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Solvent and Ion-Pairing Effects on the Photochemical Arene Replacement Reactions of $[(\eta^5\text{-}C_5H_5)Fe(\eta^6\text{-}p\text{-xyl})]^+$ (*p*-xyl = *p*-Xylene). Evidence for a Medium-Assisted Photochemical Ligand Replacement Pathway from a LF Excited State

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The photochemical removal of *p*-xylene from $[(\eta^5\text{-}C_5H_5)Fe(\eta^6\text{-}p\text{-xyl})]^+$ (*p*-xyl = *p*-xylene) has been studied as a function of solvent (propylene carbonate, CH_3OH, CH_3CN, CH_2Cl_2) and as a function of the anion present ($CF_3SO_3^-$, BF_4^-, Br^-, ClO_4^-, PF_6^-, AsF_6^-, SbF_6^-) in CH_2Cl_2 solution. The quantum yield for *p*-xylene release varies from a high of 0.81 in water to a low of 0.084 in dichloromethane. The variation in quantum yield is indicative of solvent or anion assistance in the chemical step in which *p*-xylene is released from Fe. This interpretation of the quantum yield data establishes the relative nucleophilicity of the solvents and anions studied: $H_2O \approx$ propylene carbonate $\approx CH_3OH \geq CH_3CN > CF_3SO_3^- > BF_4^- > Br^- \approx ClO_4^- >> PF_6^- > CH_2Cl_2 \approx AsF_6^- \approx SbF_6^-$. The medium assistance observed in these arene replacement reactions contrasts the dissociative behavior observed for LF excited states in other organometallic transition-metal systems.

Introduction

For the past several years, our group has been investigating the photochemical reactivity of $[(\eta^5\text{-}C_5H_5)M(\eta^6\text{-arene})]^+$ cations (M, arene = Fe, *p*-xylene; Ru, benzene).[1-4] Ligand field (LF) irradiation of dichloromethane or acetonitrile solutions of these cations in the presence of appropriate ligands yields products in which the arene has been replaced. These reactions are synthetically useful[2,3] because of the range of entering ligands that can be used, the high chemical yields generally obtained, and the ease of the experimental procedures involved.

Recently, we initiated studies designed to elucidate the mechanism(s) of these reactions because they formally involve the breakage of three metal–ligand bonds. Of particular interest to us is the question of whether all three metal–arene bonds are broken in a dissociative step prior to interaction with incoming ligands or whether an associative step, which involves bond making between the metal and the surrounding medium (counterions or solvent), is necessary to achieve arene release. Extension of the experimental information[5] and the theoretical models available for the LF photochemistry of low-spin d^6 metal carbonyl complexes[6] to this system suggests that dissociative pathways for photochemical arene release would be favored.

We have obtained a partial answer to these mechanistic questions by studying an arene replacement reaction of $[(\eta^5\text{-}C_5H_5)Fe(\eta^6\text{-}p\text{-xylene})]^+$ as a function of solvent (propylene carbonate, methanol, acetonitrile, dichloromethane) and anion ($CF_3SO_3^-$, BF_4^-, Br^-, ClO_4^-, PF_6^-, AsF_6^-, SbF_6^-).

Our results indicate that the quantum yield for arene replacement exhibits not only a significant solvent dependence but also to our surprise a dependence on the counterions present in dichloromethane solutions.

The solvent and counterion dependence observed for the quantum yields suggests the medium functions as a nucleophile in this arene replacement reaction and allows the ranking of the nucleophilicity of the solvents and anions studied.

Experimental Section

General Information. The organic solvents used in this study were of spectroscopic grade and were dried over activated alumina prior to use. $NaBF_4$, NH_4PF_6, $NaSbF_6$, and H_3OAsF_6 were purchased from the Ozark-Mahoning Co. (TBA)Br, $(TBA)BF_4$, and $(TBA)ClO_4$ (TBA = tetra-*n*-butylammonium ion) were purchased from Southwestern Analytical Chemicals. HSO_3CF_3 was obtained as a gift from the 3M Co. All other reagents were purchased as reagent grade and used as received.

$(TBA)SO_3CF_3$, $(TBA)AsF_6$, and $(TBA)SbF_6$ were synthesized by the slow addition of HSO_3CF_3, H_3OAsF_6, or $NaSbF_6$ to aqueous solutions of (TBA)Br. (In the case of SbF_6^-, the (TBA)Br solution was made strongly acidic by the addition of HCl to avoid the hydrolysis of the SbF_6^- anion.) The resulting white crystalline solids were recrystallized from dichloromethane and dried at 50 °C.

A strongly acidic aqueous solution of $[(\eta^5\text{-}C_5H_5)Fe(\eta^6\text{-}p\text{-xyl})]^+$ was obtained by the synthetic method of Nesmeyanov et al.[7] with the improvement suggested by Roman.[8] BF_4^-, PF_6^-, $CF_3SO_3^-$, AsF_6^-, and SbF_6^- salts were obtained by the addition of $NaBF_4$, NH_4PF_6, HSO_3CF_3, H_3OAsF_6, and $NaSbF_6$ to portions of the aqueous solution of the Fe cation. The solid products obtained were dissolved in dichloromethane and chromatographed *in the dark* on alumina to remove Fe(II) impurities. Dichloromethane was then removed *in the dark*, and the crystalline solids were vacuum-dried over P_2O_5.

All of the compounds were checked for purity by comparison of their ^1H NMR data (Varian CFT-20 spectrometer) to the data previously reported for $[(\eta^5\text{-}C_5H_5)Fe(\eta^6\text{-}p\text{-xyl})]PF_6$[9] and by UV–vis spectroscopy (Cary 17-D spectrophotometer).

Quantum Yield Determinations. Quantum yields were determined for the appearance of $[Fe(phen)_3]^{2+}$ (spectrophotometry at 510 nm) with irradiation at 21 ± 1 °C on solutions 0.02 M in $[(\eta^5\text{-}C_5H_5)Fe(\eta^6\text{-}p\text{-xyl})]^+$ and 0.05 M in 1,10-phenanthroline by a method similar to one previously described.[1] To ensure that the nonaqueous solutions remained dry during the time of photolysis (15–180 s), approximately 0.1 g of activated 3-Å molecular sieves was placed in the photolysis cells, which were sealed and stored for at least 3 h prior to photolysis. All solutions were stirred during photolysis.

The highly reproducible and convenient photochemical reaction of 0.02 M $[(\eta^5\text{-}C_5H_5)Fe(\eta^6\text{-}p\text{-xyl})]BF_4$ and 0.05 M phenanthroline

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Table I. Quantum Yields and Conductivities for $[(\eta^5\text{-}C_5H_5)Fe(\eta^6\text{-}p\text{-xyl})]X$

anion	conditions	ϕ^a	Λ^b
BF_4^-	H_2O/0.1 M H_2SO_4	0.81[c]	
BF_4^-	propylene carbonate	0.79	
BF_4^-	methanol	0.77	
BF_4^-	CH_3CN	0.72	137
SbF_6^-	CH_3CN	0.72	138
$CF_3SO_3^-$	CH_2Cl_2	0.60	9.3
BF_4^-	CH_2Cl_2	0.58[c]	7.9
PF_6^-	CH_2Cl_2	0.12	11.5
AsF_6^-	CH_2Cl_2	0.087	10.9
SbF_6^-	CH_2Cl_2	0.084	12.5
BF_4^-	CH_2Cl_2/0.1 M (TBA)BF_4	0.64	
SbF_6^-	CH_2Cl_2/0.1 M (TBA)Br	0.59	
SbF_6^-	CH_2Cl_2/0.02 M (TBA)Br	0.40	
SbF_6^-	CH_2Cl_2/0.1 M (TBA)ClO_4	0.55	
SbF_6^-	CH_2Cl_2/0.1 M (TBA)SbF_6	0.11	

[a] Values are measured for 0.02 M solutions of $[(\eta^5\text{-}C_5H_5)Fe(\eta^6\text{-}p\text{-xyl})]X$ in the presence of 0.05 M 1,10-phenanthroline. Esd's average 4% for these measurements. [b] Conductivities (Ω^{-1} cm^2 mol^{-1}) are measured for 0.02 M solutions and have esd's of 5%. [c] This value is taken from ref 1 (also see footnote 10).

in dichloromethane (ϕ taken as 0.58)[10] was used as an actinometer. Quantum yields reported are corrected for inner-filter effects[11] and incomplete absorption of the incident radiation.

The ease of the procedure developed permitted three or four independent determinations of four or five of the different conditions studied to be conducted in 1 day. Among the determinations of a given day, a minimum of four actinometric measurements was made. Because ϕ was determined for different combinations of the conditions studied on a given day, very high relative precision was obtained. The esd's (±4%) of the quantum yields (at least three independent measurements) reported in Table I reflect this high relative precision. The absolute accuracy of these measurements (±10%) is traceable to the accuracy of the Reineckate actinometry[12] used to determine the quantum yields previously reported.[1,10]

Conductivity Measurements. Conductivities were determined by using a standard 10-mL conductivity cell and an Industrial Instruments Type RC conductivity bridge. The cell constant was determined to be 1.441 Ω^{-1} cm^{-1} at 24 °C with a 0.01 M aqueous KCl solution. Corrections for the conductivities of the pure solvents (less than 10^{-6} Ω^{-1} cm^2 mol^{-1}) were negligible.

Solutions were dried for several hours over 3-Å molecular sieves before measurement. No change was observed in the conductivities measured on addition of a small amount of water to the nonaqueous solutions. The conductivities of $[(\eta^5\text{-}C_5H_5)Fe(\eta^6\text{-}p\text{-xyl})]X$ solutions were determined *in the dark*. Equivalent conductivities of the $[(\eta^5\text{-}C_5H_5)Fe(\eta^6\text{-}p\text{-xyl})]X$ compounds are reported in Table I. For comparison, the equivalent conductivities of 0.02 M solutions of (TBA)X in CH_2Cl_2 (X = BF_4^-, PF_6^-, AsF_6^-, $CF_3SO_3^-$, Br^-, and ClO_4^-) were determined to be 11.4, 12.7, 13.3, 10.5, 8.3, and 10.9 Ω^{-1} cm^2 mol^{-1}, respectively.

Results and Discussion

The quantum yields determined for reaction 1 in various media are listed in Table I.

$$[(\eta^5\text{-}C_5H_5)Fe(\eta^6\text{-}p\text{-xyl})]^+ \xrightarrow[0.05\text{ M phen}]{h\nu\ (\lambda\ 436\text{ nm})} [Fe(phen)_3]^{2+} + p\text{-xyl} + C_5H_5^- \quad (1)$$

The quantum yield for reaction 1 in dichloromethane solution is nearly independent of [phen] for [phen] > 0.01 M, suggesting that at high [phen] essentially *all* of the photogenerated intermediate(s) is (are) scavenged and converted to $[Fe(phen)_3]^{2+}$.[1] The presence of the phenanthroline in the solutions during photolysis greatly facilitates the measurement of the extent of reaction and inhibits back-reactions without influencing the primary photochemical step. Previous studies[1,4] of the photochemical behavior of $[(\eta^5\text{-}C_5H_5)Fe(\eta^6\text{-}p\text{-xyl})]^+$ indicate that the removal of the arene is the initial chemical step in reaction 1, followed by a sequence of relatively fast ligand replacement reactions that yield $[Fe(phen)_3]^{2+}$ as the final product. The quantum yields for the formation of $[Fe(phen)_3]^{2+}$ under the conditions studied here are taken as the rate of arene removal from the starting complex divided by the sum of this rate and the rates of all unproductive excited-state deactivational processes. The discussion that follows assumes that the rates of the unproductive excited-state deactivational processes are independent of the medium; i.e., changes in ϕ exclusively reflect the influence of the medium on the rate of arene removal. This assumption is appropriate because none of the solvents or anions studied here have excited states or redox potentials appropriate for their involvement in energy or electron-transfer quenching processes. Additionally, no strong ground- or excited-state interactions between $[(\eta^5\text{-}C_5H_5)Fe(\eta^6\text{-}p\text{-xyl})]^+$ and the media studied that might perturb nonproductive decay pathways of the reactive excited state are apparent. ϵ_{max} and λ_{max} of the band due to the $S_0 \rightarrow S_1$ LF transition of $[(\eta^5\text{-}C_5H_5)Fe(\eta^6\text{-}p\text{-xyl})]^+$ reached on 436-nm excitation are independent of solvent and anion.[13]

Quantum yield data determined for reaction 1 ($X^- = BF_4^-$) in dichloromethane, acetonitrile, methanol, propylene carbonate, and water show a small systematic increase consistent with at least a portion of the $[Fe(phen)_3]^{2+}$ formed arising from a solvent-assisted arene removal step. This solvent effect is even more pronounced for $X^- = SbF_6^-$ in dichloromethane and acetonitrile (ϕ = 0.084 and 0.72, respectively). Further, the quantum yields for acetonitrile solutions of the BF_4^- and SbF_6^- salts of $[(\eta^5\text{-}C_5H_5)Fe(\eta^6\text{-}p\text{-xyl})]^+$ are independent of X^-, suggesting for acetonitrile solutions the assisting component of the medium *is* the solvent. Conductivity data for 0.02 M solutions of the BF_4^- and SbF_6^- salts of $[(\eta^5\text{-}C_5H_5)Fe(\eta^6\text{-}p\text{-xyl})]^+$ in CH_3CN are consistent[14] with the nearly total dissociation of these salts into free ions.

The quantum yields for dichloromethane solutions of $[(\eta^5\text{-}C_5H_5)Fe(\eta^6\text{-}p\text{-xyl})]X$ indicate a strong dependence on the counterion X^- with the ordering $SO_3CF_3^- > BF_4^- \gg PF_6^- > AsF_6^- \approx SbF_6^-$. Comparison of the conductivity data determined for solutions of the Fe-containing salts and TBA^+ salts (see Experimental Section) in dichloromethane indicates *substantial and nearly identical* fractions (~85%) of the ions in *all* of these solutions are present as ion pairs.[15] The involvement of photoactive ion pairs in these solutions is further supported by the increase in the quantum yield obtained when photolysis occurs in the presence of added (TBA)X. This increase is consistent with the formation of additional $[(\eta^5\text{-}C_5H_5)Fe(\eta^6\text{-}p\text{-xyl})]X$ ion pairs as required by the law of mass

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[10] In ref 1, the quantum yield is reported as 0.58 for the PF_6^- salt of $[(\eta^5\text{-}C_5H_5)Fe(\eta^6\text{-}p\text{-xyl})]^+$. This determination was actually made on the BF_4^- salt.

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[13] A reviewer has pointed out that the lack of a medium effect on the singlet–singlet LF spectral feature reached on 436-nm excitation does not ensure the absence of medium effects on the corresponding singlet–triplet transition involving the (presumed) photoactive ^{3}LF state. We have observed a broad electronic transition at ~650 nm (ϵ ~1 M^{-1} cm^{-1}) in concentrated solutions of $[(\eta^5\text{-}C_5H_5)Fe(\eta^6\text{-}p\text{-xyl})]^+$, which we tentatively assign to the lowest $^1\text{LF} \rightarrow {}^3\text{LF}$ transition in this system. The position and intensity of this band are independent of the solvent (CH_2Cl_2, CH_3CN).

[14] For a completely dissociated 1:1 electrolyte in CH_3CN solutions, the equivalent conductances fall into the range 120–160 Ω^{-1} cm^2 mol^{-1}: Geary, W. J. *Coord. Chem. Rev.* **1971**, *7*, 81.

[15] The limiting conductivity *at infinite dilution* of (TBA)BF_4 in 1,2-dichloroethane (ϵ ~10.4) is 68.9 Ω^{-1} cm^2 mol^{-1}: Boggess, R. K.; Zatko, D. A. *J. Chem. Educ.* **1975**, *10*, 649. Our measurement of the conductivity of 0.02 M (TBA)BF_4 in dichloromethane (ϵ ~8.9) of 11.4 Ω^{-1} cm^2 mol^{-1} indicates that at this concentration a significant portion (~85%) of the (TBA)BF_4 is associated. The conductivity measurements of the other (TBA)X salts and the $[(\eta^5\text{-}C_5H_5)Fe(\eta^6\text{-}p\text{-xyl})]X$ (also 0.02 M solutions in dichloromethane) indicate a similar degree of association for these salts.

action.

The quantum yields for CH_2Cl_2 solutions of 0.02 M $[(\eta^5\text{-}C_5H_5)Fe(\eta^6\text{-}p\text{-xyl})]SbF_6$ ($\phi = 0.084$) increase significantly with the addition of 0.1 M (TBA)Br ($\phi = 0.59$) or $(TBA)ClO_4$ ($\phi = 0.55$), consistent with the formation of the relatively more reactive $[(\eta^5\text{-}C_5H_5)Fe(\eta^6\text{-}p\text{-xyl})]Br$ or $[(\eta^5\text{-}C_5H_5)Fe(\eta^6\text{-}p\text{-xyl})]ClO_4$ ion pairs.

The systematic variation in the quantum yield for dichloromethane solutions with the identity of the anion present and the extent of ion pairing suggest in dichloromethane the paired anion assists in the removal of *p*-xylene *as a nucleophile*, decreasing in the order $CF_3SO_3^- > BF_4^- > Br^- \approx ClO_4^- >> PF_6^- > AsF_6^- \approx SbF_6^-$. The much smaller quantum yield values obtained for PF_6^- and especially AsF_6^- and SbF_6^-, even though these anions exhibit ion pairing to approximately the same extent as BF_4^-, indicate them to be the poorest nucleophiles studied. This result is also consistent with the poor coordinating ability of these anions.[16] The nearly constant quantum yield values obtained for AsF_6^- and SbF_6^- may be due to a substantial fraction of the photochemical reaction proceeding by nucleophilic attack of dichloromethane on the active excited state of $[(\eta^5\text{-}C_5H_5)Fe(\eta^6\text{-}p\text{-xyl})]^+$. Quantum yield determinations in less nucleophilic solvents than CH_2Cl_2 such as SO_2 or SO_2ClF[17] would be needed to discern more accurately the nucleophilicities of CH_2Cl_2, PF_6^-, AsF_6^-, and SbF_6^- and to determine whether a parallel, purely dissociative pathway for arene removal also exists in this system.

Conclusions

The data presented here are consistent with arene removal reactions of $[(\eta^5\text{-}C_5H_5)Fe(\eta^6\text{-}p\text{-xyl})]^+$ that occur predominantly through pathways involving solvent-assisted steps (in polar, nucleophilic solvents) or anion-assisted steps (in nonpolar, weakly nucleophilic solvents). The assistance order determined in this system is $H_2O \approx$ propylene carbonate $\approx CH_3OH \gtrsim CH_3CN > CF_3SO_3^- > BF_4^- > Br^- \approx ClO_4^- >> PF_6^- > CH_2Cl_2 \approx AsF_6^- \approx SbF_6^-$.

The nature of the assistance observed for the arene replacement reaction studied here is consistent with nucleophilic attack of the medium on a LF excited state of Fe. This behavior stands in contrast to the dissociative behavior observed for LF excited states in other low-spin d^6 systems.[5] Without more detailed studies, we can only speculate that the factors that differentiate the photochemical behavior of $M(\eta^6\text{-arene})$ and analogous $M(CO)_3$ moieties are (1) the availability of alternate (η^4 or η^2) bonding modes in the M–arene system,[18] (2) the higher *total* $M\text{–}\eta^6$-arene bond energy as compared to the energy of a M–CO bond,[19] and (3) the decrease in the relative labilization gained by populating a M(arene) σ^* level as compared to a $M(CO)_3$ σ^* level.[20] This latter idea is supported by the recent crystal structure report[21] on $[(\eta^5\text{-}C_5H_5)Fe^I(\eta^6\text{-}C_6Et_6)]$ with a $(e_2)^4(a_1)^2(e_1^*)^1$ electronic configuration. The $Fe^I\text{–}\eta^6$-arene bond in this compound shows considerable thermal stability and is lengthened only 0.03 Å over the distance found for a similar Fe(II) compound.

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Registry No. $[(\eta^5\text{-}C_5H_5)Fe(\eta^6\text{-}p\text{-xyl})]BF_4$, 74176-24-2; H_2O, 7732-18-5; CH_3OH, 67-56-1; CH_3CN, 75-05-8; $CF_3SO_3^-$, 37181-39-8; BF_4^-, 14874-70-5; Br^-, 24959-67-9; ClO_4^-, 14797-73-0; PF_6^-, 16919-18-9; CH_2Cl_2, 75-09-2; AsF_6^-, 16973-45-8; SbF_6, 17111-95-4; propylene carbonate, 108-32-7.

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Enantiomerism in (*R**,*R**)-(±)- and (*R**,*S**)-(±)-1-(Methylphenylarsino)-2-(methylphenylphosphino)benzene: Resolution of Both Diastereoisomers by Metal Complexation

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The resolution of the *R**,*R** and *R**,*S** diastereoisomers of the new asymmetric bidentate 1-(methylphenylarsino)-2-(methylphenylphosphino)benzene has been achieved by the method of metal complexation. Fractional crystallization of internally diastereoisomeric palladium(II) complexes containing the different forms of the bidentate and ortho-metalated (*R*)-dimethyl[1-(1-ethyl)phenyl]amine (*R**,*R** diastereoisomer) or (*R*)-dimethyl[1-(1-ethyl)naphthyl]amine (*R**,*S** diastereoisomer) gives diastereoisomers from which the four enantiomers of the ligand can be individually liberated by stereospecific displacements. This is the first resolution of an asymmetric bidentate containing dissimilar asymmetric donor atoms. The optically pure enantiomers are air-stable crystalline solids with $[\alpha]_D$ ±79° (CH_2Cl_2) (*R**,*R**) and $[\alpha]_D$ ±15.5° (CH_2Cl_2) (*R**,*S**). Absolute configurations have been assigned by comparison of ^1H NMR spectra of certain internally diastereoisomeric palladium(II) complexes containing a particular enantiomer with similar compounds of known structure. Interconversions between the enantiomers of the *R**,*R** and *R**,*S* forms of the bis(tertiary) species take place under thermal conditions that do not affect the integrity of the asymmetric arsenic centers. Mineral acid catalysis does not epimerize the arsenic centers in these compounds: optically active protonated phosphonium salts are formed.

Metal complexation has been shown to be a powerful method for the resolution of chiral ligands.[1] The generality of the approach has been vividly demonstrated by the large-scale resolution of several important types of asymmetric and dis-

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