Table VI. Distances (Å) and Angles (Deg) Relevant to M-SO_2 Binding

	a	*b*	*c*	*d*
M-S	2.326 (2)	2.337 (2)	2.532 (3)	2.496 (2)
M-O_M	2.342 (5)	2.144 (6)	2.223 (5)	2.111 (4)
S-O_M	1.493 (5)	1.504 (5)	1.468 (5)	1.550 (4)
S-O	1.430 (5)	1.459 (5)	1.435 (8)	1.452 (5)
O_M-M-S	37.3 (1)	38.9 (1)	35.2 (1)	38.2 (1)
M-S-O_M	71.9 (2)	63.6 (2)	60.8 (2)	57.4 (2)
M-S-O	106.4 (2)	117.6 (2)	117.5 (4)	113.2 (2)
O_M-S-O	115.1 (4)	113.7 (3)	117.3 (4)	113.4 (3)
e	100.3 (3)	110.3 (3)	108.1 (3)	103.4 (4)
$\nu(SO_M)$, cm^{-1}	948	895	935[f]	873[f]

[a] $Rh(NO)(\eta^2\text{-}SO_2)(PPh_3)_2$.[1] [b] $RuCl(NO)(\eta^2\text{-}SO_2)(PPh_3)_2$.[2] [c] $Mo(CO)_3(phen)(\eta^2\text{-}SO_2)$. [d] $Mo(CO)_2(bpy)(\eta^2\text{-}SO_2)_2$ (values were averaged). [e] Dihedral angle between SO_2 and c-MSO_M. [f] Reference 4.

whenever metal π donation to the ligand is strongly favored over ligand–metal σ donation. The tendency toward the η^2 geometry would then be favored by factors such as increased metal basicity, ancillary ligands which are strong σ donors, or, in general, any perturbation which increases the energy of the potentially σ-accepting orbital or enhances the π basicity of the metal.

The orientation of the SO_2 ligand (i.e., the dihedral angle between the SO_2 plane and the plane defined by Mo and the S–O_M bond, which ranges between 103 and 110°) is consistent with the view that the SO_2 LUMO b_1 orbital is the major component of the π-accepting orbital. Additionally, we point out that some interesting correlations exist among the data presented in Table VI. The lower vibrational frequencies observed in complexes b and d are associated not only with the shorter metal–oxygen distances but also with the longer S–O_M distances, the latter point being in accord with a model which incorporates π donation from the metal to an antibonding (with respect to S–O) π SO_2 orbital such as the b_1 LUMO. We also note that this orbital is bonding with respect to O–O and that the O–S–O angles are significantly smaller for complexes b and d.

The assumption that the η^2–SO_2 ligands in these complexes effectively occupy only one coordination site is based at least in part on the observation that the average Mo–O distance of 2.111 Å in II represents a bond strength of 0.5 according to Zachariasen's recently derived bond length–bond strength relationships.[20] A bond length of 2.55 Å can then be estimated from the difference in ionic radii[21] ($\Delta(S^{2-}–O^{2-}) = 0.44$ Å) for a Mo–S bond of strength 0.5, placing the total bond strength for one Mo–SO_2 interaction in II at slightly greater than one (observed Mo–S = 2.52 Å). Similarly for complex I the Mo–O bond distance of 2.211 Å implies a strength of 0.35 and a total bond strength slightly less than in complex II, in accord with the frequencies exhibited for the S–O_M stretching mode in the two complexes (see Table VI).

Further synthetic and structural studies of complexes of the type $Mo(CO)_n(L)_{5-n}(SO_2)$ (n = 2, 3; L = various combinations of ligands such as phosphines, isocyanides, etc.) are in progress.

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Registry No. I, 68297-98-3; II, 74096-90-5.

Supplementary Material Available: A listing of calculated and observed structure factors with $10\sigma(F_o)$ plus stereoviews of the unit cell contents (11 pages). Ordering information is given on any current masthead page.

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Photochemical Generation of a Reactive Transition-Metal Fragment. Photochemically Induced Arene Replacement Reactions of the Cyclopentadienyl(*p*-xylene)iron(II) Ion

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Visible-light irradiation of $FeCp(p\text{-}xyl)^+$ (Cp = cyclopentadienyl, *p*-xyl = *p*-xylene) in organic solvents in the presence of suitable ligands leads to the formation of products in which the three coordination sites occupied by *p*-xylene have been replaced to give complexes of the form $FeCpL_3^+$ ($L_3 = (p\text{-}CNPhCH_3)_3$, $(CO)_3$, hexamethylbenzene, and triphos), which have been isolated and characterized as PF_6^- or BF_4^- salts. The quantum yields for the formation of these products are rather large. For example, irradiation (436 nm) of the LF bands of $FeCp(p\text{-}xyl)^+$ in methylene chloride in the presence of 0.05 M triphos (bis(2-(diphenylphosphino)ethyl)phenylphosphine) yields $FeCp(triphos)^+$ with $\phi = 0.57 \pm 0.06$. The course of the photochemical reaction was different in methylene chloride solution with 1,10-phenanthroline added or in aqueous 0.1 N H_2SO_4 solution. The 436-nm irradiation of $FeCp(p\text{-}xyl)^+$ in methylene chloride in the presence of 0.1 M 1,10-phenanthroline leads to the formation of $Fe(phen)_3^{2+}$ with a quantum yield of 0.58 ± 0.06. Similarly, 436-nm-irradiation of $FeCp(p\text{-}xyl)^+$ in 0.1 N aqueous H_2SO_4 solution leads to the formation of $Fe^{2+}(aq)$ with a quantum yield of 0.81 ± 0.08. The possible mechanisms for these reactions are tentatively discussed in terms of replacement of *p*-xylene to produce a reactive transition-metal fragment containing the $FeCp^+$ unit, which undergoes addition of incoming ligand L to form complexes of the form $FeCpL_3^+$ or FeL_n^{2+}.

Introduction

Except for several studies using ferrocene as a quencher[1] and the photochemical oxidation of ferrocene in halogenated solvents,[2] photochemists have for the most part been frustrated by ferrocene's distinct lack of photochemical reactivity.[3] Two types of photochemical reactivity which might be expected of ferrocene, but to our knowledge have not been observed[4] in-

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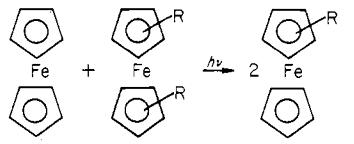
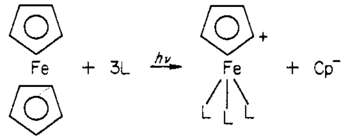
solution, are simple ring interchange reactions (reaction 1) and ring replacement reactions (reaction 2). These reactions, in addition to being mechanistically interesting, could have considerable synthetic utility. Both of these reactions might be expected to arise from LF excitation, since the predominant reaction pathway for LF excited states in the majority of transition-metal systems studied is the formation of products arising from M–L bond scission.[5] For example, both reactions 1 and 2 might be expected to involve solvated $FeCp^+$ fragments generated as reactive intermediates. Of considerable interest is the possibility of photochemically generating this type of intermediate from a source other than ferrocene. A system which was particularly attractive to us in this regard was the $FeCp(arene)^+$ system.



(1)



(2)

A variety of compounds[6] of this type having ring substituents are known and are easily synthesized by the method of Nesmeyanov et al.[7] Hendrickson and co-workers[8] have conducted preliminary studies suggesting that the electronic spectral properties of mononuclear $FeCp(arene)^+$ systems are very similar to those of ferrocene, exhibiting spin-allowed LF bands in the 400–500-nm spectral region. In a subsequent publication Nesmeyanov et al.[9] also reported some qualitative photochemical experiments which suggest that the $FeCp(arene)^+$ systems undergo a photochemically induced decomposition reaction to yield Fe^{2+} and $FeCp_2$ in a variety of organic solvents. We have begun a detailed study of the photochemical reactivity of the $FeCp(arene)^+$ system in the hope of generating reactive transition-metal fragments with multiple open coordination sites and also illucidating the mechanisms of photochemical substitution reactions of η^6-bound M(arene) systems. Our preliminary study of the photochemical reactions of $FeCp(p\text{-xyl})^+$ indicates that LF excitation leads to the efficient formation of a reactive intermediate which exhibits the reactivity of a coordinatively unsaturated iron-containing fragment.

Experimental Section

Reagents and Apparatus. Solvents used in this study (methylene chloride and acetone) were of spectroscopic quality. Acetone was dried[10] over B_2O_3. All other reagents were purchased as reagent grade or better. *p*-$CNPhCH_3$ was synthesized[11] from *p*-NH_2PhCH_3. $FeCp(p\text{-xyl})PF_6$ and $FeCp(p\text{-xyl})BF_4$ were synthesized by the method of Nesmeyanov et al.[7] $FeCp(p\text{-xyl})PF_6$ NMR spectrum (acetone-d_6): aromatic, τ 3.72 (4 H, s); Cp, τ 4.93 (5 H, s); CH_3, τ 7.52 (6 H, s). [Literature NMR spectrum[12] (acetone-d_6): aromatic, τ 3.72 (4 H, s); Cp, τ 4.92 (5 H, s); CH_3, τ 7.52 (6 H, s).] $FeCp(p\text{-xyl})BF_4$ NMR spectrum (acetone-d_6): aromatic, τ 3.67 (4 H, s); Cp, τ 4.89 (5 H, s); CH_3, τ 7.49 (6 H, s). [Literature NMR spectrum[13] (acetone-d_6): aromatic, τ 3.68 (4 H, s); Cp, τ 4.90 (5 H, s); CH_3, τ 7.50 (6 H, s).]

Synthetic-scale photolyses were carried out by using Pyrex-filtered sunlight or a 175-W medium-presure mercury lamp equipped with a Corning 0-52 filter. Photolyses for quantum yield measurements were carried out by isolating (interference filter) the 436-nm mercury line from the output of an Oriel Model 6281 100-W mercury lamp. IR, NMR, and UV–vis spectra were obtained by using a Perkin-Elmer 283, a Varian Associates CFT 20 equipped with a 79.5-MHz proton accessory, and a Cary 17D spectrophotometer, respectively.

Quantum yields were determined at 20 ± 1 °C by photolysis of 3.0-mL samples contained in standard 1-cm path length cuvettes. Analysis of the extent of reaction was made spectrophotometrically. Actinometry was carried out with the use of Reinecke's salt.[14] The light intensity striking the cell was typically 4.0×10^{-6} einstein min^{-1}. Quantum yields were corrected for inner filter effects.[15]

Photochemical Reaction of $FeCp(p\text{-xyl})PF_6$ with *p*-$CNPhCH_3$. $FeCp(p\text{-xyl})PF_6$ (63.8 mg, 0.17 mmol), *p*-$CNPhCH_3$ (77.7 mg, 0.66 mmol), 15 mL of dry acetone, and a spinbar were placed in a Pyrex test tube. A serum stopper was used to seal the test tube which was degassed by bubbling with cylinder nitrogen for about 15 min. The reaction mixture was then stirred in bright sunlight for 3 h. Evaporation of the solvent, followed by recrystallization of the residue from acetone/ether, afforded $FeCp(p\text{-CNPhCH}_3)_3PF_6$ (89.0 mg, 0.14 mmol) in 84% yield, which was characterized by NMR and IR spectroscopy. IR spectrum (KBr pellet): $\bar{\nu}$(C≡N) 2190 (s), 2140 (s) cm^{-1}. NMR spectrum: (acetone-d_6): aromatic τ 2.61 (12 H, A_2B_2 pattern); Cp, τ 4.59 (5 H, s); CH_3, τ 7.61 (9 H, s). In the literature an analogous complex of CNPh, $FeCp(CNPh)_3Cl$, has been reported:[16] $\bar{\nu}$(C≡N) 2190, 2123 cm^{-1}.

Thermal Reaction of $FeCp(p\text{-xyl})PF_6$ with *p*-$CNPhCH_3$. In a control reaction, 54.3 mg (0.15 mmol) of $FeCp(p\text{-xyl})PF_6$, 50 mg (0.43 mmol) of *p*-$CNPhCH_3$, and 10 mL of methylene chloride were placed in a test tube which was then sealed with a serum stopper. The solution was purged with dry nitrogen gas for 15 min and then stirred at room temperature in the dark for 12 h. Evaporation of the solvent, followed by recrystallization of the residue at room temperature from methylene chloride/hexane, yielded 47.0 mg (0.13 mmol, 86% recovery) of a yellow solid which was confirmed to be greater than 99% $FeCp(p\text{-xyl})PF_6$ by NMR analysis.[17]

Photochemical Reaction of $FeCp(p\text{-xyl})PF_6$ and $P(OPh)_3$. The photolysis in bright sunlight (Pyrex reaction vessel) of $FeCp(p\text{-xyl})PF_6$ (63 mg, 0.17 mmol) and $P(OPh)_3$ (175 mg, 0.56 mmol) in 15 mL of degassed methylene chloride was allowed to proceed for 1.5 h. Evaporation of the solvent, followed by recrystallization of the residue from methylene chloride/hexane, afforded $FeCp(P(OPh)_3)_3PF_6$ (105 mg, 0.09 mmol), a 52% yield. NMR spectrum (acetone-d_6): aromatic, τ 2.83–3.18 (45 H, complex multiplets); Cp, τ 5.21 (5 H, quartet, J_{P-H} = 1.5 Hz). [Literature NMR spectrum[18] (acetone-d_6): aromatic, τ 2.83–3.19 (45 H, multiplets); Cp, τ 5.22 (5 H, quartet, J_{P-H} = 1.5 Hz).]

Photochemical Reaction of $FeCp(p\text{-xyl})PF_6$ and CO. Photolysis, with the filtered (Corning 0-52) output of a 175-W medium-pressure Hg lamp, of $FeCp(p\text{-xyl})PF_6$ (80.0 mg, 0.22 mmol) in 15 mL of acetone with a CO purge yielded on evaporation 82.4 mg of a gummy residue which on recrystallization gave a 50% yield of $FeCp(CO)_3PF_6$. IR spectrum (KBr pellet): $\bar{\nu}$(CO) 2127 (s), 2074 (s) cm^{-1}. NMR

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spectrum (acetone-d_6): Cp, τ 3.83 (s). [Literature:[19] IR $\tilde{\nu}$(CO) 2135, 2072 cm^{-1} (medium not reported); NMR (acetone-d_6) Cp τ 3.82 (s).]

Photochemical Reaction of $FeCp(p\text{-xyl})BF_4$ and Hexamethylbenzene. A degassed solution of 65.7 mg (0.21 mmol) of $FeCp(p\text{-xyl})BF_4$ and 514.4 mg of hexamethylbenzene (3.2 mmol) was stirred in bright sunlight for 5 h. After evaporation of the solvent, the residue was washed repeatedly with hexane, yielding 58.5 mg of a yellow solid. NMR analysis showed the yellow solid to consist of pure (99+%) $FeCp(C_6(CH_3)_6)BF_4$, representing a 76% yield. NMR spectrum of $FeCp(C_6(CH_3)_6)BF_4$ (acetone-d_6): Cp, τ 5.23 (5 H, s); CH_3, τ 7.42 (18 H, s). [Literature NMR[13] (acetone-d_6): Cp, τ 5.22; CH_3, τ 7.42.]

Thermal Exchange Reaction of $FeCp(p\text{-xyl})BF_4$ with Hexamethylbenzene. In a control reaction, a degassed solution of 72.7 mg (0.23 mol) of $FeCp(p\text{-xyl})BF_4$ and 487.6 mg (3.0 mmol) of $C_6(CH_3)_6$ in 20 mL of methylene chloride was allowed to stir for 36 h in the dark. Evaporation of the solvent, followed by repeated washing with hexane, yielded 60.9 mg of a yellow solid. NMR analysis[17] of the solid confirmed it to be 99+% pure starting material, $FeCp(p\text{-xyl})BF_4$.

Photochemical Reaction of $FeCp(p\text{-xyl})PF_6$ with triphos. Photolysis for 3 h of $FeCp(p\text{-xyl})PF_6$ (96.8 mg, 0.26 mmol) and triphos (159.4 mg, 0.30 mmol) in 15 mL of degassed acetone was carried out with 436-nm light (interference filter) from a 100-W medium-pressure Hg lamp. Evaporation of the solvent gave a yellow solid. Recrystallization from methylene chloride/hexane gave crystals of $FeCp(triphos)PF_6$ in a 73% yield (152.5 mg, 0.10 mmol.) NMR spectrum (acetone-d_6): aromatic, τ 1.9–2.5 (25 H, complex multiplets); Cp, τ 5.52 (5 H, quartet, J_{P-H} = 1.5 Hz); methylene, partially obscured by residual acetone, τ ~8.0. Mp: 252–256 °C dec. Visible spectrum (methylene chloride): a single peak at 421 nm, $\epsilon = 790\ M^{-1}\ cm^{-1}$ ($\epsilon_{436} = 736\ M^{-1}\ cm^{-1}$). [Literature:[20] NMR spectrum (chloroform-d_1) aromatic τ ~2.7, Cp τ 5.77, methylene τ ~8; mp 253–255 °C dec.]

Quantum Yields for the Conversion of $FeCp(p\text{-xyl})^+$ to $FeCp(triphos)^+$. The absorbance changes at 436 nm upon 436-nm excitation of 3.0 mL of a solution 0.02 M in $FeCp(p\text{-xylene})PF_6$ and 0.05 M in triphos were followed. Seven points were taken at 20-s intervals. The data were corrected for the inner-filter effect[13] and then plots of the corrected absorbance vs. irradiation time were made. These plots were linear, yielding for two independent runs quantum yields for the appearance of $FeCp(triphos)^+$ of 0.54 and 0.60, giving ϕ_{av} = 0.57 ± 0.06.

Quantum Yields for the Decomposition of $FeCp(p\text{-xyl})^+$ in Aqueous 0.1 N H_2SO_4. A solution of $FeCp(p\text{-xyl})BF_4$ (0.02 M) was made up in aqueous 0.1 N H_2SO_4. Room-temperature photolysis with 436-nm light of 3.0-mL aliquots was carried out. The amount of $Fe^{2+}(aq)$ generated was determined as $Fe(phen)_3^{2+}$. The results of several runs gave ϕ for the appearance of $Fe^{2+}(aq)$ as 0.81 ± 0.08.

Decomposition Reaction of $FeCp(p\text{-xyl})^+$ in Aqueous 0.1 N H_2SO_4 in the Dark. A solution 0.02 M in $FeCp(p\text{-xyl})BF_4$ was made up in aqueous 0.1 N H_2SO_4 and stored at 20 ± 1 °C in the dark for 235 h. Analysis of the solution for $Fe^{2+}(aq)$ as $Fe(phen)_3^{2+}$ gave 6.76×10^{-6} M $Fe^{2+}(aq)$ formed during the dark storage time. This represents about 0.033% decomposition of the solution.

Quantum Yields for the Reaction of $FeCp(p\text{-xyl})^+$ and 1,10-Phenanthroline in Methylene Chloride. Methylene chloride solutions 0.02 M in $FeCp(p\text{-xyl})PF_6$ and 0.1, 0.01, and 0.001 M in 1,10-phenanthroline, respectively, were made up and dried over K_2CO_3. The absorbance at 510 nm before and after 436-nm photolysis (15-s photolysis time) for 3.0-mL aliquots of each solution were measured. The data were corrected for the inner-filter effect[15] and analyzed by assuming the ϵ_{510} for the $Fe(phen)_3^{2+}$ formed is $1.11 \times 10^4\ M^{-1}\ cm^{-1}$. ϕ's for the appearance of $Fe(phen)_3^{2+}$ were 0.58 ± 0.06, 0.52 ± 0.05, and 0.48 ± 0.05 for 0.1, 0.01, and 0.001 M 1,10-phenanthroline solutions, respectively.

Results and Discussion

Visible-light photolysis ($\lambda_{irr} > 400$ nm) of $FeCp(p\text{-xyl})PF_6$ in degassed methylene chloride or acetone in the presence of suitable incoming ligands gives products which involve replacement of the three coordination sites held by p-xylene by three new donors:

$$FeCp(p\text{-xyl})^+ \xrightarrow[\text{excess L}]{h\nu} FeCpL_3^+ + p\text{-xyl} \quad (3)$$

$$L_3 = (p\text{-CNPhCH}_3)_3,\ (P(OPh)_3)_3,\ (CO)_3,\ \text{hexamethylbenzene, triphos}$$

All of these reactions occur cleanly with high conversions at 25 °C. The products were isolated, and their spectroscopic data compared favorably with literature values.

In a typical reaction $FeCp(p\text{-CNPhCH}_3)_3PF_6$ was obtained by the sunlight photolysis of $FeCp(p\text{-xyl})PF_6$ in the presence of p-$CNPhCH_3$ in 84% yield after recrystallization. A similar reaction mixture, allowed to stir in the dark for 12 h at 20 °C, resulted in no detectable conversion[17] of $FeCp(p\text{-xyl})PF_6$ to $FeCp(p\text{-CNPhCH}_3)PF_6$. Even more remarkable are the results for the photochemical rate enhancement of the arene-exchange reaction. In the case of hexamethylbenzene as the incoming ligand, better than 99% replacement of the p-xylene of $FeCp(p\text{-xyl})^+$ by hexamethylbenzene was observed after 5 h of stirring in sunlight. The control, dark, reaction (36 h at 20 °C) after workup showed no detectable[17] $FeCp(C_6(CH_3)_6)^+$.

The photochemical process which leads to these reactions appears to be very efficient in all the cases studied here, implying a common reaction pathway. Quantum yield measurements were made on a particularly convenient system, the conversion of $FeCp(p\text{-xyl})^+$ to $FeCp(triphos)^+$. At room temperature in the presence of 0.05 M triphos, a 0.02 M solution of $FeCp(p\text{-xyl})BF_4$ in methylene chloride was irradiated with 436-nm light. The reaction was followed by UV–vis spectroscopy. The quantum yield, ϕ, for appearance of $FeCp(triphos)^+$ was measured to be 0.57 ± 0.06. The quantum yields of the other reactions (reaction 3) qualitatively appear to be of the same order of magnitude but have not been determined.

In acidic aqueous media or in organic solvents in the presence of 1,10-phenanthroline, the net photochemical reaction of $FeCp(p\text{-xyl})^+$ was found to take a different course, involving replacement of both the arene and the Cp^- ligands. In 0.1 N aqueous H_2SO_4, 436-nm irradiation leads to the formation of $Fe^{2+}(aq)$ with a quantum yield of 0.81 ± 0.08. Similarly, in methylene chloride solution with 0.1 M 1,10-phenanthroline added, 436-nm irradiation leads to formation of $Fe(phen)_3^{2+}$ with ϕ = 0.58 ± 0.06. At lower concentrations of phenanthroline ([phen] = 0.001 M), the quantum yield is not appreciably diminished, ϕ = 0.48 ± 0.05. These results are consistent with the formation of $FeCpL_n^+$ (L = H_2O, phen) complexes which are unstable with respect to thermal reactions in which Cp^- is replaced by additional molecules of L to give $Fe^{2+}(aq)$ and $Fe(phen)_3^{2+}$, respectively.

Speculation about the mechanisms of these reactions without more detailed study is somewhat premature at this time, but it appears that at least two likely possibilities exist for the replacement of arene by L_3. For simplicity these can be referred to as (A) "arene ring slippage" and (B) "arene dissociation". Mechanism A consists of conversion of an initially obtained LF excited state to a $FeCp(arene)^+$ complex in which one or at most two coordination sites are opened up at the Fe atom to solvent molecules by virtue of the arene "slipping" aside relative to the $FeCp^+$ moiety. This type of solvated intermediate could then either undergo reaction back to $FeCp(arene)^+$ by expulsion of solvent or undergo replacement of the solvent molecules by L, initiating the sequential replacement of the remaining coordination positions occupied by the arene by additional L. Mechanism B postulates the total dissociation of the arene to give $FeCp^+(solv)$ prior to attack by incoming L. At this point in our investigation, compelling evidence for either of these two mechanisms or some other mechanism in which the counterion might play an important role is lacking. Our preference at this time is for the operation

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of mechanism B since it seems unlikely that a solvated FeCp(arene)$^+$ species in which the arene is η^2 or η^4 bound could have a lifetime long enough to undergo the required second-order reaction with L at the concentrations of L employed in these studies. Laser flash photolysis and low-temperature photolysis experiments are currently in progress to further resolve the mechanistic questions. We are also investigating the possible use of the reactive intermediate generated in these reactions with respect to photoassistance reactions and the synthesis of other FeCpL$_3^+$ complexes which are either unkown or difficult to synthesize by other routes.

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Registry No. FeCp(*p*-xyl)PF$_6$, 34978-37-5; FeCp(*p*-xyl)BF$_4$, 74176-24-2; FeCp(*p*-CNPhCH$_3$)$_3$PF$_6$, 72319-47-2; FeCp(P(OPh)$_3$)$_3$PF$_6$, 35004-06-9; FeCp(CO)$_3$PF$_6$, 38834-26-3; FeCp(C$_6$(CH$_3$)$_6$)BF$_4$, 70414-95-8; FeCp(triphos)PF$_6$, 34675-96-2; Fe(H$_2$O)$_6^{2+}$, 15365-81-8; Fe(phen)$_3^{2+}$, 14708-99-7.

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Hexaisopropoxydinitrosyldichromium and Its Reactions with Nitrogen Donor Ligands

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Cr(N-*i*-Pr$_2$)$_3$NO reacts with isopropyl alcohol to give the brick red crystalline compound Cr$_2$(O-*i*-Pr)$_6$(NO)$_2$. An X-ray study shows this compound to be isostructural with the previously characterized molybdenum analogue, though a complete refinement of the chromium structure was not possible because crystals repeatedly and rapidly decomposed in the X-ray beam. The experimental data obtained from a number of physical and spectroscopic studies directly parallel those observed for Mo$_2$(O-*i*-Pr)$_6$(NO)$_2$. The structure of Cr$_2$(O-*i*-Pr)$_6$(NO)$_2$ is thus shown to contain a central Cr$_2$O$_6$(NO)$_2$ skeleton with a rigorous inversion center and virtual C_{2h} symmetry; the σ_h plane contains the two chromium atoms, the axial NO groups, and the pair of oxygen atoms from the bridging alkoxy groups. Each chromium atom is in a local trigonal-bipyramidal environment and the two trigonal bipyramids are joined along a common axial–equatorial edge. The low-temperature limiting ^{1}H NMR spectrum is entirely consistent with the retention of this structure in solution. Above 80 °C in toluene-d_8, exchange of bridging and terminal isopropoxy ligands is rapid on the NMR time scale. The mixed-metal dimer CrMo(O-*i*-Pr)$_6$(NO)$_2$ is formed upon mixing the homonuclear dimers in hydrocarbon solvents and has been detected by ^{1}H NMR, IR, and mass spectroscopy. Variable-temperature NMR studies show that for solutions containing an equilibrium mixture of the Mo$_2$-, Cr$_2$-, and CrMo-containing dimers the exchange of isopropoxy groups between the dimers is slow on the NMR time scale. Addition of nitrogen donor ligands, L, to hydrocarbon solutions of Cr$_2$(O-*i*-Pr)$_6$(NO)$_2$ leads to an equilibrium mixture of Cr$_2$(O-*i*-Pr)$_6$(NO)$_2$, Cr(O-*i*-Pr)$_3$(NO)L, and free L, where L = ammonia, pyridine, and 2,4-lutidine. The equilibration of the above species is slow on the NMR time scale and the presence of free L does not influence the rate of exchange of bridging and terminal O-*i*-Pr ligands in Cr$_2$(O-*i*-Pr)$_6$(NO)$_2$. By contrast the exchange between free and coordinated L in Cr(O-*i*-Pr)$_3$(NO)L is fast on the NMR time scale and is apparently independent of the concentration of free ligand, L. The compounds Cr(O-*i*-Pr)$_3$(NO)L have not been isolated as crystalline compounds because of the ready loss of L and formation of Cr$_2$(O-*i*-Pr)$_6$(NO)$_2$, but it is proposed that they are analogous to the previously characterized compound W(O-*t*-Bu)$_3$(py)(NO). A mechanism for bridge and terminal isopropoxy group exchange in Cr$_2$(O-*i*-Pr)$_6$(NO)$_2$ is proposed involving the formation of a monobridged dimer in which one chromium atom is four-coordinate and lacks an O-*i*-Pr ligand trans to the nitrosyl group.

Introduction

The compounds Mo$_2$(OR)$_6$ (M≡M),[2] where R = *t*-Bu, *i*-Pr, and Me$_3$CCH$_2$, react[3] with nitric oxide (2 equiv) to give dimeric compounds Mo$_2$(OR)$_6$(NO)$_2$. In a formal sense, the metal-to-metal triple bond is cleaved and replaced by two metal-to-ligand triple bonds: the Mo-to-Mo distances are 2.222 (1) and 3.335 (1) Å in Mo$_2$(OCH$_2$CMe$_3$)$_6$[2] and Mo$_2$(O-*i*-Pr)$_6$(NO)$_2$,[3] respectively. A similar cleavage of the tungsten-to-tungsten triple bond occurs in the reaction between W$_2$(O-*t*-Bu)$_6$[4] and nitric oxide (2 equiv), and by the addition of pyridine, a mononuclear compound W(O-*t*-Bu)$_3$(NO)(py) was isolated and structurally characterized.[5] Chromium, in its oxidation state +3, does not form dinuclear alkoxides with Cr-to-Cr triple bonds.[6] We show here, however, that chromium does form related nitrosyl compounds Cr$_2$(O-*i*-Pr)$_6$(NO)$_2$ and Cr(O-*i*-Pr)$_3$(NO)L, where L = ammonia, pyridine, and 2,4-lutidine, and in the case of the bulky O-*t*-Bu ligand, a monomeric compound Cr(O-*t*-Bu)$_3$(NO) has been isolated. A preliminary report of some of this work has appeared.[7]

Results and Discussion

Syntheses. The monomeric compound Cr(N-*i*-Pr$_2$)$_3$NO[8] reacts with alcohols in hydrocarbon solvents. The bulky and relatively nonacidic alcohol *tert*-butyl alcohol reacts slowly[9]

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