Multiple Oxidation States in the $[(\pi\text{-}C_5H_5)Fe(CO)]_4$ Cluster System

John A. Ferguson and Thomas J. Meyer*

Contribution from the Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina 27514. Received September 13, 1971

Abstract: Tetrakis(π-cyclopentadienyliron carbonyl) exists in four electrochemically reversible oxidation states, $[(\pi\text{-}C_5H_5)Fe(CO)]_4{}^{2+/+/0/-}$. The cluster remains intact in all four oxidation states. The monocation, $[(\pi\text{-}C_5H_5)Fe(CO)]_4{}^+$, has been isolated as the hexafluorophosphate salt and the anion, $[(\pi\text{-}C_5H_5)Fe(CO)]_4{}^-$, has been characterized in acetonitrile and tetrahydrofuran solutions. The dication has been observed as a transient in several solvents. Attempts to isolate $[(\pi\text{-}C_5H_5)Fe(CO)]_4{}^{2+}$ have resulted in the decomposition of the cluster to Fe^{2+} and $[(\pi\text{-}C_5H_5)Fe(CO)_2S]^+$ (S = acetonitrile or *n*-butyronitrile).

Tetrakis(π-cyclopentadienyliron carbonyl), $[(\pi\text{-}C_5H_5)Fe(CO)]_4$, prepared by King,[1] has the structure in Figure 1.[2] King also reported that the cluster is oxidized by bromine in dichloromethane to give the stable paramagnetic salt $[(\pi\text{-}C_5H_5)Fe(CO)]_4Br_3$ which is reduced to the neutral cluster by hydrazine. We found King's observations especially interesting since it appeared that the iron carbonyl cluster was one of the relatively few examples of compounds which contain strong metal–metal bonds and which also remain structurally intact in more than one molecular oxidation state.[3–7]

In earlier work we have demonstrated the usefulness of electrochemical techniques combined with chemical studies in understanding and exploiting the oxidation–reduction properties of compounds containing metal–metal bonds.[8,9] Here we report the application of these techniques to the iron carbonyl cluster in order to discover the extent of its multiple oxidation state behavior and to understand the chemistry of each individual (molecular) oxidation state. Part of the work reported here has already appeared in a preliminary communication.[10]

Experimental Section[11]

Measurements. Ultraviolet–visible spectra were recorded on a Cary Model 14 spectrometer and infrared spectra on a Perkin-Elmer Model 421 spectrophotometer. Epr measurements were made on a Varian E-3 spectrometer. All electrical measurements were made *vs.* the saturated sodium chloride calomel electrode (ssce) using standard three-electrode operational amplifier circuitry as described previously.[8] The total number of electrons transferred in an exhaustive electrolysis at constant potential (*n*) was determined by measuring the total area under a current *vs.* time curve with a planimeter.

Materials. Tetra-*n*-butylammonium hexafluorophosphate (TBAH) was prepared by standard techniques,[12] recrystallized three times from hot ethanol–water mixtures, and dried for 10 hr *in vacuo* at 70°. Tetrakis(π-cyclopentadienyliron carbonyl) was prepared as described by King.[1] All solvents used were dried over activated alumina, molecular sieve, or anhydrous magnesium sulfate before use. *n*-Butyronitrile was purified by vacuum distillation from sodium carbonate–potassium permanganate and *N*,*N*-dimethylformamide (DMF) from anhydrous copper sulfate. All other chemicals were spectro, reagent, or polarographic grade and used without further purification.

Preparations and Reactions. Unless otherwise stated, all manipulations were carried out under oxygen-free nitrogen in deaerated solvents. The experiments described below are typical experiments in that a given experiment was carried out more than once, sometimes under slightly different reaction conditions.

$[(\pi\text{-}C_5H_5)Fe(CO)]_4(PF_6)$. $[(\pi\text{-}C_5H_5)Fe(CO)]_4$ was dissolved in 40 ml of a 0.1 *M* TBAH dichloromethane solution and oxidized for 10 hr at +0.80 V *vs.* the ssce at a platinum electrode. *n* was 1.02. The hexafluorophosphate salt is only slightly soluble in the medium and as it formed it precipitated out onto the surface of the electrode. After the oxidation was complete, the dark green solid was scraped from the electrode onto a frit and washed with three 10-ml portions of cold dichloromethane. The solid was recrystallized from a 1:1 (by volume) acetone–carbon tetrachloride solution by slow evaporation under nitrogen. The solid was collected on a frit, washed with ether, and air-dried giving 175 mg (55% yield) of dark green crystals. *Anal.* Calcd for $C_{24}H_{20}O_4Fe_4PF_6$: C, 38.9; H, 2.72; F, 15.4. Found: C, 39.0; H, 2.75; F, 15.4.

Solutions of $[(\pi\text{-}C_5H_5)Fe(CO)]_4{}^-$. (i) In Acetonitrile. $[(\pi\text{-}C_5H_5)Fe(CO)]_4(PF_6)$ was dissolved in 15 ml of a 0.1 *M* TBAH acetonitrile solution and reduced at −1.50 V *vs.* the ssce at a platinum electrode. As the exhaustive electrolysis proceeded, the solution color changed from dark green to yellow. *n* was 2.25. In solution, $[(\pi\text{-}C_5H_5)Fe(CO)]_4{}^-$ is extremely air sensitive. It was characterized in solution as described in the next section. No attempt was made to isolate it as a salt. In order to obtain spectra or to study reactions of the anion, its solutions were transferred under nitrogen using deaerated syringes and glassware with serum caps.

(ii) In Dichloromethane. $[(\pi\text{-}C_5H_5)Fe(CO)]_4$ (10 mg) was dissolved in 20 ml of a 0.1 *M* TBAH dichloromethane solution and reduced at −1.50 *V vs.* the ssce at a platinum electrode. After 2 hr the current had not decreased from its initial value ($n > 5$). The electrolysis was stopped and the solution filtered. Ultraviolet–visible and infrared spectra of the filtrate indicated that the only carbonyl-containing species in the solution was $[(\pi\text{-}C_5H_5)Fe(CO)]_4$ and that it was present in greater than 80% of its initial concentration. No other products were observed.

(iii) Potassium Amalgam Reduction in Tetrahydrofuran. $[(\pi\text{-}C_5H_5)Fe(CO)]_4$ (20 mg) was suspended in 30 ml of tetrahydrofuran which had been freshly distilled from potassium metal under nitrogen and to which had been added 20 g of a 1% potassium amalgam. Reduction was complete after 1 hr and the infrared spectrum of the yellow solution (ν_{CO} 1592 cm^{-1}) indicated that the reduced product was the same as that formed by the electrochemical reduction of $[(\pi\text{-}C_5H_5)Fe(CO)]_4(PF_6)$ in acetonitrile, $[(\pi\text{-}C_5H_5)Fe\cdot$

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(1) R. B. King, *Inorg. Chem.*, **5**, 2227 (1966).

(2) M. A. Neuman, L. F. Dahl, and R. B. King, quoted in R. Doedens and L. F. Dahl, *J. Amer. Chem. Soc.*, 88, 4847 (1966).

(3) R. E. Dessy, P. M. Weissman, and R. L. Pohl, *ibid.*, 88, 5117 (1966).

(4) R. E. Dessy and R. L. Pohl, *ibid.*, **90**, 1995 (1968).

(5) F. A. Cotton, W. R. Robinson, and R. A. Walton, *Inorg. Chem.*, **6**, 1257 (1967).

(6) B. G. Hughes, J. L. Meyer, P. B. Fleming, and R. E. McCarley, *ibid.*, **9**, 1343 (1970); R. B. Fleming, T. A. Dougherty, and R. E. McCarly, *J. Amer. Chem. Soc.*, **89**, 159 (1967).

(7) R. J. Haines, A. L. DuPreez, and G. T. W. Wittmann, *Chem. Commun.*, 611 (1968).

(8) J. A. Ferguson and T. J. Meyer, *Inorg. Chem.*, **10**, 1025 (1971).

(9) J. A. Ferguson and T. J. Meyer, *ibid.*, **11**, 631 (1972).

(10) J. A. Ferguson and T. J. Meyer, *Chem. Commun.*, 623 (1971).

(11) Abbreviations used here include: ssce for saturated sodium chloride calomel electrode; TBAH for tetra-*n*-butylammonium hexafluorophosphate; Fe_4 for $[(\pi\text{-}C_5H_5)Fe(CO)]_4$.

(12) L. Lange and B. Müller, *Chem. Ber.*, **63**, 1058 (1930).

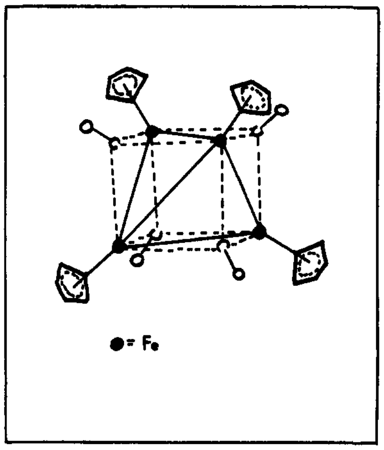

Figure 1.

$(CO)]_4^-$. Upon exposure of the reduced solution to air, $[(\pi\text{-}C_5H_5)Fe(CO)]_4$ was formed immediately.

Attempted Preparations of $[(\pi\text{-}C_5H_5)Fe(CO)]_4^{2+}$. (i) In Acetonitrile. $[(\pi\text{-}C_5H_5)Fe(CO)]_4(PF_6)$ (23 mg) was dissolved in 20 ml of 0.1 *M* TBAH acetonitrile solution and oxidized at +1.30 V *vs.* the ssce at a carbon cloth electrode. After 14 hr the reaction was complete and *n* was greater than 6. An infrared spectrum of the product solution indicated that the only carbonyl-containing species was the acetonitrile complex $[(\pi\text{-}C_5H_5)Fe(CO)_2(NCCH_3)]^+$ (ν_{CO} 2079, 2035).[8] In order to accurately determine the amount of Fe^{2+} produced in the electrolysis, the oxidized product solution was kept under nitrogen at all times to prevent any air oxidation of Fe^{2+} to Fe^{3+}. The product solution was diluted to a known volume with deaerated acetonitrile and the amounts of Fe^{2+}, Fe^{3+}, and $[(\pi\text{-}C_5H_5)Fe(CO)_2(NCCH_3)]^+$ were determined as follows.

(A) Fe^{2+}. An aliquot of the stock solution was evaporated to 1–2 ml. Deaerated water and 1,10-phenanthroline were added, the solution was diluted to the mark with water, and Fe^{2+} was determined spectrophotometrically as $Fe(phen)_3^{2+}$ [ϵ 11,100 (510 nm)].[13]

(B) $[(\pi\text{-}C_5H_5)Fe(CO)_2(NCCH_3)]^+$. The infrared spectrum of a portion of the product stock solution was recorded and the total areas under the carbonyl bands at 2079 and 2035 cm^{-1} were measured using a planimeter. The concentration of acetonitrile complex was determined by comparing the measured areas of the carbonyl bands for the stock solution with the measured areas obtained for several solutions containing known concentrations of the acetonitrile complex in the same medium. The ultraviolet-visible spectrum of the oxidized stock solution also verified the presence of the acetonitrile complex (λ_{max} 370 nm).[8]

(C) Fe^{3+}. Hydroxylamine hydrochloride {to reduce Fe^{3+} to Fe^{2+} and convert $[(\pi\text{-}C_5H_5)Fe(CO)_2(NCCH_3)]^+$ to Fe^{2+}}, and 1,10-phenanthroline were added to another aliquot of the oxidized product stock solution and the experiment was repeated giving the total concentration of iron. The concentration of Fe^{3+} was then calculated from the difference between the total iron concentration in solution and the concentration of Fe^{2+} and acetonitrile complex (determined as described above). A blank experiment verified that $[(\pi\text{-}C_5H_5)Fe(CO)_2(NCCH_3)]^+$ was quantitatively converted to Fe^{2+} by hydroxylamine hydrochloride.

The total iron concentration (Fe^{2+}, Fe^{3+}, and $(\pi\text{-}C_5H_5)Fe(CO)_2NCCH_3^+$) of the product stock solution was also determined by evaporating an aliquot to dryness and treating the resulting residue with a mixture of concentrated nitric and fuming sulfuric acids. The acid solution was evaporated to dryness, dissolved in water, buffered, and treated with hydroxylamine hydrochloride and 1,10-phenanthroline. Total iron was determined spectrophotometrically as $Fe(phen)_3^{2+}$. The value obtained from this determination agreed well with the value obtained by the hydroxylamine hydrochloride reduction of the product stock solution (72 *vs.* 73%).

(ii) **In *n*-Butyronitrile.** $[(\pi\text{-}C_5H_5)Fe(CO)]_4(PF_6)$ (10 mg) was dissolved in 20 ml of a 0.1 *M* TBAH butyronitrile solution and oxidized at +1.40 V *vs.* the ssce at a platinum electrode for 6 hr. Infrared analysis of the resulting solution indicated that the only carbonyl-containing product was the butyronitrile complex, $[(\pi\text{-}C_5H_5)Fe(CO)_2(NC(CH_2)_3CH_3)]^+$ (ν_{CO} = 2082, 2038 cm^{-1}). Qualitative tests using ferro- and ferricyanide indicated that both Fe^{2+} and Fe^{3+} were present in the solution.

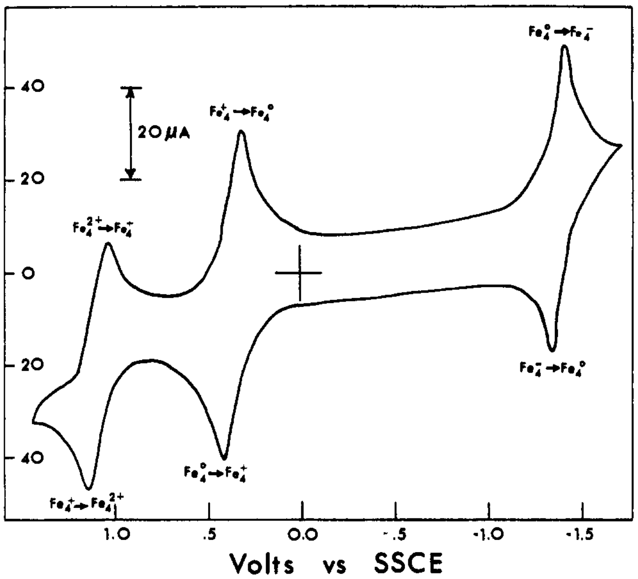

Figure 2. 100 mV/sec cyclic voltammogram of 10^{-3} *M* $[(\pi\text{-}C_5H_5)Fe(CO)]_4(PF)_6$ in 0.1 *M* TBAH acetonitrile at a Pt bead electrode *vs.* the ssce. The electron-transfer processes occurring at the various waves are indicated using Fe_4 as an abbreviation for $[(\pi\text{-}C_5H_5)Fe(CO)]_4$.

(iii) **In Dimethyl Sulfoxide.** $[(\pi\text{-}C_5H_5)Fe(CO)]_4(PF_6)$ (15 mg) was dissolved in 20 ml of a 0.1 *M* TBAH dimethyl sulfoxide solution and oxidized at +1.20 V *vs.* the ssce at a platinum electrode for 10 hr. *n* was greater than 7 and the final oxidized solution contained only ferric ion.

(iv) **In Dichloromethane.** $[(\pi\text{-}C_5H_5)Fe(CO)]_4$ (70 mg) was dissolved in 20 ml of a 0.1 *M* TBAH dichloromethane solution and oxidized at +1.40 *V vs.* the ssce at a platinum electrode. After 6 hr the current had not decreased from its initial value ($n > 10$). A precipitate, $[(\pi\text{-}C_5H_5)Fe(CO)]_4(PF_6)$, had appeared on the electrode surface. Ultraviolet-visible and infrared spectra indicated that the monocation was the only carbonyl-containing species in the solution. No other products of oxidation were detected.

Results and Discussion

Electrochemistry. A cyclic voltammogram of $[(\pi\text{-}C_5H_5)Fe(CO)]_4(PF_6)$ in 0.1 *M* TBAH acetonitrile is shown in Figure 2. The electron-transfer reactions occurring at the various waves are also indicated. From the peak separations and known *n* values all three waves are electrochemically reversible. The reversibility of the waves indicates that on the time scale of the experiment, the cluster remains intact in four discrete molecular oxidation states, +2, +1, 0, and −1. Multiple oxidation state behavior has also been observed for the structurally analogous cluster $[(\pi\text{-}C_5H_5)FeS]_4$.[10] We will report on that system in a later paper.

Voltammetric $E_{1/2}$ values relating the four oxidation states in 0.1 *M* TBAH acetonitrile measured at a platinum bead electrode at 22 ± 2° are (±0.01 V)

$$[Fe_4]^{2+} \overset{1.08\ V}{\text{———}} [Fe_4]^+ \overset{0.32\ V}{\text{———}} [Fe_4] \overset{-1.30\ V}{\text{———}} [Fe_4]^-$$

where Fe_4 is an abbreviation for $[(\pi\text{-}C_5H_5)Fe(CO)]_4$. The values are uncorrected for junction potentials and are *vs.* the ssce.

$E_{1/2}$ values in a variety of solvents for both the $[(\pi\text{-}C_5H_5)Fe(CO)]_4^{+/0}$ and ferrocene–ferricinium couples are given in Table I. The relative insensitivity of the fer-

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(13) W. B. Fortune and M. G. Mellor, *Ind. Eng. Chem., Anal. Ed.,* 10, 60 (1938).

Table I. $E_{1/2}$ Values in Various Solvents[a]

Solvent[b]	$E_{1/2}$, V, for $Fe_4^+ + e \rightarrow Fe_4$[c]	$E_{1/2}$, V, for $Fc^+ + e \rightarrow Fc$[d]
CH_3CN	0.32	0.39
$CH_3(CH_2)_3CN$	0.30	0.37
$HC(O)N(CH_3)_2$ (DMF)	0.35	0.43
$(CH_3)_2SO$ (DMSO)	0.35	0.44
CH_2Cl_2	0.38	0.46

[a] From voltammetric measurements at a platinum bead electrode *vs.* the ssce, uncorrected for junction potentials, at 22 ± 2°. [b] The supporting electrolyte in all cases is 0.1 *M* TBAH. [c] $Fe_4 = [(\pi\text{-}C_5H_5)Fe(CO)]_4$; ±0.01 V. [d] $Fc = (\pi\text{-}C_5H_5)_2Fe$; ±0.01 V.

rocene–ferricinium potential to changes in solvent is well known; the $Fe_4^{+/0}$ couple is equally insensitive. The effect of solvent on the $Fe_4^{+/0}$ couple, in which the metal–metal bonded framework remains intact in both oxidation states, is in marked contrast to solvent effects observed in the oxidations of $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$[8] or the diphos-bridged iron dimer cation $[(\pi\text{-}C_5H_5)Fe(CO)]_2(Ph_2PCH_2CH_2PPh_2)^+$ (Ph = phenyl).[9] Oxidation of the iron dimer results in cleavage of the metal–metal bond and incorporation of a solvent molecule

$$2S + [(\pi\text{-}C_5H_5)Fe(CO)_2]_2 \xrightarrow{-2e} [(\pi\text{-}C_5H_5)Fe(CO)_2S]^+$$

[S = $(CH_3)_2CO$, CH_3CN]. The reactions are electrochemically irreversible and the potentials for oxidation are greatly dependent upon solvent.

Solutions of both $[(\pi\text{-}C_5H_5)Fe(CO)]_4$ and $[(\pi\text{-}C_5H_5)Fe(CO)]_4(PF_6)$ are stable for days in the presence of light and air. The stability of the solutions combined with the electrochemical reversibility and solvent insensitivity of the $Fe_4^{+/0}$ potential make this couple an excellent electrochemical reference. We are currently investigating the uses of $[(\pi\text{-}C_5H_5)Fe(CO)]_4(PF_6)$ as an outer sphere oxidant in nonaqueous solvents.

Spectra. Important features of the ultraviolet-visible and infrared spectra of $[(\pi\text{-}C_5H_5)Fe(CO)]_4$, $[(\pi\text{-}C_5H_5)Fe(CO)]_4^+$, and $[(\pi\text{-}C_5H_5)Fe(CO)]_4^-$ are summarized in Table II. Values for $[(\pi\text{-}C_5H_5)Fe(CO)]_4^{2+}$ are not available because on time scales longer than the cyclic voltammetric experiments it decomposes in all media studied.

Table II. Spectra of the Cluster Compounds in Acetonitrile

Compound	ν_{CO}, cm^{-1} [a]	λ_{max}, nm[b]
$[(\pi\text{-}C_5H_5)Fe(CO)]_4^-$	1576[c]	770 (br, ϵ ~2500),[c] 680–700 (sh, vbr, ϵ ~1700),[c] 410 (sh, ϵ ~11,700),[c] 380 (ϵ ~12,500)[c]
$[(\pi\text{-}C_5H_5)Fe(CO)]_4$	1623	775 (ϵ ~3500), 645 (ϵ ~2500), 390 (ϵ ~18,000), 280 (sh)
$[(\pi\text{-}C_5H_5)Fe(CO)]_4^+$	1696	668 (ϵ ~4000), 388 (ϵ ~18,000), 275 (sh, ~23,000)

[a] ±3 cm^{-1}. [b] ±3 nm; ϵ values are molar extinction coefficients ±10%; sh = shoulder, br = broad, vbr = very broad. [c] In 0.1 *M* TBAH.

The bands in the visible are extremely broad for all three cluster compounds. The spectra were recorded from 1500 to 250 nm for $[(\pi\text{-}C_5H_5)Fe(CO)]_4(PF_6)$ and $[(\pi\text{-}C_5H_5)Fe(CO)]_4$ and from 1500 to 300 nm for $[(\pi\text{-}C_5H_5)Fe(CO)]_4^-$. The variation in the carbonyl stretching frequencies with the (molecular) oxidation state of the cluster is as expected, with higher frequencies being observed as the oxidation state increases. ν_{CO} for the anion appears to be the lowest value reported for a metal carbonyl compound. Infrared spectra of the anion in acetonitrile are complicated by the onset of a strong solvent band below 1550 cm^{-1} even if matched cells are used. However, in addition to the strong band at 1576 cm^{-1}, reproducible shoulders appear at 1570 and 1556 cm^{-1}. In tetrahydrofuran the three bands appear at 1592, 1589, and 1571 cm^{-1}.[14] The appearance of these shoulders implies that appreciable distortion from the tetrahedral configuration of the neutral cluster may occur in the anion.

$[(\pi\text{-}C_5H_5)Fe(CO)]_4^+$. The electrochemical oxidation of $[(\pi\text{-}C_5H_5)Fe(CO)]_4$ in 0.1 *M* TBAH–dichloromethane provides a convenient route to the hexafluorophosphate salt of the cation, $[(\pi\text{-}C_5H_5)Fe(CO)]_4(PF_6)$. The oxidation is quantitative (*n* ~ 1.0) and since the hexafluorophosphate salt is only slightly soluble in dichloromethane the cation precipitates out as it is formed. In contrast to the halide and polyhalide salts reported earlier,[1,15] the hexafluorophosphate salt is soluble in polar organic solvents. It is stable to light and air in the solid for several months and its solutions in acetonitrile are stable for at least 4 days.

Magnetic measurements on the salt using a Faraday balance gave $\chi_M = 2573 \times 10^{-6}$ at 295°K. Although the value is high (μ_{eff} = 2.46 BM), it is consistent with there being one unpaired electron per cluster unit as expected. We have been unable to observe an epr signal for the cation in acetonitrile at room temperature.

Mössbauer data for the complexes $\{[(\pi\text{-}C_5H_5)Fe(CO)]_4\}^+X^-$ (X = Cl, Br_3, I_5) and $[(\pi\text{-}C_5H_5)Fe(CO)]_4$ have been reported.[15] The data indicate that loss of an electron from the neutral cluster to give the cation affects all four iron atoms equally. It has been suggested that the electron is removed from a ligand based orbital or, if from the metal–metal bonded framework, that compensating changes leave the S electron density at the iron nuclei unchanged.[15] In either case electrons are probably gained or lost from extensively delocalized molecular orbitals and the various cluster compounds can best be described as being different molecular oxidation states of the basic cluster unit.

$[(\pi\text{-}C_5H_5)Fe(CO)]_4^-$. Because of its extreme air sensitivity in solution, no attempt was made to isolate the anion as a salt. Instead it was characterized by the following experiments. Solutions of the anion in 0.1 *M* TBAH acetonitrile were prepared by the electrochemical reduction of $[(\pi\text{-}C_5H_5)Fe(CO)]_4(PF_6)$ as described in the Experimental Section. *n* was 2.15–2.35 (*n* = 2 calculated for the reduction of the monocation to the anion). Reduced solutions were reoxidized at 0.00 V *vs.* the ssce giving $[(\pi\text{-}C_5H_5)Fe(CO)]_4$ (*n* = 0.98) and at 0.80 V *vs.* the ssce giving $[(\pi\text{-}C_5H_5)Fe(CO)]_4^+$ (*n* = 2.05). Upon exposure to air, reduced solutions rapidly gave $[(\pi\text{-}C_5H_5)Fe(CO)]_4$. In all cases the identity of the oxidized product was verified by infrared measurements (see Table II). Epr measurements on a reduced solution at room temperature gave

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(14) Solutions of the anion in THF were prepared by potassium amalgam reduction as described in the Experimental Section.

(15) R. Greatrex and N. N. Greenwood, *Discuss. Faraday Soc.*, No. 77, 126 (1969).

a single resonance with a g value of 2.013 verifying that the anion is paramagnetic. Ultraviolet–visible and infrared data for the anion in 0.1 M TBAH acetonitrile are given in Table II. The anion was also prepared by the potassium amalgam reduction of suspensions of $[(\pi\text{-}C_5H_5)Fe(CO)]_4$ in tetrahydrofuran.

From the experiments presented here it is apparent that the cluster can accept an electron reversibly to give the paramagnetic anion $[(\pi\text{-}C_5H_5)Fe(CO)]_4^-$. In the anion the metal–metal framework remains intact although some distortion from the regular tetrahedral configuration of the neutral cluster may occur (*vide supra*).

The reaction between the anion and oxygen to give $[(\pi\text{-}C_5H_5)Fe(CO)]_4$ is quantitative: at least 95% recovery as the neutral cluster is obtained and no decomposition products are observed. The anion also reacts with the monocation in the time required for mixing to yield the neutral cluster.

$$[(\pi\text{-}C_5H_5)Fe(CO)]_4^+ + [(\pi\text{-}C_5H_5)Fe(CO)]_4^- \longrightarrow 2[(\pi\text{-}C_5H_5)Fe(CO)]_4$$

From our attempts to study net electron-transfer reactions in solution, it is apparent that the various cluster compounds transfer electrons rapidly. This is probably a consequence of low reorganizational contributions to the barrier to electron transfer[16] in these highly delocalized systems.

The reduction of the neutral cluster in 1,2-dimethoxyethane was reported previously.[3] In the earlier work it was found that the reduction product cycles with $n > 5$.[3] We observed the same kind of behavior in dichloromethane and it may be the result of catalytic reduction of solvent or of an impurity in the medium. From our cyclic voltammetry and coulometry results, reduction of the neutral cluster in acetonitrile occurs smoothly to give the anion with $n = 1$. Values slightly higher than two ($n = 2.25$) are observed for the reduction of $[(\pi\text{-}C_5H_5)Fe(CO)]_4^+$ to $[(\pi\text{-}C_5H_5)Fe(CO)]_4^-$ possibly because the anion catalytically removes traces of oxygen from the solution.

$[(\pi\text{-}C_5H_5)Fe(CO)]_4^{2+}$. Cyclic voltammograms of $[(\pi\text{-}C_5H_5)Fe(CO)]_4^+$ at 200 mV/sec sweep rates at a platinum bead electrode in dichloromethane, n-butyronitrile, dimethyl sulfoxide, and acetonitrile (Figure 2) show waves for both

$$[(\pi\text{-}C_5H_5)Fe(CO)]_4^+ \xrightarrow{-e} [(\pi\text{-}C_5H_5)Fe(CO)]_4^{2+}$$

and

$$[(\pi\text{-}C_5H_5)Fe(CO)]_4^{2+} \xrightarrow{+e} [(\pi\text{-}C_5H_5)Fe(CO)]_4^+$$

The chemical and electrochemical reversibility of the reactions demonstrates that the cluster framework remains intact in the dication $[(\pi\text{-}C_5H_5)Fe(CO)]_4^{2+}$. The dication once formed can be completely recovered by reduction to $[(\pi\text{-}C_5H_5)Fe(CO)]_4^+$ within the time scale (seconds) of the cyclic voltammetry experiment. However, attempts to prepare the dication by exhaustive electrolysis of $[(\pi\text{-}C_5H_5)Fe(CO)]_4^+$ (with a time scale of at least several minutes) in several solvents gave only decomposition products $\{Fe^{2+}, Fe^{3+}$, and $[(\pi\text{-}C_5H_5)Fe(CO)_2S]^+$, $S = CH_3(CH_2)_3CN$ or $CH_3CN\}$.

The products of decomposition were analyzed in detail in 0.1 M TBAH acetonitrile at 22 ± 2°. The results indicate that the dication breaks apart in a predictable way

$$[(\pi\text{-}C_5H_5)Fe(CO)]_4^{2+} + 2CH_3CN \xrightarrow{-2e} 2Fe^{2+} + 2(\pi\text{-}C_5H_5)Fe(CO)_2NCCH_3^+ \quad (1)$$

The actual results obtained as described in the Experimental Section were

$$[(\pi\text{-}C_5H_5)Fe(CO)]_4^{2+} \xrightarrow[CH_3CN]{} 6\%\ Fe^{2+} + 30\%\ Fe^{3+} + 36\%\ (\pi\text{-}C_5H_5)Fe(CO)_2NCCH_3^+$$

We arrive at reaction 1 from the following considerations. All of the iron in the solution after complete electrolysis (73% of that present initially as $[(\pi\text{-}C_5H_5)Fe(CO)]_4^+$) can be accounted for as Fe^{2+}, Fe^{3+}, or $(\pi\text{-}C_5H_5)Fe(CO)_2NCCH_3^+$. Mass balance with regard to iron is not obtained because after the long reaction times (several hours) for complete reaction, noticeable diffusion had occurred into the reference and auxillary compartments of the cell. The appearance of Fe^{3+} can be accounted for by the slow electrochemical oxidation of Fe^{2+} to Fe^{3+}.[9] The addition of water (up to 3% by volume) shortens reaction times considerably and gives mainly Fe^{3+} (76%) and $(\pi\text{-}C_5H_5)Fe(CO)_2NCCH_3^+$ (10%). Electrochemical conversion of Fe^{2+} to Fe^{3+} is much more rapid in this medium.

The dication then has a lifetime of seconds to minutes in a variety of solvents. However, loss of the second electron from the delocalized molecular framework results in ultimate degradation of the cluster. Rather than giving $(\pi\text{-}C_5H_5)Fe(CO)_2NCCH_3^+$ directly, the cluster may break apart initially to give the iron dimer

$$[(\pi\text{-}C_5H_5)Fe(CO)]_4^{2+} \longrightarrow 2(\pi\text{-}C_5H_5)Fe^+ + [(\pi\text{-}C_5H_5)Fe(CO)_2]_2$$

followed by its oxidation to the acetonitrile complex[8]

$$[(\pi\text{-}C_5H_5)Fe(CO)_2]_2 + 2CH_3CN \xrightarrow{-2e} 2(\pi\text{-}C_5H_5)Fe(CO)_2NCCH_3^+$$

In either case it is interesting to note that all of the coordinated CO groups are retained in the iron products.

For the net reaction

$$[(\pi\text{-}C_5H_5)Fe(CO)]_4^+ + 2CH_3CN \xrightarrow{-3e} 2Fe^{2+} + 2(\pi\text{-}C_5H_5)Fe(CO)_2NCCH_3^+$$

observed n values ($n > 6$) are considerably higher than calculated ($n = 3$). This may result from the oxidation of fragments released upon decomposition of an intermediate like $(\pi\text{-}C_5H_5)Fe^+$ [9] and partly from oxidation of Fe^{2+} to Fe^{3+}.

Acknowledgments. Acknowledgments are made to the National Science Foundation, through Grant No. GP 17083, for support of this research.

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[16] R. A. Marcus, *Annu. Rev. Phys. Chem.*, **15**, 155 (1964).