J. Am. Chem. Soc. 1989, 111, 6195-6201

Summary and Perspectives. We have synthesized and characterized $Fe^{II}Fe^{III}$ complexes of the binucleating ligand BPMP, which serve as models for the mixed valence oxidation state in binuclear iron-oxo proteins such as hemerythrin, methane monooxygenase, and purple acid phosphatase. These complexes exhibit novel Mössbauer, EPR, NMR, magnetic, and electronic spectral properties, which contribute to our understanding of the mixed valence sites in proteins. In addition, we have discovered a general method for obtaining heterobimetallic complexes containing iron in one of the metal sites. The $Zn^{II}Fe^{III}$ and $Fe^{II}Ga^{III}$ complexes, in particular, will be useful for determining the properties of the isolated iron centers in the absence of antiferromagnetic coupling and will thus aid in unraveling the complexities of the $Fe^{II}Fe^{III}$ interaction that give rise to their novel Mössbauer, EPR, and magnetic properties. Furthermore, the $Zn^{II}Fe^{III}$ complex and other $M^{II}Fe^{III}$ complexes that can be synthesized by similar procedures may also serve as useful models for the $M^{II}Fe^{III}$ forms of the purple acid phosphatases[49-53] and the $Cu^{II}Fe^{III}$ center in cytochrome oxidase.[54]

Acknowledgment. We thank Prof. J. D. Britton for his generous help in solving the structure of the mixed valence complex and Carlos Juarez-Garcia for his assistance in some of the Mössbauer experiments. This work has been supported by the National Institutes of Health through Grants GM-38767 (L.Q.), GM-22701 (Eckard Münck), and GM-30306 (O.P.A.) and an NIH postdoctoral fellowship for A.S.B. (GM-11533). The Nicolet R3m/E X-ray diffractometer and computing system at Colorado State University was purchased with funds provided by the National Science Foundation.

Note Added in Proof. Recently, Buchanan, Hendrickson, and co-workers reported a complex similar to **1**, with *N*-methylimidazole ligands instead of pyridines, that exhibits valence detrapping at temperatures above 100 K (*J. Am. Chem. Soc.* **1989**, *111*, 2745-2746).

Supplementary Material Available: Tables of atomic positional parameters and their estimated standard deviations, general thermal parameters, and complete bond lengths and bond angles for **1′** and **4′** (30 pages); tables of calculated and observed structure factors (105 pages). Ordering information is given on any current masthead page.

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Photodissociation of Cyclopentadienyliron(II) Arene Cations: Detection and Characterization of Reactive Intermediates by Means of Time-Resolved Laser Spectroscopy

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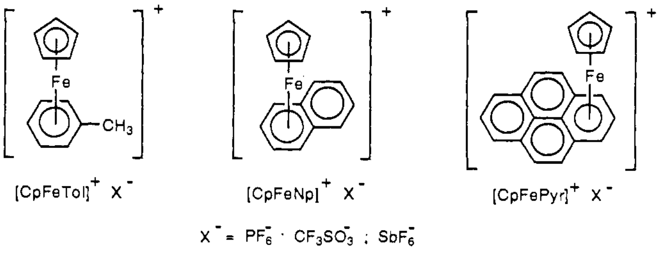
Abstract: Cyclopentadienyliron(II) arene cations ($[CpFeArH]^+$) exist in solution as a mixture of freely solvated ions and as ion pairs with an anionic counterion (X^-). Irradiation of either the free ion or the ion pair in solutions containing benzonitrile (PhCN) leads to loss of the arene ligand and formation of a tris-nitrile complex ($[CpFe(PhCN)_3]^+$). Two important reactive intermediates are detected by time-resolved laser spectroscopy. One, formed from irradiation of the ion pair, is assigned as the ring-slipped η^4-arene-Cp-iron compound covalently bound to its counterion. The other, formed from irradiation of freely solvated cations, is assigned as the coordinatively unsaturated ring-slipped Cp-iron-η^4-arene compound. The role of these intermediates in the ligand-exchange reaction was examined.

Irradiation of an organometallic compound with light often leads to chemical processes that are not observed under thermal reaction conditions. Such is the case for the cationic (cyclopentadienyl)(arene)iron(II) complexes $[(CpFeArH)^+X^-]$. These readily prepared compounds[1] are stable in the dark but undergo efficient dearylation when exposed to light. The investigation of this reaction was focused at first on its synthetic applications.[2] However, these materials have recently taken on special significance. Meier and Zweifel report that certain $[CpFeArH]^+X^-$ complexes are highly efficient, visible-light-sensitive photoinitiators for the polymerization of epoxides.[3] Since only a few compounds are known to have properties satisfactory for application in this area, it is important to probe in detail the mechanism of photodearylation and its connection to the photoinitiation of polymerization.

Chart I



The electronic structure of $[CpFeArH]^+X^-$ complexes was investigated by Hendrickson and co-workers.[4] They showed by

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(1) Sutherland, R. G. *J. Organomet. Chem. Libr.* **1976**, *3*, 311. Green, M. L. H.; Pratt, L.; Wilkinson, G. *J. Chem. Soc. A* **1960**, 989.

(2) Gill, T. P.; Mann, K. R. *Inorg. Chem.* **1980**, *19*, 3007.

(3) Meier, K.; Zweifel, H. *J. Imaging Sci.* **1986**, *30*, 174. Roloff, A.; Meier, K.; Riediker, M. *Pure Appl. Chem.* **1986**, *9*, 1267. Klingert, B.; Riediker, M.; Roloff, A. *Comments Inorg. Chem.* **1988**, *7*, 109.

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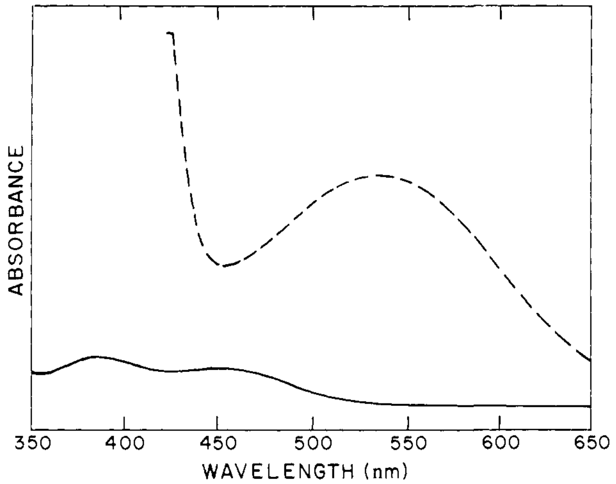


Figure 1. UV-vis spectra of a solution of $[CpFeTol]^+PF_6^-$ and PhCN in dichloroethane before (solid line) and after (dashed line) irradiation with visible light.

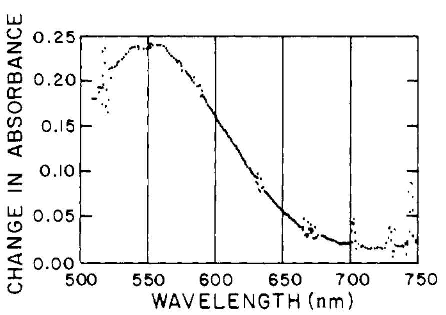


Figure 2. Absorption spectrum of the product observed 4 μs after laser irradiation (532 nm) of $[CpFePyr]^+PF_6^-$ in a dichloroethane solution containing PhCN.

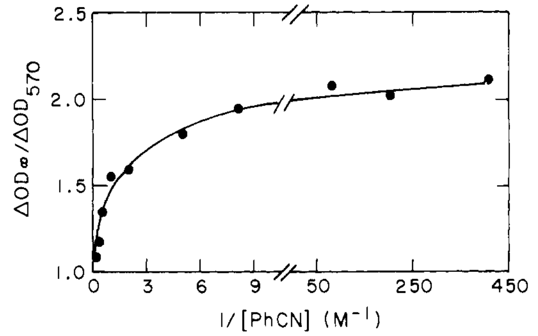
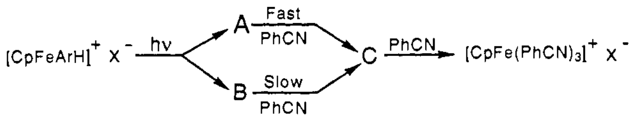


Figure 3. Plot of $\Delta OD_\infty/\Delta OD$ at 570 nm against the reciprocal of PhCN concentration for irradiation of $[CpFePyr]^+PF_6^-$ in dichloroethane solution.

Scheme I



analogy to ferrocene that the low-energy optical absorptions are spin-allowed d–d transitions leading to a^1E_{1g}, $^1E_{2g}$, and b^1E_{1g} states. Analysis of these states by means of molecular orbital theory leads to the prediction that excitation of the iron complex will labilize the ligands.[5] This prediction is supported by experiments. Nesmeyanov and co-workers were the first to report that irradiation of a THF solution of $[CpFeC_6H_6]^+BF_4^-$ leads to release of benzene and the formation of ferrocene in high yield.[6] Mann and co-workers discovered that this reaction can generally be used to exchange the iron-bound arene for other ligands.[2,7] Their further investigation of this reaction revealed that its quantum yield depends strongly on the identity of the counterion and on the nature of the arene. They also observed that triplet sensitizers initiated the ligand substitution reaction as did direct irradiation with long-wavelength light into the presumed singlet–triplet absorption band of the complex.[8-12] These experiments and others led Mann to propose that the photoactive species in this reaction is the a^3E_{1g} ligand field state of the iron–arene complex. They conclude that arene loss occurs from this state with assistance by the solvent or the counterion. We report herein the time-resolved spectroscopic investigation of the photochemistry of the cationic iron complexes shown in Chart I. Our findings reveal a multistep process in which the mechanism for replacement of the arene is controlled by the identity of the counterion and the concentration of the attacking ligand.

Results

(1) Products from the Irradiation of $[CpFeArH]^+X^-$ in the Presence of Nitriles. Gill and Mann report[9] that irradiation of an acetonitrile solution of $[CpFeXy]^+PF_6^-$ (Xy is *p*-xylene) results in efficient dissociation of the xylene ligand and formation of $[CpFe(N{\equiv}CCH_3)_3]^+$. This tris-$CH_3CN$ complex is purple (λ_{max} = 550 nm), stable for several hours at −40 °C in the dark but unstable at room temperature, and sensitive to photolysis. We observe a similar reaction when $[CpFeTol]^+PF_6^-$ is (Tol is toluene) is irradiated (500–550 nm, Na vapor lamp) in a 1,2-dichloroethane solution containing 1.0 M benzonitrile (PhCN), eq 1. The absorption spectra of the starting toluene compound and the unisolated tris-PhCN complex are shown in Figure 1. As is often the case for the d–d transitions of coordination compounds, the absorption maxima of the $[CpFe(RCN)_3]^+$ complexes appear to be relatively insensitive to the change in the ligand from CH_3CN to PhCN.[13]

$$[CpFeTol]^+PF_6^- + PhCN \xrightarrow{h\nu} [CpFe(PhCN)_3]^+PF_6^- \quad (1)$$

(2) Time-Resolved Transient Absorption Spectra. Irradiation of a dichloroethane solution of $[CpFePyr]^+PF_6^-$ (Pyr is pyrene) with the output of a frequency-doubled, pulsed Nd:YAG laser (532 nm, 20 ns, 8–10 mJ) leads to bleaching of the absorption of the iron–arene complex but does not give detectable new absorption features that may be attributed to the formation of short-lived reactive intermediates. However, similar irradiation of the $[CpFePyr]^+$ complex in a dichloroethane solution containing 0.82 M PhCN reveals the formation of a new absorbing species whose spectrum, recorded 4 μs after the laser pulse, is shown in Figure 2. Neither the shape nor the intensity of this absorption spectrum changes after it is formed. On this basis and by comparison of the spectra in Figures 1 and 2, we assign the species detected in the time-resolved experiment to the final tris-PhCN complex.

The relative yield for the formation of the $[CpFe(PhCN)_3]^+$ complex from $[CpFePyr]^+PF_6^-$ in time-resolved experiments was determined as the concentration of PhCN in the solution was varied by monitoring the absorbance change at 570 nm (ΔOD_{570})

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(4) Morrison, W. H.; Ho, E. Y.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1974**, *96*, 3603. Morrison, W. H.; Ho, E. Y.; Hendrickson, D. N. *Inorg. Chem.* **1975**, *14*, 500.

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(7) Gill, T. P.; Mann, K. R. *J. Organomet. Chem.* **1981**, *216*, 65.

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(9) Gill, T. P.; Mann, K. R. *Inorg. Chem.* **1983**, *22*, 1986.

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(12) Schrenk, J. L.; Mann, K. R. *Inorg. Chem.* **1986**, *25*, 1906.

(13) Sohn, Y. S.; Hendrickson, D. N.; Gray, H. B. *J. Am. Chem. Soc.* **1971**, *93*, 3603.

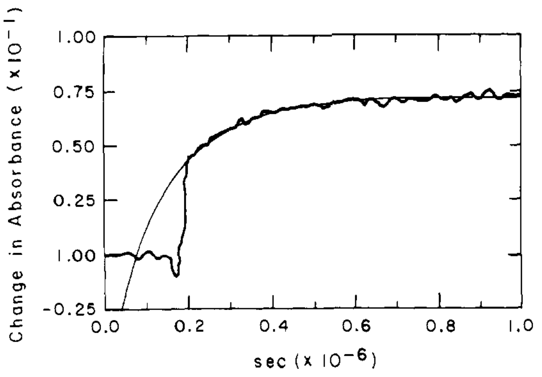

Figure 4. Time response of the ΔOD at 570 nm for irradiation of a dichloroethane solution containing PhCN and $[CpFePyr]^+PF_6^-$.

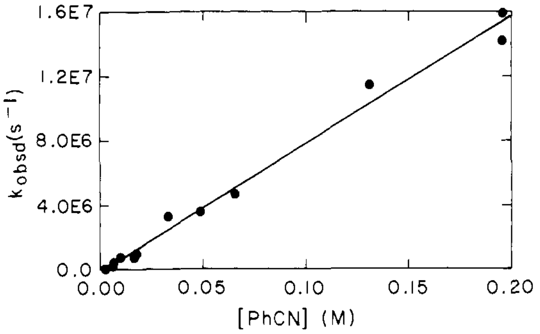

Figure 5. Response of the observed rate constant for growth of the absorption at 570 nm to change of the PhCN concentration in dichloroethane solution.

200 μs or more after the laser pulse. There is no interference from absorption of the starting complex at this wavelength, and product formation is complete at this time even in solutions that are dilute in PhCN. Figure 3 is a plot of reciprocal ΔOD_{570} that has been normalized by multiplication by ΔOD_∞ (the absorbance change at this wavelength at extrapolated infinite PhCN concentration) against the reciprocal PhCN concentration. The form of the plot in Figure 3 is characteristic of reactions where there are at least two intermediates that are capable of going on to form the detected product, Scheme I. The first intermediate (A) is short-lived and is captured efficiently at high PhCN concentrations. The second intermediate (B) is formed when the PhCN concentration is low, is longer-lived than A, and also can be captured by PhCN to give, eventually, $[CpFe(PhCN)_3]^+$.

Additional evidence for the general reaction mechanism outlined in Scheme I comes from an examination of the time dependence for the formation of the $[CpFe(PhCN)_3]^+$ complex at intermediate PhCN concentrations. Figure 4 is a plot of ΔOD_{570} following laser excitation of a solution of $[CpFePyr]^+PF_6^-$ containing 0.2 M PhCN. Two kinetic phases are easily discerned in the data. The first is unresolved (i.e., within the width of the laser pulse) initial fast growth in absorption attributed to the reaction of A with PhCN. This is followed by a slower growth in absorbance that is attributed to the reaction of B with the nitrile. The observed rate constant for the reaction during the slow phase of the reaction (k_{obsd}) depends upon the concentration of PhCN. A plot of k_{obsd} against PhCN concentration, Figure 5, is linear for nitrile concentrations above 1×10^{-2} M; the slope of this line is a measure of the bimolecular rate constant for reaction of B with PhCN (k_B) and is equal to $(7.9 \pm 0.5) \times 10^7$ M^{-1} s^{-1} in this case. Related rate constants for other reactions are reported in Table I. Implicit in the analysis of these data is the assumption that the slow step in the sequence leading to the tris-PhCN complex outlined in Scheme I is the formation of C. We will return to the examination of these data in the Discussion section.

(3) Identification of Intermediates A, B, and C. (A) Triplet Sensitization. Mann and co-workers[11] showed convincingly that the a^3E_{1g} state ($E_{triplet}$ = 42 kcal/mol) is a reactive intermediate in the photochemistry of the $[CpFeArH]^+$ complexes. In principle, intermediate A or B identified in Scheme I could be the required triplet state. This possibility was examined by means of a sensitization experiment. Figure 6 is a double-reciprocal plot of ΔOD_{570} against PhCN concentration for the 2-acetonaphthone ($E_{triplet}$ = 59 kcal/mol) sensitized irradiation (337 nm, 13 ns, 8 mJ) of $[CpFeNp]^+PF_6^-$ (the fluorescence of pyrene complicated the use of $[CpFePyr]^+$ in this experiment). The critical observation is that both the short-lived intermediate A and the long-lived intermediate B are present in the triplet-sensitized reaction. An attempt to quench the reaction of $[CpFePyr]^+$ and PhCN with perylene (up to 0.01 M, $E_{triplet}$ = 36 kcal/mol) was unsuccessful. This finding points to a very short lifetime for the triplet state of the complex, $\tau < 1.5$ ns, assuming that the rate of quenching by perylene would be diffusion limited. On this basis, it is possible that intermediate A, or a precursor to A and B, is the triplet state of the $[CpFeArH]^+$ complexes since electronically excited states must precede reactive ground-state intermediates in a photochemical reaction.

Table I. Bimolecular Rate Constants for the Reaction of Intermediate B with Ligands

ArH	X^-	ligand	k_B, M^{-1} s^{-1}
Pyr	PF_6	C_6H_5CN	7.9×10^7
Pyr	PF_6	$4\text{-}Me_2NC_6H_4CN$	11.5×10^7
Pyr	PF_6	$4\text{-}MeOC_6H_4CN$	8.1×10^7
Pyr	PF_6	$4\text{-}ClC_6H_4CN$	6.3×10^7
Pyr	PF_6	$4\text{-}FC_6H_4CN$	5.9×10^7
Pyr	PF_6	$4\text{-}BrC_6H_4CN$	2.8×10^7
Pyr	PF_6	$4\text{-}NCC_6H_4CN$	1.8×10^7
Pyr	PF_6	$4\text{-}F_3CC_6H_4CN$	1.4×10^7
Pyr	PF_6	$4\text{-}O_2NC_6H_4CN$	0.8×10^7
Pyr	PF_6	CH_3CN	2.6×10^7
Np	PF_6	C_6H_5CN	6.7×10^7
Tol	PF_6	C_6H_5CN	5.0×10^7
Pyr	Tf	C_6H_5CN	3.7×10^5
Tol	Tf	C_6H_5CN	1.8×10^5

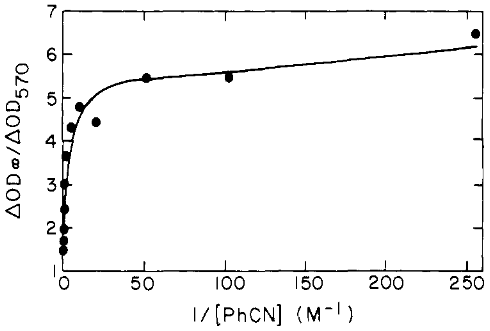

Figure 6. Plot of $\Delta OD_\infty/\Delta OD$ at 570 nm against the reciprocal PhCN concentration from triplet sensitization of $[CpFeNp]^+PF_6^-$ with 2-acetonaphthone irradiated at 337 nm.

(B) Effect of Solvent Composition. It is critically important in the consideration of these experiments to assess the degree of association of $[CpFeArH]^+$ cations with their corresponding X^- anions under the conditions of the irradiation. Mann and co-workers[11] have shown that these iron–arene complexes may exist in at least two forms with nearly identical absorption spectra. The first of these occurs in relatively nonpolar solvents such as dichloroethane. Here the $[CpFeArH]^+X^-$ complexes are believed to be associated into ion pairs. In contrast, when dissolved in a relatively polar solvent such as PhCN, the $[CpFeArH]^+X^-$ complexes are thought to exist primarily as freely solvated ions. We examined the conductivity of solutions of $[CpFeArH]^+X^-$ complexes to ascertain their degree of association under the conditions of the photochemical experiments.

Equivalent conductivities (Λ_{eq}) were measured for a series of solutions of $[CpFePyr]^+PF_6^-$ dissolved in dichloroethane containing variable amounts of PhCN.[14] As expected, Λ_{eq} increases as the

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(14) Geary, W. J. *Coord. Chem. Rev.* **1971**, *7*, 81. Boggess, R. K.; Zatko, D. A. *J. Chem. Educ.* **1975**, *52*, 649.

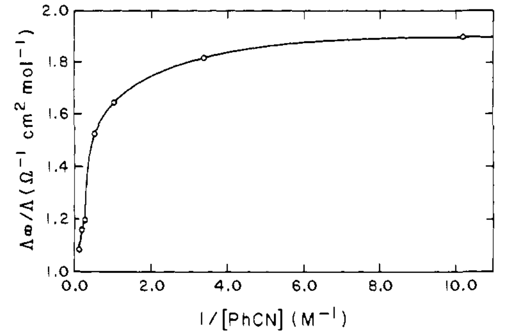

Figure 7. Response of Λ_∞/Λ to changes of PhCN concentration for 0.0138 M solutions of $[CpFePyr]^+PF_6^-$ in dichloroethane solutions.

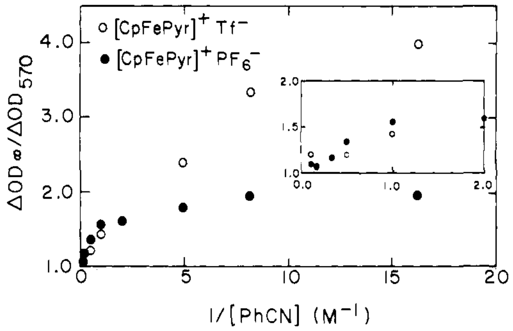

Figure 8. Plot of $\Delta OD_\infty/\Delta OD$ at 570 nm against the reciprocal PhCN concentration for irradiation of $[CpFePyr]^+$ with PF_6^- and Tf^- counterions in dichloroethane solution. The inset expands the scale for higher PhCN concentrations.

mole fraction of PhCN in the solution becomes greater. Figure 7 is a plot of these data in a format that permits comparison with the reciprocal ΔOD_{570} plots. It is clear from inspection of Figures 3 and 7 that the state of association of the $[CpFeArH]^+PF_6^-$ complex when it absorbs light parallels precisely the response of ΔOD_{570} to PhCN concentration. These results show that slowly reacting intermediate B is formed by irradiation of ion pairs in solutions containing relatively small amounts of PhCN and that rapidly reacting intermediate A is formed from irradiation of freely solvated $[CpFeArH]^+$ ions in solutions containing greater amounts of PhCN.

Finally, we searched for possible active participation of dichloroethane in the photolysis of the $[CpFeArH]^+X^-$ complexes by changing the solvent to 1,2-dibromoethane. There are recent examples of coordination by halogen-containing solvents to unsaturated metals.[15] If intermediate A or B somehow incorporated the halogenated solvent, then its measurable properties should respond to the change to dibromoethane. However, there is no significant effect of this change on the reaction. On this basis, we exclude an active role for the halogenated solvent.

(C) Effect of the Counterion. The efficiency of the dearylation reaction and the effectiveness of the $[CpFeArH]^+$ complexes as photoinitiators both depend strongly on the identity of the counterion.[3] When the irradiated complex exists as the associated ion pair, reaction between the counterion and a short-lived excited state or intermediate formed by its excitation will be greatly facilitated. We examined the effect of counterion identity on the properties of intermediates A and B.

Mann and co-workers[10] report that the quantum efficiency of the photodearylation of $[CpFeXy]^+X^-$ in methylene chloride solution decreases from 0.60 to 0.12 when X^- is changed from Tf^- to PF_6^-. We compared the photochemistry of these two complexes by means of time-resolved spectroscopy. Figure 8 shows double-reciprocal plots of ΔOD_{570} against PhCN concentration for $[CpFePyr]^+PF_6^-$ and $[CpFePyr]^+Tf^-$. These data reveal that the change of counterion affects strongly the reaction of long-lived

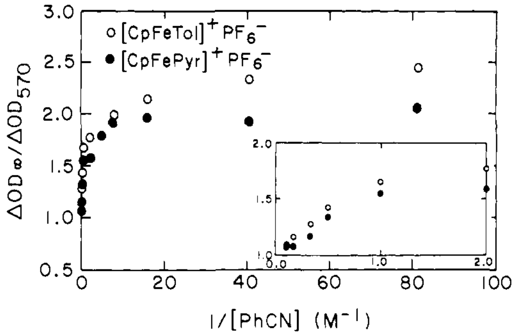

Figure 9. Plot of $\Delta OD_\infty/\Delta OD$ at 570 nm against the reciprocal PhCN concentration for irradiation of $[CpFePyr]^+PF_6^-$ and $[CpFeTol]^+PF_6^-$ complexes in dichloroethane solution. The inset expands the scale for higher PhCN concentrations.

intermediate B (low-PhCN-concentration region) but leaves essentially unchanged the reaction of short-lived intermediate A (high-concentration region). The effect of the X^- can be placed on a more quantitative basis by comparing the rates of reaction of B with PhCN formed from $[CpFeArH]^+X^-$ complexes having different counterions; the data are reported in Table I. It is apparent that the reaction of B with PhCN is ca. 200 times slower when Tf^- is the counterion than when the PF_6^- salt is irradiated.

Significantly, the rate of reaction of intermediate B formed from irradiation of $[CpFePyr]^+PF_6^-$ in nitrile-containing dichloroethane solutions is only slightly affected by additional common counterion. The lifetime of intermediate B in the presence of 4×10^{-3} M *p*-nitrobenzonitrile (the most sensitive test case: additional data on the reactions of substituted nitriles are presented below) is 12 μs in the absence of added salt. The lifetime of B increases linearly with the addition of $(n\text{-Bu})_4N^+PF_6^-$ to the reaction mixture. When 50 equiv (0.7 M) of salt has been added, the lifetime of B is 28 μs. This result might be due to an affect of the ionic strength of the medium on the rate of reaction of nitrile with B, or it might signal operation of a reaction mechanism where equlibrium dissociation of the counterion precedes combination of B with the nitrile. If the latter route is operative, then *p*-nitrobenzonitrile must be more than 100 times as reactive as PF_6^-.

The results of these experiments reveal two clear counterion effects. First, the degree of association with the counterion controls whether the reaction proceeds through intermediate A or intermediate B. Second, the rate of reaction of B with nitriles is strongly affected by the identity of the counterion. These results lead to the reasonable hypothesis that intermediate B has somehow incorporated the counterion into its structure. We will return to this topic in the Discussion section.

(D) Effect of the Arene. The effect of the structure of the arene ligand on the properties of the detected intermediates was probed by comparison of the pyrene and toluene complexes. Figure 9 is a double-reciprocal plot of ΔOD_{570} against PhCN concentration for the toluene– and pyrene–PF_6^- compounds. Examination of these data reveals that short-lived intermediate A appears relatively insensitive to this change of structure, but intermediate B formed from the toluene complex is slightly less effective in its reaction with PhCN than is its counterpart formed from the pyrene complex. This difference is also apparent in the rates of reaction of B with PhCN. Pulsed irradiation of the Tf^- salts of either $[CpFePyr]^+$ or $[CpFeTol]^+$ in dichloroethane solution containing 1.0 M PhCN shows the clean pseudo-first-order growth of $[CpFe(PhCN)_3]^+$ in both cases. Significantly, the lifetime of this reaction for $[CpFePyr]^+$ is 2.7 μs, while that for $[CpFeTol]^+$ is 6.9 μs, Table I. These findings require that intermediate B still contain the arene group. If the arene had been lost before formation of B, its rate of reaction with PhCN would have to be independent of the identity of the arene.

(4) Effect of the Attacking Ligand Structure on k_B. The rate constant for the reaction of intermediate B is sensitive to the structure of the attacking ligand. This effect was examined by measuring the rate of reaction of B formed from laser irradiation of $[CpFePyr]^+PF_6^-$ with CH_3CN and with a series of substituted

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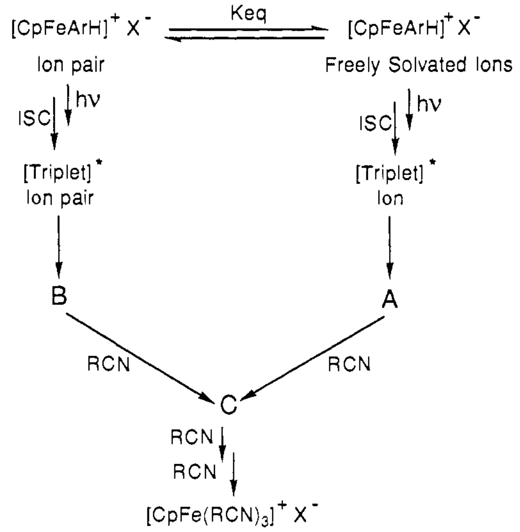
[15] Winter, C. H.; Arif, A. M.; Gladysz, J. A. *J. Am. Chem. Soc.* **1987**, *109*, 7560. Fernández, J. M.; Gladysz, J. A. *Inorg. Chem.* **1986**, *25*, 2672.

Scheme II



benzonitriles: the data are reported in Table I. The findings show that benzonitriles substituted with electron-withdrawing groups react more slowly with B than does PhCN itself. On the other hand, donor-substituted nitriles react with a somewhat greater rate constant than does PhCN. These findings are consistent with a supposed nucleophilic role for the nitrile in its reaction with intermediate B.

Discussion

The central issues associated with photodearylation of the [CpFeArH]$^+$X$^-$ complexes are the identification of the key reactive intermediates that are formed and a description of the path followed by these species to the ultimate, stable, ligand-exchanged product. Overall the reaction seems quite simple: arene leaves and is replaced by three nitrile ligands. Mechanistically, however, this reaction could be very complex. There could possibly be four electronically excited state intermediates invovled—singlets and triplets of the associated ion pair and the freely solvated iron–arene cation—and there could be participation by four or more ground-state intermediates—counterion-bound species and nitrile–ligand-bound species of variable stoichiometry. The experiments described above were designed to examine the identity and the role played by intermediates in this reaction and to allow formulation of a supported mechanistic hypothesis. Scheme II is a proposal for the mechanism of photodearylation and ligand capture by [CpFeArH]$^+$X$^-$ complexes consistent with the data.

A basic tenet of the mechanism shown in Scheme II is that there are two limiting structures for the iron–arene compounds in solution: ion paired with its counterion or existing as a freely solvated ion. The relative concentrations of these forms depend on the solvent. In relatively nonpolar solvents, ion pairs predominate. As the solvent becomes more polar through addition of increasing amounts of PhCN, the conductivity experiments reveal a shift in the position of the ion-pair equilibrium. When the iron–arene compound is dissolved in relatively polar solvent mixtures, its predominant form is as freely solvated ions.

Irradiation of either the ion pair or the freely solvated ion with green light (532 nm) must give their singlet excited states. However, we include no role for these first-formed states in Scheme II except for intersystem crossing (ISC) to their corresponding lower energy triplets. The view is supported by the sensitization experiment which shows that both intermediates A and B are formed even though the singlet excited states are bypassed. This result demands a reactive role for the triplets but does not necessarily exclude participation of the singlets in the direct irradiation.

The lifetimes of both the ion-paired and the freely solvated triplets of these iron–arene complexes must be very short since their reactions cannot be quenched by perylene. In the mechanism shown in Scheme II, rapid reaction to form intermediate B consumes the ion-pair triplet, and intermediate A is likewise formed from the triplet state of the free ion. Not shown on the scheme but probably active are energy-wasting deactivation paths from these triplets that regenerate the ground state of the starting iron–arene complex. The key remaining questions, of course, center on identifying the structures of intermediates A, B, and C.

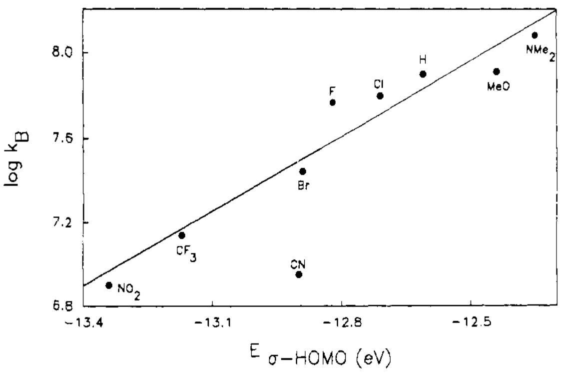
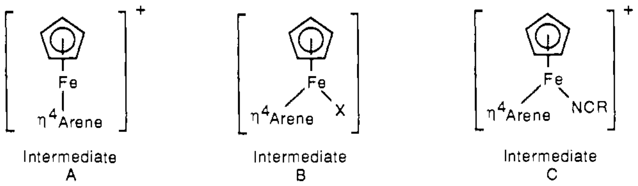


Figure 10. Correlation of log k_B against $E_{\sigma\text{-HOMO}}$ calculated by MNDO methods. The highest occupied orbital of σ symmetry in all cases corresponds to the $E_{2g}A$ orbital derived from the D_{6h} point group of benzene. The observed rate constant for p-dicyanobenzene was divided by 2 for correction of a statistical nature. Even without this correction, this nitrile reacts with a rate constant slower than predicted from the calculations.

Chart II



Intermediate B is formed by a reaction originating with the ion-paired triplet state of the iron–arene complex. Since the rate of the subsequent reaction of B with PhCN depends on the identity of the counterion and the arene, both of these components must be somehow incorporated into its structure. Recently, several examples of stable organometallic compounds having apparent covalent bonds to "noncoordinating" anions such as BF_4^-, SbF_6^-, and PF_6^- have been isolated and characterized.[16] In these cases, bonding to the metal occurs through a lone pair of electrons of one the ligand's fluorine atoms. We propose a related structure for intermediate B, Chart II. In one scenario, the anion associated with the excited ion pair reacts directly with the triplet state of the iron–arene complex to form a covalent bond with simultaneous ring slippage to reduce the hapticity of the coordinating arene ligand from η^6 to η^4. A second possibility is that the triplet complex first undergoes ring slippage to form the coordinatively unsaturated η^4-arene species, which then rapidly captures the neighboring anion. Although the experimental results cannot distinguish between these two paths for the formation of intermediate B, we favor the latter since the former requires intersystem crossing to occur simultaneously with bond formation.

Once formed, intermediate B may react with an attacking nucleophilic ligand (RCN of Scheme II) or, in an energy-wasting step not shown in the scheme, return to the starting iron–arene complex. The rate of reaction of B with the attacking ligand is dependent on the bound counterion. For example, Tf^-, expected to form relatively strong bonds to the iron,[17] is displaced more slowly than is more weakly bound PF_6^-. Similarly, the structure of the attacking nucleophile affects the rate constant for its reaction with intermediate B in a sensible way: the greater the nucleo-

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philicity of the ligand, the greater the rate of its reaction.

The reactivity of the nitriles can be put on a more quantitative basis by comparison of the rate data with the results of MNDO[18] semiempirical calculations. Figure 10 is a plot of log k_B against the calculated energy of σ-HOMO. Related examination of the π-HOMO and π-LUMO energies does not show a reasonable correlation with the measured rates of reaction. This finding is not consistent with the notion that π-complex formation precedes bond formation between the iron and the nitrile but implies that the σ-donor ability of the nitrile group controls the rate of reaction.

According to the mechanism proposed in Scheme II, reaction of intermediate B with the attacking nitrile forms C. Since the data reveal a nitrile-concentration-sensitive, counter-ion-dependent rate for this reaction, and in light of the computational findings, we propose that C is the η^4-arene–mono-nitrile complex formed by an S_N2-like reaction of B and nitrile. Subsequent fast reactions of C with an additional 2 equiv of nitrile (probably sequentially) generate the detected tris-nitrile complex and results in arene release. This proposal requires that the rate-limiting step in the reaction mechanism occur before the formation of intermediate C. If it didn't, then there would be no kinetic distinction between irradiation of the ion-paired and freely solvated iron–arene complex.

The mechanism outlined in Scheme II requires the reaction of intermediate B with PhCN to be much slower than the corresponding reaction of nitrile with intermediate C. Both B and C are proposed to have similar overall structure: each contains an η^4-bound arene ligand. For B, the opened coordination site is filled by reaction with the counterion; in C, electronic saturation is achieved by bonding to a PhCN ligand. A major difference between B and C, and the factor we consider to control the rate of reaction with incoming ligand, is their charge. Intermediate B is electrically neutral; its reaction with PhCN will displace the counterion to form positively charged intermediate C. Recall that B is formed from ion pairs under reaction conditions that do not favor charge separation. Thus, the conversion of B to C is slow because it requires separation of charge in a medium of low dielectric constant. On the other hand, addition of another PhCN ligand to C does not result in charge separation and therefore occurs without inhibition. This concept also accounts readily for the curvature observed in the plots of k_{obsd} against nitrile concentration. When the concentration of PhCN is low and the reaction medium relatively nonpolar, the rate constant for the reaction of intermediate B with nitrile is smaller than it is at higher nitrile concentrations where separation of charge is facilitated.

Intermediate A is formed from the triplet state of the freely solvated iron–arene complex. This intermediate reacts with PhCN at a rate faster than can be resolved with the nanosecond spectrometer. However, the efficiency of this reaction is unaffected when the solution contains high concentrations of triplet-quenching perylene. On this basis and with a prejudice toward the reaction of nucleophiles with singlet-state intermediates, we conclude that intermediate A is not a triplet excited state but a ground-state species derived from the short-lived triplet. The simplest structure that satisfies this requirement is the ring-slipped η^4-arene complex shown in Chart II. We plan to pursue picosecond time-scale measurements in hopes of reaching a firmer conclusion on this point.

Conclusions

Analysis of the photosubstitution of three nitriles for the η^6-arene ligand of the $[CpFeArH]^+X^-$ complexes by time-resolved spectroscopy reveals a complex reaction with a rather simple mechanism. Irradiation of either the freely solvated or ion-paired iron–arene complex initiates the same first steps: the excited singlet intersystem crosses to the triplet and a labilized arene ligand slips from η^6 to η^4, opening a coordination site on the iron. For the ion pair, the vacant coordination site is filled by bonding to the counterion to form intermediate B. For the freely solvated complex, the η^4 species is intermediate A, and it is trapped by the nitrile that must be present in relatively high concentration to form the freely solvated complex in the first place. Both routes converge at η^4-arene–mono-nitrile intermediate C, and the relatively rapid displacement of the arene by incoming nucleophile from this species yields the ligand-exchanged reaction product. We plan to examine the generality of this proposal by studying the reactions of non–nitrile–containing ligands.

Experimental Section

General. Melting points were determined on a Buchi melting point apparatus in open capillaries and are uncorrected. ^1H and ^{13}C NMR spectra were determined on Varian XL-200 or General Electric QE300 spectrometers in CD_2Cl_2, CD_3CN, or acetone-d_6 solvent and referenced to internal Me_4Si. UV–visible spectra were determined on a Perkin-Elmer 552 spectrometer. Elemental analyses were performed by the University of Illinois Microanalytical Laboratory.

Solvents and Reagents. Acetonitrile was distilled from CaH_2 and stored over 4A molecular sieves. Benzonitrile was fractionally distilled under reduced pressure from CaH_2 or P_2O_5 and stored over molecular sieves. Anhydrous 1,2-dichloroethane (Aldrich, <0.005% H_2O) was stored over molecular sieves before use. The substituted benzonitrile derivatives were recrystallized from ethanol before use.

Laser Apparatus. The laser spectroscopy was performed as previously described[19] with irradiation by a frequency-doubled Nd:YAG laser at 532 nm, 8–10 mJ, or a N_2 laser at 337 nm, 5–6 mJ. Sample photolysis by the probe beam was reduced by filtering (OG 515 cut-off), and scattered laser light was reduced at the monochromator by means of a CS 3-67 cut-off filter. Spectra were obtained from a Princeton Instruments IRY-512G-V optical multichannel analyzer.

Synthesis of Iron–Arene Complexes. The general procedure follows that of Sutherland.[20] Anions were exchanged by treatment of the aqueous solutions of the chloride salt with HPF_6, $NaSbF_6$, or CF_3SO_3H. Precipitated solids were purified by chromatography on neutral alumina, eluting with CH_2Cl_2 or acetone. Sometimes a second precipitation from acetone/Et_2O was performed. All the iron–arene complexes except $[CpFeTol]^+Tf^-$ have been previously reported;[20,21] they were characterized in this work by mp, ^1H NMR spectroscopy, and elemental analysis.

$[CpFeTol]^+CF_3SO_3^-$: mp 171–3 °C (dec); ^1H NMR (200 MHz, $(CD_3)_2CO$) δ 6.43 (s, 5 H, arom), 5.20 (s, 5 H, Cp), 2.56 (s, 3 H, CH_3); ^{13}C NMR (50 MHz, $(CD_3)_2CO$) δ 104.7, 89.7, 88.6, 87.4 (arom), 77.8 (Cp), 20.8 (CH_3).

Anal. Calcd for $C_{13}H_{13}F_3FeO_3S$: C, 43.11; H, 3.62; S, 8.85. Found: C, 43.16; H, 3.65; S, 8.72.

Typical Laser Spectroscopy Conditions. The concentrations of the pyrene complexes were 0.0138 M (OD_{532} = 1.6) and naphthalene complexes were 0.0247 M (OD_{532} = 1.6). Low solubility limited toluene complexes to 0.147 M (OD_{532} = 0.6). Solutions were prepared under a nitrogen atmosphere in a glovebag and then purged with nitrogen for several minutes. Typically, 4-mL samples were placed in 1-cm-square quartz or Pyrex cells, closed with Teflon stopcocks, and protected from light until use. The probe beam was perpendicular to the irradiation beam throughout.

Determination of ΔOD values was most often performed by inspection. The ΔOD is defined as the common logarithm of the ratio of the photomultiplier output before the laser pulse and after the growth at 550 or 570 nm is complete. To adjust for laser power variations, a fraction of the laser beam (ca. 15%) was reflected by a transparent glass plate to a Gentec ED-200 Joulemeter connected to a Tektronix 7834 storage oscilloscope. The height of the trace indicated the relative power of each laser pulse.

Determination of rate constants from the waveforms was accomplished by a nonlinear least-squares analysis. In all cases, the first-order portion of each waveform was analyzed to generate k_{obsd}. Plots of k_{obsd} versus nitrile concentration were always linear with a slope equal to the bimolecular rate constant. Electronic filtering of the signal was limited to a filter rise time of no more than ca. 5% of the rise due to the growth of the product.

Triplet sensitization experiments used $[CpFeNp]^+PF_6^-$ (9×10^{-4} M) in dichloroethane solution (OD_{337} = 0.4). All samples contained 2.5 ×

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10^{-3} M 2-acetylnaphthalene (OD_{337} = 3.8). The concentration of PhCN was varied from 1.96×10^{-3} to 8.64 M, and the ΔOD was determined in the usual fashion.

Triplet quenching experiments used $[CpFePyr]^+PF_6^-$ at typical concentrations for laser irradiation at 532 nm. The samples contained 3.92×10^{-3} M PhCN and 10^{-5}–10^{-3} M perylene. Typical ΔOD determinations were made, and a plot of ΔOD versus perylene concentration was flat.

Conductivity measurements were performed in the flow cell of a Dionex CDM-1 conductivity detector by pumping, via syringe, 5 mL of solution through the cell. A series of solutions of increasing conductivity were measured without removing the previous solution. The narrow bore tubing and small volume of the cell ensured that the previous solution was displaced by the first 1–1.5 mL of the succeeding solution. The remaining solution resulted in very stable readings which were rather insensitive to the flow rate of 5–10 mL/min.

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Transition-Metal-Promoted Reactions of Boron Hydrides. 12.[1] Syntheses, Polymerizations, and Ceramic Conversion Reactions of *B*-Alkenylborazines

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Abstract: High yield synthetic routes for the production of new *B*-alkenylborazines and poly(*B*-alkenylborazine) polymers and oligomers as well as the use of the poly(*B*-alkenylborazines) as polymeric precursors to boron nitride ceramics are reported. The syntheses of the *B*-alkenylborazines are based on the use of transition-metal reagents to activate the B–H bonds of borazine for either alkyne-addition or olefin-dehydrocoupling reactions and are the first examples of transition-metal-catalyzed reactions of borazine to be reported. Thus, the complexes $RhH(CO)(PPh_3)_3$ and $IrCl(CO)(PPh_3)_2$ were found to activate borazine/alkyne-addition reactions with acetylene, propyne, 1-butyne, and 2-butyne to give the previously unknown B-substituted alkenylborazines, *B*-$(RHC{=}CR')$-$B_3N_3H_5$ (R, R′ = H, Me, or Et). For reactions employing $RhH(CO)(PPh_3)_3$, typical yields of *B*-alkenylborazines range from 70 to 85% with the catalyst undergoing 25–50 turnovers an hour. Palladium bromide was found to catalyze the dehydrocoupling reactions of either borazine or *N*-trimethylborazine with olefins, such as ethylene and propene, to give the corresponding *B*-alkenyl- and *B*-alkylborazine products. The *B*-alkenylborazines were found to readily undergo thermally induced polymerizations to produce insoluble poly(*B*-alkenylborazines). Soluble, low molecular weight (<1500) oligomers were formed when the thermal polymerization reactions were carried out in the presence of additional borazine. The spectroscopic data for the soluble oligomers confirm that they have structures composed of carbon backbones containing pendant borazines. The ceramic conversion reactions of both the soluble and insoluble polymers were explored as potential routes to boron nitride ceramics. It was found that pyrolysis of these polymers yielded ceramic materials with B/N ratios of ~1.0 which, depending upon the polymer and pyrolysis conditions, ranged from black, high carbon materials to white, crystalline h-boron nitride. In all cases, the polymer/ceramic conversions were found to take place with both high ceramic and chemical yields.

Interest in the use of polymer precursor[2] routes to ceramics has initiated new studies of the design and synthesis of inorganic polymer systems. In our own work we have been interested in the development of synthetic pathways for the construction of new boron-containing polymers which might serve as precursors to nonoxide ceramics, such as boron carbide or boron nitride. For example, we have previously shown[3,4] that transition-metal reagents can be used to catalyze the reactions of pentaborane(9) with acetylenes to form 2-alkenylpentaboranes in high yields. Subsequent work[5] then demonstrated that 2-vinylpentaborane can be readily polymerized and that soluble oligomers of poly(2-vinylpentaborane) can, depending upon pyrolysis conditions, be converted in high yields to either boron carbide or boron nitride. Other workers have also studied polymer precursor routes to these materials.[6-16]

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