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ELECTROCHEMICAL ACTIVATION OF ACYL LIGANDS IN ORGANOMETALS. ESR STUDIES OF ACETYL- AND BENZOYLIRON(III) COMPLEXES

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Summary

The anodic oxidation of two series of acyliron(II) complexes, the neutral $CpFe(CO)_2COR$(I) and the anionic $CpFe(CO)(CN)COR^-$ (II) where R = CH_3 and C_6H_5, are examined in acetonitrile solutions. The cyclic voltammograms of II are reversible, whereas those of I are irreversible even at sweep rates as high as 10 V s^{-1}. The neutral $CpFe^{III}(CO)(CN)COCH_3$ radical is sufficiently stable at 20°C to examine its ESR spectrum, as well as the kinetics and mechanism of thermal decomposition to afford acetone in high yields. However the cation-radical $CpFe^{III}(CO)_2COCH_3^+$ from I is too reactive to observe directly, and it undergoes rapid solvolytic substitution in the presence of ethanol to afford ethyl acetate. The distinction between neutral and cationic acyliron(III) radicals is discussed in the context of acyl activation of organometals by electrochemical methods.

Introduction

Transition metal acyl complexes are the principal intermediates in a number of catalytic processes, including the hydroformylation of olefins and the carbonylation of methanol or organic halides. Although all of these processes involve changes in the formal oxidation states of the organic functionalities, nothing is known about the consequences of oxidation-reduction of the acylmetal intermediates. By contrast, transition metal hydrides [1] and alkylmetals [2] have been shown to undergo facile electron transfer at relatively modest potentials. In this study, we wish to establish the feasibility of effecting similar electron transfer with stable transition metal acyl complexes, and to relate such processes to the labilization of the acyl—metal bond in the context of the catalytic reactions described above. Of prime importance is the use of transient electrochemical techniques, particularly cyclic voltammetry, in conjunction

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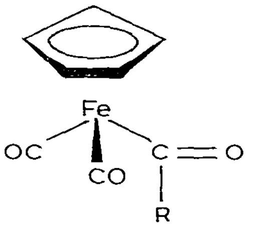
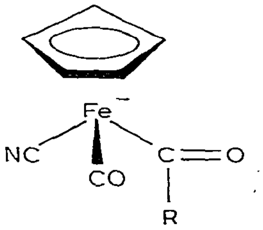
with electron spin resonance spectroscopy to probe the nature of the mestastable acylmetal intermediates.

Results

The electrochemistry of two classes of acylmetals were examined in this study, both containing the cyclopentadienyliron(II) moiety as either the neutral or the anionic complex I and II, respectively,



(I)

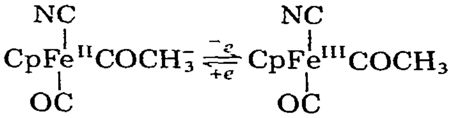


(II)

where R is methyl and phenyl in both series. The anionic complex II was prepared as the tetraethylammonium salt to allow solubilization in acetonitrile, used as the medium for electrochemistry.

Electrochemical identification of paramagnetic acyliron(II) intermediates

The anodic oxidation of the acyliron(II) complexes I and II was examined at 25°C with a stationary platinum microelectrode in acetonitrile solutions containing 0.10 *M* tetraethylammonium perchlorate (TEAP). The cyclic voltammogram of $\mathrm{CpFe(CO)(CN)(COCH_3)^-}$ in Figure 1 exhibits a well-defined anodic wave as well as a cathodic wave on the reverse scan. Both the peak current ratio $i_p(c)/i_p(a)$ and the potential separation Δ of the cathodic and anodic waves in Table 1 correspond to the expected values * for a reversible electrochemical couple as indicated in eq. 1 **.



$$\mathrm{Cp}\underset{\mathrm{OC}}{\overset{\mathrm{NC}}{\mathrm{Fe}}}{}^{\mathrm{II}}\mathrm{COCH_3^-} \underset{+e}{\overset{-e}{\rightleftharpoons}} \mathrm{Cp}\underset{\mathrm{OC}}{\overset{\mathrm{NC}}{\mathrm{Fe}}}{}^{\mathrm{III}}\mathrm{COCH_3} \qquad (1)$$

On the other hand, the cyclic voltammograms of the neutral acyliron(II) complexes I showed only an anodic peak, being irreversible even at CV sweep rates as high as 10 volts sec^{-1}. No reductive process was evident in the initial cathodic CV scan of both series of acyliron(II) complexes up to —1.50 volts.

The controlled-potential electrolysis of $\mathrm{CpFe(CO)(CN)(COCH_3)^-}$ in acetonitrile solutions at a platinum gauze electrode at 0.40 volts and 0°C, required 0.95 ± 0.05 electrons per Fe. During the electrolysis, there is a gradual change in color of the solution from pale yellow to dark brown. The cyclic voltammo-

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* The peak separation is expected to be somewhat larger than 59 mV for systems involving slow electron transfer [3], as is often observed for organometals [2].

** The formal oxidation states are included only to emphasize the redox change.

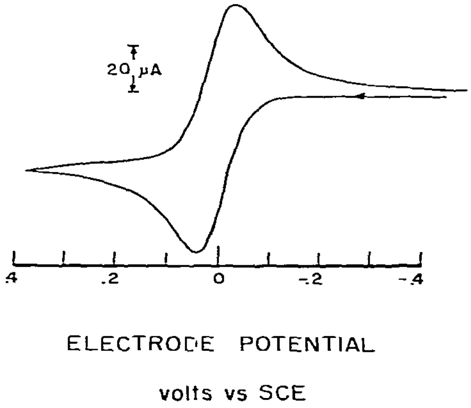

Fig. 1. First scan cyclic voltammogram of 4.0×10^{-3} M $[Et_4N][CpFe(CO)(CN)(COCH_3)]$ in acetonitrile containing 0.10 M tetraethylammonium perchlroate at a Pt microelectrode with a scan rate of 100 mV sec^{-1}.

gram of the resultant solution exhibited a reversible reduction centered at the same standard potential ($E^\circ = 0.10$ volts) observed in the oxidation of the anionic acetyliron(II) complex in Table 1. Furthermore, the controlled-potential reduction at 0.0 volts of the dark brown electrolyzed solution regenerates the anionic $CpFe(CO)(CN)(COCH_3)^-$ starting material in 90 ± 5% yield, as determined by the intensity of the carbonyl bonds at 2080 and 1905 cm^{-1} in the IR spectrum.

ESR spectra of acyliron(III) species

The electron spin resonance spectrum of the dark brown acetonitrile solution obtained from the controlled-potential electrolysis of $CpFe(CO)(CN)(COCH_3)^-$ consists of an intense, unresolved single absorption at $g = 2.059$. The lineshape of the first derivative ESR spectrum in Figure 2 (left) is Lorentzian, and the linewidth ($\Delta H_{pp} = 5.2$ gauss) is unaffected by dilution. As expected for a neutral radical, the ESR spectrum is not measurably changed in nonpolar solvents such as n-hexane. We were unable to resolve any nitrogen or proton hyperfine splittings, which must be negligible compared to the natural line-

TABLE 1

CYCLIC VOLTAMMETRIC DATA FOR ACYLIRON(II) COMPLEXES [a]

Acyliron(II) complex	E_p [b] (volts)	E^0 (volts)	$i_p(c)$ [c] / $i_p(a)$	Δ [d] (mV)
$CpFe(CO)_2(COCH_3)$	1.20	—	irrev.	—
$[CpFe(CO)(CN)(COCH_3)][Et_4N]$	0.20	0.10	1.01	98
$CpFe(CO)_2(COPh)$	1.22	—	irrev.	—
$[CpFe(CO)(CN)(COPh)][Et_4N]$	0.18	0.15	0.98	105

[a] Measured at 25°C in 7×10^{-5} M acyliron(II) complex in acetonitrile containing 0.10 M $(Et_4N)ClO_4$ as supporting electrolyte. [b] CV anodic peak potential in volts versus saturated NaCl SCE. [c] Ratio of peak currents for the cathodic and anodic waves. [d] Voltage separation of the cathodic and anodic peaks at a sweep rate of 20 mV sec^{-1}.

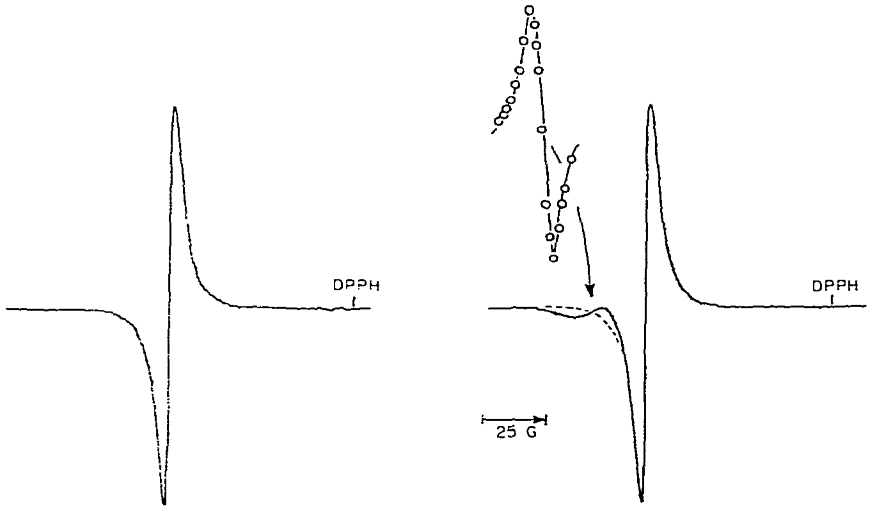

Fig. 2. Left: ESR spectrum of $CpFe^{III}(CO)(CN)(COCH_3)$ in acetonitrile solution at 25°C. Right: ESR spectrum of $CpFe^{III}(CO)(CN)COCH_3$ in the presence of PPh_3. The dashed curve is the tail expected from a Lorentzian lineshape. The inset shows the difference spectrum corresponding to the minor component.

width for an iron(III) radical to accord with the Lorentzian lineshape [4]. An odd-electron spin density which is metal centred is also indicated by the large isotropic *g*-values for both the acetyl and benzoyl radicals in Table 2 [5]. (Only a limited number of ESR spectra of organoiron radicals are available, and the ESR parameters listed in Table 2 also include those of the iron(I) analogs [6])

1. *Persistence of acyliron(III) radicals.* The acetonitrile solution of $CpFe^{III}$-$(CO)(CN)(COCH_3)$ showed no measurable change upon standing for a period of hours at —30°C, as indicated by reproducibility of the ESR spectrum. However, upon gradually warming the solution to room temperature, there is a concomitant diminution of the amplitude of the ESR signal without percep-

TABLE 2

ESR PARAMETERS OF ACYLIRON(III) AND IRON(I) RADICALS

Acyliron(III) complex	*g*	ΔH_{pp} (gauss)	Solvent	Reference
$CpFe(CO)(CN)(COCH_3)$	2.059	5.2	CH_3CN	[a]
$CpFe(CO)(CN)(COCH_3)$	2.059	6.0	$n\text{-}C_6H_{14}$	[a]
$CpFe(CO)(CN)(COPh)$	2.060	5.8	CH_3CN	[a]
$Fe(CO)_3(PPh_3)_2^+$	2.051	19.2	CH_2Cl_2	7
$Fe(NO)(S_2CNEt_2)_2$	2.040	15	EPA [b]	8
$FeH(Ph_2PCH_2CH_2PPh_2)_2$	2.085 2.206		$PhCH_3$	9
$Fe(C_6H_5)$(tetraene N_4)	2.070 2.002	(solid)		10
$Fe(C_3H_5)(CO)_2$	2.0459		$PhCH_3$	11
$Fe(C_3H_5)[P(OMe)_3]_3$	2.057	~10	THF	12

[a] This work. [b] A 2 : 5 : 5 ethanol-isopentane-diethyl ether mixture.

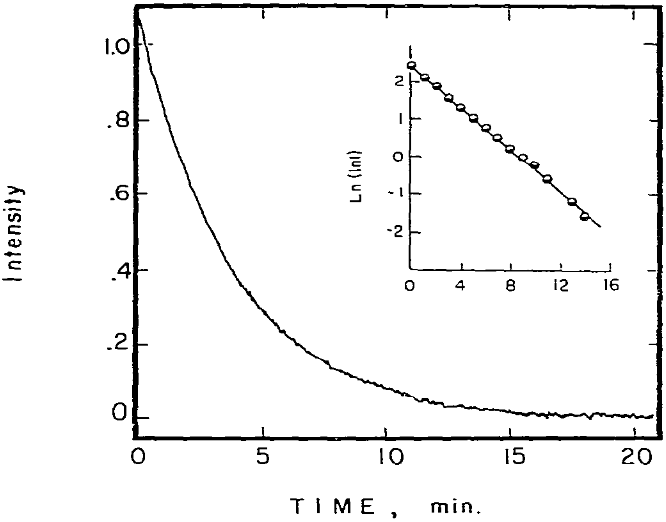

Fig. 3. The decay of the ESR signal of $CpFe^{III}(CO)(CN)(COCH_3)$ at 20°C in 0.10 M TEAP acetonitrile solution. The insert is the first order plot of the signal intensity (Int. in arbitrary units), showing a half-life of 3.6 min.

tible line broadening. The rate of decay of the radical followed first order kinetics (τ = 3.6 min) for more than four half-lives, as illustrated in Figure 3.

2. *Effect of added ligands.* If a solution of $CpFe^{III}(CO)(CN)(COCH_3)$ is saturated with carbon monoxide at 1 atmosphere, there is no change in the ESR spectrum: the g value remains constant and there are no additional signals. However, the first order decay is significantly retarded, the half-life increasing to 6.2 min compared to τ = 3.6 min obtained under an argon atmosphere. The presence of triphenylphosphine leads to an additional singlet absorption. Thus, two singlets are observed in the ESR spectrum in Figure 2 (right) of a solution of $CpFe^{III}(CO)(CN)(COCH_3)$ with added triphenylphosphine, saturated (~0.06 M) in acetonitrile. In addition to the main component due to $CpFe(CO)(CN)(COCH_3)$, a weaker absorption (5% of the principal intensity) appears at $\langle g \rangle$ = 2.045. Attempts to follow the rate of appearance of the new absorption band by mixing the reagents at low temperatures were

TABLE 3

THE DECAY OF $CpFe^{III}(CO)(CN)(COCH_3)$ IN THE PRESENCE OF TRIPHOSPHINE [a]

Time (sec)	A_1 [b]	A_2 [c] (× 10)	A_2/A_1 (%)
0	9.0	4.5	5.0
18	8.4	4.0	4.8
58	6.6	3.5	5.3
114	5.0	2.5	5.0
156	4.2	2.1	5.0
188	3.8	1.8	4.7
480	1.0	0.5	5.0

[a] In 0.10 M TEAP acetonitrile solution of $CpFe(CO)(CN)(COCH_3)$ and saturated with PPh_3 under argon at 20°C. The ESR intensities (A) are in arbitrary units. [b] Signal at $\langle g \rangle$ = 2.059. [c] Signal at $\langle g \rangle$ = 2.045.

unsuccessful, since it appears within 15 sec of mixing, even at —30°C. The rates of decay of the two ESR signals were followed at room temperature in an acetonitrile solution saturated with triphenylphosphine under 1 atmosphere of argon. As shown in Table 3, the rate of disappearance of CpFe(CO)(CN)-($COCH_3$) is to within experimental error unchanged (τ = 3.8 min) by the presence of added triphenylphosphine. Moreover, the relative intensities of the two ESR signals are invariant with time, strongly suggesting that the two paramagnetic species are in equilibrium with one another. (The alternative possibility that the two species have the same lifetimes would be highly fortuitous.)

Thermal decomposition of $CpFe^{III}(CO)(CN)(COCH_3)$

Acetone is always observed as one of the products of decomposition of $CpFe(CO)(CN)(COCH_3)$, but the yield is highly dependent on the reaction conditions, as described below. Unfortunately we were unable to identify the iron products of decomposition owing to the complex mixtures obtained. For example, even in the presence of 1 atmosphere of carbon monoxide, the decomposition of $CpFe^{III}(CO)(CN)(COCH_3)$ did not appear to yield carbonyliron species since the region between 1800—2100 cm^{-1} in the IR spectrum was transparent.

1. Effect of conversion percentage. Since the acetyl ligand is the sole source of methyl groups, acetone must arise at some stage of the decomposition from a bimolecular reaction of organoiron species. The latter could be reflected in a yield dependent on the fraction of $CpFe^{III}(CO)(CN)(COCH_3)$ converted. To examine this experimental parameter, solutions of $[Et_4N][CpFe^{II}(CO)(CN)$-$(COCH_3)]$ were first anodically oxidized at 0.40 volts according to eqn. 1, allowed to react for a set period of time, and finally the remaining $CpFe^{III}(CO)$-$(CN)(COCH_3)$ was rapidly reconverted by cathodic reduction at 0.0 volts. The amount of the acetyliron(III) which had thoroughly decomposed, was ascertained from the difference between the integrated anodic and cathodic currents. The yield of acetone was determined by gas chromatographic analysis using the internal standard method (see Experimental Section). It is noteworthy in Table 4 that acetone is produced in quantitative yields during the initial stages

TABLE 4

ACETONE YIELDS AS A FUNCTION OF THE CONVERSION OF $CpFe^{III}(CO)(CN)(COCH_3)$

$CpFe(CO)(CN)(COCH_3)$ consumed [a]			Acetone produced [b]	
10^5 M_i	10^5 M_f	Conversion (%)	10^5 M	(%)
6.8	6.2	10	0.3	100
7.0	4.9	30	1.0	95
7.5	2.4	68	1.8	70
6.9	0	100	1.4	40

[a] Decomposition of 0.1 M TEAP acetonitrile solutions of $CpFe(CO)(CN)(COCH_3)$ at 20°C under 1 atmosphere of carbon monoxide. The initial (M_i) and final (M_f) concentrations of $CpFe(CO)(CN)(COCH_3)$ monitored by coulommetry. [b] By gas chromatographic analysis.

TABLE 5

EFFECT OF ADDED LIGANDS ON THE ACETONE YIELDS FROM $CpFe(CO)(CN)(COCH_3)$ [a]

$CpFe^{III}(CO)(CN)(COCH_3)$ (10^5 M)	Ligand	Acetone (10^5 M) [b]	Acetaldehyde (10^5 M) [b]
6.9	CO	1.4(40)	0.4(6)
7.5	PPh_3	0.6(16)	0.4(5)
7.1	S_2Ph_2	3.3(93)	0.3(4)

[a] Thermal decomposition of $CpFe(CO)(CN)(COCH_3)$ in 0.10 M TEAP acetonitrile solutions at 20°C in the presence of 2 equivalents of added ligand (except carbon monixide runs were carried out at 1 atmosphere. [b] Percent yields in parentheses.

of the decomposition, but drops to more modest levels toward the final phases of decomposition.

2. *Effect of added ligands.* The ESR results point to the substitutional lability of $CpFe^{III}(CO)(CN)(COCH_3)$. Accordingly, various nucleophiles listed in Table 5 were added in an attempt to alter the efficiency of the coupling process. In these experiments, two equivalents of the appropriate nucleophile were added immediately following the anodic synthesis of $CpFe^{III}(CO)(CN)(COCH_3)$. The thermal decomposition was allowed to run its course completely before the acetone was analyzed. Triphenylphosphine induced a small decrease in the yield of acetone, as shown in Table 5. In marked contrast, the addition of diphenyldisulfide effected a quantitative production of acetone. The ligand is known to act as an effective bridge in bimetallic complexes [13], and its effect on the acetyliron(III) species is consistent with a coupling process as the route to acetone. Acetaldehyde is always produced as a minor product in these reactions, and as noted in column 4 of Table 5, its yields are relatively unaffected by added ligands. Only traces of ethane (0.1—0.5%) and methane (1—4%) were formed during the decomposition.

Anodic oxidation of $CpFe(CO)_2(COCH_3)$

The electrolysis of $CpFe^{II}(CO)_2(COCH_3)$ is somewhat complicated in acetonitrile solution by filming of the electrode surface. However, the presence of 10% by volume ethanol in acetonitrile is sufficient to obviate this difficulty without significantly altering the anodic peak potential at 1.20 volts versus SCE. (The cyclic voltammogram is still irreversible, showing no cathodic wave on the reverse scan.) Controlled-potential oxidation of $CpFe^{II}(CO)_2(COCH_3)$ at 1.30 volts required 2.90 ± 0.05 electrons per Fe. Since this coulometric value is significantly higher than one obtained for the anodic oxidation of the anionic analog $CpFe^{II}(CO)(CN)(COCH_3)^-$, it suggests a further oxidative fate of the putative acetyliron(III) cation radical, $CpFe(CO)_2COCH_3^+$. In accord with this expectation, ethyl acetate was found in 70% yield by gas chromatographic analysis. Extensive degradation of the iron moiety was qualitatively noted by the absence of carbonyl absorptions in the IR spectrum of the residue, and further product analysis was suspended.

Anodic oxidation of $CpFe(CO)_2(CH_3)$

The cyclic voltammogram of the alkyl analog $CpFe(CO)_2CH_3$ was also examined in acetonitrile solutions containing 0.1 *M* TEAP at 25°C. At a stationary platinum electrode, the CV showed an anodic peak at +0.98 volts versus SCE. The reverse scan indicated the presence of a coupled cathodic process at E_p +0.10 volts, but the current ratio i_c/i_a was only 0.20 at a sweep rate of 100 mV sec^{-1}. Similar to the behaviour of the acyl analog $CpFe(CO)_2COCH_3$, the peak potential was reproducible upon multiple scans. However, the peak current decreased successively after each cycle, suggesting a filming of the electrode surface. The addition of ethanol (10% by volume) eliminated this problem (although the CV was still irreversible), without affecting the peak potential at 0.98 volts. Controlled potential oxidation of $CpFe(CO)_2CH_3$ in a solution of acetonitrile/ethanol at +1.00 volts required 2.20 ± 0.05 electrons per Fe. Quantitative analysis of the resultant solution by gas liquid chromatography using the internal standard method, revealed the presence of ethyl acetate in 60% yield. A small quantity (10%) of acetaldehyde was also present in the electrolyzed solution. The IR spectrum lacked any absorption in the region between 1600 and 2200 cm^{-1}.

Discussion

The series of acyliron(II) complexes listed in Table 1 are all oxidized readily at a platinum electrode. The resultant acyliron(III) radicals are highly labile, in marked contrast to the stability of their diamagnetic precusors [14,15]. Electrochemical oxidation thus represents an effective means of activating the acyl functionality in an organometallic compound. In the following discussion we wish to describe in greater detail the nature of such an activation, particularly in comparison to the well-known photochemical activation of metal acyls [16].

Existence of discrete paramagnetic acyliron(III) complexes

The anodic oxidation of the cyano-substituted acyliron(II) anions II results in a completely reversible one-electron wave, as depicted by the cyclic voltammogram in Figure 1, and expressed in eq. 1. Furthermore, bulk electrolysis at a controlled potential close to E^0 demonstrates that the process is also reversible on the chemical time scale of 5—10 min. The resultant neutral acyliron(III) species may be separated from the electrochemical medium simply by extraction with hexane, as described in the Experimental. Unfortunately its thermal lability discouraged isolation and an ultimate determination of the crystal structure. The electrochemical studies, however, prove without reservation that the structures of the acetyl- and benzoyliron(III) radicals are directly related to their diamagnetic precursors by the loss of an electron. (For example, rearrangement to an isomeric methyliron(III) or phenyliron(III) carbonyl is precluded.) Although these observations are sufficient to conclude that the paramagnetic acyliron(III) in eq. 1 exists as a discrete species, it is possible that it may subsequently be involved as dimeric species, e.g.,

$$2\,CpFe(CO)(CN)(COCH_3) \rightleftharpoons Cp_2Fe_2(CO)_2(CN)_2(COCH_3)_2 \qquad (2)$$

since the reversible dimerization of iron-centered radicals is known [11].

The reactions embodied in eqs. 1 and 2, together correspond to a standard electrochemical EC process, for which the kinetic theory is well-developed [17].

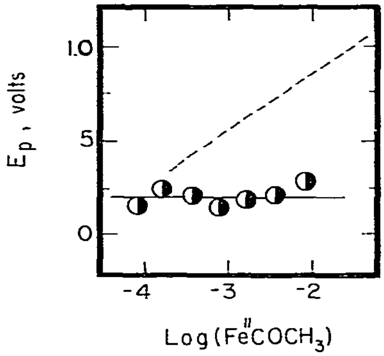

Fig. 4. Dependence of the anodic peak potential E_p on the concentration of $CpFe(CO)(CN)(COCH_3)^-$ during cyclic voltammetry in acetonitrile solution at 25°C.

Upon analysis of the CV wave parameters however, we find that it leads only to a reversible one-electron process, uncomplicated by any follow-up chemical reaction (such as that in eq. 2) on the electrochemical time scale. Thus Figure 4 shows that there is no dependence of the anodic peak potential with the concentration of $CpFe^{II}(CO)(CN)(COCH_3)^-$. Such a behavior is consistent only with an electrochemically reversible electron transfer process. The extent to which a follow-up reaction may participate, such as the second-order dimerization in eq. 2, is given by the dashed line in Figure 4. The well-behaved nature of the cyclic voltammogram is further corroborated in Figure 5, showing the linear dependence of the anodic peak current with both (a) the square root of the sweep rate $v^{1/2}$, as well as (b) the variation in the concentration of $CpFe(CO)(CN)(COCH_3)^-$ over two decades. Furthermore, the cathodic cyclic voltammogram of the resultant solution after bulk anodic electrolysis of $CpFe^{II}(CO)(CN)(COCH_3)^-$, exhibited only the reversible couple expressed in eq. 1 and listed in Table 1. No new cathodic waves were observed which could be attributed to the reduction of a dimer, e.g., *

$$Cp_2Fe_2^{III}(CO)_2(CN)_2(COCH_3)_2 \xrightarrow{+e} CpFe^{III}(CO)(CN)(COCH_3) + CpFe^{II}(CO)(CN)(COCH_3)^- \qquad (3)$$

In other words, the mononuclear acyliron(III) radical in eq. 1 is the only species extant in solution following the bulk anodic electrolysis of the anionic acyliron(II) complex. Any dimerization of such a paramagnetic species must be considered separately, since it can only occur in a subsequent process of higher activation energy.

Chemical lability of acyliron(III) radicals

The rate of decay of $CpFe^{III}(CO)(CN)(COCH_3)$, conveniently monitored by ESR spectroscopy, follows first order kinetics for more than 4 half-lives. Thus the acyliron(III) radical is not reacting by a slow reversible dimerization (com-

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* In contrast, several bimetallic dimers such as $Cp_2Fe_2(CO)_4$ or $Cp_2Mo_2(CO)_6$ are known to yield well defined cathodic waves [18].

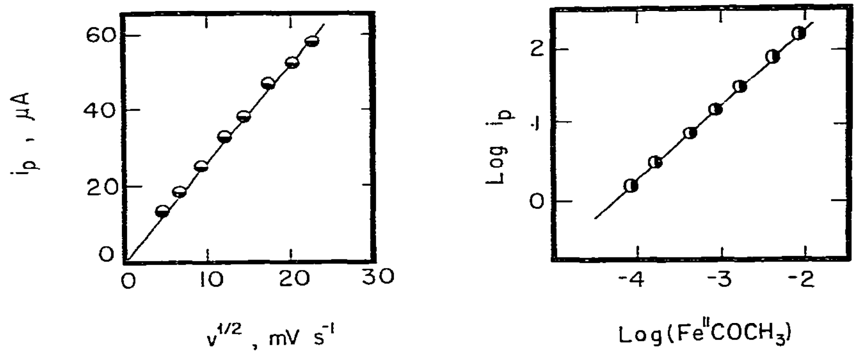
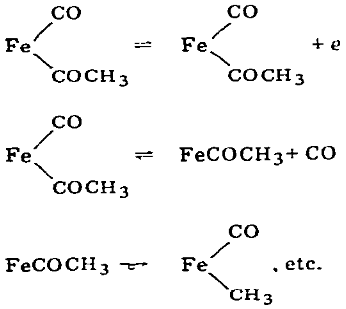


Fig. 5. Anodic peak current i_p(a) as a linear function of (a) the sweep rate ($v^{1/2}$) and (b) the concentration of $\mathrm{CpFe(CO)(CN)(COCH_3)^-}$ in acetonitrile at 25°C.

pare eq. 2). Instead, we interpret the retardation of the decomposition by carbon monoxide as arising from a dissociative process in eq. 5, included in the simplified mechanism below.

SCHEME I:



$$\mathrm{Fe}\begin{smallmatrix}\mathrm{CO}\\ \mathrm{COCH_3}\end{smallmatrix} \rightleftharpoons \mathrm{Fe}\begin{smallmatrix}\mathrm{CO}\\ \mathrm{COCH_3}\end{smallmatrix} + e \qquad (4)$$

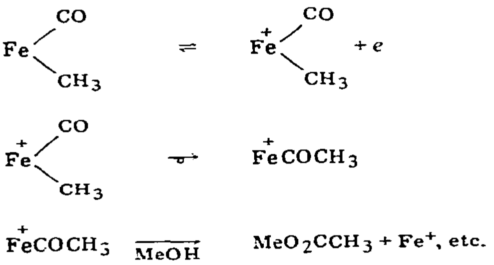
$$\mathrm{Fe}\begin{smallmatrix}\mathrm{CO}\\ \mathrm{COCH_3}\end{smallmatrix} \rightleftharpoons \mathrm{FeCOCH_3} + \mathrm{CO} \qquad (5)$$

$$\mathrm{FeCOCH_3} \rightarrow \mathrm{Fe}\begin{smallmatrix}\mathrm{CO}\\ \mathrm{CH_3}\end{smallmatrix}\text{, etc.} \qquad (6)$$

where *Fe* = CpFe(CN).

The facile CO insertion into a paramagnetic organometal as in eq. 6 has been directly observed with nickel(III) species [19], and it has been suggested as the primary step in the oxidative cleavage of a group of alkylmetal carbonyls to yield carboxylic esters, e.g. scheme 2 [20]. (Similar observations have been

SCHEME 2



$$\mathrm{Fe}\begin{smallmatrix}\mathrm{CO}\\ \mathrm{CH_3}\end{smallmatrix} \rightleftharpoons \overset{+}{\mathrm{Fe}}\begin{smallmatrix}\mathrm{CO}\\ \mathrm{CH_3}\end{smallmatrix} + e \qquad (7)$$

$$\overset{+}{\mathrm{Fe}}\begin{smallmatrix}\mathrm{CO}\\ \mathrm{CH_3}\end{smallmatrix} \rightarrow \overset{+}{\mathrm{Fe}}\mathrm{COCH_3} \qquad (8)$$

$$\overset{+}{\mathrm{Fe}}\mathrm{COCH_3} \xrightarrow[\mathrm{MeOH}]{} \mathrm{MeO_2CCH_3} + \mathrm{Fe^+}\text{, etc.} \qquad (9)$$

where *Fc* = CpFe(CO).

made with $\mathrm{CpMo(CO)_3CH_3}$ and $\mathrm{CpW(CO)_3CH_3}$.) Thus in eq. 9, alcohol is an efficient trap for the cationic acylmetal species [21]. In a similar manner, the electrochemical oxidation of an acetonitrile solution of $\mathrm{CpFe(CO)_2(COCH_3)}$ in the presence of ethanol results in high yields of ethyl acetate,

$$\mathrm{CpFe(CO)_2COCH_3} \xrightarrow[\mathrm{EtOH}]{-e} \mathrm{EtO_2CCH_3}, \text{ etc.} \tag{10}$$

which is analogous to the formation of methyl acetate in Scheme 2. Indeed the facile rearrangement in eq. 8 is supported by the observation of ethyl acetate when the methyliron complex $\mathrm{CpFe(CO)_2CH_3}$ is directly oxidized anodically in the presence of ethanol.

Since acetyliron(III) radicals are intermediates in both Schemes 1 and 2, we might ask why one radical leads to acetone, whereas the other radical affords acetate esters. An obvious, fundamental difference between the two lies in the charge on the resultant paramagnetic acyliron(III) species. Since cation-radicals of transition metal carbonyl complexes are well-known to be highly susceptible to nucleophilic attack [22], solvolytic substitution of the acetyliron(III) cation in eq. 9 to afford acetate esters is not unreasonable. Consistent with this formulation, the anodic wave in the cyclic voltammogram of $\mathrm{CpFe(CO)_2COCH_3}$ in Table 1 is observed to be irreversible even at high sweep rates. In contrast, the anodic oxidation of the cyano-substituted acetyliron(II) anion is totally reversible, allowing the neutral radical of relatively increased stability to compete in alternative reaction pathways (vide infra) *. The electrochemical activation of the acyl—metal bond depicted in eq. 5 is reminiscent of decarbonylations induced photochemically [14,16,23]. The distinction between the electrochemical and photochemical processes lies in the nature of the resultant alkylmetal species. Thus, the photochemical decarbonylation of $\mathrm{CpFe(CO)_2COCH_3}$ stops at the stable $\mathrm{CpFe(CO)_2CH_3}$ derivative (with no change in formal oxidation state), whereas the electrochemical activation presented in Scheme 1 goes on to yield ketone, as discussed in the next section.

Coupling reactions of paramagnetic organometals

Reductive elimination of coupled alkyl ligands is developing into a rather general concept for the oxidative activation of alkylmetal complexes [19,21], one of the most striking results being the high yield of alkyl dimers obtained even with halogens, e.g.

$$(\mathrm{Bipy})_2\mathrm{FeR}_2 + \mathrm{Br}_2 \left[\begin{array}{ll} \rightarrow \mathrm{RR} + (\mathrm{Bipy})_2\mathrm{FeBr}_2 & (11) \\ \\ \rightarrow 2\,\mathrm{RBr} + (\mathrm{Bipy})_2\mathrm{FeBr}_2 & (12) \end{array} \right.$$

Application of an analogous line of reasoning to the paramagnetic organoiron(III) intermediates in Scheme 1 suggests that three possible coupled products can result from the reductive elimination from acetyliron species, viz., biacetyl, acetone and ethane. Such an expectation, in conjunction with the electrochem-

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[*] An equivalent situation with respect to β-hydride elimination from transition metal alkyls is well documented. See ref. 21, Chapter 12.

ical and ESR results, may be used to understand the products observed in the thermal decomposition of $CpFe^{III}(CO)(CN)COCH_3$. Thus the acetyliron(III) radical is persistent, as established by ESR spectroscopy, and shows no measurable tendency toward dimerization within the experimental limits of the electrochemical probe. Consistent with these observations, biacetyl is not detected (<0.1%) in the reaction mixture. In contrast to the acetyliron(III) radical, the methyliron(III) species, if formed as in Scheme 1, is too reactive to be observed directly. (The first order decay of $CpFe^{III}(CO)(CN)COCH_3$ together with the CO retardation form the primary basis for the postulation of this reactive intermediate.) Furthermore, the formation of only traces of ethane, suggest that bimolecular reactions of the methyliron(III) species are not important. We tentatively ascribe the formation of acetone as arising as a result of the cross coupling of the methyliron(III) species with the acetyliron(III) radical. Notably, acetone is formed in quantitative yields only in the initial stages of decomposition (see Table 4), when the high concentration of the acetyliron(III) radical is optimized to efficiently trap the methyliron(III) species. This is followed by the precipitous drop in the acetone yield in the latter stages of reaction, as expected from such a formulation. The effect of diphenyl disulfide on the acetone yield in Table 5 also accords with the coupling of paramagnetic organoiron intermediates, since it is known to be an effective bridge in bimetallic complexes [13]. In this regard, the direct dimerization of the 17-electron organoiron species will lead to binuclear intermediates, probably analogous to those previously generated in the cobalt analogue $Cp_2Co_2(CO)_2(CH_3)_2$ by Bergman and coworkers [24]. Indeed, it remains to be seen whether the reductive elimination of acetone follows the same route in both systems.

Conclusion

The electrochemical oxidation of diamagnetic acyliron(II) complexes results in the labilization of the acyl ligands. The acetyl and benzoyl derivatives of the neutral complex $CpFe^{II}(CO)_2COR$ are irreversibly oxidized to unstable cationic acyliron(III) intermediates which may be trapped by ethanol to yield organic esters in good yields. Substitution of a carbonyl ligand by cyanide reduces the charge on the acyliron(III) moiety by one unit, and the oxidation of $CpFe^{II}(CO)(CN)COR^-$ as the tetraethylammonium salts afford paramagnetic complexes showing narrow ESR linewidths, sufficiently stable to be prepared as standard reagents. Analysis of the thermal decomposition of $CpFe^{III}(CO)(CN)COCH_3$ indicates a reversible decarbonylation followed by the facile coupling of 17-electron methyliron(III) and acetyliron(III) radicals to afford acetone in high yields.

Experimental

Materials

$CpFe(CO)_2COCH_3$, $CpFe(CO)_2CH_3$, $CpFe(CO)_2COC_6H_5$, and $CpFe(CO)_2C_6H_5$ were prepared according to published procedures [14]. The corresponding cyano derivatives were obtained by the cyanide-induced insertion of carbon monoxide into the iron—alkyl bond [15]. Reagent grade acetonitrile was further purified by refluxing over calcium hydride, followed by treatment with potassium permanganate, and redistillation from P_2O_5 through a 19-plate bubble cap Oldershaw column. All solvents and reagents were stored under argon in Schlenk flasks. Tetraethylammonium perchlorate (TEAP) was obtained from G.F. Smith Chemical Co., and used without further purification.

Electrochemical measurements

Electrochemistry was performed on a Princeton Applied Research Model 173 potentiostat equipped with a Model 176 current-to-voltage converter which provided a feedback compensation for ohmic drop between the working and reference electrodes. The voltage follower amplifier (PAR model 178) was mounted external to the main potentiostat with a minimum length of high impedance connection to the reference electrode (for low noise pickup). Cyclic voltammograms were recorded on a Houston Series 2000 X-Y recorder. The electrochemical cell was constructed according to the design of Van Duyne and Reilley [25]. The distance between the platinum working electrode and the tip of the salt bridge was 1 mm to minimize ohmic drop. Bulk coulometry was carried out in a 3-compartment cell of conventional design with a platinum gauze electrode. Complete electrolysis of 0.2 mmol electroactive material generally required 5—10 min, and was graphically recorded on a Leeds and Northrup Speedomax strip chart recorder. The current-time curve was manually integrated.

Anodic oxidation of $[Et_4N][CpFe(CO)(CN)(COCH_3)]$

A solution of $[Et_4N][CpFe(CO)(CN)(COCH_3)]$ (30.0 mg) in 8 ml of acetonitrile containing 0.1 *M* tetraethylammonium perchlorate at 0°C was electrolyzed at +0.40 V versus SCE. The electrolysis was continued for 5 half-lives in the exponential decay of the current. The measured area was 7.89 Amp sec, which yields 0.95 ± 0.05 electrons per Fe. Aliquots of the solution were removed by a hypodermic syringe for analysis in either the cyclic voltammetric cell or the ESR tube equipped with a Schlenk top. The oxidized product could be separated from the supporting electrolyte by extracting the acetonitrile solution with n-hexane. The upper hexane layer was removed and analyzed by ESR spectroscopy.

Products from the thermal decomposition of $CpFe(CO)(CN)(COCH_3)$

Solutions of $CpFe^{III}(CO)(CN)(COCH_3)$, prepared as described above, were allowed to react at room temperature for 30 minutes. During this period, the dark brown solution became lighter in color. Analysis of the gaseous products by gas chromatography on a column of Porapak Q, indicated the presence of trace amounts of ethane (0.1—0.5%) and methane (1—4%) using the internal standard method. The solution was also analyzed by gas chromatography on a 15-ft Apiezon L column at 80°C for acetone and acetaldehyde, using benzene as the internal standard. To within experimental error, the same product distribution was obtained when a separate solution of $CpFe^{III}(CO)(CN)(COCH_3)$ was allowed to react for 2 h at 0°C.

Anodic oxidation of $CpFe(CO)_2(COCH_3)$

The electrolysis cell was charged with $CpFe(CO)_2COCH_3$ (42.7 mg) in 8 ml of a solution consisting of 10% by volume of ethanol in acetonitrile, containing 0.1 *M* tetraethylammonium perchlorate at 0°C. The solution was electrolyzed at +1.3 V versus SCE to give a measured current of 54.0 Amp sec, which corresponds to 2.90 ± 0.05 electrons per Fe. The solution was analyzed by gas chromatography on a 15-ft Apiezon L column at 80°C for ethyl acetate (0.14 mmol, 70%), using cyclohexane as an internal standard.

Anodic oxidation of $CpFe(CO)_2CH_3$

Bulk electrolysis of 6.88×10^{-5} mol of $CpFe(CO)_2CH_3$ in 8 ml of 10% v ethanol in acetonitrile containing 0.1 *M* tetraethylammonium perchlorate at +1.00 V versus NaCl-SCE required 14.6 Amp sec or 2.20 ± 0.05 electrons per Fe. A transient deep green color was observed during the electrolysis. At the end of the oxidation the color of the solution returned to its original yellow color. Analysis of the resultant solution by gas chromatography on a 17 foot carbowax column at 60°C using n-pentane as an internal standard yielded 4.1×10^{-5} mol (60%) of ethyl acetate.

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References

1 R.J. Klingler, J.C. Huffman and J.K. Kochi, J. Amer. Chem. Soc., 102 (1980) 208.

2 (a) L.C. Wong and J.K. Kochi, J. Amer. Chem. Soc., 101 (1979) 5593. (b) R.J. Klingler and J.K. Kochi, J. Amer. Chem. Soc., 102 (1980) 4790. (c) R.J. Klingler, K. Mochida and J.K. Kochi, J. Amer. Chem. Soc., 101 (1979) 6626. (d) S. Fukuzumi, K. Mochida and J.K. Kochi, J. Amer. Chem. Soc., 101 (1979) 5961.

3 R.S. Nicholson, Anal. Chem., 37 (1965) 1351.

4 J.E. Wertz and J.R. Bolton, Electron Spin Resonance, McGraw-Hill, New York, 1972, Chapt. 9, p. 196.

5 A. Carrington and A.D. McLachlan, Introduction ot Magnetic Resonance, Harper and Row, New York, 1967, Chapt. 9 and 10.

6 E. Konig, in E.A. Koerner von Gustorf, F.W. Grevels and I. Fischler, The Organic Chemistry of Iron, Academic Press, New York, 1978, p. 257.

7 N.G. Connelly and K.R. Somers, J. Organometal. Chem., 113 (1976) C39.

8 B.A. Goodman, J.B. Raynor and M.C.R. Symons, J. Chem. Soc. A, (1969) 2572.

9 M. Gargano, P. Giannocaro, M. Rossi, G. Vasapollo and A. Sacco, J. Chem. Soc. Dalton Trans., 9 (1975).

10 M.C. Rakowski and D.H. Busch, J. Amer. Chem. Soc., 97 (1975) 2570.

11 E.L. Muetterties, B.A. Sosinsky and K.L. Zamaraev, J. Amer. Chem. Soc., 97 (1975) 5299.

12 S.D. Ittel, P.J. Krusic and P. Meakin, J. Amer. Chem. Soc., 100 (1978) 3264.

13 (a) R.B. King, P.M. Treichel and F.G.A. Stone, J. Amer. Chem. Soc., 83 (1961) 3600. (b) P.M. Treichel, J.H. Morris and F.G.A. Stone, J. Chem. Soc., (1963) 720. (c) R.H. Holm, R.B. King and F.G.A. Stone, Inorg. Chem., 2 (1963) 219. (d) P.M. Treichel, J. Chem. Soc. B, (1971) 14. (e) R.J. Klingler, W. Butler and M.D. Curtis, J. Amer. Chem. Soc., 97 (1975) 3535.

14 R.B. King and M.B. Bisnette, J. Organometal. Chem., 2 (1964) 15.

15 T. Kruck, L. Höfler and L. Liebig, Chem. Ber., 105 (1972) 1173.

16 A. Vogler, in A.W. Adamson and P.D. Fleischauer, (Eds.), Concepts of Inorganic Photochemistry, Wiley-Interscience, New York, 1975, p. 269.

17 (a) J.M. Saveant and E. Vianello, Comp. Rend., 256 (1963) 2597. (b) A. Streitwieser, in A. Weissberger and B.W. Rossiter, (Eds.), Physical Methods of Chemistry Part IIa, Electrochemical Methods, Wiley-Interscience, New York, 1971.

18 R.E. Dessy, P.M. Weissman and R.L. Pohl, J. Amer. Chem. Soc., 88 (1966) 5117.

19 T.T. Tsou and J.K. Kochi, J. Amer. Chem. Soc., 101 (1979) 6319.

20 G.W. Daub, Prog. Inorg. Chem., 22 (1977) 409.

21 J.K. Kochi, Organometallic Mechanisms and Catalysis, Academic Press, New York, 1978, Chapt. 18 III B and references therein.
22 J.C. Pickett, D.J. Pletcher, J. Chem. Soc. Dalton, (1975) 879; (1976) 636.
23 F. Calderazzo, Angew. Chem.,Int. Ed., 16 (1977) 299.
24 (a) N.E. Schore, C. Ilenda and R.G. Bergman, J. Amer. Chem. Soc., 98 (1976) 7436. (b) H.E. Bryndza and R.G. Bergman, J. Amer. Chem. Soc., 101 (1979) 4766.
25 R.P. Van Duyne and C.N. Reilley, Anal. Chem., 44 (1972) 142.