Journal of Organometallic Chemistry, 216 (1981) 65—71
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

SYNTHETIC APPLICATIONS OF THE PHOTOLYSIS OF THE CYCLOPENTADIENYLIRON-(*p*-XYLENE) CATION

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(Received December 31st, 1980)

Summary

Photolysis of CpFe(*p*-xylene)$^+$ (Cp = η^5-cyclopentadienyl) in the presence of suitable 6- or 2-electron donor ligands results in replacement of the aromatic ring with one 6-electron or three 2-electron donor ligands. The compounds $[CpFe(\eta^6\text{-}C_7H_8)]BF_4$ (C_7H_8 = cycloheptatriene), $[CpFe(\eta^6\text{-}C_8H_8)]PF_6$ (C_8H_8 = cyclooctatetraene), $[CpFe(\eta^6\text{-PCP})]PF_6$ (PCP = 2,2-paracyclophane), $[CpFe(P(OCH_3)_3)_3]PF_6$ and $[CpFe(P(OCH_2CH_3)_3)_3]PF_6$ were prepared in this manner. The compound $[CpFe(TM4)_3FeCp](PF_6)_2 \cdot CH_3COCH_3$ (TM4 = 2,5-dimethyl-2,5-diisocyanohexane) was prepared in two steps. First, [CpFe(*p*-xylene)]PF_6 was irradiated with an excess of the free TM4 ligand producing a mixture of $[CpFe(TM4)_3]^+$ and $[CpFe(TM4)_3FeCp]^{2+}$. An additional equivalent of [CpFe(*p*-xylene)]PF_6 was added to this mixture and photolysis yielded $[CpFe(TM4)_3FeCp](PF_6)_2 \cdot CH_3COCH_3$.

Introduction

The photochemistry of cyclopentadienyl iron arene cations has been studied recently. Nesmeyanov and coworkers have studied the photodecomposition reaction, which forms Fe^{II} and ferrocene, in a variety of solvents [1], while our group has studied ring replacement reactions [2]. The reactions studied thus far have been of the following nature:

$$CpFe(Arene^+) + 3\,L \xrightarrow{h\nu} CpFe(L)_3^+ + Arene$$

$$CpFe(Arene^+) + L_3 \xrightarrow{h\nu} CpFe(L_3)^+ + Arene$$

where L is a two electron donor and L_3 is a six-electron donor. These reactions show synthetic promise since only one ionic product is isolated in the systems studied to date and the degree of substitution is always three. Other alternatives such as products containing an arene bound to iron in an η^2 or η^4 fashion have not been observed in this reaction.

0022-328X/81/0000—0000/$02.50,

A variety of cyclopentadienyl Fe^{II} compounds have been prepared from ferrocene and the cyclopentadienyliron dicarbonyl halides [3—8]. The reaction of ferrocene with a variety of arenes in the presence of aluminum chloride and aluminum metal affords cyclopentadienyliron arene cations [3]. This reaction has also been utilized in the synthesis of the cyclopentadienyliron tricarbonyl cation [4]. Unfortunately, the harsh conditions necessary for these reactions to occur are unsuitable for the preparation of compounds with many arenes as well as more basic two-electron donor ligands. Another mode of synthesis of these compounds is by photolysis or heating of a mixture containing a cyclopentadienyliron dicarbonyl halide and the desired ligand [5—8]. The drawbacks of this method are that the degree of substitution is not always three, the halide ion is often coordinated to iron in the final product, and frequently a mixture of products is formed. For example, when $CpFe(CO)_2I$ is reacted with phenylisocyanide in refluxing benzene, a mixture of products containing $CpFe(CNPh)(CO)I$ and $CpFe(CNPh)_2I$ is formed [5]. No $[CpFe(CNPh)_3]^+$ was formed in this reaction. In comparison, photolysis of $CpFe(p\text{-xylene})^+$ in the presence of $p\text{-}CNPhCH_3$ results in the formation of $[CpFe(p\text{-}CNPhCH_3)_3]PF_6$ in 84% yield [2]. To further examine the synthetic potential of the photochemical ring replacement reaction, we have irradiated $CpFe(p\text{-xylene})^+$ in the presence of a number of ligands which we felt would yield interesting compounds that would be difficult to prepare by the other routes discussed here.

Experimental

The BF_4^- and PF_6^- salts of $CpFe(p\text{-xylene})^+$ were prepared by the method of Nesmeyanov [3]. Trityl tetrafluoroborate was prepared from triphenylcarbinol and fluoroboric acid [9]. *p*-Tolylisocyanide was prepared from *p*-toluidine and TM4-bridge was prepared from 2,5-diamino-2,5-dimethylhexane by the phase transfer method [10]. Cycloheptatriene was purified by passage through a short alumina column. All other reagents were purchased and used without additional purification.

The preparations of all of the compounds, except $[CpFe(TM4)_3FeCp](PF_6)_2 \cdot CH_3COCH_3$ are by the same general route. As an example, the preparation of $[CpFe(\eta^6\text{-}C_7H_8)]BF_4$ will be given in detail. In all photolyses the solvent was CH_2Cl_2 and the light source was the sun. Proton NMR spectra were recorded on a Varian CFT-20 spectrometer equipped with a 79.5 MHz proton accessory. The ^{13}C NMR spectrum was recorded on a Varian CFT-20 spectrometer. The proton NMR spectra were recorded in acetone-d_6 and referenced to TMS (internal standard). The ^{13}C NMR spectrum was recorded in dichloromethane-d_2 and referenced to TMS (internal standard). The IR spectrum was recorded on a Perkin-Elmer 283 infrared spectrophotometer. Conductance measurements were performed using a Yellow Springs Instruments Co. Model 31 conductivity bridge. Analytical data are given in Table 1.

$[CpFe(\eta^6\text{-}C_7H_8)]BF_4$

$[CpFe(p\text{-xylene})]BF_4$ (87.9 mg), cycloheptatriene (3 ml), and 20 ml of CH_2Cl_2 were placed in a Pyrex test tube. The tube was equipped with a magnetic stir bar and a serum septum. The solution was degassed by bubbling with tank

TABLE 1

ANALYTICAL DATA

Complex	Empirical formula	Found (calcd.)(%)	
		C	H
$[CpFe(\eta^6\text{-}C_7H_8)]PF_6$	$C_{12}H_{13}BF_4Fe$	47.98 (48.06)	4.40 (4.37)
$[CpFe(\eta^6\text{-}C_8H_8)]PF_6$	$C_{13}H_{13}F_6FeP$	42.18 (42.19)	3.77 (3.54)
$[CpFe(\eta^6\text{-}PCP)]PF_6$	$C_{21}H_{21}F_6FeP$	52.99 (53.19)	4.49 (4.46)
$[CpFeCp(OCH_2CH_3)_3)_3]PF_6$ [a]	$C_{23}H_{50}F_6FeO_9P_4$	36.83 (36.14)	6.94 (6.59)
$[CpFe(P(OCH_3)_3)_3]PF_6$	$C_{14}H_{32}F_6FeO_9P_4$	26.45 (26.35)	5.03 (5.05)
$[CpFe(TM4)_3FeCp](PF_6)_2$	$C_{40}H_{58}F_{12}Fe_2N_6P_2$	46.90 (46.89)	5.91 (5.71)

Analyses performed at Galbraith Laboratories, Knoxville, Tenn., unless otherwise noted.
[a] Performed at MHW Laboratories, Phoenix, Arizona.

nitrogen for 15 minutes. The test tube was then placed on the roof of Kolthoff Hall and stirred in sunlight at —10 ± 3° C. After three hours of photolysis, the dichloromethane was removed at room temperature on a rotary evaporator. The resulting residue was dissolved in a minimum amount of dichloromethane and the product, $[CpFe(\eta^6\text{-}C_7H_8]BF_4$ precipitated as golden crystals upon addition of hexane. The product was filtered, washed with hexane, and air dried. 60.1 mg (72% yield) of $[CpFe(\eta^6\text{-}C_7H_8)]BF_4$ were recovered. m.p. 214—215°C with decomposition. ^{1}H NMR: τ 4.74 (Cp)5Hs, τ 3.20 (H(3,4)) 2Hm, τ 3.90 (H(2,5)) 2Hm, τ 5.69 (H(1,6)) 2Hm, τ 7.18 (H(7) *endo*) 1Hm, τ 10.10 (H(7) *exo*) 1Hm.

$[CpFe(\eta^6\text{-}C_8H_8)]PF_6$

This compound was prepared by irradiating [CpFe(*p*-xylene)]PF_6 (57.3 mg) in the presence of cyclooctatetraene (724 mg) for 3 hours at 3 ± 3°C. 45.1 mg (79% yield) of orange crystalline $[CpFe(\eta^6\text{-}C_8H_8)]PF_6$ were obtained from CH_2Cl_2/hexane. m.p. 186—187°C with decomposition. ^{1}H NMR: τ 4.58 (Cp)5Hs, τ 3.46 (H(1,2,5,6))4H overlapping pair of multiplets, τ 2.78 (H(3,4)) 2Hm, τ 5.14 (H(7,8)) 2H broad singlet.

$[CpFe(\eta^6\text{-}PCP)]PF_6$ (PCP = 2,2-paracyclophane)

This compound was prepared by irradiating [CpFe(*p*-xylene)]PF_6 (57.8 mg) in the presence of PCP (110 mg) for 2.5 hours at 16 ± 4°C. The product, $[CpFe(\eta^6\text{-}PCP)]PF_6$ (64.7 mg), was recovered in 88% yield as an orange powder when hexane was added to a concentrated CH_2Cl_2 solution of the reaction mixture. m.p. 192—193°C with decomposition. ^{1}H NMR: τ 5.16 (Cp) 5Hs, τ 2.29 (protons on ring not bound to Fe) 4Hs, τ 4.22 (protons on bound ring) 4Hs, τ 6.86 (CH_2CH_2) 8Hm.

$[CpFe(P(OCH_3)_3)_3]PF_6$

This compound was prepared by photolyzing [CpFe(*p*-xylene)]PF_6 (78.1 mg) in the presence of $P(OCH_3)_3$ (765.5 mg) for 1 hour 10 minutes at 3 ± 3°C. The product, $[CpFe(P(OCH_3)_3)_3]PF_6$ (110.5 mg, 82% yield), was isolated as a light yellow powder when hexane was added to a concentrated CH_2Cl_2 solution of the reaction mixture. m.p. 265—268°C with decomposition. ^1H NMR: τ 5.16 (Cp) 5Ha, $J(P—H) = 1.2$ Hz, τ 6.21 (CH_3) 27Hm, $J(POCH) = 10.8$ Hz (taken as the separation of the outer lines of the CH_3 resonance).

$[CpFe(P(OCH_2CH_3)_3)_3]PF_6$

Photolysis of $[CpFe(p\text{-xylene})]PF_6$ (73.0 mg) in the presence of triethylphosphite (834 mg) for 2.5 hours at 10 ± 3°C produced $[CpFe(P(OCH_2CH_3)_3)_3]PF_6$ (144.5 mg) in 96% yield. The product was recovered as a yellow powder when hexane was added to a concentrated CH_2Cl_2 solution of the reaction mixture. m.p. 254—255°C with decomposition. ^1H NMR: τ 5.27 (Cp) 5Hq $J(P—H) = 1.3$ Hz, τ 5.82 (CH_2) 18Hm, τ 8.67 (CH_3) 27Ht $J = 7.0$ Hz. A spectrum was recorded while irradiating the resonance due to the methyl protons and the methylene region was observed. τ 5.82 (CH_2)m, $J(POCH) = 4.1$ Hz (taken as the separation of the outer lines of the CH_2 resonance).

$[CpFe(TM4)_3FeCp](PF_6)_2 \cdot CH_3COCH_3$ (TM4 = 2,5-dimethyl-2,5-diisocyanohexane)

This compound was prepared via a two-step procedure. In the first step a CH_2Cl_2 solution of $[CpFe(p\text{-xylene})]PF_6$ (91.1 mg) and the free TM4 ligand (454.5 mg) was irradiated for 3 hours at 10 ± 3°C. The solvent was removed on a rotary evaporator and the residue was washed repeatedly with hexane yielding a brown oil. A ^1H NMR spectrum of the oil showed to resonances in the cyclopentadienyl region at τ 4.98 and τ 5.02 in a ratio of 20 : 1. These resonances were presumed to be due to $[CpFe(TM4)_3]^+$ and $[CpFe(TM4)_3FeCp]^{2+}$ respectively (vide infra). The oil was then redissolved in CH_2Cl_2 and an additional equivalent of $[CpFe(p\text{-xylene})]PF_6$ (99.5 mg) was added. The mixture was then irradiated for 2 hours 40 minutes at 15 ± 3°C, the solution was filtered to remove Fe^{II} degradation products and the solvent was evaporated, yielding a yellow residue. The residue was dissolved in acetone and yellow crystals of $[CpFe(TM4)_3FeCp](PF_6)_2 \cdot CH_3COCH_3$ (90.8 mg, overall yield 34%) were obtained upon addition of hexane. m.p. 196—187°C with decomposition. ^1H NMR: τ 5.01 (Cp) 5Hs, τ 8.11 (CH_2) 6Hs, τ 8.37 (CH_3) 18 Hs. ^{13}C NMR (proton decoupled): δ 83.16 (Cp), 61.67 (quaternary C), 35.71 (CH_2), 29.23 ppm (CH_3). The signal due to the isocyanide carbon was not observed. This type of behavior is common for the isocyanide carbon of complexed isocyanides [11,12]. The presence of one mole of acetone per mole of binuclear complex was determined by recording the spectrum in CD_2Cl_2. IR: $\nu(C{\equiv}N)$ 2180vs, 2133vs cm^{-1}. (KBr pellet). Recrystallization from CH_2Cl_2/hexane gave solvent-free material with otherwise identical spectroscopic properties.

Conductivity measurements

The conductivity measurements were made on 10^{-3} *M* solutions of the appropriate compound in CH_3NO_2 at 24°C. The conductivity cell was calibrated by measuring the conductance of a standard aqueous KCl solution. All measurements are corrected for the conductivity of pure solvent. The conductivity of $[(CpFe(TM4)_3FeCp](PF_6)_2$ was measured along with a similar 2 : 1 electrolyte, and a 1 : 1 electrolyte. The conductances (cm^2-mhos/mol) were measured as follows: $[Rh_2(TM4)_4](PF_6)_2$ [13], 194; $[CpFe(TM4)_3FeCp](PF_6)_2$, 174; $CpFe(p\text{-}CNPhCH_3)_3PF_6$ [2], 93. These values are consistent with conductivities of 2 : 1 and 1 : 1 electrolytes previously measured in CH_3NO_2 [14].

Thermal control reactions

Solutions of the starting material, CpFe(*p*-xylene)PF_6, and the appropriate ligand were prepared in acetone-d_6. The ligands used were $P(OCH_3)_3$, $P(OCH_2CH_3)_3$, TM4, C_7H_8, C_8H_8, and PCP. Proton NMR spectra were recorded of the mixtures approximately 10 minutes after mixing and 19 hours later. The solutions were maintained in the dark at room temperature (22 ± 2°C). During that time no disappearance of starting material or conversion to products was observed. To further demonstrate the inertness of the starting material with regard to substitution reactions, 70.9 mg of CpFe(*p*-xylene)PF_6, and 1 ml of $P(OCH_3)_3$ were added to 15 ml of CH_2Cl_2. This mixture was refluxed under nitrogen in the dark. After 2.5 hours, the mixture was removed and the solvent was evaporated on a rotary evaporator. The trimethylphosphite was removed by repeated hexane washes, and the resulting solid was crystallized from CH_2Cl_2/hexane. 62.3 mg of yellow crystalline CpFe(*p*-xylene)PF_6 were recovered. NMR analysis of the product showed no detectable amounts of $CpFe(P(OCH_3)_3)_3PF_6$ or any other product.

Discussion

The synthesis of new cyclopentadienyl-iron(II) compounds is easily accomplished via the photolysis of solutions of CpFe(*p*-xylene)$^+$ and a suitable ligand. However, if the ligand is an arene, the product would be expected to be photochemically active. Indeed, photolysis of $[CpFe(\eta^6\text{-PCP})]PF_6$ leads to products associated with the ring dissociation reaction. Our preliminary results indicate that the photochemical efficiency of the ring dissociation reaction may be related to the basicity of the arene ring; as the ring becomes more basic, the efficiency of the ring dissociation [15] reaction decreases. Paracyclophane is more basic [16] than *p*-xylene and as a result a pure compound can be obtained by photolyzing [CpFe(*p*-xylene)]PF_6 in the presence of paracyclophane. We judge that the replacement of an arene ring bound to the $FeCp^+$ unit with a less basic arene by this method would be difficult since the photoproduct would be more photochemically labile than the starting material. In order to obtain a reasonable yield of product under such conditions, one would have to use a large excess of the less basic arene and perhaps develop a method of removing the original arene from solution as it is released from the $FeCp^+$ unit.

As might be expected by virtue of their similarity to CpFe(*p*-xylene)PF_6, the compounds $[CpFe(\eta^6\text{-}C_7H_8)]BF_4$ and $[CpFe(\eta^6\text{-}C_8H_8)PF_6$ are also photochemically active, undergoing ring dissociation reactions upon photolysis. However, neither of these compounds is inert to thermal substitution at room temperature. This is probably due to the ease of alternative bonding modes of cycloheptatriene and cyclooctatetraene in transition metal complexes. Both ligands can easily be distorted to accommodate η^2 or η^4 coordination [17] to the iron atom, possibly allowing an incoming ligand to displace cycloheptatriene or cyclooctatetraene in a sequential manner. For example, a solution of [CpFe(η^6-C_7H_8)]$^+$ and *p*-CNPhCH$_3$ yields CpFe(*p*-CNPhCH$_3$)$_3$$^+$ when allowed to react in the dark at room temperature for several hours. Similarly, reaction of [CpFe(η^6-C_8H_8)]$^+$ and triethylphosphite yields [CpFe(P(OCH$_2$CH$_3$)$_3$)$_3$]$^+$ in the dark at room temperature after several hours.

The cycloheptatriene complex is one of a number of transition metal complexes in which cycloheptatriene acts as a 6-electron donor [18—20]. A reaction which has been observed with several cycloheptatriene complexes, but which we have been unable to observe for CpFe(η^6-C_7H_8)$^+$ is hydride abstraction by a trityl salt [20]. Attempts at removing the *exo* proton from [CpFe(η^6-C_7H_8)]BF$_4$ with (trityl)BF$_4$ were unsuccessful both at room temperature (CH_2Cl_2) and in refluxing CH_2ClCH_2Cl.

The complex [CpFe(η^6-C_8H_8)]PF$_6$ contains an η^6-bound cyclooctatetraene and can be considered an analog of CpMn(η^6-C_8H_8). The four complex signals observed in the ^{1}H NMR for the η^6-COT moiety in CpFe(η^6-C_8H_8)$^+$ at room temperature are similar to those previously observed for W(CO)$_3$(η^6-C_8H_8) and CpMn(η^6-C_8H_8) [20,22]. These results indicate that the C_8H_8 ring in all of these compounds does not exhibit fluxional behavior at room temperature. An attempt was made to observe a fluxional rearrangement by recording the ^{1}H NMR of [CpFe(η^6-C_8H_8)]PF$_6$ in DMSO-d_6 at higher temperatures. Spectra which were obtained at temperatures from 30 to 80°C in approximately 10° intervals gave no evidence for any type of fluxional rearrangement. The compound did, however, decompose slowly at 80°C in DMSO.

The previously unknown phosphite complexes [CpFe(P(OCH$_3$)$_3$)$_3$]PF$_6$ and [CpFe(P(OCH$_2$CH$_3$)$_3$)$_3$]PF$_6$ are isoelectronic analogs of the known manganese complexes [24]. The proton NMR spectra of both iron complexes are interesting. The cyclopentadienyl protons of these compounds appear as quartets. This is due to coupling with the three equivalent phosphorous nuclei. These coupling constants are 1.2 and 1.3 Hz for the trimethylphosphite and triethylphosphite complexes, respectively. These compare with coupling constants of 2.1 Hz and 1.8 Hz in the corresponding manganese complexes [24]. This reduction in coupling may be attributed to the lower covalency of the iron(II)—phosphorous bond compared to the manganese(I)—phosphorous bond. The methylene protons of the triethylphosphite complex and the methyl protons of the trimethylphosphite complex both exhibit complex spin—spin splitting due to the phosphorous—phosphorous coupling. These protons constitute the X portion of an $X_nX'_nX''_nAA'A''$ system, where A = P [25]. The spectra of both complexes were not sufficiently resolved to allow a direct determination of all the coupling constants. However, *J*(POCH) of 10.8 Hz and 4.1 Hz could be determined from the NMR spectra of the trimethylphosphite complex and the methyl-irradiated triethylphosphite complex, respectively *.

The synthesis of [CpFe(TM4)$_3$FeCp](PF$_6$)$_2$ illustrates the use of sequential photoreactions to introduce two FeCp$^+$ units into one molecular unit. In the first step, [CpFe(*p*-xylene)]PF$_6$ is reacted photochemically with a large excess of the bidentate ligand, so that the formation of CpFe(TM4)$_3$$^+$ with three dang-

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* We define *J*(POCH) as equal to *J*(PH) + *J*(P'H) + *J*(P''H).

ling TM4 ligands will predominate. Another equivalent of $FeCp^+$ is then added by photolyzing $[CpFe(p\text{-xylene})]PF_6$ in the presence of $CpFe(TM4)_3^+$. Both NMR (^1H and ^{13}C) and conductance measurements support the formulation of this complex as a binuclear dication. (See Experimental section.) We are planning further investigations of the binuclear complex and similar analogs to determine if complexes with Fe—Fe interactions can be synthesized using this photochemical method.

Acknowledgement

Support of this research through a Dupont Young Faculty Grant, the University of Minnesota Graduate School, Research Corporation, and the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

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