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Binuclear Transition-Metal Complexes of Cyclophanoid Cyclopentadienone and Cyclopentadienyl Ligands

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The double-layered cyclophanoid cyclopentadienone 2,3,10,11-tetraphenyltricyclo[12.2.1.1^{9,12}]octadeca-1,3,9,11-tetraene-17,18-dione (**7**) is obtained by aldol condensation of cyclotetradecane-1,8-dione (**8**) with 2 equiv of benzil (**9**). **7** (= L) reacts with Ni(COD)$_2$, Fe$_2$(CO)$_9$, and Cp*Co(C$_2$H$_4$)$_2$ to give the binuclear cyclopentadienone complexes (COD)Ni–L–Ni(COD) (**11a**), (CO)$_3$Fe–L–Fe(CO)$_3$ (**11b**), and Cp*Co–L–CoCp* (**11c**). **11a** reacts with tetrafluoroboric acid and trifluoromethanesulfonic acid to yield the respective (hydroxycyclopentadienyl)nickel complexes [(COD)Ni–LH$_2$–Ni(COD)]$^{2+}\cdot$2BF$_4^-$ (**14a**) and [(COD)Ni–LH$_2$–Ni(COD)]$^{2+}\cdot$2CF$_3$SO$_3^-$ (**14b**); likewise, (tetracyclone)Ni(COD) (**13a**) reacts with tetrafluoroboric acid to give the mononuclear hydroxycyclopentadienyl complex [(Ph$_4$CpOH)Ni]$^+$BF$_4^-$ (**14e**); **11a** and **11c** react with triethyloxonium tetrafluoroborate to afford the binuclear ethoxycyclopentadienyl complexes [(COD)Ni–LEt$_2$–Ni(COD)]$^{2+}\cdot$2BF$_4^-$ (**14c**) and [Cp*Co–LEt$_2$–CoCp*]$^{2+}\cdot$2BF$_4^-$ (**14d**). The electrochemical properties of the binuclear (cyclopentadienone)cobalt complex **11c** and the binuclear (ethoxycyclopentadienyl)nickel complex **14c** are examined; both complexes show interacting redox sites. X-ray structural investigations on **11a** show an anti conformation of the two quasi-planar cyclopentadienone rings, the distance between them being approximately 410 pm; each nickel atom is bonded η^4 to its cyclopentadienone moiety, the Ni–Ni distance being 805 pm; the whole molecule is centrosymmetric (crystal system monoclinic; space group $C2/c$; a = 2433.1 (10) pm, b = 1425.1 (6) pm, c = 1850.0 (7) pm, β = 97.83 (3)°; Z = 4).

Introduction

Several one-dimensional organometallic compounds show highly anisotropic, and thus very interesting, physical properties (e.g. one-dimensional conductivity), which could make them technically important.[1] One possibility of realizing such one-dimensional compounds is to connect metal centers by double-layered organic π-ligands whose π-systems interact strongly, thus allowing efficient metal–metal communication (Figure 1). Although undoubtedly the anisotropy of some of their macroscopic properties provides the main stimulus for investigating such columnar-polymeric organometallics, the requirements for these properties are as yet hardly well-defined. Furthermore, analyzing polymeric materials, which are frequently insoluble, is fraught with problems. Consequently, monomeric, dimeric, and oligomeric metal complexes have recently attracted a lot of attention as model compounds for polymeric species of type **1**, the focus being on synthetic aspects and on the requirements for, and the mechanisms of, electron density transfer from one metal center to another.[2-4] So far, three types of double-layered organic π-ligands have been utilized for the construction of model-type units for columnar-polymeric metal complexes: Boekelheide has employed cyclophanes,[2] Hopf has used indenophanes,[3] and Rosenblum has made use of a sterically fixed, naphthalene-bridged cyclopentadienyl system[4] (representative examples are shown in Figure 2).

Up to now, no attempt has been made to use a cyclophanoid cyclopentadienyl ligand ("cyclopentadienylophane") as a building block for columnar metal complexes (Figure 3), whether oligomeric or polymeric. This is surprising, since such cyclopentadienylophanes would be very advantageous: They combine the synthetic versatility of cyclopentadienyl ligands with the structural simplicity of paracyclophanes. So far, the only example of this fascinating class of ligands is the binuclear ferrocenophane **6**, which shows a weak intramolecular ring–ring interaction[5] (Figure 4). Attempts to prepare the corresponding uncomplexed cyclopentadienylophane by reductive demetalation of [3]-(1,1′)[3](3,3′)ferrocenophane have failed.[6] Analogous efforts using **6** have not been made due to its very tedious synthesis. As part of our investigations concerning cyclopentadienylophanes with various bridge lengths, we now report the syntheses and properties of some doubly bridged cyclopentadienone and cyclopentadienyl complexes with four methylene groups per bridge.

Results and Discussion

We were able to prepare the first doubly bridged cyclopentadienone **7** using the standard two-step procedure by Allen and VanAllan:[7] When cyclotetradecane-1,8-dione (**8**) is reacted with benzil (**9**) under mild, basic conditions, the double-layered cyclopentenolone **10** is obtained in reasonable yield; further elimination of water under more rigorous conditions cleanly leads to the doubly bridged cyclopentadienone **7** (Scheme I).

Like its precursor **10**, **7** is only sparingly soluble in all common organic solvents. It precipitates from the reaction mixture as a bright orange powder and forms red needles upon recrystallization from boiling toluene. Prolonged heating (several hours reflux in toluene), however, leads to the formation of a colorless Diels–Alder product; likewise, a colorless [2 + 2] cycloaddition product is formed upon irradiation of a benzene suspension of **7** with UV light.[8] Spectroscopic data are in accord with, but do not

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† X-ray structure analysis.

(1) Böhm, M. C. *Lect. Notes Chem.* **1987**, *45*.

(2) (a) Laganis, E. D.; Finke, R. G.; Boekelheide V. *Proc. Natl. Acad. Sci. U.S.A.* **1981**, *78*, 2657. (b) Laganis, E. D.; Voegeli, R. H.; Swann, R. T.; Finke, R. G.; Hopf, H.; Boekelheide, V. *Organometallics* **1982**, *1*, 1415. (c) Boekelheide, V. *Pure Appl. Chem.* **1986**, *58*, 1. (d) Voegeli, R. H.; Kang, H. C.; Finke, R. G.; Boekelheide, V. *J. Am. Chem. Soc.* **1986**, *108*, 7010. (e) Plitzko, K.-D.; Boekelheide, V. *Organometallics* **1988**, *7*, 1573.

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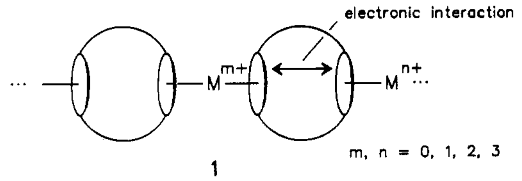

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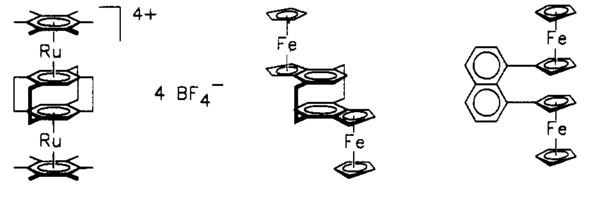
Figure 1. Building principle for one-dimensional organometallics utilizing double-layered organic π-ligands.



2 3 4

Boekelheide (1986) Hopf (1988) Rosenblum (1985)

Figure 2. Examples of model compounds for one-dimensional organometallics of type 1.

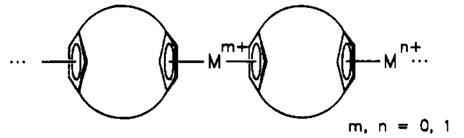
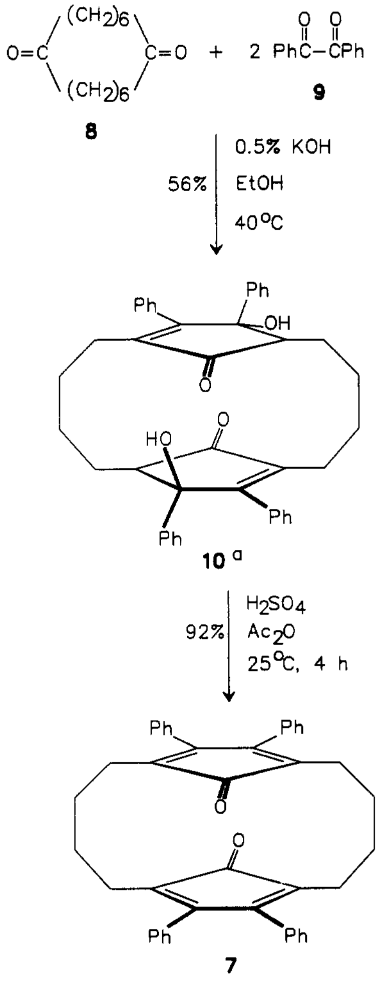


Figure 3. Cyclopentadienylophanes as building blocks for columnar-polymeric organometallics.

Scheme I. Synthesis of the Cyclophanoid Cyclopentadienone 7



a only one isomer is shown

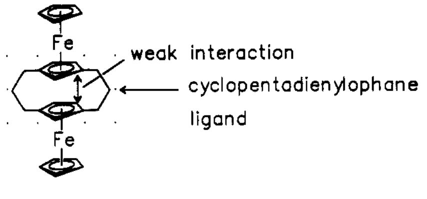


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Figure 4. [3.3](1,3)Ferrocenophane (6): the only example so far of a cyclopentadienylophane complex.

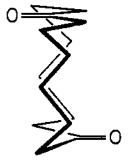

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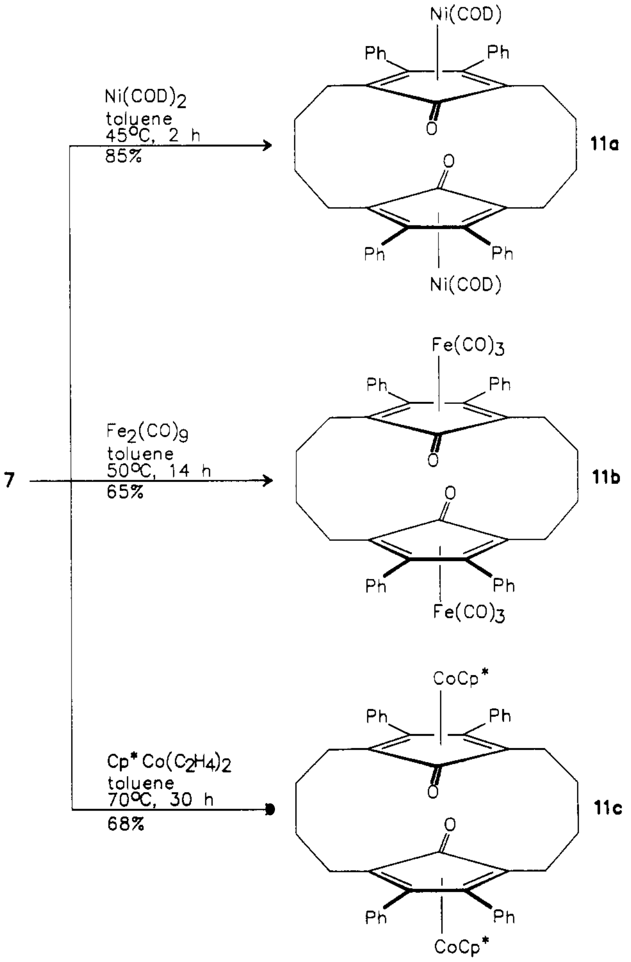
Figure 5. Conformation of cyclotetradecane-1,8-dione (8).

Scheme II. Syntheses of the Doubly Bridged Cyclopentadienone Complexes 11a–11c



prove, the exclusive formation of the anti conformer of 7 (cf. Scheme I): (1) only a single, sharp C=O stretching mode is observed in the IR spectrum of 7; (2) likewise, the ^{13}C NMR spectrum shows the presence of one conformer only (unless the syn and anti conformers equilibrate rapidly on the NMR time scale); (3) the assumption that only the anti conformer is formed is strongly supported by a single-crystal X-ray structure analysis of the binuclear nickel complex **11a** (vide infra); (4) furthermore, the

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(8) Results concerning the organic chemistry of 7 will be published soon.

Table I. Atomic Coordinates and Temperature Factors (10^4 pm^2) for 11a

atom	*x*	*y*	*z*	*U*
Ni	0.0080 (1)	1.2479 (1)	0.0059 (1)	0.042 (1)^a
O(1)	−0.0378 (2)	1.1535 (5)	−0.0298 (3)	0.048 (3)^a
C(1)	0.1781 (3)	0.9880 (5)	0.0007 (4)	0.054 (4)^a
C(2)	0.2263 (3)	0.9490 (5)	−0.0196 (4)	0.090 (6)^a
C(3)	0.2527 (3)	0.9924 (5)	−0.0730 (4)	0.091 (7)^a
C(4)	0.2310 (3)	1.0748 (5)	−0.1061 (4)	0.092 (7)^a
C(5)	0.1828 (3)	1.1138 (5)	−0.0858 (4)	0.051 (4)^a
C(6)	0.1564 (3)	1.0705 (5)	−0.0323 (4)	0.043 (4)^a
C(7)	0.1280 (2)	1.0862 (5)	0.1977 (4)	0.051 (4)^a
C(8)	0.1694 (2)	1.0831 (5)	0.2577 (4)	0.056 (4)^a
C(9)	0.2230 (2)	1.1130 (5)	0.2508 (4)	0.074 (5)^a
C(10)	0.2353 (2)	1.1460 (5)	0.1838 (4)	0.060 (5)^a
C(11)	0.1939 (2)	1.1492 (5)	0.1238 (4)	0.053 (4)^a
C(12)	0.1403 (2)	1.1193 (5)	0.1307 (4)	0.038 (4)^a
C(13)	0.0115 (3)	1.1408 (6)	−0.0087 (5)	0.034 (3)^a
C(14)	0.0557 (4)	1.1211 (6)	−0.0563 (5)	0.037 (3)^a
C(15)	0.1045 (4)	1.1038 (6)	−0.0097 (5)	0.034 (3)^a
C(16)	0.0954 (4)	1.1247 (7)	0.0667 (4)	0.035 (3)^a
C(17)	0.0383 (4)	1.1441 (6)	0.0667 (4)	0.029 (3)^a
C(18)	0.0043 (4)	1.1610 (7)	0.1284 (5)	0.043 (4)^a
C(19)	−0.0343 (4)	1.0752 (7)	0.1321 (5)	0.042 (4)^a
C(20)	−0.0035 (4)	0.9833 (7)	0.1477 (5)	0.047 (4)^a
C(21)	−0.0403 (4)	0.8952 (7)	0.1355 (5)	0.046 (4)^a
C(22)	0.0371 (4)	1.3471 (6)	−0.0619 (6)	0.053 (4)^a
C(23)	0.0203 (4)	1.3504 (7)	0.0077 (6)	0.060 (4)^a
C(24)	0.0421 (5)	1.4203 (8)	0.0688 (6)	0.066 (5)^a
C(25)	0.1054 (5)	1.4343 (9)	0.0781 (7)	0.072 (5)^a
C(26)	0.1359 (4)	1.3444 (8)	0.0618 (7)	0.063 (5)^a
C(27)	0.1513 (4)	1.3209 (7)	−0.0058 (6)	0.050 (4)^a
C(28)	0.1390 (5)	1.3825 (8)	−0.0759 (6)	0.071 (5)^a
C(29)	0.0787 (5)	1.4167 (8)	−0.0891 (6)	0.064 (5)^a
C(30)^b	0.1460 (7)	1.3221 (11)	0.3076 (8)	0.106 (5)
C(31)^b	0.1184 (5)	1.2353 (9)	−0.3530 (7)	0.082 (4)
Cl(1)^b (0.333)^c	0.1964 (8)	1.3903 (13)	0.2883 (10)	0.188 (7)
Cl(2)^b (0.333)^c	0.1799 (5)	1.4313 (9)	0.2847 (7)	0.082 (4)
Cl(3)^b (0.333)^c	0.1949 (5)	1.4159 (9)	0.3127 (7)	0.085 (4)
Cl(4)^b (0.500)^c	0.0766 (4)	1.3449 (7)	0.2750 (5)	0.102 (3)
Cl(5)^b (0.250)^c	0.0960 (10)	1.3181 (16)	0.2599 (13)	0.136 (9)
Cl(6)^b (0.250)^c	0.0750 (7)	1.3823 (12)	0.2745 (9)	0.119 (6)
Cl(7)^b (0.333)^c	0.1542 (8)	1.3080 (14)	0.3991 (10)	0.188 (7)
Cl(8)^b (0.333)^c	0.1539 (5)	1.2751 (9)	0.3927 (7)	0.114 (4)
Cl(9)^b (0.333)^c	0.1360 (5)	1.3142 (8)	0.4083 (6)	0.094 (3)
Cl(10)^b (0.500)^c	0.1565 (4)	1.1513 (6)	−0.3018 (4)	0.112 (3)
Cl(11)^b (0.100)^c	0.1849 (12)	1.1758 (21)	−0.3341 (15)	0.066 (8)
Cl(12)^b (0.200)^c	0.1412 (5)	1.1605 (9)	−0.2839 (7)	0.048 (3)
Cl(13)^b (0.500)^c	0.1661 (5)	1.2803 (8)	−0.4082 (6)	0.132 (4)
Cl(14)^b (0.200)^c	0.1229 (9)	1.3483 (16)	−0.3708 (13)	0.107 (7)
Cl(15)^b (0.200)^c	0.1892 (10)	1.2313 (16)	−0.3923 (12)	0.108 (7)
Cl(16)^b (0.500)^c	0.0958 (5)	1.3284 (8)	−0.2974 (6)	0.142 (4)
Cl(17)^b (0.200)^c	0.0804 (9)	1.2792 (16)	−0.2747 (11)	0.100 (7)
Cl(18)^b (0.200)^c	0.1146 (7)	1.3532 (12)	−0.3213 (10)	0.080 (5)
Cl(19)^b (0.200)^c	0.1160 (12)	1.1904 (20)	−0.2750 (15)	0.152 (9)
Cl(20)^b (0.200)^c	0.1428 (9)	1.3140 (15)	−0.3960 (10)	0.070 (5)

^{a} Equivalent isotropic *U* defined as one-third of the trace of the $\mathbf{U}_{ij}$ tensor. ^{b} Disordered chloroform molecules. ^{c} Site occupancy factor (<1 due to disordering); the sum of all Cl site occupancy factors is 6.000, indicating that four chloroform molecules per **11a** molecule are included in the crystal.

starting material cyclotetradecane-1,8-dione (**8**) has an anti conformation in the solid state as well as in solution[9] (Figure 5).

Cyclopentadienones are known to be able to act as 4π-diene ligands forming a wide variety of stable transition-metal complexes. The doubly bridged cyclopentadienone **7** reacts smoothly with coordinatively labile reagents like $Ni(COD)_2$, $Fe(CO)_9$, and $Cp^*Co(C_2H_4)_2$[10] to form the corresponding binuclear complexes **11a–c** in high yield (Scheme II).

The nickel complex **11a** is isolated as a light brown, the iron complex **11b** as a light yellow, and the cobalt complex **11c** as an orange powder; all three compounds are air-stable. Whereas **11b** is moderately soluble in toluene and chloroform, **11a** and **11c** are only slightly soluble in these and in all other common organic solvents. Nevertheless, single crystals could be grown of **11a** by slow cooling of a hot chloroform solution, so that a single-crystal X-ray structure analysis could be made. A view of the molecule is shown in Figure 6; atomic coordinates are collected in Table I; relevant bond lengths and angles are collected in Table II. **11a** is a centrosymmetric molecule. The cyclopentadienone rings are arranged in an anti conformation to each other; they are very nearly planar: The plane defined by C14, C15, C16, C17 and that defined by C13, C14, C17[11] intersect each other at an angle of 2.6°, which to our knowledge is the smallest value for a cyclo-

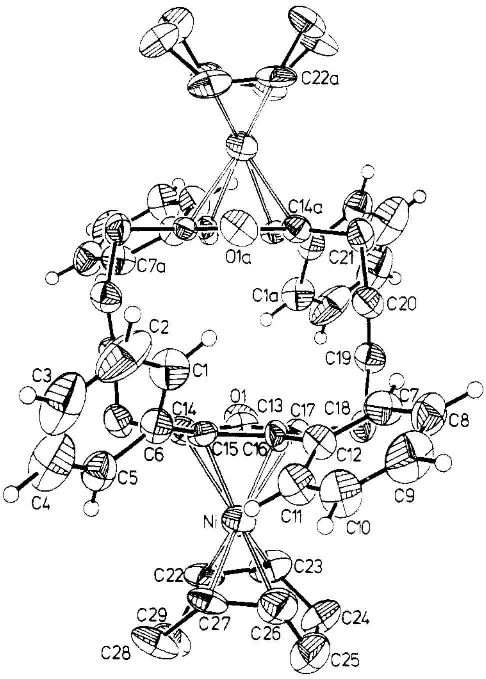

Figure 6. Molecular structure of **11a**.

Table II. Selected Bond Lengths and Angles for 11a

Bond Lengths (pm)			
Ni–C(13)	224.8 (8)	C(15)–C(16)	147.9 (12)
Ni–C(14)	218.1 (9)	C(16)–C(17)	141.7 (12)
Ni–C(15)	210.8 (9)	C(17)–C(18)	151.8 (13)
Ni–C(16)	209.1 (9)	C(18)–C(19)	154.9 (13)
Ni–C(17)	218.9 (9)	C(19)–C(20)	151.7 (13)
Ni–C(22)	207.4 (10)	C(20)–C(21)	154.0 (14)
Ni–C(23)	206.3 (11)	C(21)–C(14a)	148.0 (13)
Ni–C(26)	210.5 (11)	C(22)–C(23)	140.5 (17)
Ni–C(27)	206.0 (10)	C(22)–C(29)	154.8 (16)
O(1)–C(13)	122.5 (10)	C(23)–C(24)	154.6 (16)
C(6)–C(15)	148.3 (12)	C(24)–C(25)	153.9 (17)
C(12)–C(16)	149.9 (10)	C(25)–C(26)	153.1 (17)
C(13)–C(14)	150.6 (13)	C(26)–C(27)	139.5 (17)
C(13)–C(17)	145.7 (12)	C(27)–C(28)	156.1 (16)
C(14)–C(15)	138.2 (12)	C(28)–C(29)	153.3 (16)
Bond Angles (deg)			
O(1)–C(13)–C(14)	126.0 (8)	C(18)–C(19)–C(20)	113.8 (8)
O(1)–C(13)–C(17)	126.3 (8)	C(19)–C(20)–C(21)	114.4 (8)
C(6)–C(15)–C(16)	124.8 (7)	C(20)–C(21)–C(14a)	109.7 (8)
C(12)–C(16)–C(15)	124.0 (7)	C(22)–C(23)–C(24)	125.3 (10)
C(13)–C(14)–C(15)	106.3 (8)	C(22)–C(29)–C(28)	124.1 (9)
C(13)–C(17)–C(16)	107.7 (7)	C(23)–C(22)–C(29)	124.1 (9)
C(13)–C(17)–C(18)	120.5 (7)	C(23)–C(24)–C(25)	113.8 (10)
C(14)–C(13)–C(17)	107.8 (7)	C(24)–C(25)–C(26)	112.0 (9)
C(14)–C(15)–C(16)	110.4 (8)	C(25)–C(26)–C(27)	125.1 (10)
C(15)–C(16)–C(17)	107.8 (7)	C(26)–C(27)–C(28)	124.4 (9)
C(17)–C(18)–C(19)	107.7 (7)	C(27)–C(28)–C(29)	112.4 (10)

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[9] Alvik, T.; Borgen, G.; Dale, J. *Acta Chem. Scand.* **1972**, *26*, 1805.

[10] Cp* is used as an abbreviation for η^5-1,2,3,4,5-pentamethylcyclopenta-2,4-dien-1-yl.

[11] Crystallographers' numbering.

Table III. ν(C=O) and δ(*C*=O) for a Number of Cyclopentadienone Complexes and for the Ligands 7 and Tetracyclone (12)

	7	11a	11b	11c	12	13a	13b
ν(C=O),[a] cm^{-1}	1702	1574	1620	1565	1700	1605	1633[b,14]
δ(*C*=O),[c] ppm	204.0	161.6	167.3	148.6	200.3	163.2	173.8[15]

[a] Measured in the solid state (CsI or KBr pellet). [b] Measured in solution ($CHCl_3$). [c] In $CDCl_3$.

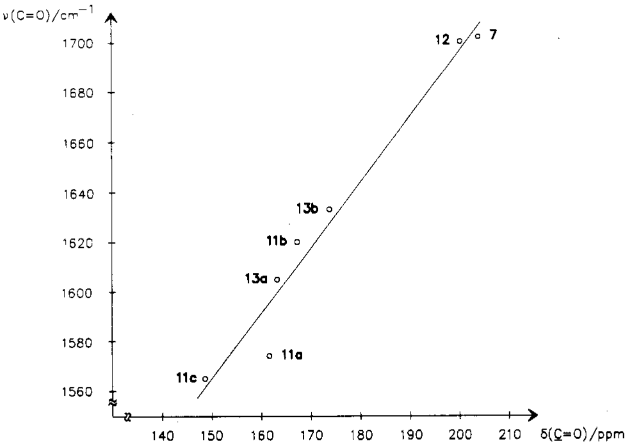

Figure 7. Correlation diagram of ν(C=O) and δ(*C*=O) for the complexes and ligands listed in Table III.

pentadienone complex so far observed. Each nickel atom is bonded η^4 to its cyclopentadienone moiety.[12] The intramolecular distance between the cyclopentadienone rings is approximately 410 pm; the Ni–Ni distance is 805 pm. The molecules are arranged in stacks along the *y* axis with the nickel atoms forming zigzag chains. The intramolecular Ni–Ni vectors intersect the *y* axis at an angle of very nearly 30°. Each nickel atom is surrounded by three nearest nickel neighbors in the *xy* plane, one neighbor belonging to the same molecule, one to the next molecule within the same stack, and one belonging to the next molecule within the neighboring stack. The Ni–Ni distances are approximately equal (805–831 pm).

The frequency of the C=O stretching mode in the IR spectra of **11a–c** can be used for a qualitative assessment of the electron density transferred to the cyclopentadienone moiety by the 14-electron metal fragments Ni(COD), $Fe(CO)_3$, and CoCp*.[13] It can be seen from Table III that this metal cyclopentadienone back-donation increases in the order **11b** < **11a** < **11c**; it stands to reason that the negative charge density, and thus the nucleophilicity, of the cyclopentadienone O atom increases accordingly. The same trend can be observed regarding the chemical shift of the carbonyl C atom in the ^{13}C NMR spectra of **11a–c**; corresponding data for tetracyclone (tc) (**12**), and for its complexes (tc)Ni(COD) (**13a**) and (tc)Ru$(CO)_3$ (**13b**), fit well into the pattern observed for **7** and **11a–c**, the correlation of IR and ^{13}C NMR data being roughly linear (Table III; Figure 7). The carbonyl O atoms of (cyclopentadienone)metal complexes are nucleophilic centers (vide supra). Thus, **11a**, **11c**, and **13a** react cleanly with good electrophiles (strong acids, Meerwein reagents) to yield the corresponding cyclopentadienyl complexes **14a–e** (Scheme III). Analogous experiments with the iron complex **11b** or the ruthenium complex **13b** have not been made by us.

Table IV. Electrochemical Data for 11c and 14c

compd	concn, M	ΔE_{p1}, mV	$E_1°$, mV	ΔE_{p2}, mV	$E_2°$, mV	scan rate, mV s^{-1}
11c	3.5 × 10^{-5}	61	972	66	1121	2000
		59	981	84	1125	10000
14c	6.3 × 10^{-5}	61	-321	59	-560	20
		56	-325	62	-561	100
		61	-327	68	-558	500

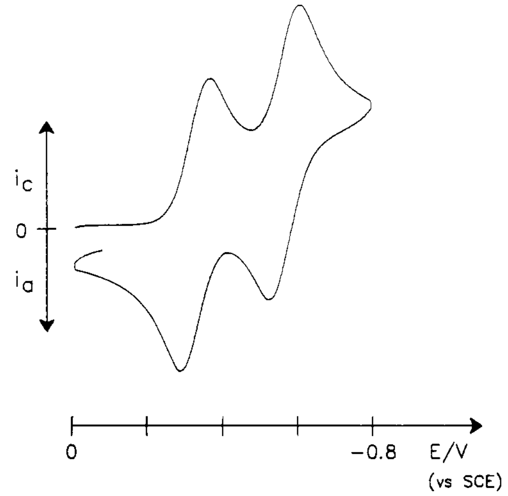

Figure 8. Cyclic voltammogram of **14c**.

The nickel complexes **14a–c** and **14e** are obtained as green powders; the cobalt complex **14d** forms a bright yellow powder. The binuclear hydroxycyclopentadienyl complex **14a** is totally insoluble in all common nonbasic organic solvents except dichloromethane, where its solubility still is extremely low but sufficient for recording a ^1H NMR spectrum. The solubilities of **14a–e** in dichloromethane increase "in alphabetical order", and ^{13}C NMR spectra could be recorded for all compounds except **14a**. In the case of the hydroxycyclopentadienyl complexes **14a**, **14b**, and **14e**, basic solvents lead rapidly to the regeneration of the respective cyclopentadienone complexes **11a** and **13a** through proton transfer to solvent molecules.

The formation of cyclopentadienyl complexes from their respective cyclopentadienone precursors is evidenced by IR and NMR data: (1) no C=O stretching mode can be detected in the IR spectra of **14a–e**; (2) owing to the aromatic ring current of the cyclopentadienyl moiety formed upon protonation or ethylation at the carbonyl O atom, the ^{13}C NMR signal of its neighboring C atom experiences an upfield shift of ca. 22 ppm; (3) the change of the formal oxidation state of the Co atom from +I in **11c** to +III in **14d** coincides with a downfield shift of its ^{59}Co NMR signal of more than 1100 ppm. Our findings concerning the IR and ^{13}C NMR data are in accord with literature values;[15,16] ^{59}Co or other metal nuclei have not been used before as a probe in analogous investigations.

The electrochemical behavior of **11c** and **14c** was studied by cyclic voltammetry. **11c** undergoes two reversible one-electron oxidations at high scan rates and irreversible oxidation at low scan rates, indicating that probably a slow follow-up reaction of the oxidized species ensues. **14c**

---

(12) The distance between the nickel atom and the carbonyl C atom of the cyclopentadienone ring is significantly longer than the distances between the nickel atom and the other four carbon atoms of the cyclopentadienone ring, indicating an η^4-bonding of the metal; however, this does not rule out a weak bonding interaction between the nickel atom and the carbonyl C atom.

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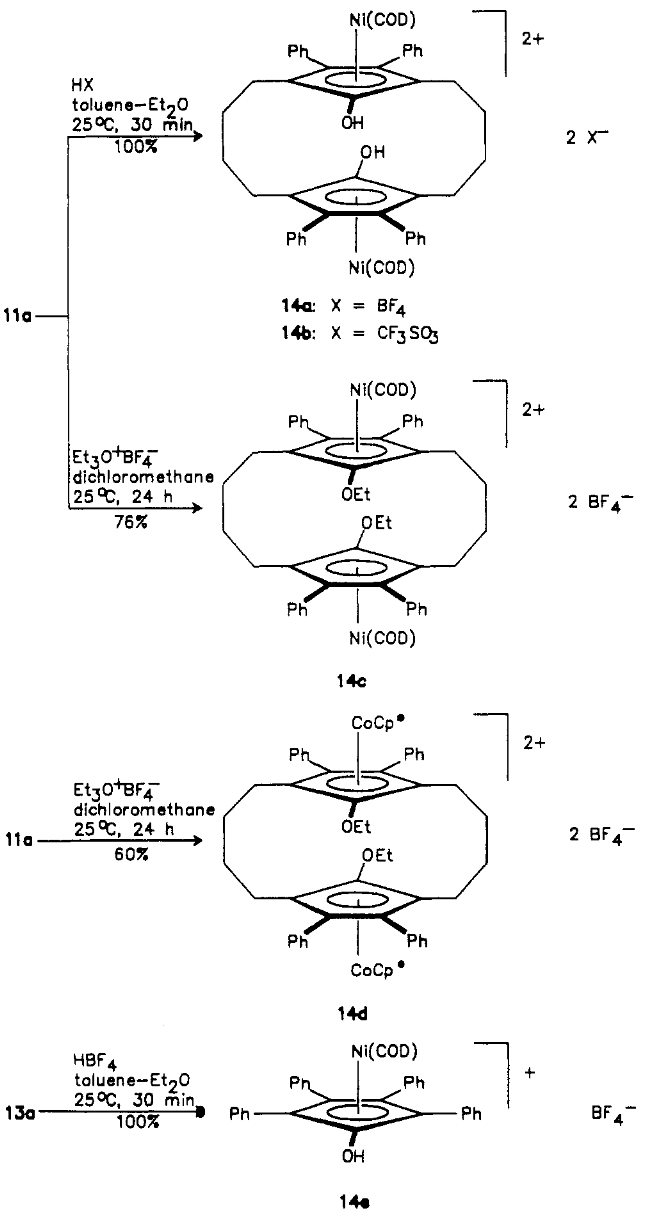
Scheme III. Syntheses of the Cyclopentadienyl Complexes 14a–14e



undergoes two reversible one-electron reductions. The pertinent electrochemical data are listed in Table IV; the cyclic voltammogram of **14c** is shown in Figure 8. **11c** and **14c** contain two equivalent redox sites (metal centers). According to the model developed by Savéant, Bard, and Anson,[17] the fact that **11c** and **14c** exhibit two clearly separated one-electron waves in their respective cyclic voltammograms can be accounted for only, if it is assumed that the redox sites interact with one another. The exact nature of this interaction[18] has not been resolved. However, results obtained from similar homobinuclear transition-metal complexes and their respective mixed-valence ions indicate that a wave splitting of the magnitude observed ($\Delta E° \simeq 149$ mV for **11c** and 235 mV for **14c**) often does not stem from electronic delocalization.[4a,19] Regarding the respective spatial separations of the cyclopentadienone rings and of the metal centers in the nickel complex **11a** (vide supra), it seems reasonable to assume that at the most only weak electronic interactions contribute to the observed overall metal–metal interaction in **11c** and **14c**.

Mixed-valence Ni(II)/Ni(III) complexes of monobridged bis(tetraazamacrocyclic) ligands have been demonstrated to show an electrostatic metal–metal interaction, which is effective up to a Ni–Ni distance of at least 700 pm; the observed $\Delta E°$ values are, however, rather small (<100 mV).[20] Compared with these mixed-valence ions, electrostatic metal–metal interactions should be much smaller in our M(I)/M(II) mixed-valence systems, although it is difficult to estimate the influences of the bridging ligands on this repulsion.

Experimental Section

General Consideration. All reactions were carried out under an atmosphere of purified argon by using standard Schlenk techniques. Solvents and reagents were appropriately dried and purified. The following instruments were used: melting points (uncorrected), Büchi 510 melting point apparatus; NMR spectra, Bruker AM 300 (300.133 MHz, ^{1}H, external TMS; 96.279 MHz, ^{11}B, external B(OMe)$_3$; 75.453 MHz, ^{13}C, external TMS; 282.407 MHz, ^{19}F, external CFCl$_3$; 70.859 MHz, ^{59}Co, external K$_3$[Co(CN)$_6$]; mass spectra, Varian 311 A (70 eV, 300 μA emission; only characteristic fragments are listed); IR spectra (CsI pellets), Perkin-Elmer 180 grating IR spectrophotometer and Mattson Polaris TM FTIR spectrophotometer; cyclic voltammograms, Princeton Applied Research (PAR) 173 potentiostat–galvanostat with integrated PAR 179 digital coulometer and PAR 175 universal programmer (measurements were made with Pt electrodes and a SCE reference electrode in a 0.1 M solution of tetra-*n*-butylammonium tetrafluoroborate in dichloromethane). Elemental analyses were carried out by "Mikroanalytisches Laboratorium Beller" (Göttingen) or by the analytical laboratory of the Universität Bielefeld. Chlorine was determined by Schöniger's method in our laboratory.

Cyclotetradecane-1,8-dione (8). We simplified and optimized the procedure developed by Blomquist and Spencer.[21] A solution of 92.3 g (437 mmol) of suberic acid dichloride in 150 mL of diethyl ether is added dropwise over a period of 4 h through an Allihn condenser to a well-stirred mixture of 450 mL (6.1 mol) of triethylamine and 1.20 L of diethyl ether. During the addition a gentle reflux is maintained. The reaction mixture is allowed to stand overnight; the white precipitate is removed by filtration and washed with diethyl ether (2 × 50 mL). The combined ether solutions are cooled in an ice bath and carefully acidified with dilute hydrochloric acid. The ether phase is separated, washed with water (2 × 300 mL), and dried over magnesium sulfate. The ether is distilled off by using a rotary evaporator; the remaining viscous yellow oil is diluted with 30 mL of methanol and cooled to −10 °C. A solution of 71.5 g (1.27 mol) of potassium hydroxide in 220 mL of methanol is added dropwise to the well-stirred mixture; the first few drops have to be added very carefully, since a vigorous exothermic reaction ensues. During the addition a white solid (probably potassium carbonate) precipitates. The alkaline mixture is refluxed for 1.5 h, then 200 mL of water is added, and refluxing is continued for another 1.5 h. After being cooled to room temperature, the turbid yellow solution is extracted with diethyl ether (3 × 300 mL), the combined extracts are washed neutral with water and dried over calcium chloride. The solvent is distilled off by using a rotary evaporator; recrystallization of the crude product from ethanol and then from *n*-hexane affords 11.2 g (23%) of shiny white plates, mp 139–144 °C (147.5–148 °C[17]). The product thus obtained is pure enough for synthetic purposes.

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Dihydroxy-2,3,10,11-tetraphenyltricyclo[12.2.1.$1^{9,12}$]octadecadiene-17,18-dione (10) (Mixture of Isomers). A solution of 22.4 g (99.8 mmol) of 8, 63.0 g (300 mmol) of benzil (9), and 7.00 g (125 mmol) of potassium hydroxide in 900 mL of ethanol is stirred at 40 °C for 3 days. The precipitate is filtered off with suction, washed with ethanol (100 mL), diethyl ether (100 mL), and *n*-pentane (50 mL), and dried in vacuo to give 34.1 g (56%) of a white powder, mp 276–278 °C dec. IR (cm^{-1}): 3460 s, 3088 w, 3059 w, 3029 w, 2949 m, 2931 m, 2861 m, 1697 vs, 1598 m, 701 s. MS: *m/e* 608 (M$^+$, 1.1%), 590 ((M – H_2O), 88%), 572 ((M – $2H_2O$), 52%), 105 (100%). Anal. Calcd for $C_{42}H_{40}O_4$ (608.78): C, 82.86; H, 6.62. Found: C, 82.31; H, 6.89.

2,3,10,11-Tetraphenyltricyclo[12.2.1.$1^{9,12}$]octadeca-1,3,9,11-tetraene-17,18-dione (7). A few drops of concentrated sulfuric acid are added to a suspension of 34.1 g (56.0 mmol) of **10** in 220 mL of acetic anhydride, whereupon the mixture turns orange and warms slightly. After the mixture is stirred for 4 h, the product is filtered off with suction, washed with ethanol (2 × 100 mL), diethyl ether (100 mL), and *n*-pentane (50 mL), and dried in vacuo to give 29.5 g (92%) of a bright orange powder, which is analytically pure. Upon recrystallization from toluene, red needles are obtained. No melting point can be determined because a white Diels–Alder product is formed during the heating process. ^{1}H NMR ($CDCl_3$): δ 1.52 (br s, 8 H, $CH_2CH_2CH_2CH_2$), 2.24 (br s, 8 H, $CH_2CH_2CH_2CH_2$), 6.99–7.02 (m, 8 H, Ph), 7.17–7.25 (m, 12 H, Ph). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 23.0 ($CH_2CH_2CH_2CH_2$), 25.4 ($CH_2CH_2CH_2CH_2$), 127.0, 127.8, 128.5 (Ph), 133.8, 154.9 (olefinic C's), 204.0 (C=O). IR (cm^{-1}): 3078 w, 3055 w, 3030 w, 3019 w, 2951 m, 2921 m, 2905 m, 2878 m, 2842 w, 1702 vs, 1596 w, 703 (sh) s. MS: *m/e* 572 (M$^+$, 100%), 286 (M$^+$/2, 20.8%). Anal. Calcd for $C_{42}H_{36}O_2$ (572.75): C, 88.08; H, 6.34. Found: C, 87.83; H, 6.54.

Bis(η^4-1,5-cyclooctadiene)[μ-(1–4-η:9–12-η)-2,3,10,11-tetraphenyltricyclo[12.2.1.$1^{9,12}$]octadeca-1,3,9,11-tetraene-17,18-dione]dinickel(0,0) (11a). Bis(η^4-1,5-cyclooctadiene)nickel(0) (3.00 g, 10.9 mmol) and 2.92 g (5.10 mmol) of **7** are stirred in 350 mL of toluene at 45 °C for 2 h and then at room temperature overnight. The precipitate is isolated by filtration, washed with toluene (2 × 20 mL) and *n*-pentane (2 × 20 mL), and dried in vacuo to give 3.93 g (85%) of a light brown powder, decomposition above ca. 240 °C. ^{1}H NMR ($CDCl_3$): δ 1.24–1.32 (br m, 4 H, CH_2), 2.11–2.16 (br m, 12 H, CH_2), 2.39–2.52 (br m, 12 H, CH_2), 2.62–2.66 (br m, 4 H, CH_2), 3.58 (br s, 8 H, CH), 6.99–7.02 (m, 8 H, Ph), 7.10–7.13 (m, 12 H, Ph). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 23.5 ($CH_2CH_2CH_2CH_2$), 25.5 ($CH_2CH_2CH_2CH_2$), 29.4, 31.6 (CH_2(COD)), 94.7 (CH), 99.2 (olefinic C (cyclopentadienone)), 103.0 (CH), 105.8 (olefinic C (cyclopentadienone)), 126.4, 127.6, 130.4, 133.5 (Ph), 161.6 (C=O). IR (cm^{-1}): 3060 w, 3003 w, 2942 m, 2892 w, 2860 w, 2838 w, 1574 s, 760 s, 745 s, 705 s, 660 m. MS: *m/e* 796 ((M – COD), 1.2%), 630 ((M – 2COD – Ni), 2.9%), 572 (**7**$^+$, 52.1%). Anal. Calcd for $C_{58}H_{60}Ni_2O_2$ (906.54): C, 76.85; H, 6.67. Found: C, 77.12; H, 6.90.

11a may be recrystallized from chloroform to afford brownish red crystals. The elemental analysis suggests that four chloroform molecules per **11a** molecule are included in the crystals; this is confirmed by single-crystal X-ray diffraction data (vide supra). Anal. Calcd for $C_{62}H_{64}Cl_{12}Ni_2O_2$ (1384.05): C, 53.80; H, 4.66; Cl, 30.7. Found: C, 54.01; H, 4.71; Cl, 30.5.

Bis(tricarbonyl)[μ-(1–4-η:9–12-η)-2,3,10,11-tetraphenyltricyclo[12.2.1.$1^{9,12}$]octadeca-1,3,9,11-tetraene-17,18-dione]diiron(0,0) (11b). **7** (1.05 g, 1.83 mmol) and 1.36 g (3.74 mmol) of nonacarbonyldiiron are stirred in 150 mL of toluene at 50 °C for 14 h. The suspension is filtered to remove excess iron carbonyl; the yellow filtrate is concentrated and cooled to –30 °C to yield 1.01 g (65%) of a light yellow powder, decomposition above ca. 190 °C. ^{1}H NMR ($CDCl_3$): δ 1.50 (br s, 4 H, CH_2), 1.94–2.02 (br m, 4 H, CH_2), 2.12–2.19 (br m, 4 H, CH_2), 2.49–2.56 (br m, 4 H, CH_2), 7.21 (br s, 12 H, Ph), 7.38 (br s, 8 H, Ph). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 24.3 ($CH_2CH_2CH_2CH_2$), 25.7 ($CH_2CH_2CH_2CH_2$), 89.5, 105.4 (olefinic C's), 127.8, 128.1, 130.6, 132.3 (Ph), 167.3 (>C=O), 209.6 ($Fe(CO)_3$). IR (cm^{-1}): 3060 w, 2961 w, 2930 m, 2878 w, 2060 vs, 2005 vs, 1985 (sh) vs, 1620 vs, 700 s, 625 s, 615 s, 594 s, 572 s. MS: *m/e* 852 (M$^+$, 1.1%), 824 ((M – CO), 7.9%), 796 ((M – 2CO), 22.4%), 768 ((M – 3CO), 23.7%), 740 ((M – 4CO), 3.2%), 712 ((M – 5CO), 14.1%), 684 ((M – 6CO), 100%), 342 ((M – 6CO)/2, 52.2%). Anal. Calcd for $C_{48}H_{36}Fe_2O_8$ (852.50): C, 67.63; H, 4.26. Found: C, 67.34; H, 4.77.

Bis(η^5-1,2,3,4,5-pentamethyl-2,4-cyclopentadien-1-yl)[μ-(1–4-η:9–12-η)-2,3,10,11-tetraphenyltricyclo[12.2.1.$1^{9,12}$]octadeca-1,3,9,11-tetraene-17,18-dione]dicobalt(I,I) (11c). Bis(η^2-ethene)(η^5-1,2,3,4,5-pentamethyl-2,4-cyclopentadiene-1-yl)cobalt(I) (1.42 g, 5.67 mmol) and 1.60 g (2.79 mmol) of **7** are stirred in 200 mL of toluene at 70 °C for 30 h. After the solution is cooled to room temperature, the precipitate is filtered off, washed with toluene (2 × 20 mL) and *n*-pentane (2 × 10 mL), and dried in vacuo to give 1.82 g (68%) of an orange powder, which is pure enough for synthetic purposes. An analytical sample may be obtained by recrystallization from chloroform and removal of the chloroform included in the dark red crystals by grinding them to a fine powder which is then heated in vacuo to 80 °C for 5 days: decomposition above ca. 260 °C. ^{1}H NMR ($CDCl_3$): δ 1.40 (s, 30 H, Cp*), 1.70–1.93 (br m, 12 H, CH_2), 2.12–2.20 (br m, 4 H, CH_2), 7.13–7.20 (m, 12 H, Ph), 7.25–7.37 (m, 8 H, Ph). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 8.0 ($C_5(CH_3)_5$), 21.7 ($CH_2CH_2CH_2CH_2$), 24.2 ($CH_2CH_2CH_2CH_2$), 83.5, 90.0 (olefinic C's), 90.7 ($C_5(CH_3)_5$), 126.1, 129.3, 131.5, 134.5 (Ph), 148.6 (C=O). ^{59}Co NMR ($CDCl_3$): δ –1445 ($\nu_{1/2}$ = 13 000 Hz). IR (cm^{-1}): 3060 w, 2980 w, 2957 w, 2921 m, 2900 w, 2854 w, 1601 w, 1565 vs, 696 s. MS: *m/e* 960 (M$^+$, 100%), 825 ((M$^+$ – Cp*), 10.3%), 480 (M$^+$/2, 74.2%). Anal. Calcd for $C_{62}H_{66}Co_2O_2$ (961.07): C, 77.48; H, 6.92. Found: C, 77.58; H, 6.88.

(η^4-1,5-Cyclooctadiene)[(2–5-η)-2,3,4,5-tetraphenyl-2,4-cyclopentadien-1-one]nickel(0) (13a). This compound was prepared by variation of the method described by Eisch et al.[22] Bis(η^4-1,5-cyclooctadiene)nickel(0) (430 mg, 1.56 mmol) and 565 mg (1.47 mmol) of tetracyclone (**12**) are stirred in 130 mL of toluene at 45 °C for 2 h and then at room temperature overnight. Concentration of the black solution and cooling to –60 °C yield 542 mg (67%) of black crystals, mp 215–217 °C (216–217 °C[18]). ^{1}H NMR ($CDCl_3$): δ 2.00–2.09 (br m, 2 H, CH_2), 2.26–2.35 (br m, 2 H, CH_2), 2.41–2.52 (br m, 2 H, CH_2), 2.68–2.79 (br m, 2 H, CH_2), 4.00–4.07 (br m, 2 H, CH), 4.21–4.28 (br m, 2 H, CH), 6.83–6.86 (m, 4 H, Ph), 7.04–7.31 (m, 12 H, Ph), 7.67–7.70 (m, 4 H, Ph). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 28.6, 31.6 (CH_2), 94.7 (CH), 96.6 (olefinic C), 103.1 (CH), 105.0 (olefinic C), 126.5, 127.3, 127.7, 130.6, 130.8, 132.4, 132.8 (Ph), 163.2 (C=O). IR (cm^{-1}): 3060 w, 2970 w, 2938 w, 2909 w, 2882 w, 2838 w, 1605 vs, 719 s, 710 s, 695 s, 634 m, 547 m, 517 m. MS: *m/e* 550 (M$^+$, 47.3%), 442 ((M – COD), 100%), 384 (**12**$^+$, 68.1%).

Bis(η^4-1,5-cyclooctadiene)[μ-(η^5:η^5)-17,18-dihydroxy-2,3,10,11-tetraphenyltricyclo[12.2.1.$1^{9,12}$]octadeca-1,3,9,11-tetraene-17,18-diyl]dinickel(II,II) Bis(tetrafluoroborate) (14a). Tetrafluoroboric acid–diethyl etherate (700 mg, 4.32 mmol) in 20 mL of diethyl ether is added dropwise to a suspension of 1.81 g (2.00 mmol) of **11a** in 150 mL of toluene and 40 mL of diethyl ether. After the solution was stirred for 30 min, the precipitate is filtered off, washed with toluene–diethyl ether (20 mL), diethyl ether–*n*-pentane (20 mL), and *n*-pentane (20 mL), and dried in vacuo to give 2.16 g (100%) of a green powder, decomposition above ca. 250 °C. ^{1}H NMR (CD_2Cl_2): δ 1.52–1.70 (br m, 8 H, CH_2), 2.33–2.45 (br m, 8 H, CH_2), 2.70–2.89 (br m, 12 H, CH_2), 3.01–3.13 (br m, 4 H, CH_2), 4.33 (br s, 8 H, CH), 6.98–7.01 (m, 8 H, Ph), 7.25–7.38 (m, 12 H, Ph), 8.35 (br s, 2 H, OH). ^{11}B NMR (CD_2Cl_2): δ –20.5. ^{19}F NMR (CD_2Cl_2): δ –148.4 ($\nu_{1/2}$ = 10 Hz). IR (cm^{-1}): 3225 m, 3052 w, 2953 m, 2883 w, 2833 w, 1600 w, 1575 w, 1485 m, 1455 m, 1440 m, 1430 m, 1095 (sh) vs, 760 s, 711 s. Anal. Calcd for $C_{58}H_{62}B_2F_8Ni_2O_2$ (1082.16): C, 64.38; H, 5.78. Found: C, 64.30; H, 5.72. No interpretable mass spectrum could be obtained.

Bis(η^4-1,5-cyclooctadiene)[μ-(η^5:η^5)-17,18-dihydroxy-2,3,10,11-tetraphenyltricyclo[12.2.1.$1^{9,12}$]octadeca-1,3,9,11-tetraene-17,18-diyl]dinickel(II,II) Bis(trifluoromethanesulfonate) (14b). By a procedure identical with that described for **14a**, 1.20 g (100%) of **14b** is obtained from 906 mg (1.00 mmol) of **11a** and 380 mg (2.53 mmol) of trifluoromethanesulfonic acid as a green powder, decomposition above ca. 250 °C. ^{1}H NMR (CD_2Cl_2): δ 1.52–1.72 (br m, 8 H, CH_2), 2.32–2.45 (br m, 8 H, CH_2), 2.70–2.88 (br m, 12 H, CH_2), 3.07–3.16 (br m, 4 H, CH_2), 4.34 (br s, 8 H, CH), 6.97–7.00 (m, 8 H, Ph), 7.26–7.39 (m, 12 H, Ph), 9.73 (br s, 2 H, OH). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 22.7 ($CH_2CH_2CH_2CH_2$),

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Table V. Crystal Data, Intensity Measurement, and Refinement Parameters for 11a

empirical formula: $C_{58}H_{60}Ni_2O_2 \cdot 4CHCl_3$
cryst system: monoclinic ($Z = 4$)
space group: $C2/c$
$a = 2433.1$ (10) pm, $b = 1425.1$ (6) pm, $c = 1850.0$ (7) pm
$\beta = 97.83$ (3)°
$V = 6354.6 \times 10^6$ pm^3
$d_{\text{calcd}} = 1.45$ g cm^{-3}
μ(Mo Kα) = 11.45 cm^{-1}
$F(000) = 2848$ electrons
radiatn: Mo Kα (graphite monochromator, $\lambda = 71.069$ pm)
scan mode: ω-scan
scan range (2θ): 4–52°
scan width: 1° in ω bisected by K$\alpha_{1,2}$ maximum
scan speed: 2.9–29.3° min^{-1}
bkgd/scantime ratio: 0.6
temp: 294 K
check reflctns: 3 reflctns every 100 reflctns
no. of reflctns measd: 6969 ($+h,+k,\pm l$)
no. of unique reflctns obsd ($F_o > 4.5\sigma(F_o)$): 3317
no. of variables: 354
$R = 0.106^a$
$R_w = 0.117^a$

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = (\sum(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$, $1/w = \sigma^2(F_o) + 0.0001F_o^2$.

26.6 ($CH_2CH_2CH_2CH_2$), 30.9 (CH_2(COD)), 102.9 (cyclopentadienyl rings), 104.7 (CH), 109.5 (cyclopentadienyl rings) 128.6, 129.1, 129.4, 130.5 (Ph), 138.9 (C–OH). ^{19}F NMR (CD_2Cl_2): δ −77.0 ($\nu_{1/2}$ = 2 Hz). IR (cm^{-1}): 3453 m, 3061 w, 2956 m, 2925 m, 2887 w, 1618 w, 1578 w, 1457 m, 1299 s, 1278 s, 1261 s, 1230 s, 1165 s, 1030 s, 763 m, 710 m, 636 s. Anal. Calcd for $C_{60}H_{62}F_6Ni_2O_8S_2$ (1206.66): C, 59.72; H, 5.18. Found: C, 60.08; H, 5.29. No interpretable mass spectrum could be obtained.

Bis(η^4-1,5-cyclooctadiene)[μ-(η^5:η^5)-17,18-diethoxy-2,3,10,11-tetraphenyltricyclo[12.2.1.1^{9,12}]octadeca-1,3,9,11-tetraene-17,18-diyl]dinickel(II,II) Bis(tetrafluoroborate) (14c). **11a** (2.38 g, 2.63 mmol) and 1.07 g (5.80 mmol) of triethyloxonium tetrafluoroborate are stirred in 20 mL of dichloromethane for 24 h. The precipitate is filtered off, washed with dichloromethane (2 × 2 mL), diethyl ether (5 mL), and *n*-pentane (2 × 5 mL), and dried in vacuo to give 2.28 g (76%) of a green powder, decomposition above ca. 250 °C. ^{1}H NMR (CD_2Cl_2): δ 1.30 (t, J = 7.0 Hz, 6 H, OCH_2CH_3), 1.61 (br s, 8 H, CH_2), 2.37–2.46 (br m, 8 H, CH_2), 2.65 (br s, 8 H, CH_2), 2.76–2.90 (br m, 8 H, CH_2), 4.16 (q, J = 7.0 Hz, 4 H, OCH_2CH_3), 4.61 (br s, 8 H, CH), 7.03–7.06 (m, 8 H, Ph), 7.33–7.48 (m, 12 H, Ph). ^{11}B NMR (CD_2Cl_2): δ −17.6 ($\nu_{1/2}$ = 14 Hz). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 16.2 (OCH_2CH_3), 23.0 ($CH_2CH_2CH_2CH_2$), 27.5 ($CH_2CH_2CH_2CH_2$), 31.0 (CH_2(COD)), 70.3 (OCH_2CH_3), 103.8 (CH), 105.9, 108.2 (cyclopentadienyl rings), 129.2, 129.6, 130.2, 130.4 (Ph), 138.9 (*C*–OEt). ^{19}F NMR (CD_2Cl_2): δ −151.1 ($\nu_{1/2}$ = 5 Hz). IR (cm^{-1}): 3059 w, 2981 m, 2933 m, 2892 w, 1600 w, 1517 w, 1503 w, 1440 m, 1379 w, 1342 w, 1284 w, 1207 w, 1100 s, 1062 vs, 1033 s, 781 m, 772 m, 761 m, 706 s. Anal. Calcd for $C_{62}H_{70}B_2F_8Ni_2O_8$ (1138.24): C, 65.42; H, 6.20. Found: C, 64.49; H, 5.70. No interpretable mass spectrum could be obtained.

(μ-η^5:η^5-17,18-Diethoxy-2,3,10,11-tetraphenyltricyclo[12.2.1.1^{9,12}]octadeca-1,3,9,11-tetraene-17,18-diyl)bis(η^5-1,2,3,4,5-pentamethyl-2,4-cyclopentadien-1-yl)dicobalt(III,III) Bis(tetrafluoroborate) (14d). By a procedure identical with that described for **14c**, 603 mg (60%) of **14d** is obtained from 810 mg (0.843 mmol) of **11c** and 322 mg (1.75 mmol) of triethyloxonium tetrafluoroborate as a bright yellow powder, decomposition above ca. 280 °C. ^{1}H NMR (CD_2Cl_2): δ 1.28 (t, J = 6.9 Hz, 6 H, OCH_2CH_3), 1.38–1.56 (br m, 8 H, CH_2), 1.61 (s, 30 H, Cp*), 2.33–2.48 (br m, 8 H, CH_2), 3.99 (q, J = 6.9 Hz, 4 H, OCH_2CH_3), 7.02–7.07 (m, 8 H, Ph), 7.32–7.46 (m, 12 H, Ph). ^{11}B NMR (CD_2Cl_2): δ −19.0 ($\nu_{1/2}$ = 24 Hz). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 9.5 ($C_5(CH_3)_5$), 16.9 (OCH_2CH_3), 21.1 ($CH_2CH_2CH_2CH_2$), 28.1 ($CH_2CH_2CH_2CH_2$), 68.7 (OCH_2CH_3), 90.0, 93.3 (cyclopentadienyl rings), 97.1 ($C_5(CH_3)_5$), 127.4 (*C*–OEt), 128.5, 129.3, 130.0, 131.4 (Ph). ^{19}F NMR (CD_2Cl_2): δ −150.7 ($\nu_{1/2}$ = 4 Hz). ^{59}Co NMR (CD_2Cl_2): δ −292 ($\nu_{1/2}$ = 17000 Hz). MS: *m/e* 1018 ((M − 2BF$_4$), 3.9%), 960 (**11c**$^+$, 100%), 480 (**11c**$^+$/2, 71.8%). IR (cm^{-1}): 3059 w, 2989 m, 2965 m, 2923 m, 1618 w, 1578 w, 1458 m, 1443 m, 1102 s, 1059 vs, 1031 s, 765 m, 710 s. Anal. Calcd for $C_{66}H_{76}B_2Co_2F_8O_2$ (1192.80): C, 66.46; H, 6.42. Found: C, 66.67; H, 6.54.

(η^4-1,5-Cyclooctadiene)(η^5-1-hydroxy-2,3,4,5-tetraphenyl-2,4-cyclopentadien-1-yl)nickel(II) Tetrafluoroborate (14e). By a procedure identical with that described for **14a**, 347 mg (100%) of **14e** is obtained from 300 mg (0.544 mmol) of **13a** and 120 mg (0.741 mmol) of tetrafluoroboric acid–diethyl etherate as a green powder, decomposition above ca. 250 °C; ^{1}H NMR ($CDCl_3$): δ 2.34–2.40 (br m, 4 H, CH_2), 2.87 (br s, 4 H, CH_2), 4.65 (br s, 4 H, CH), 6.78 (br "d", 4 H, Ph), 7.08–7.45 (br m, 13 H, Ph and OH), 7.65 (br "d", 4 H, Ph). ^{11}B NMR $CDCl_3$): δ −19.3 ($\nu_{1/2}$ = 14 Hz). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 30.3 (CH_2), 101.9 (cyclopentadienyl ring), 104.2 (CH), 107.0 (cyclopentadienyl ring), 127.1, 128.4, 128.7, 129.0, 129.2, 130.4, 131.1 (Ph), 140.5 (C–OH). ^{19}F NMR ($CDCl_3$): δ −151.8 ($\nu_{1/2}$ = 18 Hz). IR (cm^{-1}): 3452 w, 3060 w, 2960 w, 2895 w, 2842 w, 1602 m, 1578 m, 1480 (sh) m, 1440 m, 1097 vs, 1079 vs, 1000 s, 971 s, 759 s, 700 vs. MS: *m/e* 550 (**13a**$^+$, 28.5%), 442 ((**13a**$^+$ − COD), 100%), 384 (**12**$^+$, 41.1%). Anal. Calcd for $C_{37}H_{33}BF_4NiO$ (639.18): C, 69.53; H, 5.20. Found: C, 69.66; H, 5.52.

X-ray Structure Determination of 11a. The structure of **11a** was determined from single-crystal X-ray diffraction data (Syntex P2$_1$ four-circle diffractometer). Single crystals were obtained by slow cooling of a hot chloroform solution; they contained four chloroform molecules per **11a** molecule (vide supra). Crystal data and details concerning the intensity data collection and structure refinement are given in Table V. The unit cell parameters were obtained at 21 °C by the least-squares refinement of the angular settings of high-angle reflections (22° < 2θ < 32°). The data were corrected for Lorentz and polarization effects. The check reflections decreased to one-third of the starting intensity due to a decomposition of the crystal (probably due to a loss of $CHCl_3$). All three check reflections decreased by approximately the same amount. From these reflections a decay curve was calculated on which the intensity data were scaled. The structure was solved by direct methods (SHELXTL program package).[23] The H atoms of the phenyl rings were included in the calculations in calculated positions (C–C = 139.5, C–H = 96 pm; C–C–C = C–C–H = 120°). The final least-squares refinements converged at the values given in Table V. The occupancy factors for the disordered $CHCl_3$ molecules were chosen so that the Cl atoms approximately had the same (reliable) U values. They were not refined due to the limited data set. During the last cycles of refinement no parameter shifted more than 0.1σ, where σ is the standard deviation of the parameter. The last difference Fourier synthesis showed no significant maxima; the highest peak in the last difference Fourier map had a magnitude of 0.8 e/Å^3 and was close to a $CHCl_3$ molecule. The atomic scattering factors for all atoms were taken from standard sources.[24] Anomalous dispersion corrections were applied to all atoms.

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Supplementary Material Available: Tables of anisotropic thermal parameters, additional bond lengths and angles, and hydrogen coordinates with temperature factors for **11a** (9 pages); a listing of observed and calculated structure factors (20 pages). Ordering information is given on any current masthead page.

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[23] Nicolet Analytical Instruments, SHELXTL, Revision 5.1, December 1985.

[24] *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.