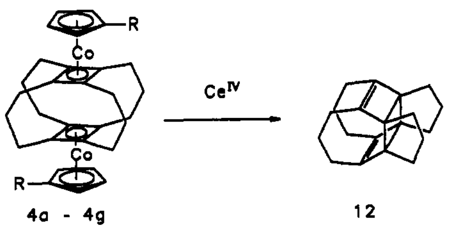
31%) of the superphane **9** are also found. No intramolecular product has been detected.



The reaction between **2** and **3** (Table II) shows almost no substituent effect on the yields. We found about the same yield with **3c**[13] and **3d–3f**, only **3a** gives a lower yield. X-ray investigations of single crystals of **5a**,[11] **5c**,[13] and **5d**[11] show distances between the two cyclobutadiene moieties of 5.34–5.38 Å, respectively. For **5a** and **5d** a pinwheel conformation is adopted for the pentamethylene bridges, and the substituents on the Cp rings adopt a trans orientation.

The reaction between **2** and **8** yields only the intramolecular reaction product **11** in 28–30% yield. The oxidation of **4a–4g** with Ce^{IV} gives the cage hydrocarbon **12** in yields between 60 and 80%.[3] Thus **12** is available in two steps from **1** in acceptable yields. Under similar reaction conditions we have not yet obtained any characterizable product from **5**.





Discussion

Table II. Conditions and Yields for the Reaction of (η^4-Cyclooctadiene-1,5)(η^5-R-cyclopentadienyl)cobalt with 1,8-Cyclotetradecadiyne

product	R	time (days)	eluent	yield (%)[a]
5a	Me	4	pentane	1–2[b]
5d	$SiMe_3$	4	pentane	7–11
5e	C_6H_5	4	pentane → pentane/benzene = 10/1	6–7
5f	CO_2CH_3	4	pentane/ether = 1/1 → ether	7–10[b]

[a] The yields were determined from five runs. [b] The yield of the intramolecular complex **7a** is 33–36%; that of **7f** is 4–5%.

Our original goal, to improve the yields of the superphanes, has been achieved at least for 1,6-cyclodecadiyne by using electron-withdrawing groups in the Cp ring or by using the indenyl fragment. We are, however, far away from rationalizing this observation in detail, especially since we have no kinetic data available. It is possible to argue that the electronic effect of electron-withdrawing groups is transmitted to the cobalt atom, as evidenced by the increased ^{59}Co shift (see Table I).[10] (Note that there seems to be a correlation between the yields of **4** and the δ (^{59}Co) values for **3**.) As a consequence the metal to ligand back-donation is decreased. This has also been observed in NMR, IR, and PE investigations.[8b] Thus, the replacement of the ligand should be facilitated. Furthermore the η^5 to η^3 change of the cyclopentadienyl ligand in the transition state is facilitated by an electron-withdrawing substituent[8,14] or by using the indenyl group.[12]

These arguments suggest that, for the reaction of **1** with **3**, the early stages of the reaction, the 2-fold nucleophilic replacement of the COD ligand by two 1,6-cyclodecadiyne molecules, are important. However, this cannot be the entire story since the reaction of **2** with **3** is essentially independent of the substituent. Possibly, the larger rings give rise to more low-energy conformations which do not allow coordination of the second triple bond with the cobalt. However, the isolated yields probably do not represent suitable data for a detailed discussion of the mechanism because they often depend on uncontrollable parameters. Therefore kinetic measurements in connection with calculations are needed to understand the mechanistic aspects of the reactions reported.

Experimental Section

Equipment. All melting points are uncorrected. The NMR spectra are measured with a Bruker AS 200 or AS 300 (^{1}H NMR at 200 and 300 MHz and ^{13}C at 50.23 MHz) using the solvent as the internal standard (δ; J (Hz)). The mass spectra refer to data from a Vacuum Generators ZAB instrument (EI, 70 eV); IR spectra were recorded with Perkin-Elmer 580 B and Beckmann 4200 instruments. UV light absorption data were recorded in CH_2Cl_2 by using a Varian Cary 17 D spectrometer.

General Procedures for the Reactions of the Diynes 1 and 2 with 3a–3g. All reactions were conducted in dry and oxygen-free solvents under argon atmosphere. After all the alkyne has disappeared, all volatiles were removed in vacuum. The residue is adsorbed on 3 mL of Al_2O_3 (neutral, 7% H_2O) and chromatographed on Al_2O_3 (neutral, 6% H_2O) with the solvent given in Table I or II.

Reaction of (η^4-Cyclooctadiene-1,5)(η^5-R-cyclopentadienyl)cobalt with 1,6-Cyclodecadiyne. 1,6-Cyclodecadiyne (264 mg, 2 mmol) and 2 mmol of the cobalt complex are refluxed in 20 mL of *n*-octane for the time given in Table I.

(η^4:η^4-[3$_4$]Cyclobutadienophane)bis[(η^5-methylcyclopentadienyl)cobalt] (4a). The product was crystallized from

---

[13] Gleiter, R.; Treptow, B.; Kratz, D.; Nuber, B. *Tetrahedron Lett.* **1992**, *33*, 1733.

[14] Schuster-Woldan, H. G.; Basolo, F. *J. Am. Chem. Soc.* **1966**, *88*, 1657.

pentane as an orange red solid: mp >250 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 4.30 (t, J = 1.7 Hz, 4H), 4.23 (t, J = 1.7 Hz, 4H), 2.22 (m, 16H), 1.92 (s, 6H), 1.72–1.59 (m, 8H); ^{13}C NMR (50.32 MHz, C_6D_6) δ 91.52 (C), 81.71 (CH), 80.01 (CH), 77.75 (C, cyclobutadiene), 28.01 (CH_2), 26.48 (CH_2, double intensity), 13.02 (CH_3); IR ($CDCl_3$) 2926, 2886, 2844, 1696, 1511, 1445, 1428, 1343, 1258, 1241, 1182, 1118, 1069, 1033, 1017; UV (CH_2Cl_2) [λ_{max}, nm (log ϵ)] 222 (4.45), 252 (4.34), 304 (4.92); HRMS (EI, 70 eV) calcd for $C_{32}H_{38}Co_2$ 540.1630, found 540.1608; MS *m/z* (relative intensity) 540.1608 (M^+, 19), 402.1711 (M^+ – MeCpCo, 6). Anal. Calcd for $C_{32}H_{38}Co_2$ (540.5): C, 71.11; H, 7.21. Found: C, 71.33; H, 7.21.

(η^4:η^4-[3$_4$]Cyclobutadienophane)bis[(η^5-chlorocyclopentadienyl)cobalt] (4b). The product was crystallized from pentane as an orange red solid: mp >250 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 4.49 (t, J = 2.1 Hz, 4H), 4.35 (t, J = 2.1 Hz, 4H), 2.21 (m, 16H), 1.70 (m, 8H); ^{13}C NMR (50.32 MHz, $CDCl_3$) δ 94.54 (C), 80.25 (C, cyclobutadiene), 79.87 (CH), 78.32 (CH), 27.25 (CH_2), 25.67 (CH_2, double intensity); IR ($CDCl_3$) 2926, 2886, 2844, 1695, 1511, 1445, 1428, 1343, 1258, 1241, 1182, 1118, 1069, 1033, 1017; UV (CH_2Cl_2) [λ_{max}, nm (log ϵ)] 222 (4.45), 252 (4.34), 304 (4.92; HRMS (EI, 70 eV) calcd for $C_{30}H_{32}{}^{35}Cl_2Co_2$ 580.0538, found 580.0520, calcd for $C_{30}H_{32}{}^{35}Cl^{37}ClCo_2$ 582.0509, found 582.0570; MS *m/z* (relative intensity) 582.0509 (M^+ + 2, 6), 580.0538 (M^+, 8), 422.1154 (M^+ –^{35}ClCpCo, 3).

(η^4:η^4-[3$_4$]Cyclobutadienophane)bis[(η^5-(trimethylsilyl)cyclopentadienyl)cobalt] (4d). The product was crystallized from pentane as an orange red solid: mp >250 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 4.49 (t, J = 1.7 Hz, 4H), 4.43 (t, J = 1.7 Hz, 4H), 2.24 (m, 16H), 1.63 (m, 8H), 0.16 (s, 18H); ^{13}C NMR (50.32 MHz, $CDCl_3$) δ 84.25 (CH), 84.10 (CH), 79.82 (C), 78.50 (C, cyclobutadiene), 27.42 (CH_2), 26.80 (CH_2, double intensity), 0.17 (CH_3); IR (KBr) 3072, 2932, 2912, 2898, 2830, 1445, 1427, 1242, 1161, 1029, 894, 845, 829, 808, 802, 625, 579, 559, 513; UV (CH_2Cl_2) [λ_{max}, nm (log ϵ)] 222 (4.54), 256 (4.20), 304 (8.84); HRMS (EI, 70 eV) calcd for $C_{36}H_{50}Co_2Si_2$ 656.2102, found 656.2010; MS *m/z* (relative intensity 656.2010 (M^+, 0.3). Anal. Calcd for $C_{36}H_{50}Co_2Si_2$ (656.8): C, 65.83; H, 7.67. Found: C, 66.06; H, 7.82.

(η^4:η^4-[3$_4$]Cyclobutadienophane)bis[(η^5-phenylcyclopentadienyl)cobalt] (4e). The product was crystallized from pentane as an orange red solid: mp 226–229 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.28 (m, 8H), 7.07 (m, 2H), 4.82 (t, J = 2.0 Hz, 4H), 4.54 (t, J = 2.0 Hz, 4H), 1.98 (m, 16H), 1.50 (m, 8H); ^{13}C NMR (50.32 MHz, $CDCl_3$) δ 136.99 (C, phenyl), 128.14 (CH, double intensity), 125.04 (CH, double intensity) 124.89 (CH), 94.97 (C), 81.32 (CH), 79.05 (C, cyclobutadiene), 77.26 (CH), 27.22 (CH_2), 25.73 (CH_2, double intensity); IR (KBr) 3050, 2926, 2904, 2838, 1596, 1510, 1447, 1427, 798, 761, 756, 689; UV (CH_2Cl_2) [λ_{max}, nm (log ϵ)] 222 (4.41), 246 (4.29), 316 (4.69); HRMS (EI, 70 eV) calcd for $C_{42}H_{42}Co_2$ 664.1940, found 664.1940; MS *m/z* (relative intensity) 664.1940 (M^+, 100). Anal. Calcd for $C_{42}H_{42}Co_2$ (664.2): C, 75.90; H, 6.37. Found: C, 75.87; H, 6.53.

(η^4:η^4-[3$_4$]Cyclobutadienophane)bis[(η^5-(methoxycarbonyl)cyclopentadienyl)cobalt] (4f). The product was crystallized from pentane/ether as an orange red solid: mp >250 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 4.98 (t, J = 2.1 Hz, 4H), 4.61 (t, J = 2.1 Hz, 4H), 3.75 (s, 6H), 1.67 (m, 8H), 1.65 (m, 16H); ^{13}C NMR (50.32 MHz, $CDCl_3$) δ 168.30 (C, COOMe), 84.09 (CH), 83.28 (C), 81.48 (CH), 80.87 (C, cyclobutadiene), 50.98 (CH_3), 27.05 (CH_2), 25.45 (CH_2, double intensity); IR (KBr) 3027, 2920, 2842, 1702, 1459, 1425, 1360, 1279, 1183, 1130, 802, 765, 563, 515, 485; UV (CH_2Cl_2) [λ_{max}, nm (log ϵ)] 222 (4.17), 306 (4.57); HRMS (EI, 70 eV) calcd for $C_{34}H_{38}Co_2O_4$ 628.1424, found 628.1424; MS *m/z* (relative intensity) 628.1424 (M^+, 100). Anal. Calcd for $C_{34}H_{38}Co_2O_4$ (628.5): C, 64.97; H, 6.09. Found: C, 64.95; H, 6.09.

(η^4:η^4-[3$_4$]Cyclobutadienophane)bis[(η^5-formylcyclopentadienyl)cobalt] (4g). The product was crystallized from pentane/ether as an orange red solid: mp >250 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 9.56 (s, 2H), 4.97 (t, J = 2.1 Hz, 4H), 4.79 (t, J = 2.1 Hz, 4H), 2.15 (m, 16H), 1.65 (m, 8H); ^{13}C NMR (50.32 MHz, $CDCl_3$) δ 189.18 (C, CHO), 92.26 (C), 86.52 (CH), 82.25 (CH), 80.75 (C, cyclobutadiene), 27.11 (CH_2), 25.82 (CH_2, double intensity); IR (KBr) 2916, 2832, 2800, 2748, 1670, 1645, 1610, 1448, 1428, 1405, 1355, 1344, 1251, 1033, 514, 409; UV (CH_2Cl_2) [λ_{max}, nm (log ϵ)] 222 (3.86), 236 (3.80), 288 (3.98), 308 (4.07); MS (EI) calcd for $C_{32}H_{34}Co_2O_2$ 568.1, found 568.3. Anal. Calcd for $C_{32}H_{34}Co_2O_2$ (568.5): C, 67.61; H, 6.03. Found: C, 67.54; H, 5.99.

(η^4:η^4-[3$_4$]Cyclobutadienophane)bis[(η^5-indenyl)cobalt] (9). A solution of 1.32 g of 1,6-cyclodecadiyne (10 mmol) and 2.82 g of (η^4-cyclooctadiene-1,5)(η^5-indenyl)cobalt (10 mmol) in 100 mL of dry xylene was refluxed for 14 days. The reaction mixture was cooled, alumina (deactivated by 6% water) was added, and the solvent was removed in vacuo. The residue was then placed on an alumina-packed column and eluted with 10/1 cyclohexane/toluene. Evaporation of the solvent afforded 920 mg (30%) of (η^4:η^4-[3$_4$]cyclobutadienophane)bis[(η^5-indenyl)cobalt] as an orange red solid. The product was crystallized from pentane as an orange red solid: mp >250 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.17 (m, 4H), 6.83 (m, 4H), 6.81 (d, J = 2.7 Hz, 4H), 4.65 (t, J = 2.7 Hz, 2H), 1.75 (m, 16H), 1.42 (m, 8H); ^{13}C NMR (50.32 MHz, $CDCl_3$) δ 123.90 (CH), 120.90 (CH), 98.08 (C), 85.19 (CH), 77.21 (C, cyclobutadiene), 72.43 (CH), 26.96 (CH_2), 24.93 (CH_2, double intensity); IR ($CDCl_3$) 2920, 2888, 2846, 1708, 1428, 1342, 1325, 1258, 1212, 1121, 1025, 815, 557, 511, 444; UV (CH_2Cl_2) [λ_{max}, nm (log ϵ)] 206 (3.82), 252 (3.88), 328 (3.82); HRMS (EI, 70 eV) calcd for $C_{38}H_{38}Co_2$ 612.1628, found 612.1801 (M^+ – IndCo, 23). Anal. Calcd for $C_{38}H_{38}Co_2$ (612.6): C, 74.51; H, 6.25. Found: C, 74.46; H, 6.33.

Reaction of (η^4-Cyclooctadiene-1,5)(η^5-R-cyclopentadienyl)cobalt with 1,8-Cyclotetradecadiyne. 1,8-Cyclotetradecadiyne (940 mg, 5 mmol) and 5 mmol of the cobalt complex are refluxed in 10 mL of *n*-nonane for the time given in Table II.

(η^4:η^4-[5$_4$]Cyclobutadienophane)bis[(η^5-methylcyclopentadienyl)cobalt] (5a). The product was crystallized from pentane as an orange red solid: mp >250 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 4.30 (m, 4H), 4.22 (m, 4H), 2.22 (s, 16H), 1.92 (s, 6H), 1.30 (s, 24H); ^{13}C NMR (50.32 MHz, $CDCl_3$) δ 91.93 (C), 81.40 (CH), 80.42 (CH), 78.94 (C, cyclobutadiene), 30.06 (CH_2, double intensity), 26.83 (CH_2, double intensity), 26.30 (CH_2), 12.60 (CH_3); IR (KBr) 2922, 2896, 2844, 1618, 1310, 1159, 1113, 1035, 666, 555, 479; UV (CH_2Cl_2) [λ_{max}, nm (log ϵ)] 234 (4.01), 272 (4.38), 304 (3.23); HRMS (EI, 70 eV) calcd for $C_{40}H_{54}Co_2$ 652.2876, found 652.2823; MS *m/z* (relative intensity) 652.2823 (M^+, 18). Anal. Calcd for $C_{40}H_{54}Co_2$ (652.7): C, 73.60; H, 8.34. Found: C, 73.68; H, 8.33.

(η^4:η^4-[5$_4$]Cyclobutadienophane)bis[(η^5-(trimethylsilyl)cyclopentadienyl)cobalt] (5d). The product was crystallized from pentane as an orange red solid: mp >250 °C; ^{1}H NMR (200 MHz, CD_2Cl_2) δ 4.50 (t, J = 1.7 Hz, 4H), 4.44 (t, J = 1.7 Hz, 4H), 2.27 (s, 16H), 1.27 (s, 24H), 0.15 (s, 18H); ^{13}C NMR (50.32 MHz, $CDCl_3$) δ 85.09 (CH), 84.90 (CH), 80.70 (C), 79.71 (C, cyclobutadiene), 29.94 (CH_2, double intensity), 27.51 (CH_2, double intensity), 26.40 (CH_2), 0.18 (CH_3); IR (KBr) 2929, 2898, 2844, 1459, 1244, 1162, 1029, 846, 829, 803, 513, 479; UV (CH_2Cl_2) [λ_{max}, nm (log ϵ)] 222 (3.01), 272 (4.16); HRMS (EI, 70 eV) calcd for $C_{44}H_{66}Co_2Si_2$ 768.3350, found 768.3373. Anal. Calcd for $C_{44}H_{66}Co_2Si_2$ (768.04): C, 68.72; H, 8.65. Found: C, 68.63; H, 8.62.

(η^4:η^4-[5$_4$]Cyclobutadienophane)bis[(η^5-phenylcyclopentadienyl)cobalt] (5e). The product was crystallized from pentane as an orange red solid: mp >250 °C; ^{1}H NMR (200 MHz, CD_2Cl_2) δ 7.28 (m, 8H), 7.06 (m, 4H), 2.27 (s, 16H), 4.82 (t, J = 2 Hz, 4H), 4.54 (t, J = 2 Hz, 4H), 2.01 (s, 16H), 1.18 (s, 24H); ^{13}C NMR (50.32 MHz, CD_2Cl_2) δ 137.34 (C, phenyl), 128.60 (CH, double intensity), 125.56 (CH, double intensity), 125.40 (CH), 95.95 (C), 82.86 (CH), 80.74 (C, cyclobutadiene), 78.43 (CH), 30.29 (CH_2), 26.92 (CH_2, 1.5 intensity); IR (KBr) 2920, 2892, 2844, 1599, 1510, 1459, 1427, 801, 757, 688; UV (CH_2Cl_2) [λ_{max}, nm (log ϵ)] 220 (4.52), 238 (4.50), 280 (4.71); HRMS (EI, 70 eV) calcd for $C_{50}H_{58}Co_2$ 776.3202, found 776.3221; MS *m/z* (relative intensity) 575.3037 (M^+ – $C_{11}H_{10}Co$, 100). Anal. Calcd for $C_{50}H_{58}Co_2$ (776.9): C, 77.30; H, 7.53. Found: C, 77.32; H, 7.47.

(η^4:η^4-[5$_4$]Cyclobutadienophane)bis[(η^5-(methoxycarbonyl)cyclopentadienyl)cobalt] (5f). The product was crystallized from pentane as an orange red solid: mp >250 °C; ^1H NMR (200 MHz, $CDCl_3$) δ 4.99 (t, *J* = 2.1 Hz, 4H), 4.62 (t, *J* = 2.1 Hz, 4H), 3.75 (s, OMe, 6H) 2.16 (s, 16H), 1.27 (s, 24H); ^{13}C NMR (50.32 MHz, $CDCl_3$) δ 168.27 (C), 85.16 (CH), 83.81 (C), 82.21 (CH), 82.11 (C, cyclobutadiene), 51.05 (CH3), 29.58 (CH_2, double intensity), 26.38 (CH_2), 26.29 (CH_2, double intensity); IR ($CDCl_3$) 2924, 2902, 2848, 1699, 1599, 1517, 1460, 1428, 1367, 1359, 1282, 1252, 1187, 1139, 1047, 1025, 848, 810, 567, 510; UV (CH_2Cl_2) [λ_{max}, nm (log ϵ)] 220 (4.45), 272 (4.71), 312 (3.90), 388 (4.10); HRMS (EI, 70 eV) calcd for $C_{42}H_{54}Co_2O_4$ 740.2668, found 740.2655; MS *m/z* (relative intensity) 740.2655 (M^+, 100). Anal. Calcd for $C_{42}H_{54}Co_2O_4$ (740.8): C, 68.10; H, 7.35. Found: C, 68.20; H, 7.44.

(η^5-Methylcyclopentadienyl)(η^4-Tricyclo[7.5.0.0^{2,8}]-tetradeca-1,8-diene)cobalt (7a). The product was crystallized from pentane as an orange red solid: mp 102–103 °C; ^1H NMR (200 MHz, $CDCl_3$) δ 4.71 (s, 2H), 4.60 (s, 2H), 1.69 (s, 13H) 1.62 (m, 8H), 0.92 (s, 2H); ^{13}C NMR (50.32 MHz, $CDCl_3$) δ 92.00 (C), 80.16 (CH), 78.58 (C, cyclobutadiene), 77.83 (CH), 30.56 (CH_2), 30.35 (CH_2, double intensity), 27.49 (CH_2, double intensity), 13.32 (CH_3); IR (KBr) 2902, 2835, 2806, 2664, 1435, 1426, 1418, 1344, 1323, 1297, 1257, 1220, 1212, 1034, 1018, 835, 793, 727, 508, 435, 409; UV (CH_2Cl_2) [λ_{max}, nm (log ϵ)] 222 (3.72), 268 (4.27); MS (EI) calcd for $C_{20}H_{27}Co$ 326.1, found 326.0; MS *m/z* (relative intensity) 326.0 (M^+, 43), 137.9 ($MeCpCo^+$, 57). Anal. Calcd for $C_{20}H_{27}Co$ (326.4): C, 73.60; H, 8.34. Found: C, 73.56; H, 8.42.

(η^5-(Methoxycarbonyl)cyclopentadienyl)(η^4-tricyclo-[7.5.0.0^{2,8}]tetradeca-1,8-diene)cobalt (7f). The product was crystallized from pentane as an orange red solid mp 89–92 °C; ^1H NMR (200 MHz, $CDCl_3$) δ 5.41 (t, *J* = 2.0 Hz, 2H), 4.89 (t, *J* = 2.0 Hz, 2H), 3.74 (s, 3H), 1.95 (m, 9H), 1.58 (m, 9H), 0.91 (m, 2H); ^{13}C NMR (50.32 MHz, $CDCl_3$) δ 168.97 (C), 83.21 (C), 82.42 (CH), 81.81 (C, cyclobutadiene), 81.13 (CH), 50.87 (CH_3), 30.24 (CH_2), 29.83 (CH_2, double intensity), 27.22 (CH_2, double intensity); IR (CH_2Cl_2) 2916, 2844, 2810, 1708, 1476, 1461, 1439, 1363, 1325, 1280, 1264, 1186, 436; UV (CH_2Cl_2) [λ_{max}, nm (log ϵ)] 222 (4.71), 268 (4.22), 318 (3.27), 380 (2.74); HRMS (EI, 70 eV) Calcd for $C_{21}H_{27}CoO_2$ 370.1569 (M^+, 100), found 370.1307.

(η^5-Indenyl)(η^4-tricyclo[7.5.0.0^{2,8}]tetradeca-1,8-diene)cobalt (11). The product was crystallized from pentane as an orange red solid: mp 143 °C; ^1H NMR (200 MHz, $CDCl_3$) δ 7.24 (m, 2H), 6.85 (m, 2H), 5.39 (d, *J* = 2.7 Hz, 2H), 4.85 (t, *J* = 2.7 Hz, 1H), 2.05–1.86 (m, 6H), 1.74–1.22 (m, 12H) 0.91–0.75 (m, 2H); ^{13}C NMR (50.32 MHz, $CDCl_3$) δ 124.05 (CH), 121.51 (CH), 99.07 (C), 78.85 (C, cyclobutadiene), 72.21 (CH), 30.53 (CH_2), 26.67 (CH_2); IR ($CDCl_3$) 2914, 2842, 2802, 1598, 1498, 1438, 1425, 1261, 1246, 1220, 1200, 1025, 798, 510; UV (CH_2Cl_2) [λ_{max}, nm (log ϵ)] 224 (4.16), 248 (4.19), 254 (4.26), 296 (4.13); HRMS (EI, 70 eV) calcd for $C_{23}H_{27}Co$ 362.1438, found 362.1454; MS *m/z* (relative intensity) 362.1454 (M^+, 2). Anal. Calcd for $C_{20}H_{27}Co$ (326.4): C, 73.60; H, 8.34. Found: C, 73.56; H, 8.42.

Acknowledgment. We are grateful to the Deutsche Forschungsgemeinschaft (SFB 247), the Fonds der Chemischen Industrie, the BASF Aktiengesellschaft, and the Metallgesellschaft Frankfurt for financial support.

OM920567R