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Contribution from the Department of Chemistry, University of Birmingham, P.O. Box 363,
Birmingham B15 2TT, United Kingdom, and MediSense, 38 Nuffield Way, Abingdon Oxon OX14 1RL, United Kingdom

Redox-Responsive Crown Ethers Containing a Conjugated Link between the Ferrocene Moiety and a Benzo Crown Ether

Paul D. Beer,*[†] Christopher Blackburn,[‡] Jerome F. McAleer,[‡] and Harrison Sikanyika[†]

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The syntheses of new redox-active crown ethers **8a**, **8b**, **9a**, and **9b** containing cis- and trans-conjugated olefinic linkages between the ferrocene redox center and respectively benzo-15-crown-5 and *N*-phenylaza-15-crown-5 are described. The sodium cation forms 1:1 stoichiometric complexes with the trans ferrocenyl ionophores **8b** and **9b**, whereas potassium produces 1:2 intermolecular sandwich complexes with the same ligands, which were also observed by fast atom bombardment mass spectrometry. Electrochemical investigations reveal the binding of Na$^+$, K$^+$, and Mg^{2+} guest cations at the respective crown ether coordinating sites results in shifts of the ferrocene oxidation wave to more positive potentials if a conjugated π-electron system links the heteroatoms of the ionophore to the redox center. The magnitude and type (one or two waves) of the anodic shift are related to the charge:radius ratio of the cationic guest, Mg^{2+} producing the largest value and K$^+$ the smallest.

With a view toward advancement of chemical sensor technology, considerable interest is being shown in the syntheses of redox-active macrocyclic receptor molecules that contain a redox center in close proximity to a cation binding site.[1-6] These systems can be designed to electrochemically recognize the binding of a metal guest cation either through space interactions (Figure 1a) or via various bond linkages between the receptor site and redox center (Figure 1b). In contrast to the alkali-metal coordination studies of electrochemically *reducible* quinone[2,4,7,8] and nitroaromatic[3,9] macrocyclic systems, little has been reported about the effects of cation binding on the oxidation potential of redox-active macrocycles containing oxidizable moieties[10] such as ferrocenyl.[11-14]

We report here the syntheses of new redox-active crown ethers **8** and **9** containing a conjugated (olefinic) link between the ferrocene redox center and a benzo crown ether and demonstrate using electrochemical techniques that group IA and group IIA guest cation binding perturbs the ferrocenyl redox couple by a mesomeric mechanism involving transmission of the electrostatic effect through the π-electron system.

Results and Discussion

Syntheses. Treatment of the phosphonium salt **1**[15] with *n*-butyllithium afforded the phosphonium ylide **2**, which on reaction with the aldehydes **3**, **4**,[16] **5**,[17] and **6** gave the olefins **7**–**10**, respectively (Scheme I). Thin-layer chromatography (TLC) analysis of all four products revealed the presence of two major components in each case. With **7** and **8** the respective cis and trans isomers were separated by column chromatography using silica gel and eluting with a 75% petroleum ether–25% dichloromethane solvent mixture. In the case of **9** and **10** preparative thin-layer chromatography (PLC) eluting with 60% diethyl ether–40% petroleum ether gave the cis and trans isomers **9a**,**b** and **10a**,**b**. Alternatively, **9b** could also be isolated by crystallization from diethyl ether solution mixtures of **9**. Hydrogenation of **9** using a Pd–carbon catalyst gave **11** in near-quantitative yield.

The structures of the new olefinic ferrocene benzo crown ethers were characterized by elemental analyses, mass spectrometry, and ^{1}H and ^{13}C NMR spectroscopy (see Experimental Section). It is noteworthy that in each case the ^{1}H NMR spectra of the respective cis isomer's olefinic protons give doublets with *J* values of 12 Hz whereas, with the exception of **9b**, which shows a two-proton singlet in the olefinic region, the trans isomers exhibit larger *J* values of 16 Hz.

Coordination Studies. Refluxing aqueous methanolic solutions of the trans isomers **8b** and **9b** with excess amounts of sodium and potassium hexafluorophosphate yielded orange crystalline solids of respective stoichiometry [(**8b**)Na]PF$_6$, [(**9b**)Na]PF$_6$, [(**8b**)$_2$K]PF$_6$, and [(**9b**)$_2$K]PF$_6$, characterized by elemental analyses. These stoichiometric formulations were also observed by fast atom bombardment mass spectrometry[6] and suggest the larger K$^+$ forms the preferred 1:2 intermolecular sandwich complex with the ferrocene ionophores whereas Na$^+$ forms a 1:1 complex.

Electrochemical Studies. The electrochemical properties of the ferrocene benzo crown ethers **8** and **9** and the "model" compounds **7** and **10** were investigated in acetonitrile by using cyclic voltammetry with [*n*-Bu$_4$N]BF$_4$ as the supporting electrolyte. Each compound exhibited a reversible redox oxidation wave in the +0.3- to +0.45-V region (versus SCE) typical of a substituted ferrocene derivative (Table I). The amino compounds **9**–**11** showed an additional redox wave in the +0.6- to +0.8-V region at a potential similar to that observed for unsubstituted *N*-phenylaza-15-crown-5 (+0.85 V). On this basis the second wave may be attributed to the removal of an electron from the respective dialkylaniline derivative bearing a ferrocenium substituent.

Cyclic voltammograms were also recorded after progressively adding stoichiometric equivalents of Na$^+$, K$^+$, or Mg^{2+} cations to the electrochemical solutions, and the results are summarized in Table I. We noted previously[14] that addition of Li$^+$ to solutions of **9b** led to the appearance of a new ferrocene redox couple at more positive potentials associated with oxidation of a complex FcILi$^+$ (Scheme II) whereas addition of Na$^+$ or K$^+$ salts did not give rise to a new wave. Gradual shifts in the position of the original ferrocene redox wave are observed however on Na$^+$ or K$^+$ addition for both the cis (**9a**) and trans (**9b**) isomers (Table I).

[†] University of Birmingham.

[‡] MediSense.

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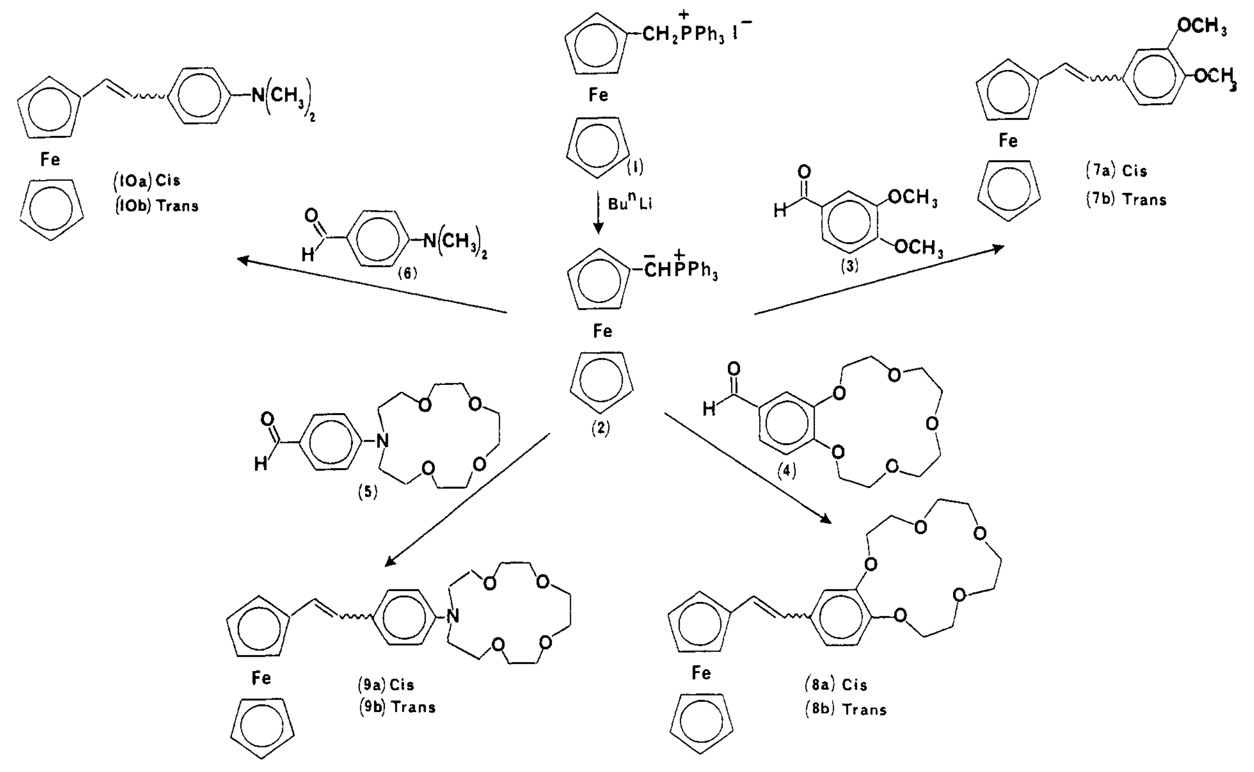
Table I. Electrochemical Data

	compound									
	7a	**7b**	**8a**	**8b**	**9a**	**9b**	**10a**	**10b**	**11**	**12b**
E_f, V[a]	+0.43	+0.43	+0.43	+0.40	+0.33 +0.61[d]	+0.34 +0.64[d]	+0.34 +0.63[d]	+0.35 +0.63[d]	+0.36 +0.79[d]	+0.45
ΔE_p, mV[b]	70	90	70	90	80	75	75	75	80	70
$\Delta E(Na^+)$, mV[c]	<10	<10	30	30	50	65	<5	<5	<5	
$\Delta E(K^+)$, mV[c]	<10	<10	20	20	20	20	<5	<5	<5	
$\Delta E(Mg^{2+})$, mV[c]	<10	<10	70	60	100	110	120	100	<20	

[a] Obtained in acetonitrile solution containing 0.2 M $[n\text{-}Bu_4N]BF_4$ as supporting electrolyte. Solutions were ca. 2×10^{-3} M in complex, and potentials were determined with reference to SCE. [b] Separation between anodic and cathodic peak potentials of cyclic voltammograms; values for ferrocene under the same conditions ranged from 75–85 mV. [c] Shift in ferrocenyl oxidation potential produced by presence of metal cations (4 equiv) added as their hexafluorophosphate (for sodium and potassium) and thiocyanate (for magnesium) salts. [d] Dialkylaniline oxidation wave.

Scheme I



Scheme II. Redox and Complexation Equilibria for a Ferrocene-Substituted Ionophore, FcI[a]

$$\begin{tikzcd}
\mathrm{FcI} \arrow[d, shift left] & + & \mathrm{M}^{n+} \arrow[r, rightleftharpoons, "K_1"] & \mathrm{FcIM}^{n+} \arrow[d, shift left, "E_{1c}"] \\
\mathrm{Fc^{+}I} \arrow[u, shift left, "E_{1f}"] \arrow[d, shift left] & + & \mathrm{M}^{n+} \arrow[r, rightleftharpoons, "K_2"] & \mathrm{Fc^{+}IM}^{n+} \arrow[u, shift left] \arrow[d, shift left, "E_{2c}"] \\
\mathrm{Fc^{+}I^{+}} \arrow[u, shift left, "E_{2f}"] & + & \mathrm{M}^{n+} \arrow[r, rightleftharpoons, "K_3"] & \mathrm{Fc^{+}I^{+}M}^{n+} \arrow[u, shift left]
\end{tikzcd}$$

[a] f denotes free (uncomplexed) ionophore; c denotes complexed species; $K_j = \overrightarrow{k}_j/\overleftarrow{k}_j$.

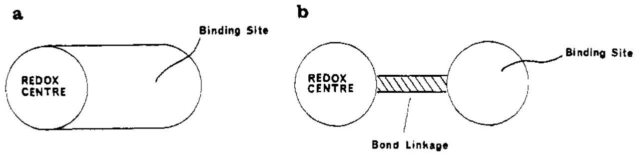


Figure 1. Depiction of the concept of electrochemical recognition, the binding of a metal guest cation in close proximity to a redox-active center, electrochemically detectable (a) through space interactions and (b) through various bond linkages.

The dialkylaniline wave is little affected in peak position or height by these latter ions. The effect of the small highly charged Mg^{2+} ion is similar to that observed with Li^+ in that a new ferrocene redox couple evolves on titration of either **9a** or **9b** (Figure 2).

It should be noted that the ferrocene wave due to uncomplexed **9** has also shifted. After 1.5 equiv of the Mg^{2+} guest cation had been added both the ferrocene and dialkylaniline waves due to uncomplexed **9** had disappeared, suggesting that all of the ionophore **9** had been complexed (Figure 2). With the benzo-15-crown-5 derivatives **8a** and **8b**, gradual anodic shifts of the ferrocene wave were observed with *all* the cations Na^+, K^+, and Mg^{2+} with shift magnitudes increasing with increasing charge density (polarizing power) of the guest cation. No notable shifts were observed with the model compounds **7a** and **7b**.

Compound **11**, in which the conjugated π-electron system be-

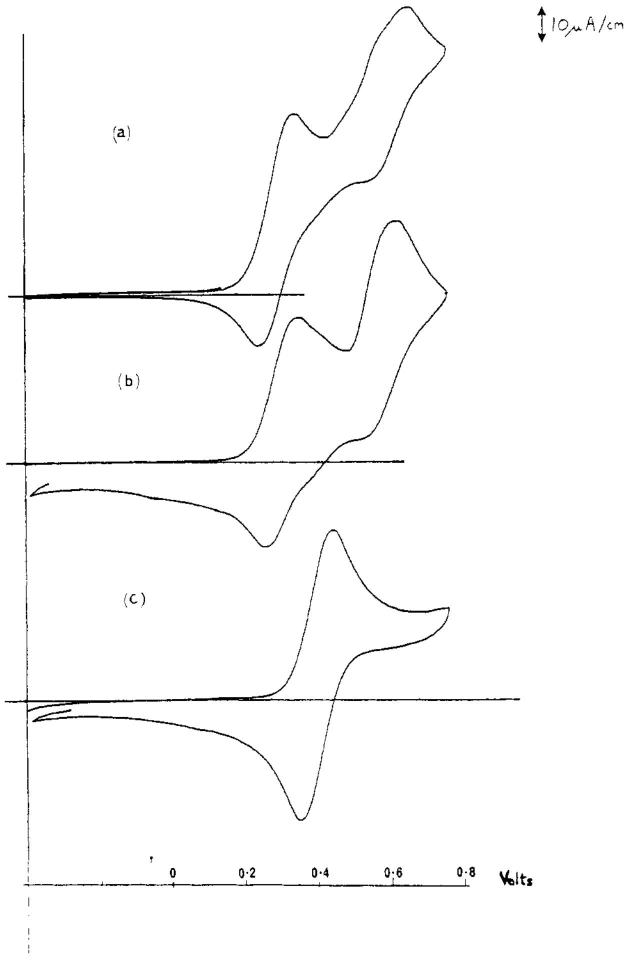
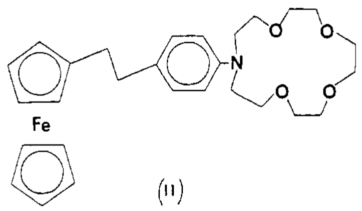
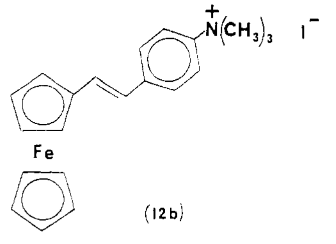


Figure 2. Cyclic voltammetry in acetonitrile solutions (sweep rate 100 mV/s) of (a) compound **9a** (3 mM), (b) compound **9a** + 0.75 equiv of Mg^{2+}, and (c) compound **9a** + 1.5 equiv of Mg^{2+}.

tween the nitrogen atom of the aza crown system and the ferrocenyl redox center has been modified to a saturated linkage, was unaffected by addition of Na^+ or K^+ ions. Addition of Mg^{2+}



(11)



(12b)

again gave behavior similar to that for Li^+ addition,[14] with the ferrocene wave little affected in position and dialkylaniline wave decreasing in height. These electrochemical results indicate that in this type of system, with the metal cation binding site remote from the redox center, any electrochemical perturbation (gradual shift or the appearance of a new couple) requires a continuous π-electron path between the ferrocene redox center and donor atoms (nitrogen or oxygen) of the crown ether binding site. It is also noteworthy that no significant differences between the magnitudes of the metal cation induced shifts of the respectively cis and trans isomers were observed suggesting the cis olefinic linkage can communicate the metal's positive charge to the redox center as effective as the trans olefinic linkage.

Discussion

The origins of metal ion induced shift of one redox wave or the appearance of two waves, one due to free ionophore and the other to the metal-complexed species of redox-active crown ethers containing *reducible* organic redox centers, have been discussed recently by Gokel and co-workers.[18] We have studied in detail *N*-(4-ferrocenylphenyl)aza crown ethers[12] and noted a sweep rate dependent crossover between these alternative electrochemical behaviors.[19] For the compounds described here several qualitative features concerning redox-active ionophore design are evident. Although significant anodic shifts are observed under the conditions employed, crown ethers **8** show one-wave behavior with Na^+, K^+, and Mg^{2+} and aza crowns **9** one-wave behavior with Na^+ and K^+, suggesting low values of the binding constants K_1[18] (Scheme II). Moreover, the *rate* of the decomplexation $\bar{k}_1$ is fast on the cyclic voltammetric (CV) time scale and thus oxidation of a ferrocene-substituted ionophore FcI (where Fc stands for the ferrocene redox moiety and I the appended crown or aza crown ether) at a potential E_{1f} (Scheme II) drives the first equilibrium toward decomplexation, preventing the detection of a discrete redox couple due to the ferrocene-substituted ionophore metal complexed species $FcIM^{n+}$. In the case of the aza crown **9**, continued scanning to higher potentials then leads to the detection (at potential E_{2f}) of the unperturbed dialkylaniline wave due to free **9**.

The sole observation of a new ferrocene redox couple (at E_{1c}) for **9a** or **9b** in the presence of excess Mg^{2+} (Figure 2c) implies that, for complexed **9** $FcIMg^{2+}$, $\bar{k}_1$ is slow on the cyclic voltammetric (CV) time scale. Furthermore, since the dialkylaniline aza crown ether oxidation wave (at potential E_{2f} in Scheme II) is not observed, the ferrocenium form of this complex Fc^+IMg^{2+} does not decomplex on the CV time scale either ($\bar{k}_2$ slow). Oxidation at potential E_{2c} of Fc^+IMg^{2+} was not detected below the solvent oxidation. On the reverse sweep, reduction of Fc^+IMg^{2+} is observed with no detectable reduction wave of Fc^+I found, indicating that the Mg^{2+} ion remains complexed throughout the scan. The complex formed between **9a** and excess Li^+ showed electrochemical behavior intermediate between these extremes.[14] Thus, on the forward sweep, oxidation of complex $FcILi^+$ only was observed, but further scanning led to the detection of a small current due to Fc^+I oxidation and, on the reverse sweep, due to Fc^+I reduction. In this case, then, $\bar{k}_1$ is slow and $\bar{k}_2$ comparable to the CV time scale.

The electrochemistry of the model amines **10a** and **10b** was unaffected by Na^+ or K^+ ions, but Li^+ or Mg^{2+} addition led to the evolution of a new ferrocene wave. This observation, of behavior similar to that of the aza crown compounds, indicates the importance of the nitrogen atom in the complexation process of these two particular cations. The redox potentials of the ferrocene wave for complexes formed between **9** or **10** and Li^+ or Mg^{2+} are close to that observed for the methiodide **12b**, suggesting that ions of high charge density induce a positive charge near unity on the nitrogen atom.

Conclusions

A series of crown ethers have been synthesized with a ferrocene redox center remote from the metal binding site, linked via an olefinic bond. Anodic shifts in the ferrocene oxidation wave are observed if a conjugated π-electron system links the heteroatoms of the ionophore to the redox center. These compounds represent the first examples of an alternative design of redox-active ionophores to the well-established lariat ethers[18] that function by through-space electrostatic perturbation. The charge:radius ratio or polarizing power of the guest cation is of great importance in

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determining the magnitude and type (one or two waves) of the shift in redox potential of the ferrocenyl redox center.

Experimental Section

Reactions were carried out under an atmosphere of dry nitrogen, and solvents were distilled prior to use from an appropriate drying agent. ^{1}H NMR spectra were recorded at 400 and 270 MHz and ^{13}C NMR spectra at 100 and 67.8 MHz by using tetramethylsilane (TMS) as an internal standard. Microanalyses were performed by the Birmingham University Chemistry Department microanalytical service. Electrochemical measurements were performed by using a PAR 174A polarographic analyzer. Cyclic voltammetric measurements were carried out in acetonitrile solution containing 0.2 mol dm^{-3} n-Bu$_4$NBF$_4$ as supporting electrolyte by using a platinum-bead working electrode with ferrocene internal reference. Values are quoted relative to the saturated calomel reference electrode (SCE). Positive ion fast atom bombardment mass spectrometry was performed by using a primary atom beam of argon (6 keV) on a Kratos MS80 RF mass spectrometer coupled to a Kratos DS55 data system.

(Ferrocenylmethyl)triphenylphosphonium iodide (**1**),[15] (4-formylbenzo)aza-15-crown-5 (**5**),[17] and (4-formylbenzo)-15-crown-5 (**4**)[16] were prepared by literature procedures. The aldehydes **3** and **6** were obtained commercially from Aldrich Chemical Co. and used without purification.

General Procedure for Preparation of *cis*- and *trans*-1-Aryl-2-ferrocenylethylenes. A suspension of the phosphonium salt **1** (4.0 g, 6.8 mmol) in anhydrous tetrahydrofuran (100 mL) was treated dropwise with a solution of n-butyllithium in hexane (4.7 mL of 1.55 M, 7.3 mmol). The deep red solution that formed was stirred under a nitrogen atmosphere at room temperature for 2 h.

A solution of the appropriate aldehyde (6.8 mmol) in anhydrous tetrahydrofuran (50 mL) was then added dropwise and the reaction mixture stirred for a further 16 h under a nitrogen atmosphere at room temperature with exclusion of light. The reaction mixture was treated with water (100 mL) and the tetrahydrofuran–water solvent mixture removed under reduced pressure. The residue was extracted several times with dichloromethane, the combined extracts were dried (MgSO$_4$), and the solvent was evaporated. The crude product was chromatographed on a silica gel 60 column by eluting with CH$_2$Cl$_2$–Et$_2$O gradient. The main orange band(s) afforded compounds **7**–**10** in yields of 70–80%. ^{1}H NMR and TLC analysis indicated, in each case, a mixture of cis and trans stereoisomers in approximately equal proportions. The isomers were separated by careful chromatographic techniques as follows:

7a and 7b. Column chromatography (silica gel 60; 75% petroleum ether (60–80 °C)–25% dichloromethane) gave the cis isomer (**7a**): mp 74.5–76.5 °C; m/z 348. (Anal. Found: C, 68.0; H, 6.3. Calcd for $C_{20}H_{20}FeO_2$: C, 68.9; H, 5.8.) ^{1}H NMR (CDCl$_3$): δ 3.75 (s, 3 H, OCH$_3$), 3.88 (s, 3 H, OCH$_3$), 4.11 (s, 5 H, Fc H), 4.16 (t, J = 1.7 Hz, 2 H, Fc H), 4.22 (t, J = 1.7 Hz, 2 H, Fc H) 6.26 (d, J = 12 Hz, olefinic H), 6.37 (d, J = 12 Hz, olefinic H), 6.77–6.90 (m, 3 H, Ar H).

Trans isomer (**7b**): mp 133–135 °C; m/z 348. (Anal. Found: C, 68.2; H, 6.2. Calcd for $C_{20}H_{20}FeO_2$: C, 68.9; H, 5.8.) ^{1}H NMR (CDCl$_3$): δ 3.89 (s, 3 H, OCH$_3$), 3.95 (s, 3 H, OCH$_3$), 4.14 (s, 5 H Fc H), 4.26 (t, J = 1.7 Hz, 2 H, Fc H), 4.44 (t, J = 1.7 Hz, 2 H, Fc H), 6.64 (d, J = 16 Hz, olefinic H), 6.73 (d, J = 16 Hz), olefinic H), 6.82–6.98 (m, 3 H, Ar H).

8a and 8b. Column chromatography (silica gel 60; 75% petroleum ether (60–80 °C)–25% dichloromethane) gave the cis isomer (**8a**): mp 79.5–81.5 °C; m/z 478. (Anal. Found: C, 64.2; H, 6.6. Calcd for $C_{26}H_{30}FeO_5$: C, 65.1; H, 6.3.) ^{1}H NMR (CDCl$_3$): δ 3.70–3.94 (m, 16 H, crown H), 4.05 (s, 5 H, Fc H), 4.15 (t, J = 1.7 Hz, 2 H, Fc H), 4.20 (t, J = 1.7 Hz, 2 H, Fc H) 6.25 (d, 1 H, J = 12 Hz, olefinic H), 6.36 (d, 1 H, J = 12 Hz, olefinic H), 6.78–6.89 (m, 3 H, Ar H). ^{13}C NMR (CDCl$_3$): δ 68.84, 69.03, 69.22, 69.39, 70.11 (OCH$_2$), 75.63, 77.03, 78.46 (ferrocene C), 81.81 (ferrocene C ipso), 113.58, 114.52, 121.96, 126.97, 127.26, 131.43 (aromatic C), 147.94, 148.43 (cis C=C).

Trans isomer (**8b**): mp 110–101.5 °C; m/z 478; ^{1}H NMR (CDCl$_3$) δ 3.77–4.01 (m, 16 H, crown H), 4.13 (s, 5 H, Fc H), 4.26 (t, 2 H, J = 1.8 Hz, Fc H), 4.43 (t, 2 H, J = 1.8 Hz, Fc H), 6.61 (d, 1 H, J = 16 Hz, olefinic H), 6.70 (d, 1 H, J = 16 Hz, olefinic H), 6.82–6.98 (m, 3 H, ArH); ^{13}C NMR (CDCl$_3$) δ 66.62, 68.77, 69.13, 70.59, 71.08 (OCH$_2$), 75.63, 77.03, 78.48 (ferrocene C), 83.69 (ferrocene C ipso), 111.56, 114.32, 119.43, 124.99, 125.84, 131.69 (aromatic C), 148.50, 149.38 (trans C=C).

9a and 9b. Preparative thick-layer chromatography (PLC) on silica gel eluting with 3:2 diethyl ether–petroleum ether gave the cis isomer (**9a**): mp 94 °C; m/z 510; ^{1}H NMR (CDCl$_3$) δ 3.60–3.80 (m, 20 H, crown H), 4.11 (s, 5 H, Fc H), 4.16 (t, 2 H, J = 1.9 Hz, Fc H), 4.28 (t, 2 H, J = 1.9 Hz, Fc H), 6.14 (d, 1 H, J = 12 Hz, olefinic H), 6.32 (d, 1 H, J = 12 Hz, olefinic H), 6.56 (d, 2 H, J = 9 Hz, Ar H), 7.23 (d, 2 H, J = 9 Hz, Ar H). (Anal. Found: C, 66.6; H, 6.9; N, 2.8. Calcd for $C_{28}H_{35}FeNO_4$: C, 66.5; H, 6.9; N, 2.8.)

Trans isomer (**9b**): mp 105 °C. (Anal. Found: C, 66.7; H, 7.0; N, 2.8. Calcd for $C_{28}H_{35}FeNO_4$: C, 66.5; H, 6.9; N, 2.8.) ^{1}H NMR (CDCl$_3$): δ 3.61–3.80 (m, 20 H crown H), 4.12 (s, 5 H, Fc H), 4.23 (t, 2 H, J = 1.9 Hz, Fc H), 4.43 (t, 2 H, J = 1.9 Hz, Fc H), 6.63 (s, 2 H, olefinic H), 6.64 (d, 2 H, J = 9 Hz, Ar H), 7.30 (d, 2 H, J = 9 Hz, Ar H).

Alternatively, **9b** could be obtained as orange needles by allowing a diethyl ether solution of **9a** and **9b** to evaporate slowly.

10a and 10b. Preparative thick-layer chromatography (PLC) on silica gel eluting with toluene gave the cis isomer (**10a**): mp 73 °C; m/z 331. (Anal. Found: C, 71.6; H, 6.4; N, 4.1. Calcd for $C_{20}H_{21}FeN$: C, 72.5; H, 6.3; N, 4.2.) ^{1}H NMR (CDCl$_3$): δ 2.97 (s, 6 H, NMe$_2$), 4.11 (s, 5 H, Fc H), 4.17 (t, 2 H, J = 1.8 Hz, Fc H), 4.28 (t, 2 H, J = 1.8 Hz, Fc H), 6.18 (d, 1 H, J = 12 Hz, olefinic H), 6.37 (d, 1 H, J = 12 Hz, Ar H), 6.66 (d, 2 H, J = 9 Hz, Ar H), 7.27 (d, 2 H, J = 9 Hz, Ar H).

Trans isomer (**10b**): mp 164 °C; ^{1}H NMR (CDCl$_3$) δ 2.98 (s, 6 H, NMe$_2$), 4.13 (s, 5 H, Fc H); 4.24 (t, 2 H, J = 1.8 Hz, Fc H), 4.43 (t, 2 H, J = 1.8 Hz, Fc H), 6.65 (s, 2 H, olefinic H), 6.72 (d, 2 H, J = 9 Hz, Ar H, 7.34 (d, 2 H, J = 9 Hz, Ar H).

Preparation of 11. A mixture of cis and trans olefins **9** (0.51 g, 1 mmol) was hydrogenated (3% Pd–carbon catalyst, 0.2 g, 1 atm H$_2$) in ethanol (50 mL) and dichloromethane (5 mL) for 24 h. The mixture was filtered (Celite), solvent removed, and the residue column chromatographed by using silica gel with a 1:1 diethyl ether–dichloromethane eluent to give **11** (0.45 g, 89%) as an orange oil: m/z 512; ^{1}H NMR (CDCl$_3$) δ 2.61 (m, 4 H, CH$_2$), 3.31–3.69 (m, 20 H, crown H), 4.00 (m, 9 H, Fc H), 6.53 (d, 2 H, J = 9 Hz, Ar H), 6.95 (d, 2 H, J = 9 Hz, Ar H).

Preparation of 12a and 12b. A solution of **10a** or **10b** (0.33 g, 1 mmol) in acetonitrile (30 mL) was treated with excess methyl iodide (5 mL) and the reaction mixture stirred at room temperature for 24 h. After removal of the solvent under vacuo the product was dissolved in dichloromethane (20 mL) and the solution filtered and added dropwise to diethyl ether (100 mL). The resulting suspension was cooled for several hours, and the precipitated methiodides were collected and dried. Yields were quantitative.

12a: mp 50 °C; ^{1}H NMR (CDCl$_3$) δ 4.01 (s, 9 H, Me$_3$N$^+$–), 4.12 (s, 5 H, Fc H), 4.15 (t, 2 H, J = 1.8 Hz, Fc H), 4.22 (t, 2 H, J = 1.8 Hz, Fc H), 6.33 (d, 1 H, J = 12 Hz, olefinic H), 6.48 (d, 1 H, J = 12 Hz, olefinic H), 7.55 (d, 2 H, J = 9 Hz, Ar H), 7.81 (d, 2 H, J = 9 Hz, Ar H).

12b: mp 175 °C dec; ^{1}H NMR (CDCl$_3$) δ 4.03 (s, 9 H, Me$_3$N$^+$–), 4.16 (5 H, Fc H), 4.36 (t, 2 H, J = 1.8 Hz, Fc H), 4.50 (t, 2 H, J = 1.8 Hz, Fc H), 6.66 (d, 1 H, J = 16 Hz, olefinic H), 7.01 (d, 1 H, J = 16 Hz, olefinic H), 7.62 (d, 2 H, J = 9 Hz, Ar H), 7.86 (d, 2 H, J = 9 Hz, Ar H).

Sodium and Potassium Complexes of the Trans Isomers 8b and 9b. To a methanolic solution of either **8b** or **9b** (1 mmol) was added an excess amount of alkali-metal hexafluorophosphate salt (5 mmol). The resulting solution was refluxed for 30 min, and upon cooling, an orange precipitate was collected and dried in vacuo. Recrystallization from methanol gave the respective complexes in quantitative yields.

[(8b)Na]PF$_6$·H$_2$O. Anal. Found: C, 44.5; H, 4.9. Calcd for $C_{26}H_{32}FeNaO_6PF_6$: C, 44.6; H, 5.1.

[(8b)$_2$K]PF$_6$. Anal. Found: C, 54.4; H, 5.0. Calcd for $C_{52}H_{60}Fe_2KO_{15}PF_6$: C, 54.7; H, 5.3.

[(9b)Na]PF$_6$. Anal. Found: C, 49.5; H, 5.1; N, 2.3. Calcd for $C_{28}H_{35}FeNNaO_4PF_6$: C, 49.9; H, 5.2; N, 2.1.

[(9b)$_2$K]PF$_6$. Anal. Found: C, 56.2; H, 5.7; N, 2.1. Calcd for $C_{36}H_{70}Fe_2N_2KO_8PF_6$: C, 56.3; H, 5.9; N, 2.3.

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