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Synthesis, Structural Characterization, and Properties of a New Range of Strained 2-Aza[3]ferrocenophane Ligands: Dual Behavior as Electrochemical Sensors of Metal Ions or Anions

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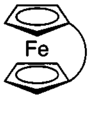
The synthesis of structurally new types of strained 2-aza[3]ferrocenophanes, **9** and **10**, which comprise a benzoquinuclidine framework incorporating a 1,1′-disubstituted ferrocene unit is reported. These compounds were prepared in four steps from the readily available 1,1′-diacetylferrocene and thoroughly characterized by spectroscopic means and electrochemical methods. The ligands **9** and **10** act as electrochemical sensors either of Mg^{2+}, Zn^{2+}, and Ni^{2+} cations (free ligands), where a new redox peak appears in the CV shifted 310−350 mV, or hydrogensulfate anion (protonated ligand) via a significant cathodic perturbation. The crystal structures of compounds **9** and **9b** (**9**·$HClO_4$) have been determined by single-crystal X-ray methods. In the latter compound the anion and cation are associated onto ribbons parallel to the *z* axis by four hydrogen bonds.

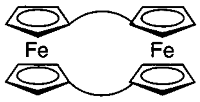
Introduction

The most prevalent organometallic analogues of cyclophanes are the ferrocenophanes with a bivalve-like structure, in which the two cyclopentadienyl rings of ferrocene are joined by an atomic or molecular bridge. In these sorts of compounds many of the desirable characteristics of the parent ferrocene are retained and they are expected to show unique chemical properties owing to functionality of the sidearm.

There have been many different classes of ferrocenophanes described; most of them possess exclusively carbon-based bridges with three modes of ring attachment[1]: mononuclear [*m*]ferrocenophanes (type I), mononuclear multiply bridged [m^n]ferrocenophanes (type II) and multinuclear [m^n]ferrocenophanes (type III).



I



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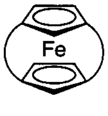

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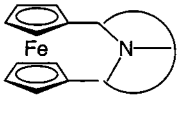

IV

Ferrocenophanes of types I and II in which the bridge contains the heteroatoms phosphorus, silicon, and sulfur have also been described.[2] To establish new properties and further potential applications of these fascinating compounds, one avenue of special interest would be to create ferrocenophane architectures which additionally incorporate sites in the bridge for the purpose of binding metal ions. The combined structural features comprising rigid preorganization, spatially well-defined shape, and electronically linked metal ions would yield a new class of organometallic materials that would be expected to display a range of physicochemical properties in addition to those of the parent ferrocene. However, despite the rich functionality on the sidearm aza[*m*]ferro-

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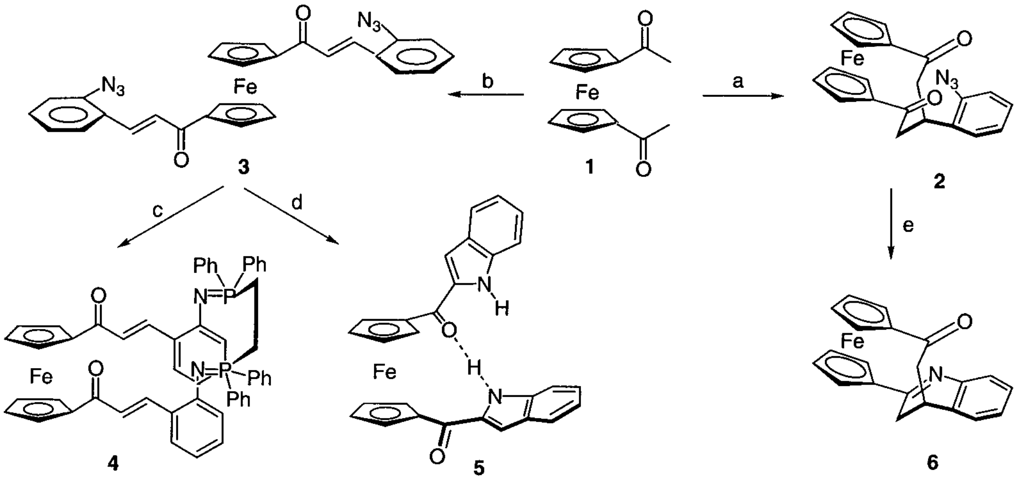
(1) For a recent review see: Heo, R. W.; Lee, T. R. *J. Organomet. Chem.* **1999**, *578*, 31 and references therein.

(2) Phosphorus: (a) Osborne, A. G.; Whiteley, R. H.; Meads, R. E. *J. Organomet. Chem.* **1980**, *193*, 345. (b) Seyferth, D.; Withers, H. P., Jr. *Organometallics* **1982**, *1*, 1275. (c) Brunner, H.; Blankermayer, J.; Zabel, M. *J. Organomet. Chem.* **2000**, *601*, 211. Sulfur: (d) Johnston, E. R.; Brandt, P. F. *Organometallics* **1998**, *17*, 1460. (e) Brandt, P. F.; Compton, D. L.; Rauchfuss, T. B. *Organometallics* **1998**, *17*, 2702. (f) Compton, D. L.; Rauchfuss, T. B. *Organometallics* **1994**, *13*, 4367. (g) Pudelski, J. K.; Gates, D. P.; Rulkens, R.; Lough, A. J.; Manners, I. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1506. (h) Stendel, R.; Hassenberg, K.; Pickardt, J. *Organometallics* **1999**, *18*, 2910. Silicon: (i) Kumada, M.; Kondo, T.; Mimura, K.; Ishikawa, M.; Yamamoto, K.; Ikeda, S.; Kondo, M. *J. Organomet. Chem.* **1972**, *42*, 293. (j) Osborne, A. G.; Whiteley, R. H. *J. Organomet. Chem.* **1975**, *101*, C27. (k) Stoeckli-Evans, H.; Osborne, A. G.; Whiteley, R. H. *Helv. Chim. Acta* **1976**, *59*, 2402. (l) Fischer, A. B.; Kinney, J. B.; Staley, R. H.; Wrighton, M. S. *J. Am. Chem. Soc.* **1979**, *101*, 6501. (m) Butler, I. R.; Cullen, W. R.; Tettig, S. J. *Can. J. Chem.* **1987**, *65*, 1452. (n) Foucher, D. A.; Tang, B. Z.; Manners, I. *J. Am. Chem. Soc.* **1992**, *114*, 6246. (o) Zechel, D. L.; Foucher, D. A.; Pudelski, J. F.; Yap, G. P. A.; Rheingold, A. L. *J. Chem. Soc., Dalton Trans.* **1995**, 1893. (p) Dementiev, V. V.; Cervantes-Lee, F.; Parkanyi, L.; Sharma, M.; Pannell, K. H. *Organometallics* **1993**, *12*, 1983.

10.1021/om010979c CCC: $22.00

Scheme 1[a]



[a] Legend: (a) *o*-azidobenzaldehyde (1 equiv), KOH (excess), EtOH; (b) *o*-azidobenzaldehyde (5 equiv), KOH (cat.), EtOH; (c) 1,2-bis(diphenylphosphino)ethane, CH_2Cl_2, room temperature; (d) toluene/*o*-xylene (1:1), reflux; (e) Ph_2MeP, toluene, reflux, or *n*-Bu_3P, CH_2Cl_2, room temperature.

cenophanes have barely been studied. To the best of our knowledge, there have only been reports on the preparation of N-substituted 2-aza[3]ferrocenophanes either from the reaction of 1,1′-ferrocenedimethanol with aryl isocyanates or arylamines in the presence of $RuCl_2(PPh_3)_2$[3] or by condensation of [1,1′-ferrocenediylbis(methylene)]bis(pyridinium) tosylate with methylamine.[4]

Following our work on the preparation of aza-heteroaryl-substituted ferrocene derivatives displaying redox-switchable character,[5] we now wish to report on the synthesis of a new range of ferrocenophanes containing an aza-substituted bridge in which all the atoms belong to a rigid aza-fused tricyclic ring system (type IV). This unprecedented structure combines the typical 2-aza[3]ferrocenophane framework with the otherwise not readily available 2,9-disubstituted benzoquinuclidine ring.

Results and Discussion

Synthesis. The reaction of 1,1′-diacetylferrocene (**1**) with *o*-azidobenzaldehyde in a basic medium may be driven toward the formation of 3-(*o*-azidophenyl)[5]ferrocenophane (**2**) or 1,1′-bis(*o*-azidocinnamoyl)ferrocene (**3**) as the only reaction products, simply by changing the sequence of addition of the reagents as well as the amount of base. Addition of *o*-azidobenzaldehyde (1 equiv) to an ethanolic solution of 1,1′-diacetylferrocene containing an excess of KOH gave **2** in 74% yield, which was separated as a stable yellow solid. However, addition of a catalytic amount of ethanolic KOH to a mixture of 1,1′-diacetylferrocene and *o*-azidobenzaldehyde (1:5) provided **3** in 61% yield as an stable solid. In this case, the use of catalytic amounts of base prevents the conversion **3** → **2** by a reverse aldol condensation[6] (Scheme 1).

The ^1H and ^{13}C NMR spectra of the [5]ferrocenophane **2** clearly revealed the highly ordered and asymmetric conformation of the molecule. In the ^1H NMR spectrum, the protons of the Cp rings appeared as four broad, well-separated singlets at δ 4.92, 4.89, 4.62, and 4.55 (2:2:2:2), whereas the two protons within the two equivalent methylene groups of the bridge are magnetically nonequivalent (at 318 K a broad doublet at δ 2.54 and a broad triplet at δ 2.99 are detected for both methylene groups). The signal of the methine proton is included in the ferrocene region and hence cannot be seen. However, in the analogue 3-(4-methylphenyl)[5]ferrocenephane-1,5-dione, prepared in 50% yield by the same way, the methine proton appeared at δ 4.31 ppm as a broad triplet. Probably, the anisochrony of the two protons within each of the two equivalent methylene groups in **2** could be due to the fact that the ferrocene develops a diamagnetic anisotropy.[7] Thus, the signals of the two quasi-axial hydrogen atoms in the endo position directed toward the iron atom are shifted downfield, whereas the signals of the two quasi-equatorial hydrogen atoms in the exo position that point away from the iron atom are shifted to higher magnetic field. With regard to the asymmetry observed for the Cp ring protons, it is known that in [5]ferrocenophanes the iron-to-ring distance is the same as in ferrocene,[8] since the bridge is long enough to span the rings without strain. In the [5]ferrocenophane **2**, the four signals for the two Cp rings strongly suggest a staggered conformation of the two rings as the bridge forces them out of coplanarity, with the two rings now being magnetically nonequivalent.

The ^1H and ^{13}C NMR spectra of compound **3** reveal high symmetry, only showing one set of signals for the two cinnamoyl substituents which are almost identical with those found in the monosubstituted analogue.[9] These data suggest that the two groups placed at the 1,1′-positions of the ferrocene unit in compound **3** are constrained to an anti geometry.

A Staudinger reaction between the bis(azide) **3** and 1,2-bis(diphenylphosphino)ethane in dry dichloromethane at room temperature afforded the 18-membered mac-

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[3] (a) Lorkowski, H. J.; Kieselack, P. *Chem. Ber.* **1966**, *99*, 3619. (b) Yamaguchi, Y.; Sakano, T.; Ishii, H.; Osakada, K.; Yamamoto, T. *J. Organomet. Chem.* **1999**, *584*, 213.

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[6] Winstead, A. J. *J. Org. Chem.* **1972**, *37*, 1271.

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[8] Hillman, M.; Fujita, E.; Dauplaise, H.; Kuick, A.; Kerber, R. C. *Organometallics* **1984**, *3*, 1170.

[9] Molina, P.; Tárraga, A.; López, J. L.; Martínez, J. C. *J. Organomet. Chem.* **1999**, *584*, 147.

rocycle **4** in 20% yield after chromatographic purification (Scheme 1). The syn spatial arrangement in compound **4** is induced by the diphosphine in an optimal manner by the "ball bearing"[10] motion of the two Cp rings of the ferrocene unit. The proposed structure **4** was deduced from NMR spectroscopic data (^1H, ^{13}C, ^{31}P) and MS in FAB mode. The ^1H and ^{13}C NMR spectra of **4** do not show significant differences with respect to the precursor bis(azide) **3**, and the resonances corresponding to the diphosphine framework are in good agreement with the proposed structure. Macrocycle **4** could be of valuable interest for the construction of heterobimetallic ferrocene-based complexes, because the iminophosphorane group has demonstrated its versatility toward forming M−N σ bonds to transition metals. [11]

Bis(azide) **3** was converted in 30% yield into 1,1′-bis(2-indolylcarbonyl)ferrocene (**5**) by heating at reflux temperature in a mixture of toluene and *o*-xylene (1:1) (Scheme 1). All attempts to improve the yield of **5** by changing the solvent and reaction time failed. The ^1H and ^{13}C NMR spectra of **5** clearly revealed that the top and bottom parts of the molecule are magnetically nonequivalent. The ^1H NMR spectrum showed two distinct N−H resonances at 9.63 and 8.76 ppm, respectively, and in the ferrocene region four broad singlets appeared at δ 5.10, 4.95, 4.63, and 4.52 ppm (2:2:2:2), respectively, due to the α-, α′-, β-, and β'-protons.[12] In contrast to these data, it is worth noting those exhibited by the 2-(ferrocenylcarbonyl)indole,[9] which shows the N−H signal at 9.60 ppm and the two triplets, due to the α- and β-protons of the substituted cyclopentadienyl ring, at δ 5.15 and 4.63 ppm, respectively. The ^{13}C NMR spectrum also displayed two sets of signals for all carbon atoms, one of them being identical with that observed in the above-mentioned 2-(ferrocenylcarbonyl)indole.

All the data and molecular models indicate an intramolecular hydrogen bonding between the carbonyl group of one substituent and the N−H group of the opposing one, as suggested by the structural drawing of **5**. In this compound the ferrocene serves as a reliable organometallic scaffold for the construction of an ordered structure via intramolecular hydrogen bonding.[13] This kind of interaction has been found in 1,1′-bis(azaaryl)-substituted ferrocenes[14] and bis(amino acid) derivatives of 1,1′-ferrocenedicarboxylic acid,[15] and it has been successfully used for nucleobase recognition.[16]

[5]Ferrocenophane **2** underwent an intramolecular aza-Wittig reaction by the action of *n*-Bu_3P in dichloromethane at room temperature to give the cryptand **6** in 55% yield. However, better yield (80%) was obtained when the reaction was carried out using diphenylmethylphosphane in toluene at reflux temperature (Scheme 1). The unusual structure of **6**, which can be considered either as a [5]ferrocenophane bearing a 2,4-bridged dihydroquinoline ring or a [4](2,4)quinolinophane containing a 1,1′-disubstituted ferrocene bridge, was deduced from NMR spectroscopic data as well as mass spectrometry. The ^1H NMR spectrum of **6** clearly detailed the asymmetry of the molecule, showing the two methylene groups as two double doublets and two doublets. The $\Delta\delta$ value for the geminal protons within each of the two methylene groups ranged from 0.84 ppm for the α-position to 0.4 for the γ-position. The signals corresponding to the two Cp rings were very illustrative. The ^1H NMR spectrum displayed six singlets (2:1:1:1:2:1) for the 8 ring protons, and the ^{13}C NMR spectrum gave 10 signals for the ferrocene carbon atoms.

It is worth noting that the transformation **2** → **6**, involving an intramolecular aza-Wittig reaction, constitutes the first example of the conversion of a ferrocenophane into a cryptand bearing a ferrocene moiety and also shows the applicability of this reaction to build strained carbon−nitrogen double bonds.[17]

Reduction of **6** with $LiAlH_4$−$AlCl_3$ (3:1) in ether at room temperature gave the fully reduced [5]ferrocenophane **7** in 85% yield as an orange solid, which was characterized by spectroscopic methods (see Experimental Section). Selective reduction of the C=N double bond in **6** with $NaBH_3CN$ in ethanol in the presence of HBF_4 afforded **8** in 80% yield. We were surprised to discover that on treatment of **8** with $LiAlH_4$−$AlCl_3$ (3:1) in ether at room temperature the only product isolated from this reaction was the rigid 2-aza-[3]ferrocenophane **9**, rather than the expected [5]ferrocenophane **7**, which was recovered in almost quantitative yield (95%) by flash chromatographic separation over silica gel. A similar result was obtained when BH_3−Me_2S was used as reducing agent (Scheme 2). Taking into account that this reagent has successfully been applied for the reduction of ferrocenyl ketones into ferrocenylalkyl alcohols,[18] we think that the formation of **9** probably involves initial reduction of the carbonyl group at the hydroxyl stage with concomitant cyclization by nucleophilic attack of the amino group on the α-position of ferrocene.[19]

Compound **9** is thermally and photochemically (daylight) stable, and crystals suitable for X-ray structural analysis could be obtained by recrystallization from chloroform/pentane (1:1). As observed in other ferrocenophane compounds, the presence of the bridge results in ring strain. This strain is conveniently described by the tilt angle α of the rings and the deformation angle δ formed between the two ring centroids and the iron atom. The molecular structure of **9** (Figure 1 and Table 1) reveals a tilt angle between the planes of the Cp rings of 10.9°. This Cp ring tilting is accompanied by a RC1−Fe−RC2 (RC = ring centroid) angle of 172.2°. The C(17)−N−C(21) angle of 111.5° is slightly smaller than those found in the previously reported 2-aza[3]ferrocenophanes,[3,4] and the appended carbon atoms deviate outside the Cp rings by 12 pm,

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(14) Gelin, F.; Thummel, R. P. *J. Org. Chem.* **1992**, *57*, 3780.

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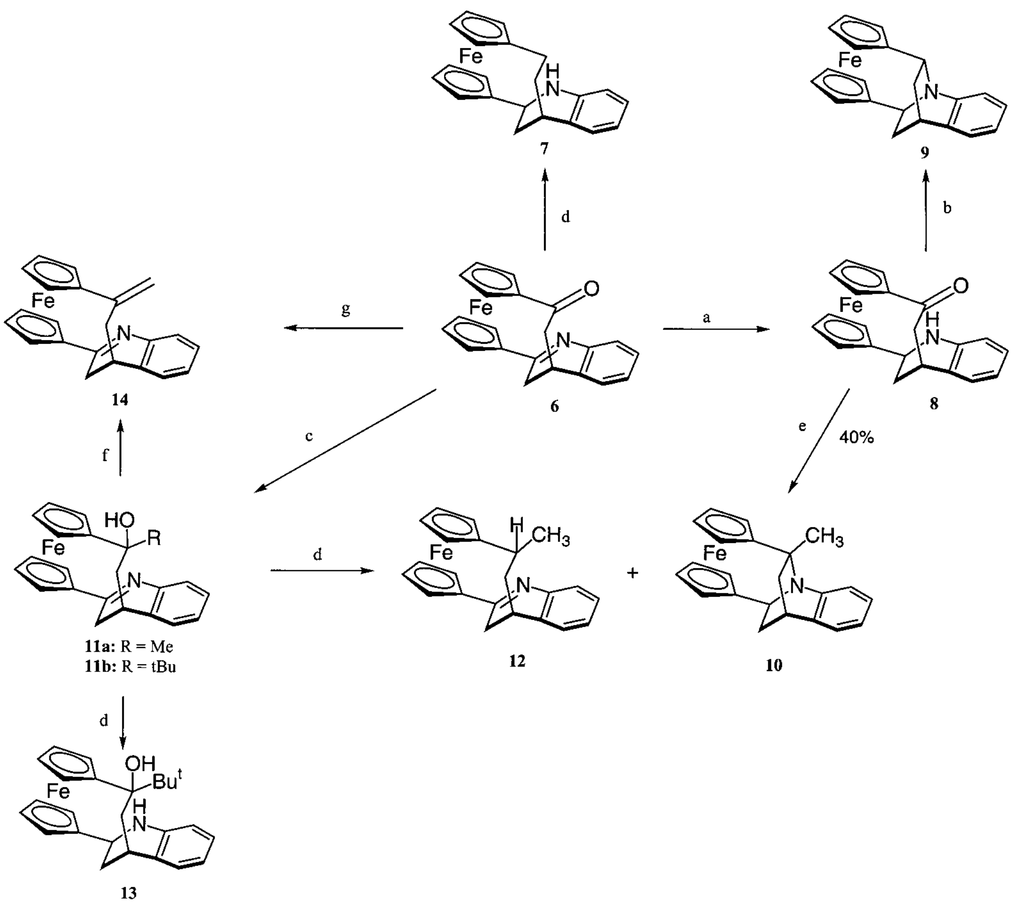
Scheme 2[a]



[a] Legend: (a) $NaBH_3CN$, HBF_4, EtOH, room temperature; (b) $LiAlH_4-AlCl_3$ (3:1), Et_2O, room temperature or $BH_3{\cdot}Me_2S$, Et_2O, room temperature; (c) MeLi or *t*-BuLi (2 equiv), Et_2O, −30 °C to room temperature; (d) $LiAlH_4-AlCl_3$ (3:1), Et_2O, room temperature; (e) (i) MeLi (2 equiv), Et_2O, −30 °C to room temperature, (ii) $AlCl_3$, room temperature; (f) 10-camphorsulfonic acid, toluene, reflux or $CF_3-COOH/AcOH$, THF, room temperature; (g) Nysted's reagent, $TiCl_4$, THF, −50 °C to room temperature.

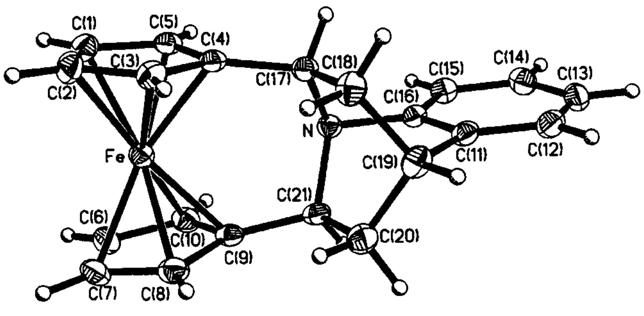


Figure 1. Perspective view (ORTEP) of compound **9**. Bond distances (Å) and angles (deg) (errors in last digits in parentheses): N−C(17), 1.510(3); N−C(21), 1.517(2); N−C(16), 1.452(2); C(4)−C(17), 1.506(3); C(9)−C(21), 1.502(3); C(17)−N−C(21), 111.51(14); C(16)−N−C(17), 105.37(14); C(16)−N−C(21), 106.33(14); C(4)−C(17)−N, 110.9(2); C(9)−C(21)−N, 111.2(2).

both closer to the central iron atom. The most important features of this structure are as follows: (a) there is a short Fe···N distance of only 323.4 pm, which is enforced by the rigid geometry of the bridge; (b) interestingly, the Cp rings are eclipsed with respect to each other; (c) the N atom has a distorted-tetrahedral environment.

In light of this remarkable result, it was of interest to extend the study to 1-alkyl-2-aza[3]ferrocenophane. Methylation of **6** with MeLi afforded the alcohol derivative **11a** in 70% yield, whereas with *t*-BuLi compound **11b** was obtained in 65% yield. Treatment of **11a** with $LiAlH_4-AlCl_3$ gave **10**, albeit in low yield (20%), along with a small amount of **12**. However, **10** is much more conveniently obtained from **8** (40% yield after chromatography) by sequential treatment with MeLi and an excess of $AlCl_3$. All attempts to prepare 1-*tert*-butyl-2-aza[3]ferrocenophane using the two approaches failed, and only compound **13** was obtained in 20% yield when **11b** was treated with an excess of AlH_3, which on standing in solution at room temperature undergoes spontaneous dehydrogenation to give **11a**.

On the other hand, dehydration of **11a** under acidic conditions (10-camphorsulfonic acid or CF_3COOH/AcOH) afforded **14** in 80% yield. This compound was also prepared in 30% yield directly from **6** by reaction with *cyclo*-dibromodi-*m*-methylene(*m*-tetrahydrofuran)-trizine (Nysted's reagent) in the presence of $TiCl_4$.[20] While it may be surprising that the exocyclic olefin in **14** does not isomerize into the endocyclic olefin under the acidic conditions employed for its preparation, analysis of molecular models reveals the endocyclic isomer to be much more strained than the exocyclic isomer. This assumption is supported by the fact that compound **11b** remained unaltered when it was treated under the above acidic conditions.

The relatively rigid structure of **9** and **10** enforces a tetrahedral arrangement of the nitrogen lone pair that

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[20] Matsubara, S.; Sugihara, M.; Utimoto, K. *Synlett.* **1998**, 313.

Table 1. Crystal Data for Compounds 9 and 9b

	9	9b
mol formula	$C_{21}H_{19}FeN$	$C_{21}H_{20}ClFeNO_4$
mol wt	341.22	441.68
wavelength (Å)	0.710 73	0.710 73
temp (K)	173(2)	133(2)
cryst size (mm)	0.45 × 0.38 × 0.23	0.27 × 0.24 × 0.24
cryst syst	orthorhombic	orthorhombic
space group	*Pbca*	$Cmc2_1$
a (Å)	9.7648(5)	9.2909(6)
b (Å)	8.3409(5)	19.5021(14)
c (Å)	36.968(2)	9.9261(6)
vol (Å^3), *Z*	3010.9(3), 8	1798.5(2), 4
ρ(calcd) (Mg m^{-3})	1.505	1.631
F(000)	1424	912
μ (mm^{-1})	1.000	1.017
θ range for data collecn (deg)	3.03−25.00	2.09−30.02
limiting indices		$-12 \le h \le 13$, $-27 \le k \le 27$, $-13 \le l \le 13$
no. of rflns collected		10 329
no. of indep rflns	2641 (*R*(int) = 0.0295)	2768 (*R*(int) = 0.0246)
abs cor	ψ scans	none
max and min transmissn	0.971 and 0.709	
no. of data/restraints/ params	2640/223/208	2768/1/145
goodness of fit on F^2		1.07
R1[a]	0.0301	0.0226
wR2[b]	0.0807	0.0629
largest diff peak and hole (e Å^{-3})	0.258 and −0.427	0.430 and −0.225

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$ for reflections with $I > 2\sigma(I)$. [b] $wR2 = [\sum[w(F_o{}^2 - F_c{}^2)^2]/\sum[w(F_o{}^2)^2]]^{0.5}$ for all reflections; $w^{-1} = \sigma^2(F^2) + (aP)^2 + bP$, where $P = (2F_c{}^2 + F_o{}^2)/3$ and *a* and *b* are constants set by the program.

would be expected to be able to bind metal ions, and consequently, the redox potential of the ferrocene/ferrocenium couple would also undergo perturbation upon coordination. Subsequent experimental investigations confirmed that this was indeed the case. At first, the electrochemical behavior of ferrocenophanes **9**−**11** in the presence of variable concentrations of HBF_4 was investigated in order to obtain a detailed picture of the coordination properties. The cyclic voltammograms (CVs) of **9**−**11** display a single anodic process with features of electrochemical reversibility, with no subsidiary amine oxidation being observed. Electrochemical reversibility was demonstrated by the peak-to-peak separation between the resolved reduction and oxidation wave maxima; the relationship of the cathodic and anodic peak currents was constantly equal to 1, and oxidation peaks are diffusion-controlled ($i \approx v^{1/2}$). Upon protonation by addition of 1 equiv of HBF_4 in acetonitrile to a solution of compounds **9**−**11** in the same solvent, the redox potential of the ferrocene nucleus was shifted anodically in each case. The magnitude of the electrochemical shift on protonation provides important thermodynamic information. The shift in the redox potential on protonation is related to the ratio of protonation constant for the oxidized and reduced forms of the ligand. For compound **9** the potential shift on protonation was 390 mV (Figure 2a) and, consequently, the binding enhancement factor (BEF) is 2.5×10^{-7} and the reaction coupling efficiency (RCE)[21] is 3.9×10^6. This means that it is 3 900 000 times more difficult to protonate the oxidized form than the reduced one. Similar values were found for compounds **10** and **11** (Table 2).

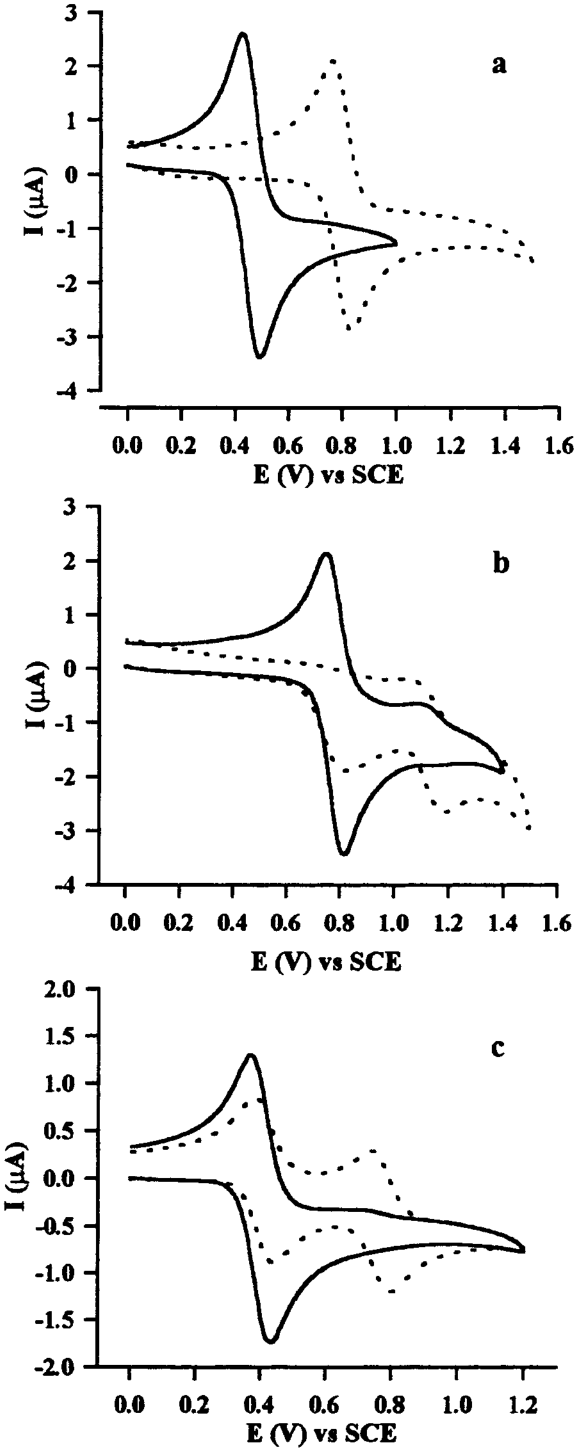

Figure 2. (a) Cyclic voltammogram of compound **9** before (continuous line) and after protonation with 1 equiv of HBF_4 (dotted line). Conditions: 1 mM **9** and 0.1 M Bu_4NClO_4 in CH_3CN at a Pt-disk electrode, scan rate 0.2 V/s. (b) Cyclic voltammogram of compound **6** before (continuous line) and after protonation with 0.6 equiv of HBF_4 (dotted line); other conditions as in (a). (c) Cyclic voltammogram of compound **9** before (continuous line) and after addition of 0.5 equiv of $Mg(ClO_4)_2$ (dotted line); 0.5 mM in sample, and other conditions as in (a).

The high values of the redox potential shift on protonation are in good agreement with the linear

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[21] (a) Beer, P. D.; Gale, P. A.; Chen, Z. *Adv. Phys. Org. Chem.* **1998**, *31*, 1. (b) Beer, P. D.; Gale, P. A.; Chen, Z. *Coord. Chem. Rev.* **1999**, *185−186*, 3.

Table 2. Cyclic Voltammetric Data

ligand	$E^{\circ\prime}_{\text{free}}$ (V)[a]	$E^{\circ\prime}_{\text{complex}}$ (V)[a]	$\Delta E^{\circ\prime}$ (mV)	K_1/K_2[b]
9a	0.410	0.800	390	3.9×10^6
9/Mg	0.410	0.760	350	8.2×10^5
9/Zn	0.410	0.740	330	5.6×10^5
9/Ni	0.410	0.740	330	5.6×10^5
10/H$^+$	0.450	0.770	320	2.6×10^5
10/Mg	0.450	0.790	330	5.6×10^5
10/Zn	0.450	0.760	310	1.7×10^5
10/Ni	0.450	0.760	310	1.7×10^5
11a/H$^+$	0.580	0.940	360	1.2×10^6
11b/H$^+$	0.570	0.940	370	1.8×10^6

[a] Data from acetonitrile solutions at a scan rate of 200 V s^{-1} vs SCE. CV recorded from 0 to 1 V. [b] The equilibrium constants K_1 and K_2 correspond to the complexation processes by the neutral and oxidized forms of the ligand.

relationship ($y = (-2.7 \times 2.1x)10^2$) between the inverse iron−nitrogen separation (x) and the shifts of the potentials (y) found upon protonation of several kinds of aza-substituted ferrocenes.[4]

The CV of compound **6** also displays a single anodic process with the feature of electrochemical reversibility $E^{\circ\prime} = 0.800$ V vs SCE. The redox potential is also shifted toward the more positive value $E_{\text{p,a}} = 1.190$ V by protonation under the same conditions. However, this shift is accompanied by a drastic flattening of the cathodic peak, which is indicative of an EC mechanism making the redox process irreversible: after the electron transfer of the oxidation, a chemical process occurs which prevents reduction from being observed (Figure 2b).

Recognition properties of the redox-active compounds **9** and **10** were also evaluated by CV. Whereas no perturbation of the CV of **9** was observed upon addition of Li$^+$ and Ca^{2+} cations, significant modifications of the CVs could be observed upon addition of Mg^{2+}, Zn^{2+}, and Ni^{2+} cations. On addition of Mg(ClO$_4$)$_2$ a second redox peak appeared in the CV, anodically shifted by ca. 350 mV. This "two-wave" behavior is diagnostic of a large value for the equilibrium constant for cation binding by the neutral ligand[22] (Figure 2c). Further addition of Mg^{2+} up to 16 equiv had no effect on the CV. We presume that the electrochemical response observed arises from Mg^{2+} coordination to the nitrogen atom of the ligand. We have discounted the fact that the electrochemical response is due to the adventitious protonation or hydration of the ligand because, after H$_2$O addition, the CV was identical with that obtained before the addition of Mg(ClO$_4$)$_2$. The presence of the methyl group in **10** slightly decreased the strengh of binding of Mg^{2+}: $\Delta E^{\circ\prime} = 330$ mV. Notably, compounds **9** and **10** showed an identical affinity for Zn^{2+} and Ni^{2+}, although the latter cations required a considerably higher concentration (14 equiv) than the other cations before the original ferrocene redox peak was lost. Data comparing the redox behavior of these ligands in the presence of Mg^{2+}, Zn^{2+}, and Ni^{2+} cations are collected in Table 2.

As ligand **9** acts as a base, when it is protonated it may be also used to detect anions. In this context, the synthesis of receptors containing a ferrocene as a functional antenna to detect anion binding has only recently been reported.[23] The protonated species **9a** (**9**·HBF$_4$), readily prepared as a crystalline solid in almost quantitative yield by addition of 1 equiv of HBF$_4$ to a solution of **9** in dichloromethane, was used to investigate its ability to electrochemically sense anion binding. The electrochemical responses were investigated in an acetonitrile solution with NBu$_4$BF$_4$ as supporting electrolyte. The addition of dihydrogenphosphate and hydrogensulfate anions elicited different electrochemical responses. For dihydrogenphosphate anion a new reversible redox wave evolved, which was shifted cathodically from the original ferrocene redox potential. The evolving peak appeared at virtually the same potential as that the free ferrocenophane **9**. A control experiment with addition of K$_2$CO$_3$/H$_2$O to the final solution, which caused no further change in the redox behavior, showed that this response was equivalent to deprotonation. However, significant modification of the CV of **9a** was observed upon addition of hydrogensulfate anion. The ferrocene oxidation wave shifted 60 mV cathodically (with 5 equiv of guest), indicative of oxidation being facilitated by the proximate coordination of a negative charge (Figure 3). Similar electrochemical findings have recently been reported with charged transition-metal-coordinated ferrocene phosphine amides as receptors.[24]

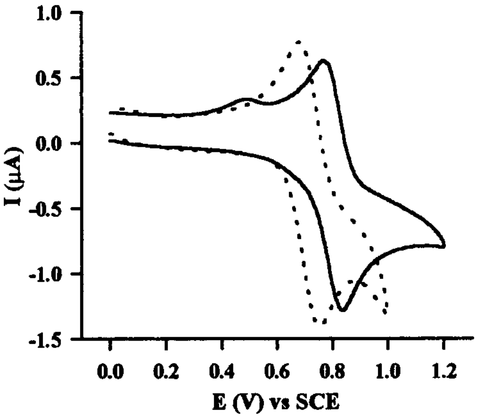

Figure 3. Voltammetric response of compound **9a** before (continuous line) and after addition of 0.5 equiv of hydrogensulfate ion (dotted line). The solution was 0.5 mM in **9a** and 0.1 M in Bu$_4$NBF$_4$ in CH$_3$CN. Working electrode: Pt-disk electrode. Scan rate: 0.2 V/s.

A ^{1}H NMR investigation was undertaken in order to complement the electrochemistry study. The spectra of the protonated species **9a** and **9b** (**9**·HClO$_4$) in CDCl$_3$ have been carefully analyzed. We find that in both species all signals are downfield shifted as compared with the analogous resonances of the free ligand **9**. Thus, while the aromatic protons in **9** appear as a singlet at δ 7.26 ppm, in the protonated species **9a** and **9b** appear as three multiplets: two of them are centered at δ 7.45 ppm (1H) and δ 7.54 ppm (2H), and the third one, corresponding to one proton, is centered at δ 8.20 ppm in the case of **9a** or at δ 8.40 ppm for **9b**. The magnitude of the downfield shift upon protonation is higher in **9b** (1.14 ppm) than in **9a** (0.94 ppm). Closer examination of the signals observed for the cyclopen-

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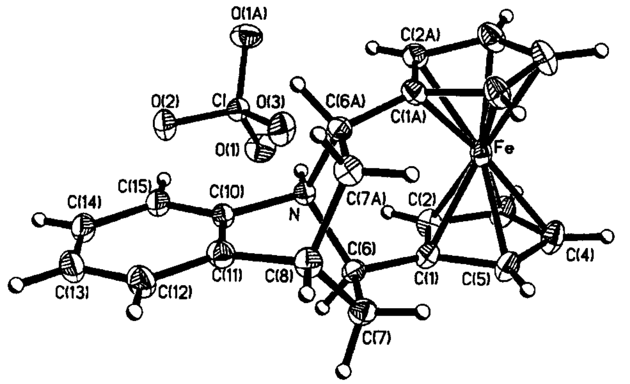

Figure 4. Perspective view (ORTEP) of compound **9a**. Bond distances (Å) and angles (deg) (errors in last digits in parentheses): N−C(10), 1.471(2); N−C(6), 1.5589(14); C(10)−N−C(6), 107.37(9); C(6)#1−N−C(6), 114.06 (14).

Table 3. Hydrogen Bonds (Å and deg)[a]

D−H···A	*d*(D−H)	*d*(H−A)	*d*(D···A)	∠(DHA)
C(5)−H(5)···O(1)#2	0.95	2.55	3.490(2)	172.1
C(6)−H(6)···O(1)#3	1.00	2.68	3.4832(16)	137.6
C(6)−H(6)···O(2)#3	1.00	2.60	3.4171(11)	139.3
C(15)−H(15)···O(2)	0.95	2.55	3.496(3)	174.4
C(2)−H(2)···O(3)	0.95	2.50	3.238(2)	134.5
N−H(0)···O(3)	0.93	2.02	2.942(2)	173.4

[a] Symmetry transformations used to generate equivalent atoms: (#1) $-x + 1, y, z$; (#2) $x, y, z - 1$; (#3) $-x + {}^1/_2, -y + {}^1/_2, z - {}^1/_2$.

tadienyl protons showed that in **9a** they appear as three multiplets centered at δ 4.29 (2H), δ 4.49 (4H), and δ 4.96 (2H) whereas in **9b** these eight ferrocenyl protons appear now as four multiplets centered at δ 4.37 (2H), δ 4.47 (2H), δ 4.52 (2H), and δ 5.04 (2H). It is worth noting that the downfield signal in the ferrocene region at δ 4.28 ppm in the free ligand **9** upon protonation is also shifted downfield by 0.68 ppm for **9a** and 0.76 ppm for **9b**, respectively.

These NMR data clearly show that in the protonation process the aforementioned ferrocenyl and aromatic protons are strongly deshielded in a value which seem to be dependent on the nature of the anion used. For both type of protons this value is higher in **9b** than in **9a**.

Further support for our NMR-based predictions was obtained through a single-crystal X-ray analysis of **9b** from suitable crystals obtained by recrystallization from deuterated acetonitrile/pentane (Figure 4 and Table 1).

Compound **9b** displays crystallographic mirror symmetry, with the plane passing through the atoms Fe, N, C8, and C10−C15. The tilt angle between the planes of the Cp rings is 8.5° associated with a RC1−Fe−RC2 (RC = ring centroid) angle of 175.1°. The C(6)−N−C(6A) angle is 114.06(14)°, and the Fe···N distance is only 322.8 pm. The anions and cations of **9b** are associated into ribbons parallel to the *z* axis (Figure 5) by the four shortest hydrogen bonds, shown in Table 3. These contacts may be described as C−H···O hydrogen bonds, as defined in the literature, between slightly acidic protons and oxygen acceptors.[25] Indeed, all C−O distances and all C−H···O angles fall into the expected range for such bonds (3.23−3.49 Å and 134−174°, respectively).[24b] Such C−H···O interactions correspond to a bifurcated interaction between one oxygen atom and two Fec-H atoms and one interaction between one oxygen atom and one Ar−H. Again, two Fec-H atoms of the neighbor participate in two single interactions with the remaining oxygen atoms of the anion. Recently, a ferrocene-substituted calix[4]pyrrole has been described a a new electrochemical sensor for anions involving this kind of direct Fec-H···anion binding interactions.[26]

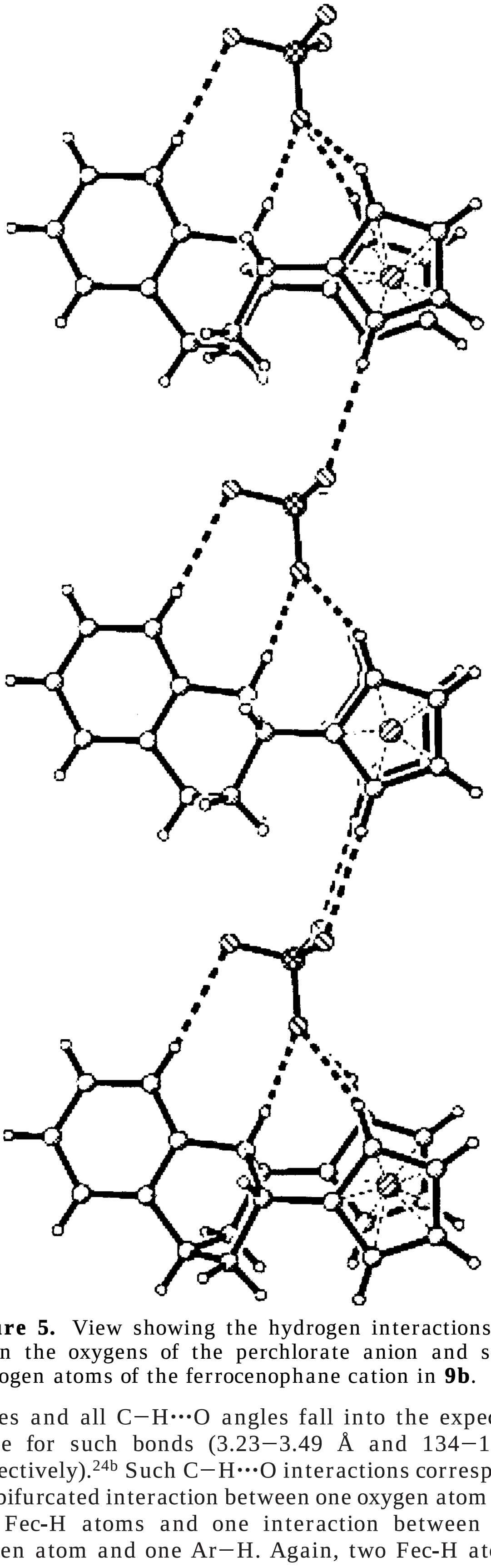

Figure 5. View showing the hydrogen interactions between the oxygens of the perchlorate anion and some hydrogen atoms of the ferrocenophane cation in **9b**.

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Conclusions

In summary, the above work describes the successful preparation of a number of functionalized ferrocenophanes from which 2-aza[3]ferrocenophanes **9** and **10** are the first representative members of a new class of strained metal-ion-coordinating ferrocenophanes. The synthesis was readily accomplished in a relatively small number of steps, starting from the commercially available 1,1′-diacetylferrocene (**1**). Formation of the tricyclic architecture is achieved by initial formation of the functionalized [5]ferrocenophane **5** from the reaction of **1** with *o*-azidobenzaldehyde under controlled reaction conditions. The second cyclization is based on an intramolecular aza Wittig reaction to give the hydroquinoline ring in **6**. Selective reduction of the C═N double bond in **6** followed by either reduction with the $LiAlH_4/AlCl_3$ system or methylation with MeLi and further treatment with $AlCl_3$ provides **9** and **10**, respectively. The convenience of this synthetic pathway makes this approach very attractive as a potentially general method for the preparation of structurally related 1-substituted 2-aza[3]ferrocenophane ligands.

The structural assignment of **9** and **10** was established on the basis of mass spectrometry and IR and NMR spectroscopy. These compounds possess specific structural features such as (1) a rigid framework with a blocked rotation of cyclopentadienyl rings, (2) a highly basic benzoquinuclidine ring, and (3) a short Fe···N distance. The summed effects of these characteristics suggested that **9** and **10** not only might experience electron cloud perturbation upon coordination and may function as a sensors for metal ions but also could give them particular stereoelectronic properties. Investigations into the metal ion coordination behavior of **9** and **10** showed that they responded electrochemically to a narrow range of cations, comprising Mg^{2+}, Zn^{2+}, and Ni^{2+}. Of particular significance is the fact that the protonated species **9a** functions as a selective electrochemical sensor for hydrogen sulfate.

Azaferrocenophanes **9** and **10** and related structures may therefore find potential applications in the detection and monitoring of Mg^{2+} and Zn^{2+}, and they may also be of interest for electrochemically modifying reactions in which cation coordination plays a pivotal role. On the other hand, the observed hydrogen-bonding motifs in **9b** may be useful for a better understanding of the role of weak hydrogen bonds in the design of new ferrocene-based electrochemical anion sensors.

Experimental Section

General Procedures. All reactions were carried out under N_2 and using solvents which were dried by routine procedures. Column chromatography was performed with the use of a column of dimensions 60 × 4.5 cm and of silica gel (60 A CC 70−200 μm, sds) as the stationary phase. All melting points were determined on a Kofler hot-plate melting point apparatus and are uncorrected. IR spectra were determined as Nujol emulsions or films on a Nicolet Impact 400 spectrophotometer. ^1H, ^{13}C, and ^{31}P NMR spectra were recorded on a Bruker AC200 (200 MHz) or a Varian Unity 300 instrument (300 MHz). Chemical shifts refer to signals of tetramethylsilane in the case of ^1H and ^{13}C spectra and to 85% aqueous phosphoric acid in the case of ^{31}P spectra. The EI and FAB^+ mass spectra were recorded on a Fisons AUTOSPEC 500 VG spectrometer, using 3-nitrobenzyl alcohol as a matrix. Microanalyses were performed on a Perkin-Elmer 240C instrument. The cyclic voltammetric measurements were performed on a QUICELTRON potentiostat/galvanostat controlled by a personal computer and driven by dedicated software. Cyclic voltammetry was performed with a conventional three-electrode configuration consisting of platinum working and auxiliary electrodes and a SCE reference electrode. The experiments were carried out with a 10^{-3} M solution of sample in dry CH_3CN containing 0.1 M $(n\text{-}C_4H_9)_4ClO_4$ as supporting electrolyte. All the potential values reported are relative to a SCE electrode at room temperature. Deoxygenation of the solutions was achieved by bubbling nitrogen for at least 10 min, and the working electrode was cleaned after each run. The cyclic voltammograms were recorded with a scan rate increasing from 0.05 to 1.00 V s^{-1}. Typically, the receptor (1×10^{-3} mol) was dissolved in solvent (5 mL) and TBAP (base electrolyte) (0.170 g) added. The guest under investigation was then added as a 0.1 M solution in acetonitrile using a microsyringe, while the cyclic voltammetric properties of the solution were monitored. Ferrocene was used as an external reference both for potential calibration and for reversibility criteria. Under similar conditions the ferrocene has $E°' = 0.390$ V vs SCE and the anodic peak−cathodic peak separation is 67 mV.

X-ray Crystallographic Analysis of 9 and 9b. The crystals were mounted in inert oil on glass fibers and transferred to the diffractometer (**9**, Siemens P4 with LT2 low-temperature attachment; **9b**, Bruker Smart 1000 CCD LT3 low-temperature attachment) as summarized in Table 1. The structures were solved by the heavy-atom method and refined anisotropically on F^2 (**9**, SHELXL-93; **9b**, SHELXL-97). Hydrogen atoms were included using a riding method. For compound **9b**, the absolute structure parameter[27] is −0.011-(12).

1,1′-[3-(*o*-Azidophenyl)-1,5-dioxo-1,5-pentanediyl]ferrocene (2). To a cooled (0 °C) solution of KOH (0.5 g, 8.9 mmol) in EtOH (15 mL) was added 1,1′-diacetylferrocene (**1**; 0.5 g, 1.85 mmol), and the reaction mixture was stirred at that temperature for 20 min. Then *o*-azidobenzaldehyde (0.272 g, 1.85 mmol) was added, and the reaction mixture was allowed to reach room temperature. After the mixture was stirred for 12 h, the yellow solid that formed was filtered and recrystallized from $CHCl_3$ to give **2** in 74% yield; mp 193−196 °C dec. IR (Nujol; cm^{-1}): 2127, 1663, 1652, 1492, 1456, 1379, 1293, 1252, 1240, 1105, 1084, 831, 765. ^1H NMR ($CDCl_3$): δ 2.54 (bd, 2H, $J = 11$ Hz), 2.99 (bt, 2H, $J = 11$ Hz), 4.55 (bs 3H), 4.62 (bs, 2H), 4.88 (bs, 2H), 4.92 (bs, 2H), 7.15−7.32 (m, 4H). ^{13}C NMR ($CDCl_3$): δ 45.5 (2 × CH_2), 63.88 (CH), 70.71 (2 × CH, Cp), 71.5 (2 × CH, Cp), 118.4 (CH), 125.20 (CH), 127.90 (CH), 128.11 (CH), 135.61 (q), 137.13 (q), 198.30 (C═O). EIMS (*m*/*z* (relative intensity)): 399 (M^+, 17), 371 (100), 355 (14), 251 (21), 185 (11), 130 (34). Anal. Calcd for $C_{21}H_{17}FeN_3O_2$: C, 63.18; H, 4.29; N, 10.53. Found: C, 63.20; H, 4.18; N, 10.39.

1,1′-Bis(*o*-azidocinnamoyl)ferrocene (3). To a solution of 1,1′-diacetylferrocene (0.5 g, 1.85 mmol) and *o*-azidobenzaldehyde (1.4 g, 1.85 mmol) in EtOH (20 mL) was added a solution of a saturated solution of KOH in the same solvent (0.5 mL). The reaction mixture was stirred at room temperature for 36 h, and the precipitated solid obtained was washed with ethanol (3 × 10 mL) and recrystallized from EtOH to give **3** as red prisms in 61% yield; mp 144−146 °C. IR (Nujol; cm^{-1}): 2128, 1659, 1652, 1603, 1575, 1489, 1456, 1377, 1325, 1282, 1241, 1082, 1035, 1007, 984, 975, 987, 846. ^1H NMR ($CDCl_3$): δ 4.60 (bs, 4H, Cp), 5.00 (bs, 4H, Cp). 7.10−7.40 (m, 8H), 7.63−7.65 (m, 2H), 7.93 (d, 2H, $J = 16$ Hz). ^{13}C NMR ($CDCl_3$): δ 71.49 (2 × CH), 74.10 (2 × CH), 81.92 (q, Fc ipso), 118.75 (CH), 124.14 (CH), 124.84 (CH), 126.44 (q), 128.42 (CH), 121.11 (CH),

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136.16 (CH), 139.50 (q), 192.04 (C=O). EIMS (*m*/*z* (relative intensity)): 528 (M^+, 51), 472 (58), 329 (10), 456 (12), 186 (18), 119 100), 91 (99). Anal. Calcd for $C_{28}H_{20}FeN_6O_2$: C, 63.65; H, 3.82; N, 15.91. Found: C, 63.78; H, 3.70; N, 15.79.

1,1′-[1,2-Ethanediylbis[(diphenylphosphoranylidyne)nitrilo-2,1-phenylene(1-oxo-2-propene-3,1-diyl)]] (4). To a solution of bis(diphenylphosphino)ethane (0.26 g, 0.34 mmol) in freshly distilled CH_2Cl_2 (20 mL) was added a solution of the bis(azide) **3** (0.2 g, 0.34 mmol) in the same solvent (10 mL) dropwise at room temperature and under nitrogen. The solution was stirred at room temperature for 12 h and the solvent removed under vacuum, giving a residue which was chromatographed on a silica gel column, using 9:1 EtOAc/*n*-hexane as eluent to give **4** in 20% yield, which was crystallized from CH_2Cl_2/*n*-hexane; mp 158−160 °C. IR (Nujol; cm^{-1}): 1652, 1649, 1457, 1382, 1226, 1313, 1081, 1055, 1025, 787, 751. ^1H NMR ($CDCl_3$): δ 2.67 (d, 4H, $^1J_{H-P} = 1.34$ Hz), 4.47 (m, 4H, Cp), 4.90 (m, 4H, Cp), 6.34 (d, 2H, $J = 7.8$ Hz), 6.67 (t, 2H, $J = 7.32$ Hz), 6.83 (t, 2H, $J = 7.0$ Hz), 7.25−7.64 (m, 24H), 8.55 (d, 2H, $J = 16$ Hz). ^{13}C NMR ($CDCl_3$): δ 22.87 (qt, 2 × CH_2, $|^1J + {}^2J| = 45.4$ Hz), 71.33 (4 × CH, Cp), 74.51 (4 × CH, Cp), 82.07 (2 × q, Cp), 117.8 (2 × CH), 122.41 (t, 2 × CH, $|^3J + {}^6J| = 11.90$ Hz), 123.16 (2 × CH), 126.7 (q, t, $|^1J + {}^4J| = 66.00$ Hz), 128.80 (q), 129.12 (t, 8 × CH, $|^3J + {}^6J| = 11.20$ Hz), 129.91 (2 × CH), 129.98 (4 × CH), 131.76 (8 × CH, $|^2J + {}^5J| = 9.32$ Hz), 132.14 (2 × CH), 142.54 (CH), 151.93 (q), 194.11 (C=O). ^{31}P NMR: δ 9.86. FABMS (*m*/*z* (relative intensity)): 872 ($M^+ + 2$, 41), 871 ($M^+ + 1$, 58). Anal. Calcd for $C_{54}H_{44}FeN_2O_2P_2$: C, 74.49; H, 5.09; N, 3.22. Found: C, 74.28; H, 5.15; N, 3.17.

1,1′-Bis(2-indolylcarbonyl)ferrocene (5). A solution of the bis(azide) **3** (0.4 g, 0.68 mmol) in a mixture of toluene and *o*-xylene (1:1, 20 mL) was heated at reflux temperature for 24 h. Then, the solvent was evaporated under reduced pressure and the residue chromatographed on a silica gel column, using 9:1 EtOAc/*n*-hexane as eluent to give the final product in 30% yield, which was crystallized from CH_2Cl_2/*n*-hexane; mp 158−160 °C. IR (Nujol; cm^{-1}): 3303, 1598, 1576, 1520, 1450, 1378, 1342, 1309, 1224, 1268, 1138, 1058, 1033, 821. ^1H NMR ($CDCl_3$): δ 4.52 (bs, 2H), 4.63 (bs, 2H), 4.95 (bs, 2H), 5.10 (bs, 2H), 7.13 (t, 1H, $J = 7.6$ Hz), 7.26−7.37 (m, 5H), 7.46 (d, 1H, $J = 8.3$ Hz), 7.55 (d, 1H, $J = 7.9$ Hz), 7.84 (bs, 1H), 8.44 (m, 1H), 8.76 (bs, 1H, NH), 9.63 (bs, 1H, NH). ^{13}C NMR ($CDCl_3$): δ 72.24 (CH, Cp), 72.40 (CH, Cp), 73.14 (CH, Cp), 74.06 (CH, Cp), 80.10 (q, Cp), 83.50 (q, Cp), 108.97 (CH), 111.35 (CH), 112.17 (CH), 117.71 (q), 120.83 (CH), 122.51 (CH), 122.64 (CH), 122.89 (CH), 123.90 (CH), 125.85 (CH), 126.24 (q), 127.77 (q), 131.15 (CH), 135.17 (q), 136.00 (q), 136.80 (q), 188.00 (C=O), 190.97 (C=O). FABMS (*m*/*z* (relative intensity)): 473 ($M^+ + 1$, 53). Anal. Calcd for $C_{28}H_{20}FeN_2O_2$: C, 71.20; H, 4.27; N, 5.93. Found: C, 71.35; H, 4.36; N, 5.70.

1,1′-[(3,4-Dihydro-2,4-quinolinediyl)(2-oxo-1,2-ethanediyl)]-ferrocene (6). Method A. To a cooled (0 °C) solution of **2** (0.2 g, 0.5 mmol) in freshly distilled CH_2Cl_2 (10 mL) and under nitrogen was added *n*-Bu_3P (0.75 mL) dropwise. The solution was warmed to room temperature and then was stirred for 12 h, at which point the solvent was removed under vacuum and the residue chromatographed on a silica gel column, using 9:1 EtOAc/*n*-hexane as eluent to give the final product in 55% yield, which was crystallized from CH_2Cl_2/*n*-hexane; mp 157−160° C.

Method B. To a solution of **2** (1 g, 2.5 mmol) in dry toluene (50 mL) was added diphenylmethylphosphane (0.47 mL, 2.5 mmol), and the mixture was stirred at room temperature for 1 h. Then, the solution was heated at reflux temperature for 24 h, and the product was isolated as above (0.71 g, 80%). IR (Nujol; cm^{-1}): 1661, 1596, 1575, 1457, 1387, 1296, 1274, 1092, 1038, 829, 727, 789, 775. ^1H NMR ($CDCl_3$): δ 2.26 (dd, 1H, $J = 13.5$, $J = 6.6$ Hz), 2.60 (dd,1H, $J = 14.7$, $J = 5.1$ Hz), 3.00 (d, 1H, $J = 14.7$ Hz), 3.10 (d, 1H, $J = 13.5$ Hz), 3.46−3.53 (m, 1H), 4.41 (bs, 2H, Cp), 4.60 (s, 1H, Cp), 4.65 (s, 1H, Cp), 4.80 (s, 1H, Cp), 4.90 (s, 2H, Cp), 5.31 (s, 1H, Cp), 7.00−7.11 (m, 2H), 7.25−7.33 (m, 2H). ^{13}C NMR ($CDCl_3$): δ 29.90 (CH_2), 35.26 (CH), 41.58 (CH_2), 66.68 (CH), 68.30 (CH), 70.08 (CH), 72.07 (CH), 72.90 (CH), 72.96 (CH), 74.00 (CH), 74.34 (CH), 75.32 (q, Cp), 83.75 (q, Cp), 125.60 (CH), 125.81 (CH), 126.49 (CH), 128.20 (CH), 131.50 (q), 143.05 (q), 169.12 (C=N), 207.56 (C=O). EIMS (*m*/*z* (relative intensity)): 355 (M^+, 100), 353 (13), 312 (18), 248 (51), 222 (6), 191 (16), 164 (15). Anal. Calcd for $C_{21}H_{17}FeNO$: C, 71.01; H, 4.82; N, 3.94. Found: C, 71.12; H, 4.77; N, 3.86.

Compound 6·HBF₄. To a solution of **6** (0.1 g, 0.28 mmol) in dry CH_2Cl_2 (20 mL) was added HBF_4 (1 equiv, 0.044 mL of a 54% solution of HBF_4 in Et_2O), and immediately a change of color in the solution, from red to deep purple, was observed. The solvent was removed under reduced pressure and the residue was triturated with diethyl ether to give **6**·HBF_4 as a solid in almost quantitative yield (95%), which was crystallized from CH_2Cl_2/Et_2O; mp 148−150 °C. IR (Nujol; cm^{-1}): 1664, 1573, 1464, 1303, 1277, 1091 (BF_4^-), 870, 778, 727. ^1H NMR ($CDCl_3$): δ 2.3 (dd, 1H, $J = 13.4$, $J = 6.63$ Hz), 2.65 (dd, 1H, $J = 14.8$, $J = 5.0$ Hz), 3.03−3.18 (m, 2H), 3.42−3.70 (m, 1H), 4.40 (m, 1H, Cp), 4.59 (m, 1H, Cp), 4.72 (m, 2H, Cp), 4.82 (m, 1H, Cp), 4.94 (m, 1H, Cp), 5.03 (m, 1H, Cp), 5.50 (m, 1H, Cp), 7.14−7.21 (m, 2H), 7.26−7.33 (m, 1H), 7.43 (d, 1H, $J = 7.6$ Hz). ^{13}C NMR ($CDCl_3$): δ 30.25 (CH_2), 35.56 (CH), 41.63 (CH_2), 67.27 (CH, Cp), 68.55 (CH, Cp), 72.49 (CH, Cp), 73.23 (CH, Cp), 73.39 (CH, Cp), 73.46 (CH, Cp), 75.27 (CH, Cp), 75.38 (CH, Cp), 78.89 (q), 106.15 (q), 124.95 (CH), 126.04 (CH), 127.26 (CH), 128.57 (CH), 131.2 (q), 147.47 (q), 171.0 (C=N). FAB^+ (*m*/*z* (relative intensity)): 357 ($M^+ + 1$, 25), 356 (M^+, 43). Anal. Calcd for $C_{21}H_{18}BF_4FeNO$: C, 56.93; H, 4.10; N, 3.16. Found: C, 56.81; H, 3.89; N, 3.31.

1,1′-[(1,2,3,4-Tetrahydro-2,4-quinolinediyl)(1,2-ethanediyl)]ferrocene (7). Under a nitrogen atmosphere a suspension of $AlCl_3$ (37.4 mg, 0.28 mol) in dry Et_2O (10 mL) was prepared. Then, $LiAlH_4$ (0.84 mmol, 0.84 mL of an 1 M ethereal solution of $LiAlH_4$) was added and the mixture was stirred at room temperature and under nitrogen for 10 min. A solution of the cryptand **6** (0.1 g, 0.28 mmol) in THF/Et_2O (5:10 mL) was added dropwise, and the resulting mixture was stirred for 30 min. At this point, a saturated solution of K_2CO_3 (20 mL) was added, the solution was extracted with CH_2Cl_2 (3 × 50 mL), and the organic layer was dried over anhydrous Na_2SO_4. After filtration, the solvent was removed under reduced pressure and the residue chromatographed on a silica gel column, using 20:1 CH_2Cl_2/EtOAc as eluent to give the final product in 85% yield as an orange unstable solid. IR (Nujol; cm^{-1}): 3340, 1465, 1445, 1386, 1282, 1111, 1080, 1036, 822, 768. ^1H NMR ($CDCl_3$): δ 1.93−2.09 (m, 2H), 2.22−2.36 (m, 2H), 2.53−2.62 (m, 1H), 2.80 (d, 1H, $J = 13.8$ Hz), 2.83−2.91 (m, 1H), 3.90 (bs, 1H, Cp), 3.98 (bs, 1H, Cp), 4.04−4.06 (m, 1H, Cp), 4.12−4.13 (m, 2H), 4.46−4.48 (m, 1H, Cp), 4.52 (bs, 1H, Cp), 6.60 (d, 1H, $J = 7.8$ Hz), 6.72 (t, 1H, $J = 7.8$ Hz), 7.02−7.10 (m, 2H). ^{13}C NMR ($CDCl_3$): δ 24.91 (CH_2), 31.50 (CH_2), 33.53 (CH_2), 40.57 (CH), 48.59 (CH), 64.91 (CH, Cp), 65.40 (CH, Cp), 65.59 (CH, Cp), 66.61 (CH, Cp), 66.86 (CH, Cp), 67.69 (CH, Cp), 67.96 (CH, Cp), 69.23 (CH, Cp), 95.23 (q, Cp), 99.43 (q, Cp), 113.82 (CH), 117.80 (CH), 127.17 (CH), 127.46 (CH), 128.80 (q), 144.50 (q). EIMS (*m*/*z* (relative intensity)): 343 (M^+, 8), 342 (37), 341 (100), 248 (30), 167 (10), 121 (4). Anal. Calcd for $C_{21}H_{21}FeN$: C, 73.48; H, 6.17; N, 4.08. Found: C, 73.25; H, 6.09; N, 4.15.

1,1′-[(1,2,3,4-Tetrahydro-2,4-quinolinediyl)(2-oxo-1,2-ethanediyl)]ferrocene (8). To a solution of **6** (0.1 g, 0.28 mmol) and $NaBH_3CN$ (53 mg, 0.84 mmol) in dry EtOH (10 mL) was added HBF_4 (1 equiv, 0.044 mL of a 54% solution of HBF_4 in ether). The reaction mixture was stirred at room temperature and under nitrogen for 3 h, and then H_2O (20 mL) was added. The solution was extracted with CH_2Cl_2 (3 × 50 mL) and the organic layer dried over anhydrous Na_2SO_4. The solution was filtered and the solvent removed under vacuum to give a residue which was crystallized from EtOH to give **8** in 80% yield as an orange solid; mp 198−200 °C. IR (Nujol; cm^{-1}): 3349, 1652, 1375, 1308, 1262, 1054, 1031, 868, 817, 738. ^{1}H NMR (CDCl$_3$): δ 2.1 (m, 1H), 2.31 (d, 1H, J = 13.2 Hz), 2.55 (dd, 1H, J = 14.7, J = 5.1 Hz), 3.53 (m, 2H), 3.98 (bs, NH), 4.15 (m, 2H, Cp), 4.26 (m, 1H, Cp), 4.47−4.55 (m, 2H), 4.64 (m, 1H, Cp), 4.76 (m, 1H, Cp), 6.68 (d, 1H, J = 7.8 Hz), 6.73 (t, 1H, J = 7.96 Hz), 7.06−7.14 (m, 2H). ^{13}C NMR (CDCl$_3$): δ 29.66 (CH$_2$), 33.09 (CH), 41.92 (CH$_2$), 47.88 (CH), 65.29 (CH, Cp), 66.31 (CH, Cp), 66.84 (CH, Cp), 67.31 (CH, Cp), 70.11 (CH, Cp), 72.15 (CH, Cp), 72.38 (CH, Cp), 73.02 (CH, Cp), 74.46 (q, Cp), 98.70 (q, Cp), 114.66 (CH), 118.66 (CH), 127.08 (CH), 127.53 (CH), 128.17 (q), 144.14 (q), 204.55 (C═O). EIMS (m/z (relative intensity)): 357 (M$^+$, 100), 343 (14), 314 (26), 248 (14), 167 (6), 130 (21), 121 (7). Anal. Calcd for C$_{21}$H$_{19}$FeNO: C, 70.61; H, 5.36; N, 3.92. Found: C, 70.50; H, 5.15; N, 3.70.

1,1′-(2,9-Benzoquinuclidinediyl)ferrocene (9). Method A. This compound was prepared in 95% yield by following the same procedure described above for the preparation of **7**, but using 1:4 EtOAc/n-hexane as eluent.

Method B. To a solution of **8** (0.1 g, 0.28 mmol) in THF/Et$_2$O (5/10 mL) was added a solution of Me$_2$S·BH$_3$ (0.28 mL, 0.56 mmol; 1 M in THF) dropwise, and the mixture was stirred under nitrogen for 2 h. Then, MeOH (15 mL) was added dropwise and the mixture was poured into H$_2$O. The mixture was extracted with CH$_2$Cl$_2$ (3 × 50 mL), and the organic layers were dried over anhydrous Na$_2$SO$_4$. After filtration, the solution was evaporated to dryness and the residue was crystallized from CHCl$_3$/pentane to give **9** in 95% yield as a yellow solid; mp 210−211 °C. IR (Nujol; cm^{-1}): 1463, 1303, 1185, 1031, 1301, 1089, 850, 753, 732. ^{1}H NMR (CDCl$_3$): δ 1.69−1.81 (m, 4H), 3.21−3.22 (m, 1H), 3.40 (dd, 2H, J = 9.7, J = 7.0 Hz), 4.11−4.13 (m, 2H, Cp), 4.23−4.25 (m, 4H, Cp), 4.27−4.29 (m, 2H, Cp), 7.26 (bs, 4H). ^{13}C NMR (CDCl$_3$): δ 32.43 (2 × CH$_2$), 33.72 (CH), 55.80 (2 × CH), 68.35 (2 × CH, Cp), 69.54 (2 × CH, Cp), 69.92 (2 × CH, Cp), 70.42 (2 × CH, Cp), 86.74 (2 × q, Cp), 123.04 (CH), 124.35 (CH), 126.31 (CH), 126.78 (CH), 143.00 (q), 153.43 (q). EIMS (m/z (relative intensity)): 341 (M$^+$, 100), 248 (44), 225 (35), 212 (33), 194 (34), 165 (25), 147 (30), 121 (34), 77 (25). Anal. Calcd for C$_{21}$H$_{19}$FeN: C, 73.92; H, 5.61; N, 4.10. Found: C, 74.03; H, 5.50; N, 4.22.

Compound 9a (9·HBF$_4$). To a solution of **9** (0.1 g, 0.3 mmol) in dry CH$_2$Cl$_2$ (10 mL) was added 0.3 mL of a 0.1 M solution of HBF$_4$ in CH$_2$Cl$_2$. The solvent was removed under reduced pressure, and the residue was triturated with Et$_2$O to give **9a** in almost quantitative yield (95%), which was crystallized from CH$_2$Cl$_2$/Et$_2$O; mp >320 °C. IR (Nujol; cm^{-1}): 1467, 1432, 1253, 1081, 1034, 977, 758. ^{1}H NMR (CDCl$_3$): δ 2.04−2.21 (m, 4H), 3.63 (m, 1H), 4.29−4.37 (m, 4H), 4.48−4.50 (m, 4H), 4.95−4.96 (m, 2H), 7.43−7.47 (m, 1H), 7.51−7.57 (m, 2H), 8.18−8.21 (m, 1H), 9.24 (s, 1H). ^{13}C NMR (CDCl$_3$): δ 29.22 (2 × CH$_2$), 32.45 (CH), 59.22 (2 × CH), 69.14 (2 × CH, Cp), 71.04 (2 × CH, Cp), 74.10 (2 × CH, Cp), 120.52 (CH9, 125.27 (CH), 129.34 (CH), 130.94 (CH), 135.61 (q), 139.20 (q). FAB$^+$ (m/z (relative intensity)): 343 (M$^+$ + 1, 30), 342 (M$^+$, 100). Anal. Calcd for C$_{21}$H$_{20}$BF$_4$FeN: C, 58.79; H, 4.70; N, 3.26. Found: C, 58.60; H, 4.55; N, 3.12.

Compound 9b (9·HClO$_4$). To a solution of **9** (0.1 g, 0.3 mmol) in dry CH$_2$Cl$_2$ (10 mL) was added a solution of HClO$_4$ (70%; 0.025 mL, 1 equiv). The solvent was removed under reduced pressure, and the residue was triturated with Et$_2$O to give a solid in almost quantitative yield (95%), which was crystallized from CH$_3$CN/n-pentane; mp 225 °C dec. IR (Nujol; cm^{-1}): 1437, 1111, 1054, 869, 745. ^{1}H NMR (CDCl$_3$): δ 2.10−1.10 (m, 4H), 3.62 (m, 1H), 4.31−4.40 (m, 4H), 4.46−4.48 (m, 2H), 4.50−4.54 (m, 2H), 5.03−5.06 (m, 2H), 7.44−7.47 (m, 1H), 7.51−7.63 (m, 2H), 8.34−8.44 (m, 1H). ^{13}C NMR (CDCl$_3$): δ 29.34 (2 × CH$_2$), 32.32 (CH), 59.22 (2 × CH), 69.33 (2 × CH, Cp), 71.04 (4 × CH, Cp), 71.28 (2 × CH, Cp), 74.11 (2 × CH, Cp), 120.68 (CH), 125.22 (CH), 129.26 (CH), 130.92 (CH), 138.62 (q), 139.21 (q). FAB$^+$ (m/z (relative intensity)): 343 (M$^+$ + 1, 28), 342 (M$^+$, 100). Anal. Calcd for C$_{21}$H$_{20}$ClFeNO$_4$: C, 57.11; H, 4.56; N, 3.17. Found: C, 57.30; H, 4.42; N, 2.98.

1,1′-[(2-Methyl)-2,9-benzoquinuclidinediyl)]ferrocene (10). Method A. To a cooled (−30 °C) solution of **8** (0.1 g, 0.28 mmol) in dry Et$_2$O (30 mL) under nitrogen was added MeLi (4 equiv, 1 mL of an 1.6 M ethereal solution) dropwise. The solution was warmed to room temperature and then was stirred for 3 h, at which point an excess of anhydrous AlCl$_3$ (100 mg, 3.3 equiv) was added and the mixture was stirred for 12 h. A saturated solution of K$_2$CO$_3$ (10 mL) was added and the organic phase extracted with CH$_2$Cl$_2$ (3 × 50 mL) and dried over anhydrous Na$_2$SO$_4$. The solvent was removed under vacuum and the residue chromatographed on a silica gel column, using 1:4 EtOAc/n-hexane as eluent to give **10** in 40% yield, which was crystallized from CH$_2$Cl$_2$/n-hexane; mp 220−222 °C. IR (Nujol; cm^{-1}): 1460, 1300, 1184, 1005, 908, 853, 753, 731. ^{1}H NMR (CDCl$_3$): δ 0.90 (s, 3H), 1.47 (d, 1H, J = 12.4 Hz), 1.75.1.78 (m, 2H), 2.05 (d, 1H, J = 11.6 Hz), 3.23 (bs, 1H), 3.55 (dd, 1H, J = 9.6, J = 8.6 Hz), 4.06 (m, 1H, Cp), 4.10 (m, 1H, Cp), 4.21 (m, 2H, Cp), 4.28 (m, 1H, Cp), 4.34 (m, 1H, Cp), 7.23−7.26 (m, 4H). ^{13}C NMR (CDCl$_3$): δ 31.5 (CH$_3$), 33.94 (CH$_2$), 34.42 (CH$_2$), 40.42 (CH), 53.82 (CH), 67.75 (CH, Cp), 67.83 (CH, Cp), 68.53 (CH, Cp), 68.87 (CH, Cp), 69.51 (CH, Cp), 69.78 (CH, Cp), 70.23 (CH, Cp), 70.62 (CH, Cp), 70.43 (q), 84.76 (q, Cp), 93.76 (q, Cp), 124.20 (CH), 124.94 (CH), 126.24 (CH), 126.44 (CH), 142.22 (q), 152.64 (q). EIMS (m/z (relative intensity)): 355 (M$^+$, 100), 353 (67), 340 (24), 248 (50), 167 (7). Anal. Calcd for C$_{22}$H$_{21}$FeN: C, 74.38; H, 5.96; N, 3.91. Found: C, 74.19; H, 5.70; N, 3.82.

Method B. This compound was also prepared by starting from **11a** and LiAlH$_4$/AlCl$_3$ following the same procedure described above for the preparation of **7**, although in this case it was obtained in lower yield (20%). Using this procedure, formation of the side product **12** was also observed, which was isolated in 10% yield as an oil. IR (Nujol; cm^{-1}): 1580, 1564, 1472, 1455, 1249, 1119, 872, 614. ^{1}H NMR (CDCl$_3$): δ 1.1 (d, 3H, J = 7.2 Hz), 1.45−1.73 (m, 2H), 2.17−2.52 (m, 2H), 2.85−2.87 (m, 1H), 3.10 (d, 1H, J = 13.4 Hz), 3.97 (m, 1H, Cp), 4.03 (m, 1H, Cp), 4.06 (m, 1H, Cp), 4.17 (m, 1H, Cp), 4.48−4.49 (m, 2H, Cp), 4.60 (m, 1H, Cp), 4.95 (m, 1H, Cp), 7.07−7.17 (m, 2H), 7.21−7.30 (m, 1H), 7.37 (d, 1H, J = 8.0 Hz). ^{13}C NMR (CDCl$_3$): δ 28.53 (CH$_3$), 28.8 (CH), 29.66 (CH$_2$), 35.31 (CH), 38.04 (CH$_2$), 64.86 (CH, Cp), 67.02 (CH, Cp), 67.69 (CH, Cp), 67.90 (CH, Cp), 68.95 (CH, Cp), 69.83 (CH, Cp), 71.17 (CH, Cp), 72.11 (CH, Cp), 86.25 (q, Cp), 96.76 (q, Cp), 125.42 (CH), 125.91 CH), 126.20 (CH), 127.69 (CH), 132.5 (q), 144.86 (q), 166.92 (C═N). EIMS (m/z (relative intensity)): 355 (M$^+$, 100), 353 (23), 248 (34), 130 (24), 121 (13).

General Procedure for the Preparation of 1,1′-[(3,4-Dihydro-2,4-quinolinediyl)(2-alkyl-2-hydroxy-1,2-ethanediyl)]ferrocene (11). To a cooled (−30 °C) solution of **6** (0.1 g, 0.28 mmol) in dry Et$_2$O (30 mL) was added the appropriate alkyllithium derivative (2 equiv), under nitrogen. The stirred solution was then allowed to reach room temperature (3 h), and then H$_2$O (30 mL) was added. The reaction mixture was extracted with CH$_2$Cl$_2$ (3 × 50 mL), and the combined organic layers were dried over anhydrous Na$_2$SO$_4$, filtered off, and evaporated under reduced pressure. The crude product was then chromatographed on a silica gel column using 1:1 EtOAc/n-hexane as eluent to give the final product.

11a (R = CH$_3$): 70%; mp 224−226 °C from CH$_2$Cl$_2$/n-hexane. IR (Nujol; cm^{-1}): 3389, 1582, 1562, 1472, 1450, 1254, 1119, 872. ^{1}H NMR (CDCl$_3$): δ 1.32 (3H, CH$_3$), 1.80 (d, 1H, J = 14.1 Hz), 1.86 (s, 1H, OH), 1.95 (dd, 1H, J = 14.1, J = 5.1 Hz), 2.44 (dd, 1H, J = 13.8, J = 5.4 Hz), 3.25 (m, 1H), 3.48 (dd, 1H, J = 13.8, J = 1.8 Hz), 3.86 (m, 1H, Cp), 4.15 (m, 1H, Cp), 4.19 (m, 1H, Cp), 4.27 (m, 1H, Cp), 4.46 (m, 1H, Cp), 4.54 (m, 1H, Cp), 4.65 (m, 1H, Cp), 4.98(m, 1H, Cp), 7.10−7.20 (m, 2H), 7.24−7.29 (m, 1H), 7.4 (d, 1H, J = 7.8 Hz). ^{13}C NMR (CDCl$_3$): δ

31.65 (CH_3), 31.25 (CH_2), 39.85 (CH), 42.3 (CH_2), 64.26 (CH, Cp), 64.78 (CH, Cp), 66.95(CH, Cp), 67.31 (CH, Cp), 68.99 (CH, Cp), 70.23 (CH, Cp), 70.80 (CH, Cp), 72.80 (CH, Cp), 86.47 (q, Cp), 99.42 (q, Cp), 125.32 (CH), 125.73 (CH), 126.12 (CH), 127.52 (CH), 132.35 (q), 145.1 (q), 168.3 ($C{=}N$). EIMS (*m/z* (relative intensity)): 371 (M^+, 51), 353 (100), 313 (39), 248 (90), 221 (32), 167 (35), 121 (33). Anal. Calcd for $C_{22}H_{21}FeNO$: C, 71.17; H, 5.70; N, 3.77. Found: C, 71.32; H, 5.49; N, 3.63.

11b (R = *t*-Bu): 65%; mp 139−141 °C from Et_2O/*n*-hexane. IR (Nujol; cm^{-1}): 3380, 1582, 1562, 1435, 1116, 1091, 737. ^1H NMR ($CDCl_3$): δ 0.88 (s, 9H, *t*-Bu), 1.59 (dd, 1H, $J = 14.6$, $J = 12.8$ Hz), 1.72 (s, 1H, OH), 2.04 (dd, 1H, $J = 14.6$, $J = 4.4$ Hz), 2.41 (dd, 1H, $J = 13.8$, $J = 5.4$ Hz), 3.10 (m, 1H), 3.60 (dd, 1H, $J = 13.8$, $J = 2.0$ Hz), 3.97 (m, 1H, Cp), 4.10 (m, 1H, Cp), 4.24 (m, 2H, Cp), 4.27 (m, 2H, Cp), 4.67 (m, 1H, Cp), 5.02 (m, 1H, Cp), 7.12−7.23 (m, 2H), 7.28−7.32 (m, 1H), 7.40 (d, 1H, $J = 7.8$ Hz). ^{13}C NMR ($CDCl_3$): δ 24.86 (3 × CH_3), 31.38 (CH_2), 32.91 (CH), 35.84 (CH_2), 41.06 (q, *t*-Bu), 66.90 (CH, Cp), 66.98 (CH, Cp), 67.00 (CH, Cp), 67.12 (CH, Cp), 68.73 (CH, Cp), 70.53 (CH, Cp), 71.25 (CH, Cp), 72.56 (CH, Cp), 74.32 (q), 86.30 (q, Cp), 95.26 (q, Cp), 125.34 (CH), 125.62 (CH), 126.16 (CH), 127.73 (CH), 133.10 (q), 145.51 (q), 169.2 ($C{=}N$). EIMS (*m/z* (relative intensity)): 413 (M^+, 62), 356 (10), 293 (14), 248 (8), 167 (15), 149 (100). Anal. Calcd for $C_{25}H_{27}FeNO$: C, 72.65; H, 6.58; N, 3.39. Found: C, 72.84; H, 6.35; N, 3.12.

1,1′-[(3,4-Dihydro-2,4-quinolinediyl)(2-*tert*-butyl-2-hydroxy-1,2-ethanediyl)]ferrocene (13). To a suspension of $AlCl_3$ (32 mg, 0.24 mmol) in dry Et_2O (10 mL) was added $LiAlH_4$ (0.72 mmol, 0.72 mL of a 1 M ethereal solution of $LiAlH_4$) under nitrogen. The mixture was stirred at room temperature for 10 min, and then a solution of **11b** (0.1 g, 0.24 mmol) in THF/Et_2O (5:10 mL) was added dropwise. The resulting mixture was stirred for an additional 30 min. At this point, a saturated solution of K_2CO_3 (20 mL) was added, the solution was extracted with CH_2Cl_2 (3 × 50 mL), and the organic layer was dried over anhydrous Na_2SO_4. After filtration, the solvent was removed under reduced pressure and the residue chromatographed on a silica gel column, using 1:4 EtOAc/*n*-hexane as eluent to give **13** in 20% yield; mp 205−208 °C from EtOAc/*n*-hexane. IR (Nujol; cm^{-1}): 3351, 1595, 1575, 1478, 1371, 1095, 922. ^1H NMR ($CDCl_3$): δ 0.80 (s, 9H, *t*-Bu), 1.95 (s, 1H, OH), 2.02 (dd, 1H, $J = 10.8$, $J = 4.3$ Hz), 2.15−2.28 (m, 1H), 2.7 (t, 1H, $J = 13.2$ Hz), 3.05 (d, 1H, $J = 14.6$ Hz), 3.20 (m, 1H), 3.91−3.92 (m, 1H, Cp), 4.01−4.02 (m, 1H, Cp), 4.04−4.07 (m, 1H, Cp), 4.15−4.24 (m, 3H), 4.29−4.31 (m, 1H), 4.34−4.36 (m, 1H, Cp), 4.46 (d, $J = 9.4$ Hz), 6.6 (d, 1H, $J = 8.2$ Hz), 6.73 (t, 1H, $J = 6.4$ Hz), 7.00−7.10 (m, 2H). ^{13}C NMR ($CDCl_3$): δ 24.96 (3xCH_3), 29.78 (CH_2), 32.34 (CH_2), 36.32 (CH), 40.56 (q, *t*-Bu), 48.04 (CH), 64.40 (CH, Cp), 65.37 (CH, Cp), 65.42 (CH, Cp), 65.97 (CH, Cp), 67.10 (2 × CH, Cp), 67.98 (CH, Cp), 68.20 (CH, Cp), 99.55 (q, Cp), 100.71 (q, Cp), 114.05 (CH), 118.02 (CH), 127.04 (CH), 127.20 (CH), 131.00 (q), 144.88 (q). EIMS (*m/z* (relative intensity)): 415 (M^+, 13), 413 (31), 356 (100), 313 (34), 248 (74), 191 (11), 130 (94), 121 (9). Anal. Calcd for $C_{25}H_{29}FeNO$: C, 72.29; H, 7.04; N, 3.37. Found: C, 72.42; H, 7.29; N, 3.07.

1,1′-[(3,4-Dihydro-2,4-quinolinediyl)(2-methylidene-1,2-ethanediyl)]ferrocene (14). Method A. To a cooled (−30 °C) suspension of the Nysted reagent (1.3 g, 0.56 mmol) in anhydrous THF (30 mL) was added a solution of 1 M $TiCl_4$ in CH_2Cl_2 (0.56 mmol), and the resulting mixture was stirred for 5 min under nitrogen. Then, a solution of **6** (0.2 g, 0.56 mmol) in dry THF (5 mL) was added and the reaction mixture was warmed to room temperature (3 h). After that, the reaction mixture was poured into a saturated solution of K_2CO_3 and extracted with CH_2Cl_2 (3 × 50 mL). The combined organic layers were dried over anhydrous Na_2SO_4, and after filtration, the solvent was removed under reduced pressure and the residue chromatographed on a silica gel column, using 1:4 EtOAc/*n*-hexane as eluent to give **14** in 30% yield, which was crystallized from $CHCl_3$/pentane; mp 141−143 °C. IR (Nujol; cm^{-1}): 1584, 1570, 1484, 1451, 1121, 1031, 825, 763. ^1H NMR ($CDCl_3$): δ 1.96 (td, 1H, $J = 13.85$, $J = 1.8$ Hz), 2.28 (dd, 1H, $J = 14.8$, $J = 5.1$ Hz), 2.42 (m, 1H), 3.02 (m, 2H), 4.1 (m, 1H, Cp), 4.2 (m, 1H, Cp), 4.24−4.25 (m, 1H, Cp), 4.34 (m, 1H, Cp), 4.4 (m, 1H, Cp), 4.43−4.44 (m, 1H, Cp), 4.60 (m, 1H Cp), 5.00−5.01 (m, 1H, Cp), 5.1 (s, 1H), 5.36 (d, $J = 1.2$ Hz), 7.12−7.2 (m, 2H), 7.22−7.30 (m, 1H), 7.37 (d, 1H, $J = 8.0$ Hz). ^{13}C NMR ($CDCl_3$): δ 29.7 (CH_2), 35.17 (CH_2), 36.80 (CH), 64.66 (CH, Cp), 67.10 (CH, Cp), 67.14 (CH, Cp), 68.14 (CH, Cp), 69.34 (CH, Cp), 70.30 (CH, Cp), 70.45 (CH, Cp), 71.57 (CH, Cp), 72.46 (CH, Cp), 84.97 (q, Cp), 88.13 (q, Cp), 113.55 ($=CH_2$), 125.65 (CH), 125.80 (CH), 126.30 (CH), 127.87 (CH), 127.70 (q, $C{=}CH_2$), 131.74 (q), 141.67 (q), 168.00 ($C{=}N$). EIMS (*m/z* (relative intensity)): 353 (M^+, 100), 248 (85), 191 (20), 167 (23), 121 (6). Anal. Calcd for $C_{22}H_{19}FeN$: C, 74.80; H, 5.42; N, 3.97. Found: C, 76.65; H, 5.30; N, 3.77.

Method B. To a solution of 10-camphorsulfonic acid (0.125 g, 0.54 mmol) in dry toluene (30 mL) heated at 80 °C was added a solution of the alcohol **11a** (0.1 g, 0.27 mmol) in the same solvent (5 mL), and the resultant solution was heated at that temperature for 2 h. After addition of H_2O (20 mL) and a saturated solution of K_2CO_3, the suspension was extracted with CH_2Cl_2 (3 × 50 mL) and the combined organic layers were dried over anhydrous Na_2SO_4. The solvent was then removed under reduced pressure and the residue purified as above to give **14** in 80% yield.

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Supporting Information Available: Tables of atomic coordinates, anisotropic thermal parameters, bond lengths and angles, and hydrogen atom parameters for **9** and **9b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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