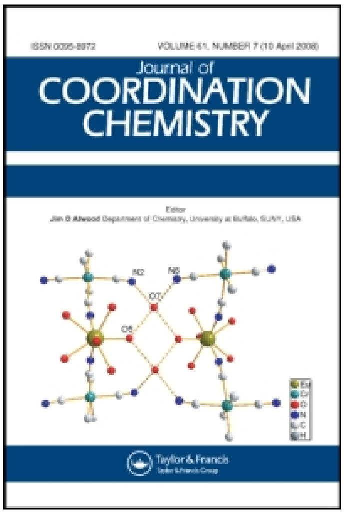

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ELECTROCHEMICAL INVESTIGATION OF METAL CARBONYL-ISOCYANIDE COMPLEX CATIONS

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Polarographic measurements on the cations $CpFe(CO)_{3-n}{}^+$ (L = PPh_3, n = 1,2; L = CH_3NC, n = 1–3) show an increasingly anodic one-electron reduction wave as CO is successively substituted by L. The effect is greater for L = $CNCH_3$ than for L = PPh_3. The reduced species then either lose L and dimerize (giving rise to a second reduction wave) or decompose. Heretofore unreported Mössbauer parameters for the isocyanide complexes are given and correlated with the polarographic results.

INTRODUCTION

Organometallic cations of the type $CpFe(CO)_{3-n}L_n{}^+$ (Cp = η^5-C_5H_5; L = PPh_3, n = 1,2; L = CNR, n = 1–3) exhibit varied reaction patterns with nucleophiles. Examples from recent literature for tricarbonyl and tris(isocyanide) cations include the following:

Ligand substitution[1]

$$CpFe(CO)_3^+ + X^- \rightarrow CpFe(CO)_2X + CO \qquad X = Cl^-, CN^-, NCS^- \tag{1}$$

Attack on coordinated ligands[2,3]

$$CpFe(CO)_3^+ + N_3^- \rightarrow CpFe(CO)_2NCO + N_2 \tag{2}$$

$$CpFe(CNCH_3)_3^+ + LiC_6F_5 \xrightarrow{H^+} CpFe(CNCH_3)_2(C(C_6F_5) = NHCH_3) \tag{3}$$

Reduction[4]

$$CpFe(CO)_3^+ + LiC_6H_5 \rightarrow 1/2[CpFe(CO)_2]_2 \tag{4}$$

Reduction to the dimer also occurs with CH_3Li and $C_6H_5CH_2MgCl$.[4b]

Some investigations on mixed carbonyl-isocyanide complexes have also been conducted with $C_6F_5^-$ as the nucleophile.[5] The results may be summarized as follows:

$$CpFe(CO)_2(CNCH_3)^+ + C_6F_5^- \rightarrow exo\text{-}\eta^4\text{-}C_6F_5C_5H_4Fe(CO)_2(CNCH_3) + [CpFe(CO)_2]_2 \tag{5}$$

$$CpFe(CO)(CNCH_3)_2^+ + C_6F_5^- \rightarrow CpFe(CNCH_3)_2C_6F_5 + CpFe(CNCH_3)_2(C{=}NCH_3)C_6F_5 \tag{6}$$

Also, reaction of the $CpFe(CO)_2PPh_3^+$ cation with $C_6H_5CH_2MgCl$ has been found[4b] to lead to ring addition.

Three general reaction patterns emerge: ligand substitution, attack on coordinated ligand and reduction. The limited data available seem to indicate that isocyanide-containing cations display some preference for attack on the coordinated RNC ligand.

In order to try to relate these differences in reactivity to the ground state electron distribution in these complexes, we undertook an investigation of ground state electronic structures of these cations employing ir, nmr as well as Mössbauer spectroscopy. These investigations should provide valuable comparisons of bonding properties of carbonyl, isocyanide and triphenylphosphine ligands.

Moreover, we have investigated the polarographic behavior of the series of compounds $[CpFe(CO)_{3-n}(CNCH_3)_n]PF_6$ (n = 0-3). A simple picture of the chain of events involved in nucleophilic attack on $CpFe(CO)_{3-n}L_n^+$ is incipient transfer of an electron pair from the HOMO of the nucleophile to the LUMO of the cation. Formally, this is also the first step in the redox process.

The rate and mechanism of a redox process $Ox_1 + Red_2 \rightarrow Ox_2 + Red_1$ depend on the properties of both coupled redox systems. In his classic paper, Vlček[6] has pointed out that a formally equivalent system may be set up by combining a redox system with an inert polarized electrode.[7] In such a case the rate and mechanism of the reduction process depend only on the properties of the redox system studied. Because this model system does not undergo a redistribution of energy levels or atomic configuration with a change in the charge density on the electrode, it may be advantageous over a single chemical system for use as a standard of comparison for various redox systems.

In particular, an inert electrode may be useful as a model for attacking nucleophiles at least in identifying qualitatively the LUMO on the substrate reduced. It has been speculated[7] that species undergoing reduction at an electrode surface can suffer any of three fates depending on where localized electronic change occurs. First, electron transfer to the metal atom can lead to reduction possibily followed by decomposition of the complex. Second, electron transfer to a π orbital localized on a ligand could occur. Finally, electron addition to an orbital antibonding between metal and ligand might take place resulting in ligand dissociation. Insofar as these are actually distinct possibilities, the behavior of complexes on polarographic reduction would correspond, respectively, to the reduction, ligand attack and ligand displacement reactions seen with nucleophiles.

Hence, we have investigated the reactivities of the organometallic cations $CpFe(CO)_{3-n}L_n^+$ ($L = CH_3NC$, $n = 1-3$; $L = PPh_3$, $n = 1,2$) with electrons at a dropping mercury electrode. Our hope was that differences in their behavior toward nucleophiles might be reflected in differences in their polarographic behavior.

EXPERIMENTAL

Measurements. Polarograms were recorded using a Sargent Model XV polarograph equipped with the Model A IR Compensator. The cell contained a typical three-electrode geometry with a silver wire as the reference and a platinum coil auxiliary electrode. The stability of the reference was demonstrated by the reproducibility of the half-wave potential for $[CpFe(CO)]_2$ which remained unchanged over a period of weeks. The characteristics of the dme capillary employed were $m = 1.665$ mg sec^{-1} and $t = 4.21$ sec measured under open circuit conditions. The height of the mercury reservoir was 65 cm. and the cell temperature was 26–7° C.

Millimolar solutions of the complexes were prepared by dissolving a weighed quantity in a measured volume of acetonitrile which was 0.10 M in tetrabutylammonium perchlorate (TBAP). All solutions were degassed with N_2 for 20 min. prior to the measurements. The polarograms were recorded from −0.2V to −3.0V (vs. Ag reference). When the reduction stoichiometry was required, it was calculated from the Ilkovic Equation.[8] The diffusion coefficient required for the calculations was taken to be the same for all species measured. Its value ($D = 3.27 \times 10^{-6}$ $cm^2 sec^{-1}$) was obtained by solving the Ilkovic Equation using polarographic data on $[CpFe(CO)_2]_2$ in acetonitrile and the coulometric measurements[9] on this compound which indicate that it undergoes a two-electron reduction.

Infrared spectra were recorded on a Perkin-Elmer 331 instrument in Nujol mulls. Nmr spectra were recorded in $CDCl_3$ with a TMS reference on a Varian Model T-60. Mössbauer measurements were made on an Austin Science Associates Model S3 spectrometer relative to a stainless steel reference.

Reagents. Acetonitrile for polarography was glass-distilled grade from Burdick and Jackson Laboratories and was used without further purification. The supporting electrolyte tetrabutylammonium perchlorate (TBAP) obtained from Eastman was dried for 6–8 hours at 120° C and stored in a desiccator. Background currents remained less than 0.06 μA during long periods of storage.

Ethyl chloroformate from Eastman, ammonium hexafluorophosphate from Apache and methyl fluorosulfonate from Aldrich were used without further purification.

Starting Materials and Complexes. $[CpFe(CO)_3]PF_6$,[10] $[CpFe(CO)_2]_2$,[11] $CpFe(CO)_2CN$,[12] $K[CpFe(CN)_2CO]$,[12] $CpFe(CO)_2Br$,[13] $[CpFe(CO)_2(PPh_3)]PF_6$,[14c] $[CpFe(CO)(PPh_3)_2]PF_6$,[14c] and CH_3NC[15] were all prepared by literature methods.

Preparation of $[CpFe(CO)_2CNCH_3]PF_6$[14i]

A 0.50 g sample (0.40 mmoles) of the starting material $CpFe(CO)_2CN$, was placed in a round-bottom flask fitted with a nitrogen inlet and an addition funnel. An excess amount (~2 ml) of methyl fluorosulfonate was added dropwise while the reaction mixture was cooled in an ice bath. The mixture was slowly allowed to come to room temperature and stirred for 30 minutes. The unreacted methyl fluorosulfonate was then removed under reduced pressure. CAUTION: *Methyl fluorosulfonate is toxic. Care must be taken not to breathe the vapors or allow it to come in contact with the skin.*

This treatment resulted in a yellow oil, which was subsequently dissolved in a water-acetone solution. A saturated aqueous solution of ammonium hexafluorophosphate was added until no more precipitate formed. The yellow hexafluorophosphate salt was collected on a frit, washed with water, and dried. The dry solid was recrystallized several times from a chloroform-pentane solution cooled to dry ice temperature. The reaction gave a 46% yield. $\delta_{C_5H_5} = 5.48$, $\delta_{CH_3} = 3.52$, $\nu_{CN} = 2250\ cm^{-1}$, $\nu_{CO} = 2060, 2012\ cm^{-1}$.

Preparation of $[CpFe(CO)(CNCH_3)_2]PF_6$

A 0.50 g sample (2.1 mmoles) of $K[CpFe(CO)(CN)_2]$ was added to a roundbottom flask as before. The methyl fluorosulfonate (~2 ml) was added and the mixture stirred for 30 minutes. At the end of this time the excess methylating agent was removed under pressure and the residue was extracted with dichloromethane. To the resulting yellow solution, diethyl ether was added to precipitate a yellow powder. This powder was collected on a glass frit and washed with several volumes of cold ether. The crude product was dissolved in water and a saturated aqueous solution of ammonium hexafluorophosphate was added dropwise until precipitation ceased. The salt was collected on a frit and washed with water. It was then recrystallized several times as above, lit.[10] 2200 and 2000 cm^{-1}. Yield 37%. $\delta_{C_5H_5} = 5.13$, $\delta_{CH_3} = 3.47$; $\nu_{CN} = 2217\ cm^{-1}$, $\nu_{CO} = 2000\ cm^{-1}$, respectively for the iodide salt in KBr.

Preparation of $[CpFe(CNCH)_3)_3]PF_6$

The synthesis of this cation was carried out using a modification of the method suggested by Pauson *et al.*[16] A 0.50 g sample (1.9 mmoles) of $CpFe(CO)_2Br$ was dissolved in a minimum amount of benzene. Methyl isocyanide (0.24 g, 5.9 mmoles) was added dropwise with stirring. This mixture was refluxed for 1.5 hours. The benzene was removed *in vacuo* and the residue was extracted with hot water which was subsequently decanted and allowed to cool. A saturated aqueous solution of ammonium hexafluorophosphate was added to precipitate the product. This material was recrystallized following the procedure previously described. $\delta_{C_5H_5} = 4.80$, $\delta_{CH_3} = 3.47$, $\nu_{CN} = 2195, 2161\ cm^{-1}$.

The polarographic characteristics of the compounds studied are given in Table I. Half-wave potentials varied no more than 0.02 volts between experiments. All the compounds showed diffusion-controlled limiting currents since plots of i_{lim} versus the height of the mercury reservoir (corrected for back pressure) gave slopes near the value 0.5 expected for a diffusion-controlled process. In addition, actual measurements at elevated temperatures revealed an increase in limiting current with temperature. This behavior is consistent with diffusion control.

In acetonitrile most of the compounds exhibit what appear to be two one-electron waves. The reduction potential of the first wave shows a strong dependence on the nature and extent of CO substitution. This wave is generally well defined and plots of $\log(i/i_d - i)$ versus E indicate irreversible one-electron reductions.[17] The second wave is usually less well defined and often distorted by maxima located on the limiting plateau of the first wave or directly on the second wave. If the maximum is ignored, this wave appears roughly equal in size to the first. This wave is also irreversible.

TABLE I
Polarographic Data in Acetonitrile

Compound	$E_{1/2}$[a](volts)	I_d[b]	n[c]
$[CpFe(CO)_3]PF_6$	−0.46	3.46	0.85
	−1.45	4.05	0.99
$[CpFe(CO)_2(CNCH_3)]PF_6$	−0.86	3.33	0.82
	−1.45	4.05	0.99
$[CpFe(CO)(CNCH_3)_2]PF_6$	−1.14	2.50	0.62
	−1.52	0.45	
	−1.75	1.38	0.89[d]
$[CpFe(CNCH_3)_3]PF_6$	−1.74[e]	6.49	1.60
$[CpFe(CO)_2PPh_3]PF_6$	−0.78	3.21	0.78
	−1.45	3.38	0.82
$[CpFe(CO)(PPh_3)_2]PF_6$	−0.88[e]	4.32	1.05
$[CpFe(CO)_2]_2$	−1.41	8.35	2.06
$[CpFe(CO)(CNCH_3)]_2$	−1.50	5.96	
	−1.74	2.47	2.08[d]

[a] Relative to Ag reference
[b] $I_d = i_d/Cm^{2/3}t^{1/6}$
[c] n = number of electrons; calculated from the Ilkovic Equation
[d] Calculated using i_d of second wave (combined waves)
[e] Estimated due to occurrence of maxima

Measurements were also made in DMF with similar results except in the case of $[CpFe(CO)_3]PF_6$; this compound displayed three reduction waves of equal height.

Both methyl isocyanide and cyclopentadiene were found to be electrochemically inactive within the range of study.

Table II reports some Mössbauer parameters while infrared spectral parameters are given in Table III.

TABLE II
Mössbauer Effect Parameters[a]

Compound	δ(mm sec^{-1})	ΔE_Q(mm sec^{-1})
$[CpFe(CO)_3]PF_6$	+0.094	1.85
$[CpFe(CO)_2(CNCH_3)]PF_6$	+0.104	1.86
$[CpFe(CO)(CNCH_3)_2]PF_6$	+0.150	1.92
$[CpFe(CNCH_3)_3]PF_6$	+0.160	1.96
$[CpFe(CO)_2PPh_3]PF_6$	+0.124	1.81
$[CpFe(CO)(PPh_3)_2]PF_6$	+0.234	1.91

[a] Measured relative to stainless steel reference.

TABLE III
Infrared Spectral Data[a]

Compound	$\nu_{CO}(cm^{-1})$	$\nu_{CN}(cm^{-1})$
$[CpFe(CO)_3]PF_6$	2048, 2072, 2108	
$[CpFe(CO)_2(CNCH_3)]PF_6$	2012, 2060	2250
$[CpFe(CO)(CNCH_3)_2]PF_6$	2000	2217
$[CpFe(CNCH_3)_3]PF_6$		2195, 2161
$[CpFe(CO)_2(PPh_3)]PF_6$	2009, 2056	
$[CpFe(CO)(PPh_3)_2]PF_6$	1970	

[a] In Nujol.

These data compare well with measurements reported by other workers.[12,14,17,18]

DISCUSSION

Comparison of the first half-wave potentials of the iron derivatives in Table I suggests that this wave is determined by the character of the ligand field surrounding the iron atom. The half-wave potential decreases from -0.47 V for $CpFe(CO)_3^+$ to -1.74 V for $CpFe(CNCH_3)_3^+$ and to -0.88 volts for $CpFeCO(PPh_3)_2^+$. The increasing negative potential needed for reduction as the extent of substitution increases seems to reflect the buildup of electron density on the central metal atom since it parallels trends in sigma donor-pi acceptor abilities of the various ligands as seen in Mössbauer and infrared data (*vide infra*).

Analysis of the limiting currents for the first waves indicate a one-electron reduction, presumably of a molecular orbital primarily localized on the iron atom. The degree of difficulty of this event seems to depend upon the electron density present on the iron as mentioned above. The odd electron species generated at this step most likely follows a path leading to ligand dissociation. This would fit nicely with the observation that the first wave observed in the polarography experiments appears irreversible. From cyclic voltammetric experiments, it has not been possible to establish the reversibility of this first electrochemical event. This seems plausible if the rate of dissociation were greater than the sweep rate of the oxidation reduction cycle or the lifetime of the dme. Placement of an electron into an antibonding orbital is likely since the eighteen electrons of the starting complex presumably fill all bonding orbitals. This would likely lead to ligand dissociation.

The most probable leaving group would be the ligand that least stabilized the radical, the strongest net (sigma plus pi) electron donors, i.e. PPh_3 or CH_3NC. However, loss of a carbon monoxide could occur if no other ligand were present. Once this chemical event occurs, the metal would be left coordinately unsaturated.

Following the dissociation, the radical complex could follow either of two routes. An abstraction of hydrogen from either the solvent or supporting electrolyte would result in formation of a metal hydride. This could go on to dimerize with elimination of H_2. Alternatively, the iron radical could couple with a like radical species and form a dimeric compound. Organometallic species containing an odd number of electrons are known to dimerize.[19] At this point it is not clear which pathway is followed, but the eventual outcome is the production of a dimeric product.

The second wave, then, is thought to arise from reduction of a dimer formed by one of the above mechanisms. In agreement with this interpretation, no second wave was observed with $CpFe(CO)(PPh_3)_2^+$ and $CpFe(CNCH_3)_3^+$ when the corresponding dimeric species are unknown.

The identity of dimeric material as a product was established by massive electrolysis of the starting material at the first half-wave potential and noting that the first wave was converted to the second wave.[20] The half-wave potential of the second wave compared favorably to the $E_{1/2}$ of authentic samples of dimers. Also, upon addition of known dimeric material to the orginal solutions, it was noted that the second wave increased in height while the first wave was unchanged.

From the stoichiometry of the reduction it appears that the second wave is a two-electron reduction of the dimeric species resulting in cleavage and generation of a metalloanion.

$$CpFe(CO)_{3-n}L_n^+ + e^- \rightarrow 0.5[CpFe(CO)_{3-n}L_{n-1}]_2 + L \quad (7)$$

$$0.5[CpFe(CO)_{3-n}L_{n-1}]_2 + e^- \rightarrow CpFe(CO)_{3-n}L_{n-1} \quad (8)$$

$(L = CO, n = 1; L = CH_3NC, n = 1,2; L = PPh_3, n = 1)$

Equations (7) and (8) make it clear why both waves correspond to reductions involving the same number of electrons.

As pointed out previously, only a single wave is observed on reduction of $CpFe(CO)(PPh_3)_2^+$ and $CpFe(CNCH_3)_3^+$. This is consistent with the failure to prepare the hypothetical $[CpFe(CO)(PPh_3)]_2$ and $[CpFe(CNCH_3)_2]_2$.

It is noteworthy that reduction of $[CpFe(CO)(CNCH_3)]_2$ gives rise to two waves closely spaced and not very well resolved. This is in contrast to $[CpFe(CO)_2]_2$ which displays only a single wave. We have no very satisfactory explanation for this result. It is possible that the bridging-terminal and all terminal isomers of $[CpFe(CO))(CNCH_3)]_2$ are reduced at different potentials. Adams and Cotton have[21] shown that two forms of this dimer exist in solution. The equilibrium position for the related dimer $[Cp_2Mo_2(CNCH_3)(CO)_5]$ depends on solvent polarity.[22] In our experiments addition of up to 40% by volume of toluene to the acetonitrile solutions effects a 9% change in the ratio of wave heights. Although this value is small, the effect is consistent with the above proposal.

Mössbauer data in Table II show that the isomer shift δ increases with increasing substitution of the parent carbonyl. The increase is greater when triphenylphosphine rather than methyl isocyanide is substituting ligand. Although we have not used a numerical procedure to fit our data to Lorentizian line shape,[18] the large variations in δ leave no doubt that a genuine effect is being observed. The increasing isomer shifts reflect a decreasing *s*-electron density at iron with increasing substitution. This is reasonable since both triphenylphosphine and methyl isocyanide are considered to be better σ donors and worse π-acids than CO. The increase in isomer shift on increasing substitution measures the $(\sigma + \pi)$ effect of the substituting ligands on *s*-electron density. Results indicate that triphenylphosphine has a greater total effect than methyl isocyanide. This is evidence that triphenylphosphine is a worse σ-donor and/or π-acceptor than the isocyanide. Results for triphenylphosphine substituted compounds were reported previously.[14]

The quadrupole splittings ΔE_Q show variation which seems to be more dependent on the extent of substitution than on the nature of the substituting ligand. A small variation in ΔE_Q has been observed by Bancroft, *et al.*[14] in a series of similar cationic Fe complexes. These authors suggested that carbonyl and cyclopentadienyl ligands are capable of varying their bonding properties so as effectively to neutralize changes in electron asymmetry about Fe resulting from substitution.

Infrared data given in Table III show that substitution of isocyanide or triphenylphosphine lowers the CO stretching frequency. This is expected for ligands of lower π-acidity than CO.

From the experimental data it is seen that substituting carbonyl for various weaker pi-acid acceptor ligands increases the electron density on the iron atom resulting in lower carbonyl stretching frequencies, higher Mössbauer shifts, and more anodic reduction potentials. A parallel observation was made by Treichel, *et al.*[23] who found that the oxidation of $CpFe(CO)_{2-n}(CNC_6H_5)_nI$ was more facile for n = 2 than for n = 1. In all cases, reduction of these organometallic species seems to involve transfer of one electron to a molecular orbital localized on the metal atom. This decrease in oxidation state of iron necessitates ligand dissociation, leaving the metal atom coordinately unsaturated. A possible mechanism for this dissociation is that once the iron atom has been readuced, either by a nucleophile or by an electrode process, its orbitals are raised in energy with respect to the bonding molecular orbitals in the complex. This would place them in an energetically more favorable position to interact with antibonding orbitals, causing ligand dissociation.

By analogy, an incoming nucleophile could transfer electron density to metal orbitals without complete reduction leading to ligand dissociation, or, if the nucleophile is strongly coordinating, occupy the vacant site on the metal. A more weakly-coordinating ligand may merely reduce the iron species to the dinuclear state. In the electrochemical experiments, dimerization was observed in all cases because there were no strongly coordinating ligands to fill the vacant site on the iron atom.

Our experiments do not seem to offer an electrochemical analogy to attack by nucleophiles on coordinated ligands.

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