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Photochemistry of $[(\eta\text{-}C_5H_5)Fe(\eta\text{-}p\text{-xyl})]PF_6$ in Acetonitrile Solution. Characterization and Reactivity of $[(\eta\text{-}C_5H_5)Fe(CH_3CN)_3]^+$

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The photolysis of $[(\eta\text{-}C_5H_5)Fe(\eta\text{-}p\text{-xyl})]^+$ (xyl = xylene) in acetonitrile solution at −40 °C produces a purple intermediate that we have characterized as $[(\eta\text{-}C_5H_5)Fe(CH_3CN)_3]^+$ by ^1H NMR, electronic spectroscopy, and chemical reaction studies. Room-temperature photolysis of $[(\eta\text{-}C_5H_5)Fe(\eta\text{-}p\text{-xyl})]^+$ in acetonitrile also generates this species, which rapidly yields ferrocene and Fe(II) as the final products. Mechanistic studies on this system suggest that ferrocene is generated when $[(\eta\text{-}C_5H_5)Fe(CH_3CN)_3]^+$ releases $C_5H_5^-$, which subsequently replaces three CH_3CN molecules on an unreacted $[(\eta\text{-}C_5H_5)Fe(CH_3CN)_3]^+$ ion. This tris(acetonitrile) complex is a convenient starting material for the synthesis of substituted complexes of the form $[(\eta\text{-}C_5H_5)Fe(CH_3CN)(L)_2]^+$, $[(\eta\text{-}C_5H_5)Fe(CH_3CN)(L)(L')]^+$, $[(\eta\text{-}C_5H_5)Fe(L)(L')_2]^+$, and $[(\eta\text{-}C_5H_5)Fe(L)(L')(L'')]^+$, where L, L′, and L″ = isocyanides, phosphites, or phosphines. Room-temperature photolysis of $[(\eta\text{-}C_5H_5)Fe(\eta\text{-}p\text{-xyl})]^+$ in CH_3CN in the presence of excess L produces $[(\eta\text{-}C_5H_5)Fe(CH_3CN)(L)_2]^+$. Photolysis at −40 °C in CH_3CN, followed by the addition of 1 equiv of L and a warm-up step in the presence of excess L′, produces $[(\eta\text{-}C_5H_5)Fe(CH_3CN)(L)(L')]^+$. The reaction of the disubstituted compounds with excess ligand produces complexes of the form $[(\eta\text{-}C_5H_5)Fe(L')(L)_2]^+$ and $[(\eta\text{-}C_5H_5)Fe(L)(L')(L'')]^+$, respectively. Reactivity comparisons of $[(\eta\text{-}C_5H_5)Fe(CH_3CN)_n(L)_{3-n}]^+$ and $[(\eta\text{-}C_5H_5)Ru(CH_3CN)_n(L)_{3-n}]^+$ ($n \neq 0$) have also been made. In every case the Fe complex has been found to undergo substitution reactions more readily than the corresponding Ru analogue.

Introduction

In recent work, we have found that photolysis of $[(\eta\text{-}C_5H_5)Ru(\eta\text{-}C_6H_6)]PF_6$ in acetonitrile solution results in the formation of $[(\eta\text{-}C_5H_5)Ru(CH_3CN)_3]PF_6$ in high yield.[1] This ruthenium–acetonitrile complex is a useful starting material for a variety of $(\eta\text{-}C_5H_5)Ru^{II}$ compounds, because the acetonitrile ligands are labile[2] and the extent of substitution can be controlled. The synthetic utility of this ruthenium compound has prompted us to pursue the generation of the iron analogue $[(\eta\text{-}C_5H_5)Fe(CH_3CN)_3]^+$ from $[(\eta\text{-}C_5H_5)Fe(\eta\text{-}p\text{-xyl})]^+$[3] (xyl = xylene). Previously, Nesmeyanov reported that the photolysis of $[(\eta\text{-}C_5H_5)Fe(\eta\text{-arene})^+$ compounds in acetonitrile solution yields Fe(II) and ferrocene as the Fe-containing products (eq 1).[4]

$$2[(\eta\text{-}C_5H_5)Fe(arene)]^+ \xrightarrow[CH_3CN]{h\nu} Fe(II) + (\eta\text{-}C_5H_5)_2Fe + 2(arene) \quad (1)$$

We now wish to report that a reinvestigation of this reaction indicates the intermediacy of a purple species that is stable at −40 °C. This intermediate has been characterized in solution as $[(\eta\text{-}C_5H_5)Fe(CH_3CN)_3]^+$ by low-temperature ^1H NMR and electronic spectroscopy. The reactivity of this acetonitrile complex has allowed us to develop its chemistry as a reagent for the synthesis of substituted $[(\eta\text{-}C_5H_5)Fe(CH_3CN)_{3-n}(L)_n]^+$ complexes.

Experimental Section

General Procedures. Photolyses were performed with the sun or the Pyrex-filtered output of an Oriel Model 6281 100-W mercury lamp. IR spectra were recorded on a Perkin-Elmer 297 instrument. ^1H NMR spectra were recorded on a Varian Associates CFT-20 equipped with a 79.50-MHz proton accessory. Chemical shifts (δ) are relative to Me_4Si. ^{31}P NMR spectra were recorded on a Nicolet NT 300-MHz WB instrument at 121.5 MHz, and chemical shifts (δ) are referenced to an 85% orthophosphoric acid external standard. Elemental analyses were performed at MHW Laboratories, Phoenix, AZ.

The acetonitrile was used as purchased from Burdick and Jackson without further purification. All other solvents were of spectroscopic quality. *tert*-Butyl isocyanide ($CNC(CH_3)_3$) and 2,6-dimethylphenyl isocyanide (2,6-DMP) were prepared from the corresponding amines.[5] The complex $[(\eta\text{-}C_5H_5)Fe(\eta\text{-}p\text{-xyl})]PF_6$ was synthesized by the method of Nesmeyanov.[6] Similarly, the compound $[(\eta\text{-}C_5H_4CH_3)Fe(\eta\text{-}p\text{-xyl})]BF_4$ was prepared by the ligand-exchange reaction of dimethylferrocene with *p*-xylene. Photochemical reactions were performed at ambient temperatures (20 ± 5 °C), unless otherwise noted. All reactions were stirred magnetically.

Control Reactions. Solutions containing $[(\eta\text{-}C_5H_5)Fe(\eta\text{-}p\text{-xyl})]PF_6$ and the ligands used in this study showed no evidence (^1H NMR) of chemical reaction after being stored in the dark for 1 day at room temperature.

Preparation of Complexes

$[(\eta\text{-}C_5H_4CH_3)Fe(\eta\text{-}p\text{-xyl})]BF_4$. This compound was synthesized by the method of Nesmeyanov.[6] Because the dimethylferrocene (Alfa) was contaminated (~10%) with methylferrocene, the compound $[(\eta\text{-}C_5H_5)Fe(\eta\text{-}p\text{-xyl})]BF_4$ was also formed. Purification of $[(\eta\text{-}C_5H_4CH_3)Fe(\eta\text{-}p\text{-xyl})]BF_4$ was performed by column chromatography.[7] Anal. Calcd for $C_{14}H_{17}BF_4Fe$: C, 51.28; H, 5.22. Found: C, 50.76; H, 5.20. ^1H NMR (acetone-d_6): C_5H_4 (4 H), δ 5.01, singlet; aryl protons (4 H), δ 6.27, singlet; *p*-xylene methyl protons (6 H), δ 2.51, singlet; $C_5H_4CH_3$ (3 H), δ 2.08, singlet.

$[(\eta\text{-}C_5H_5)Fe(CH_3CN)(P(OCH_3)_3)_2]PF_6$. $[(\eta\text{-}C_5H_5)Fe(\eta\text{-}p\text{-xyl})]PF_6$ (55.8 mg), $P(OCH_3)_3$ (0.5 mL), 20 mL of acetonitrile, and a stir bar were placed in a Pyrex test tube. The test tube was equipped with a serum septum, and the solution was degassed by bubbling with dry nitrogen for 15 min. The solution was irradiated with sunlight for 1 h. During this time, the solution changed from yellow to orange. The solvent was removed by rotary evaporation, and the excess $P(OCH_3)_3$ was removed by washing with ether. The solid remaining was crystallized from CH_3CN/ether. $[(\eta\text{-}C_5H_5)Fe(CH_3CN)(P(OCH_3)_3)_2]PF_6$ (77.3 mg) was recovered in 93% yield as orange crystals, mp 158–160 °C dec. Anal. Calcd for $C_{13}H_{26}F_6FeNO_6P_3$: C, 28.13; H, 4.72. Found: C, 27.97; H, 4.94. ^1H NMR (acetone-d_6): C_5H_5 (5 H), δ 4.67, triplet, J = 1.2 Hz; OCH_3 (18 H), δ 3.81, apparent triplet, J_{POCH} = 10.9 Hz; CH_3CN (3 H), δ 2.56, triplet, J = 1.3 Hz.

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[1] T. P. Gill and K. R. Mann, *Organometallics*, **1**, 485 (1982).

[2] B. N. Storhoff and H. C. Lewis, *Coord. Chem. Rev.*, **23**, 1 (1977), and references therein.

[3] We have previously investigated the photochemical reactions of $(\eta\text{-}C_5H_5)Fe(\eta\text{-}p\text{-xyl})^+$ in CH_2Cl_2 solutions and found ϕ for arene release to be 0.58 ± 0.06: (a) T. P. Gill and K. R. Mann, *Inorg. Chem.*, **19**, 3007 (1980); (b) T. P. Gill and K. R. Mann, *J. Organomet. Chem.*, **216**, 65 (1981).

[4] A. N. Nesmeyanov, N. A. Vol'Kenau, and L. S. Shilovtseva, *Dokl. Akad. Nauk. SSSR*, **190**, 857 (1970).

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[6] A. N. Nesmeyanov, N. A. Vol'Kenau, and I. N. Bolesova, *Dokl. Akad. Nauk SSSR*, **149**, 612 (1963).

[7] A. N. Nesmeyanov, N. A. Vol'Kenau, and L. S. Shilovtseva, *Dokl. Chem.* (*Engl. Transl.*), **160**, 203 (1965).

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$[(\eta\text{-}C_5H_5)Fe(CH_3CN)(CNC(CH_3)_3)_2]PF_6$. A 101-mg sample of $[(\eta\text{-}C_5H_5)Fe(\eta\text{-}p\text{-xyl})]PF_6$, 0.1 mL of *tert*-butyl isocyanide, and 20 mL of CH_3CN were placed in a test tube. The tube was equipped with a stir bar and a serum septum. The solution was degassed by bubbling with nitrogen for 15 min. The reaction mixture was then exposed to sunlight for 2 h 15 min. The solution turned from yellow to orange during the photolysis. The solvent was removed by rotary evaporation, and the excess ligand was removed by an ether wash. The residue was dissolved in CH_3CN and precipitated upon addition of ether. $[(\eta\text{-}C_5H_5)Fe(CH_3CN)(CNC(CH_3)_3)_2]PF_6$ (105.6 mg) was recovered as an orange powder in 82% yield; mp 128–130 °C dec. Anal. Calcd for $C_{17}H_{26}F_6FeN_3P$: C, 43.15; H, 5.54. Found: C, 43.09; H, 5.57. IR (CH_3CN solution): $\bar{\nu}(C\equiv N)$ 2160 (s), 2134 (s) cm^{-1}. ^1H NMR (acetone-d_6): C_5H_5 (5 H), δ 4.69, singlet; $CNC(CH_3)_3$ (18 H), δ 1.59, singlet; CH_3CN (3 H), δ 2.38, singlet.

$[(\eta\text{-}C_5H_5)Fe(CH_3CN)(2,6\text{-DMP})_2]PF_6$ (2,6-DMP = 2,6-Dimethylphenyl Isocyanide). This compound was prepared by irradiating an acetonitrile solution of $[(\eta\text{-}C_5H_5)Fe(\eta\text{-}p\text{-xyl})]PF_6$ (72.6 mg) and 2,6-DMP (57.6 mg). This solution was placed in a test tube equipped with a stir bar and a serum septum. The reaction mixture was degassed by bubbling with nitrogen for 15 min. Upon exposure to sunlight, the solution turned reddish orange. Photolysis was continued for 1 h 40 min. The solvent was removed by rotary evaporation, and the product was washed with ether to remove excess ligand. The product (102.5 mg) was recovered as an orange crystalline solid. Analysis by ^1H NMR indicated that the major product was $[(\eta\text{-}C_5H_5)Fe(CH_3CN)(2,6\text{-DMP})_2]PF_6$ and that a minor product $[(\eta\text{-}C_5H_5)Fe(\eta^6\text{-}2,6\text{-DMP})]PF_6$ was present in 5% yield. Because the photolysis of $(\eta\text{-}C_5H_5)Fe(\eta^6\text{-arene})^+$ complexes in CH_3CN forms Fe(II) and ferrocene,[4] $(\eta\text{-}C_5H_5)Fe(\eta^6\text{-}2,6\text{-DMP})^+$ was conveniently removed from the desired product via selective photodecomposition. A portion of the mixture (61.9 mg) was dissolved in 20 mL of acetonitrile and exposed to sunlight for 3 h 40 min. The solvent was removed by rotary evaporation, and the product was washed with ether to remove any ferrocene that may have formed. The product was redissolved in acetonitrile and eluted through a short alumina column. The acetonitrile was removed, yielding 52.8 mg of crystalline product. Pure $[(\eta\text{-}C_5H_5)Fe(CH_3CN)(2,6\text{-DMP})_2]PF_6$ was recovered in 78% yield; mp 164–166 °C dec. Anal. Calcd for $C_{25}H_{26}F_6FeN_3P$: C, 52.74; H, 4.60. Found: C, 52.67; H, 4.57. IR spectrum (CH_3CN solution): $\bar{\nu}(C\equiv N)$ 2145 (s), 2109 (s) cm^{-1}. ^1H NMR (acetone-d_6): C_5H_5 (5 H), δ 5.15, singlet; aryl protons (6 H), δ 7.27, singlet; CH_3CN (3 H), η 2.99, singlet; isocyanide methyl (12 H), δ 2.52, singlet.

$[(\eta\text{-}C_5H_5)Fe(CH_3CN)(P(OCH_2CH_3)_3)_2]PF_6$. A solution was prepared by dissolving $[(\eta\text{-}C_5H_5)Fe(\eta\text{-}p\text{-xyl})]PF_6$ (103.9 mg) and $P(OCH_2CH_3)_3$ (0.15 mL) in 10 mL of acetonitrile. The solution was placed in a test tube equipped with a stir bar and a serum septum. The solution was degassed, and the reaction mixture was irradiated with the Oriel lamp for 3 h 40 min. Evaporation of the solvent yielded an oil. The oil was washed with ether to remove excess $P(OCH_2CH_3)_3$. An additional portion of ether (20 mL) was added to the oil, and this was placed in a refrigerator (5 °C) overnight. The next day, 142.1 mg of $[(\eta\text{-}C_5H_5)Fe(CH_3CN)(P(OCH_2CH_3)_3)_2]PF_6$ (80% yield) was recovered as waxy orange crystals. The carbon analysis of the compound is low although the compound appeared to be pure by ^1H NMR. ^1H NMR (acetone-d_6): C_5H_5 (5 H), δ 4.58, triplet, J = 1.3 Hz; CH_2 (12 H), δ 4.17, multiplet; OCH_2CH_3 (18 H), δ 1.33, triplet, J = 7.0 Hz; CH_3CN (3 H), δ 2.36, triplet, J = 1.3 Hz. Anal. Calcd for $C_{19}H_{38}F_6FeNO_6P_3$: C, 35.70; H, 5.99. Found: C, 34.64; H, 3.95. A derivative of this compound ($[(\eta\text{-}C_5H_5)Fe(P(OCH_3)_3)(P(OCH_2CH_3)_3)_2]PF_6$) (vide infra) was prepared in high yield and gave a satisfactory analysis.

$[(\eta\text{-}C_5H_5)Fe(CH_3CN)(P(OPh)_3)_2]PF_6$. This compound was prepared by irradiating an acetonitrile solution (20 mL) containing 102.1 mg of $[(\eta\text{-}C_5H_5)Fe(\eta\text{-}p\text{-xyl})]PF_6$ and 0.3 mL of $P(OPh)_3$. This solution was placed in a test tube and degassed prior to photolysis. The test tube was placed in sunlight for 4 h 30 min. The solvent was removed, and the residue was washed with ether. The ether wash was lightly colored and cloudy, indicating some product loss. The remaining residue was dissolved in acetonitrile. Elution down a short alumina column followed by evaporation of solvent yielded a dark orange oil. Ether was added to the oil and the product crystallized. A 151-mg sample of $[(\eta\text{-}C_5H_5)Fe(CH_3CN)(P(OPh)_3)_2]PF_6$ was recovered (60% yield); mp 154–165 °C dec. Anal. Calcd for $C_{43}H_{38}F_6FeNO_6P_3$: C, 55.68; H, 4.13. Found: C, 54.90; H, 4.10. ^1H NMR (acetone-d_6): C_5H_5 (5 H), η 4.36, triplet, J = 1.3 Hz; phenyl protons (30 H), δ 7.36, complex multiplet; CH_5CN (3 H), δ 2.47, triplet, J = 1.4 Hz.

$[(\eta\text{-}C_5H_5)Fe(CH_3CN)(\text{diphos})]PF_6$. This compound was prepared by irradiating an acetonitrile solution containing 98.6 mg of $[(\eta\text{-}C_5H_5)Fe(\eta\text{-}p\text{-xyl})]PF_6$ and 122.3 mg of 1,2-bis(diphenylphosphino)ethane (diphos). This solution was placed in a test tube, degassed, and exposed to sunlight for 2 h. The solvent was then removed, leaving an orange solid. The crude product was washed with toluene to remove unreacted diphos. This solid was then dissolved in acetone. Elution through a short alumina column, followed by evaporation of solvent and recrystallization from acetone/hexane, yielded 184 mg of red-orange crystals. The product, $[(\eta\text{-}C_5H_5)Fe(CH_3CN)(\text{diphos})]PF_6$, was recovered in 96% yield; mp 210–211 °C dec. Anal. Calcd for $C_{33}H_{32}F_6FeNP_3$: C, 56.22; H, 4.57. Found: C, 56.28; H, 4.80. ^1H NMR (acetone-d_6): C_5H_5 (5 H), δ 4.48, triplet, J = 1.4 Hz; phenyl protons (20 H), δ 7.54, multiplet; CH_2 (4 H), δ 2.48, 2.66, two multiplets; CH_3CN (3 H), δ 1.64, triplet, J = 1.3 Hz. The $B(C_6H_5)_4^-$ salt of this cation has been previously characterized.[8]

$[(\eta\text{-}C_5H_5)Fe(P(OCH_3)_3)_2(2,6\text{-DMP})]PF_6$. This compound was prepared by reacting $[(\eta\text{-}C_5H_5)Fe(P(OCH_3)_3)_2(CH_3CN)]PF_6$ with 2,6-DMP. A 45.1-mg sample of $[(\eta\text{-}C_5H_5)Fe(P(OCH_3)_3)_2(CH_3CN)]PF_6$ and 77.3 mg of 2,6-DMP were dissolved in 15 mL of dichloromethane. This solution was refluxed under nitrogen for 64 h. The color of the reaction mixture changed from orange to yellow. After the reaction was complete, the solvent was removed by rotary evaporation, yielding an oil. Addition of ether to the oil caused the product to crystallize. The excess isocyanide was removed by repeated washes with ether. The product, $[(\eta\text{-}C_5H_5)Fe(P(OCH_3)_3)_2(2,6\text{-DMP})]PF_6$ (47.2 mg), was recovered in 90% yield as a yellow crystalline material, mp 155–156 °C dec. Anal. Calcd for $C_{20}H_{32}F_6FeNO_6P_3$: C, 37.23; H, 5.00. Found: C, 37.04; H, 4.92. IR (CH_3CN solution): $\bar{\nu}(C\equiv N)$ 2111 (s) cm^{-1}. ^1H NMR (acetone-d_6): C_5H_5 (5 H), δ 5.11, triplet, J = 1.3 Hz; aryl protons (3 H), δ 7.20, singlet; OCH_3 (18 H), δ 3.82, apparent triplet, J_{POCH} = 11.3 Hz; isocyanide methyl (6 H), δ 2.47, singlet.

$[(\eta\text{-}C_5H_5)Fe(P(OCH_3)_3)(2,6\text{-DMP})_2]PF_6$. A solution was prepared by dissolving 34.8 mg of $[(\eta\text{-}C_5H_5)Fe(CH_3CN)(2,6\text{-DMP})_2]PF_6$ and 0.5 mL of $P(OCH_3)_3$ in 15 mL of dichloromethane. This solution was refluxed under nitrogen for 18 h. During the reaction, the color of the solution changed from orange to yellow. Upon completion of the reaction, the solvent was removed by rotary evaporation to yield a yellow oil. Addition of hexane to the oil caused the product to crystallize. The product was washed repeatedly with hexane to remove all unreacted $P(OCH_3)_3$. $[(\eta^5\text{-}C_5H_5)Fe(P(OCH_3)_3(2,6\text{-DMP})_2]PF_6$ (38 mg) was recovered in 95% yield; mp 197–198 °C dec. Anal. Calcd for $C_{26}H_{32}F_6FeN_2O_3P_2$: C, 47.87; H, 4.94. Found: C, 47.55; H, 4.97. IR (CH_3CN solution): $\bar{\nu}(C\equiv N)$ 2144 (s), 2112 (s) cm^{-1}. ^1H NMR (acetone-d_6): C_5H_5 (5 H), δ 5.36, doublet, J = 1.3 Hz; aryl protons (6 H), δ 7.22, singlet; OCH_3 (9 H), δ 3.89, doublet, J = 11.8 Hz; isocyanide methyl (12 H), δ 2.48, singlet.

$[(\eta\text{-}C_5H_5)Fe(P(OCH_2CH_3)_3)_2(P(OCH_3)_3)]PF_6$. $[(\eta\text{-}C_5H_5)Fe(CH_3CN)(P(OCH_2CH_3)_3)_2]PF_6$ (53.5 mg) and $P(OCH_3)_3$ (1 mL) were dissolved in 15 mL of dichloromethane. This solution was refluxed for 22 h. During this time, the reaction mixture changed from orange to yellow. The product was crystallized by adding hexane to the oil. Additional hexane washes were necessary to remove all of the unreacted $P(OCH_3)_3$. The product $[(\eta\text{-}C_5H_5)Fe(P(OCH_2CH_3)_3)_2(P(OCH_3)_3)]PF_6$ (54.3 mg) was recovered in 90% yield; mp 247–249 °C dec. Anal. Calcd for $C_{20}H_{44}F_6FeO_9P_4$: C, 33.26; H, 6.14. Found: C, 33.51; H, 6.25. ^1H NMR (acetone-d_6): C_5H_5 (5 H), δ 4.77, quartet, J = 1.3 Hz; CH_2 (12 H), δ 4.14, multiplet; OCH_3 (9 H), δ 3.81, multiplet characteristic of the X portion of an A_2BX spectrum, J_{POCH} = 10.9 Hz; CH_2CH_3 (18 H), δ 1.32, triplet, J = 7 Hz. ^{31}P NMR (acetone-d_6; broad band, proton decoupled; eight-line A_2B pattern): $P(OCH_2CH_3)_3$ (2 P), δ 177.84; $P(OCH_3)_3$ (1 P), δ 172.45; $J_{PP'}$ = 143.35 Hz.

$[(\eta\text{-}C_5H_5)Fe(P(OCH_2CH_3)_3)(P(OCH_3)_3)_2]PF_6$. A solution containing 36.6 mg of $[(\eta\text{-}C_5H_5)Fe(CH_3CN)(P(COCH_3)_3)_2]PF_6$ and 1 mL of $P(OCH_2CH_3)_3$ dissolved in 10 mL of dichloromethane was prepared. This solution was refluxed under nitrogen for 38 h. The initially orange solution changed gradually to a yellow solution as the reaction proceeded. After the reaction was complete, the solvent was removed by rotary evaporation. The oil that remained was washed

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(8) P. E. Riley, C. E. Capshew, R. Pettit, and R. E. Davis, *Inorg. Chem.*, 17, 408 (1978).

with ether and hexane to remove unreacted $P(OCH_2CH_3)_3$. The oil was dissolved in acetonitrile. Elution through a short alumina column followed by evaporation of the solvent yielded 39.1 mg of $[(\eta\text{-}C_5H_5)Fe(P(OCH_2CH_3)_3)(P(OCH_2)_3)_2]PF_6$ (90% yield) as a yellow powder, mp 257–259 °C dec. Anal. Calcd for $C_{17}H_{38}F_6FeO_9P_4$: C, 30.02; H, 5.63. Found: C, 29.83; H, 5.70. ^1H NMR (acetone-d_6): C_5H_5 (5 H), δ 4.80, quartet, J = 1.3 Hz; CH_2 (6 H), δ 4.15, pentet, J = 6.8 Hz; OCH_3 (18 H), δ 3.79, multiplet; CH_2CH_3 (9 H), δ 1.32, triplet; J = 7.0 Hz. ^{31}P NMR (acetone-d_6 broad band, proton decoupled; eight-line AB_2 pattern): $P(OCH_2CH_3)_3$ (1 P), δ 177.90; $P(OCH_3)_3$ (2 P), δ 172.10; $J_{PP'}$ = 142.84 Hz.

$[(\eta\text{-}C_5H_5)Fe(P(OCH_3)_3)_2(P(OPh)_3)]PF_6$. This compound was prepared by reacting $[(\eta\text{-}C_5H_5)Fe(CH_3CN)(P(OCH_3)_3)_2]PF_6$ with $P(OPh)_3$. A 51.5-mg sample of $[(\eta\text{-}C_5H_5)Fe(CH_3CN)(P(OCH_3)_3)_2]PF_6$ and 0.5 mL of $P(OPh)_3$ were dissolved in 20 mL of dichloromethane. This solution was refluxed under nitrogen for 24 h. As the reaction proceeded, the solution changed from orange to yellow. The solvent was removed by rotary evaporation, and the unreacted $P(OPh)_3$ was removed by hexane and ether washes. $[(\eta\text{-}C_5H_5)Fe(P(OCH_3)_3)_2P(OPh)_3]PF_6$ (68.1 mg) was recovered in 89% yield as a yellow crystalline material, mp 172–174 °C dec. Anal. Calcd for $C_{29}H_{38}F_6FeO_9P_4$: C, 42.25, H, 4.65. Found: C, 41.85; H, 4.71. ^1H NMR (acetone-d_6): C_5H_5 (5 H), δ 4.75, quartet, J = 1.3 Hz; phenyl protons (15 H), δ 7.24, multiplet; OCH_3 (18 H), δ 3.87, multiplet characteristic of the X portion of an A_2BX spectrum, J_{POCH} = 10.6 Hz. ^{31}P NMR (acetone-d_6; broad band, proton decoupled; eight-line A_2B spectrum): $P(OCH_3)_3$ (2 P), δ 173.16; P(OPh) (1 P), δ 165.60; $J_{PP'}$ = 139.15 Hz.

$[(\eta\text{-}C_5H_5)Fe(CH_3CN)(P(OCH_3)_3)(2,6\text{-}DMP)]PF_6$. This compound was prepared in three steps from $[(\eta\text{-}C_5H_5)Fe(\eta\text{-}p\text{-}xyl)]PF_6$. A solution was prepared by dissolving 33.3 mg of $[(\eta\text{-}C_5H_5)Fe(\eta\text{-}p\text{-}xyl)]PF_6$ in 10 mL of acetonitrile. This solution was placed in a test tube along with a stir bar. The test tube was stoppered, and the solution was degassed by bubbling with nitrogen. The test tube was then placed in a dry ice/acetonitrile bath and exposed to sunlight. The solution turned dark purple soon after the photolysis was begun. The photolysis was continued for 30 min to ensure complete conversion to $(\eta\text{-}C_5H_5)Fe(CH_3CN)_3^+$. Next, a solution of 12 mg of 2,6-DMP in 1 mL of acetonitrile was added to the reaction mixture. The solution turned reddish brown immediately. This reaction was allowed to continue for 5 min. Finally, 0.1 mL of $P(OCH_3)_3$ was added to the reaction. This caused the solution to turn orange. Evaporation of the solvent yielded an orange oil. The oil was washed with ether and hexane to remove excess $P(OCH_3)_3$. The remaining solid was crystallized from acetone/hexane. A 43-mg sample of $[(\eta\text{-}C_5H_5)Fe(CH_3CN)(P(OCH_3)_3)(2,6\text{-}DMP)]PF_6$ (86% yield) was recovered. Anal. Calcd for $C_{19}H_{26}F_8FeN_2O_3P_2$: C, 40.59; H, 4.66. Found: C, 40.51; H, 4.78. ^1H NMR (acetone-d_6): C_5H_5 (5 H), δ 4.94, doublet, J = 1.2 Hz; aryl protons (3 H), δ 7.24, singlet; OCH_3 (9 H), δ 3.82, doublet, J = 1.2 Hz; isocyanide methyl (6 H), δ 2.52, singlet; CH_3CN (3 H), δ 2.44, doublet, J = 1.0 Hz.

$[(\eta\text{-}C_5H_5)Fe(P(OCH_2CH_3)_3)(P(OCH_3)_3)(2,6\text{-}DMP)]PF_6$. A solution was prepared by dissolving $[(\eta\text{-}C_5H_5)Fe(CH_3CN)(P(OCH_3)_3)(2,6\text{-}DMP)]PF_6$ (27 mg) and 0.5 mL of $P(OCH_2CH_3)_3$ in 15 mL of dichloromethane. This solution was refluxed under nitrogen for 23 h. The solvent was then removed by rotary evaporation, and the oil that remained was washed with hexane. Ether was added to this oil, and the material was allowed to crystallize in a refrigerator (5 °C). After several hours, the ether was decanted and 20 mg of yellow crystalline $[(\eta\text{-}C_5H_5)Fe(P(OCH_2CH_3)_3)(P(OCH_3)_3)(2,6\text{-}DMP)]PF_6$ (61% yield) was recovered; mp 121–122 °C dec. Anal. Calcd for $C_{23}H_{38}F_6FeNO_6P$: C, 40.19; H, 5.57. Found: C, 39.94; H, 5.56. IR (KBr pellet): $\bar{\nu}(C{\equiv}N)$ 2098 (s) cm^{-1}. ^1H NMR (acetone-d_6): C_5H_5 (5 H), δ 5.08, triplet, J = 1.3 Hz; aryl protons (3 H), δ 7.19, singlet; CH_2 (6 H), δ 4.20, pentet, J = 7 Hz; OCH_3 (9 H), four-line spectrum characteristic of the X portion of a A_2BX_n spectrum, J_{POCH} = 11.2 Hz; isocyanide methyl (6 H), δ 2.48, singlet; CH_2CH_3 (9 H), δ 1.32, triplet, J = 7 Hz.

Reactions

Photochemical Reaction of $[(\eta\text{-}C_5H_5)Fe(\eta\text{-}p\text{-}xyl)]PF_6$ with $P(OCH_3)_3$ and 2,6-DMP. A solution was prepared by placing 33.3 mg of $[(\eta\text{-}C_5H_5)Fe(\eta\text{-}p\text{-}xyl)]PF_6$, 12 mg of 2,6-DMP, 0.1 mL of $P(OCH_3)_3$, and 10 mL of acetonitrile into a test tube. A stir bar was added, and the solution was degassed by bubbling with nitrogen for 10 min. After exposure to sunlight for 3 h, the acetonitrile was removed, leaving an oily residue. This residue was washed with hexane to remove unreacted ligand. ^1H NMR analysis of the crude product indicated that three $(\eta\text{-}C_5H_5)Fe^{II}$ products were present. The products $[(\eta\text{-}C_5H_5)Fe(P(OCH_3)_3)_2CH_3CN]PF_6$ and $[(\eta\text{-}C_5H_5)Fe(CH_3CN)(P(OCH_3)_3)(2,6\text{-}DMP)]PF_6$ were present in approximately equal amounts. The third product, present in only a trace amount (5%), was $[(\eta\text{-}C_5H_5)Fe(CH_3CN)(2,6\text{-}DMP)_2]PF_6$.

Low-Temperature ^1H NMR of $(\eta\text{-}C_5H_5)Fe(CD_3CN)_3^+$. A sample of $[(\eta\text{-}C_5H_5)Fe(\eta\text{-}p\text{-}xyl)]PF_6$ was dissolved in approximately 0.5 mL of CD_3CN. This solution was placed in an NMR tube, and a serum septum was used to seal the tube. The solution was degassed by bubbling with nitrogen for 5 min. The tube was then placed in a dry ice/acetonitrile bath. This solution was irradiated with the Oriel lamp for 10 min. At this time, the color of the solution was deep purple. A ^1H NMR spectrum of this solution was recorded at −40 °C. A number of peaks were observed. Five of the peaks could be assigned to the starting complex $[(\eta\text{-}C_5H_5)Fe(\eta\text{-}p\text{-}xyl)]PF_6$ and free *p*-xylene. Two additional resonances were observed at δ 4.15 and 4.06. The peak at δ 4.15 was assigned to ferrocene and was of lesser intensity. The peak of δ 4.06 was assigned to the intermediate $(\eta\text{-}C_5H_5)Fe(CD_3CN)_3^+$. As the sample was warmed, the peak at δ 4.06 diminished in intensity and the amount of ferrocene increased. By the time the sample had reached 0 °C, all of the intermediate had been converted to ferrocene.

Photolysis of $[(\eta\text{-}C_5H_5)Fe(\eta\text{-}p\text{-}xyl)]PF_6$ in Neat CH_3CN. Samples of $[(\eta\text{-}C_5H_5)Fe(\eta\text{-}p\text{-}xyl)]PF_6$ (100 mg) were placed in two test tubes. To one of the tubes were added 10 mL of acetonitrile, a stir bar, and a serum septum. This sample was degassed by bubbling with nitrogen for 10 min. The other sample was similarly prepared by using 20 mL of acetonitrile. The test tube containing the 20 mL of solution was exposed to sunlight for 3 h 25 min, and the other solution was irradiated with an Oriel lamp for the same period of time. Ferrocene was recovered from both samples by evaporating the solvent and extracting the residue with cyclohexane. In both cases the purity of ferrocene was verified by ^1H NMR and a melting pont determination. The yield of ferrocene, based on $C_5H_5^-$ from the complex $[(\eta\text{-}C_5H_5)Fe(\eta\text{-}p\text{-}xyl)]PF_6$, was 97% in the sunlight-irradiated sample and 93% in the sample that was irradiated with the Oriel lamp.

Results and Discussion

Characterization of the Purple Intermediate $(\eta\text{-}C_5H_5)Fe(CH_3CN)_3^+$. When a degassed acetonitrile solution of $[(\eta\text{-}C_5H_5)Fe(\eta\text{-}p\text{-}xyl)]PF_6$ is irradiated at room temperature, an intense purple color is observed. As the photolysis is continued, the purple coloration gradually decreases in intensity, resulting in a yellow-orange solution. The disappearance of the purple color is due to three factors. First, the intermediate is thermally unstable, as evidenced by the rapid bleaching of the photogenerated purple solution in the dark. Second, the final products of the reaction, Fe(II) and ferrocene, begin to produce a marked inner-filter effect, so that less light is available to promote the formation of the purple intermediate. Finally, the recombination (vide infra) of the intermediate with *p*-xylene may increase with time due to the buildup of *p*-xylene to further reduce the lifetime of the intermediate.

Appreciable concentrations of the intermediate are formed if the photolysis is performed at lower temperatures. When an acetonitrile solution of $[(\eta\text{-}C_5H_5)Fe(p\text{-}xyl)]PF_6$ is placed in a dry ice/acetonitrile slush bath and irradiated, the purple color of the intermediate is more intense and is persistent over several hours at the bath temperature. The high chemical yields obtained in low-temperature synthetic reactions (vide infra) also suggest that the purple intermediate is generated in appreciable amounts.

The increase in stability of the purple intermediate at low temperature has enabled the determination of its visible absorption spectrum. The purple color (lowest energy absorption band λ_{max} = 550 nm) is consistent with the formulation of the intermediate as $(\eta\text{-}C_5H_5)Fe(CH_3CN)_3^+$. Since CH_3CN is a relatively weak-field ligand,[9] it is reasonable to expect the

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[9] G. M. Bancroft, R. E. B. Garrod, A. G. Maddock, M. J. Mays, and B. F. Prater, *J. Am. Chem. Soc.*, **94**, 647 (1972).

ligand field absorption of the cation $(\eta\text{-}C_5H_5)Fe(CH_3CN)_3^+$ to be shifted significantly to the red of the absorption band of $[(\eta\text{-}C_5H_5)Fe(\eta\text{-}p\text{-xyl})]PF_6$ (lowest energy absorption band $\lambda_{max} = 450$ nm). Indeed, the lowest energy absorption band of the yellow complex $[(\eta\text{-}C_5H_5)Ru(CH_3CN)_3]PF_6$ ($\lambda_{max} = 365$ nm) is also shifted substantially from the lowest energy absorption band of the white compound $[(\eta\text{-}C_5H_5)Ru(\eta\text{-}C_6H_6)]PF_6$ ($\lambda_{max} = 320$ nm).[1] The shift between the lowest bands of the purple intermediate and the complex $[(\eta\text{-}C_5H_2)Fe(\eta\text{-}p\text{-xyl})]PF_6$ is ~4000 cm^{-1}, in good agreement with the ~3850-cm^{-1} shift between $[(\eta\text{-}C_5H_5)Ru(CH_3CN)_3]PF_6$ and $[(\eta\text{-}C_5H_5)Ru(\eta\text{-}C_6H_6)]PF_6$. The similarity of the shift in the Fe and Ru systems and the position of λ_{max} supports the formulation of the purple intermediate as $(\eta\text{-}C_5H_5)Fe(CH_3CN)_3^+$.

We have also obtained information concerning the structure of the intermediate by utilizing low-temperature ^1H NMR spectroscopy. Photolysis of $[(\eta\text{-}C_5H_5)Fe(\eta\text{-}p\text{-xyl})]PF_6$ in acetonitrile-d_3 solution in an NMR tube at −40 °C yields the purple solution that exhibits a single resonance ascribable to the intermediate at δ 4.06. This peak is assigned to the cyclopentadienyl protons of the species $(\eta\text{-}C_5H_5)Fe(CD_3CN)_3^+$. The position of this resonance is shifted 1.11 ppm upfield of the cyclopentadienyl resonance of the complex $[(\eta\text{-}C_5H_5)Fe(\eta\text{-}C_6H_6)]PF_6$.[9] In comparison, the cyclopentadienyl resonance of the complex $[(\eta\text{-}C_5H_5)Ru(CH_3CN)_3]PF_6$ is shifted 1.23 ppm upfield from the cyclopentadienyl resonance of $[(\eta\text{-}C_5H_5)Ru(\eta\text{-}C_6H_6)]PF_6$. The absence of any other peaks in the ^1H NMR spectrum of the purple intermediate suggests that *p*-xylene is not coordinated to the iron in the intermediate. If an η^2- or η^4-*p*-xylene moiety were present in the purple intermediate, signals consistent with this coordination mode would have been observed for the aryl protons. After the sample was allowed to warm to 0 °C, a subsequent ^1H NMR spectrum showed that the solution contained ferrocene and free *p*-xylene.

Indirect evidence for the formulation of the purple intermediate as $(\eta\text{-}C_5H_5)Fe(CH_3CN)_3^+$ also comes from the photolysis of acetonitrile solutions containing $[(\eta\text{-}C_5H_5)Fe(\eta\text{-}p\text{-xyl})]PF_6$ and a ligand, L. Reactions of the intermediate with a variety of ligands yielded products of the general formula $[(\eta\text{-}C_5H_5)Fe(CH_3CN)L_2]PF_6$, where L = $P(OCH_3)_3$, $P(OCH_2CH_3)_3$, $P(OPh)_3$, $CNC(CH_3)_3$, 2,6-DMP, and L_2 = diphos. The preparations of these compounds will be discussed in a later section of this paper.

Mechanism of Ferrocene Formation. The amount of ferrocene formed by irradiating acetonitrile solutions of $[(\eta\text{-}C_5H_5)Fe(\eta\text{-}p\text{-xyl})]PF_6$ was measured for typical photolysis conditions at room temperature. With the sun and the Oriel lamp as irradiation sources, the yields of ferrocene were 97% and 93%, respectively. These yields are based on the stoichiometry of reaction 1. The presence of Fe(II) was confirmed by treating the photolyte with 1,10-phenanthroline and observing the bright red-orange color of the $Fe(phen)_3^{2+}$ ion.

A mechanism that accounts for the formation of ferrocene and Fe(II) in this system is

$$(\eta\text{-}C_5H_5)Fe(\eta\text{-}p\text{-xyl})^+ \xrightarrow[CH_3CN]{h\nu} (\eta\text{-}C_5H_5)Fe(CH_3CN)_3^+ + p\text{-xyl} \quad (2)$$

$$(\eta\text{-}C_5H_5)Fe(CH_3CN)_3^+ \overset{CH_3CN}{\rightleftharpoons} Fe(CH_3CN)_6^{2+} + C_5H_5^- \quad (3a)$$

$$(\eta\text{-}C_5H_5)Fe(CH_3CN)_3^+ + C_5H_5^- \rightarrow (\eta\text{-}C_5H_5)_2Fe + 3CH_3CN \quad (4)$$

Alternate mechanisms for the formation of ferrocene include the bimolecular reaction of two intermediate ions (eq 3b) or an intermediate ion with a parent ion (eq 3c).

$$(\eta\text{-}C_5H_5)Fe(CH_3CN)_3^+ + (\eta\text{-}C_5H_5)Fe(CH_3CN)_3^+ \rightarrow (\eta\text{-}C_5H_5)_2Fe + Fe(II) + 6CH_3CN \quad (3b)$$

$$(\eta\text{-}C_5H_5)Fe(CH_3CN)_3^+ + (\eta\text{-}C_5H_5)Fe(\eta\text{-}p\text{-xyl})^+ \rightarrow (\eta\text{-}C_5H_5)_2Fe + Fe(II) + p\text{-xyl} + 3CH_3CN \quad (3c)$$

The first step common to *all* of the possible mechanisms is the photochemical replacement of *p*-xylene from the complex $[(\eta\text{-}C_5H_5)Fe(\eta\text{-}p\text{-xyl})]PF_6$ by three acetonitrile molecules. In the proposed mechanism, a portion of the intermediate decomposes to give one of the final products Fe(II) (reaction 3a) and $C_5H_5^-$, which reacts with unreacted $(\eta^5\text{-}C_5H_5)Fe(CH_3CN)_3^+$ to form ferrocene[10] (reaction 3b).

Reaction 3a is supported by the results obtained when a solution of $(\eta\text{-}C_5H_5)Fe(CD_3CN)_3^+$ is treated with HBF_4 at −40 °C followed by a warm-up step. The products of this reaction observed by ^1H NMR are Fe(II) and cyclopentadiene. This result is not unequivocal for step 3a, because direct protonation of the bound $\eta\text{-}C_5H_5$ may be possible, although in our view is much less likely.

The dissociation of Cp^- is also supported by the original study[4] of the photodecomposition of $[(\eta\text{-}C_5H_5)Fe(\eta\text{-}C_6H_6)]BF_4$ in other solvents. In this study, it was reported that the photodecomposition of $[(\eta\text{-}C_5H_5)Fe(\eta\text{-}C_6H_6)BF_4$ in protic solvents does *not* yield ferrocene. When the solvent was CH_3OH, CH_3CH_2OH, H_2O, or CH_3CO_2H, the only iron-containing decomposition product observed was Fe(II). These results are consistent with the generation of *free* $C_5H_5^-$ as a precursor in the formation of ferrocene. Protic solvents such as these would be expected to lead to the rapid protonation of the free $C_5H_5^-$, removing it from the reaction sequence before reaction 4 can occur.

When $(\eta\text{-}C_5H_4CH_3)Fe(CH_3CN)_3^+$ (generated by irradiating an acetonitrile solution of $[(\eta\text{-}C_5H_4CH_3)Fe(\eta\text{-}p\text{-xyl})]^+$ at −40 °C) is allowed to react with thallium cyclopentadienide, the *exclusive* product is methylferrocene. This result is inconsistent with steps 3b or 3c, which would be expected to generate dimethylferrocene. Step 3c is further ruled out as a viable step in the production of ferrocenes in this system because the product obtained on warm-up of $[(\eta\text{-}C_5H_4CH_3)Fe(CH_3CN)_3]^+$ in the presence of $[(\eta\text{-}C_5H_5)Fe(\eta\text{-}p\text{-xyl})]^+$ is *exclusively* dimethylferrocene. If step 3c obtains, some methylferrocene would be expected in this experiment.

Reactivity of $(\eta\text{-}C_5H_5)Fe(CH_3CN)_3^+$. Room-temperature photolysis of acetonitrile solutions containing a two-electron-donor ligand L and $[(\eta\text{-}C_5H_5)Fe(\eta\text{-}p\text{-xyl})]PF_6$ has proven to be a very useful method for preparing compounds of the form $[(\eta\text{-}C_5H_5)Fe(CH_3CN)L_2]PF_6$ with a variety of ligands, L (see Experimental Section). All six of the $[(\eta\text{-}C_5H_5)Fe(CH_3CN)L_2]PF_6$ complexes that we have isolated by this route are orange crystals or powders that have been characterized by ^1H NMR, elemental analysis and infrared spectroscopy (where appropriate). These compounds are air stable and soluble in polar organic solvents (acetone, acetonitrile, dichloromethane) and for the most part exhibit unexceptional physical properties. However, $[(\eta\text{-}C_5H_5)Fe(CH_3CN)(diphos)]PF_6$ exhibits an unexpected feature in its ^1H NMR spectrum. The resonance due to the acetonitrile protons was observed as a triplet at δ 1.64. The triplet structure is due to coupling with two phosphorus atoms bound to the iron and is expected. However, the position of the resonance is far upfield of where the acetonitrile protons of the other complexes have been observed. These occur in the range δ 2.36–2.56. We believe that the upfield shift of approximately 0.8 ppm in this diphos complex is caused by diamagnetic shielding of the methyl protons by the phenyl rings of the diphos ligand.[11]

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[10] G. Wilkinson, *Org. Synth.*, **36**, 31 (1956), and references therein.

Table I. ^{31}P NMR Spectral Results[a]

complex	peak position[b] (rel intens)	chem shifts[b,c]	P-P′ coupling const[c,d]
$[(\eta\text{-}C_5H_5)Fe(P(OCH_2CH_3)_3)(P(OCH_3)_3)_2]PF_6$[e]	178.63 (540)	177.90	142.84
	178.48 (497)	172.10[f]	
	177.43 (787)		
	177.35 (822)		
	173.16 (651)		
	172.10 (346)		
	171.87 (389)		
	170.83 (159)		
$[(\eta\text{-}C_5H_5)Fe(P(OCH_2CH_3)_3)_2(P(OCH_3)_3)]PF_6$	179.13 (200)	177.84	143.35
	178.09 (314)	172.45[f]	
	177.84 (381)		
	176.80 (529)		
	173.01 (894)		
	172.92 (871)		
	171.88 (542)		
	171.71 (545)		
$[(\eta\text{-}C_5H_5)Fe(P(OCH_3)_3)_2(P(OPh)_3)]PF_6$[e]	173.83 (440)	173.16[f]	139.15
	173.72 (527)	165.60	
	172.67 (817)		
	172.60 (568)		
	166.65 (397)		
	165.60 (303)		
	165.42 (277)		
	164.37 (228)		

[a] ^1H-decoupled ^{31}P spectra were obtained at room temperature in acetone-d_6. The probe frequency was 121.487 (4) MHz. [b] In δ units. [c] These values derived from analysis in ref 12. [d] In Hz. [e] A small impurity peak (less than 1%) due to $[(\eta\text{-}C_5H_5)Fe(P(OCH_3)_3)_2CH_3CN]PF_6$ was observed at δ 177.95. [f] Chemical shift of $P(OCH_3)_3$.

Examination of the X-ray structure[8] that has been obtained on the $B(C_6H_5)_4^-$ salt of the complex suggests the methyl protons are held between roughly parallel phenyl rings of the diphos ligand.

The room-temperature photolysis of $(\eta\text{-}C_5H_5)Fe(\eta\text{-}p\text{-xyl})^+$ is not a convenient method for the preparation of $[(\eta\text{-}C_5H_5)Fe(CH_3CN)(L)(L')]PF_6$ compounds because the direct photolysis of $[(\eta\text{-}C_5H_5)Fe(\eta\text{-}p\text{-xyl})]PF_6$ in the presence of both L and L′ yields $(\eta\text{-}C_5H_5)Fe(L)_2(CH_3CN)^+$ and $(\eta\text{-}C_5H_5)Fe(L')_2(CH_3CN)^+$ in addition to the desired product. However, the sequential substitution of the acetonitrile ligands in $(\eta\text{-}C_5H_5)Fe(CH_3CN)_3^+$ can be obtained as in the analogous Ru system if the first substitution is performed at −40 °C with a stoichiometric amount of the ligand. An excess of the second ligand is then added at low temperature followed by a warming-up step. The complex $[(\eta\text{-}C_5H_5)Fe(CH_3CN)(P(OCH_3)_3)(2,6\text{-DMP})]PF_6$ was prepared with use of this method by treating the intermediate $[(\eta\text{-}C_5H_5)Fe(CH_3CN)_3]^+$ with 1 equiv of 2,6-DMP followed by a slow warm-up step in the presence of excess $P(OCH_3)_3$. The isolation of only one product from this reaction indicates that the substitution rate for the replacement of the first acetonitrile by 2,6-DMP is significantly faster than the subsequent substitution rates at −40 °C. If the second substitution occurred at the same rate or at a faster rate than the first, $[(\eta\text{-}C_5H_5)Fe(CH_3CN)(2,6\text{-DMP})_2]PF_6$ would also have been observed. Consistent with the previously discussed room-temperature photolysis results, photolysis of a room-temperature solution containing the identical amounts of $[(\eta\text{-}C_5H_5)Fe(\eta\text{-}p\text{-xyl})]PF_6$, 2,6-DMP, and $P(OCH_3)_3$ used to prepare $[(\eta\text{-}C_5H_5)Fe(CH_3CN)P(OCH_3)_3(2,6\text{-DMP})]PF_6$ yielded a mixture of compounds that were identified by ^1H NMR as $[(\eta\text{-}C_5H_5)Fe(CH_3CN)(P(OCH_3)_3)_2]PF_6$, $[(\eta\text{-}C_5H_5)Fe(CH_3CN)(P(OCH)_3)(2,6\text{-DMP})]PF_6$, and $[(\eta\text{-}C_5H_5)Fe(CH_3CN)(2,6\text{-DMP})_2]PF_6$. The first two of these complexes were produced in greatest yield, because of the large $P(OCH_3)_3$/2,6-DMP ratio used.

Trisubstituted compounds are readily formed by replacing the remaining acetonitrile ligand of $[(\eta\text{-}C_5H_5)Fe(CH_3CN)L_2]PF_6$ or $[(\eta\text{-}C_5H_5)Fe(CH_3CN)(L)(L')]PF_6$ with a ligand L″ in refluxing dichloromethane. In this manner, the following compounds were prepared: $[(\eta\text{-}C_5H_5)Fe(P(OCH_2CH_3)_3)_2(P(OCH_3)_3)]PF_6$, $[(\eta\text{-}C_5H_5)Fe(P(OCH_2CH_3)_3)(P(OCH_3)_3)_2]PF_6$, $[(\eta\text{-}C_5H_5)Fe(P(OCH_3)_3)_2(P(OPh)_3)]PF_6$, $[(\eta\text{-}C_5H_5)Fe(P(OCH_3)_3)_2(2,6\text{-DMP})]PF_6$, and $[(\eta\text{-}C_5H_5)Fe(P(OCH_3)_3)(2,6\text{-DMP})_2]PF_6$. Of special interest is the compound $[(\eta\text{-}C_5H_5)Fe(P(OCH_2CH_3)_3)(P(OCH_3)_3(2,6\text{-DMP})]PF_6$, in which all three CH_3CN ligands have been replaced by different ligands. Both this compound and the precursor ($[(\eta\text{-}C_5H_5)Fe(CH_3CN)(P(OCH_3)_3)(2,6\text{-DMP})]PF_6$, from which it was prepared in refluxing dichloromethane) should exist as equal amounts of two optical isomers. At this time we have not attempted their resolution.

The progress of these reactions was easily monitored by visual inspection because, as the displacement of the final acetonitrile molecule proceeds, the color of the solution changes from orange (characteristic of the mono(acetonitrile) complexes) to yellow (characteristic of the trisubstituted complexes). At this point, these reactions were usually allowed to reflux for a few additional hours to ensure complete conversion to product.

Of special interest are the proton-decoupled ^{31}P NMR spectra of the complexes $[(\eta\text{-}C_5H_5)Fe(P(OCH_2CH_3)_3)(P(OCH_3)_3)_2]PF_6$, $[(\eta\text{-}C_5H_5)Fe(P(OCH_2CH_3)_3)_2(P(OCH_3)_3]PF_6$, and $[(\eta\text{-}C_5H_5)Fe(P(OCH_3)_3)_2(P(OPh)_3)]PF_6$, which exhibit the eight-line pattern expected for an A_2B spectrum (Table I, Figure 1). By a straightforward analysis,[12] the chemical shifts of the phosphorus nuclei and the relevant coupling constants were determined. Even though the spectra vary somewhat in appearance, the P-P′ coupling constants are relatively constant (141 ± 2 Hz). This variation is predicted because of the strong dependence of the spectrum on the ratio $J_{AB}/|\nu_A - \nu_B|$.[13] The large value for the phosphorus-phosphorus coupling constant is also consistent with the complex

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(11) For an explanation of diamagnetic shielding by phenyl rings see V. J. Pasto and C. R. Johnson, "Organic Structure Determinatin", Prentice Hall, Englewood Cliffs, NJ, 1969, p 171.

(12) H. Günther, "NMR Spectroscopy", Wiley, New York, 1980, p 131.

(13) Reference 12, p 157.

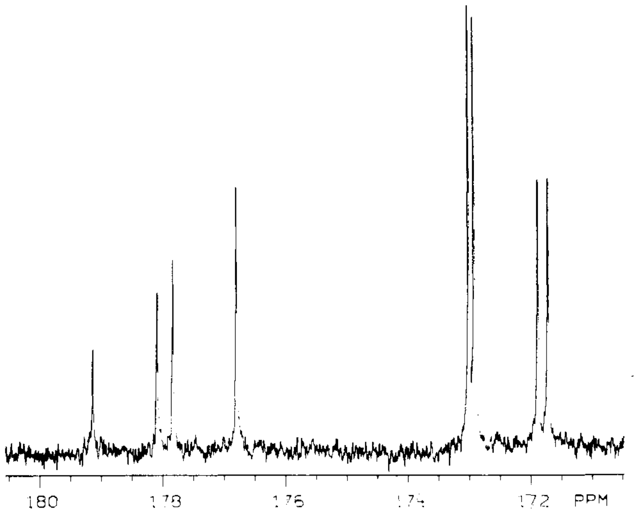

Figure 1. 121.5-MHz ^{31}P NMR spectrum of $[(\eta\text{-}C_5H_5)Fe(P(OCH_2CH_3)_3)_2(P(OCH_3)_3)]PF_6$.

^1H NMR spectral pattern observed in these and previously reported phosphite complexes.[3]

Reactivity Comparison of $[(\eta\text{-}C_5H_5)Fe(CH_3CN)_n(L)_{3-n}]^+$ and $[(\eta\text{-}C_5H_5)Ru(CH_3CN)_n(L)_{3-n}]^+$. The cyclopentadienyliron acetonitrile compounds prepared here are in every case more reactive than the corresponding cyclopentadienylruthenium acetonitrile complexes that we have previously investigated. This difference in reactivity is most evident in the thermally unstable $(\eta\text{-}C_5H_5)Fe(CH_3CH)_3^+$ ion compared with the isolable ruthenium complex, $[(\eta\text{-}C_5H_5)Ru(CH_3CN)_3]PF_6$. Addition of two-electron-donor ligands at room temperature to the ruthenium complex results in the replacement of exclusively one CH_3CN upon mixing. Further substitution of the complex $[(\eta\text{-}C_5H_5)Ru(CH_3CN)_2L]PF_6$ with an additional ligand proceeds slowly at room temperature. In contrast, the iron analogue $(\eta\text{-}C_5H_5)Fe(CH_3CN)_3^+$ reacts rapidly at room temperature in CH_3CN with a variety of two-electron-donor ligands to yield disubstituted complexes $(\eta\text{-}C_5H_5)Fe(CH_3CN)L_2^+$. The third acetonitrile ligand can be displaced in the disubstituted iron compounds in refluxing dichloromethane solution, while its replacement in the corresponding ruthenium complexes occurs in refluxing dichloroethane. Although these reactions proceed at similar rates, the Ru system is significantly less labile, as judged by the significantly higher boiling point of dichloroethane (44 °C difference). Finally, the increased reactivities of these iron acetonitrile complexes over the ruthenium analogues are consistent with the general observation that, in analogous first- and second-row complexes, reactions generally proceed more rapidly for the first-row transition-metal complex.

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Registry No. $[(\eta\text{-}C_5H_4CH_3)Fe(\eta\text{-}p\text{-}xyl)]BF_4$, 85709-81-5; $[(\eta\text{-}C_5H_5)Fe(CH_3CN)(P(OCH_3)_3)_2]PF_6$, 85701-91-3; $[(\eta\text{-}C_5H_5)Fe(CH_3CN)(CNC(CH_3)_3)_2]PF_6$, 85701-93-5; $[(\eta\text{-}C_5H_5)Fe(CH_3CN)(2,6\text{-}DMP)_2]PF_6$, 85701-95-7; $[(\eta\text{-}C_5H_5)Fe(CH_3CN)(P(OCH_2CH_3)_3)_2]PF_6$, 85701-97-9; $[(\eta\text{-}C_5H_5)Fe(CH_3CN)(P(OPh)_3)_2]PF_6$, 33307-64-1; $[(\eta\text{-}C_5H_5)Fe(CH_3CN)(diphos)]PF_6$, 83172-78-5; $[(\eta\text{-}C_5H_5)Fe(P(OCH_3)_3)_2(2,6\text{-}DMP)]PF_6$, 85701-99-1; $[(\eta\text{-}C_5H_5)Fe(P(OCH_3)_3)(2,6\text{-}DMP)_2]PF_6$, 85702-01-8; $[(\eta\text{-}C_5H_5)Fe(P(OCH_2CH_3)_3)_2(P(OCH_3)_3)]PF_6$, 85702-03-0; $[(\eta\text{-}C_5H_5)Fe(P(OCH_2CH_3)_3)(P(OCH_3)_3)_2]PF_6$, 85702-05-2; $[(\eta\text{-}C_5H_5)Fe(P(OCH_3)_3)_2(P(OPh)_3)]PF_6$, 85702-07-4; $[(\eta\text{-}C_5H_5)Fe(CH_3CN)(P(OCH_3)_3)(2,6\text{-}DMP)]PF_6$, 85702-09-6; $[(\eta\text{-}C_5H_5)Fe(P(OCH_2CH_3)_3)(P(OCH_3)_3)(2,6\text{-}DMP)]PF_6$, 85702-11-0; $[(\eta\text{-}C_5H_5)Fe(\eta\text{-}p\text{-}xyl)]PF_6$, 34978-37-5; $P(OCH_3)_3$, 121-45-9; CH_3CN, 75-05-8; $CNC(CH_3)_3$, 7188-38-7; 2,6-DMP, 2769-71-3; $P(OCH_2CH_3)_3$, 122-52-1; $P(OPh)_3$, 101-02-0; diphos, 1663-45-2; $(\eta\text{-}C_5H_5)Fe(CD_3CN)_3^+$, 85702-12-1; CD_3CN, 2206-26-0; $(\eta\text{-}C_5H_5)Fe(CH_3CN)_3^+$, 85702-13-2; thallium cyclopentadienide, 34822-90-7.

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Sublimation of Bis(1,3-propanedial) Chelates of Palladium(II) and Chromium(III)

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The bis(1,3-propanedial) chelates of palladium(II) and chromium(III) have been synthesized and characterized, and their volatility has been studied. Both chelates sublime below 120 °C in a fractional sublimator in a stream of air at 1 torr and are recoverable, but not quantitatively. Sublimation of the Pd(II) chelate was accompanied by a partial decomposition with Pd metal deposited as a mirror. It is proposed that the Pd(II) chelate may be used in the preparation of palladium front-surface mirrors in spectroscopic instrumentation and for the deposition of catalytic palladium in porous supports. Attempts to synthesize the bis(1,3-propanedial) chelates of Al(III), Co(II), Co(III), Cu(II), Fe(III), Ni(II), Mn(II), Mn(III), Pt(II), and Rh(III) were unsuccessful.

Numerous β-diketone ligands have been investigated in this laboratory for their ability to form volatile metal chelates, but of all the ligands studied, 1,3-propanedial (malonaldehyde) is unique. Malonaldehyde (MDA) is the simplest molecule capable of providing the basic 1,3-diketo structure, which may enolize and thereby coordinate with metal ions to form β-diketo chelates, but unlike other 1,3-diketones it will coordinate with a very limited number of ions and forms a palladium chelate with unusual sublimation characteristics.

MDA has been extensively studied by organic chemists but has been almost ignored as a possible chelating agent. Schuster[1] used the metal chelates of MDA as models in LCAO-MO calculations on the enol form of acetylacetone and its metal complexes, but the chomium(III) complex of MDA is the only chelate of the ligand reported in the literature as having been isolated and characterized. Kwon and Watts[2]

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(1) Schuster, P. *Chem. Phys. Lett.* **1969**, *3*, 433.
(2) Kwon, T. W.; Watts, B. M. *J. Food Sci.* **1964**, *29*, 294.