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SYNTHESES, AN ELECTROCHEMICAL STUDY, AND SOME CHEMICAL REACTIONS OF $Fe(C_5H_5)(CNR)_2X$ COMPOUNDS

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Summary

Reactions of $Fe(C_5H_5)(CO)_2Br$ with two equivalents of CNR give $Fe(C_5H_5)(CNR)_2Br$ compounds (R = C_6H_5, *p*-C_6H_4Me, *m*-C_6H_4Me, *p*-C_6H_4OMe, *m*-C_6H_4OMe, *p*-C_6H_4F, *m*-C_6H_4Cl, *m*-$C_6H_4CF_3$, *p*-$C_6H_4NO_2$). With excess CNR cationic complexes $[Fe(C_5H_5)(CNR)_3]^+$ are formed. Reactions of $[Fe(C_5H_5)(CO)_2(THF)]PF_6$ and *p*-CNC_6H_4F give $[Fe(C_5H_5)(CO)_{3-n}(p\text{-}CNC_6H_4F)_n]PF_6$ (n = 1 or 2, determined by stoichiometry). The $Fe(C_5H_5)(CNR)_2Br$ compounds are shown to undergo one-electron oxidation processes; the required potentials for oxidation ($E_{1/2}$) correlate well with Hammett σ_p or σ_m constants for substituents on the aryl rings. Chemical and electrochemical oxidations of several $Fe(C_5H_5)(CNR)_2Br$ compounds were attempted but only $[Fe(C_5H_5)(CNR)_3]PF_6$ species are obtained. The process using $AgPF_6$ in acetone was followed by NMR. A rapid reaction of these reagents to give a red solution is seen; this red solution may contain as many as six intermediates. These intermediates convert slowly (a period of hours) to the final product, $[Fe(C_5H_5)(CNR)_3]PF_6$. Speculation is offered that among the intermediates are the compounds $[Fe(C_5H_5)(CNR)_2(acetone)]PF_6$ and $[Fe(C_5H_5)(CNR)_2BrFe(C_5H_5)(CNR)_2]PF_6$; the latter is a halide bridged species. Using a different solvent, MeCN, a stable product, $[Fe(C_5H_5)(CNPh)_2(MeCN)]PF_6$, analogous to the acetone complex is obtained.

Introduction

Some time ago, we reported on the electrochemical and chemical oxidations of various $Fe(C_5H_5)(dpe)X$ compounds. This work was distinguished by the isolation of stable 17*e* products $[Fe(C_5H_5)(dpe)X]^+$ [1]. At that time we also looked briefly at the oxidations of several related species, including $Fe(C_5H_5)(CNPh)(CO)I$ and $Fe(C_5H_5)(CNPh)_2I$, finding by cyclic voltammetry that these compounds undergo chemically reversible electron transfer reactions at moderately low potentials. However, unlike the analogous dpe compounds, these spe-

cies reacted with $NOPF_6$ (intended as an oxidizing agent) in a different fashion, with halide loss, to give the cationic 18*e* species $[Fe(C_5H_5)(CO)(CNPh)_2]PF_6$ and $[Fe(C_5H_5)(CNPh)_3]PF_6$. A similar type of behavior has been found for the compounds $Mn(CO)_{5-n}(CNPh)_nX$ (n = 4, 5) [1] and these reactions were utilized for specific syntheses of various cationic manganese compounds [2]. Electron richness appears to facilitate loss of a halide ion as a mechanism to decrease electron richness at the metal site.

We have now expanded our earlier study of $Fe(C_5H_5)(CNR)_2X$ species. Reported here are the syntheses of nine compounds of this formula and their electrochemistry. In addition we have attempted a controlled potential oxidation of one of these compounds and have looked further at the $AgPF_6$ reactions of these species in several solvents. These latter reactions were unexpectedly complex, several intermediates being implicated.

Experimental

Reactions were carried out under nitrogen. Melting points were determined using a Thomas-Hoover capillary melting point apparatus, and are uncorrected. High resolution infrared spectra (±1 cm^{-1}) in the region 2500—1800 cm^{-1} were recorded on a Digilab FTS-20 spectrometer using chloroform solutions. Proton NMR spectra were recorded on a JEOL-NM-MH-100 or a Bruker WH-270 spectrometer in chloroform-d_1, acetone-d_6, acetonitrile-d_3 with TMS, δ = 0 ppm, as an internal standard. Molecular weight determinations for nonionic compounds were made with chloroform solutions using a Mechrolab Osmometer, Model 301 A. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee.

Electrochemical measurements were made using a three electrode configuration, employing a stationary platinum bead working electrode, platinum spiral counter electrode, and saturated calomel (aq. KCl) reference electrode. Voltage and current functions were controlled using a Princeton Applied Research Electrochemistry System, Model 170, incorporating compensation for internal resistive potential drop or an A.S.S. 169 Electrochemistry System utilizing a Princeton Applied Research, Model 173, Potentiostat/Galvanostat, a Princeton Applied Research, Model 175, Universal Programmer and a Houston 2000 X-Y recorder. Sweep rates were normally varied from 50 to 200 mV/sec in order to obtain optimum peak shapes. Acetonitrile was used as the solvent with the solution 5×10^{-3} *M* in substrate. Tetrabutylammonium perchlorate (0.1 *M*) was employed as base electrolyte. Data are given in Table 1.

Controlled potential electrolyses were carried out in acetonitrile using an H-shaped three electrode electrolysis cell with a platinum gauze working electrode, a platinum spiral counter (auxillary) electrode and a saturated calomel reference electrode. The voltage function was controlled using an A.S.S. 169 Electrochemistry System Incorporating a Princeton Applied Research Potentiostat/Galvanostat, Model 173 with a digital coulometer, Model 179. The electrode compartments were separated by a sintered Pyrex disc. Tetrabutylammonium perchlorate was employed as the base electrolyte.

The acetonitrile used for electrochemical measurements distilled from phosphorus pentoxide. All other solvents were reagent grade and were used without

TABLE 1

CYCLIC VOLTAMMETRY DATA [a]

Compound	$\frac{1}{2}[E_{p,a} + E_{p,c}]$	$E_{p,a} - E_{p,c}$ (V)
$Fe(C_5H_5)(p\text{-}CNC_6H_4OMe)_2Br$	0.450	0.088
$Fe(C_5H_5)(p\text{-}CNC_6H_4Me)_2Br$	0.477	0.081
$Fe(C_5H_5)(m\text{-}CNC_6H_4Me)_2Br$	0.508	0.084
$Fe(C_5H_5)(CNPh)_2Br$	0.508 [c]	0.105
$Fe(C_5H_5)(m\text{-}CNC_6H_4OMe)_2Br$	0.528	0.081
$Fe(C_5H_5)(p\text{-}CNC_6H_4F)_2Br$	0.540	0.080
$Fe(C_5H_5)(m\text{-}CNC_6H_4Cl)_2Br$	0.569	0.069
$Fe(C_5H_5)(m\text{-}CNC_6H_4CF_3)_2Br$	0.578	0.087
$Fe(C_5H_5)(p\text{-}CNC_6H_4NO_2)_2Br$	0.630	0.071
$[Fe(C_5H_5)(p\text{-}CNC_6H_4Me)_3]PF_6$	1.390	0.169
$[Fe(C_5H_5)(CNPh)_3]PF_6$	1.403	0.156
$[Fe(C_5H_5)(p\text{-}CNC_6H_4F)_3]PF_6$	1.428	0.156
$[Fe(C_5H_5)(CO)(p\text{-}CNC_6H_4F)_2]PF_6$	1.8 [e]	—
$[Fe(C_5H_5)(CO)_2(p\text{-}CNC_6H_4F)]PF_6$	[e]	
$[Fe(C_5H_5)(CNMe)_3]PF_6$	1.29	0.079
$[Fe(C_5H_5)(CO)(CNMe)_2]PF_6$	1.68 [d]	—

[a] Obtained in MeCN; concentration of compound 5×10^{-3} *M*: 0.1 *M* $(Bu_4N)ClO_4$ used as supporting electrolyte. [b] Reported in V vs. saturated calomel electrode (aq. KCl). [c] Reported value of 0.58 vs. SCE in CH_2Cl_2 [1]. [d] Oxidation wave only, no reduction observed. [e] No oxidation at potentials <2.2 V.

further purification. Aryl isocyanides used in this study were prepared by the reaction of the appropriate formamide with triphenylphosphine, carbon tetrachloride, and triethylamine [3]. If liquids, these ligands were purified by distillation; solid ligands were purified by sublimation or recrystallization. The preparations of $Fe(C_5H_5)(CNPh)_2Br$ [4], $[Fe(C_5H_5)(CNPh)_3]PF_6$ [4], $[Fe(C_5H_5)(CNMe)_3]PF_6$ [4,5], $[Fe(C_5H_5)(CO)(CNMe)_2]PF_6$ [5,6], and $[Fe(C_5H_5)(CO)_2(THF)]PF_6$ [7] were accomplished according to literature methods.

Preparation of new $Fe(C_5H_5)(CNR)_2Br$ complexes

The complexes $Fe(C_5H_5)(CNC_6H_4X)_2Br$ (X = *p*-NO_2, *m*-CF_3, *m*-Cl, *m*-OCH_3, *p*-F, *m*-CH_3, *p*-CH_3, *p*-OCH_3) were prepared by a method similar to that used to prepare $Fe(C_5H_5)(CNPh)_2Br$. The distribution of products from the reaction of $Fe(C_5H_5)(CO)_2Br$ with aryl isocyanides among $Fe(C_5H_5)(CO)(CNR)Br$, $Fe(C_5H_5)(CNR)_2Br$ and $[Fe(C_5H_5)(CNR)_3]Br$ is determined primarily by the reaction stoichiometry. When two equivalents of the ligand are used the major product is $Fe(C_5H_5)(CNR)_2Br$, accompanied by smaller amounts of the other two species. Column chromatography allowed the separation of these compounds. Separations carried out on acidic alumina with chloroform as eluent gave bands in the following order and colors: orange-clear, ferrocene and unreacted isocyanide; red-brown, $Fe(C_5H_5)(CNR)_2Br$; brown, $Fe(C_5H_5)(CO)(CNR)Br$; yellow, $[Fe(C_5H_5)(CNR)_3]Br$. The last band does not move appreciably using chloroform, but can be eluted with acetone. The products obtained from the respective fractions were purified by recrystallization.

Specific details of these syntheses are presented below.

$Fe(C_5H_5)(p\text{-}CNC_6H_4NO_2)_2Br$. After refluxing the two reactants in benzene, the solution was filtered; cooling gave dark-purple crystals (62% yield) m.p. 183—184° C.

Found: C, 45.86; H, 2.70; N, 11.12; mol. wt. 520. $C_{19}H_{13}BrFeN_4O_4$ calcd.: C, 45.91; H, 2.70; N, 11.27%; mol. wt. 497. IR ν(CN): 2113vs, 2056vs, 2006(sh) cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.5—8.5 (AA'BB', C_6H_4), 4.89 (s, C_5H_5) ppm.

$Fe(C_5H_5)(m\text{-}CNC_6H_4CF_3)_2Br$. The reagents were refluxed in benzene for 1 h, then filtered. Chromatography separated the designated product which was purified by recrystallization from diethyl ether (36% yield); m.p. 136—137°C.

Found: C, 46.25; H, 2.42; N, 5.08; mol. wt. 554. $C_{21}H_{13}BrF_6FeN_2$ calcd.: C, 46.44; H, 2.41; N, 5.16%; mol. wt. 543. IR ν(CN): 2126vs, 2095s, 2063vs cm^{-1}. ^1H NMR ($(CD_3)_2CO$): δ 7.6—7.9 (m, C_6H_4), 4.85 (s, C_5H_5) ppm.

$Fe(C_5H_5)(m\text{-}CNC_6H_4Cl)_2Br$. The reactants were refluxed in toluene (15 min). Chromatography separated the desired product. It precipitated slowly from a $MeCN/CHCl_3$ solution as purple crystals (70% yield); m.p. 127.5—129°C.

Found: C, 45.52; H, 2.66; N, 5.51; mol. wt. 489. $C_{19}H_{13}BrCl_2FeN_2 \cdot 0.25$ $CHCl_3$ calcd.: C, 45.71; H, 2.64; N, 5.54%; mol. wt. 476 (without $CHCl_3$). The presence of $CHCl_3$ was verified by NMR. IR ν(CN): 2125s, 2095m, 2060s cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.2—7.5 (m, C_6H_4), 4.76 (s, C_5H_5) ppm.

$Fe(C_5H_5)(m\text{-}CNC_6H_4OMe)_2Br$. A solution of the reactants in toluene was refluxed 2.5 h. After chromatographic separation from other compounds, the product was recrystallized from $MeCN/Et_2O$ as dark purple crystals (41% yield); m.p. 91—92°C.

Found: C, 53.82; H, 4.20; N, 5.93; mol. wt. 457. $C_{21}H_{19}BrFeN_2O_2$ calcd.: C, 53.99; H, 4.03; N, 6.00%; mol. wt. 467. IR ν(CN): 2125s, 2075s cm^{-1}. ^1H NMR ($CDCl_3$): δ 6.7—7.3 (m, C_6H_4), 4.73 (s, C_5H_5), 3.81 (s, CH_3) ppm.

$Fe(C_5H_5)(p\text{-}CNC_6H_4F)_2Br$. Refluxing of the reactants in benzene for 16 h followed by crystallization of the crude product from Et_2O gave this compound as dark brown crystals, (44% yield), m.p. 121—122.5°C.

Found: C, 51.39; H, 3.00; N, 6.26; mol. wt. 435. $C_{19}H_{13}BrF_2FeN_2$ calcd.: C, 51.51; H, 2.95; N, 6.32%; mol. wt. 443. IR ν(CN): 2126s, 2084s, 2037(sh) cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.0—7.6 (m, C_6H_4), 4.74 (s, C_5H_5) ppm.

$Fe(C_5H_5)(m\text{-}CNC_6H_4Me)_2Br$. 3 h reflux in toluene gave the product which was purified by chromatography and crystallization from $MeCN/Et_2O$ (55% yield); m.p. 124—125°C.

Found: C, 57.90; H, 4.54; N, 6.53; mol. wt. 432. $C_{21}H_{19}BrFeN_2$ calcd.: C, 57.96; H, 4.40; N, 6.43%; mol. wt. 435. IR ν(CN): 2124s, 2085s, 2062(sh) cm^{-1}. ^1H NMR ($CDCl_3$): δ 6.9—7.4 (m, C_6H_4), 4.71 (s, C_5H_5), 2.32 (s, CH_3) ppm.

$Fe(C_5H_5)(p\text{-}CNC_6H_4Me)_2Br$. 8 h reflux in benzene was required. The reaction mixture was filtered, evaporated and the residue crystallized from $CHCl_3$/hexane and recrystallized from hexane (67% yield); m.p. 122—124°C.

Found: C, 57.86; H, 4.60; N, 6.49; mol. wt. 435. $C_{21}H_{19}BrFeN_2$ calcd.: C, 57.96; H, 4.40; N, 6.43%; mol. wt. 435. IR ν(CN): 2128s, 2087s, 2042m cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.1—7.4 (AA'BB', C_6H_4), 4.68 (s, C_5H_5), 2.55 (s, CH_3) ppm.

$Fe(C_5H_5)(p\text{-}CNC_6H_4OMe)_2Br$. Prepared from the reactants upon 16 h reflux in benzene. Filtration and evaporation gave the crude product which was recrystallized from Et_2O/hexane as dark brown crystals (51% yield); m.p. 115—117°C.

Found: C, 54.19; H, 4.13; N, 5.97; mol. wt. 469. $C_{21}H_{19}BrFeN_2O_2$ calcd.: C, 53.99; H, 4.03; N, 6.00%; mol. wt. 467. IR ν(CN): 2128s, 2088s, 2048(sh) cm^{-1}. ^1H NMR ($CDCl_3$): δ 6.8—7.6 (AA'BB'), C_6H_4), 4.68 (s, C_6H_5); 3.80 (s, CH_3) ppm.

Preparations of several $[Fe(C_5H_5)(CO)_{3-n}(CNR)_n]PF_6$ compounds

$[Fe(C_5H_5)(CO)_2(p\text{-}CNC_6H_4F)]PF_6$. A solution of $[Fe(C_5H_5)(CO)_2(THF)]PF_6$ (1.0 g, 2.6 mmol) and p-CNC_6H_4F (0.31 g, 2.6 mmol) in acetone (30 ml) was stirred under N_2 for 20 h. The acetone was evaporated and the residue chromatographed on alumina with acetone as eluent. Two bands were apparent. The first was yellow in color and was collected. The second band was red and did not move with acetone; perhaps this was unreacted starting material. Solvents was removed from the fraction collected and the residue remaining was crystallized from acetone/chloroform to give a yellow powder (0.40 g, 36% yield); m.p. 169—170.5°C.

Found: C, 38.00, H, 2.15; N, 3.13. $C_{14}H_9F_7FeO_2NP$ calcd.: C, 37.95; H, 2.05; N, 3.16%. IR ν(CN): 2192s, ν(CO) 2088s, 2046s cm^{-1}. ^1H NMR ($(CD_3)_2CO$) δ 7.2—7.9 (m, C_6H_4), 5.94 (s, C_5H_5) ppm.

$[Fe(C_5H_5)(CO)(p\text{-}CNC_6H_4F)_2]PF_6$. An acetone solution of $[Fe(C_5H_5)(CO)_2$-$(THF)]PF_6$ (1.0 g, 2.6 mmol) and p-CNC_6H_4F 90.63 g, 5.2 mmol) was stirred under N_2 for 4 h. The solvent was removed on a rotary evaporator, and the residue was chromatographed on alumina. Elution with chloroform gave four bands. The first three bands contained ferrocene, unreacted isocyanide and some other unidentified neutral products. The fourth band collected was yellow in color and contained the product. This material was purified by crystallization from $MeOH/Et_2O$ (0.46 g, 33% yield); m.p. 167—168°C.

Found: C, 44.78; H, 2.51; N, 5.15. $C_{20}H_{13}F_8FeN_2OP$ calcd.: C, 44.81; H, 2.44; N, 5.22%. IR ν(CN): 2188vs; 2158vs; ν(CO): 2018vs cm^{-1}. ^1H NMR ($(CD_3)_2CO$): δ 7.1—7.8 (m, C_6H_4), 5.66 (s, C_5H_5) ppm.

$[Fe(C_5H_5)(p\text{-}CNC_6H_4F)_3]PF_6$. This compound was prepared following the general procedure used for the synthesis of similar compounds [4]. An excess of p-CNC_6H_4F (1.4 g, 11.6 mmol) was added to a solution of $Fe(C_5H_5)(CO)_2Br$ (0.89 g, 3.5 mmol) in benzene (70 ml). The solution was then refluxed for 4 h. The resulting yellow precipitate was collected by filtration. This material was dissolved in acetone and added to a saturated solution of NH_4PF_6 in acetone. The product precipitated as orange crystals upon the addition of hexane (1.2 g, 54% yield); m.p. 223—224°C.

Found: C, 49.73; H, 2.89; N, 6.56. $C_{26}H_{17}F_9FeN_3P$ calcd.: C, 49.63; H, 2.72; N, 6.68%. IR ν(CN): 2176s, 2126s cm^{-1}. ^1H NMR ($(CD_3)_2CO$): δ 7.2—7.7 (m, C_6H_4), 5.50 (s, C_5H_5) ppm.

$[Fe(C_5H_5)(p\text{-}CNC_6H_4Me)_3]PF_6$. This compound, prepared by the procedure outlined above, crystallized from acetone/Et_2O as orange crystals (55% yield) m.p. 212.5—214°C.

Found: C, 56.19; H, 4.23; N, 6.73. $C_{29}H_{26}F_6FeN_3P$ calcd.: C, 56.42; H, 4.24; N, 6.81%. IR ν(CN): 2178s, 2123s, 2043w cm^{-1}. ^1H NMR ($(CD_3)_2CO$): δ 7.2—7.5 (AA'BB', C_6H_4), 5.33 (s, C_5H_5), 2.34 (CH_3) ppm.

$[Fe(C_5H_5)(m\text{-}CNC_6H_4Cl)_3]PF_6$. Prepared as yellow crystals by the method outlined above (65% yield) m.p. 220—221°C.

Found: C, 42.88; H, 2.50; N, 6.09. $C_{26}H_{17}Cl_3F_6FeN_3P$ calcd.: C, 44.0; H, 2.52; N, 6.19%. IR ν(CN): 2178s, 2125s, 2076(sh) cm^{-1}. ^1H NMR ($(CD_3)_2CO$): δ 7.4—7.7 (m, C_6H_4), 5.52 (s, C_5H_5) ppm.

Attempted oxidation of $Fe(C_5H_5)(CNR)_2X$ compounds

Controlled potential electrolysis of $Fe(C_5H_5)(p\text{-}CNC_6H_4F)_2Br$. A sample of $Fe(C_5H_5)(p\text{-}CNC_6H_4F)_2Br$ (1.0 g, 2.2 mmol) was dissolved in acetonitrile (25 ml) along with $(Bu_4N)ClO_4$ (0.87 g, 2.5 mmol) as base electrolyte. The electrolysis was carried out at a potential of 0.60 V vs. SCE over a period of 14.5 h. A total of 39.5 Coulombs or approximately 0.4 mmol of electrons were utilized in this period. Workup of the reaction gave 0.32 g $[Fe(C_5H_5)(p\text{-}CNC_6H_4F)_3]Br$ (36% yield based on available $p\text{-}CNC_6H_4F$), identified by IR spectroscopy.

Attempted oxidation of $Fe(C_5H_5)(p\text{-}CNC_6H_4F)_2Br$ with $AgPF_6$. An 0.5 g (1.12 mmol) sample of $Fe(C_5H_5)(p\text{-}CNC_6H_4F)_2Br$ was dissolved in 5 ml acetone, and 0.29 g (1.4 mmol) of $AgPF_6$ in 5 ml acetone was added. The solution quickly became dark red in color. After stirring several hours the solution was filtered and the solvent evaporated giving a red oil. This was dissolved in MeCN; upon addition of Et_2O and petroleum ether yellow crystals began to form. This product was filtered and identified as $[Fe(C_5H_5)(p\text{-}CNC_6H_4F)_3]PF_6$ by its infrared spectrum (0.44 g, 94% yield based on available $p\text{-}CNC_6H_4F$).

Thr grey-white solid which precipitates in this reaction dissolves completely in $NH_{3(aq)}$, indicating it is only AgBr; no Ag metal is formed.

Similar reactions were carried out using $Fe(C_5H_5)(p\text{-}CNC_6H_4Me)_2Br$, giving a 94% yield of $[Fe(C_5H_5)(p\text{-}CNC_6H_4Me)_3]PF_6$, and $Fe(C_5H_5)(m\text{-}CNC_6H_4Cl)_2Br$, giving a 37% yield of $[Fe(C_5H_5)(m\text{-}CNC_6H_4Cl)_3]PF_6$. Both compounds were identified by infrared and NMR data.

In the latter reaction an attempt was made to determine what the red intermediate product(s) were. After mixing the reactants the solution was placed on a neutral alumina chromatography column. A red band eluted with acetone. Upon evaporation a hard red oil was obtained which could not be purified further. Attempts to dissolve this material in other solvents ($CHCl_3$) hastened its decomposition to $[Fe(C_5H_5)(m\text{-}CNC_6H_4Cl)_3]PF_6$. The ^1H NMR of this substance, run in $(CD_3)_2CO$, showed resonances δ 7.5—7.8 and 4.87, which do not correspond to starting material or product.

NMR Studies on reaction with $AgPF_6$

Interested in obtaining more information concerning possible intermediates in these reactions, we attempted a series of experiments in which the course of the reaction was followed by ^1H NMR. These experiments entailed using accurately measured samples of the starting material and $AgPF_6$ dissolved in $(CD_3)_2CO$. Periodically the solution was sampled by syringe, filtered and placed in a NMR tube, and the spectrum recorded.

In Fig. 1, spectra at several times (0.5, and 18 h) are portrayed for a reaction of equimolar quantities of $Fe(C_5H_5)(p\text{-}CNC_6H_4F)_2Br$ and $AgPF_6$. The C_5H_5 resonance of the starting material at δ 4.84 is replaced by a group of six singlet resonances at slightly lower field (in order: δ 4.86, 4.93, 4.98, 5.00, 5.03, 5.17 ppm). At 0.5 h only a very small resonance at δ 5.50 ppm for the ultimate

(Continued on p. 283)

Fig. 1. Progress of the reaction of equivalent amounts $Fe(C_5H_5)(p\text{-}CNC_6H_4F)_2Br + AgPF_6$ in $(CD_3)_2CO$ with time as shown by 100 MHz ^1H NMR spectra. A, t 0, B, t 0.5 h; C, t 18 h; b, expansion of B.

Fig. 2. Progress of the reaction $Fe(C_5H_5)(CNPh)_2Br$ + 0.8 equiv. $AgPF_6$ in $(CD_3)_2CO$ with time as shown by 270 MHz ^1H NMR spectra (δ 5.646—4.546 ppm). a, t 0; b, t 4 min; c, t 22 min; d, t 67 min; e, t 120 min.

product $[Fe(C_5H_5)(p\text{-}CNC_6H_4F)_3]PF_6$ is seen; this peak slowly increases in intensity until at 18 h it is the only C_5H_5 proton resonance seen in the spectrum.

Similar series of spectra were recorded for reactions of $Fe(C_5H_5)(p\text{-}CNC_6H_4Me)_2Br$ and $Fe(C_5H_5)(CNPh)_2Br$ with $AgPF_6$ in acetone.

The 270 MHz ^1H NMR spectra presented in Fig. 2 shows the progress of the reaction that occurs when 0.80 equivalents of $AgPF_6$ are added to $Fe(C_5H_5)(CNPh)_2Br$ in $(CD_3)_2CO$. The spectra are of the region δ 4.546—5.646 ± 0.01 ppm. Spectrum a shows the cyclopentadienyl resonance for the starting material at δ 4.779 ppm. The spectra b—e were obtained 4, 22, 67, and 120 minutes after the addition of $AgPF_6$. These spectra are qualitatively similar to the spectra in Fig. 1. The presence of eight resonances of different intensities in spectrum b is noted. None of these resonances corresponds exactly with starting material. The low field resonance (δ 5.46 ppm) which continues to grow in intensity with time corresponds to the cationic product $[Fe(C_5H_5)(CNPh)_3]PF_6$. The two resonances at δ 4.88 and 5.10 ppm remain small and are unidentified. The three larger resonances at δ 4.910, 4.937 and 4.973 ppm appear to be a triplet, but this is ruled out since the separations are not equal (7.4 and 8.8 Hz) and the relative intensities vary with time (spectra b—d). Also spectra obtained on a 100 MHz instrument show all separations to be reduced by a factor of 2.7 which indicates that the observed resonances are singlets. The relatively small resonance at δ 4.814 ppm grows to a maximum in spectrum c while at the same time the resonance at δ 4.801 ppm disappears. 45 min later, the resonance at δ 4.814 ppm has disappeared, and a resonance corresponding to the starting material has reappeared (spectrum d).

In a different experiment, the effect of adding excess phenyl isocyanide was considered. Two NMR samples were obtained six minutes after the addition of 0.80 equivalents of $AgPF_6$ to $Fe(C_5H_5)(CNPh)_2Br$ in acetone-d_6 and were stored on dry ice. Excess CNPh (~1.5 equivalents) was added to one of the samples and the ^1H NMR spectra were recorded. The spectrum of the sample without added isocyanide resembles spectrum b in Fig. 2. The sample containing excess phenyl isocyanide has a spectrum containing only two cyclopentadienyl resonances due to the starting material and $[Fe(C_5H_5)(CNPh)_3]PF_6$.

Reaction of $Fe(C_5H_5)(CNPh)_2Br$ and $AgPF_6$ in acetonitrile, studies on the compound $[Fe(C_5H_5)(CNPh)_2(MeCN)]PF_6$

One of the possible intermediates in the reactions described above is an acetone complex $[Fe(C_5H_5)(CNR)_2(acetone)]PF_6$. In this experiment we sought indirect evidence for such a species by attempting to prepare analogous stable species with a better ligand, MeCN.

Preparation of $[Fe(C_5H_5)(CNPh)_2(MeCN)]PF_6$. Solid $AgPF_6$ (0.5 g, 1.98 mmol) was added to a solution of $Fe(C_5H_5)(CNPh)_2Br$ (0.5 g, 1.23 mmol) in acetonitrile (20 ml). The reaction mixture was stirred for 10 min at room temperature and then filtered to remove the AgBr that had formed. The acetonitrile was removed on a rotary evaporator yielding a red oil. Hexane was added on top of the oil. After 2 h at room temperature rust colored crystals had formed; these were collected by filtration and washed with water and diethyl

TABLE 2

QUALITATIVE STUDY ON THE STABILITY OF $[Fe(C_5H_5)(CNPh)_2(MeCN)]PF_6$

Solvent, reagent	Temp (°C)	Time (h)	Ratio of St. mat./prod. [a]	Conversion [b] (%)
CD_3CN	RT	<20		0
	85	48	~9	~10
CD_3CN + CNPh [c]	40	17.5	2	33
$(CD_3)_2CO$	RT	12	1.5	40
	RT	24	1.0	50
	RT	75	0.7	60
$(CD_3)_2CO$ + CNPh [c]	RT	1/6	9	10
	RT	10	1.5	40
	RT	20	0.8	55

[a] Approximate ratio of $[Fe(C_5H_5)(CNPh)_2(MeCN)]PF_6$ to $[Fe(C_5H_5)(CNPh)_3]PF_6$ as determined by integrated intensities of the $C_5\underline{H}_5$ proton resonances. [b] Conversion assumes no other products are formed. (No soluble compounds with $C_5\underline{H}_5$ resonances were seen and no decomposition was observed in RT reactions). [c] ~1.5 equiv. CNPh added.

ether. The crude product was recrystallized from acetonitrile/hexane (0.58 g, 92%) m.p. 144—145° C.

Found: C, 49.08; H, 3.54; N, 7.99. $C_{21}H_{18}Fe_6N_3P$ calcd.: C, 49.15; H, 3.54; N, 8.19%. IR KBr ν(CN): 2138s, 2100s cm^{-1}. ^1H NMR ($(CD_3)_2CO$): δ 7.4—7.8 (m, C_6H_5), 5.14 (s, C_6H_5), 2.47 (s, CH_3); (CD_3CN) 7.4—7.7 (m, C_6H_5); 4.99 (s, C_5H_5), 2.50 (s, CH_3) ppm.

Stability of $[Fe(C_5H_5)(CNPh)_2(MeCN)]PF_6$

A series of qualitative experiments were performed to determine how readily this compound converted to $[Fe(C_5H_5)(CNPh)_3]PF_6$. These experiments consisted of dissolving of a measured amount of this compound in a solvent ($(CD_3)_2CO$ or CD_3CN) in an NMR tube and monitoring intensities of the cyclopentadienyl proton resonances in the ^1H NMR spectrum. The starting material shows a singlet at δ 5.14 in $(CD_3)_2CO$ or at 4.99 ppm in CD_3CN while the product spectrum has singlets at either δ 5.46 in $(CD_3)_2CO$ or 5.40 ppm in CD_3CN. In some experiments CNPh (~1.5 equivalents) was added. The results are presented below in Table 2.

Discussion

Reactions of $Fe(C_5H_5)(CO)_2X$ compounds (X = Cl, Br, I) with an isocyanide, CNPh, were first reported by Joshi, Pauson, and Stubbs in 1963 [3]. The products obtained, $Fe(C_5H_5)(CNPh)(CO)I$, $Fe(C_5H_5)(CNPh)_2X$ (X = Br, I) and $[Fe(C_5H_5)(CNPh)_3]Cl$, were determined by the choice of starting material and the stoichiometry of the reactants. There are later reports of the syntheses of two other $[Fe(C_5H_5)(CNR)_3]Cl$ compounds (R = p-C_6H_4OMe [8], Me [4]) by the procedure used to synthesize the analogous CNPh compound. Also the compounds $[Fe(C_5H_5)(CO)_2(CNMe)]PF_6$ and $[Fe(C_5H_5)(CO)(CNMe)_2]PF_6$ have been made by alkylation of cyanometallate precursors [5].

In this paper we report the syntheses of a series of $Fe(C_5H_5)(CNR)_2Br$ com-

pounds, by the reaction of $Fe(C_5H_5)(CO)_2Br$ and various CNR ligands; viz.:

$$Fe(C_5H_5)(CO)_2Br + 2\ CNR \rightarrow Fe(C_5H_5)(CNR)_2Br + 2\ CO$$

(R = C_6H_5, p-C_6H_4Me, p-C_6H_4OMe, m-C_6H_4OMe, p-C_6H_4F, m-C_6H_4Cl, m-$C_6H_4CF_3$, p-$C_6H_4NO_2$)

These reactions were run in refluxing benzene or toluene for several hours; the progress of the reaction could be followed by monitoring the disappearance of ν(CO) absorptions in an infrared spectrum. Reactions run in toluene are of shorter duration but otherwise identical to reactions in benzene. Use of slightly over two equivalents of ligand is advantageous in the workup of reaction products; the amount of $Fe(C_5H_5)(CO)(CNR)Br$ is minimized, and although some of the ionic compound $[Fe(C_5H_5)(CNR)_3]Br$ does form this is easily separated. Good yields of the brown or purple, crystalline, air stable products, $Fe(C_5H_5)(CNR)_2Br$ are usually obtained. Characterization was accomplished by standard means.

One usual feature of these compounds is the fact that, excepting $Fe(C_5H_5)(p\text{-}CNC_6H_4OMe)_2Br$, all have three rather than two IR absorptions in the ν(CN) region. This number of absorptions may arise because of coupling of ν(CN) with certain vibrations of the phenyl rings, or because of the existence of two forms differing by virtue of the orientations of the planes of the two phenyl rings. Whatever the reason, this observation is not uncommon in isocyanide complex chemistry; a larger than predicted number of absorptions in the ν(CN) region is also seen for octahedral $Cr(CNR)_6$ (R = aryl) compounds [9,10].

Excess CNR ($\geqslant$3/1) reacts with $Fe(C_5H_5)(CO)_2Br$ to precipitate ionic products $[Fe(C_5H_5)(CNR)_3]Br$ from the reaction mixture. These were isolated and converted to PF_6 salts by metathetical reaction with NH_4PF_6.

$$Fe(C_5H_5)(CO)_2Br + xs\ CNR \rightarrow [Fe(C_5H_5)(CNR)_3]Br + 2\ CO$$

(R = p-C_6H_4F, p-C_6H_4Me)

Similar reactions have been reported using $Fe(C_5H_5)(CO)_2Cl$ [3,4,8]. Reactions of $Fe(C_5H_5)(CO)_2Br$ are slower, and more easily interrupted at an intermediate stage, but suffice well in the preparation of these compounds.

The syntheses of $[Fe(C_5H_5)(CO)_{3-n}(CNC_6H_4F)_n]PF_6$ compounds (n = 1, 2) are accomplished from reactions of $[Fe(C_5H_5)(CO)_2(THF)]PF_6$ [7], the stoichiometry determining whether one or two CNR groups are found in the final product.

Using cyclic voltammetry, we observed that each $Fe(C_5H_5)(CNR)_2Br$ compound undergoes a single one electron oxidation in MeCN, viz.:

$$Fe(C_5H_5)(CNR)_2Br \rightleftharpoons [Fe(C_5H_5)(CNR)_2Br]^+ + e$$

Oxidation potentials ($E_{1/2}$ values) are in the range 0.45—0.63 V vs. SCE. No other oxidations or reductions are observed. The ratio of anodic to cathodic peak currents is near unity indicating a chemically reversible process with no decomposition of oxidized products over the span of time associated with the experiment (roughly 2—20 s for sweep rates of 50—500 mV/s). These systems do not meet the criterion for electrochemical reversibility, $E_{p,c}-E_{p,a} \leqslant$ 0.059 V. However they are quasi-reversible, implying a slow rate of electron transfer relative to sweep rate [11]. This phenomenon has been encountered

regularly in the non-aqueous electrochemistry of organometallic complexes [9,12].

Previously we reported good correlations between $E_{1/2}$ data for metal complexes of aryl isocyanides and Hammett substituent group parameters σ_p or σ_m for substituent groups on the aryl ring [9,12]. A similar excellent correlation is found using these data for the nine $Fe(C_5H_5)(CNC_6H_4R)_2Br$ compounds reported here. The degree of correlation can be seen in a graph of these data (Fig. 3), and verified in a numerical analysis which gives a least squares equation $\sigma = 5.90\ E_{1/2} - 3.00$ with a correlation coefficient at 0.982 [13,14]. The reaction constant can be determined from the slope of this line, taking into account the fact that two ligands are present; its value is 0.0847. This value is similar to ρ values for oxidation reactions of $Cr(CNC_6H_4R)_6$ [9] and $[Mn(CNC_6H_4R)_6]PF_6$ [12].

In passing we note one other very good correlation, between $E_{1/2}$ data and the chemical shift of the C_5H_5 protons. Chemical shifts ranged from δ 4.681 (p-OMe) to 4.890 (p-NO_2) ppm and are related to Hammett σ_p or σ_m values by the equation $\delta = 1.139\sigma + 4.142$, with a correlation coefficient [14] of 0.955.

Additional electrochemical data were accumulated for the cationic compounds $[Fe(C_5H_5)(CO)_{3-n}(CNR)_n]PF_6$ (n = 2, 3; R = p-C_6H_4F, CH_3). Chemically reversible processes are found for the two $[Fe(C_5H_5)(CNR)_3]PF_6$ compounds, with the methyl isocyanide compounds being more easily oxidized. This result has some precedence [12].

The electrochemical data for the $Fe(C_5H_5)(CNR)_2Br$ compounds suggest that chemical oxidations of these species to the 17 electron complexes $[Fe(C_5H_5)(CNR)_2Br]^+$ ought to be possible. Such compounds would be analogous to the known 17 electron complexes $[Fe(C_5H_5)(dpe)X]PF_6$ isolated earlier by reactions of the 18 electron precursors with $AgPF_6$ [1]. However, in preliminary

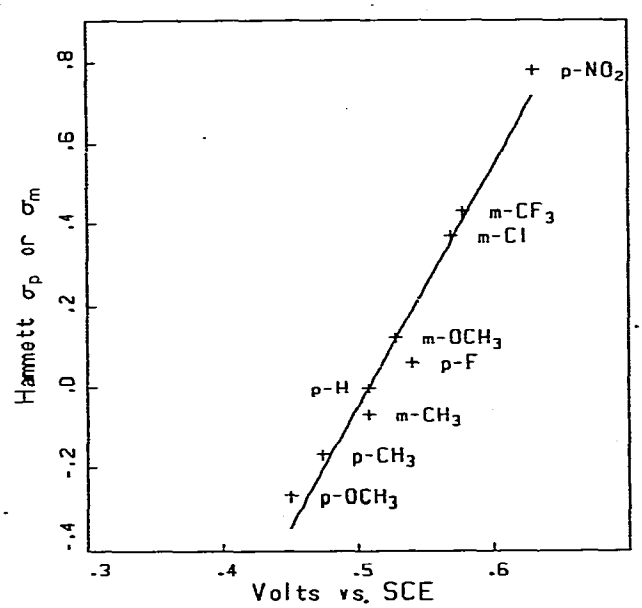

Fig. 3. Hammett σ_p or σ_m parameters vs. $E_{1/2}$ data for the $Fe(C_5H_5)(CNC_6H_4X)_2Br$ series.

work, an attempt had been made to oxidize both $[Fe(C_5H_5)(CNPh)_2I$ and $Fe(C_5H_5)(CO)(CNPh)I$ with $NOPF_6$; products obtained were $[Fe(C_5H_5)(CNPh)_3]^+$ and $[Fe(C_5H_5)(CO)(CNPh)_2]^+$ respectively [1]. Similar reactions of $Mn(CO)(CNR)_4X$ and $Mn(CNR)_5X$ with $AgPF_6$ give the 18 electron products $[Mn(CO)(CNR)_5]^+$ and $[Mn(CNR)_6]^+$ [2]. Only AgX is found in these reactions; the absence of Ag metal precludes oxidation having occurred. We believe that halide loss (as AgX) from these precursors precedes a rapid reaction wherein additional isocyanide (probably arising from decomposition) is scavenged to give high yields of the isolated products. In no instance is evidence found for the 17 electron compounds predicted from electrochemical studies.

The best chance to isolate the 17 electron $[Fe(C_5H_5)(CNR)_2Br]^+$ complexes was expected in oxidative processes not utilizing a halide ion acceptor such as Ag^+. Thus a controlled potential electrolysis of $Fe(C_5H_5)(p\text{-}CNC_6H_4F)_2Br$ was run in acetonitrile in ambient temperature and a potential of 0.60 V vs. SCE, slightly above the measured $E_{1/2}$ value for this compound. Over a period of 14.5 h approximately 0.19 equivalents of electrons were utilized. Workup of the reaction products yielded only $[Fe(C_5H_5)(p\text{-}CNC_6H_4F)_3]Br$. The amount of this product, 36% based on iron, exceeded the input of electrons in this process by roughly a factor of two. This leads us to speculate that the reaction ought to follow the sequence:

$$Fe(C_5H_5)(p\text{-}CNC_6H_4F)_2Br \rightarrow [Fe(C_5H_5)(p\text{-}CNC_6H_4F)_2Br]^+ + e \quad (1)$$

$$Fe(C_5H_5)(p\text{-}CNC_6H_4F)_2Br]^+ \rightarrow 2\ p\text{-}CNC_6H_4F + [C_5H_5FeBr]^+ \quad (2)$$

$$Fe(C_5H_5)(p\text{-}CNC_6H_4F)_2Br + CNC_6H_4F \rightarrow [Fe(C_5H_5)(p\text{-}CNC_6H_4F)_3]Br \quad (3)$$

A key point here is that the sought after 17*e* products are unstable at room temperature, decomposing to give isocyanide into solution. The lifetime of the 17*e* products is apparently greater than a few seconds according to the cyclic voltammograms data but less than the several hours of this electrolysis experiment. The third step in the sequence is a known reaction.

We also ran a number of reactions between $AgPF_6$ and various $Fe(C_5H_5)(CNR)_2Br$ compounds, first in acetone and later in acetonitrile. In acetone a grey solid precipitates leaving a deep red solution. The solid dissolves in $NH_{3(aq)}$ and is thus identified as AgBr and not Ag. On standing, the red solution gradually becomes yellow and the cationic product $[Fe(C_5H_5)(CNR)_3]PF_6$ can be isolated in high yield based on available isocyanide. Attempts to isolate an intermediate species were unsuccessful.

In order to obtain further information concerning the nature of the intermediate species and their rate of decomposition, we monitored these reactions by NMR. After $AgPF_6$ was added, the reaction mixture was sampled at intervals and the NMR spectrum (C_5H_5 proton region) was recorded. The result for one experiment on the reaction of $AgPF_6$ and $Fe(C_5H_5)(p\text{-}CNC_6H_4F)_2Br$ is shown in Fig. 1. Following $AgPF_6$ addition the singlet C_5H_5 resonance for the starting material was replaced by a group of seven singlet resonances at slightly lower field. At this point the resonance of the ultimate product, $[Fe(C_5H_5)(p\text{-}CNC_6H_4F)_3]PF_6$, is visible but of low intensity. 20 h are required before the intermediates in this reaction are completely converted to this product.

Figure 2 gives another series of spectra from the reaction of $Fe(C_5H_5)(CNPh)_2Br$ with 0.8 equivalents of $AgPF_6$. As in Fig. 1 a series of resonances representing intermediates are seen, and slow conversion to $[Fe(C_5H_5)(CNPh)_3]PF_6$ occurs. No starting material is seen immediately after addition of $AgPF_6$ even though less than one equivalent of $AgPF_6$ is used. After about an hour the starting material resonance reappears. One possible explanation for this observation is that the halide bridged intermediate $[Fe(C_5H_5)(CNPh)_2BrFe(C_5H_5)(CNPh)_2]PF_6$ forms when a deficiency of $AgPF_6$ is used. This would be expected [15] to react quickly with additional ligand giving $[Fe(C_5H_5)(CNPh)_3]PF_6$ and $Fe(C_5H_5)(CNPh)_2Br$.

In one further experiment excess free isocyanide was added to the solution containing the intermediates from the reaction of $Fe(C_5H_5)(CNPh)_2Br$ and 0.8 equivalents of $AgPF_6$. In the time it took to record an NMR spectrum of this mixture the reactants was converted to $[Fe(C_5H_5)(CNPh)_3]PF_6$ and $Fe(C_5H_5)(CNPh)_2Br$.

It is difficult to predict what other intermediates are present in this system. One obvious possible species is an acetone complex, $[Fe(C_5H_5)(CNR)_2(acetone)]PF_6$. Another possibility is that traces of water, present in the solvent, lead to complex $[Fe(C_5H_5)(CNR)_2(H_2O)]PF_6$. From this one could derive various other intermediates by loss of H^+.

Since the presence of an acetone complex was suspected it seemed worthwhile to look at reactions in other solvents. Thus the reaction of $AgPF_6$ and $Fe(C_5H_5)(CNPh)_2Br$ was run in acetonitrile. The reaction proceeds quickly and in good yield to an isolable acetonitrile complex:

$$Fe(C_5H_5)(CNPh)_2Br + AgPF_6 \xrightarrow{MeCN} [Fe(C_5H_5)(CNPh)_2(MeCN)]PF_6 + AgBr$$

This rust colored compound, $[Fe(C_5H_5)(CNPh)_2(MeCN)]PF_6$, proved remarkably stable. It could be converted to $[Fe(C_5H_5)(CNPh)_3]PF_6$ at 85°C in acetonitrile only slowly. In acetone it is less stable, being 50% converted to $[Fe(C_5H_5)(CNPh)_3]PF_6$ in about 24 h. Addition of free CNPh in either solvent accelerates this process only slightly.

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