

# Oxaferrocene Cryptands as Efficient Molecular Switches for Alkali and Alkaline Earth Metal Ions

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The reactions of 3,4-diphenylcyclopent-2-en-1-one, cyclopent-2-en-1-one, 3,4-dimethylcyclopent-2-en-1-one, and 2,3,4,5-tetramethylcyclopent-2-en-1-one with various trialkylsilyl triflates ( $\text{SiR}_3 = \text{SiMe}_3, \text{SiEt}_3, \text{SiMe}_2^t\text{Bu}, \text{Si}^i\text{Pr}_3$ ) result in the formation of the respective cyclopentadienyl silyl ethers in virtually quantitative yields. The reactions of these cyclopentadienes with *n*-BuLi and  $\text{FeCl}_2$  give the respective substituted ferrocenyl trialkylsilyl ethers in 48–57% yields, which are synthetic equivalents of hydroxyferrocenes as generated by a suitable cleavage protocol:  $\text{SiMe}_3$ -protected ferrocene alcohols ( $\text{CH}_3\text{CN} + 10\% \text{H}_2\text{O} + \text{Na}_2\text{CO}_3$ );  $\text{SiEt}_3$  ( $\text{CH}_3\text{CN} + 10\% \text{H}_2\text{O} + \text{Na}_2\text{CO}_3 + \text{NaF}$ ); and  $\text{SiMe}_2^t\text{Bu}$  protection ( $\text{NBu}_4\text{F} \cdot 3\text{H}_2\text{O}$  in  $\text{CH}_3\text{CN}$ ). Carrying out the deprotection in the presence of carbon electrophiles leads to the respective ferrocenyl alkyl ethers in excellent yields. Using 1-chloro-2-tosylethane results in 1,1'-bis(2-chloroethoxy)-3,3',4,4'-tetraphenylferrocene which was converted into 1,1'-bis(2-iodoethoxy)-3,3',4,4'-tetraphenylferrocene in 89% yield, to be finally reacted with diaza-crown ethers (diaza-12-C-4, diaza-15-C-5, diaza-18-C-6). In this manner the respective ferrocene cryptands **23**, **24**, and **25** were generated as the 1 + 1 products in yields of 67–80%. The coordination of alkali and alkaline earth metal ions within the cavities of these ferrocene cryptands results in large anodic shifts of the redox potentials of the ferrocene units (**23**,  $E = +0.290 \text{ V}$ ; **23** +  $\text{Ca}^{2+}$ ,  $E = +0.670 \text{ V}$ ; **23** +  $\text{Na}^+$ ,  $E = +0.505 \text{ V}$ ; **24**,  $E = +0.285 \text{ V}$ ; **24** +  $\text{K}^+$ ,  $E = +0.455 \text{ V}$ ) as determined by cyclic voltammetry. These anodic shifts are correlated with a decrease in the complex stability constant *K* of the respective metal ion complex (redox-switching effect) and in the case of **23** and  $\text{Ca}^{2+}$  amounts to a reduction of *K* by  $3.4 \times 10^6$ .

## Introduction

The making of molecules capable of performing certain tasks has been termed property-directed synthesis.<sup>1</sup> Consequently the investigation of specifically designed molecular devices constitutes a subdivision of supramolecular chemistry.<sup>2,3</sup> Examples for such devices are molecular switches, in which a characteristic property such as conductivity along a molecular wire,<sup>4</sup> fluorescence,<sup>5</sup> refractive index,<sup>6</sup> magnetic behavior,<sup>7</sup> photochromism,<sup>8</sup> catalytic behavior,<sup>9</sup> or affinity toward a guest molecule can be switched on or off.<sup>10</sup> The minimum requirements for the switched complexation of guests are the ability to incorporate molecular or ionic units into a suitable receptor framework as well as the reversible change of the binding properties triggered by a chemical or physi-

cal stimulus, which may be a light- or chemically-driven conformational change,<sup>11</sup> a variation of proton concentration,<sup>12</sup> or an electron transfer (redox reaction).<sup>13,14</sup>

For our work we have chosen to investigate the redox-switched bonding of alkali or alkaline earth metal ions within the cavities of ferrocene-crown ethers. Consequently the guest is a metal ion, whose binding properties within a ferrocene cryptand are switched on or off, depending on the redox state of the ferrocene unit. Group I and II metal ions are ideally suited for such switching devices, since their coordination chemistry is characterized by fast complexation and decomplexation reactions.

(10) The term switch may be somewhat misleading, in that it suggests an all or nothing situation, which is, quite in contrast to a mechanical switch, not possible on a molecular level. According to the laws of thermodynamics there can only be a certain increase or decrease in the binding affinity as expressed by a change of the stability constant *K* for the equilibrium under observation.

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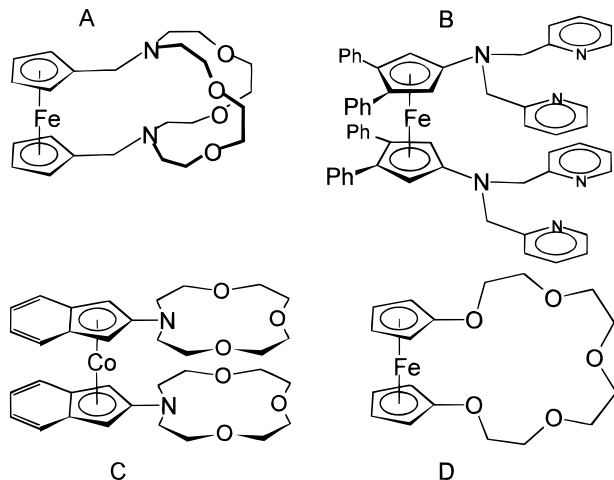
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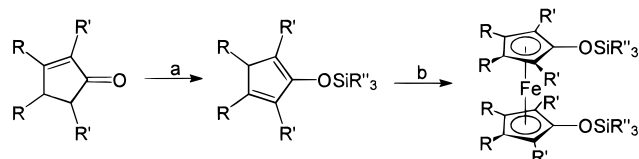
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Chart 1



For an optimum performance of such molecular devices it is very important to allow an efficient electronic communication between the metal ion coordinated within the macrocyclic cavity and the redox active unit. Recently it was shown by us that the switching process in most ferrocene cryptands relies predominantly on electrostatic interactions.<sup>15</sup> One of the best molecular devices based on this principle is (1,1'-ferrocenylenedimethylene) bis(1,4,10,13-tetraoxa-7,16-diazacyclooctadecane) (A in Chart 1),<sup>16</sup> but it is difficult to see how such switches primarily relying on Coulomb type interactions could be further optimized. Consequently, to develop such molecular machines to the point at which they can be used to emulate naturally occurring switching molecules such as for example calmodulin,<sup>17</sup> the previous concept based only on electrostatic interactions has to be modified and extended. In this vein we have recently demonstrated in an investigation of transition metal complexes of bis(1,1'-di(2-picolyl)-amino)-3,3',4,4'-tetraphenylferrocene (B in Chart 1) that the electronic communication between the two metal centers can be improved drastically when at least one of the donor atoms coordinated to the metal ion is directly coupled electronically to the metallocene unit.<sup>18</sup>

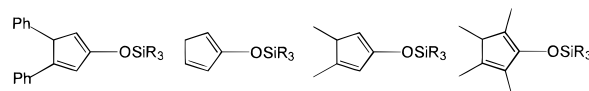
Due to the often unfavorable thermodynamic and kinetic properties (with respect to switching action!) transition metal complexes are not well suited for redox-switching, while unfavorable soft-hard interactions in the complexes of the hard alkali metal ions with the soft nitrogen donors of aminoferrocenes did not result in significantly improved devices (C in Chart 1).<sup>19</sup> The obvious solution therefore was to synthesize ferrocene cryptands in which one or two hard oxygen donor centers are directly attached to the redox-active moiety. In fact the first ferrocene crown ethers prepared used this concept (D in Chart 1),<sup>20</sup> which was abandoned later

Scheme 1. General Synthesis of the Cyclopentadienyl Silyl Ethers and Ferrocenyl Silyl Ethers<sup>a</sup>

R = H, -Me, -Ph; R' = -H, -Me; R'' = -Me<sub>3</sub>, -Et<sub>3</sub>, -tBuMe<sub>2</sub>, -iPr<sub>3</sub>

<sup>a</sup> Reagents: (a) CF<sub>3</sub>SO<sub>3</sub>SiR''', Et<sub>3</sub>N, petroleum ether; (b) *n*-BuLi, FeCl<sub>2</sub>, THF.

Scheme 2. Cyclopentadienyl Silyl Ethers



R <sub>3</sub> = Me <sub>3</sub>	1	4	8	12
R <sub>3</sub> = Et <sub>3</sub>	2	5	9	13
R <sub>3</sub> = Me <sub>2</sub> tBu	-	6	10	-
R <sub>3</sub> = iPr <sub>3</sub>	3	7	11	14

on, probably due to the difficult availability of the hydroxyferrocenes needed to synthesize such compounds<sup>21</sup> and because the coronand type ligands synthesized then did not allow the stable bonding of alkali metal ions required for an efficient switching device.

To overcome these problems we present here a new and facile synthesis of a number of different silylated hydroxyferrocenes,<sup>22</sup> their reactions to yield oxaferrocene cryptands, and an investigation into the electrochemistry, i.e., switching behavior, of such redox-active macrocycles.

## Results and Discussion

**Syntheses of Oxygen-Substituted Cyclopentadienes.** Cyclopentenones are very versatile starting materials for the synthesis of various cyclopentadienes,<sup>23,24</sup> and we have recently communicated the reactions of 3,4-diphenylcyclopent-2-en-1-one, cyclopent-2-en-1-one, 3,4-dimethylcyclopent-2-en-1-one, and 2,3,4,5-tetramethylcyclopent-2-en-1-one with a variety of trialkylsilyl triflates (SiMe<sub>3</sub>, SiEt<sub>3</sub>, Si<sup>t</sup>BuMe<sub>2</sub>, Si<sup>i</sup>Pr<sub>3</sub>) yielding the respective cyclopentadienyl silyl ethers 1–14 in almost quantitative yields (Scheme 1, Scheme 2) when applying procedures related to those by Simchen et al.<sup>25</sup> and Reetz et al.<sup>26</sup> for silyl enol ether formation.

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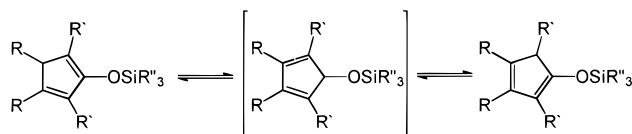
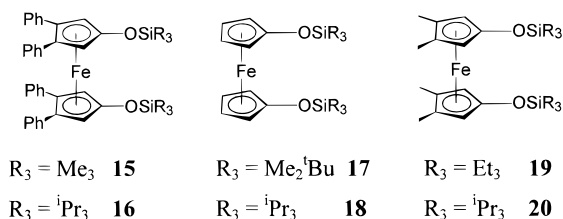
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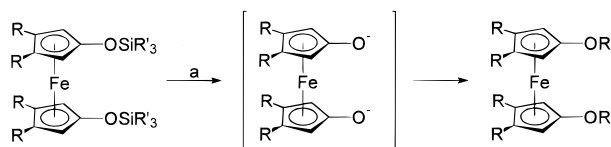
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**Scheme 3. Different Isomers of the Silyl Cyclopentadienyl Ethers****Scheme 4. 1,1'-Disiloxyferrocenes**

The cyclopentadienes **1–3** and **8–14** derived from 3,4-diphenylcyclopent-2-en-1-one, 3,4-dimethylcyclopent-2-en-1-one, and 2,3,4,5-tetramethylcyclopent-2-en-1-one, respectively, are stable compounds. However, the cyclopentadienes synthesized from the unsubstituted cyclopent-2-en-1-one are prone to Diels–Alder dimerization and must be stored at temperatures below  $-20\text{ }^{\circ}\text{C}$  but can be handled without special precautions during workup at room temperature. All yields were excellent, as long as an excess of acid (trialkylsilyl triflate) with respect to the added base ( $\text{Et}_3\text{N}$ ) was avoided, since this invariably leads to the decomposition of the products.

The characterization of the cyclopentadienyl silyl ethers by NMR spectroscopy is not straightforward since they exist as a mixture of double-bond isomers (Scheme 3).<sup>27</sup> The product formed under kinetic control is the 1,4-diene, which rearranges within a time interval ranging from a few minutes to several days to give the thermodynamically favored 1,3-diene. Both isomers have the siloxy groups in the vinyl position, while another possible isomer with the siloxy substituents in the allyl position was never observed in detectable concentrations.

**Synthesis of Ferrocenyl Silyl Ethers and Ferrocenyl Alkyl Ethers.** We have synthesized a number of cyclopentadienylsilyl ethers with different protective groups to evaluate which of them is best suited for the synthesis of the respective ferrocenes (Scheme 1, Scheme 4). Ideally the protective group is just stable enough to survive the reaction conditions during the formation of the ferrocenyl silyl ethers and can be easily cleaved off afterward under basic conditions, to allow the in situ functionalization to ferrocenyl alkyl ethers. The stability of the protective group primarily depends on the steric bulk of the trialkylsilyl unit<sup>28</sup> and to a minor extent also on the additional substituents attached to the cyclopentadiene. Accordingly we found that  $\text{SiMe}_3$ -protected **1** is ideally suited for the synthesis of the corresponding tetraphenylferrocene **15**, when using a standard procedure in which the cyclopentadienyl silyl ethers are deprotonated with  $n\text{-BuLi}$  and the respective anions reacted with  $\text{FeCl}_2$ . For the more electron-rich metallocenes at least  $\text{SiEt}_3$  protection is required and the synthesis of the corresponding ferrocenes is possible under carefully controlled reaction conditions. However,

**Scheme 5. Synthesis of the 1,1'-Dialkoxyferrocenes<sup>a</sup>**

<sup>a</sup> Conditions: (a) cleavage reagents for  $\text{OSiMe}_3$ ,  $\text{CH}_3\text{CN}/10\%\text{ H}_2\text{O}/\text{Na}_2\text{CO}_3$ ; and  $\text{OSiEt}_3$ ,  $\text{CH}_3\text{CN}/10\%\text{ H}_2\text{O}/\text{Na}_2\text{CO}_3/\text{NaF}$ ; and  $\text{Si}^t\text{BuMe}_2$ ,  $\text{Bu}_4\text{N}^+\text{F}^-\cdot 3\text{H}_2\text{O}/\text{Na}_2\text{CO}_3$ .

for more reliable results  $\text{SiMe}_2^t\text{Bu}$  protection is to be preferred. Quite in contrast the synthesis of the 1,1'-bis(trialkylsiloxy)octamethylferrocenes is unreliable. We were able to isolate a dark red oil, which most likely appears to contain the desired ferrocene. The reason for these problems appears to be that small protective groups are unstable with respect to cleavage reactions, while the anions of the extremely bulky tetramethyl-(trialkylsiloxy)cyclopentadienes are rather oxidatively coupled upon attempted ferrocene synthesis. The redox potentials of the ferrocenes reflect the electronic effects of the different substituents, and it is obvious that siloxy groups are strongly electron-donating substituents, with each being responsible for a cathodic shift of about 100 mV: **15**  $E_{1/2} = +0.28\text{ V}$ ; **17**  $E_{1/2} = +0.18\text{ V}$ ; **19**  $E_{1/2} = -0.03\text{ V}$ .<sup>29</sup>

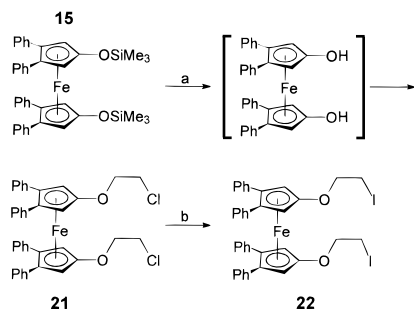
The ferrocenyl silyl ethers described here are masked alcohols forming stable compounds, quite unlike the closely related hydroxyferrocenes.<sup>21</sup> For the synthesis of the desired ferrocenyl alkyl ethers, it is most convenient to cleave the silyl ether and in situ react the formed alcohol with carbon electrophiles to generate the ferrocenyl alkyl ethers (Scheme 5). The cleavage of the alcohol as well as formation of the alkyl ether ideally proceeds in one step under basic conditions, and we have performed a number of experiments with  $\text{SiMe}_3$ -,  $\text{SiEt}_3$ -, and  $\text{SiMe}_2^t\text{Bu}$ -protected alcohols in the presence of different cleavage reagents and benzyl bromide to determine the optimum conditions. The  $\text{SiMe}_3$ -protected ferrocene **15** is best reacted in acetonitrile containing 10% of water and excess  $\text{Na}_2\text{CO}_3$ . Performing this cleavage in the presence of benzyl bromide leads directly to the respective benzyl ether in more than 85% yield. This procedure does not work very well in the case of the  $\text{SiEt}_3$ - and  $\text{SiMe}_2^t\text{Bu}$ -protected ferrocenes and it is much more convenient to cleave the latter two silyl ethers in a different manner:  $\text{SiEt}_3$  protection (excess  $\text{NaF} + \text{Na}_2\text{CO}_3$  in  $\text{CH}_3\text{CN}$  with 10% water) and  $\text{SiMe}_2^t\text{Bu}$  protection ( $n\text{-Bu}_4\text{N}^+\text{F}^-\cdot 3\text{H}_2\text{O}$  in  $\text{CH}_3\text{CN}$ ). The fluoride reagent is highly reactive and quantitatively cleaves the silyl ethers within a few minutes at room temperature. Carrying out both cleavage reactions in the presence of benzyl bromide leads after several hours under reflux to the respective ferrocenyl benzyl ethers.

**Synthesis of the Ferrocene Cryptands.** After synthesizing a number of ferrocenyl silyl ethers as well as working out conditions for their cleavage and transformation into the respective alkyl ethers, we had to decide which ferrocene was best suited for the synthesis of ferrocene cryptands. While an obvious choice might have been the unsubstituted ferrocene **17**, we prefer the tetraphenylferrocene **15** instead, because it is much

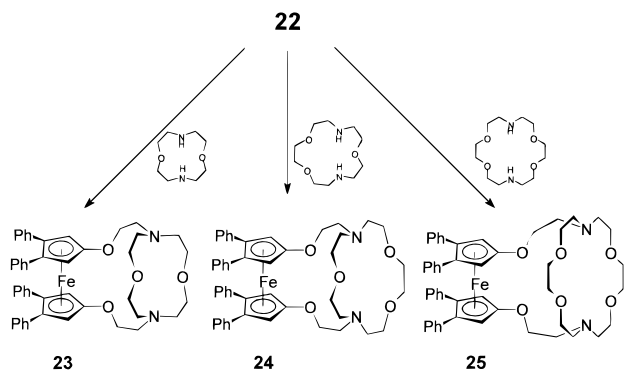
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**Scheme 6. Synthesis of 1,1'-Bis(2-iodoethoxy)-3,3',4,4'-tetraphenylferrocene<sup>a</sup>**

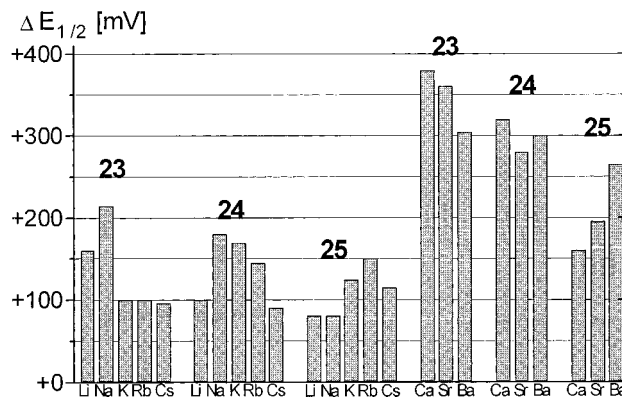
<sup>a</sup> Reagents and conditions: (a) CH<sub>3</sub>CN + 10% H<sub>2</sub>O, Na<sub>2</sub>CO<sub>3</sub>; ClC<sub>2</sub>H<sub>4</sub>(tosylate), reflux; (b) NaI, acetone reflux.

**Scheme 7. Synthesis of the Oxaferrocene Cryptands**

more convenient for a number of reasons: (I) 3,4-diphenylcyclopentenone can be synthesized in two steps from easily available starting materials in large amounts (>100 g).<sup>18a,30</sup> (II) The steric bulk of the two phenyl groups hinders the Diels–Alder dimerization of the respective cyclopentadienylsilyl ethers. (III) The electron-withdrawing effect of the phenyl groups renders the resulting ferrocenes less sensitive toward oxidation, which facilitates chromatographic workup. (IV) The SiMe<sub>3</sub> protective group can be cleaved off very easily.

The tetraphenylferrocene **15** was cleaved according to Scheme 6 and the resulting dihydroxyferrocene in situ reacted with a 5-fold excess of 1-tosyl-2-chloroethane. This reaction yields after chromatographic purification 1,1'-bis(2-chloroethoxy)-3,3',4,4'-tetraphenylferrocene (**21**) in 80% yield together with a small amount (<5%) of the undesired ferrocenophane, resulting from an intramolecular ring closure of the second hydroxy group with the OCH<sub>2</sub>CH<sub>2</sub>Cl unit. Iodide can be replaced more easily than chloride, and a Finkelstein reaction was employed to generate the iodide **22** from the chloride **21** in 89% yield.

This iodide was reacted with three different macrocycles (diaz-12-crown-4, diaza-15-crown-5, diaza-18-crown-6) in the presence of Na<sub>2</sub>CO<sub>3</sub> or K<sub>2</sub>CO<sub>3</sub> to yield the desired ferrocene cryptands in excellent yields: **23** (yield 80%), **24** (yield 67%), and **25** (yield 68%) (Scheme 7). Such extremely high yields are quite unusual in the formation of macrocycles, especially since no high dilution conditions were applied.<sup>31</sup>

**Scheme 8. Histogram of the Shifts of the Redox Potentials ( $\Delta E_{1/2}$ ) As Induced by the Coordination of the Alkali and Alkaline Earth Metal Ions within the Cavities of the Oxaferrocene Cryptands **23**, **24**, and **25****

**Cyclic Voltammetric Investigations of the Ferrocene Cryptands and their Metal Complexes.** In the metal complexes of the oxaferrocene cryptands **23**, **24**, and **25** two oxygen donors are shared between the redox-active metallocene and the group I or II metal ion bonded within the macrocyclic cavity. These two oxygen atoms are vital for the electronic communication between the two metal centers for two reasons: (I) A chelating coordination of a metal ion by the two oxygen centers bonded directly to the cyclopentadienyl rings will result in a short iron to metal ion distance and consequently in an increase of the electrostatic interaction between the two metal centers. (II) The coordination of a metal ion by the same two oxygen atoms will allow a through bond interaction between the two metal centers via the cyclopentadienyl units. More evidence for the participation of the two oxygen atoms attached to the five-membered ring in the complexation of the metal cations could have been obtained from crystal structure analysis; however, all crystals investigated (**23**·NaClO<sub>4</sub>, **23**·NaCF<sub>3</sub>SO<sub>3</sub>, **24**·KCF<sub>3</sub>SO<sub>3</sub>) either proved to be high-order twins or poorly diffracting species.

We expected that the aforementioned two effects would give rise to a highly efficient switching device, to be quantified by measuring the redox potentials of the oxaferrocene cryptands ( $E_1$ ) as well as the anodically shifted redox potentials ( $E_2$ ) of the respective complexes with group I or II metal ions. The difference  $E_2 - E_1 = \Delta E_{1/2}$  is correlated with the difference in the stability constants for the metal ion complexes of the neutral and the oxidized oxaferrocene cryptand.<sup>32</sup>

Upon analyzing the CV data obtained for the oxaferrocene cryptands **23**, **24**, and **25** and their group I or II metal ion complexes, two overlapping trends are visible (Scheme 8, Table 1): (I) The larger the cavity, i.e., the more donor atoms present (**23** → **24** → **25**), the smaller the anodic shift  $\Delta E_{1/2}$  of the redox potentials. (II) Those metal ions which are complementary to the size of the cavity of the ferrocene cryptand produce the largest anodic shift  $\Delta E_{1/2}$  of the redox potentials upon complexation.

Both trends can be identified, when the  $\Delta E_{1/2}$  values of the different alkaline earth metal ion complexes of

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**Table 1. Summary of the Redox Potentials of the Ferrocene Cryptands **23**, **24**, and **25** and Their Different Alkaline and Alkaline Earth Metal Ion Complexes. All CV's Were Recorded in Acetonitrile at Ambient Temperatures Using Group I and II Triflates or Perchlorates**

metal ion	Li <sup>+</sup>	Na <sup>+</sup>	K <sup>+</sup>	Rb <sup>+</sup>	Cs <sup>+</sup>	Ca <sup>2+</sup>	Sr <sup>2+</sup>	Ba <sup>2+</sup>
<b>Ferrocene <b>23</b></b>								
$E_{1/2}$ [V]	+0.290	+0.450	+0.505	+0.390	+0.390	+0.385	+0.670	+0.650
$\Delta E_{1/2}$ [mV]		+160	+215	+100	+100	+95	+380	+360
<b>Ferrocene <b>24</b></b>								
$E_{1/2}$ [V]	+0.285	+0.385	+0.465	+0.455	+0.430	+0.375	+0.605	+0.585
$\Delta E_{1/2}$ [mV]		+100	+180	+170	+145	+90	+320	+280
<b>Ferrocene <b>25</b></b>								
$E_{1/2}$ [V]	+0.285	+0.365	+0.365	+0.410	+0.435	+0.400	+0.445	+0.480
$\Delta E_{1/2}$ [mV]		+80	+80	+125	+150	+115	+160	+195

**23**, **24**, and **25** are compared. With **23** for Ca<sup>2+</sup>, Sr<sup>2+</sup>, and Ba<sup>2+</sup> the largest  $\Delta E_{1/2}$  of +380, +360, and +305 mV within the whole series was observed. But it is also obvious that the cavity of **23** is best suited for Ca<sup>2+</sup>, since in the complexes of this metal with **23**, **24**, and **25**  $\Delta E_{1/2}$  drops very significantly from +380 → +320 → +160 mV. On the other hand the drop of  $\Delta E_{1/2}$  in the same series of ligands is much less pronounced for the Ba<sup>2+</sup> complexes, i.e., +305 → +300 → +265 mV.

The second trend is more obvious upon analyzing the  $\Delta E_{1/2}$  values of the alkali metal complexes with **23**, **24**, and **25**. For **23** the Na<sup>+</sup> complex displays the largest  $\Delta E_{1/2}$  value by a wide margin; while **24**/Na<sup>+</sup> still shows the strongest anodic shift of all alkali metal ions, but now by a much smaller margin. When **23** and **24** are compared, the Na<sup>+</sup> value decreases from +215 → +180 mV, whereas the K<sup>+</sup>  $\Delta E_{1/2}$  value has increased from +100 → +170 mV; this trend continues with **25** and here the +80 mV of Na<sup>+</sup> is substantially smaller than the +125 mV determined for K<sup>+</sup>, while the largest shift is observed with the larger Rb<sup>+</sup> +150 mV. It is quite remarkable that in **24** even the comparatively soft Cs<sup>+</sup> shows a larger  $\Delta E_{1/2}$  than that of Na<sup>+</sup>. The  $\Delta E_{1/2}$  values were calculated to correspond to the following reductions in the stability constants: **23**/Na<sup>+</sup> =  $5 \times 10^3$ , **23**/Ca<sup>2+</sup> =  $3.5 \times 10^6$ , and **24**/K<sup>+</sup> =  $8.4 \times 10^2$ .

An explanation for the trends described above can be easily given. The general drop of  $\Delta E_{1/2}$  upon increasing the size of the ligand cavity is caused by the decreased relative importance of the two oxygen atoms directly bonded to the cyclopentadienyl ring for metal coordination, as evidenced by the increasing number of donor atoms in the diaza crown ether substructure. This also causes an increase in the iron–metal ion distance and hence a reduced electrostatic interaction. The two oxygen atoms directly bonded to the ferrocene will be most important when the metal ion is complementary to the cavity of the respective ferrocene cryptand.

It should finally be noted that the anodic shifts of the redox potentials observed in the ferrocene cryptands **23**, **24**, and **25** are the largest ever observed in ferrocene crown ethers and this is also the first time that substantial effects have been observed for the larger alkali metal ions K<sup>+</sup>, Rb<sup>+</sup>, and Cs<sup>+</sup>. The switching effects are extremely strong for the alkaline earth metal ions, and the Ca<sup>2+</sup> value of  $\Delta E_{1/2}$  = +380 mV is 110 mV more positive than the previous best of  $\Delta E_{1/2}$  = +270 mV observed by Gokel et al.<sup>16</sup> in a ferrocene cryptand, which appears to rely mainly on electrostatic interactions.

**Conclusions.** The work described here is based on the development of a new and facile synthesis of

ferrocenyl silyl ethers which are used as stable synthetic equivalents of the otherwise unstable hydroxyferrocenes and on the fact that the new oxafferrocene cryptands are available in excellent yields from fairly simple starting materials. Consequently, we have described the synthesis of highly efficient molecular switches based on ferrocenyl alkyl ether cryptands, in which two oxygen atoms act as an electronic relays between the redox-active ferrocene unit and a group I or II metal ion coordinated by the macrocyclic unit. The performance of these devices by far exceeds that of other known redox switches and is especially high for the biologically relevant metal ions calcium, sodium, and potassium with switching effects of up to  $3.5 \times 10^6$  for calcium complexation. It can be finally concluded that the development of molecular switching devices based on ferrocenes has now reached a point at which one can seriously envisage applications in terms of imitating naturally occurring switching and regulatory device.<sup>33</sup> The systems presented here appear well suited for this purpose. In this context it is quite significant that calcium is the element responsible for controls and triggers in organisms.<sup>34</sup>

## Experimental Section

Commercially available solvents and reagents were purified according to literature procedures. Chromatography was carried out on silica MN60. NMR spectra were recorded at 300 K on a Bruker Avance (<sup>1</sup>H NMR 200 MHz, <sup>13</sup>C NMR 50.3 MHz) instrument. <sup>1</sup>H NMR were referenced to residual <sup>1</sup>H impurities in the solvent and <sup>13</sup>C NMR to the solvent signals: CDCl<sub>3</sub> (7.26 ppm, 77.0 ppm), C<sub>6</sub>D<sub>6</sub> (7.16, 128.0 ppm), CD<sub>3</sub>CN (1.93 ppm, 1.30 ppm). For the purpose of <sup>1</sup>H NMR signal assignment CpH denotes a proton attached to the sp<sup>2</sup> carbon of cyclopentadiene or to the carbon of a ferrocene η<sup>5</sup>-cyclopentadienyl ring. 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. All cyclic voltammograms were recorded in dry CH<sub>3</sub>CN under an argon atmosphere at ambient temperature and processed 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 with a Pt wire counter electrode. The pseudoreference electrode was an Ag wire. Potentials were calibrated internally against the formal potential of cobalti-

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cinium perchlorate ( $-0.94$  V vs Ag/AgCl) or octamethylferrocene ( $-0.025$  V vs Ag/AgCl). Solutions were ca.  $2 \times 10^{-4}$  mol dm $^{-3}$  in compound. NBu $_4$ PF $_6$  (0.1 M) was used as a supporting electrolyte. In all complexes the separation of anodic and cathodic peak potentials is smaller than 100 mV (scan speed 100 mV/s). 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 and Geissman/Koelsch.<sup>18a,30</sup> Starting materials were available commercially or prepared according to literature procedures: diaza-12-crown-4,<sup>35</sup> 3,4-dimethylcyclopent-2-en-1-one.<sup>36</sup>

**Synthesis of 1-(Trialkylsiloxy)-3,4-diphenylcyclopentadienes 1, 2, and 3.** 3,4-Diphenylcyclopent-2-enone was added to 30/50 petroleum ether and treated with Et $_3$ N. CF $_3$ SO $_3$ SiR $_3$  (R = Me, Et,  $^i$ Pr) was added dropwise to the ice-cooled, stirred suspension. The reaction mixture was allowed to warm to room temperature and stirring continued for 12 h. Precipitated Et $_3$ NH $^+$ CF $_3$ SO $_3^-$  was filtered off and the solvent removed from the filtrate in vacuo, whereupon a red-brown oil remains behind.

**1-(Trimethylsiloxy)-3,4-diphenylcyclopentadiene (1).** Scale: 3,4-diphenylcyclopent-2-en-1-one (1.00 g, 4.3 mmol), Et $_3$ N (1.20 mL, 5.20 mmol), CF $_3$ SO $_3$ SiMe $_3$  (0.80 mL, 4.30 mmol). Yield: 1.3 g (97%) red-brown oil.  $^1$ H NMR (CDCl $_3$ ):  $\delta$  0.27 (s, 9H, SiCH $_3$ ), 3.43 (s, 2H, CH $_2$ ), 5.56 (s, 1H, CpH), 7.14–7.30 (m, 10H, ArH).  $^{13}$ C NMR (CDCl $_3$ ):  $\delta$  -0.24, 54.69, 113.21, 125.83, 126.31, 126.87, 127.70, 128.19, 128.30, 128.61, 139.30, 150.52, 154.78.

**1-(Triethylsiloxy)-3,4-diphenylcyclopentadiene (2).** Scale: 3,4-diphenylcyclopent-2-en-1-one (1.00 g, 4.3 mmol), Et $_3$ N (1.20 mL, 5.20 mmol), CF $_3$ SO $_3$ SiEt $_3$  (0.90 mL, 4.30 mmol). Yield: 1.43 g (96%) red-brown oil.  $^1$ H NMR (CDCl $_3$ ):  $\delta$  0.78 (q,  $J$  = 15.2 Hz, 6H, CH $_2$ CH $_3$ ), 1.05 (t,  $J$  = 15.1 Hz, 9H, CH $_2$ CH $_3$ ), 3.45 (s, 2H, CH $_2$ ), 5.58 (s, 1H, CpH), 7.11–7.39 (m, 10H, ArH).

**1-(Triisopropylsiloxy)-3,4-diphenylcyclopentadiene (3).** Scale: 3,4-diphenylcyclopent-2-en-1-one (1.00 g, 4.30 mmol), Et $_3$ N (1.20 mL, 5.20 mmol), CF $_3$ SO $_3$ Si $^i$ Pr $_3$  (1.10 mL, 4.30 mmol). Yield: 1.63 g (97%) red-brown oil.  $^1$ H NMR (CDCl $_3$ ):  $\delta$  1.05–1.13 (m, 21H,  $^i$ Pr), 3.43 (s, 2H, CH $_2$ ), 4.55 (d,  $J$  = 2.6 Hz, 1H, CpH), 5.34 (s, 1H, CpH), 6.70 (d,  $J$  = 2.7 Hz, 1H, ArCH), 7.08–7.34 (m, 10H, ArH).  $^{13}$ C NMR (CDCl $_3$ ):  $\delta$  12.48 (SiCH(CH $_3$ ) $_2$ ), 17.90 (CH $_3$ ), 54.62, 113.09, 125.47, 125.82, 126.25, 126.79, 127.43, 127.75, 128.27, 128.56, 128.62, 134.87, 139.48, 150.21, 155.31.

**Syntheses of 1-(Trialkylsiloxy)cyclopentadienes 4, 5, 6, and 7.** A solution of cyclopent-2-en-1-one and NEt $_3$  in 30/50 petroleum ether (50 mL) was cooled to 0 °C and CF $_3$ SO $_3$ SiR $_3$  (R $_3$  = Me $_3$ , Et $_3$  or  $^i$ Pr $_3$ ) added dropwise. The reaction mixture was allowed to warm to room temperature and the Et $_3$ NH $^+$ CF $_3$ SO $_3^-$  precipitate filtered off after 15 min. The solvents were carefully evaporated from the filtrate in vacuo without warming, and the products were stored at  $-20$  °C to retard Diels–Alder dimerizations. It is very important that there is no excess of acid present.

**1-(Trimethylsiloxy)cyclopentadiene (4).** Scale: cyclopent-2-en-1-one (430 mg, 5.00 mmol), Et $_3$ N (0.84 mL, 6.00 mmol), CF $_3$ SO $_3$ SiMe $_3$  (0.93 mL, 5.00 mmol). Yield: 733 mg (95%) yellow oil.  $^1$ H NMR (CDCl $_3$ ):  $\delta$  0.24 (s, 9H, Si(CH $_3$ ) $_3$ ), 2.87–2.91 (m, 2H, CH $_2$ ), 5.23 (m, 1H, CpH), 6.19–6.34 (m, 2H, CpH).

**1-(Triethylsiloxy)cyclopentadiene (5).** Scale: cyclopent-2-en-1-one (430 mg, 5.00 mmol), Et $_3$ N (0.84 mL, 6.00 mmol), CF $_3$ SO $_3$ SiEt $_3$  (1.05 mL, 5.00 mmol). Yield: 953 mg (97%) yellow oil.  $^1$ H NMR (CDCl $_3$ ):  $\delta$  0.72 (q,  $J$  = 7.8 Hz, 6H, SiCH $_2$ CH $_3$ ), 0.99 (t,  $J$  = 7.7 Hz, 9H, CH $_2$ CH $_3$ ), 2.91 (d,  $J$  = 1.5 Hz, 2H, CH $_2$ ), 5.24 (t,  $J$  = 1.8 Hz, 1H, CpH), 6.24–6.35 (m, 2H, CpH).

**1-(Triisopropylsiloxy)cyclopentadiene (7).** Yield: cyclopent-2-en-1-one (430 mg, 5.00 mmol), Et $_3$ N (0.84 mL, 6.00 mmol), CF $_3$ SO $_3$ Si $^i$ Pr $_3$  (1.30 mL, 5.00 mmol). Yield: 1.13 g (95%) yellow oil.  $^1$ H NMR (CDCl $_3$ ):  $\delta$  1.11 (m, 21H, Si $^i$ Pr), 2.91 (m, 2H, CH $_2$ ), 5.25 (m, 1H, CpH), 6.27–6.38 (m, 2H, CpH).

**Syntheses of 1-(Trialkylsiloxy)-3,4-dimethylcyclopentadienes 8–11 and 1-(Trialkylsiloxy)-2,3,4,5-tetramethylcyclopentadienes 12–14.** A solution of 3,4-dimethylcyclopent-2-en-1-one or 2,3,4,5-tetramethylcyclopent-2-en-1-one and NEt $_3$  in 30/50 petroleum ether (50 mL) was cooled to 0 °C and CF $_3$ SO $_3$ SiR $_3$  (R $_3$  = Me $_3$ , Et $_3$ ,  $^i$ BuMe $_2$ , or  $^i$ Pr $_3$ ) added dropwise. The reaction mixture was allowed to warm to room temperature and the Et $_3$ NH $^+$ CF $_3$ SO $_3^-$  precipitate filtered off after 15 min. The solvents were removed from the filtrate and the residue dried under vacuo for 30 min resulting in a yellow oil.

**1-(Trimethylsiloxy)-3,4-dimethylcyclopentadiene (8).** Scale: 3,4-dimethylcyclopent-2-en-1-one (570 mg, 5.00 mmol), Et $_3$ N (0.84 mL, 6.00 mmol), CF $_3$ SO $_3$ SiMe $_3$  (0.93 mL, 5.00 mmol). Yield: 856 mg (94%) yellow oil.  $^1$ H NMR (CDCl $_3$ ):  $\delta$  0.05–0.26 (m, 9H, SiCH $_3$ ), 1.03–1.37 (m, CpCH $_3$ ), 1.75–2.30 (m, CpCH $_3$ ), 2.57–2.80 (m, CH $_2$ ), 4.41–4.57 (m, CpH), 5.04–5.23 (m, CpH), 5.74–5.96 (m, CpH).

**1-(Triethylsiloxy)-3,4-dimethylcyclopentadiene (9).** Scale: 3,4-dimethylcyclopent-2-en-1-one (570 mg, 5.00 mmol), Et $_3$ N (0.84 mL, 6.00 mmol), CF $_3$ SO $_3$ SiEt $_3$  (1.05 mL, 5.00 mmol). Yield: 1.08 g (96%) yellow oil.  $^1$ H NMR (CDCl $_3$ ):  $\delta$  0.69 (q,  $J$  = 15.4 Hz, 6H, SiCH $_2$ ), 0.84–1.21 (m, CH $_3$ ), 1.89 (m, CpCH $_3$ ), 2.17 (m, CpCH $_3$ ), 4.41–4.76 (m, CpH), 5.05–5.32 (m, CpH), 5.76–5.96 (m, CpH).

**1-(tert-Butyldimethylsiloxy)-3,4-dimethylcyclopentadiene (10).** Scale: 3,4-dimethylcyclopent-2-en-1-one (570 mg, 5.00 mmol), Et $_3$ N (0.84 mL, 6.00 mmol), CF $_3$ SO $_3$ SiMe $_2^i$ Bu (1.15 mL, 5.00 mmol). Yield: 1.09 g (97%) yellow oil.  $^1$ H NMR (CDCl $_3$ ):  $\delta$  0.15 (s, 6H, SiCH $_3$ ), 0.92 (s, 9H, Si $^i$ Bu), 1.02–1.42 (m, CpCH $_3$ ), 1.88–2.07 (CpCH $_3$ ), 4.39–4.57 (m, CpH), 5.15–5.25 (m, CpH), 5.72–5.92 (m, CpH).

**1-(Triisopropylsiloxy)-3,4-dimethylcyclopentadiene (11).** Scale: 3,4-dimethylcyclopent-2-en-1-one (570 mg, 5.00 mmol), Et $_3$ N (0.84 mL, 6.00 mmol), CF $_3$ SO $_3$ Si $^i$ Pr $_3$  (1.30 mL, 5.00 mmol). Yield: 1.30 g (98%) yellow oil.  $^1$ H NMR (CDCl $_3$ ):  $\delta$  1.03–1.28 (m, CH $_3$ ), 1.89 (br, CpCH $_3$ ), 2.08 (m, CpCH $_3$ ), 4.40–4.56 (m, CpH), 5.05–5.25 (m, CpH), 5.70–5.82 (m, CpH).

**1-(Trimethylsiloxy)-2,3,4,5-tetramethylcyclopentadiene (12).** Scale: 2,3,4,5-tetramethylcyclopent-2-en-1-one (690 mg, 5.00 mmol), Et $_3$ N (0.84 mL, 6.00 mmol), CF $_3$ SO $_3$ SiMe $_3$  (0.93 mL, 5.00 mmol). Yield: 1.00 g (94%) yellow oil.  $^1$ H NMR (CDCl $_3$ ):  $\delta$  0.05 (s, 9H, SiCH $_3$ ), 0.93–0.99 (m, CpCH $_3$ ), 1.48–1.79 (m, CpCH $_3$ ), 4.45–4.50 (m, 1H, CpH).

**1-(Triethylsiloxy)-2,3,4,5-tetramethylcyclopentadiene (13).** Scale: 2,3,4,5-tetramethylcyclopent-2-en-1-one (690 mg, 5.00 mmol), Et $_3$ N (0.84 mL, 6.00 mmol), CF $_3$ SO $_3$ SiEt $_3$  (1.05 mL, 5.00 mmol). Yield: 1.20 g (95%) yellow oil.  $^1$ H NMR (CDCl $_3$ ):  $\delta$  0.68 (q,  $J$  = 8.0 Hz, 6H, SiCH $_2$ ), 0.86–1.16 (m, CH $_3$ ), 1.57–1.94 (m, CpCH $_3$ ), 4.44–4.51 (m, 1H, CpH).

**1-(Triisopropylsiloxy)-2,3,4,5-tetramethylcyclopentadiene (14).** Scale: 2,3,4,5-tetramethylcyclopent-2-en-1-one (690 mg, 5.00 mmol), Et $_3$ N (0.84 mL, 6.00 mmol), CF $_3$ SO $_3$ Si $^i$ Pr $_3$  (1.30 mL, 5.00 mmol). Yield: 1.44 g (96%) yellow oil.  $^1$ H NMR (CDCl $_3$ ):  $\delta$  1.00–1.18 (m, CH $_3$ ), 1.51–1.96 (m, CpCH $_3$ ), 4.44–4.53 (m, CpH).

**Syntheses of 1,1'-Bis(trialkylsiloxy)-3,4-diphenylferrocenes 15 and 16.** A solution of the respective 1-(trialkylsiloxy)cyclopentadiene **1** or **3** in THF (50 mL) was cooled to  $-40$  °C and treated with  $n$ -BuLi (2.5 M in hexane), resulting in the green fluorescent lithium cyclopentadienide. After stirring for 15 min, the solution was warmed to 0 °C, FeCl $_2$  was added, and the reaction mixture was slowly allowed to warm to room temperature and stirred until the green fluorescence had disappeared. The solvents were evaporated, the oily residue was extracted with cyclohexane, and the

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solution was filtered over a silica plug. Finally the cyclohexane was evaporated and the residue dried in vacuo.

**1,1'-Bis(trimethylsiloxy)-3,3',4,4'-tetraphenylferrocene (15).** Scale: 1-(trimethylsiloxy)-3,4-diphenylcyclopentadiene (2.00 g, 6.51 mmol), *n*-BuLi (2.60 mL, 6.51 mmol, 2.5 M in hexane), FeCl<sub>2</sub> (0.40 g, 3.26 mmol). Yield: 1.23 g (57%) orange-colored powder. Anal. Calcd for C<sub>40</sub>H<sub>42</sub>O<sub>2</sub>Si<sub>2</sub>Fe (666.8): C, 72.73; H, 6.48. Found: C, 72.05; H, 6.35. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 0.20 (s, 18H, SiCH<sub>3</sub>), 4.16 (s, 4H, CpH), 7.00–7.26 (m, 20H, ArH). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 0.30, 65.76, 81.21, 120.42, 125.56, 127.23, 130.01, 136.79.

**1,1'-Bis(triisopropylsiloxy)-3,3',4,4'-tetraphenylferrocene (16).** Scale: 1-(triisopropylsiloxy)-3,4-diphenylcyclopentadiene (2.00 g, 5.12 mmol), *n*-BuLi (2.60 mL, 5.12 mmol, 2.5 M in hexane), FeCl<sub>2</sub> (0.40 g, 2.56 mmol). Yield: 1.17 g (55%) orange-colored powder. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 1.12–1.26 (m, 42H, <sup>i</sup>Pr), 4.23 (s, 4H, CpH), 6.88–7.26 (m, 20H, ArH). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 12.17, 17.92, 66.70, 81.56, 121.80, 125.46, 127.17, 130.04, 136.67.

**Syntheses of 1,1'-Bis(trialkylsiloxy)ferrocenes 17–20.** A solution of the respective 1-(trialkylsiloxy)cyclopentadiene in THF (50 mL) was cooled to –40 °C and treated with *n*-BuLi (2.5 M in hexane). After stirring for 15 min, the solution was warmed to 0 °C, FeCl<sub>2</sub> was added, and the reaction mixture was slowly allowed to warm to room temperature and stirred. The solvents were evaporated, the oily residue was extracted with cyclohexane, and the solution was filtered over a silica plug. Finally the cyclohexane was evaporated and the residue dried in vacuo.

**1,1'-Bis(*tert*-butyldimethylsiloxy)ferrocene (17).** Scale: 1-(*tert*-butyldimethylsiloxy)cyclopentadiene (1.00 g, 5.09 mmol), *n*-BuLi (2.04 mL, 5.09 mmol, 2.5 M in hexane), FeCl<sub>2</sub> (0.31 g, 2.50 mmol). Yield: 0.58 g (52%); orange-colored oil. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 0.15 (s, 12H, SiCH<sub>3</sub>), 0.97 (s, 18H, <sup>t</sup>Bu), 3.78 (br, 4H, CpH), 4.05 (br, 4H, CpH). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>): δ –4.44, 18.31, 25.88, 60.75, 63.21, 122.45.

**1,1'-Bis(triisopropylsiloxy)ferrocene (18).** Scale: 1-(triisopropylsiloxy)cyclopentadiene (1.00 g, 5.09 mmol), *n*-BuLi (2.04 mL, 5.09 mmol, 2.5 M in hexane), FeCl<sub>2</sub> (0.31 g, 2.50 mmol). Yield: 1.11 g (56%); mp. 172 °C; orange-colored powder. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 1.02–1.14 (m, 42H, <sup>i</sup>Pr), 3.75 (<sup>t</sup>t, *J* = 1.9 Hz, 4H, CpH), 3.98 (<sup>t</sup>t, *J* = 1.9 Hz, 4H, CpH). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 12.28, 17.82, 60.88, 62.52, 122.29.

**1,1'-Bis(triethylsiloxy)-3,3',4,4'-tetramethylferrocene (19).** Scale: 1-(triethylsiloxy)-3,4-dimethylcyclopentadiene (1.50 g, 6.67 mmol), *n*-BuLi (2.67 mL, 6.67 mmol, 2.5 M in hexane), FeCl<sub>2</sub> (0.42 g, 3.34 mmol). Yield: 0.81 g (48%) dark yellow oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 0.45–0.71 (m, 12H, SiCH<sub>2</sub>CH<sub>3</sub>), 0.88–0.99 (m, 4H, CH<sub>2</sub>CH<sub>3</sub>), 1.78 (s, 12H, CpCH<sub>3</sub>), 3.55 (s, 4H, CpH). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 11.97, 12.19, 17.90, 63.44, 76.52, 118.13.

**1,1'-Bis(triisopropylsiloxy)-3,3',4,4'-tetramethylferrocene (20).** Scale: 1-(triisopropylsiloxy)-3,4-dimethylcyclopentadiene (2.00 g, 7.50 mmol), *n*-BuLi (3.00 mL, 7.50 mmol, 2.5 M in hexane), FeCl<sub>2</sub> (0.47 g, 3.75 mmol). Yield: 1.19 g (54%) dark yellow oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 1.07 (s, 42H, <sup>i</sup>Pr), 1.81 (s, 12H, CpCH<sub>3</sub>), 3.58 (s, 4H, CpH). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 11.98, 12.19, 17.89, 63.42, 76.36, 117.95.

**1,1'-Bis(2-chloroethoxy)-3,3',4,4'-tetraphenylferrocene (21).** A mixture of 1,1'-bis(trimethylsiloxy)-3,3',4,4'-tetraphenylferrocene (5.00 g, 7.50 mmol), 1-tosyl-2-chloroethane (17.5 g, 75.0 mmol), Na<sub>2</sub>CO<sub>3</sub> (10.0 g, 95.5 mmol), CH<sub>3</sub>CN (500 mL) and H<sub>2</sub>O (50 mL) were heated under reflux for 3 d. After the reaction mixture was cooled to room temperature, the Na<sub>2</sub>CO<sub>3</sub> was filtered off and the solvents were evaporated in vacuo. The residue was purified by chromatography (silica, cyclohexane–ethyl acetate: 4/1). Yield: 3.88 g (80%), mp 154 °C; orange-colored powder. In addition to the desired product a small amount of 3,3',4,4'-tetraphenyldioxa[4]ferrocenophane was isolated. Anal. Calcd for C<sub>38</sub>H<sub>32</sub>Cl<sub>2</sub>FeO<sub>2</sub> (647.4): C, 70.50; H, 4.98. Found: C, 70.20; H, 5.23. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 3.52 (t, *J* = 5.7 Hz, 4H, CH<sub>2</sub>Cl), 3.82 (t, *J* = 5.9 Hz, 4H, OCH<sub>2</sub>),

4.37 (s, 4H, CpH), 7.02–7.24 (m, 20H, ArH). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 41.80, 60.95, 70.08, 81.20, 124.77, 126.16, 127.60, 129.74, 136.26. 3,3',4,4'-Tetraphenyldioxa[4]ferrocenophane. MS, *m/z* (%): 548 (36) [M<sup>+</sup>]. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 4.35 (s, 4H, CpH), 4.84 (s, 4H, CpOCH<sub>2</sub>), 6.90–7.08 (m, 20H, ArH).

**1,1'-Bis(2-iodoethoxy)-3,3',4,4'-tetraphenylferrocene (22).** 1,1'-Bis(2-chloroethoxy)-3,3',4,4'-tetraphenylferrocene (2.70 g, 4.20 mmol) and NaI (6.22 g, 42.00 mmol) were dissolved in acetone (250 mL) and heated under reflux for 6 d. The cold solution was filtered, and the volatiles were evaporated. The residue was taken up in CH<sub>2</sub>Cl<sub>2</sub> and washed with Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (10% aqueous). The organic layer was separated, dried over MgSO<sub>4</sub>, and filtered and the solvent evaporated. The crude product was purified by chromatography (cyclohexane–ethyl acetate = 10/1). Yield: 3.10 g (89%), mp 158 °C, orange-colored solid. Anal. Calcd for C<sub>38</sub>H<sub>32</sub>FeI<sub>2</sub>O<sub>2</sub> (830.3): C, 55.14; H, 4.03. Found: C, 54.97; H, 3.88. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 2.81 (t, *J* = 6.6 Hz, 4H, CH<sub>2</sub>I), 3.54 (t, *J* = 6.8 Hz, 4H, OCH<sub>2</sub>), 4.30 (s, 4H, CpH), 7.05–7.40 (m, 20H, ArH). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 1.00 (CH<sub>2</sub>I), 61.07 (CpH), 70.74 (OCH<sub>2</sub>), 81.15, 124.51, 126.18, 127.62, 129.74, 136.30.

**1,1'-[(1,7-Dioxa-4,10-diazacyclododecane-4,10-diyl)-3,3',4,4'-tetraphenylferrocene (23).** A mixture of 1,1'-bis(2-iodoethoxy)-3,3',4,4'-tetraphenylferrocene (250 mg, 0.30 mmol), diaza-12-crown-4 (52 mg, 0.30 mmol), and Na<sub>2</sub>CO<sub>3</sub> (160 mg, 1.50 mmol) in CH<sub>3</sub>CN (50 mL) was heated under reflux for 5 d. The cold reaction mixture was filtered, the volatiles were evaporated in vacuo, and the residue was dissolved in a mixture of CH<sub>2</sub>Cl<sub>2</sub> (20 mL) and water (10 mL). The organic layer was separated and washed with water twice (10 mL), dried over MgSO<sub>4</sub>, filtered, and evaporated. The residue was purified by chromatography (ethyl acetate–diethylamine: 20/1). Yield: 180 mg (80%), mp 215 °C; orange-colored powder. Anal. Calcd for C<sub>46</sub>H<sub>48</sub>FeN<sub>2</sub>O<sub>4</sub> (748.7): C, 73.79; H, 6.46; N, 3.74. Found: C, 73.88; H, 6.42; N, 3.70. MS, *m/z* (%): 748 (55) [M<sup>+</sup>]. <sup>1</sup>H NMR (CD<sub>3</sub>CN): δ 2.64–2.88 (m, 8H, NCH<sub>2</sub>), 2.94 (t, *J* = 6.8 Hz, 4H, CpOCH<sub>2</sub>CH<sub>2</sub>N), 3.53–3.61 (m, 8H, CH<sub>2</sub>O), 4.28 (t, *J* = 6.8 Hz, 4H, CpOCH<sub>2</sub>), 4.43 (s, 4H, CpH), 6.92–7.08 (m, 20H, ArH). <sup>13</sup>C NMR (CD<sub>3</sub>CN): δ 55.74, 57.00, 62.38, 70.69, 72.55, 82.71, 126.86, 127.00, 128.12, 128.42, 130.81, 137.65.

**1,1'-[(1,4,10-Trioxa-7,13-diazacyclopentadecane-7,13-diyl)diethoxy]-3,3',4,4'-tetraphenylferrocene (24).** A mixture of 1,1'-bis(2-iodoethoxy)-3,3',4,4'-tetraphenylferrocene (500 mg, 0.60 mmol), diaza-15-crown-5 (127 mg, 0.60 mmol), and Na<sub>2</sub>CO<sub>3</sub> (320 mg, 3.0 mmol) in CH<sub>3</sub>CN (50 mL) was heated under reflux for 7 d. The cold reaction mixture was filtered, the volatiles were evaporated in vacuo, and the residue was dissolved in a mixture of CH<sub>2</sub>Cl<sub>2</sub> (20 mL) and water (10 mL). The organic layer was separated and washed with water twice (10 mL), dried over MgSO<sub>4</sub>, filtered, and evaporated. The residue was purified by chromatography (ethyl acetate–diethylamine: 20/1). Yield: 320 mg (67%), mp 210 °C; orange-colored powder. Anal. Calcd for C<sub>48</sub>H<sub>52</sub>FeN<sub>2</sub>O<sub>5</sub> (792.8): C, 72.72; H, 6.61; N, 3.53. Found: C, 72.63; H, 6.77; N, 3.66. MS, *m/z* (%): 792 (39) [M<sup>+</sup>]. <sup>1</sup>H NMR (CD<sub>3</sub>CN): δ 2.65–2.69 (m, 8H, NCH<sub>2</sub>), 2.87 (t, *J* = 6.8 Hz, 4H, CpOCH<sub>2</sub>CH<sub>2</sub>N), 3.47–3.52 (m, 12H, CH<sub>2</sub>O), 4.21 (t, *J* = 6.9 Hz, 4H, CpOCH<sub>2</sub>), 4.33 (s, 4H, CpH), 6.79–7.00 (m, 20H, ArH). <sup>13</sup>C NMR (CD<sub>3</sub>CN): δ 55.89, 57.63, 58.41, 61.94, 70.75, 70.97, 71.36, 71.68, 82.87, 126.85, 127.01, 127.64, 128.41, 130.84, 137.45.

**1,1'-[(1,4,10,13-Tetraoxa-7,16-diazacyclooctadecane-7,16-diyl)diethoxy]-3,3',4,4'-tetraphenylferrocene (25).** A mixture of 1,1'-bis(2-iodoethoxy)-3,3',4,4'-tetraphenylferrocene (500 mg, 0.60 mmol), diaza-18-crown-6 (156 mg, 0.60 mmol), and K<sub>2</sub>CO<sub>3</sub> (840 mg, 6.0 mmol) in CH<sub>3</sub>CN (75 mL) was heated under reflux for 7 d. The cold reaction mixture was filtered, the volatiles were evaporated in vacuo, and the residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (20 mL) and water (10 mL). The organic layer was separated and washed with water twice (10 mL), dried over MgSO<sub>4</sub>, filtered, and evaporated. The residue was

purified by chromatography (ethyl acetate–diethylamine: 20/1). Yield: 340 mg (68%), mp 208 °C, orange-colored powder. Anal. Calcd for  $C_{50}H_{56}FeN_2O_6$  (836.8): C, 71.76; H, 6.74; N, 3.35. Found: C, 71.55; H, 6.87; N, 3.27. MS,  $m/z$  (%): 836 (53) [ $M^+$ ].  $^1H$  NMR ( $CD_3CN$ ):  $\delta$  2.71–2.77 (m, 8H,  $NCH_2$ ), 2.94 (t,  $J = 7.0$  Hz, 4H,  $CpOCH_2CH_2N$ ), 3.55–3.62 (m, 16H,  $CH_2O$ ), 4.21 (t,  $J = 6.9$  Hz, 4H,  $CpOCH_2$ ), 4.40 (s, 4H,  $CpH$ ), 6.91–7.09 (m, 20H,  $ArH$ ).  $^{13}C$  NMR ( $CDCl_3$ ):  $\delta$  54.90, 56.72, 60.45, 69.75, 70.08, 71.02, 81.95, 125.61, 125.86, 127.28, 129.83, 135.91.

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