Journal of Organometallic Chemistry, 174 (1979) 191—197
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NEW 17 ELECTRON COMPLEXES OF IRON

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(Received February 26th, 1979)

Summary

One electron oxidation reactions are predicted for $Fe(C_5H_5)(dpe)X$ * compounds according to cyclic voltammetry. These oxidations have been carried out using $AgPF_6$ as an oxidant, and a number of 17*e* complexes of the formula $[Fe(C_5H_5)(dpe)X]PF_6$ (X = Cl, Br, I, H, Me, $SnMe_3$, CN, SCN (N bonded isomer), SPh) has been isolated. The compound $[Fe(C_5H_5)(dpe)SPh]BF_4$ also is formed from addition of HBF_4 to the appropriate 18 electron precursor, while addition of a potentially stronger oxidizing agent $NOPF_6$ gives $[Fe(C_5H_5)(dpe)NO](PF_6)_2$. The compound $[Fe(C_5H_5)\{P(OPh)_3\}_2I]PF_6$ has been isolated. The 17*e* species $Fe(C_5H_5)(dpe)S_2O_3$ forms from $[Fe(C_5H_5)(dpe)(MeCN)]PF_6$ and $Na_2S_2O_3$. This may be the first organometallic compound having an S_2O_3 ligand. The 17*e* compounds are paramagnetic, with all but the CN compound having magnetic moments corresponding to one unpaired electron; the magnetic moment of the CN^- compound is abnormally low (0.55 BM).

Introduction

There has been abundant recent interest in organometallic compounds which are one electron short of the 18 electron, or EAN, configuration. Part of this interest arises because such species have been implicated as intermediates in many chemical reactions. For example much interesting chemistry associated with dinuclear metal carbonyl compounds ($Mn_2(CO)_{10}$, $Re_2(CO)_{10}$, $[M(C_5H_5)(CO)_3]_2$, etc.) begins with cleavage of the metal—metal bond in these species to generate reactive 17 electron intermediates [1]. Once generated, these 17 electron species undergo a variety of reactions of significance, or they can be trapped with a spin trapping agent or they may dimerize and regenerate the 18 electron precursor.

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* dpe ≡ 1,2-bis(diphenylphosphino)ethane.

Isolable 17 electron complexes have been known for some time (viz. $V(CO)_6$, $[Fe(C_5H_5)_2]^+$) but not until recently had much effort been directed to syntheses of wide numbers of these compounds. In 1975 we described [2] our initial work on synthesis and characterization of the 17 electron manganese and iron species, $[Mn(C_5H_4R)(CO)(dpe)]PF_6$ (R = H, Me) and $[Fe(C_5H_5)(dpe)X]$-PF_6 (X = Cl, Br, I, $SnMe_3$, Me). In this paper we describe results of a more extensive study on these and other compounds having the latter formulation.

Experimental

All reactions were routinely carried out under nitrogen, unless otherwise noted. Melting points were determined using a Thomas-Hoover capillary melting point apparatus and are uncorrected. Infrared spectra were recorded on a Beckman IR-10. Proton NMR spectra were recorded on a Jeol-NM-MH-100 spectrometer employing TMS, $\delta = 0$, as an internal standard. UV—visible spectra were recorded on a Cary-14 spectrometer. Molecular weight determinations were made in chloroform using a Mechrolab osmometer, Model 301-A. Conductivity measurements were determined at 26° C using a Beckman conductivity bridge, Model RC-18A, and a Beckman conductivity cell with cell constant $k = 0.195$ cm^{-1} on 4.0—7.0 × 10^{-4} M solutions in CH_2Cl_2. Conductivity values are corrected for conductivity due to the solvent. Magnetic susceptibility measurements were performed at five field strengths between 5.9 and 7.9 kOe on a Faraday balance calibrated against $Hg[Co(SCN)_4]$. Several complexes exhibited field dependence which was corrected for by the standard method of Honda and Owen [3]. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee.

Electrochemical measurements were made in dichloromethane using a three electrode configuration, with a stationary platinum bead working electrode, platinum spiral counter electrode, and saturated calomel (aq. KCl) reference electrode. Voltage and current functions were controlled with an A.S.S. 169 Electrochemistry System utilizing a Princeton Applied Research Model 173 Potentiostat/Galvanostat, a PAR Model 175 Universal Programmer and a Houston 2000 XY recorder. Sweep rates were varied from 50 to 200 mV/s to obtain optimum peak shapes. Tetrabutylammonium perchlorate (~ 0.1 M) served as base electrolyte. Solute concentrations were 5.0 × 10^{-3} M. Data are given in Table 1. The dichloromethane used for electrochemical measurements was distilled from phosphorus pentoxide. Tetrahydrofuran (THF) was distilled from $LiAlH_4$. Other solvents were reagent grade and were used without further purification.

Starting materials

The syntheses of most of the starting materials, $Fe(C_5H_5)(dpe)X$ (X = I, Br, CN, SCN, SPh, H, Me), were accomplished by reactions of $[Fe(C_5H_5)(dpe)(MeCN)]Br$ with X^- according to a procedure we described earlier [4]; other $Fe(C_5H_5)(dpe)X$ compounds (X = Cl, [5], $SnCl_3$, $SnBr_3$, and $SnMe_3$ [6]) and $Fe(C_5H_5)[P(OPh)_3]_2I$ [7] were prepared by procedures given in the cited references.

TABLE I

CYCLIC VOLTAMMETRIC DATA FOR $Fe(C_5H_5)$ (dpe)X COMPLEXES

X	$1/2[E_{p,a} + E_{p,c}]$ [a]	$[E_{p,c} - E_{p,a}]$ [a]
S_2O_3	−0.366	0.119
	0.769 [c]	0.113
CH_3	−0.26	0.279
SPh	−0.252	0.153
	1.166 [c]	0.144
H [b]	−0.08	0.115
Cl [b]	0.08	0.055
$SnMe_3$ [b]	0.065	0.121
Br [b]	0.11	0.065
I [b]	0.15	0.066
NCS	0.316	0.194
CN	0.535	0.136
$SnCl_3$ [b]	0.90	0.105

[a] Solutions in CH_2Cl_2; concentration of compound approximately 5×10^{-3} *M*; $[Bu_4N]ClO_4$, 0.1 *M* used as supporting electrolyte. Cathiodic and anodic peak potentials are in volts vs. saturated calomel electrode. [b] Value previously reported (ref. 2). [c] Irreversible oxidation.

Preparation of 17e complexes

$[Fe(C_5H_5)(dpe)NCS]PF_6$. To a solution of $Fe(C_5H_5)(dpe)NCS$ (1.0 g, 1.7 mmol) in acetone (200 ml) was added $AgPF_6$ (0.46 g, 1.8 mmol). The blue solution was stirred at room temperature for 30 min. The reaction mixture was then filtered to remove the precipitated silver metal. The acetone was removed from the filtrate at reduced pressure. Crystallization of the residue from MeCN/Et_2O gave burgundy crystals of the product (0.85 g, 68%) which decomposes >200°C without melting.

Anal.: found: C, 53.36; H, 4.01; P, 12.70. $C_{32}H_{29}F_6FeNP_3S$ calcd.: C, 53.20; H, 4.05; P, 12.86%. IR (KBr): $\nu(CN)$ 2040w cm^{-1}; intensity 11.2×10^4 M^{-1} cm^{-1} as determined by the method of Ramsay [8], identifies this as the *N*-bonded isomer [9]. UV (CH_2Cl_2): λ = 5820 Å (ϵ = 2300), 2310 Å ($\epsilon = 3.4 \times 10^5$) 2600 Å (sh) ($\epsilon \sim 35000$); μ_{eff} = 1.97 BM.

If excess $AgPF_6$ was used, or if additional $AgPF_6$ was added after stoichiometric quantities of the reactants were mixed, the solution changed color from blue to red. Addition of polar solvents like MeCN, or addition of KBr, reversed this change. An infrared spectrum of the red solution showed a shift of the 2040 cm^{-1} peak to 2050 cm^{-1}; we take this to indicate possible complexation of Ag^+ to the sulfur end of the —NCS ligand. Attempts to isolate a red product from this system did not succeed.

$[Fe(C_5H_5)(dpe)CN]PF_6$. To a solution of $Fe(C_5H_5)(dpe)CN$ (1.0 g, 1.8 mmol) in acetone (250 ml) was added $AgPF_6$ (0.47 g, 1.9 mmol). The solution was stirred at room temperature for 20 min, then filtered to remove precipitated silver. The acetone was removed at reduced pressure. The residue was crystallized from acetone/MeOH giving $[Fe(C_5H_5)(dpe)CN]PF_6$ as a yellow powder (0.9 g, 71%); decomposes at 200°C, without melting.

Anal.: found: C, 55.47; H, 4.45; P, 13.26. $C_{32}H_{29}Fe_6FeNP_3$ calcd.: C, 55.68; H, 4.23; P, 13.46%. IR (KBr): $\nu(CN)$ 2055ms cm^{-1}. μ_{eff} = 0.486—0.566 BM (slight field dependence); Λ_M (in MeCN) = 66.75 cm^2 S mol^{-1}.

[Fe(C$_5$H$_5$)(dpe)Me]PF$_6$. Obtained in a similar reaction, and recrystallized as brown-yellow plates from CHCl$_3$/Et$_2$O (79%), m.p. 155°C (dec.).

Anal.: found: C, 57.12; H, 4.77; P, 13.54. $C_{32}H_{32}F_6P_3Fe$ calcd.: C, 56.57; H, 4.75, P, 13.68%. μ_{eff} = 2.18 BM, Λ_M (CH$_2$Cl$_2$) = 62.5 cm^2 S mol^{-1}.

[Fe(C$_5$H$_5$)(dpe)Cl]PF$_6$. Prepared in a similar fashion; orange-red prisms obtained from CH$_2$Cl$_2$/Et$_2$O (58%), m.p. 175—177°C.

Anal.: found: C, 53.88; H, 4.12; P, 13.58. $C_{31}H_{29}ClF_6P_3Fe$ calcd.: C, 53.22; H, 4.15; P, 13.02%. μ_{eff} = 2.13 BM, Λ_M = 55.0 cm^2 S mol^{-1}.

[Fe(C$_5$H$_5$)(dpe)Br]PF$_6$. Obtained in a similar fashion; red-brown prisms from CH$_2$Cl$_2$/Et$_2$O (37%), m.p. 188—189°C.

Anal.: found: C, 49.55; H, 3.75; P, 12.52. $C_{31}H_{29}BrF_6P_3Fe$ calcd.: C, 50.00; H, 3.90; P, 12.23%. μ_{eff} = 2.12 BM, Λ_M = 53.5 cm^2 S mol^{-1}.

[Fe(C$_5$H$_5$)(dpe)I]PF$_6$. Prepared in a similar reaction. This product proved very difficult to crystallize and consequently was not obtained pure enough for good microanalyses. (Crude yield, 70%); m.p. 145°C (dec.).

[Fe(C$_5$H$_5$)(dpe)SnMe$_3$]PF$_6$. Prepared in a similar manner, crystallized from MeOH/i-C$_5$H$_{12}$ as orange prisms (33%).

Anal: found: C, 49.20; H, 4.54; P, 10.65; $C_{34}H_{38}F_6P_3SnFe$ calcd.: C, 49.39; H, 4.60; P, 11.02%. Λ_M = 51.4 cm^2 S mol^{-1}.

[Fe(C$_5$H$_5$)(dpe)SPh]PF$_6$. Addition of AgPF$_6$ (0.15 g, 0.59 mmol) to Fe(C$_5$H$_5$)(dpe)SPh (0.3 g, 0.48 mmol) in acetone resulted in a rapid color change from black to red-brown. After stirring for 5 min, the solvent was removed on a rotary evaporator. The residue was dissolved in CH$_2$Cl$_2$ and filtered. The CH$_2$Cl$_2$ was then removed and the product was crystallized from MeOH/Et$_2$O as black crystals (0.15 g, 40%); m.p. 205—207°C.

UV (CH$_2$Cl$_2$): λ_{max} = 5820 Å, $\epsilon = 1.39 \times 10^3$. (Slow decomposition in CH$_2$Cl$_2$ noted.)

The same complex as the BF$_4^-$ salt was also obtained by oxidation using H$_3$O$^+$. Addition of excess aqueous HBF$_4$ (~50 mmol) to a solution of Fe(C$_5$H$_5$)(dpe)SPh (0.2 g, 0.32 mmol) in acetone caused an immediate color change from green-brown to blue. The volume of solution was reduced to approximately 10 ml on a rotary evaporator. On standing for 12 h, a black microcrystalline complex formed. The product, [Fe(C$_5$H$_5$)(dpe)SPh]BF$_4$, was recrystallized from MeOH/Et$_2$O as a methanol solvate (0.17 g, 75%); softens at 120°C, m.p. 200—202°C.

Anal.: found: C, 60.99; H, 5.17; P, 8.49. $C_{37}H_{34}BF_4FeP_2S \cdot CH_3OH$ calcd.: C, 61.07; H, 5.12; P, 8.28%. Λ_M (MeCN) = 138 cm^2 S mol^{-1}.

Attempted oxidation of Fe(C$_5$H$_5$)(dpe)SPh by NOPF$_6$

Addition of excess NOPF$_6$ to a solution of Fe(C$_5$H$_5$)(dpe)SPh (0.1 g, 0.16 mmol) in acetone (20 ml) resulted in a color change from dark brown to dark red to orange within 5 min. The solvent was removed on a rotary evaporator. Addition of methanol and diethyl ether to the residual oil resulted in the formation of a yellow precipitate which was collected by filtration. On standing for 15 h at room temperature an additional product (orange crystals) formed in the filtrate. These were collected by filtration and washed with Et$_2$O (0.074 g, 55%), decomposes at 153—154°C. This complex was identified as [Fe(C$_5$H$_5$)(dpe)NO](PF$_6$)$_2$.

Anal.: found: C, 44.11; H, 3.75. $C_{31}H_{29}F_{12}FeNOP_4$ calcd.: C, 44.36; H, 3.48%. IR (KBr): ν(NO) 1885s cm^{-1}. ^{1}H NMR ($(CD_3)_2CO$), δ 7.6—8.3 (m, $C_6\underline{H}_5$), 6.4 (br, C_5H_5), 4.0 (m, $C\underline{H}_2$).

$Fe(C_5H_5)(dpe)S_2O_3$. Sodium thiosulfate (1.2 g, 7.8 mmol) and [$Fe(C_5H_5)$(dpe)(MeCN)]Br (1.0 g, 1.6 mmol) were added to 50 ml of methanol and the solution was refluxed for 10 min which resulted in a color change from red to purple. The methanol was removed on a rotary evaporator and the residue was chromatographed on acidic alumina (2 × 15 cm). Elution with CH_2Cl_2/MeOH (9/1) yielded a purple band which was collected. The solvent was removed from this band and acetonitrile was added to the residue. The product precipitated on standing as a dark purple powder and was recrystallized from CH_2Cl_2 by slow evaporation as dark red crystals (0.25 g, 25%), m.p. 172.5—173°C.

Anal.: found: C, 58.64; H, 4.89; S, 9.96%; mol. wt., 615. $C_{31}H_{29}FeO_3P_2S_2$ calcd.: C, 58.96; H, 4.63; S, 10.15%; mol. wt., 631.5. IR (KBr): 1475w, 1430m, 1302vw, 1210s *, 1155(sh), 1085w, 1010s *, 870w, 825w, 785w, 738w, 690m, 665(sh), 600m *, 520m cm^{-1}. UV (CH_2Cl_2): λ_{max} = 5700 Å ($\epsilon = 1.68 \times 10^3$); μ_{eff} (field dependent, extrapolated to 1/H = 0) = 1.95 BM.

[$Fe(C_5H_5)\{P(OPh)_3\}_2I$]$PF_6$. To a solution of $Fe(C_5H_5)\{P(OPh)_3\}_2I$ (0.50 g, 0.58 mmol) in dry benzene (30 ml) was added solid $NOPF_6$ (0.11 g, 0.63 mmol) and the solution stirred for 6 h at room temperature, after which time a dark green solid had precipitated. Filtration and washing with Et_2O afforded the product (0.537 g, 92% yield) as blue green crystals. Crystallization form acetone/Et_2O gave blue green needles, m.p. 112—114°C.

Anal.: found: C, 48.91; H, 3.51; P, 8.98. $C_{41}H_{35}F_6IO_6P_3Fe$ calcd.: C, 48.57; H, 3.46; P, 8.98. μ_{eff} = 2.20 BM, Λ_M = 58.8 cm^2 S mol^{-1}.

Attempted preparation of [$Fe(C_5H_5)(dpe)H$]PF_6. When $AgPF_6$ (0.062 g, 0.4 mmol) was added to a solution of $Fe(C_5H_5)$(dpe)H (0.20 g, 0.38 mmol) in acetone, the yellow solution immediately blackened. Removal of the solvent, extraction with chloroform and evaporation gave a yellow oil; crystallization from CH_2Cl_2/Et_2O gave [$Fe(C_5H_5)$(dpe)Cl]PF_6 (0.057 g, 21%) as the only product, identified by its infrared spectrum.

Discussion

Most of the electron rich 18 electron precursors used in this study were known previously, having been prepared either by direct reaction of dpe with $Fe(C_5H_5)(CO)_2X$, by anion exchange from $Fe(C_5H_5)$(dpe)X, or by displacement of acetonitrile from the complex [$Fe(C_5H_5)$(dpe)(MeCN)]Br [4]. The third method is probably the most convenient route to a large number of compounds.

The product of the reaction of [$Fe(C_5H_5)$(dpe)(MeCN)]Br with sodium thiosulfate in methanol, a dark red crystalline material, turned out to be the 17*e* compound, $Fe(C_5H_5)(dpe)S_2O_3$. This formulation was determined by elemental analyses and the paramagnetic nature of this compound (low-spin, one unpaired electron per molecule) was confirmed by magnetic susceptibility measurements.

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* Peaks due to S_2O_3.

Why a 17 electron species rather than an 18 electron compound was isolated is not clear, but it may be noted that the 18 electron precursor was found to have a very low oxidation potential by cyclic voltammetry. No oxidizing agent was identified in this synthesis, and perhaps oxidation was a consequence of contact with air in the work up.

The most logical structure for $Fe(C_5H_5)(dpe)S_2O_3$ is one containing a unidentate sulfur bonded $S_2O_3^{2-}$ ligand. The infrared spectrum contains absorptions at 1210s, 1010s, adn 600m cm^{-1} in accord with this formulation [10]. As far we can determine, this is the first known organometallic complex with the S_2O_3 ligand.

Each of the starting materials was shown by cyclic voltammetry to undergo a single electron oxidation:

$$Fe(C_5H_5)(dpe)X \rightleftharpoons [Fe(C_5H_5)(dpe)X]^+ + e$$

Cathodic and anodic peak currents are equal, indicative of chemical reversibility. The peak separation are greater than 0.059 V, and vary with sweep rate, in a manner typical of a quasi-reversible electron transfer process [11]. The required potentials for oxidations vary widely, from —0.366 V (vs. SCE) for the S_2O_3 compound to +0.90 V for the $SnCl_3$ compound. There is no good correlation between $E_{1/2}$ value and the ligands involved, expect that the complexes of two ligands which are generally believed to be π acceptors ($SnCl_3^-$, CN^-) have significantly higher $E_{1/2}$ values. The $SnCl_3^-$ complex has a particularly high $E_{1/2}$ value and, in fact, it was not possible to oxidize this compound to a 17*e* system by chemical means.

Excepting the $SnCl_3^-$ complex and of course the 17 electron complex $Fe(C_5H_5)(dpe)S_2O_3$, all of the $Fe(C_5H_5)(dpe)X$ complexes could be chemically oxidized by $AgPF_6$. In this process silver metal precipitates:

$$Fe(C_5H_5)(dpe)X + AgPF_6 \rightarrow [Fe(C_5H_5)(dpe)X]PF_6 + Ag$$

Isolated products are the 17*e* species. These compounds were characterized by analyses. They were found to be paramagnetic, as expected, with magnetic moments equivalent to one unpaired electron excepting the cyano compound which has an anomalously low value. This latter compound also has an unusually low conductivity value for a 1 : 1 electrolyte, 66.8 cm^2 S mol^{-1} in MeCN vs an expected value in the range of 135—155 cm^2 S mol^{-1}.

An attempt was made to protonate the compound $Fe(C_5H_5)(dpe)SPh$, in hopes of preparing $[Fe(C_5H_5)(dpe)(PhSH)]^+$. Such a compound would have been of particular interest to us. Earlier we prepared the compound $[Fe(C_5H_5)(CO)_2(PhSH)]PF_6$ and studied its acid strength [12], and we were interested in determining the effect of dpe substitution on this property. However, addition of acid, even at low temperature, gave the oxidized product and hydrogen.

The cyclic voltammetry study on $Fe(C_5H_5)(dpe)SPh$ identified a second reversible one electron oxidation for this substance at a relatively low potential, 1.17 V vs. SCE. We tried unsuccessfully to duplicate this process using the chemical oxidant $NOPF_6$, but obtained only the 18 electron product $[Fe(C_5H_5)(dpe)NO](PF_6)_2$. Here NO^+ has replaced SPh^- as a ligand.

Although both isomers, $Fe(C_5H_5)(CO)_2SCN$ and $Fe(C_5H_5)(CO)_2NCS$, are known [13] and are presumably of similar stability, the dpe compound $Fe(C_5H_5)(dpe)NCS$ exists only as the *N*-bonded isomer. This was established by determining the intensity of the $\nu(CN)$ stretching mode at 2108 cm^{-1} ($\epsilon = 7.0 \times 10^4\ M^{-1}\ cm^{-2}$) [8,9]. A second absorption at 810 cm^{-1} due to $\nu(CS)$ was also recorded. On oxidation to $[Fe(C_5H_5)(dpe)NCS]PF_6$ the former absorption shifted to 2040 cm^{-1} ($\epsilon = 11.2 \times 10^4\ M^{-1}\ cm^{-2}$). The latter was obscured by $\nu(PF)$ of the anion. Again the integrated intensity of $\nu(CN)$ is in accord with an *N*-bonded isomer.

This compound also was interesting for another reason. A blue solution of the 17*e* species $[Fe(C_5H_5)(dpe)NCS]PF_6$ became red if excess Ag^+ was added. Addition of acetonitrile, a more polar solvent, or KBr, caused a return to the original blue color. An infrared spectrum of the red solution showed that $\nu(CN)$ had shifted to 2050 cm^{-1}. This new value is in the region anticipated for a NCS group bridging two metals [13] and suggests that complexation of Ag^+ to the sulfur end of this ligand may be occurring. Unfortunately, attempts to isolate such a species were not successful.

The formation of $[Fe(C_5H_5)[P(OPh)_3]_2I]PF_6$ using $NOPF_6$ as an oxidant is also noted. The weaker oxidizing agent Ag^+ does not give this product, but gave $[Fe(C_5H_5)[P(OPh)_3]_3]^+$ [14]. Formation of a 17 electron product contrasts with the reaction of a similar compound $Fe(C_5H_5)(CNPh)_2I$, with various reagents to give only $Fe(C_5H_5)(CNR)_3]^+$ [2].

Acknowledgement

We thank Mr. C. Feldmann for assistance in determining magnetic susceptibilities.

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