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Indenyl Crown Ethers: Heterotopic Ligands with π- and σ-Faces and the Synthesis of Cymantrene and Cobaltocene Crown Ethers and Their Alkaline Metal Ion Complexes

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2-Indanone reacts with aza-12-crown-4, aza-15-crown-5, aza-18-crown-6 and diaza-18-crown-6 to give the corresponding enamine 2-indenyl crown ethers **1**−**4** in almost quantitative yields. The indene subunits of **1**−**3** can be deprotonated with *n*-BuLi and reacted with Co(THF)$_3$Br$_2$ to yield—after oxidation—the cobaltocenium salts **5**−**7**. Four oxidation states of the cobaltocene **5** are readily accessible in the CV experiment: $E_{1/2} = -1.99$ V (−I/0, quasireversible), −0.94 V (0/+I), and +0.97 V (+I/+II), with the +I/+II oxidation occurring at an unusually low potential. Addition of LiClO$_4$ or NaClO$_4$ to **5** results in anodic shifts of the 0/+I redox wave of up to +190 mV, whereas the +I/+II redox pair is not at all influenced. The reaction of lithiated **2** with BrMn(CO)$_3$(py)$_2$ gives the corresponding cymantrene crown ether **8**. The X-ray crystal structure of **8** displays a very short indenyl−nitrogen bond distance of 136.2(4) pm. Complexation of Li$^+$ and Na$^+$ by **8** [$E_{1/2}$(0/+I) = +0.91 V] leads to anodic shifts of the redox potential of +100 and +90 mV, respectively, and represents the first example of redox-switched bonding of metal ions involving a cymantrene derivative. Complexation of Li$^+$ and Na$^+$ within the crown ether subunit of **8,** or protonation of the nitrogen atom, gives rise to shifts of the CO-stretching frequencies of up to 36 cm^{-1}; thus it is apparent that the basicity of the metal center can be influenced reversibly by added metal ions.

Introduction

The cyclopentadienyl group is the most common ligand within organometallic chemistry, and a large number of different substitution patterns are known.[1] Crown ethers on the other hand are of similar importance in the coordination chemistry of group I and group II metal ions, since they form highly stable complexes with these metal ions.[2]

We are interested in ligands which combine these two features by offering a π-face (cyclopentadienyl, indenyl) for the coordination of redox-active organometallic fragments and a σ-face (crown ether) for the complexation of group I metal ions.[3] Ideally these two metal sites should interact electronically as close as possible since attractive properties can result from the combination of hard and soft metal centers. One such feature is the redox-switched bonding of alkaline metal ions; another could be the reversible modification of organometallic reactivity[4] and/or catalytic activity by influencing the electron density or basicity at the transition metal center in a subtle way through alkaline metal ions coordinated within the crown ether unit.[5,6]

Macrocycles with appended redox-active groups are of interest since the affinity of the crown ether unit toward metal complexation can be modified by the oxidations state, i.e. the charge at the redox-active substituent (redox-switched crown ether).[7,8] Typical redox-active units include ferrocenes, cobaltocenes, or anthraquinones which are usually connected to the crown ether by a CH$_2$ group.[9] Whereas this methylene linker is advantageous from a synthetic point of view, it is on the other hand effectively blocking the direct electronic communication between the redox-active unit and the metal ion encapsulated within the crown ether, resulting in modest redox responses.[10,11]

We wish to report on the synthesis of novel 2-indenyl crown ethers and the corresponding cobaltocene and cymantrene crown ethers and on the influence of crown

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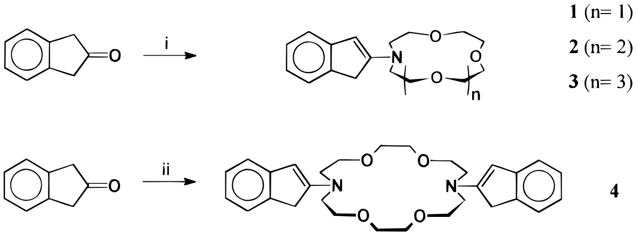
Scheme 1[a]



1 (n= 1)
2 (n= 2)
3 (n= 3)
4

[a] Reagents and conditions: (i) aza-$(3n + 9)$-crown-$(n + 3)$, methanol, reflux; (ii) diaza-18-crown-6, methanol, reflux.

ether complexed alkaline metal ions on the redox potentials and the CO-stretching frequency of the organometallic complexes.

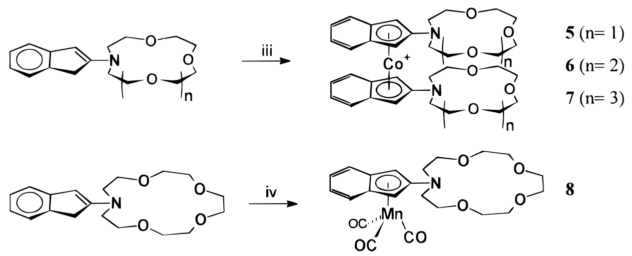
Results and Discussion

We have recently demonstrated that reactions of 3,4-diphenylcyclopent-2-enone or 2-indanone with secondary amines provide facile access to numerous aminocyclopentadienes, in which the nitrogen atom is directly bonded to the five-membered ring. These ligands can be deprotonated and reacted with iron or cobalt salts to yield the respective ferrocenes and cobaltocenes.[12,13] For this study we were interested if the enamine route provides access to the synthesis of azacrown ether substituted indenes even though these macrocycles are sterically demanding amines.

The reactions of aza-12-crown-4, aza-15-crown-5, aza-18-crown-6, or diaza-18-crown-6 with 2-indanone in refluxing methanol result in the formation of the corresponding enamines **1**−**4** and allow the easy synthesis of multigram quantities of these heterotopic ligands (Scheme 1). The yields are almost quantitative, and since purification of the oily products **1**−**3** is difficult, the crude materials were used for all reactions.

The 2-indenyl crown ethers can be deprotonated with n-BuLi in THF without decomposition of the macrocyclic polyether ring. The anion should in principle provide access to numerous η^5-bound metal complexes. We tested the reactions of the lithiated indenes **1**−**3** with $Co(THF)_3Br_2$ in THF at low temperatures and were able to generate the corresponding cobaltocenes and—after oxidative workup with iodine and chromatographic purification—to isolate the cobaltocenium iodides **6** and **7** as dark green highly viscous oils and **5** as a green solid in yields from 43 to 61% (Scheme 2). The iodides were converted into the corresponding perchlorate salts for the electrochemical experiments by reaction with $LiClO_4$. The reaction of lithiated **2** with $BrMn(CO)_3(py)_2$ [$BrMn(CO)_5$ gives much poorer yields] in THF leads in a 60% yield to the cymantrene derivative **8** which also has a crown ether directly linked to the η^5-bonded indenyl unit (Scheme 2). This organometallic crown ether forms complexes with Na^+ as evidenced by a NMR-titration experiment.

Scheme 2[a]



5 (n= 1)
6 (n= 2)
7 (n= 3)
8

[a] Reagents and conditions: (iii) n-BuLi, $Co(THF)_3Br_2$, THF; (iv) n-BuLi, $BrMn(CO)_3(py)_2$, THF.

Table 1. Selected Bond Lengths (Å) for 8

Mn(1)−C(1)	2.147(3)	Mn(1)−C(8)	2.152(3)
Mn(1)−C(7)	2.179(3)	Mn(1)−C(2)	2.184(3)
Mn(1)−C(9)	2.258(3)	C(1)−C(2)	1.430(4)
C(1)−C(9)	1.440(4)	C(2)−C(3)	1.424(4)
C(2)−C(7)	1.425(4)	C(3)−C(4)	1.352(5)
C(4)−C(5)	1.413(6)	C(5)−C(6)	1.356(5)
C(6)−C(7)	1.432(5)	C(7)−C(8)	1.435(4)
C(8)−C(9)	1.427(4)	C(9)−N(1)	1.362(4)

X-ray Crystal Structure of 8. The result of the crystal structure determination (Tables 1 and 2) of **8** is displayed in Figure 1. The indenyl−nitrogen ligand is not planar, and the two planes formed by N(1)−C(9)−C(8)−C(1) and C(1)−C(2)−C(7)−C(8) are tilted by 9° with N(1) and C(9) pointing away from the CO ligands. The C−C distances within the six-membered ring display alternating bond lengths and are best described by a diene structure (Scheme 2), which is not untypical.[14] The indenyl−nitrogen bond of 136.2(4) pm is remarkably short and comparable to the Cp−nitrogen bond in $(C_5H_4NMe_2)_2TiCl_2$.[15] Both short nitrogen bond distances reflect the electron deficiency of the organometallic residue and are much shorter than in related aminoferrocenes (ca. 140 pm).[12]

Cyclic Voltammetry. The redox chemistry displayed by the aminocobaltocenes described here is unusual since four oxidation states are easily accessible: besides the monoanionic cobaltocene with $E_{1/2}(-I/0) = -1.99$ V (quasireversible)[16] the neutral and the monocation $E_{1/2}(0/+1) = -0.93$ V, even the dication can be generated at an unexpectedly low potential $E_{1/2}(+I/+II) = +0.97$ V (Figure 2) with the oxidation to the dication as well as to the monocation being reversible at temperatures of −40° C. This facile second oxidation contrasts the behavior displayed by $(C_5H_5)_2Co$ whose electrochemical oxidation to the dication was described by Bard et al. to occur at an extremely positive potential ($E_{1/2} = +3.15$ V vs SCE in SO_2) which is not normally accessible in organic solvents.[17] It is obvious that this differing behavior of the amino-cobaltocenes has to be attributed to the nitrogen substituents at the indenyl rings, which will help to stabilize a positive charge in the cobaltocene unit by donating lone-pair electron density toward the metal. Upon comparison of the first two redox potentials of $(C_9H_7)_2Co$ ($E_{1/2} = -1.68$ and

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Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 8

	x	*y*	*z*	*U*(eq)[a]
Mn(1)	234(1)	1900(1)	2268(1)	40(1)
C(1)	−122(3)	4364(3)	2154(1)	42(1)
C(2)	−637(3)	3862(3)	2637(1)	41(1)
C(3)	−436(3)	4354(4)	3212(1)	51(1)
C(4)	−1111(3)	3708(5)	3579(2)	61(1)
C(5)	−1970(3)	2517(5)	3405(2)	64(1)
C(6)	−2182(3)	1998(4)	2864(2)	59(1)
C(7)	−1528(3)	2696(4)	2455(1)	44(1)
C(8)	−1567(3)	2488(4)	1858(1)	48(1)
C(9)	−792(3)	3634(4)	1661(1)	43(1)
N(1)	−670(3)	3972(3)	1116(1)	51(1)
C(10)	−1298(4)	3033(4)	654(1)	59(1)
C(11)	−2369(3)	3829(4)	324(2)	64(1)
O(1)	−2761(4)	2888(3)	−153(1)	120(2)
C(12)	−3598(5)	3279(6)	−554(2)	101(2)
C(13)	−4096(8)	4524(6)	−801(3)	173(4)
O(2)	−4153(4)	5892(3)	−474(1)	104(1)
C(14)	−3976(5)	7211(5)	−770(2)	78(1)
C(15)	−3978(4)	8583(5)	−392(2)	76(1)
O(3)	−3082(2)	8526(3)	97(1)	61(1)
C(16)	−1916(3)	8964(4)	−19(1)	54(1)
C(17)	−1001(3)	8680(4)	500(1)	52(1)
O(4)	−772(2)	7047(2)	548(1)	51(1)
C(18)	115(3)	6680(4)	1017(1)	51(1)
C(19)	350(3)	4944(4)	1007(1)	55(1)
C(20)	1008(4)	1214(5)	1714(2)	60(1)
O(5)	1507(3)	764(4)	1362(1)	98(1)
C(21)	1650(3)	2097(4)	2724(2)	59(1)
O(6)	2568(3)	2228(5)	3008(1)	102(1)
C(22)	14(3)	−78(4)	2496(2)	61(1)
O(7)	−111(3)	−1336(4)	2645(2)	98(1)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

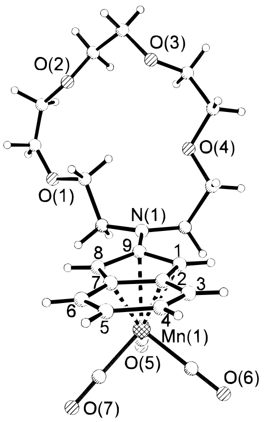

Figure 1. Crystal structure of the cymantrene **8** (indenyl carbon atoms denoted by numbers only).

+0.53 V) and **5** it becomes apparent that the −I/0 and 0/+I redox potentials differ by −290 and −410 mV, respectively.

To test the redox-switching ability, we have performed cyclic voltammetry experiments of **5** and **6** in the presence of $LiClO_4$ and $NaClO_4$. Addition of the respective salts to solutions of the cobaltocene crown ethers **5** and **6** gives continuous anodic shifts of the 0/+I redox potentials of up to +190 mV (Table 3), with the larger shifts being due to 2-to-1 metal−ligand stoichiometries. The anodic shifts observed are smaller than hoped for and indicate that the metal ions are primarily coordinated by the oxygen donors. It is interesting therefore to discuss the anodic shifts of the redox potentials determined for the Na^+ complexes of **5** and **6** in the light of the linear correlation which we observed recently between the inverse Na^+ to Fe distance and the shift of the redox potentials in several ferrocene crown ethers upon addition of Na^+ salts.[10,18] It should be kept in mind that the interaction between the metal ion and the ferrocene unit in the ferrocene crowns described previously was predominantly of an electrostatic nature. Upon comparison of the +90 mV redox shift in **5** and **5**·Na^+ with the +70 mV shift in a ferrocene crown Na^+ complex which is analogous to **5** (except that it has a CH_2 group separating each of the two twelve-membered crowns from the Cp-ring), it becomes apparent that the Co−Na^+ interactions in the compounds described here seem to be mainly of an electrostatic nature. It can thus be concluded that nitrogen is only marginally involved in Na^+ coordination.

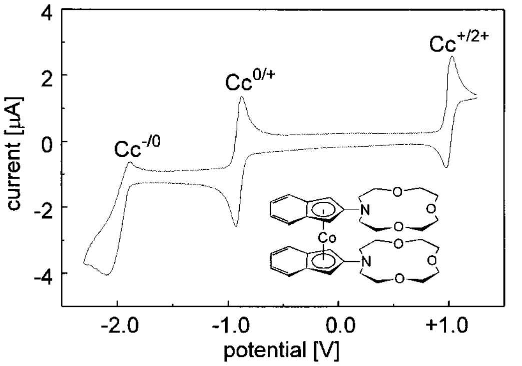

Figure 2. Cyclic voltammogram of **5**: $E_{1/2} = -1.99$ V (quasireversible), $E_{1/2} = -0.94$ V, $E_{1/2} = +0.97$ V (CH_3CN, $T = -35$ °C).

Table 3. Electrochemical Data ($E_{1/2}$, V) for the Cobaltocenes 5 and 6, Cymantrene 8, and Their Complexes with $LiClO_4$ and $NaClO_4$[a]

	ligand (0/+I)	+ Li^+	+ Na^+
5	−0.94	−0.75 (+190)	−0.85 (+90)
6	−0.92	−0.75 (+170)	−0.75 (+170)
8	+0.91	+1.01 (+100)	+1.00 (+90)

[a] Values in parentheses in mV.

It is significant in connection with the redox-switched bonding of metal ions that there is no anodic shift of the redox potentials of the +I/+II redox couple even in the presence of a large excess of metal ions. This is indicative of the fact that the monocationic cobaltocene crown ethers have no affinity toward metal ions and thereby proves the redox-switched bonding of metal ions by these ligands.

The redox chemistry of the cymantrene **8** was also investigated, but at room temperature all cyclic voltammograms only display irreversible oxidation processes. Kochi et al. have shown that a rapid electrocatalytical process leading to the substitution of one CO ligand in cymantrenes occurs if a mere trickle of current is passed through the solution containing the metal complex.[19] In the cyclic voltammogram of **8** a clean reversible oxidation was therefore only observed at scan rates faster than 100 mV/s and at low temperatures (−40 °C). When the potential window is scanned slower, the reduction wave related to the 0 → +I oxidation starts to disappear and a new reduction wave at circa +0.25 V develops

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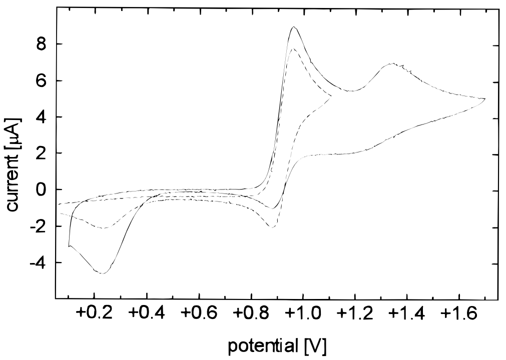

Figure 3. Cyclic voltammograms of **8** (CH_3CN, $T = -40$ °C, 70 mV/s, potential window $+0.1 \rightarrow +1.7$ V; CH_3CN, $T = -40$ °C, 70 mV/s, potential window $0.0 \rightarrow +1.1$ V, dashed line).

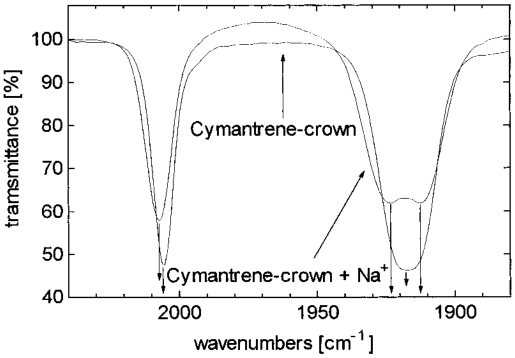

Figure 4. IR spectrum (CO region) of **8** and **8**·$NaClO_4$.

instead, typical for an ECE mechanism (Figure 3). The new reduction wave probably corresponds to a product in which one CO ligand was substituted, either by a solvent molecule or by a donor atom of the crown ether unit. This process is much more pronounced after the potential was held constant at +1.2 V for several seconds. CO substitution becomes also fast even at −40 °C when the potential is scanned up to +1.7 V to initiate a new, quasireversible oxidation process at circa +1.3 V. Upon addition of $LiClO_4$ and $NaClO_4$, respectively, the first redox wave of **8** (+0.91 V vs Ag/AgCl) displays the expected anodic shift of the redox potential of +100 and +90 mV (Table 3).

Infrared Spectroscopy. Stephenson et al. have recently reported on the use of $Cr(CO)_3$-substituted benzocrown ethers as FTIR-readable molecular sensors for metal ions,[20,21] since these compounds experience shifts of ν(CO) of up to 7 cm^{-1} upon complexation of group I metal ions.

We therefore determined the CO-stretching frequencies of the cymantrene **8** with and without added $LiClO_4$ and $NaClO_4$ and observed shifts of up to 2 cm^{-1} upon complexation of metal ions within the aza-crown ethers (Figure 4), which is less than observed by Stephenson et al. The small change of the CO-stretching frequencies may appear somewhat surprising when one considers the respectable redox shifts observed in the cyclic voltammogram. However, whereas electrostatic interactions can be responsible for shifts of the redox potential, they do not necessarily influence IR frequencies since Coulomb forces cannot produce a permanent dipole along a chemical bond which is mobile with respect to the positive charge.

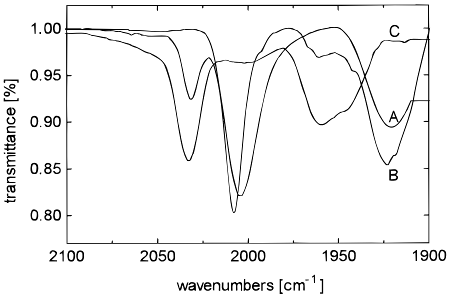

Figure 5. IR spectra of cymantrene crown ether **8** with increasing concentrations of H^+: (A) aqueous $HClO_4$ (+MeOH), pH 0.6; (B) 20% $HClO_4$(aq); (C) 70% $HClO_4$(aq).

A comparision of the ν(CO) of $(C_9H_7)Mn(CO)_3$ (2023, 1950, 1930 cm^{-1}) and **8** (2002, 1920 cm^{-1}, both compounds in KBr) shows that the donor effect of nitrogen leads to substantial shifts of the CO-stretching frequencies. It was obvious therefore to test the protonation of this nitrogen atom, to see if changes in the IR spectrum would be more pronounced. The results are plotted in Figure 5, and it is apparent that the ν-(CO) values are shifted from 2009, 1923 cm^{-1} to 2032, 1959 cm^{-1} upon protonation, which corresponds to a $\Delta\nu = 36$, 23 cm^{-1}. This large effect, however, can only be observed in strongly acidic media, since the electron-withdrawing indenyl−$Mn(CO)_3$ unit very much reduces the basicity of the nitrogen atom. It is therefore only very weakly basic, and even at pH 0.6 (trace A) the IR spectrum is virtually identical to that of the starting material. Protonation of the nitrogen atom is only possible at much higher H^+ concentrations (traces B and C), thus effecting the desired changes of ν(CO) to higher wavenumbers.[22] Addition of base quantitatively regenerates the cymantrene crown ether; therefore, a $\eta^5-\eta^6$ rearrangement of the $Mn(CO)_3$ unit appears unlikely.[23]

Conclusion

Indenyl crown ethers constitute a new class of ligands which offer a π-face for the complexation of organometallic fragments and σ-face for the reversible coordination of group I metal ions. The basicity of the organometallic complex can be changed subtly and reversibly by coordinating alkaline metal ions within the crown ether unit. This is evident from cyclic voltammetry and from IR spectroscopy, and it is hoped for that this principle can be applied to in situ exert fine control over polymerization activity, polymerization characteristics, and microstructure control within organometallic catalysts of, for example, the Ziegler−Natta type.[24]

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Experimental Section

Commercially available solvents and reagents were purified according to literature procedures.[25] All reactions were carried out in dry solvents under a nitrogen atmosphere. Chromatography was carried out with alumina N and silica. NMR spectra were recorded at 300 K with a Bruker AC200 F (^{1}H NMR 200 MHz, ^{13}C NMR 50.3 MHz,) or a Varian Unity 300 (^{1}H NMR 300 MHz, ^{13}C NMR 75.4 MHz). ^{1}H NMR were referenced to residual H-impurities in the solvent, and ^{13}C NMR to the solvent signals: $CDCl_3$ (7.26 ppm, 77.0 ppm), CD_3CN (1.93 ppm, 1.30 ppm), and CD_3COCD_3 (2.04 ppm, 29.8 ppm). Mass spectra: Finnigan MAT 3800. IR spectra were recorded on a Bruker IFS-25: solid materials as KBr tablets, liquids as pure films between NaCl plates, and aqueous solutions as 4 μm films between CaF_2 plates. Elemental analyses were performed at the Mikroanalytisches Laboratorium der Chemischen Laboratorien, Universität Freiburg. Cyclic Voltammetry: The standard electrochemical instrumentation consisted of an Amel System 5000 potentiostat/galvanostat. Cyclic voltammograms were recorded in dry CH_3CN under an argon atmosphere at −40 °C or ambient temperature using Amel software on a PC. A three-electrode configuration was employed. The working electrode was a Pt disk (diameter 1 mm) sealed in soft glass, and the counter electrode, a Pt disk (area 3 cm^2). The pseudoreference electrode was an Ag wire. Potentials were calibrated against the formal potential of cobaltocenium perchlorate (−0.94 V vs Ag/AgCl) or octamethylferrocene (−0.025 V vs Ag/AgCl). Solution were ca. 2×10^{-4} mol dm^{-3} in compound. NBu_4PF_6 (0.1 M) was used as a supporting electrolyte. Starting materials were available commercially or prepared according to literature procedures: diaza-18-crown-6,[26] aza-12-crown-4,[27] aza-15-crown-5 and aza-18-crown-6,[28] $BrMn(CO)_5$,[29] $BrMn(CO)_3(py)_2$.[30]

2-(*N*-Aza-12-crown-4)indene (1). The procedure is analogous to that for **2**. Scale: aza-12-crown-4 (1.28 g, 7.3 mmol), 2-indanone (0.96 g 7.3 mmol). Yield: >90%. ^{1}H NMR ($CDCl_3$): δ 3.45 (t, 4H, 4.8 Hz, NCH_2), 3.51 (s, 2H, Ind-CH_2), 3.61−3.71 (m, 12H, OCH_2), 5.21 (s, 1H, Ind-H), 6.82 (td, 7.3 Hz, 1.2 Hz, 1H, Ind-H), 6.97 (d, 7.3 Hz, 1H, Ind-H), 7.09 (d, 7.4 Hz, 1H, Ind-H), 7.15−7.21 (m, 1H, Ind-H). IR (NaCl) (cm^{-1}): 1570 s (Ind-N).

2-(*N*-Aza-15-crown-5)indene (2). A solution of aza-15-crown-5 (2.5 g, 11.4 mmol) in methanol (50 mL) was heated to reflux, followed by addition of 2-indanone (1.51 g, 11.4 mmol). Heating under reflux was continued for another 120 min, and then the volatiles were removed in vacuo. The remaining oil was dried under vacuo for 3 h and used without further purification. Yield: >90%. ^{1}H NMR ($CDCl_3$): δ 3.40−3.77 (m, 22H, CH_2O, CH_2N, Ind-CH_2), 5.25 (s, 1H, Ind-H), 6.78 (td, 1.2 Hz and 7.2 Hz, 1H, Ind-H), 6.93 (d, 7.0 Hz, 1H, Ind-H), 7.02−7.16 (m, 2H, Ind-H). IR (NaCl) (cm^{-1}): 1588 s (Ind-N).

2-(*N*-Aza-18-crown-6)indene (3). The procedure is analogous to that for **2.** Scale: 507 mg (1.94 mmol) of aza-18-crown-6, 256 mg (1.94 mmol) of 2-indanone in 25 mL of MeOH. Yield: >90%, brown oil. ^{1}H NMR ($CDCl_3$): δ 3.3−3.8 (m, 26H, crown ether, Ind-CH_2), 5.3 (s, 1H, Ind-H), 6.8−7.0 (m, 2H, Ind-H), 7.1−7.2 (m, 2 H, Ind-H). IR (KBr) (cm^{-1}): 1588 s (CN).

Diaza-*N*,*N*′-bis(inden-2-yl)-18-crown-6 (4). The procedure is analogous to that for **2**. Scale: 544 mg (2.1 mmol) of diaza-18-crown-6, 569 mg (4.2 mmol) of 2-indanone in 25 mL of MeOH. A yellow solid was obtained, which was recrystallized from toluene. Yield: 650 mg (63%). IR (KBr) (cm^{-1}): 1586 s (CN). ^{1}H NMR ($CDCl_3$): δ 3.39−3.72 (m, 28H, crown ether, Ind-CH_2), 5.27 (s, 2H, 2 Ind-H), 6.83 (td, 1.1 and 7.1 Hz, 2H, Ind-H), 6.96 (d, 7.1 Hz, 2H, Ind-H), 7.06−7.19 (m, 4H, Ind-H). Anal. Calcd for $C_{30}H_{38}N_2O_4$ (490.64): C, 73.44; H, 7.81; N, 5.71. Found: C, 73.76; H, 7.80; N, 5.91.

Bis[*N*-(aza-12-crown-4)-η^5-inden-2-yl]cobalt(III) Perchlorate (5). The procedure is analogous to that for **6.** The iodide was dissolved in CH_3CN and layered with a solution of $LiClO_4$ in CH_3CN. After several hours the solid perchlorates had precipitated. Scale: **1** (1.82 g, 6.3 mmol), $Co(THF)_3Br_2$ (2.67 g, 6.3 mmol), and *n*-BuLi (2.5 mL, 2.5 M) in 80 mL of THF. Yield: 2.9 g (61%) green solid. ^{1}H NMR (CD_3COCD_3): δ 3.1 (v br), 3.50 (br), 3.6 (v br), 4.0 (v br), 5.49 (s, 2H, Ind-H), 6.86−6.90 (AA′, 4H, Ind-H), 7.15−7.20 (BB′, 4H, Ind-H). ^{13}C NMR (CD_3COCD_3): δ 54.11, 54.61, 68.55, 69.33, 71.06, 91.14, 123.46, 127.34, 129.90. Anal. Calcd for $C_{34}H_{44}CoClN_2O_{10}$ (735.12): C, 55.55; H, 6.03; N, 3.81. Found: C, 55.43; H, 6.09; N 3.69. MS (*m*/*z*): 635 (M$^+$).

Bis[*N*-(aza-15-crown-5)-η^5-inden-2-yl]cobalt(III) Iodide (6). A solution of **2** (308 mg, 0.92 mmol) in THF (30 mL) was cooled to −50 °C and deprotonated with *n*-BuLi (0.41 mL, 2.5 M), whereupon the reaction mixture turned red. After 30 min $Co(THF)_3Br_2$ (195 mg, 0.46 mol) was added. After warming of the solution to room temperature, stirring was continued for another 30 min before the cobaltocene was oxidized to the cobaltocenium salt by addition of I_2 (120 mg, 0.47 mmol). The oxidation is accompanied by a color change from red to green. After removal of the solvent, **6** was obtained as a green oil. The product was purified by column chromatography (alumina N, $CHCl_3/CH_3OH$ = 50:1). Yield: 364 mg (49%). ^{1}H NMR ($CDCl_3$): δ 3.46−3.52 (m, 40H, crown ether), 5.61 (s, 4H, Ind-H), 6.90−6.95 (AA′, 4H, Ind-H), 7.11−7.16 (BB′, 4H, Ind-H). ^{13}C NMR ($CDCl_3$): δ 54.64, 68.09, 69.61, 70.01, 70.82, 91.11, 123.22, 127.34, 129.17. Anal. Calcd for $C_{38}H_{52}CoIN_2O_8$ (850.68): C, 53.65; H, 6.16; N, 3.29. Found: C, 54.06; H, 6.38; N, 3.03. MS (*m*/*z*): 722.5 (M$^+$).

Bis[*N*-(aza-18-crown-6)-η^5-inden-2-yl]cobalt(III) Iodide (7). The procedure is analogous to that for **6**. Scale: **3** (453 mg, 1.20 mmol), 2.5 M *n*-BuLi (0.54 mL, 1.32 mmol), $Co(THF)_3Br_2$ (254 mg, 0.60 mmol), and I_2 (155 mg, 0.61 mmol) in 50 mL of THF. Yield: 209 mg (43%) of a green viscous oil. ^{1}H NMR ($CDCl_3$): δ 3.33−3.54 (m, 48H, crown ether), 5.92 (s, 4H, CpH), 6.70−6.75 (AA′, 4H, Ind-H), 6.85−6.90 (BB′, 4H, Ind-H). ^{13}C NMR ($CDCl_3$): δ 54.60, 68.63, 69.60, 70.23, 70.50, 70.61, 90.93, 123.13, 127.20, 129.71. Anal. Calcd for $C_{42}H_{60}CoIN_2O_{10}$ (938.78): C, 53.74; H, 6.44; N, 2.98. Found: C, 53.61; H, 6.47; N, 3.11. MS (*m*/*z*): 808 (M$^+$).

[η^5-(2-(*N*-aza-15-crown-5)indenyl)]manganese Tricarbonyl (8). The aminoindene **2** (0.70 g, 2.1 mmol) was dissolved in THF (20 mL), and the solution was cooled to −50 °C and deprotonated with *n*-BuLi (0.92 mL, 2.3 mmol). The solution was added to $BrMn(CO)_3(py)_2$ (1.02 g, 2.7 mmol) dissolved in THF (30 mL), and the reaction mixture was stirred for 15 h. The solvent was removed in vacuo and the remaining oil purified by chromatography (silica, ethyl acetate/cyclohexane/Et_2NH). The product was recrystallized from 60/70 petroleum ether. Yield: 63%. ν(CO) = 1915, 1920, 2005 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 3.25 (t, 6.1 Hz, 4H, NCH_2), 3.60−3.66 (m, 12H, CH_2O, CH_2N), 3.73 (t, 6.1 Hz, 4H, CH_2O), 4.65 (s, 2H, Ind-H), 6.97−7.02 (AA′, 2H, Ind-H), 7.40−7.44 (BB′, 2H, Ind-H). ^{13}C NMR ($CDCl_3$): δ 53.53, 55.39, 68.73, 70.06, 70.20, 71.22, 99.68, 124.94, 125.21, 224.2 (br). Anal. Calcd for $C_{22}H_{26}MnNO_7$ (471.39): C, 56.06; H, 5.56; N, 2.97. Found: C, 56.10; H, 5.89; N, 3.34. ^{1}H NMR (CD_3CN): δ 3.19 (t, 6.0 Hz, 4H, NCH_2), 3.50 (s, 4H, CH_2O), 3.56 (s, 8H, CH_2O), 3.67 (t, 6.0 Hz, CH_2O), 4.85 (s, 2H, Ind-H), 7.00−7.05 (AA′, 2H, Ind-H), 7.46−7.51 (BB′, 2H, Ind-H). MS: *m*/*z* 418 (M$^+$ − 2CO), 443 (M$^+$ − CO). ^{13}C NMR (CD_3CN): δ 54.31, 56.90, 69.46, 70.48, 70.88, 71.45, 100.95, 125.86, 126.46, 137.24.

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8·NaClO$_4$. ^{1}H NMR (CD$_3$CN): δ 3.14 (t, 4.8 Hz, 4H, CH$_2$N), 3.57 (s, 4H, CH$_2$O), 3.61 (s, 8H, CH$_2$O), 3.67 (t, 4.8 Hz, 4H, CH$_2$O), 5.05 (s, 2H, Ind-H), 7.06−7.11 (AA′, 2H, Ind-H), 7.51−7.56 (BB′, 2H, Ind-H). ^{13}C NMR (CD$_3$CN): δ 55.10, 60.65, 67.93, 68.82, 70.37, 101.14, 126.56, 126.67, 135.67.

Crystal Structure Determination. Single crystals were prepared by slowly evaporating an ethanol solution of **8** and were mounted on top of a glass fiber. X-ray data were collected on an Enraf-Nonius CAD4 diffractometer using Mo Kα radiation (71.069 pm) and a graphite monochromator. The structure was solved using SHELXS-86[31] and refined with SHELXL-93[32] against F^2. All non-hydrogen atoms were refined using anisotropic temperature coefficients and the hydrogen atoms refined with fixed isotropic temperature coefficients (riding model). An empirical absorption correction (ψ -scans) was applied.

Crystal Data Summary: empirical formula, C$_{22}$H$_{26}$MnNO$_7$; formula weight (g mol^{-1}), 471.39; temperature (K), 293(2); wavelength (Å), 0.710 69; crystal system, monoclinic; space group, $P2_1/n$; unit cell dimensions, $a = 11.106(2)$ Å, $b = 8.524\ (2)$ Å, $c = 23.935(5)$ Å, $\beta = 98.52(3)°$; volume (Å), 2240.9 (8); $Z = 4$; density (g cm^{-3}), 1.397; absorption (mm^{-1}), 0.631; $F(000)$, 984; crystal size (mm), 0.6 × 0.6 × 0.5; θ range (deg), 2.5−26.3; reflections (collected/independent), 4792/4552; data/parameters, 3849/281; GooF = 1.086, final R indices [$I > 2\sigma(I)$] $R1$, w$R2$, 0.0913, 0.2987; extinction coefficient, 0.0074(9); largest peak and hole (e Å^{-3}), +0.524, −0.293. Further details of the crystal structure investigation are available from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany, on quoting the depository number CSD-401607.

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Supporting Information Available: Tables giving the structure determination summary and complete bond lengths, bond angles, and thermal parameters (4 pages). Ordering information is given on any current masthead page.

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