ascertain that the pigments are linked to the protein through a protonated Schiff base, we examined their resonance Raman spectra.[9] These measurements clearly reveal the contribution of $C=NH^+$ frequency to the spectra (1640 cm^{-1}), which shifted to lower frequency (1620 cm^{-1}), upon deuteration.[10] These observations confirmed the protonation of the Schiff base linkage.[11]

The observed spectral changes of the pigments may be correlated with an increase in the bulkiness of the C_4-substituent. Moreover, it is evident that the changes in going from I to V are basically due to a gradual reduction in the intensity of the red band and to a parallel increase in that of the blue band. The observations are indicative of two pigment species, characterized by different retinal–opsin interactions.

Pigments II–V were exposed to pulsed-laser photolysis. In all cases we observed an initial rise in absorption in the red, characteristic of the short-lived K intermediate of bR and a long-lived M species absorbing around 390 nm. In variance with II, V, and native bR, the photocycles of III and IV were markedly dependent on the excitation wavelength. Thus, excitation at 580 nm (in the range of the red band) led to a photocycle characteristic of a single pigment as in the case of native bR and II. However, excitation at 440 nm (in the range of the blue band) led to a K stage with two maxima in the red (520 ± 20 and 620 ± 20 nm). The formation of M was accompanied by two distinct depletions, corresponding to the red and to the blue absorption bands, respectively. It is thus evident that III and IV each consist of two species exhibiting two independent photocycles. The photocycle originating from the red absorbing species is comparable to those of I and II. The photocycle of the blue species is analogous to that of V.

The evidence presented above indicates that the retinal moiety may adopt at least two conformations while occupying the opsin binding site. Only one conformation is observed in bR (I), in which the red absorption band is indicative of a close proximity between the ring and an opsin charge as suggested by Nakanishi and Honig.[12] A second conformation, favored by increasing steric hindrance at the region of C_4, is associated with a drastic blue shift in absorption. The effect is attributed to a substantial increase in the separation between the polyene system and the "ring opsin charge". The blue absorbing species constitutes an interesting example of a bR pigment that retains the basic retinal chromophore system; however, this pigment's absorption is close to that of the corresponding free protonated Schiff base in solution ($\lambda_{max} = 460 \pm 20$ nm), which obviously lacks the neighboring ring charge. As such it provides an additional direct support to the point charge model for bacteriorhodopsin.

The spectral shift, $\Delta\nu$(bR/K), associated with the generation of K, is of the order of 2500 cm^{-1} and is essentially independent of pigment and conformer. This observation strongly supports the claim that the primary photochemical event in bR is due to a charge separation associated with the protonated Schiff base and its opsin counterion and does not involve any other charges. While the ring charge appears to be dominant in controlling the spectra of the pigments and their K intermediates, its effect on the spectrum of M (characterized by a nonprotonated Schiff base) are relatively small. Thus, all M species of I–V absorb in the range between 380 and 410 nm, exhibiting considerable red shifts, relative to the corresponding nonprotonated Schiff bases in solution ($\lambda_{max} = 350$ nm).[13] The exact cause for the spectral shift in M is still under investigation.

for supporting this work.

Electron-Transfer Chemistry of the 20-Electron Complex $(C_6Me_6)_2Fe^0$ and Its Strategic Role in C–H Bond Activation and C–C Bond Formation[1]

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Complexation of arenes in the 18-electron complexes (arene)Cr(CO)$_3$ and (arene)Fe$^+$Cp has provided specific synthetic applications because electron withdrawal by the transition-metal unit renders the arene ligand susceptible to nucleophilic attack or deprotonation.[2] We wish to describe here a different type of synthetically useful activation that results from the electron-transfer chemistry of the stable 20-electron complex $(C_6Me_6)_2Fe^0$,[3] a strong neutral reducing agent now available on a large scale.[4] This new approach is of particular significance since most of the classical, nonradical chemistry of other arene–transition-metal complexes fails with bis(arene)iron dications. For instance, it would have been desirable to make C–C bonds by nucleophilic attack of carbanions on $(C_6R_6)_2Fe^{2+}$ (R = H, Me) or to effect deprotonation (1^{2+}, R = Me) by anionic O or N bases.[5] However, C, O, and N anions react with 1^{2+}(PF$_6^-$)$_2$ at -80 °C by electron transfer, providing mainly the purple 19-electron complex 1^+PF$_6^-$, characterized by Mössbauer spectra[4] of the reaction mixtures after slow warm up and removal of solvents (Scheme I).

$(C_6H_6)_2Fe^{2+}$(PF$_6^-$)$_2$ (**4**), and $(C_6Me_6)(C_6H_6)Fe^{2+}$(PF$_6^-$)$_2$ (**5**), react similarly.[6] We find that the desired, synthetically useful processes can only be achieved using electron-transfer reactions of **1** with organic halides (C–C bond formation) or O$_2$ (C–H activation). PhCH$_2$Br, PhCOCl, NCCH$_2$Cl, BrCH$_2$CO$_2$Et, and ICH$_2$CHCH$_2$ react in toluene or pentane at -20 °C with **1** to give orange $[(C_6Me_6)(\eta^5\text{-}C_6Me_6R)Fe^+]PF_6^-$ (**3a–e**) after metathesis with NH$_4$PF$_6$ (yields on a 1-mmol scale: PhCH$_2$ and PhCO 90%; CH$_2$CN 40%; CH$_2$CO$_2$CH$_3$ and CH$_2$CHCH$_2$ 50%). As shown in Scheme II, the first step is an outer-sphere electron transfer from **1** to RX, characterized by the intermediate purple color and EPR spectra ($g = 2.091$, 2.012, 2.003 at -140 °C in acetone) of 1^+ in the reaction media before collapse to orange (**3c–e**). Thus the principle of this type of C–C bond formation lies in the coupling (within the solvent cage) of organic (R·) and organometallic (19-electron 1^+) radicals. Note that this type of activation is not suitable starting from 19-electron[7] complexes since electron transfer to RX leaves an 18-electron complex that cannot couple, thus limiting the yield of coupling products to 50%.[8]

The reaction of aqueous H$^+$PF$_6^-$ does not follow this course because H· atoms collapse rapidly to H$_2$ and 1^+PF$_6^-$ is formed

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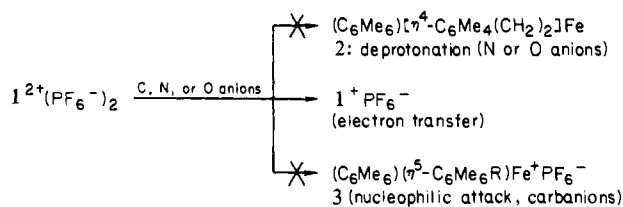
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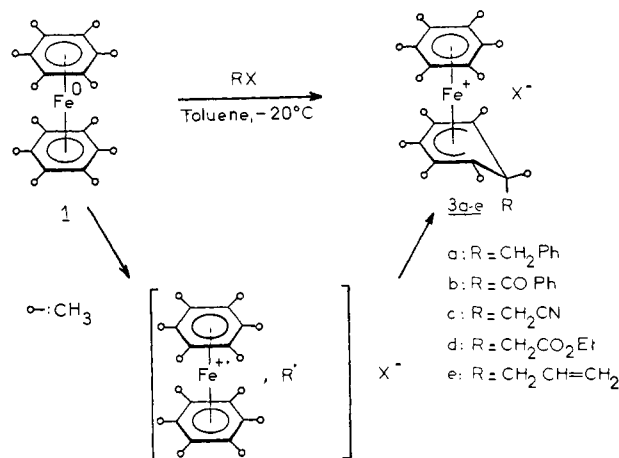
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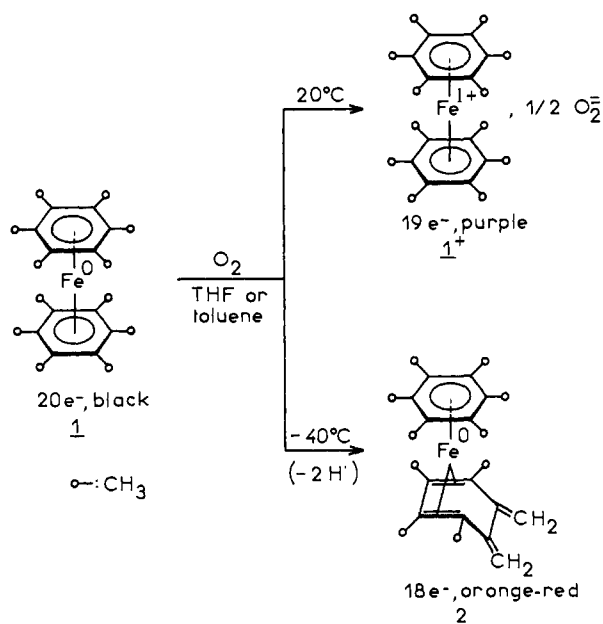(8) Nesmeyanov, A. N.; Vol'kenau, N. A.; Petrakova, V. A. *J. Organomet. Chem.* **1977**, *136*, 363–369.

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Scheme I

Scheme II

Scheme III
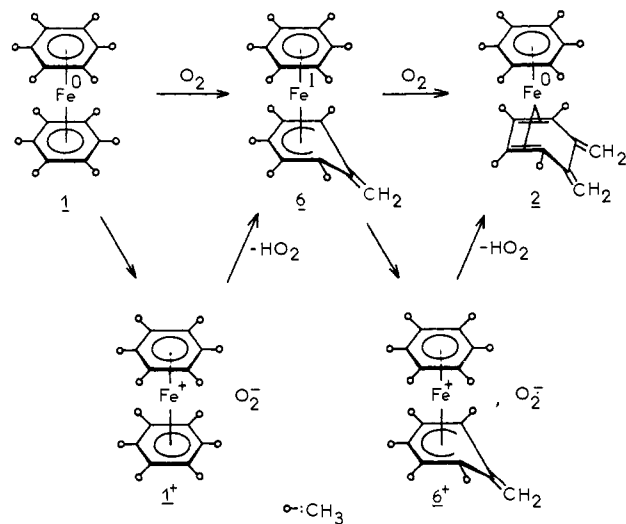

Scheme IV

Scheme V

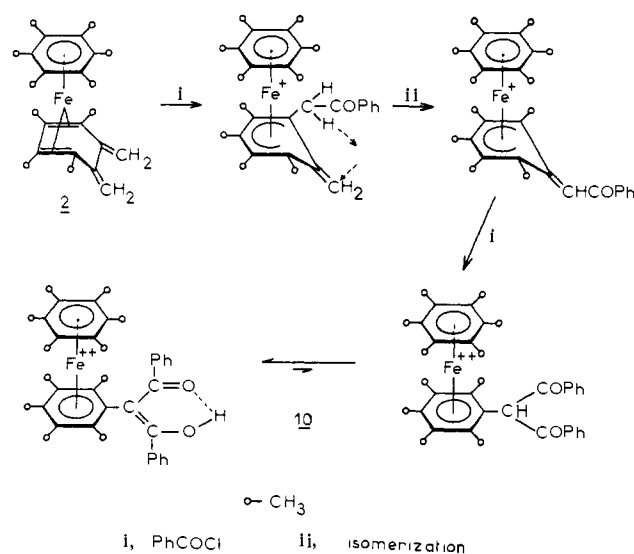i, PhCOCl   ii, isomerization

quantitatively (this is an excellent method of preparation of pure 1^+ PF_6^-). Recall that protonation of the isoelectronic 20-electron complex NiCp$_2$ provides the triple-decker sandwich Ni$_2$Cp$_3$;[9] NiCp$_2$ has a much lower oxidation potential than 1,[10] which explains why it does not reduce protons.

The reaction of 1 with O$_2$ at 20 °C gives purple 1^+,$^1/_2$O$_2^{2-}$ ($\nu_{O_2^{2-}}$ = 840 cm^{-1}) as the main reaction product, resulting from dismutation of O$_2^-$· subsequent to its escape from the cage $[1^+, O_2^-\cdot]$. However, this reaction at –40 °C (toluene or THF) gives the new *o*-xylylene complex (C$_6$Me$_6$)[η^4-C$_6$Me$_4$(CH$_2$)$_2$]Fe (2) resulting from double C–H bond activation of two *o*-methyl groups of a C$_6$Me$_6$ ligand (Scheme III). 2 is the first example of an *o*-xylylene iron complex in which this ligand is only bonded to iron by en-

docyclic coordination, although the Ru analogue is known.[11] 2 is unstable above –20 °C but could be characterized by ^{1}H and ^{13}C NMR at –50 °C when prepared in toluene-d_8.[12] Single C–H activation by O$_2$ is known for Cp(C$_6$Me$_6$)Fe^I, but fundamental differences exist in the chemistry of 1 as follows: (i) deprotonation of Cp(C$_6$Me$_6$)Fe$^+$ by bases is feasible,[13] but the analogous reaction of 1^{2+} fails; (ii) deprotonation of the mixed sandwiches according to Green's rule[14] proceeds at the even arene ligand whereas if one considers the intermediate (C$_6$Me$_6$)(η^5-C$_6$Me$_5$CH$_2$)Fe^I (6) in the reaction of 1 (Scheme IV), the second step proceeds at the odd cyclohexadienyl ligand contrary to Green's rule. We mimicked this second step by reacting O$_2$ with the stable complex (C$_6$Me$_6$)(η^5-C$_6$Me$_6$H)Fe^I (7),[15] related to the expected intermediate 6. The triene complex (C$_6$Me$_6$)(η^4-C$_6$Me$_5$HCH$_2$)Fe^0 (8), rather than (η^5-C$_6$Me$_5$CH$_2$)(η^5-C$_6$MeH)Fe^{II}, is obtained, which

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(12) (η^6-C$_6$Me$_6$)(η^4-C$_6$Me$_4$(=CH$_2$)$_2$)Fe^0 (2): ^{1}H NMR (toluene-d_8, –50 °C) δ 5.04 and 4.42 (2 s, 4 H, =CH$_2$), 1.73 (s, 18 H, C$_6$Me$_6$), 1.71 (s, 6 H, β-CH$_3$), 1.15 (s, 6 H, α-CH$_3$); ^{13}C NMR (toluene-d_8, –50 °C) δ 144.8 (s, C=CH$_2$), 90.5 (C$_6$Me$_6$), 88.0 (t, C=CH$_2$), 81.6 (β-ring C), 59.1 (α-ring C), 23.1 (β-CH$_3$), 14.8 (C$_6$Me$_6$); Mössbauer (mm/s vs. Fe, 77 K) IS 0.43, QS 1.02 (compare 8 and (η^6-C$_6$Me$_6$)(η^4-C$_6$Me$_6$H$_2$)Fe^0 IS 0.33, QS 0.98.

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strongly favors the mechanisms in Scheme IV. Like **7** (−1.6 V/SCE), **6** must have a very negative oxidation potential implying fast electron transfer to O_2 (−0.7 V/SCE) as in the first step of Scheme IV.

Protonation of **2** by HPF_6 gives 1^{2+} $(PF_6^-)_2$ directly without isolation of the intermediate complex $[(C_6Me_6)(\eta^5\text{-}C_6Me_5CH_2)Fe]^+PF_6^-$ (**9**), which indicates that the methylene carbon is more basic in **9** than in **2**. This reaction gives a 50% yield from **1**, which provides an estimate of the reaction yield **1** → **2**. Reaction of **2** with PhCOCl gives the double benzoylation product **10** (Scheme V). Again the monobenzoylated intermediate cannot be isolated; intra- or intermolecular proton transfer from a benzoylated methylene to a nonbenzoylated one occurs, affording a second benzoylation of this alkylidene unit. ^{1}H and ^{13}C NMR data indicate 75% of enolic form in the β-diketone **10**.

In conclusion, entries to functionalized bis(arene)iron complexes are provided by C–H activation and C–C bond formation using electron-transfer reactions from the readily available complex **1** and the simple substrates RX and O_2.

Supplementary Material Available: ^{1}H and ^{13}C NMR, infrared, and analytical data for **3a–e**, **8**, and **10** (2 pages). Ordering information is given on any current masthead page.

Near-Infrared f-f Transition Cotton Effects of Ytterbium(III) Ion: Experimental Evidences for Interaction between Rifamycin Antibiotics and Metal Ions

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Lanthanide ions have been used for some time as paramagnetic[1] or fluorescent[2] probes to study the binding of metals to biological molecules. Near-infrared circular dichroism (near-IR-CD) associated with f-f electronic transitions of the above ions can also be exploited to obtain this kind of information. Indeed several lanthanide ions exhibit[3,4] magnetic dipole allowed transitions between 800 and 2000 nm, and intense CD bands are to be expected when the ion is perturbed by a chiral organic ligand. Only very weak CD bands of the latter, due to the overtones of vibrational excitations,[5] are present in the above spectral region. Therefore, the appearance of near-IR-CD bands is directly connected to the metal–ligand complex formation. Furthermore, as the observed CD is dependent on the crystal field around the metal, in principle, information about the structure of the metal–ligand adduct can be obtained by means of near-IR-CD measurements.

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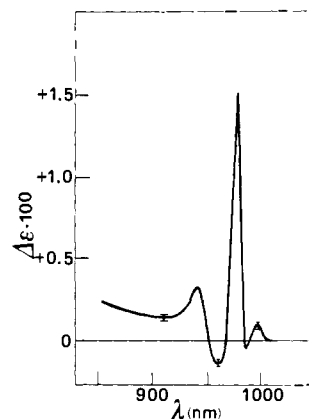(5) Keiderling, T.; Stephens, P. J. *Chem. Phys. Lett.* **1976**, *41*, 46.

Figure 1. CD curve of 1/Yb(III) adduct in $MeOH/H_2O$ (98/2) solution at pH 5–6 [$c(1)$ 2.7 mmol/L, $c(YbCl_3)$ 2 mmol/L]. $\Delta\epsilon$ values in the figure have been arbitrarily referred to the overall Yb(III) concentration. The noise level is indicated by vertical error bars.

An interesting application is provided by the use of Yb(III) ions to probe the interaction between rifampicin (**1**) and physi-

1
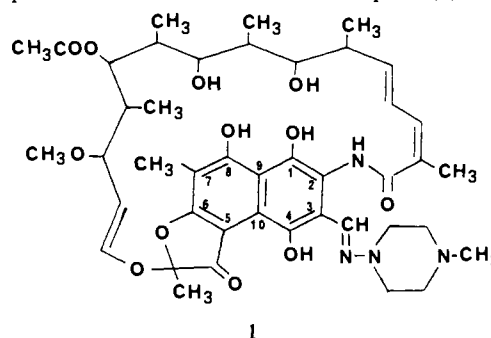
ologically important ions, like Ca(II), which lack appropriate spectroscopic characteristics for direct observation of their binding to biological molecules.[6] The Yb(III) ion exhibits[3,4] a magnetic dipole allowed transition,$^2F_{7/2} \rightarrow {}^2F_{5/2}$, at about 1000 nm, and its replacement of the Ca(II) ion may be considered as isomorphous, since the ionic radii are 0.94 and 0.99 Å, respectively.

The CD spectra of **1** in a pH 5–6 methanol/water (98/2) solution have been obtained[10] in the range 185–1200 nm both in the absence and in the presence of the metal ions, Ca(II) and Yb(III). The absorption and CD spectra in the UV–vis region are not reported here, as no remarkable variations are observed in this region, dominated by the exciton coupling of the ansadiene and naphthohydroquinone chromophores.[11] Slight differences may be due simply to different experimental conditions (pH, metal ion concentration, etc.). In Figure 1, the CD spectrum of **1** in the presence of Yb(III) ions is reported between 700 and 1100 nm. At least five oppositely signed bands can be observed in this region, the 974-nm component showing a high dissymmetry factor ($g \simeq 0.01$). The appearance of strong optically active bands, due to the crystal field splitting of the $^2F_{7/2} \rightarrow {}^2F_{5/2}$ electronic transition

(6) The mechanism of action of **1** seems to require[7,8] the inhibition of DNA-dependent RNA polymerase **2**, possibly via complexation of **1** with **2**, by means of the Zn(II) ion of **2**. Moreover it has been recently reported[9] that **1** can also be involved in the methabolism of Ca(II) ions.
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