Aminoferrocenes and Aminocobaltocenes as Redox-Active Chelating Ligands: Syntheses, Structures, and Coordination Chemistry[1]

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The enamine reaction can be applied to secondary amines and 3,4-diphenylcyclopentenone to produce the corresponding aminodiphenylcyclopentadienes in yields between 42 and 52%. Deprotonation of these cyclopentadienes and reaction with Fe(II) and Co(II) salts gave the respective diaminotetraphenylferrocenes and diaminotetraphenylcobaltocenes in yields of around 50%. In the amines chosen for our study the nitrogen atoms are part of a chelating ligand, which is able to form complexes with metal ions. Hence, the formation of stable complexes of Zn^{2+} and Co^{2+} salts with 1,1′-bis(di-2-picolylamino)-3,3′,4,4′-tetraphenylferrocene (**12**) was investigated. In the X-ray crystal structure of **12**·2$ZnBr_2$ it is apparent that the nitrogen atoms directly bonded to the ferrocene **12** take part in the coordination of Zn^{2+}. This nitrogen donor thus acts as a relay, enhancing the electronic communication between the redox-active ferrocene center and the metal ion (Zn^{2+} or Co^{2+}); consequently in the cyclic voltammograms of **12** addition of metal salts leads to very large changes in the redox potential of the ferrocene unit. The relative anodic shift upon addition of $Zn(CF_3SO_3)_2$ is $\Delta(\Delta E_{1/2}) = +330$ mV (**12**·Zn^{2+}) and $\Delta(\Delta E_{1/2}) = +720$ mV (**12**·2Zn^{2+}). Upon complexation of Co^{2+} each metal ion produces a $\Delta(\Delta E_{1/2}) = +380$ mV; thus the redox potential of **12**·2Co^{2+} is shifted by $\Delta(\Delta E_{1/2}) = +760$ mV relative to that of **12**. This corresponds to a reduction in the stability constant for the complexation of Co^{2+} by approximately 3.4×10^6 per Co^{2+}. It is apparent therefore that our concept of attaching donor atoms directly to the redox-active ferrocene unit leads to very large redox-switching effects.

Introduction

Numerous ferrocenes have been described in recent years in which the metallocene is linked to a chelating ligand. Interesting effects such as the redox-switched bonding of metal ions within ferrocene crown ethers or investigations into the potential use of such compounds as amperometric sensors for metal ions or protons have been among the highlights of this development.[2,3]

The performance of such molecular devices depends on an efficient electronic communication between the ferrocene and the metal ion coordinated within the chelating ligand. The situation so far has not been ideal as in most ferrocene chelate metal complexes the two metal centers “talk” to each other mainly via Coulomb type interactions.[4] This obviously is a structural consequence of the fact that in most substituted ferrocenes the chelating ligand and the metallocene are separated by a CH_2 group.[2,3] This linker may facilitate the synthesis of these compounds, but it is less ideal from an electronic point of view since this bridge effectively insulates the two metal centers from each other. It is obvious therefore that a transmission of electronic effects via bonding electrons would be much more efficient.[5] The best way to realize this would be to directly link at least one donor atom of a chelating ligand to the cyclopentadienyl ring of a ferrocene. The efficiency of such an approach has recently been demonstrated by Wrighton et al. for metal carbonyl complexes of 1,1′-bis(diphenylphosphino)ferrocene (dppf), where carbonyl reactivity could be modulated reversibly by changing the oxidation state of the appended ferrocene unit.[6]

Our target therefore was to synthesize ferrocenes in which a nitrogen atom bonded to the cyclopentadienyl ring is part of a chelating ligand and can thus act as a transmitter enhancing the electronic communication between two metal centers.

Metallocenes which have a nitrogen atom directly bonded to the five-membered ring are not very common since substitution reactions at the aromatic ring are not straightforward, neither with nitrogen-based nucleophiles nor with electrophiles which are strong oxidants—such as NO_2^+—or relatively unstable compounds such as hydroxylamine derivatives.[7,8]

Up to our work only very few aminocyclopentadienes[9] were known.[10] Probably the best synthesis originates from work by Boche et al., who prepared several *N*,*N*-dialkylaminocyclopentadienes in good yields from O-tosylated *N*,*N*-dialkylhydroxylamines and $C_5H_5^-$. This

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(1) Dedicated to Prof. Dr. M. Herberhold on the occasion of his 60th birthday.

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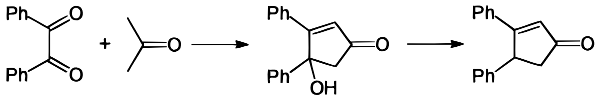
Scheme 1. Synthesis of 3,4-Diphenylcyclopent-2-enone



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approach consequently led to the synthesis of the respective aminoferrocenes as well as other η^5-bound metal complexes in good yields.[11,12] On the other hand, however, the number of hydroxylamines is rather limited and the handling of these compounds poses certain risks,[13] which severly limits the scope of this reaction. Another drawback is the fact that aminocyclopentadienes of the type $C_5H_5NR_2$ are thermally and oxidatively rather sensitive compounds.

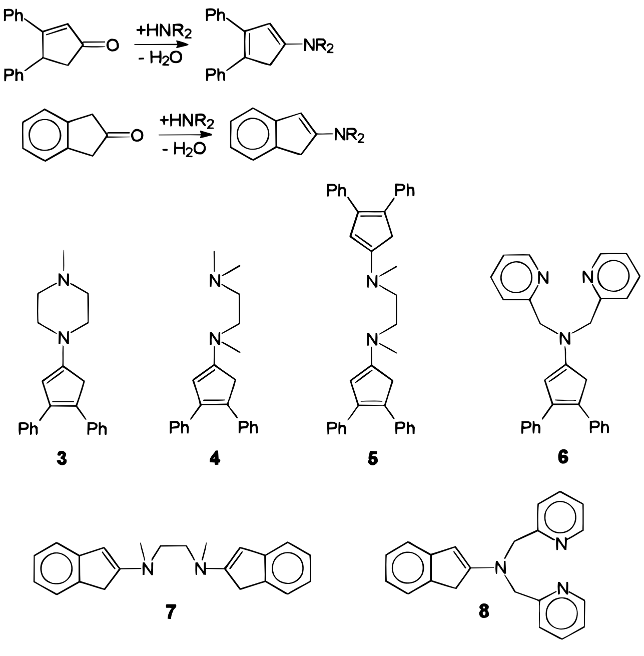
We have recently demonstrated that the enamine reaction of 2-indanone with sec-amines is very efficient in the generation of 2-aminoindenes, which can be used to synthesize the respective η^5-bound complexes such as cymantrenes,[14] zirconocenes,[15] and cobaltocenes.[16]

We wish to report here on a general synthesis of aminocyclopentadienes with chelating ligands in the side chain, on the formation of the respective aminoferrocenes and aminocobaltocenes, on the synthesis of complexes of metal salts with such metallocenes, and on the consequences of metal ion coordination on the redox behavior.[17]

Results and Discussion

Synthesis of the Aminocyclopentadienes and 2-Aminoindenes. To stabilize the aminocyclopentadienes with respect to Diels–Alder dimerization and toward oxidative attack, additional substituents attached to the five-membered ring are required. Consequently 3,4-diphenylcyclopent-2-enone was chosen as a starting material since it is easily available in large amounts (>100 g) in a two-step reaction (Scheme 1) using very cheap starting materials[18,19] and since the two phenyl groups will provide sufficient steric bulk as well as electronic stabilization in the anticipated aminocyclopentadienes.

Scheme 2. Synthesis of the Aminocyclopentadienes and the 2-Aminoindenes



For the synthesis of the aminocyclopentadienes and the 2-aminoindenes described here sec-amines were reacted with 2-indanone and 3,4-diphenylcyclopent-2-enone, respectively. The amines used in this study were deliberately chosen such that they contain additional ligating groups to later allow the formation of classical Werner type complexes. In this way a heteroditopic ligand is generated, which offers a π-face for the bonding of organometallic fragments and a σ-face for the coordination of metal ions.

While the enamine reaction with sec-amines and 2-indanone is well established,[20] up to our work only a single example of enamine formation from a cyclopentenone and an amine had been described.[21] We have thus reacted 3,4-diphenylcyclopent-2-enone with different amines such as *N*-methylpiperazine, trimethylethylenediamine, *N*,*N'*-dimethylethylenediamine, and dipicolylamine in benzene in the presence of catalytic amounts of acid. The reaction is driven to completion by removing the reaction water azeotropically, and the respective aminocyclopentadienes were isolated in yields between 42 and 52%. The enamine formation of 2-indanone with sec-amines is straightforward; consequently the reactions of 2-indanone with dipicolyamine and *N*,*N'*-dimethylethylenediamine yielded the respective 2-aminoindenes in very good yields (Scheme 2).

In principle all sec-amines can be used for the synthesis of aminocyclopentadienes; however, with sterically demanding amines the formation of enamines is rather slow. Changing the solvent from the low boiling benzene to toluene or even xylene is possible with involatile amines and leads to a marked acceleration in the formation of the enamine. Fortunately even long reaction times in high boiling solvents do not lead to significant amounts of unwanted side products as long as the condensation is carried out under strict exclusion of oxygen. Due to the reversibility of enamine formation

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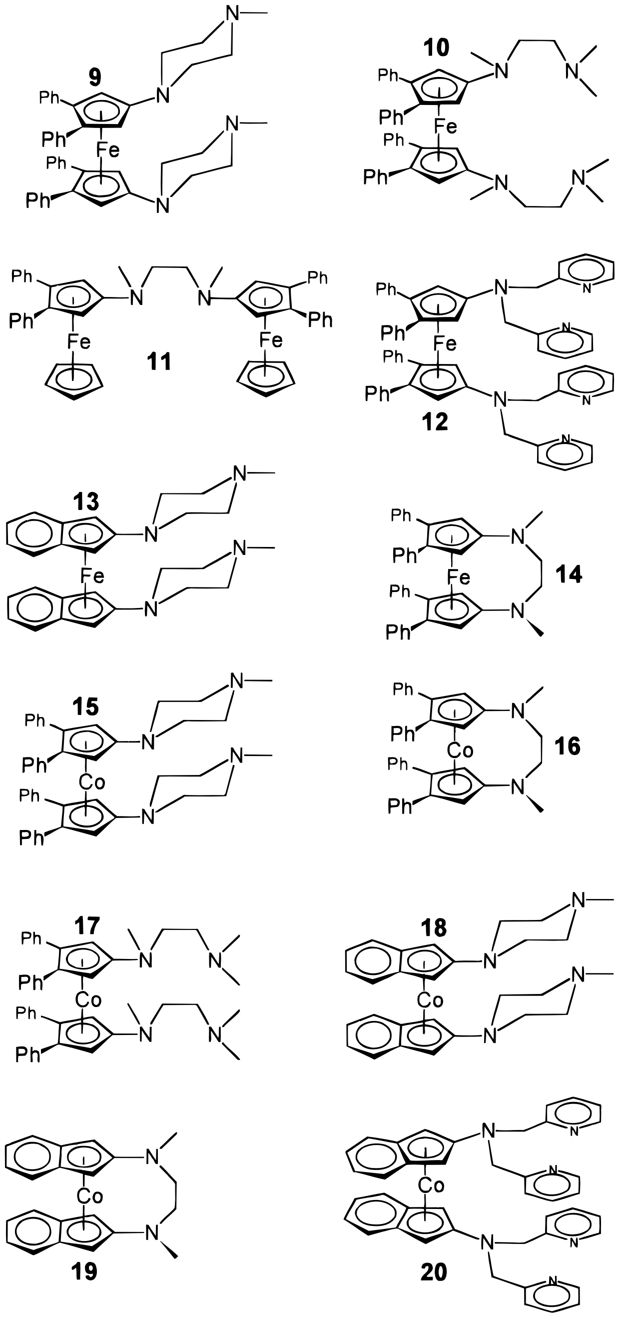
Chart 1. Schematic Drawings of the Aminocobaltocenes and Aminoferrocenes



(only the removal of water shifts the equilibrium toward the enamine side!) workup may be difficult if the crude product is contaminated; thus, care has to be taken to only use high-purity starting materials.

Synthesis of Aminoferrocenes and Aminocobaltocenes. The syntheses of aminoferrocenes and aminocobaltocenes were straightforward in most cases. Typically the aminocyclopentadiene or 2-aminoindene were deprotonated with *n*-BuLi in THF and the respective lithium salt was reacted with $FeCl_2$ or $CoBr_2 \cdot 2THF$ leading to the formation of the respective aminoferrocene or aminocobaltocene (isolated as the cobaltocenium salt after oxidation with iodine) in yields of around 50% (Chart 1). This general procedure was modified for ligands containing the dipicolyl unit such as **6**, to account for the sensitivity of this group toward basic reagents. Whereas the reaction of $Fe(N(i\text{-}Pr)_2)_2$ [generated in situ from $FeCl_2$ and $LiN(i\text{-}Pr_2)_2$] with **6** leads to the desired ferrocene **12** in only 35%, the yield was

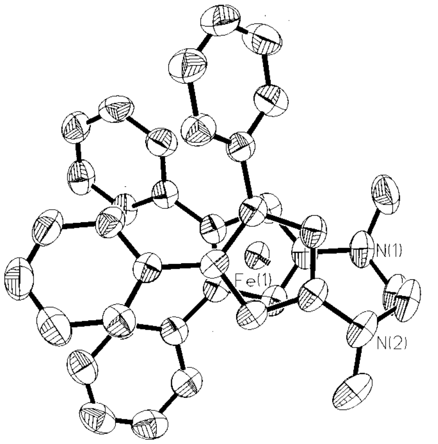
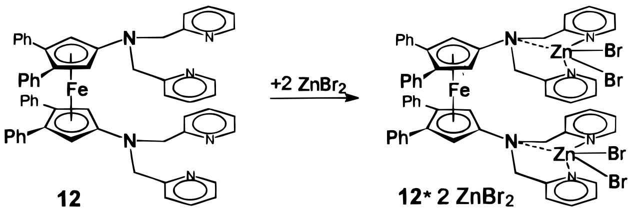


Figure 1. Crystal structure of the ferrocenophane **14** (hydrogen atoms omitted for clarity) viewed along the axis centroid−Fe−centroid.

Scheme 3. Synthesis of the Zinc Complex of 12



substantially increased to a respectable 61% when $Fe(N(i\text{-}Pr)_2)_2$ was produced by using iron(II) acetylacetonate instead of $FeCl_2$. This much higher yield is probably due to the good solubility of iron(II) acetylacetonate in THF. All aminoferrocenes and aminocobaltocenium salts are air-stable metallocenes with the exception of the bis(indenylamino)ferrocene **13** which, like bis(indenyl)ferrocene[22] itself, is a very oxidation sensitive compound that can only be handled in an inert-gas atmosphere.

Crystal Structure of the Ferrocenophane 14. In **14** the two five-membered rings are bridged by an ethylendiamino chain, which leads to a slight tilting of the planes of the two cyclopentadienyl rings by 10.2°. When the structure is viewed along the axis centroid−Fe−centroid′ (Figure 1) it is apparent that all four phenyl groups are arranged such that—upon projection into a plane—they lie in a row. We believe that this is primarily a consequence of the relative orientation of the two Cp rings as imposed by the ethylenediamino bridge and not so much due to steric crowding, since, in crystal structures of related unbridged aminoferrocenes, phenyl groups often tend to be coplanar. However, relative to the five-membered ring of ferrocene the phenyl rings are tilted (26−39° in **14**). A typical feature of all aminoferrocenes is the pronounced shortening of the Cp(C)−N bond [138.8(5), 140.0(3) pm]. This shortening is found in all η^5-complexes of aminocyclopentadienes and is roughly correlated with the electron deficiency of the transition metal center; hence, Cp(C)−N bonds may be as short as 132.5(7) pm in aminozirconocene dichlorides.[15]

Synthesis of Complexes of the Aminoferrocenes with Metal Salts. Ferrocene **10** contains two trimethylethylenediamino groups, and the ferrocene **12**, two dipicolylamino groups; both iron complexes should thus

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Table 1. Crystal Data and Parameter of Structure Refinement Summary

	compd	
	14	**12**·$2ZnBr_2$·$3CH_3CN$
empirical formula	$C_{38}H_{34}FeN_2$	$C_{62}H_{57}Br_4FeN_9OZn_2$
fw (g mol^{-1})	574.52	1416.33
temp (K)	293(2)	293(2) K
cryst system	orthorhombic	monoclinic
space group	*Pbca*	$P2_1/c$
unit cell dimens (pm, deg)		
a	16.934(3)	12.316(2)
b	14.352(3)	13.033(3)
c	23.793(5)	38.752(8)
β		91.06(3)
V (Å)	5783(2)	6219(2)
Z	8	4
D (g cm^{-3})	1.320	1.513
abs (mm^{-1})	0.552	3.610
F(000)	2416	2824
cryst size (mm)	0.6 × 0.6 × 0.5	0.8 × 0.6 × 0.6
θ range (deg)	2.41−25.98	3.06- 26.00
index range (*hkl*)	−20/0, −17/0, −29/0	−15/4, −16/0, −47/47
reflcns collcd/indepdt	5667/5667	12 778/12 179
data/params	4792/373	9289/731
GooF	1.059	1.062
final *R* indices [$I > 2\sigma(I)$]: *R*1, w*R*2	0.0354, 0.0942	0.0552, 0.141
final *R* indices (all data): *R*1, w*R*2	0.0719, 0.299	0.151, 0.202
largest peak and hole (eÅ^{-3})	+0.343, −0.277	+0.579, −0.692

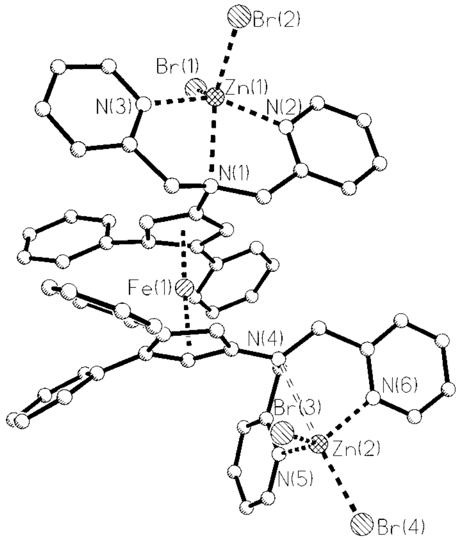

Figure 2. Crystal structure of **12**·$2ZnBr_2$ (hydrogen atoms omitted for clarity).

Table 2. Selected Bond Lengths (pm) and Angles (deg) in 12·2ZnBr₂ (Esd's in Parentheses)

Zn(1)−N(1)	249.3(5)	Zn(2)−N(4)	267.7 (7)
Zn(1)−N(2)	207.6(6)	Zn(2)−N(5)	210.5(6)
Zn(1)−N(3)	208.2(6)	Zn(2)−N(6)	206.1(6)
Zn(1)−Br(1)	238.51(12)	Zn(2)−Br(3)	236.28(14)
Zn(1)−Br(2)	245.05(13)	Zn(2)−Br(4)	244.43(13)
C(1)−N(1)	141.7(8)	C(6)−N(4)	140.1(8)

N(1)−Zn(1)−N(2)	73.5(2)	N(4)−Zn(2)−N(5)	70.8(2)
N(1)−Zn(1)−N(3)	73.5(2)	N(4)−Zn(2)−N(6)	71.1(2)
N(1)−Zn(1)−Br(1)	114.35(12)	N(4)−Zn(2)−Br(3)	89.2(2)
N(1)−Zn(1)−Br(2)	131.07(12)	N(4)−Zn(2)−Br(4)	168.7(2)
N(2)−Zn(1)−N(3)	145.4(2)	N(5)−Zn(2)−N(6)	101.3(2)
N(2)−Zn(1)−Br(1)	99.1(2)	N(5)−Zn(2)−Br(3)	125.1(2)
N(2)−Zn(1)−Br(2)	97.5(2)	N(5)−Zn(2)−Br(4)	101.8(2)
N(3)−Zn(1)−Br(2)	96.5(2)	N(6)−Zn(2)−Br(3)	120.1(2)
N(3)−Zn(1)−Br(1)	73.5(2)	N(6)−Zn(2)−Br(4)	102.8(2)
Br(1)−Zn(1)−Br(2)	114.56(5)	Br(3)−Zn(2)−Br(4)	102.16(5)

be able to form strong complexes with metal salts. To investigate the influence of the ferrocene unit onto the coordination behavior we have reacted **10** and **12** with different zinc salts. After the addition of 2 equiv of $ZnCl_2$ to a solution of **10** dissolved in ethanol, ether was slowly allowed to diffuse into the reaction mixture, which led to the precipitation of a red complex, with the stoichiometry of **10**·$2ZnCl_2$·$4H_2O$.

Addition of $ZnBr_2$ to a solution of **12** in 2-propanol held under reflux led to the precipitation of an orange-colored precipitate, which was redissolved with small amounts of acetonitrile. Slowly cooling this solution led to the formation of X-ray-quality single crystals of the composition **12**·$2ZnBr_2$.

Crystal Structure of 12·2ZnBr₂. In Figure 2 it can be seen that the two $ZnBr_2$ units are easily accommodated by **12**, since the two metal ions and the dipicolylamino unit are located above and below the ferrocene unit (Table 1). To our surprise the two Zn^{2+} ions in this complex display rather different coordination geometries and will thus be discussed separately.

The environment of Zn(1) can be described as roughly trigonal bipyramidal with N(2) and N(3) occupying axial postions, whereas Br(1), Br(2), N(1), and Zn(1) are situated in the equatorial plane, in which also lie the two coplanar pyridine rings. However, the angle N(1)−Zn(1)−N(2) does not amount to the ideal 180° but is only 145° since N(2) and N(3) are drawn toward N(1). Whereas the N(2) and N(3) distances to Zn(1) are normal [207.6(6), 208.2(6) pm], the equatorial N(1) is located at a much longer distance of 249.3(5) pm. Additional bond lengths and angles are listed in Table 2.

The coordination sphere around Zn(1) is comparable to that of L^1ZnBr_2 (L^1 = bis(2-benzimidazol-2-ylmethyl)-methylamine) described by Vahrenkamp et al.[23] and $L^2Zn(SCN)_2$ (L^2 = (bis(2-benzimidazolylmethyl)amino)-ethanol) by Takahashi et al.[24]

The coordination sphere of Zn(2) is quite different to that of Zn(1) and may be described as a distorted tetrahedron consisting of Br(3), Br(4), N(5), and N(6). The aliphatic N(4) attempts to push in between N(5) and N(6) but cannot get closer than 267.7(7) pm to Zn(2), which is almost 20 pm longer than the related Zn(1)−N(1) distance. The coordination geometry around Zn^{2+} may be compared to L^3ZnBr_2 [L^3 = bis(benzimidazol-2-ylmethyl) sulfide][25] in which the bridgehead sulfur at best weakly participates in the bonding of the metal ion.

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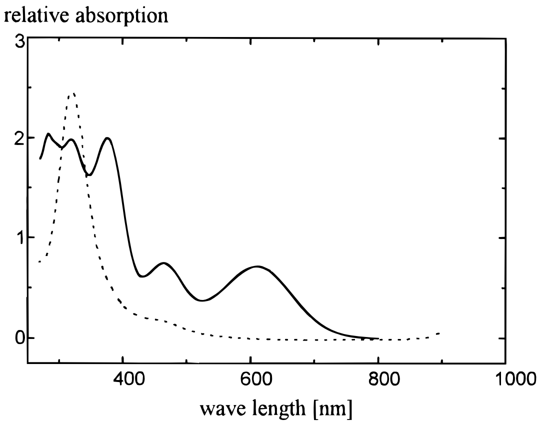

Figure 3. UV spectra of $(C_9H_7)_2Co^+ClO_4^-$ (- - -) and (2-$(Me_2NC_2H_4N(Me))C_9H_6)_2Co^+I^-$ (—).

Table 3. UV Absorptions of Aminocobaltocenes in Ethanol between 250 and 800 nm

cobaltocene	λ (nm)				
$(C_5H_5)_2Co^+PF_6^-$	263	299	405		
16$^+I^-$	249	275	347	443	545
17$^+I^-$	247	291	377	470	
$(C_9H_7)_2Co^+ClO_4^-$	323			460	
18$^+I^-$	302		382	460	608
19$^+I^-$	279		385	463	636

When the somewhat irregular coordination spheres of Zn(1) and Zn(2) are described, it should be remembered that Zn^{2+} is always highly flexible and that the arrangement of the ligating atoms is mainly dominated by the geometrical requirements of the ligand and a maximization of interatom distances around the metal ion (points-on-a-sphere approach[26]).[27]

The Zn(1) and the Zn(2) fragments in **12**·$2ZnBr_2$ have almost the same Zn−N(py) and Zn−Br distances; however, the decisive difference lies in the variable participation of the aliphatic nitrogens N(1) and N(4). The very different roles played by N(1) and N(4) are not reflected in significant differences in the Cp(C)−N bond lengths [141.7(8), 140.1(8) pm] or angles, which are around 114° and thus midway between tetrahedral and trigonal planar. In the solid-state structure of **12** itself,[17] however, angles around nitrogen are closer to trigonal planar (average 118.1°). Other than that bonding parameters within the ferrocene **12** do not change significantly upon complexation of the two $ZnBr_2$. A comparision of the Zn(1) and Zn(2) coordination spheres is therefore well suited to demonstrate that the energy price paid for a transition from a trigonal bipyramidal to a distorted, tetrahedral coordination is small.

UV Spectra. The yellow $(C_5H_5)_2Co^+$ and the yellow-orange $(C_9H_7)_2Co^+$ are very different in color from their nitrogen-substituted relatives, which are dark-red to violet (**15**−**17**) or dark green in the case of the (aminoindenyl)cobaltocenes. As can be seen upon comparing the UV spectra of $(C_9H_7)_2Co^+$ and **17** (Figure 3), the absorption structure of the aminocobaltocenes reveals much more detail.[28] Dominating in all UV spectra is the strong CT band between 247 and 302 nm; other absorptions are observed between 347 and 385, 443 and 470, and 608 and 636 nm (Table 3).

Table 4. Redox Potentials (V vs Ag/AgCl) of the Aminoferrocenes (CH_3CN, Scan 100 mV/s)

	$E_{1/2}(0/+I)$	$E_{1/2}(+I/+II)$	$E_{1/2}(+II/+III)$
$(C_5H_5)_2Fe$	+0.40		
$(C_5H_4N(CH_3)_2)_2Fe$	−0.23	+0.53	+1.23
9	−0.05		
10	−0.20	+0.91	+1.32
11	+0.07	+0.17	
12	−0.10	+0.98	
13	−0.22		
14	−0.01	+1.08	

Table 5. Redox Potentials (V vs Ag/AgCl) of the Aminocobaltocenes (*T* = −40 °C, Scan 50 mV/s)

	$E_{1/2}(-I,0)$	$E_{1/2}(0/+I)$
$(C_5H_5)_2Co$	−1.82[a]	−0.94[b]
$(C_5H_4NMe_2)_2Co$[11]		−1.35[b]
$(C_5H_4NH_2)_2Co$[38]	−2.21[a]	−1.34[a]
$(C_9H_7)_2Co$[39]	−1.68[b]	−0.53[b]
15$^+Br^-$	−1.80	−1.15
16$^+I^-$	*d*	−1.08
17$^+I^-$	−1.88	−1.27
19$^+I^-$	−1.92	−0.89
20$^+I^-$	*d*	−0.81

[a] solvent dmf. [b] solvent CH_3CN. [c] solvent SO_2. [d] not determined.

Cyclic Voltammetry of Aminoferrocenes and Aminocobaltocene. All aminoferrocenes and aminocobaltocenes described here can be oxidized reversibly to the monocation; the respective redox potentials are listed in Tables 4 and 5. For the aminoferrocenes the 0/+I redox potentials range from +0.07 to −0.21 V, which is more negative than ferrocene itself but not as negative as 1,1′-bis(dimethylamino)ferrocene, which can be attributed to the +M-effect of nitrogen on the one side and the electron-withdrawing effect of the phenyl groups on the other.[29] In the case of the aminoferrocenes **9**, **10**, and **12** a second irreversible oxidation was observed between +0.98 and +1.08 V, which is much more positive than the (irreversible) oxidation of $(C_5H_4NMe_2)_2Fe$ (+0.53 V). Another irreversible oxidation process was seen in the CV of **10** at +1.32 V [correspondingly in $Fe(C_5H_4N(CH_3)_2)_2$ at +1.23 V].[11]

The indenylcobaltocenes **18**−**20** are oxidized to the monocation between −0.81 and −0.92 V, and the cyclopentadienylcobaltocenes **15**−**17** between −1.08 and −1.27 V. If the CV experiment is carried out at low temperatures (−40 °C), a reversible reduction to the monoanion is also possible at very negative potentials of between −1.80 and −1.92 V.

Cyclic Voltammetry of the Complexes of Aminoferrocenes and Aminocobaltocenes with Metal Salts. In order to find out whether the nitrogen atoms directly bonded to the cyclopentadienyl ring are able to act as an electronic mediator between the metallocene unit and metal ions coordinated within the chelating ligand, we have determined the redox potentials of the metal complexes of the aminoferrocenes and aminocobaltocenes **10**, **12**, **17**$^+CF_3SO_3^-$, and **20**$^+CF_3SO_3^-$. In order to limit electron transfer processes to the metallocenes we have chosen to investigate complexes with $Zn(CF_3SO_3)_2$ and $Co(CF_3SO_3)_2$ since both metal ions (as well as the anion) are redox-inactive in the potential region investigated.

The redox potentials of the metallocenes **10** and **17** which each have two trimethylethylenediamino ligands

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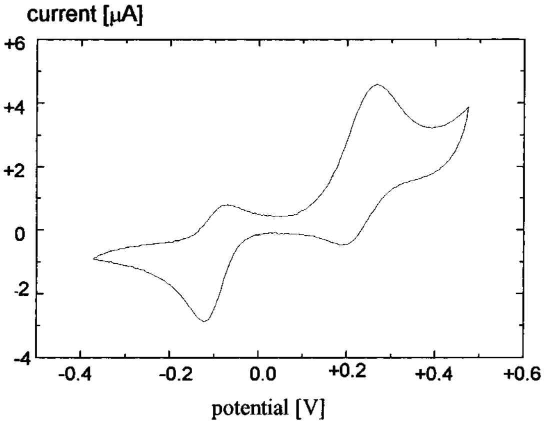

Figure 4. Cyclic voltammogram of **12** in the presence of 0.5 $Zn(CF_3SO_3)_2$.

Table 6. Redox Potentials (V vs Ag/AgCl) of the Aminoferrocenes (10, 12), the Aminocobaltocenes (17, 20), and Their Complexes with $Zn(CF_3SO_3)_2$ or $Co(CF_3SO_3)_2$

	$\Delta E_{1/2}$ (V) (no metal salt)	$\Delta E_{1/2}$ (V) + metal salt	$\Delta(\Delta E_{1/2})$ (mV)
10 + Zn^{2+}	−0.20	−0.01	+190
17 + Zn^{2+}	−1.27	−1.09	+180
12 + 1 Zn^{2+}	−0.10	+0.23	+330
12 + 2 Zn^{2+}		+0.62	+720
12 + 1 Co^{2+}	−0.10	+0.28	+380
12 + 2 CO^{2+}		+0.66	+760
20 + Zn^{2+}	−0.81	−0.20	+610
20 + Co^{2+}	−0.81	−0.17	+640

were determined with and without added zinc salt. In both cases the redox potentials were shifted toward positive potential (Table 6). However, the anodic shifts [$\Delta(\Delta E_{1/2}(\mathbf{10})) = +\ 190$ mV, $\Delta(\Delta E_{1/2}(\mathbf{17})) = +\ 180$ mV] observed are significantly smaller than expected. This becomes more apparent upon comparison of the $\Delta(\Delta E_{1/2})$ values with those obtained by Beer et al. for two ferrocene-substituted azamacrocycle, in which metallocene and chelating ligand are separated by a CH_2 group.[30] In these complexes $\Delta(\Delta E_{1/2}) = +85$ and $+135$ mV were observed upon formation of Zn(II) complexes. The +180 and +190 mV observed by us are even less impressive when considering that **10** as well as **17** coordinate two Zn(II) ions simultaneously. Considering these results, two conclusions are possible: either our concept of nitrogen acting as an electronic mediator is wrong or Zn^{2+} is preferably coordinated by the terminal nitrogen atom and the interaction between the metallocene and Zn^{2+} is mainly of an electrostatic nature. The latter explanation appears more likely since the observed shortening of the Cp(C)−N bond is indicative of a relatively weak donor ability of this nitrogen atom, resulting in a low stability of the Zn(II) complexes of **10** and **17**.

In complexes of **12** and **20** with Zn^{2+} or Co^{2+} the situation should be different since the two pyridine units will considerably increase the stability of the metal complexes.[31] In the CV experiment after addition of 0.5 molar equiv of Zn(II) to a solution of **12** a two-wave situation is observed, which is indicative of the two species **13** [$\Delta E_{1/2} = -0.10$ V] and **12**·Zn^{2+} [$\Delta E_{1/2} = +0.23$ V] (Figure 4). After addition of 2 equiv of $Zn(CF_3SO_3)_2$ only one redox wave corresponding to **12**·$2Zn^{2+}$ is present [$\Delta E_{1/2} = +0.62$ V]. This is a very remarkable result insofar as the redox potential of **12**·$2Zn^{2+}$ is shifted by $\Delta(\Delta E_{1/2}) = +720$ mV with respect to **12**, which is by far the largest metal-induced shift ever obtained! Complexation of two Co(II) ions by **12** leads to even larger shifts $\Delta(\Delta E_{1/2}) = +760$ mV, whereas the $\Delta(\Delta E_{1/2})$ values observed for the cobaltocenes are slightly smaller.

One should attempt to understand what is happening to Zn^{2+} or Co^{2+} after oxidation of the metallocene. The two-wave situation shows that both metal ions remain bound to the metallocene ligand. This may appear surprising when one calculates the reduction in the stability constants upon oxidation using the data from the CV experiments. It is a fairly good approximation to correlate $\Delta(\Delta E_{1/2})$ with the differences in the stability constants of the complexes of the redox-active ligands with metal ions in the different oxidation states.[32] For $\Delta(\Delta E_{1/2}) = +380$ mV for the Co(II) complex results a 3.4×10^6 fold decrease in the stability constant of $\mathbf{12}^{+}\cdot Co^{2+}$ with respect to **12**·Co^{2+},[33] which is an enormous value when compared to typical ferrocene derivatives with a CH_2 group.

It can also be seen in Figure 4 that the electrochemical behavior is not fully reversible for the Zn(II) and Co(II) complexes of **12**, which brings us closer to understand the fate of the metal ions (Zn^{2+} or Co^{2+}) after oxidation of the metallocene unit.

Prior to oxidation the nitrogen bonded to the cyclopentadienyl ring takes part in the bonding of the metal ion, as can be seen in the crystal structure of **12**·$2ZnBr_2$. After oxidation of the metallocene any donor ability of this nitrogen is lost, as is also evident from protonation experiments with aminocobalticinium salts and aminocymantrenes.[14] Furthermore the metal ion (Zn^{2+} or Co^{2+}) will feel a small repulsive electrostatic force from the metallocene. These two factors will lead to the metal ions being pushed toward the periphery of the aminometallocene, where they still can be bonded to the pyridine rings, whose donor ability will not be affected by the oxidation. By moving away from the nitrogen atom, the metal ions are undergoing a reorganization of their coordination sphere, since one nitrogen donor has been lost. This vacant site is probably substituted by solvent molecules or the supporting electrolyte anion (PF_6^-), which may explain the lack of full reversibility in the CV's of the metal complexes of **12**.

Conclusions

We have shown that the enamine route provides an easy access to numerous aminocyclopentadienes, which can be converted in good yields into the corresponding aminoferrocenes and aminocobaltocenes. The X-ray crystal structure of the $ZnBr_2$ complex of 1,1′-bis(di-2-picolylamino)-3,3′,4,4′-tetraphenylferrocene (**12**) shows that the nitrogen atom linked to the cyclopentadienyl ring participates in the bonding of metal ions. The investigation into the redox behavior of the aminoferrocenes and aminocobaltocenes described here proves the succesful realization of our concept in which nitrogen atoms directly bonded to the cyclopentadienyl ring of ferrocene act as highly efficient mediators of electronic

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communication. This was shown experimentally since the anodic shifts in the redox potentials of the metal complexes of **12** [$\Delta(\Delta E_{1/2}) = +720$ mV ($+2Zn^{2+}$) and $\Delta(\Delta E_{1/2}) = +760$ mV ($+2Co^{2+}$)] are by far the largest ever observed in redox-responsive systems. Two factors have been identified to be decisive for such large effects: (1) the nitrogen atom directly bonded to the ferrocene, which acts as a relay for the electronic communication between the redox-active unit and the metal ion; (2) strong additional ligating groups to stabilize the metal ion in the vicinity of the ferrocene bound nitrogen, since this nitrogen atom is not a very good donor.

The oxidation of 1,1′-bis(di-2-picolylamino)-3,3′,4,4′-tetraphenylferrocene effectively switches two donor atoms of the ferrocene, whereas the pyridine units are only marginally influenced. Metal ions which can form stable complexes with the pyridine ligands will remain bonded to **12**, but their coordination number will change, depending on the oxidation state of the ferrocene unit.

We believe that the facile access to aminoferrocenes and aminocyclopentadienes with chelating ligands, electronically coupled to the metallocene, will open the door for a substantial improvement of amperometric sensory devices as well as for the realization of abiotic enzyme models based on molecular switching devices.[34]

Experimental Section

Commercially available solvents and reagents were purified according to literature procedures. All reactions were carried out in dry solvents under a nitrogen atmosphere. Chromatography: 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). ^{1}H NMR were referenced to residual ^{1}H-impurities in the solvent, and ^{13}C NMR, to the solvent signals: $CDCl_3$ (7.26 ppm, 77.0 ppm), C_6D_6 (7.16, 128.0 ppm), CD_3CN (1.93 ppm, 1.30 ppm). Mass spectra: Finnigan MAT 3800. IR spectra: Bruker IFS-25; solid materials as KBr tablets. Elemental analyses: 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 ambient temperature (unless otherwise noted) 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 internally 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. The petroleum ether used was the 60−70 °C cut. The procedures given for 3,4-diphenyl-3-hydroxycyclopent-4-enone and 3,4-diphenylcyclopent-2-enone are modified from the publications by Japp/Knox[18] and Geissman/Koelsch.[19] Starting materials were available commercially or prepared according to literature procedures: dipicolylamine;[31] iron(II) acetylacetonate.[35]

3,4-Diphenyl-3-hydroxycyclopent-4-enone (1). To a stirred suspension of benzil (105.0 g, 0.500 mol) and KOH (0.6 g) in acetone (83 mL, 1.1 mol) and ethanol (0.75 mL) was added a solution of KOH (13.8 g, 0.25 mol) in water (45 mL), whereupon all solid material dissolved with a change of color to brown. The reaction mixture was stirred for 1 h at 60 °C and then poured into hot water, whereupon a brown solid precipitated. This crude product was filtered off, dried, recrystallized from toluene three times, and dried under vacuum. Yield: 103.2 g (82%), yellow powder, mp 147 °C.

^{1}H NMR ($CDCl_3$): δ 2.77−3.05 (m, 2H, CH_2), 3.38 (br, 1H, OH), 6.62−6.66 (m, 1H, CH), 7.23−7.51 (m, 10H, ArH).

3,4-Diphenylcyclopent-2-enone (2). A mixture of 3,4-diphenyl-3-hydroxycyclopent-4-enone (84.1 g, 0.34 mol), HI (14.5 g, 0.05 mol, 45% in H_2O), red phosphorus (18.8 g, 0.58 mol), and glacial acid (330 mL) was heated under reflux for 1 h and then filtered into a cold, vigorously stirred aqueous solution of $Na_2S_2O_3$. A yellow solid consisting of 3,4-diphenylcyclopent-2-enone precipitated, was filtered off, and then redissolved in diethyl ether. This solution was washed with aqueous Na_2CO_3, the etheral layer was separated and dried over $MgSO_4$, and the volatiles were evaporated. The crude product was recrystallized twice from petroleum ether/toluene (2/1). Yield: 47 g (60%), pale-yellow powder, mp108−110 °C.

^{1}H NMR ($CDCl_3$): δ 2.46 (dd, J = 2.0, 18.8 Hz, 1H, *cis*-PhCHC*H*$_2$), 3.12 (dd, J = 7.4, 18.8 Hz, 1H, *trans*-PhCHC*H*$_2$), 4.62 (d, J = 7.3 Hz, 1H, PhC*H*CH$_2$), 6.76 (d, J = 1.4 Hz, 1H, COCH), 7.14−7.33 (m, 8H, ArH), 7.50−7.55 (m, 2H, ArH). ^{13}C NMR ($CDCl_3$): δ 46.71, 46.81, 126.96, 127.08, 127.89, 128.71, 129.06, 129.14, 130.77, 133.26, 142.45, 175.09, 208.01.

1-(*N*-Methylpiperazinyl)-3,4-diphenylcyclopenta-1,3-diene (3). 3,4-Diphenylcyclopent-2-enone (10.0 g, 42.7 mmol), *N*-methylpiperazine (4.56 g, 45.6 mmol), and *p*-toluenesulfonic acid (0.05 g) in benzene (100 mL) were heated under reflux with a water aspirator for 72 h. After removal of the solvent in vacuum the residue was recrystallized from petroleum ether (100 mL) three times. Yield: 7.0 g (52%), pale-yellow powder, mp 88 °C.

Anal. Calcd for $C_{22}H_{24}N_2$ (316.45): C, 83.50; H, 7.64; N, 8.85. Found: C, 83.75; H, 7.84; N, 9.12. IR (KBr): ν 1593 s (CpN), 1548 s (CpN). ^{1}H NMR ($CDCl_3$): δ 2.39 (s, 3H, NCH_3), 2.55 (t, J = 5.2 Hz, 4H, NCH_2), 3.20 (t, J = 5.2 Hz, 4H, NCH_2), 3.58 (s, 2H, CpH_2), 5.43 (s, 1H, CpH), 7.10−7.40 (m, 10H, ArH). ^{13}C NMR ($CDCl_3$): δ 42.45, 46.24, 47.86, 54.47, 105.48, 124.86, 125.42, 126.82, 126.97, 127.99, 128.26, 128.29, 137.44, 138.17, 142.61, 156.73.

1-(*N*,*N*′,*N*′-Trimethylethylenediamino)-3,4-diphenylcyclopenta-1,3-diene (4). A solution of 3,4-diphenylcyclopent-2-enone (10.00 g, 42.6 mmol), trimethylethylenediamine (6.0 mL, 46.9 mmol), and *p*-toluenesulfonic acid (0.05 g) in benzene (150 mL) was heated under reflux for 48 h with a water aspirator. After removal of the solvent in vacuum the residue was recrystallized from petroleum ether three times and the product dried in vacuum. Yield: 6.1 g (45%), yellow powder, mp 77 °C.

Anal. Calcd for $C_{22}H_{26}N_2$ (318.46): C, 82.97; H, 8.23; N, 8.80. Found: C, 83.32; H, 8.50; N, 8.80. IR (KBr): ν 1593 s (CpN), 1570 s (CpN), 1548 s (CpN). ^{1}H NMR ($CDCl_3$): δ 2.29 (s, 6H, $N(CH_3)_2$), 2.51 (t, J = 7.3 Hz, 2H, NCH_2), 2.89 (s, 6H, NCH_3), 3.31 (t, J = 7.3 Hz, 2H, NCH_2), 3.55 (s, 2H, CpH_2), 5.15 (s, 1H, CpH), 7.11−7.37 (m, 10H, ArH). ^{13}C NMR ($CDCl_3$): δ 38.20, 42.52, 45.81, 51.34, 56.37, 101.94, 122.97, 124.34, 126.67, 127.92, 128.20, 128.31, 137.69, 138.52, 143.68, 156.52.

***N*,*N*′-Dimethyl-*N*,*N*′-bis(3,4-diphenylcyclopenta-1,3-dienyl)ethylenediamine (5).** A solution of 3,4-diphenylcyclopent-2-enone (22.00 g, 94.1 mmol), *N*,*N*′-dimethylethylenediamine (5.00 mL, 47.0 mmol) and *p*-toluenesulfonic acid (0.05 g) in benzene (250 mL) was heated under reflux for 48 h with a water aspirator. After removal of the solvent in vacuum the residue was recrystallized from toluene three times and the product dried in vacuum. Yield: 9.3 g (42%), yellow powder, mp 145 °C (dec).

Anal. Calcd for $C_{38}H_{36}N_2$ (520.72): C, 87.65; H, 6.97; N, 5.38. Found: C, 87.35; H, 7.00; N, 5.26. IR (KBr): ν 1593 s (CpN), 1571 s (CpN), 1543 s (CpN). ^{1}H NMR ($CDCl_3$): δ 2.93 (s, 6H, NCH_3), 3.43 (s, 4H, CH_2), 3.55 (s, 4H, CH_2), 5.19 (s, 2H, CpH), 7.09−7.41 (m, 20H, ArH). ^{13}C NMR ($CDCl_3$): δ

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38.70, 42.66, 50.34, 102.20, 123.30, 124.52, 126.78, 126.84, 128.02, 128.31, 128.37, 137.64, 138.51, 143.58, 155.93.

***N*,*N*′-Dimethyl-*N*,*N*′-diinden-2-ylethylenediamine (7).** Dimethylethylenediamine (0.67 g, 7.6 mmol) was added to a stirred solution of 2-indanone (2.00 g, 15.2 mmol) in methanol (14 mL). The white solid which formed during the next 2 h was filtered off, washed with methanol, dried in vacuo, and recrystallized from toluene. Yield: 1.96 g (82%) white powder, mp 157 °C (dec).

Anal. Calcd for $C_{22}H_{24}N_2$ (316.4): C, 83.50; H, 7.64; N, 8.85. Found: C, 82.65; H, 7.53; N, 8.39. IR (KBr): ν 1571.5 s (IndN). ^{1}H NMR ($CDCl_3$): δ 2.93 (s, 6H, NCH_3), 3.38 (s, 4H, NCH_2), 3.43 (s, 4H, $IndH_2$), 5.35 (s, 2H, IndH), 6.86 (dt, J = 1.2, 7.4 Hz, 2H, IndH), 7.02 (d, J = 7.0 Hz, 2H, IndH), 7.11−7.26 (m, 4H, IndH). ^{13}C NMR ($CDCl_3$): δ 37.41, 38.71, 50.52, 96.60, 116.74, 119.84, 122.69, 126.76, 136.46, 147.81, 156.35.

2-(Di-(2-picolylamino)indene (8). 2-Indanone (132 mg, 1.0 mmol) was added to a solution of dipicolylamine (199 mg, 1.0 mmol) and *p*-toluenesulfonic acid (3 mg) in refluxing methanol (10 mL). After the mixture was heated for another 2 h, the volatiles were removed in vacuum. The remaining oil solidified after several hours and was recrystallized from toluene/petroleum ether. Yield: 257 mg (82%), gray powder.

Anal. Calcd for $C_{21}H_{19}N_3$ (313.4): C, 80.48; H, 6.11; N, 13.41. Found: C, 80.12; H, 6.54; N, 12.91. IR (KBr): ν 1587 s, 1572 s (CpN). ^{1}H NMR ($CDCl_3$): δ 3.53 (s, 2H, $IndH_2$), 4.68 (s, 4H, NCH_2py), 5.41 (s, 1H, IndH), 6.84 (t, J = 7.2 Hz, 1H), 6.96 (d, J = 7.2 Hz, 1H), 7.06−7.29 (m, 6H, pyH, IndH), 7.61 (dt, J = 7.6, 1.6 Hz, 2H, pyH), 8.57 (d, J = 4.2 Hz, 2H, pyH).

1,1′-Bis(*N*-methylpiperazinyl)-3,3′,4,4′-tetraphenylferrocene **(9)**. A solution of 1-(*N*-methylpiperazinyl)-3,4-diphenylcyclopenta-1,3-diene (1.00 g, 3.16 mmol) in THF (30 mL) was cooled to −78 °C, and *n*-BuLi (1.36 mL, 3.4 mmol) added, followed after 15 min by $FeCl_2$ (0.20 g, 1.6 mmol). The reaction mixture was then slowly warmed to room temperature and 2 h later the solvent removed in vacuum. The brown residue was washed with acetonitrile (10 mL), and the solid material was filtered off, dried in vacuum, and recrystallized from petroleum ether. Yield: 0.46 g (46%), orange-red powder.

Anal. Calcd for $C_{44}H_{46}N_4Fe$ (686.7): C, 76.96; H, 6.75, N, 8.16. Found: C, 76.46, H, 6.79, N, 7.61. IR (KBr): ν 1639 s, 1487 s, 1451 s. ^{1}H NMR (C_6D_6): δ 2.10 (s, 6H, NCH_3), 2.23 (t, J = 5.1 Hz, 8H, NCH_2), 2.71 (t, J = 5.1 Hz, 8H, NCH_2), 4.18 (s, 4H, CpH), 7.00−7.05 (m, 12H, ArH), 7.49−7.54 (m, 8H, ArH). ^{13}C NMR (C_6D_6): δ 46.34, 49.81, 55.20, 60.32, 82.52, 114.99, 125.91, 127.88, 130.25, 138.66.

1,1′-Bis(*N*,*N*′,*N*′-trimethylethylenediamino)-3,3′,4,4′-tetraphenylferrocene (10). A solution of 1-(*N*,*N*′,*N*′-trimethylethylenediamino)-3,4-diphenylcyclopenta-1,3-diene (1.16 g, 3.63 mmol) in THF (50 mL) was cooled to −50 °C and *n*-BuLi (1.6 mL, 4.0 mmol) added, followed after 10 min by $FeCl_2$ (0.23 g, 1.8 mmol), whereupon the color changed to red-brown. The reaction mixture was slowly warmed to room temperature, and after 2 h the volatiles were removed in vacuum. The product was purified by chromatography (cyclohexane/ethyl acetate/$HNEt_2$ = 5/5/1). Yield: 0.75 g (60%), red solid, mp 46 °C.

Anal. Calcd for $C_{44}H_{50}N_4Fe$ (690.76): C, 76.51; H, 7.30; N, 8.11. Found: C, 76.81; H, 7.40; N, 8.21. IR (KBr): ν 1598 s. ^{1}H NMR (C_6D_6): δ 2.06 (s, 12H, $N(CH_3)_2$), 2.24 (t, J = 7.0 Hz, 4H, NCH_2), 2.42 (s, 6H, NCH_3), 2.90 (t, J = 7.0 Hz, 4H, NCH_2), 4.17 (s, 4H, FcH), 7.07−7.10 (m, 12H, ArH), 7.54−7.57 (m, 8H, ArH). ^{13}C NMR (C_6D_6): δ 30.06, 38.57, 45.84, 52.30, 57.27, 59.60, 81.71, 125.70, 127.83, 130.15, 139.32.

1,1′-Bis(*N*,*N*′,*N*′-trimethylethylenediamino)-3,3′,4,4′-tetraphenylferrocene·2ZnCl$_2$ (10·2ZnCl$_2$). The respective solutions of the ferrocene **10** (14.6 mg, 0.021 mmol) and $ZnCl_2$ (5.8 mg, 0.042 mmol) in ethanol (1 mL each) were mixed. The reaction mixture was filtered and Et_2O allowed to slowly diffuse into the solution. Within several days very small red needles formed.

Anal. Calcd for $C_{44}H_{50}N_4FeZn_2Cl_2 \cdot 4H_2O$ (1035.4): C, 51.01; H, 4.80; N, 5.41. Found: C, 51.57; H, 4.88; N, 5.49. IR (KBr): ν 697 m, 766 m, 1457 m, 1560 ss (CpN), 3443 br (H_2O).

2,5-Diazahexane-2,5-diylbis[(3,4-diphenylcyclopenta-1,3-dienyl)cyclopentadienyliron(II)] (11). *N*,*N*′-Dimethyl-*N*,*N*′-bis(3,4-diphenylcyclopenta-1,3-dienyl)ethylenediamine (1.30 g, 2.5 mmol) in THF (50 mL) was treated with *n*-BuLi (2.0 mL, 5.0 mmol, 2.5 M in hexane). After addition of [CpFe(p-Xylol)]$^+$PF$_6^-$ (1.14 g, 5 mmol), the solution was irradiated for 7 h with a halogen lamp (300 W). Afterward the volatiles were removed in vacuum and the residue purified by chromatography (cyclohexane/$HNEt_2$ = 10/1). Yield: 170 mg (8%), orange-red powder.

Anal. Calcd for $C_{48}H_{44}N_2Fe_2$ (760.59): C, 75.80; H, 5.83; N, 3.68. Found: C, 75.90; H, 5.58; N, 3.53. MS, *m*/*z* (%): 760 (80) [M$^+$]. IR (KBr): ν 1523 s, 1496 s. ^{1}H NMR (C_6D_6): δ 2.46 (s, 6H, NCH_3), 3.01 (s, 4H, NCH_2), 4.10 (s, 5H, CpH), 4.26 (s, 4H, CpH), 7.05−7.10 (m, 12H, ArH), 7.50−7.55 (m, 8H, ArH). ^{13}C NMR (C_6D_6): δ 39.78, 52.98, 57.42, 70.90, 81.85, 114.56, 126.27, 128.27, 130.14, 139.48.

1,1′-Bis(di-2-picolylamino)-3,3′,4,4′-tetraphenylferrocene (12). To a mixture of iron(II) acetylacetonate (50 mg, 0.5 mmol) and $Li(N(C_3H_7)_2)$ (107 mg, 1 mmol) in THF (15 mL) held at −78 °C was added 1-(di-(2-picolylamino)-3,4-diphenylcyclopenta-1,3-diene (414 mg, 1 mmol). The reaction mixture was slowly warmed to room temperature. After 2 h the volatiles were removed in vacuum and the residue was purified by chromatography (cyclohexane/ethyl acetate/$HNEt_2$ = 10/1/1) and by recrystallization from petroleum ether/toluene. Yield: 270 mg (61%), orange-red powder.

Anal. Calcd for $C_{58}H_{48}N_6Fe$ (884.9): C, 78.25; H, 5.50; N, 9.78. Found: C, 78.72; H, 5.47; N, 9.50. IR (KBr): ν 698 s, 760 vs, 1436 s, 1501 vs, 1523 vs, 1593 s. ^{1}H NMR (C_6D_6): δ 4.19 (s, 4H, CpH), 4.23 (s, 8H, NCH_2py), 6.25 (ddd, J = 1.3, 4.8, 7.4 Hz, 4H, pyH), 6.60−6.80 (m, 20H, pyH, ArH), 7.17−7.23 (m, 8H, pyH, ArH), 8.10 (ddd, J = 0.9, 1.8, 4.8 Hz, 4H, pyH). ^{13}C NMR (C_6D_6): δ 59.06, 60.81, 82.03, 116.61, 121.73, 122.40, 125.88, 127.90, 130.20, 135.92, 139.17, 149.51, 159.95.

1,1′-Bis(di-2-picolylamino)-3,3′,4,4′-tetraphenylferrocene·2ZnBr$_2$ (12·2ZnBr$_2$). To a solution of the ferrocene (28.2 mg, 0.032 mol) in 2-propanol (5 mL) held at reflux was added a solution of $ZnBr_2$ (14.4 mg, 0.064 mmol) in the same solvent. An orange-red solid immediately precipitated, which was redissolved by careful addition of CH_3CN. Upon slowly cooling this solution to room temperature, X-ray-quality crystals were grown.

Anal. Calcd for $C_{58}H_{48}N_6FeZn_2Br_4$ (1335.2): C, 51.78; H, 3.30; N, 6.13. Found: C, 52.17; H, 3.62; N, 6.29. IR (KBr): ν 699 s, 765 ss, 1442 s, 1488 ss, 1572 s.

Bis[2-(methylpiperazinyl)indenyl]iron(II) (13). 2-(*N*′-methylpiperazinyl)indene (944 mg, 4.41 mmol) was dissolved in THF (50 mL), cooled to −60 °C, and treated with *n*-BuLi (2.9 mL, 4.4 mmol, 2.5 M in hexane), whereupon the color changed from yellow to orange-red. After 15 min $FeCl_2$ (280 mg, 2.21 mmol) was added, the reaction mixture was slowly warmed to room temperature and stirred for 2 h, and then the volatiles were removed in vacuum. The residue was recrystallized from toluene/petroleum ether. Yield: 490 mg (46%), gray-green powder.

Anal. Calcd for $C_{28}H_{34}N_4Fe$ (482.39): C, 69.72; H, 7.10; N, 11.61. Found: C, 69.36; H, 6.94; N, 11.35. MS, *m*/*z* (%): 482 (95) [M$^+$]. ^{1}H NMR (C_6D_6): δ 2.19 (s, 6H, NCH_3), 2.35 (t, J = 5.1 Hz, 8H, NCH_2), 3.07 (t, J = 5.1 Hz, 8H, NCH_2), 4.01 (s, 4H, CpH), 6.97−7.02 (m, 4H, ArH), 7.31−7.36 (m, 4H, ArH). ^{13}C NMR (C_6D_6): δ 30.16, 46.41, 46.91, 49.84, 55.22, 84.18, 116.13, 122.93, 130.79.

{2,5-Diazahexane-2,5-diylbis[3,4-diphenylcyclopentadienyl]}iron(II) (14). A solution of *N*,*N*′-dimethyl-*N*,*N*′-bis(3,4-diphenylcyclopenta-1,3-dienyl)ethylenediamine in THF (50 mL) was cooled to −78 °C and *n*-BuLi (2.9 mL, 7.37 mmol) added, followed after 10 min by $FeCl_2$ (0.42 g, 3.4 mmol), whereupon the color changed to brown-red. The reaction mixture was slowly warmed to room temperature, and after 2 h the volatiles were removed in vacuum. The product was purified by chromatography (cyclohexane/ethyl acetate = 10/1, N_2 atmosphere!) and then recrystallized from petroleum ether. Yield: 0.84 g (44%), orange-red powder, mp 218 °C.

Anal. Calcd for $C_{38}H_{34}N_2Fe$ (574.55): C, 79.44; H, 5.97; N, 4.88. Found: C, 79.22; H, 6.11; N, 4.62. MS, *m*/*z* (%): 574 (95) [M$^+$]. IR (KBr): ν 1598 m, 1525 s, 1502 s. ^{1}H NMR

(C_6D_6): δ 2.60 (s, 6H, NCH_3), 2.95 (s, 4H, NCH_2), 4.60 (s, 4H, FcH), 6.92−7.02 (m, 12H, ArH), 7.34−7.39 (m, 8H, ArH). ^{13}C NMR (C_6D_6): δ 38.49, 48.86, 57.68, 82.99, 111.42, 125.96, 127.78, 129.71, 138.78.

1,1′-Bis(*N*-methylpiperazinyl)-3,3′,4,4′-tetraphenylcobaltocenium(III) Bromide (15^+Br^-). A solution of 2-(*N*-methylpiperazinyl)indene (1.50 g, 4.74 mmol) in THF (30 mL) was cooled to −78°C and treated with *n*-BuLi (2.03 mL, 5.1 mmol, 2.5 M in hexane). After addition of $CoBr_2\cdot 3THF$ (0.99 g, 2.3 mmol) the reaction mixture was slowly warmed to room temperature and stirred for 2 h, and I_2 (0.30 g, 1.2 mmol) was added. The volatiles were removed in vacuum and the residue was purified by chromatography ($MeOH/HNEt_2$ = 10/1). Yield: 0.80 g (21%), dark-red powder.

Anal. Calcd for $C_{44}H_{46}BrCoN_4$ (769.7): C, 68.66; H, 6.02; N, 7.28. Found: C, 68.95; H, 6.35; N, 7.41. IR (KBr): ν 1558 s. ^{1}H NMR (CD_3OD): δ 2.20 (s, 6H, NCH_3), 2.32 (br., 8H, NCH_2), 2.78 (br, 8H, NCH_2), 5.38 (s, 4H, CpH), 7.18−7.35 (m, 20H, ArH). ^{13}C NMR (CD_3OD): δ 6.00, 48.26, 54.82, 65.82, 96.75, 129.14, 129.83, 130.21, 131.19, 132.54.

1,1′-Bis(*N*-methylpiperazinyl)-3,3′,4,4′-tetraphenylcobaltocenium(III) Triflate ($15^+CF_3SO_3^-$). 15^+Br^- (327 mg, 0.42 mmol) was dissolved in acetonitrile (50 mL) and treated with $AgCF_3SO_3$ (103 mg, 0.41 mmol). Precipitated AgBr was filtered off, the filtrate evaporated in vacuum, and the residue recrystallized from toluene. Yield: 220 mg (65%), dark red powder. An analogous procedure was chosen to synthesize all other cobaltocenium triflates.

Anal. Calcd for $C_{45}H_{46}CoF_3N_4SO_3\cdot 2CH_3OH$ (870.9): C, 62.52; H, 6.03; N, 6.20. Found: C, 62.67; H, 5.76; N, 5.99. IR (KBr): ν 1555 s, 1260 s (CF_3SO_3), 1030 s (CF_3SO_3). ^{1}H NMR (CD_3CN): δ 2.21 (s, 6H, NCH_3), 2.30 (br, 8H, NCH_2), 2.87 (br, 8H, NCH_2), 5.21 (s, 4H, CpH), 7.21−7.43 (m, 20H, ArH). ^{13}C NMR (CD_3CN): δ 46.05, 48.31, 54.49, 65.39, 96.02, 129.20, 129.58, 129.96, 130.97, 132.28.

2,5-Diazahexan-2,5-diylbis[3,4-diphenylcyclopentadienyl]cobalt(III) Iodide (16^+I^-). Synthesis is as described for **15**: *N*,*N*′-dimethyl-*N*,*N*′-bis(3,4-diphenylcyclopenta-1,3-dienyl)ethylenediamine (474 mg, 0.91 mmol), *n*-BuLi (0.8 mL, 2.0 mmol, 2.5 M in hexane), $CoBr_2\cdot 3THF$ (396 mg, 0.91 mmol), I_2 (115 mg, 0.46 mmol), chromatography (Alu-N, $CHCl_3$), recrystallization from ethanol. Yield: 0.262 g (41%), dark purple crystals, mp 120 °C (dec).

Anal. Calcd for $C_{38}H_{34}CoIN_2\cdot 1.5C_2H_5OH$ (773.6): C, 63.65; H, 5.60; N, 3.62. Found: C, 63.71; H, 5.44; N, 3.69. MS, *m*/*z* (%): 577 (95) [M^+]. IR (KBr): ν 1549 s. ^{1}H NMR (CD_3CN, 330 K): δ 3.35 (s, 10H, NCH_3, NCH_2), 6.06 (s, 4H, 4 CpH), 7.10−7.13 (m, 16H, ArH), 7.29−7.32 (m, 4H, ArH). ^{13}C NMR (CD_3CN): δ 40.45, 48.62, 126.58, 129.43, 130.13, 130.36.

1,1′-Bis(*N*,*N*′,*N*′-trimethylethylenediamino)-3,3′,4,4′-tetraphenylcobaltocenium(III) Iodide (17^+I^-). Synthesis is as described for **15**: 1-(*N*,*N*′,*N*′-trimethylethylenediamino)-3,4-diphenylcyclopenta-1,3-diene (577 mg, 1.81 mmol), *n*-BuLi (0.8 mL, 2.0 mmol, 2.5 M in hexane), $CoBr_2\cdot 3THF$ (396 mg, 0.91 mmol), I_2 (115 mg, 0.46 mmol), chromatography (Alu-N, MeOH), recrystallization from methanol. Yield: 410 mg (55%), red solid, mp 307 °C.

Anal. Calcd for $C_{44}H_{50}CoIN_4\cdot CH_3OH$ (852.8): C, 61.97; H, 5.87; N, 6.57. Found: C, 62.23, H, 6.05; N, 6.83. IR (KBr): ν 1560 s. ^{1}H NMR (CD_3CN): δ 2.15 (s, 12H, $N(CH_3)_2$), 2.31 (m, 8H, NCH_2), 2.62 (s, 6H, NCH_3), 5.13 (br, 4H, CpH), 7.18−7.40 (m, 20H, ArH). ^{13}C NMR (CD_3CN): δ 30.06, 38.55, 45.84, 52.28, 57.29, 59.58, 81.73, 125.69, 127.82, 130.14, 139.31.

Bis[2-(*N*-methylpiperazinyl)indenyl]cobalt(III) Iodide (18^+I^-). Synthesis is as described for **15**: 2-(*N*-methylpiperazinyl)indene (273 mg, 1.3 mmol), *n*-BuLi (0.52 mL, 1.3 mmol, 2.5 M in hexane), $CoBr_2\cdot 3THF$ (280 mg, 0.64 mmol), I_2 (100 mg, 0.39 mmol), chromatography (10/1 $MeOH/Et_2NH$). Yield: 179 mg (49%), dark green solid.

Anal. Calcd for $C_{28}H_{34}N_4CoIN_4$ (612.44): C, 54.91; H, 5.56; N, 9.15. Found: C, 54.48; H, 5.52; N, 9.19. MS, *m*/*z* (%): 485 (2) [M^+]. IR (KBr): ν 1532 s. ^{1}H NMR (CD_3CN, 320 K): δ 2.54 (br, 16H, NCH_2), 3.16 (br., 6H, NCH_3), 5.54 (s, 4H, IndH), 6.65−6.70 (AA′, 4H, IndH), 7.24−7.29 (BB′, 4H, IndH). ^{13}C NMR (CD_3CN): δ 45.95, 48.47, 54.08, 54.43, 91.70, 123.44, 128.51, 130.61.

[2,5-Diazahexan-2,5-diylbis(2-indenyl)]cobalt(III) Iodide (19^+I^-). Synthesis is as described for **15**: *N*,*N*′-dimethyl-*N*,*N*′-di-inden-2-ylethylenediamine (0.40 g, 2.5 mmol), *n*-BuLi (0.24 mL, 5.6 mmol, 2.5 M in hexane), $CoBr_2\cdot 3THF$ (1.10 g, 2.5 mmol), I_2 (0.32 g, 1.3 mmol), chromatography (Alu-N, 50/1 $CHCl_3/MeOH$). Yield: 600 mg (35%), dark green powder.

Anal. Calcd for $C_{22}H_{22}N_2CoI$ (500.26): C, 52.82; H, 4.43; N, 5.60. Found: C, 52.91; H, 4.56; N, 5.60. MS, *m*/*z* (%): 373 (95) [M^+]. IR (KBr): ν 1542 s. ^{1}H NMR (CD_3CN, 335 K): δ 3.34 (s, 6H, NCH_3), 3.82 (s, 4H, NCH_2), 6.14 (s, 4H, IndH), 6.90−6.95 (AA′, 4H, IndH), 7.17−7.22 (BB′, 4H, IndH). ^{13}C NMR (CD_3CN, 330 K): δ 40.73, 48.12, 57.94, 123.53, 129.22.

Bis(2-(di-2-picolylamino)indenyl)cobalt(III) Iodide (20^+I^-). To 2-(di-2-picolylamino)indene (0.840 g, 2.7 mmol) in THF (25 mL) at −60 °C was added a solution of $Li(N(C_3H_7)_2)$ (0.28 mg, 2.7 mmol) in THF (5 mL), followed immediately by $CoBr_2\cdot 3THF$ (1.08 g, 2.5 mmol). The solution slowly allowed to room temperature and treated with I_2 (0.17 g, 0.7 mmol) after 1 h, whereupon the color changed from red to green. The volatiles were removed in vacuum and residue purified by chromatography (Alu-N; 50/1 $CHCl_3/MeOH$). Yield: 300 mg (30%), green solid.

Anal. Calcd for $C_{42}H_{36}N_6CoI$ (810.6): C, 62.23; H, 4.44; N, 10.27. Found: C, 61.40; H, 4.52; N, 10.29. IR (KBr): ν 1532 s. ^{1}H NMR ($CDCl_3$): δ 4.73 (s, 8H, CH_2py), 5.59 (s, 4H, IndH), 6.93 (AA′, 4H, IndH), 7.11 (ddd, *J* = 1.0, 4.9, 7.4 Hz, 4H, pyH), 7.21 (BB′, 4H, IndH), 7.36 (d, *J* = 8 Hz, 4H, pyH), 7.55 (dt, *J* = 1.8, 7.7 Hz, 4H, pyH), 8.46 (d, *J* = 7.2 Hz, 4H, pyH). ^{13}C NMR ($CDCl_3$): δ 38.70, 42.66, 50.34, 102.20, 123.30, 124.52, 126.78, 126.84, 128.021, 128.31, 128.37, 137.64, 138.51, 143.58, 155.93.

Crystal Structure Determinations. Single crystals 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[36] and refined with SHELXL-93[37] 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. Complex $\mathbf{12}\cdot 2ZnBr_2$ crystallizes with three solvent molecules (CH_3CN) of which two are badly disordered. The solvent molecules do not interact with the ferrocene−zinc complex. Further details of the crystal structure investigations are available on request from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany, on quoting the depository numbers CSD-405162 and CSD-405163, the names of the authors, and the journal citation.

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Supporting Information Available: Tables giving the structure determination summary and complete bond lengths, bond angles, and positional and thermal parameters (10 pages). Ordering information is given on any current masthead page.

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