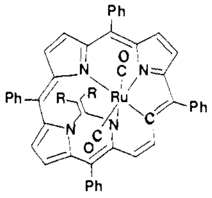

5

The composition and structure of **5** have been elucidated from an X-ray diffraction study.[6] Figure 1 presents a perspective view of the entire molecule while Figure 2 shows a different view which emphasizes the coordination environment about the ruthenium atom. These drawings show that the ruthenium atom has inserted itself into one of the pyrrole C–N bonds. The nonbonded C(3)–N(1) separation is 2.741 (7) Å while the average bonded C–N distance in the unaltered pyrrole rings is 1.375 Å. On the other hand, the C(3)–Ru and N(1)–Ru distances of 2.086 (6) and 2.206 (5) Å, respectively, are consistent with the presence of C–Ru and N–Ru single bonds. The coordination sphere of the ruthenium atom consists of two pyrrole nitrogen atoms and two mutually cis carbonyl ligands in addition to the C and N atoms of the ruptured pyrrole ring. One pyrrole nitrogen atom, N(2), is not bound to ruthenium. As Figure 2 shows, the disrupted porphyrin is no longer planar.

Compound **5** is best formulated as a complex of Ru(II) with the macrocyclic ligand present as a dianion with carbanionic and amide characteristics at C(3) and N(1). As is usual for Ru(II), the ligands are arranged into approximately octahedral geometry with the three trans angles in the range 158.8–173.6° and the 12 cis angles falling in the range 76.0–102.8°.

The oxidative addition of C–N bonds to metal centers, which is seen in the formation of **2–5**, is a little studied and infrequently observed reaction. In contrast there are a number of examples in which low-valent metals are responsible for breaking C–P bonds.[7] Since C–N bond strengths are only about 10% greater than C–P bond strengths,[8] more examples of C–N bond fragmentation are likely to be discovered. The relatively rare observation of this reaction as contrasted to P–C bond disruption probably results from the fact that phosphines are widely studied as ligands with low-valent metals while amines are infrequently used as ligands for low-valent metals. The insertion of metals into C–N bonds, however, may be a significant part of the catalytic cycle where triruthenium dodecacarbonyl catalyzes the scrambling alkyl groups between two differently substituted tertiary amines.[9]

The biochemical significance of N-substituted and N,N′-bridged porphyrins has only recently begun to be recognized.[10] It remains to be seen whether insertion of metals into these substances under other conditions can produce carbon–nitrogen bond rupture. However, it should be noted that the major metabolic pathway for heme destruction involves an oxidative process in which the porphyrin periphery is attacked while the pyrrole rings remain intact.[11]

Acknowledgment. We thank the National Institutes of Health (Grant GM26226) for financial assistance. F.E.W. held a University of California Regents' Fellowship.

Supplementary Material Available: A listing of atomic positional and thermal parameters for **5** is available (2 pages). Ordering information is given on any current masthead page.

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(5) Spectroscopic data: infrared, ν(CO), 2026, 1945 cm^{-1}; UV/vis, 384 nm (2.58 × 10^4 μ^{-1} cm^{-1}), 564 (1.35 × 10^4); ^{1}H NMR (CDCl$_3$), pyrrole, 9.41 (1 H, 10.3 Hz) d, 8.14 (1 H, 10.3 Hz) d, 7.65–7.4 (4 H) m, 7.10 (1 H, 3.8 Hz) d, 6.88 (1 H, 5.7 Hz) d; *meso*-phenyl, 8.11 (1 H, 4.9 Hz) d, 7.85 (2 H, 7.0 Hz) d, 7.80 (2 H, 6.8 Hz), 7.65–7.4 (14 H) m, 6.70 (1 H, 7.21 Hz) d; *p*-chlorophenyl, 7.03 (2 H, 7.7 Hz) d, 6.02 (2 H, 8.1 Hz), 5.66 (2 H, 7.7 Hz) d, 4.88 (2 H, 8.1 Hz) d.

(6) Single crystals of **5**·2CH$_2$Cl$_2$ were grown by diffusion of methanol into a dichloromethane solution of the complex. They belong to the space group $P\bar{1}$ (no. 2) with a = 9.796 (3) Å, b = 12.944 (4) Å, c = 22.377 (5) Å, α = 80.14 (2)°, β = 89.41 (2)°, γ = 70.25 (2)°, Z = 2 at 140 K. Refinement yielded R = 7.5% for 7658 reflections with $F > 6\sigma(F)$ and 677 parameters.

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Reaction of Nucleophiles with the Iron–Arene Complexes (η^6-C$_6$R$_6$)$_2$Fe^{2+} and (η^5-C$_6$R$_6$H)(η^6-C$_6$R$_6$)Fe$^+$ (R = H, Me) and Functionalization of a Single Arene Ligand Using Hydride as a Protecting Group

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Nucleophilic addition of carbanions to coordinated arenes has been used successfully by Semmelhack as a means of functionalization in (η^6-arene)Cr(CO)$_3$ complexes.[1] However, useful applications with other transition-metal activating groups are not known, although this area is promising as indicated by recent interesting reports with Mn[2] and Co[3] complexes. Dicationic arene complexes are of special interest because, in principle, they can react successively with two distinct nucleophiles to give functional cyclohexadiene complexes from which the ligands could be liberated by oxidation. However, the addition of carbon-centered nucleophiles apparently poses difficulties, as most previous reports concern the addition of hydride, phosphines, or phosphites.[4] Although addition of alkyl carbanions occasionally succeeds,[2,3] Vollhardt[3] showed that extension to functional carbanions is not possible with Cp(η^6-C$_6$H$_6$)Co^{2+}.

Our attention has focused on the easily available complexes (arene)$_2$Fe^{2+}.[5] In the case of (1,3,5-Me$_3$C$_6$H$_3$)$_2$Fe^{2+}, Helling showed that one nonfunctional carbanion can be added to each ring (with functional carbanions, the second addition does not occur[6b]):

$$\{(\eta^6\text{-C}_6\text{H}_3\text{Me}_3)\text{Fe}^{\text{II}}\}^{2+} \xrightarrow{2\text{R}^-} (\eta^5\text{-C}_6\text{H}_3\text{Me}_3\text{R})\text{Fe}^{\text{II}}$$

This regioselectivity (addition of the second carbanion to the even rather than to the odd ligand) was rationalized by Davies et al. in terms of charge control.[7] We suspected that this regioselectivity was in fact due to the peculiar 1, 3, 5 disposition

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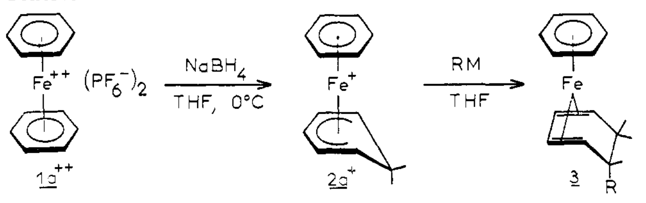
Scheme I[a]



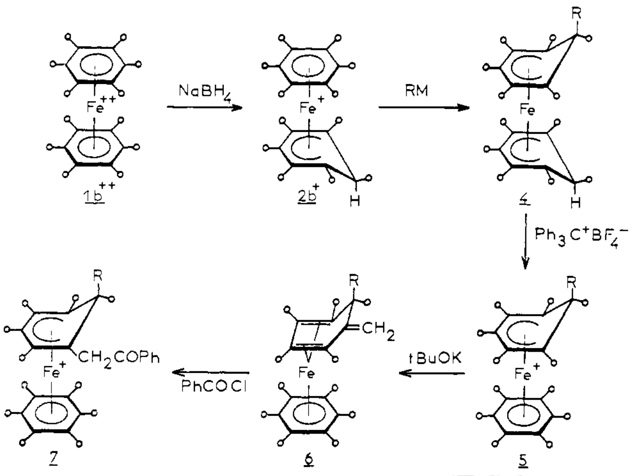
3	RM	R in 3	yield, %
a	$NaBH_4$	H	90
b	KCN	CN	85
c	$NaCH(CO_2Et)_2$	$CH(CO_2Et)_2$	75
d	$PhCH_2MgBr$	CH_2Ph	55
e	$\mathrm{Li}\overline{\mathrm{CHS(CH_2)_3S}}$	$\overline{\mathrm{CHS(CH_2)_3S}}$	62
f	$Cp(\eta^5\text{-}CH_2C_6Me_5)Fe$	$Cp(\eta^6\text{-}CH_2C_6Me_5)Fe^+$	59

[a] Conditions: **3a** 1 equiv, THF, 0 °C–room temperature, 2 h (or **1a**$^{2+}$ + 4 equiv $NaBH_4$, THF, 0 °C–room temperature, 2 h, 65%); **3b** 1 equiv, acetone, room temperature, overnight; **3c** 3 equiv, THF, room temperature, overnight; **3d** 6 equiv, THF, −60 °C, overnight; **3e** 1.1 equiv, THF, −80 °C–room temperature, 2 h; **3f** (ref 17) 1 equiv, THF, room temperature, overnight.

of the Me groups about the arene ligands and report here the reactivity of the parent complexes $(\eta^6\text{-}C_6H_6)_2Fe^{2+}$ (**1a**$^{2+}$) and $(\eta^5\text{-}C_6H_7)(\eta^6\text{-}C_6H_6)Fe^+PF_6^-$ (**2a**$^+$) and of other methyl-substituted derivatives. We find the following to be the case: (i) Carbanions fail to react with the dications **1**$^{2+}$ by C–C bond formation if the arene ≠ mesitylene; rather, hydride must be used as the first nucleophile. (ii) Functionalization proceeds cleanly by attack of a carbanion as the second nucleophile, giving only substituted cyclohexadiene Fe^0 derivatives, not the bis(cyclohexadienyl)iron(II) complexes predicted by Davies' rules. (iii) In the permethylated complexes, hydride must also be used as the first nucleophile and the carbanion then attacks on the other ring for steric reasons. (iv) Hydride can be abstracted by Ph_3C^+ from the bis(cyclohexadienyl)iron(II) complexes and thus serves as a protecting group. Subsequently, deprotonation of the substituted (arene)(cyclohexadienyl)iron cations followed by electrophilic attack provides a second functionalization of the cyclohexadienyl ligand.

The reaction of carbanions with $(C_6H_nMe_{6-n})_2Fe^{2+}(PF_6^-)_2$ (**1**$^{2+}$ ($n \neq 3$)) at low temperature in THF gives mainly the known, purple d^7 19-electron complexes **1**$^+PF_6^-$ characterized by their Mössbauer spectra typical of Fe^I.[8] Even $(\eta^6\text{-}C_6Me_6)(\eta^6\text{-}C_6H_6)Fe^{2+}(PF_6^-)_2$ reacts in this manner, although it was designed to present favorable stereoelectronic conditions for nucleophilic attack at the benzene ligand. On the other hand, all these dications **1**$^{2+}$ react cleanly with 1 mol of $NaBH_4$ to give high yields of $(\eta^5\text{-}C_6R_6H)(\eta^6\text{-arene})Fe^+$ derivatives.[9,10] $\{(\eta^5\text{-}C_6H_7)(\eta^6\text{-}C_6H_6)Fe\}^+$ (**2a**$^+$), unlike **1**$^{2+}$, reacts regio- and stereospecifically with all the carbanions examined (Li, Na, K, Grignard reagents) to give reasonable yields of the new series of functional cyclohexadiene complexes **3** (Scheme I).[11] The parent complex **3a**[12] can be obtained by reaction of **1a**$^{2+}$ or **2a**$^+$ with $NaBH_4$, and the double hydride reduction of $(\eta^6\text{-}C_6D_6)_2Fe^{2+}(PF_6^-)_2$ gives **3a**-d_{12} bearing two exo H.[12d] As is known for $(\eta^4\text{-}C_6H_7R)Fe(CO)_3$[13] (R exo), $Ph_3C^+BF_4^-$ does not react with **3b–e** (it does, however, react with **3a** to give **2a**$^+$ or **1a**$^{2+}$; it also reacts with **3f**). The reaction **2**$^+$ → **3** parallels inter alia the rich chemistry of the isolobal complex $\{(\eta^5\text{-}C_6H_7)Fe(CO)_3\}^+$[13] although the stereoelectronic constraints are different. However, arene complexes are not available in the latter series.

Scheme II



o— = CH_3 ; RM = $PhCH_2MgBr$: **4a**-**7a** ; RM = $\mathrm{Li}\overline{\mathrm{CHS(CH_2)_3S}}$: **4b**-**7b**.

The clean reaction of **2b**$^+$ with carbanions ($PhCH_2MgBr$ and $\mathrm{Li}\overline{\mathrm{CHS(CH_2)_3S}}$) gives **4**[14] (Scheme II, R = $PhCH_2$, 70% yield, **4a**; $\overline{\mathrm{CHS(CH_2)_3S}}$, 60% yield, **4b**), the regiospecificiy being opposite to that found for the parent complexes **3** or for the hydride reduction of **2b**$^+$.[15] H^- is easily removed by $Ph_3C^+BF_4^-$ (CH_2Cl_2, −80 °C) from the dissymmetrical bis(cyclohexadienyl) complexes **4** to give **5a** (R = $PhCH_2$, 76% yield) and **5b** (R = $\overline{\mathrm{CHS(CH_2)_3S}}$, 69% yield). In this fashion, the electron-transfer chemistry that dominates reactions of **1**$^{2+}$ with carbanions,[16] thus impeding C–C bond formation, can be circumvented. A second functionalization can be achieved by deprotonation of **5** followed by acylation of the triene intermediates **6**; thus reactions of **5a** and **5b** with *t*-BuOK (THF, −80 °C) followed by PhCOCl (room temperature) give a 76% yield of **7a** (R = CH_2Ph) and a 58% yield of **7b** (R = $\overline{\mathrm{CHS(CH_2)_3S}}$).

Finally, this study holds potential for organic synthesis. Oxidation of the complexes **3** affords the free, substituted cyclohexadienes[18a] in excellent yield (**3a** (R = H) 95%, **3b** (R = CN) 90%, **3d** (R = CH_2Ph) 75%, yields by GPC on Carbowax vs. internal standard, **3c** (R = $CH(CO_2Et)_2$) 90% by ^1H NMR vs. internal standard). The best results are obtained with 2 equiv of anhydrous $FeCl_3$ in ether at 0 °C or with aqueous $CuCl_2$ and **3** in toluene solution.[18b]

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Supplementary Material Available: Spectroscopic characterizations (^1H and ^{13}C NMR and infrared data) and elemental analyses for all new complexes (3 pages). Ordering information is given on any current masthead page.

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[14] New compounds were identified by ^1H and ^{13}C NMR, infrared spectral data, and elemental analysis. See supplementary material (also including data for the fitted Mössbauer spectra of **3a**, **3b**, and **4b**).

[15] The hydride reduction of **2b**$^+$ giving $(\eta^4\text{-}C_6Me_6H_2)(\eta^6\text{-}C_6Me_6)Fe^0$ proceeds by electron transfer (which gives **2b**) followed by H atom transfer.[10]

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[18] (a) The substituted cyclohexadienes were also characterized by ^1H NMR and TLC, which confirmed that they are free of the rearomatized product Ph-R. (b) Oxygen or aqueous Ce(IV) give slightly lower yields, while I_2 in toluene is unsatisfactory.