range of solvents tested. These solvents have a wide range of properties, including dielectric constant and its pressure derivative as well as molar volume, index of refraction, viscosity, and compressibility. No simple correlations between the solvent properties and $\Delta V^‡$ were found. However, an analysis of the data within a Marcus theory framework that has had reasonable success in predicting $\Delta V^‡$ values demonstrates that ion pairing can lead to a great diminution of the range of $\Delta V^‡$ values compared to what would be expected without ion pairing. Doine and Swaddle[17] have found better agreement with the Marcus theory predictions in their study of tris(hexafluoroacetylacetonato)ruthenium(II,III) in various solvents. This system is a 0/–charge type, and therefore does not suffer from as many complications from ion pairing and Coulombic interaction as the manganese isocyanides. Nevertheless, they also observed an apparent influence of ion pairing on $\Delta V^‡$ in chloroform.

In order to better interpret these results, more information on the ion paired species present is required, as well as more data on the physical properties of the solvents as a function of pressure in order to apply the Marcus theory and related equations. A better understanding of molar volumes of ions in nonaqueous solvents will also help, and development of equations for predicting molar volumes would allow $\Delta V^‡$ to be predicted by direct consideration of the reactant and transition-state structures. More sensitive instrumentation will also help improve the precision and allow us to work at a wider range of concentrations in order to manipulate the extent of ion pairing.

Further results of this study involve the variation of the ambient-pressure rate constant with solvent and the temperature dependence of the rate constants. The rate constants were found to vary in the opposite manner as did those for complexes of cyclohexyl isocyanide studied earlier. This again indicates that the specifics of the molecular interactions in solvation and not just bulk properties are significant. The values of $\Delta H^‡$ and $\Delta S^‡$ were typical of others measured, and did not show the correlation between $\Delta S^‡$ and $\Delta V^‡$ previously observed for substitution reactions.[30]

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Registry No. $\mathrm{Mn(CNC(CH_3)_3)_6}^+$, 18972-33-3; $\mathrm{Mn(CNC(CH_3)_3)_6}^{2+}$, 19154-91-7; $\mathrm{Mn(CNC_6H_{11})_6}^+$, 52438-24-1; $\mathrm{Mn(CNC_6H_{11})_6}^{2+}$, 52438-27-4.

Notes

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Synthesis, Structure, and Spectroscopic Properties of (σ-Alkyl)iron(II) Phthalocyanines

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Many years ago, it was shown that the doubly reduced iron phthalocyanine $[\mathrm{Fe^IPc}(-3)]^{2-}$ (Pc = phthalocyanine) reacts with alkyl and aryl halides to produce σ-bonded alkyl- and aryliron(II) phthalocyanine derivatives.[2] However, these complexes were never completely characterized and their chemistry has so far not been explored. The analogous iron(II) porphyrin species have been mentioned in the literature as very unstable species that form by electrochemical reduction of the corresponding iron(III) porphyrin complexes, but they were never isolated.[3–6] We have now isolated several σ-bonded alkyliron(II) phthalocyanine complexes. We describe here the synthetic methods used for the preparation of these complexes and their spectroscopic and structural properties.

Experimental Section

General Procedures. All experiments were done under an inert atmosphere by Schlenk techniques. Solvents used were rigorously purified and dried under argon. Iron(II) phthalocyanine was prepared by using known methods[7] and purified at 400 °C under reduced pressure (10^{-4}–10^{-5} Torr). The compounds 1,4,7,10,13,16-hexaoxacyclooctadecane (18-crown-6), lithium aluminum hydride, sodium borohydride, and 2-methyl-2-propanethiol were purchased from Aldrich-Chimie (France). Potassium 2-methyl-2-propanethiolate was prepared by reaction of a 10-fold excess of 2-methyl-2-propanethiol with potassium hydroxide in ethanol, precipitated by addition of diethyl ether, filtered, dried under vacuum, and stored in a glovebox. The visible spectra were recorded in chlorobenzene or THF on a Cary 210 spectrometer. The ^{1}H NMR spectra were obtained in deuteriated DMSO or THF with a 200-MHz Bruker SY 200 instrument in tubes sealed under argon. Chemical shifts are indicated in ppm relative to TMS. Coupling constants are indicated in Hz. Elemental analyses were obtained from the Centre de Microanalyse, Département de Chimie de l'Université Louis Pasteur de Strasbourg. All the analytical and spectroscopic results described here were obtained with small crystals that were sorted out under the microscope.

Synthesis of $[\mathrm{Fe(R)Pc}(-2)]^-$ (R = $\mathrm{CH_3}$ (1), $\mathrm{C_2H_5}$ (2), $\mathrm{(CH_3)_2CH}$ (3)). $\mathrm{LiAlH_4}$ (0.035 mmol, 13 mg) and 18-crown-6 (0.077 mmol, 20.3 mg) were mixed with a suspension of iron(II) phthalocyanine $[\mathrm{Fe(R)Pc}(-2)]$ (0.0355 mmol, 20 mg) in THF (15 mL), and the mixture was stirred until the color of the resulting solution became violet. This color indicated the formation of the doubly reduced species $[\mathrm{Fe^IPc}(-3)]^{2-}$. After filtration under an inert atmosphere a 15–20 fold excess of one of the halides $\mathrm{CH_3I}$ (0.56 mmol, 80 mg), $\mathrm{C_2H_5I}$ (0.064 mmol, 100 mg), or $\mathrm{(CH_3)_2CHBr}$ (0.65 mmol, 80 mg) was added and the stirring was continued until the solution became green. Red crystals of **3** mixed with colorless crystals of 18-crown-6 were obtained after filtration under an inert atmosphere and slow diffusion of pentane into these green solutions enclosed in sealed tubes.

Alternative Procedures. (a) Sodium borohydride (0.035 mmol, 1.3 mg) can also be used as reducing agent in place of lithium aluminum hydride.

(b) Potassium 2-methyl-2-propanethiolate can also be used as reducing agent. A chlorobenzene solution (10 mL) containing potassium 2-methyl-2-propanethiolate (0.21 mmol, 26.6 mg) and 18-crown-6 ($\subset$18c6; 0.077 mmol, 20.3 mg) was added under argon to a suspension of $[\mathrm{Fe^{II}Pc}]$ (0.035 mmol, 20 mg) in 12 mL of chlorobenzene and stirred until the resulting solution became violet. The procedure followed from this point on was then identical with that described above.

$[\mathrm{Fe(CH_3)Pc}][\mathrm{Li}(\subset 18c6)]\cdot\mathrm{THF}$ (1). UV–vis ($\mathrm{C_6H_5Cl}$; λ_m, nm (log ϵ)): 479 (4.94), 540 (4.75), 639 (4.75), 675 (4.76), 707 (4.96). ^{1}H NMR (δ, deuteriated DMSO): 7.70 ($\mathrm{H_a}$, Pc); 8.84 ($\mathrm{H_b}$, Pc); –7.65 ($\mathrm{CH_3}$); 3.34 ($\subset$18c6). Anal. Calcd for $\mathrm{FeLiC_{49}H_{51}N_8O_7}$: C, 63.51; H, 5.50; N, 12.09. Found: C, 62.5; H, 5.2; N, 11.8.

$[\mathrm{Fe(C_2H_5)Pc}][\mathrm{Li}(\subset 18c6)]\cdot\mathrm{THF}$ (2). UV–vis ($\mathrm{C_6H_5Cl}$; λ_m, nm (log ϵ)): 479 (4.87), 550 (4.74), 657 (4.70), 677 (4.71), 702 (4.90). ^{1}H NMR (δ, deuteriated DMSO): 7.63 ($\mathrm{H_a}$, Pc); 8.87 ($\mathrm{H_b}$, Pc); –6.27 ($\mathrm{H_\alpha}$, $\mathrm{C_2H_5}$), –3.01 ($\mathrm{H_\beta}$, $\mathrm{C_2H_5}$), $J(\mathrm{H_\alpha H_\beta})$ = 7.5 Hz); 3.34 ($\subset$18c6). Anal. Calcd for $\mathrm{FeLiC_{50}H_{52}N_8O_7}$: C, 63.84; H, 5.61; N, 11.91. Found: C, 63.6; H, 5.6; N, 12.0.

$[\mathrm{Fe(CH(CH_3)_2)Pc}][\mathrm{Li}(\subset 18c6)]\cdot\mathrm{THF}$ (3). UV–vis ($\mathrm{C_6H_5Cl}$; λ_m, nm (log ϵ)): 479 (4.81), 545 (4.64), 651 (4.63), 676 (4.64), 699 (4.82). ^{1}H

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NMR (δ, deuteriated DMSO): 7.72 (H_a, Pc); 8.81 (H_b, Pc); −5.52 (H_α, $CH(CH_3)_2$, −3.05 (H_β, $CH(CH_3)_2$), $J(H_\alpha H_\beta)$ = 7.2 Hz; 3.34 ($\subset$18c6). Anal. Calcd for $FeLiC_{51}H_{54}N_8O_7$: C, 64.10; H, 5.76; N, 11.74. Found: C, 63.9; H, 5.8; N, 11.6.

X-ray Crystallography. Suitable red single crystals of $[Fe(CH_3)Pc][Na(\subset 18c6)]\cdot THF\cdot C_6H_5Cl$ (**4**) were obtained as described above for **1** by using 2-methyl-2-propanethiolate as reducing agent.

A systematic search in reciprocal space with a Philips PW1100/16 automatic diffractometer showed that crystals of **4** belong to the monoclinic system.

The unit-cell dimensions and their standard deviations were obtained and refined at −100 °C (achieved by using a local by built gas-flow system) with Cu Kα radiation (λ = 1.5405 Å) by using 25 carefully selected reflections and the standard Philips software. Final results: $C_{55}H_{56}N_8O_7NaClFe$, M_r = 1055.4; a = 13.139 (3), b = 21.501 (6), c = 18.631 (5) Å, β = 104.91 (2)°; V = 5086 Å^3; Z = 4; d_{calcd} = 1.378 g cm^{-1}; μ = 34.49 cm^{-1}, $F(000)$ = 2208, space group $P2_1/n$.

A nearly parallelepipedic crystal of dimensions 0.35 × 0.44 × 0.45 mm was glued at the end of a copper wire mounted on a rotation-free goniometer head. All quantitative data were obtained from a Philips PW1100/16 four-circle automatic diffractometer, at −100 °C, controlled by a P852 computer, using graphite-monochromated radiation and standard software. The vertical and horizontal apertures in front of the scintillation counter were adjusted so as to minimize the background counts without loss of net peak intensity at the 2σ level. The total scan width ($\theta/2\theta$ flying step-scan mode) used was $\Delta w = [1 + 0.143 \tan \theta]°$ (deg) with a step width of 0.05° and a scan speed of 0.028° s^{-1}. A total of 7196 ($\pm h,k,l$) reflections were recorded ($4° < \theta < 57°$). The resulting data set was transferred to a MicroVAX II computer, and for all subsequent computations, the Enraf-Nonius SPD/VAX package[8] was used with the exception of a local data-reduction program.

Three standard reflections measured every 1 h during the entire data-collection period showed no significant trend.

The raw step-scan data were converted to intensities by using the Lehmann–Larsen method[9] and then corrected for Lorentz, polarization, and absorption factors the last being computed by the empirical method of Walker and Stuart[10] (transmission factors between 0.97 and 1.12).

A unique data set of 5351 reflections having $I > 3\sigma(I)$ was used for determining and refining the structure.

The structure was solved by direct methods, with use of MULTAN.[11] After refinement of the heavy atoms, a difference-Fourier map revealed maxima of residual electronic density close to the positions expected for hydrogen atoms; they were introduced in structure factor calculations by their computed coordinates (C–H = 0.95 Å) and isotropic temperature factors such that $B(H) = 1.3[B_{eq}(C)]$ Å^2 but not refined (methyl and chlorobenzene hydrogens were omitted). The chlorobenzene solvent molecule is disordered over two positions related by an inversion center (in the ratio 0.5/0.5 derived from difference-Fourier peak heights). Full least-squares refinement minimizing $\sum w(|F_o| - |F_c|)^2$ converged to $R(F$ = 0.068 and $R_w(F)$ = 0.076 ($\sigma^2(F^2) = \sigma^2(\text{counts}) + (pI)^2$). The unit-weight observation was 1.406 for p = 0.08. A final difference map revealed no significant maxima. The scattering factor coefficients and anomalous dispersion coefficients come respectively from parts a and b of ref 12.

Results and Discussion

The electronic spectra of **1**–**3** are almost identical in chlorobenzene (see Experimental Section). The Soret band, which is in general somewhat weaker than the Q band, is here almost as strong. The ^1H NMR spectra of **1**–**3** obtained in deuteriated DMSQ or THF solutions in sealed tubes show resonances close to 8.84 and 7.68 ppm, which correspond respectively to the inner (H_b, Pc) and outer (H_a, Pc) phthalocyanine ring protons (see Experimental Section). Due to the ring current effect of the phthalocyanines ligand the ^1H NMR signals of the axially bonded σ-alkyl groups are shifted upfield.

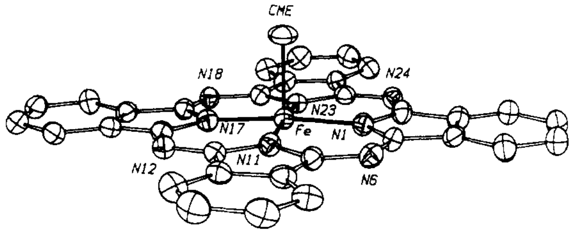

Figure 1. ORTEP drawing of the $[Fe(CH_3)Pc]^-$ anion with thermal ellipsoids at the 50% level.

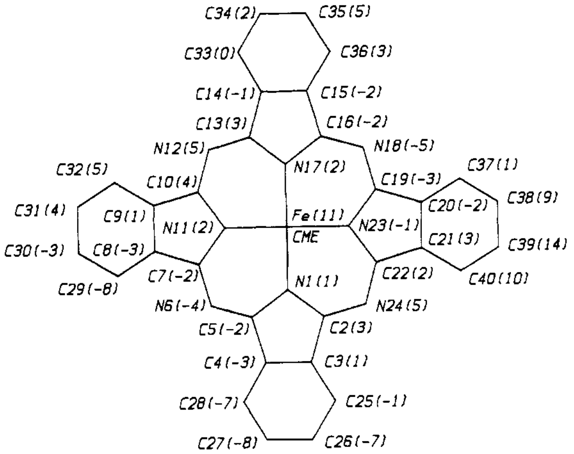

Figure 2. Formal diagram of $[Fe(CH_3)Pc]^-$ giving the numbering scheme used for the atoms and the vertical displacements in 0.01 Å of all the atoms with respect to the central 24-atom-core mean plane of the phthalocyanine ring.

Structure of $[Fe(CH_3)Pc][Na(\subset 18c6)]\cdot THF\cdot C_6H_5Cl$ (4). The asymmetric unit cells of these crystals contain one formula unit. Figure 1 displays the geometry of the $[Fe(CH_3)Pc]^-$ anion. Figure 2 is a formal diagram of the phthalocyanine core, which shows the perpendicular displacements (in units of 0.01 Å) of each atom from the central 24-atom-core mean plane. Table I lists the atomic coordinates of all the non-hydrogen atoms of **4**. Table II gives selected bond distances and bond angles found in 4.

Figure 1 shows the five-coordinate nature of this low-spin complex. The ⟨Fe–N(iso)⟩ bond distance is 1.905 (3) Å (iso = isoindole). This average distance is clearly shorter than the mean value of the four Fe–N(iso) bondlengths of 1.934 (3) Å that has been found in the low-spin six-coordinate bis(4-methylpyridine)iron(II) phthalocyanine.[13] It is also shorter than the average Fe–N(iso) bond length of 1.926 (1) Å present in the intermediate-spin, four-coordinate iron(II) phthalocyanine.[14] The mean value of the C_t- - -Ni(iso) separations is 1.902 Å. This distance indicates that a contraction of the phthalocyanine core occurs when the coordination number of low-spin ferrous phthalocyanine derivatives changes from 6 to 5. Indeed, in the six-coordinate bis(4-methylpyridine)iron(II) species, the metal lies at the center of the phthalocyanine ring; thus, the corresponding C_t–N(iso) distance is identical with the average Fe–N(iso) bond length of 1.934 (3) Å.

A similar contraction of the porphyrin core has been observed when the coordination number of low-spin ferrous porphyrin derivatives changes from 6 to 5. Indeed, the C_t–N_p separation is 1.968 Å[15] in the low-spin five-coordinate thiocarbonyliron(II) tetraphenylporphyrin complex and close to 2.000 Å in the low-spin six-coordinate iron(II) species.[16] The displacement of the iron atom in $[Fe(CH_3)Pc)]^-$ is only 0.10 Å with respect to the 4 N(iso) mean plane and 0.11 Å relative to the central 24-atom-core mean

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Table I. Positional Parameters and Their Estimated Standard Deviations[a]

atom	x	y	z	B, Å^2
Fe	0.40603 (6)	0.16533 (4)	0.76338 (4)	1.94 (2)
N1	0.4299 (3)	0.1987 (2)	0.6742 (2)	2.25 (9)
C2	0.5210 (4)	0.1939 (3)	0.6512 (3)	2.4 (1)
C3	0.5071 (4)	0.2225 (3)	0.5785 (3)	2.6 (1)
C4	0.4039 (4)	0.2449 (2)	0.5585 (3)	2.4 (1)
C5	0.3574 (4)	0.2295 (2)	0.6182 (3)	2.1 (1)
N6	0.2592 (3)	0.2434 (2)	0.6165 (2)	2.44 (9)
C7	0.2168 (4)	0.2288 (2)	0.6715 (3)	2.2 (1)
C8	0.1101 (4)	0.2433 (2)	0.6705 (3)	2.3 (1)
C9	0.0929 (4)	0.2202 (2)	0.7366 (3)	2.2 (1)
C10	0.1909 (4)	0.1922 (2)	0.7763 (3)	2.2 (1)
N11	0.2657 (3)	0.1977 (2)	0.7365 (2)	2.21 (9)
N12	0.2030 (3)	0.1673 (2)	0.8422 (2)	2.22 (9)
C13	0.2940 (4)	0.1434 (2)	0.8801 (3)	2.2 (1)
C14	0.3099 (4)	0.1174 (2)	0.9539 (3)	2.2 (1)
C15	0.4135 (4)	0.0974 (2)	0.9748 (3)	2.2 (1)
C16	0.4603 (4)	0.1124 (2)	0.9149 (3)	2.1 (1)
N17	0.3864 (3)	0.1401 (2)	0.8569 (2)	2.15 (9)
N18	0.5596 (3)	0.0999 (2)	0.9178 (2)	2.00 (9)
C19	0.6008 (4)	0.1135 (2)	0.8616 (3)	2.2 (1)
C20	0.7077 (4)	0.0987 (2)	0.8629 (3)	2.3 (1)
C21	0.7224 (4)	0.1182 (2)	0.7943 (3)	2.0 (1)
C22	0.6249 (4)	0.1453 (2)	0.7544 (3)	2.2 (1)
N23	0.5507 (3)	0.1422 (2)	0.7951 (2)	2.18 (9)
N24	0.6110 (3)	0.1689 (2)	0.6868 (2)	2.31 (9)
C25	0.5735 (4)	0.2311 (3)	0.5326 (3)	2.7 (1)
C26	0.5360 (5)	0.2619 (3)	0.4664 (3)	3.1 (1)
C27	0.4319 (5)	0.2834 (3)	0.4452 (3)	3.1 (1)
C28	0.3642 (4)	0.2754 (3)	0.4916 (3)	2.8 (1)
C29	0.0290 (4)	0.2744 (3)	0.6188 (3)	2.8 (1)
C30	−0.0673 (4)	0.2785 (3)	0.6348 (3)	3.0 (1)
C31	−0.0851 (4)	0.2545 (3)	0.7001 (3)	3.2 (1)
C32	−0.0048 (4)	0.2255 (3)	0.7518 (3)	2.9 (1)
C33	0.2429 (4)	0.1094 (3)	1.0005 (3)	2.5 (1)
C34	0.2826 (4)	0.0795 (3)	1.0678 (3)	2.8 (1)
C35	0.3866 (5)	0.0576 (3)	1.0880 (3)	3.0 (1)
C36	0.4543 (4)	0.0660 (3)	1.0424 (3)	2.8 (1)
C37	0.7874 (4)	0.0685 (3)	0.9147 (3)	2.8 (1)
C38	0.8822 (5)	0.0587 (3)	0.8966 (3)	3.4 (1)
C39	0.8978 (4)	0.0778 (3)	0.8280 (3)	3.3 (1)
C40	0.8180 (4)	0.1081 (3)	0.7766 (3)	2.8 (1)
CME	0.3648 (5)	0.0815 (3)	0.7151 (3)	3.2 (1)
NA	0.4378 (2)	0.3920 (1)	0.7960 (1)	3.05 (5)
O1C	0.6299 (3)	0.3581 (2)	0.8542 (2)	3.54 (9)
C2C	0.6542 (5)	0.3069 (3)	0.8129 (4)	4.2 (2)
C3C	0.6466 (5)	0.3293 (3)	0.7376 (4)	4.0 (2)
O4C	0.5429 (3)	0.3495 (2)	0.7058 (2)	3.32 (9)
C5C	0.5361 (5)	0.3845 (3)	0.6403 (3)	3.7 (1)
C6C	0.4316 (5)	0.4147 (3)	0.6195 (4)	4.2 (2)
O7C	0.4296 (3)	0.4577 (2)	0.6787 (2)	3.66 (9)
C8C	0.3456 (5)	0.5015 (3)	0.6619 (4)	4.1 (2)
C9C	0.2433 (5)	0.4706 (3)	0.6584 (4)	4.2 (2)
O10C	0.2520 (3)	0.4422 (2)	0.7282 (2)	3.54 (9)
C11C	0.1627 (5)	0.4033 (3)	0.7269 (4)	4.7 (2)
C12C	0.1723 (5)	0.3823 (3)	0.8040 (4)	4.6 (2)
O13C	0.2682 (3)	0.3497 (2)	0.8297 (2)	3.56 (9)
C14C	0.2821 (5)	0.3323 (3)	0.9044 (4)	4.3 (2)
C15C	0.3809 (5)	0.2966 (3)	0.9285 (4)	4.2 (2)
O16C	0.4660 (3)	0.3329 (2)	0.9194 (2)	3.55 (9)
C17C	0.5652 (5)	0.3052 (3)	0.9485 (4)	4.2 (2)
C18C	0.6468 (5)	0.3470 (3)	0.9323 (4)	3.9 (1)
OS	0.5230 (3)	0.5185 (2)	0.1340 (2)	4.0 (1)
C1S	0.5961 (5)	0.4854 (3)	0.1043 (4)	4.1 (2)
C2S	0.5635 (8)	0.4202 (3)	0.0997 (6)	7.8 (3)
C3S	0.4639 (8)	0.4177 (3)	0.1137 (6)	7.3 (2)
C4S	0.4332 (5)	0.4800 (3)	0.1318 (4)	4.6 (2)
Cl1S	0.6566 (2)	−0.0065 (1)	0.4867 (2)	5.67 (6)*
C5S	0.6338 (9)	−0.0362 (7)	0.5684 (6)	4.3 (3)
C6S	0.6462 (8)	0.0016 (5)	0.6340 (6)	3.0 (2)
C7S	0.6292 (9)	−0.0228 (5)	0.7025 (6)	2.8 (2)*
C8S	0.5948 (6)	−0.0896 (4)	0.7018 (4)	4.7 (1)*
C9S	0.5810 (9)	−0.1189 (6)	0.6365 (9)	4.6 (3)
C10S	0.5993 (8)	−0.0973 (6)	0.5750 (6)	3.1 (3)
Cl2S	0.6088 (5)	−0.0558 (3)	0.7093 (3)	8.5 (1)*
C11S	0.618 (1)	−0.0364 (8)	0.6141 (9)	6.0 (4)*
C12S	0.600 (1)	−0.0805 (9)	0.554 (1)	7.3 (4)*
C13S	0.626 (2)	−0.051 (1)	0.490 (1)	7.8 (5)*
C14S	0.644 (2)	0.041 (1)	0.533 (1)	3.9 (5)*
C15S	0.637 (2)	0.024 (1)	0.604 (1)	7.4 (5)*

[a] Starred values denote atoms refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

Table II. Selected Bond Distances (Å), Bond Angles (deg), and Averages with Their Estimated Standard Deviations Found in **4**

	Metal Coordination Sphere		
Fe–N1	1.907 (3)	CME–Fe–N1	91.8 (1)
Fe–N11	1.913 (3)	CME–Fe–N11	94.5 (1)
Fe–N17	1.904 (3)	CME–Fe–N17	93.9 (1)
Fe–N23	1.905 (3)	CME–Fe–N23	92.1 (1)
⟨Fe–N⟩	1.908 (1)		
Fe–CME	2.025 (3)		
	Isoindoles[a]		
N–C_α	1.385 (1)	C_α–N–C_α	106.0 (1)
C_α–C_β	1.440 (2)	N–C_α–C_β	110.5 (1)
C_β–C_β	1.396 (2)	N–C_α–N_m	127.1 (1)
C_α–N_m	1.321 (1)	C_α–C_β–C_β	106.4 (1)
C_α–C_{phe}	1.394 (2)	C_α–N_m–C_α	121.8 (1)
C_{phe1}–C_{phe2}	1.386 (2)		
C_{phe2}–C_{phe2}	1.401 (3)		
	Crown Ether		
O–C	1.420 (1)	C–O–C	112.7 (1)
C–C	1.478 (2)	O–C–C	108.5 (1)

[a] C_α, C_β, N_m, and C_{phe} stand respectively for the α- and β-carbon atoms of the pyrroles, the meso nitrogen atoms, and the phenyl carbon atoms.

plane. These displacements are in general larger in the porphyrin complexes: respectively 0.22 and 0.23 Å in [Fe(CS)TPP] (TPP = tetraphenylporphyrin) and 0.17 and 0.17 Å in Fe(C_2H_5)TPP[17] away from the 4 N_p and the 24-atom-core mean planes. The Fe^{II}–C(CH_3) bond distance of 2.025 (3) Å in $[Fe(CH_3)Pc]^-$ is slightly longer than that present in the low-spin, five-coordinate iron(III) species Fe(C_6H_5)TPP (1.955 (3) Å[18] and low-spin five-coordinate iron(II) macrocyclic complex Fe(C_6H_5)($C_{22}H_{22}N_4$) (1.933 (3) Å).[19] These differences are most probably due mainly to the II oxidation state of iron and the sp^3 hybridization of the carbon atom bonded to it in $[Fe(CH_3)Pc]^-$. The Fe–C bond is slightly tilted with respect to the normal to the 4 N(iso) mean plane by an angle of 1.98°.

The macrocyclic ligand is only slightly distorted from planarity. Relative to the central 24-atom-core mean plane of the ring the largest displacement of the atoms forming this central part is 0.05 Å and the largest displacement of the outermost carbon atoms of the phenyl rings is 0.145 Å. As usual, the pyrrole rings do not deviate from planarity and their dihedral angles with the mean plane of the 24 core atoms, which range from 1.31 (±3.41) to 1.82 (±2.76)°, are not significantly different. The bond distances and bond angles in the [Na(⊂18c6)] cation and in the THF and chlorobenzene molecules of crystallization present their usual values (Table II).

Registry No. **1**, 115270-66-1; **2**, 115270-68-3; **3**, 115270-70-7; **4**, 115270-73-0; [FePc], 132-16-1.

Supplementary Material Available: Thermal factors for all anisotropic atoms (Table S1), hydrogen atom positional parameters (Table S2), a complete set of bond distances (Table S3), and a complete set of bond angles (Table S4) (11 pages); observed and calculated structure factor amplitudes (×10) for all observed reflections (Table S5) (22 pages). Ordering information is given on any current masthead page.

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