formally appears to be sterically unsaturated. Clearly, the $(1,3-Me_2C_5H_3)_2YH$ unit can accommodate nine coordination as is demonstrated in $[(1,3-Me_2C_5H_3)_2(THF)Y(\mu-H)]_2$. The nine-coordinate structure must be slightly crowded as evidenced by the facile THF loss, but an eight-coordinate structure in which two of the ligands are hydrides probably does not provide optimum steric saturation. As a result, 3 contains shorter Y-C(ring) distances and the molecule is not as thermally stable in solution as 4. Hence with a dicyclopentadienyl hydride ligand set, dimethyl substitution does perturb the metal–ligand size balance enough to change the chemistry from that observed with C_5H_5 or MeC_5H_4 analogues. The result is a new type of bis(cyclopentadienyl)metal hydride trimer.

Conclusion

Dimethyl substitution of a cyclopentadienyl ring provides a small perturbation to the chemistry of trivalent bis(cyclopentadienyl)yttrium complexes. For chloride and methyl complexes, no structural or chemical consequences

are evident. For hydride complexes, the steric balance is affected to a greater extent such that nine-coordinate dimeric species desolvate to form a new class of eight-coordinate trimers. As expected the change is not as great as that caused by substituting the ring with two Me_3Si groups. Hence, the $1,3-Me_2C_5H_3$ ligand constitutes an intermediate sized cyclopentadienyl ligand which can be used to manipulate organoyttrium and organolanthanide chemistry.

Supplementary Material Available: Tables of thermal parameters (4 pages); a listing of structure factor amplitudes (28 pages). Ordering information is given on any current masthead page.

Electrochemical Studies of the Cation Radical (η-MeC₅H₄)(CO)(MeOH)FeCOMe⁺

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The oxidations of $(η-Cp)(CO)_2FeMe$ ($Cp' = MeC_5H_4$) in methanol and mixtures of methanol and acetonitrile have been studied by a combination of electrochemical, spectroscopic, and chemical techniques. The distribution of $(η-Cp)(CO)(MeOH)FeCOMe^+$ and $(η-Cp')(CO)(AN)FeCOMe^+$ formed during the oxidation of $(η-Cp')(CO)_2FeMe^0$ at low temperatures is initially kinetically determined and reflects the solvent composition. These observations coupled with the computer simulation of cyclic voltammetry experiments show that the acetonitrile and methanol complexes are formed with equal rate constants. We interpret this to be consistent with the intermediacy of a highly reactive species, possibly $(η-Cp')(CO)FeCOMe^+$. The methanol and acetonitrile complexes interconvert in the iron(III) state via an entering ligand-dependent pathway with an equilibrium constant (K_{eq}(III) = 60) favoring the acetonitrile complex; however, in the iron(II) state K_{eq}(II) = 3.5 × 10⁵.

Introduction

The dramatic kinetic and thermodynamic promotion of the alkyl to acyl migratory insertion reaction that occurs upon oxidation of alkyl transition-metal carbonyls is a well-documented phenomenon.[1,2] Several mechanisms have been proposed to account for the distribution of products, but the origins of these enhancements remain obscure.[3] In order to gain further insight about the be-

havior of intermediates generated by the oxidation of alkyl iron carbonyls, we studied the oxidation of $(η-Cp')(CO)_2FeMe^4$ in methanol and mixed methanol/acetonitrile at low temperatures.

Results

The generation and ligand exchange reactions of the complex $(η-Cp')(CO)(MeOH)FeCOMe^+$ have been studied by a combination of chemical and electrochemical techniques. The chemical oxidation of $(η-Cp')(CO)_2FeMe$ with ceric ammonium nitrate (Ce(IV)) in alcohols at -78 °C affords deep green solutions that are characteristic of the presence of cation radicals of the type $(η-Cp')(CO)LFe-COMe^+$.[1] The rapid attenuation of the green color as the solutions warmed to room temperature attests to the kinetic instability of the chromophoric species. Consonant with these observations, the cyclic voltammograms (CV's) of $(η-Cp')(CO)_2FeMe$ in MeOH at 22 °C show only the irreversible oxidation (E_{pa} = 1.25 V) of the complex; no appreciable concentrations of new electrochemically active species were detected upon scan reversal. These results

(1) (a) Magnuson, R. H.; Zulu, S. J.; Tsai, W.-M.; Giering, W. P. *J. Am. Chem. Soc.* **1980**, *102*, 6887. (b) Magnuson, R. H.; Meirowitz, R.; Zulu, S. J.; Giering, W. P. *J. Am. Chem. Soc.* **1982**, *104*, 5790. (c) Magnuson, R. H.; Meirowitz, R.; Zulu, S. J.; Giering, W. P.; *Organometallics* **1983**, *2*, 460. (d) Javaheri, S.; Giering, W. P. *Organometallics* **1984**, *3*, 1927.
(2) (a) Nicholas, K. M.; Rosenblum, M. *J. Am. Chem. Soc.* **1973**, *95*, 4449. (b) Bock, P. L.; Boschetto, D. J.; Rasmussen, J. R.; Demers, J. P.; Whitesides, G. M. *J. Am. Chem. Soc.* **1974**, *96*, 2814. (c) LaCrose, S. J.; Cutler, A. R. *J. Am. Chem. Soc.* **1982**, *104*, 2312. (d) Cameron, A.; Smith, V. H.; Baird, M. C. *Organometallics* **1983**, *2*, 465. (e) Bly, R. S.; Silverman, G. S.; Bly, R. K. *Organometallics* **1985**, *4*, 374. (f) Bly, R. S.; Silverman, G. S.; Hossain, M. M.; Bly, R. K. *Organometallics* **1984**, 642. (g) Reger, D. L.; Mintz, E. *Organometallics* **1984**, *3*, 1759. (h) Reger, D. L.; Mintz, E. *J. Am. Chem. Soc.* **1986**, *108*, 1940.
(3) (a) Anderson, S. N.; Fong, C. W.; Johnson, M. D. *J. Chem. Soc., Chem. Commun.* **1973**, 163. (b) Doxsee, K. M.; Grubbs, R. H.; Anson, F. C. *J. Am. Chem. Soc.* **1984**, *106*, 7819.

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(4) $Cp = C_5H_5$; $Cp' = MeC_5H_4$.

were obtained regardless of how the experiments were performed (vide infra). When the initial anodic wave of $(\eta\text{-Cp}')(CO)_2FeMe$ is traversed at -45 °C, we observe a cathodic wave ($E_{pa} = 0.47$ V) with no coupled anodic partner and a set of low current cathodic and anodic waves ($E° = -0.07$ V) which are assigned to the $(\eta\text{-Cp}')(CO)$-$(MeOH)FeCOMe^{0,+}$ couple (vide infra). The current of the -0.07 V couple increases dramatically, and the wave at $E_{pc} = 0.47$ V is absent when the initial anodic wave of $(\eta\text{-Cp}')(CO)_2FeMe$ is ramped but the peak is not traversed. The concentration of $(\eta\text{-Cp}')(CO)(MeOH)FeCOMe^+$ was maximized by stepping to the foot of the initial anodic wave and then holding at the switching potential for several seconds before commencing the return scan. In this manner we avoid the further oxidation of the primary electrochemical products. Similar CV's are obtained on samples of $(\eta\text{-Cp}')(CO)_2FeMe$ that had been preoxidized at -45 °C by 0.8 equiv of Ce(IV). (Addition of larger amounts of Ce(IV) results in extensive over oxidation.) Thus, immediately after mixing, the CV ($E_i = 0.53$ V with the initial scan in the negative direction) shows the irreversible wave at $E_{pa} = 0.47$ V and the couple at -0.07 V. The species responsible for the wave at $E_{pa} = 0.47$ V decayed (via a non-first-order process) over a period of 15 min whereas $(\eta\text{-Cp}')(CO)(MeOH)FeCOMe^+$ exhibited a longer lifetime. Similar results were obtained for the CV experiments in ethanol and using a glassy carbon electrode.

Cyclic voltammetry provides rich kinetic and thermodynamic data, but the short lifetimes of the intermediates present substantial problems in terms of structural characterization. Identification of $(\eta\text{-Cp}')(CO)(MeOH)Fe$-$COMe^+$ as the transient generated by the oxidation of $(\eta\text{-Cp}')(CO)_2FeMe$ rests on spectroscopic and indirect evidence. Thus, the infrared spectrum of the reaction mixture generated by the Ce(IV) oxidation of $(\eta\text{-Cp}')$-$(CO)_2FeMe$ in methanol at -45 °C exhibits a new moderate to strong absorption at 1694 cm^{-1} which disappears when the solution is warmed. We assign this absorption to the acetyl ligand of $(\eta\text{-Cp}')(CO)(MeOH)FeCOMe^+$. The analogous acetonitrile complex $(\eta\text{-Cp})(CO)(AN)FeCOMe^+$ exhibits a similar absorption at 1710 cm^{-1}.[1a] Indirect evidence also supports this interpretation: The chemically irreversible electrochemical oxidation of $(\eta\text{-Cp}')(CO)_2FeMe$ in the presence of external ligands (i.e. acetonitrile (AN), Ph$_3$P, $(p\text{-MeC}_6H_4)_3$P, $(i\text{-PrO})_3$P) all afford cation radicals of the type $(\eta\text{-Cp}')(CO)LFeCOMe^+$ even at temperatures as low as -78 °C. The structures of these complexes are well-established since they may be generated directly from $(\eta\text{-Cp}')(CO)LFeCOMe$.[1a–c,5] We know that the transformations of the initial oxidation product $(\eta\text{-Cp}')$-$(CO)_2FeMe^+$ to the observed acyl complexes are enormously fast in the presence of the external ligands because we cannot observe the reduction of $(\eta\text{-Cp}')(CO)_2FeMe^+$ at -78 °C even at high scan rates (>1.0 V s^{-1}). Thus, it seems reasonable that the transients generated by the oxidation of $(\eta\text{-Cp}')(CO)_2FeMe$ in alcohols (or in the presence of other oxygen solvents) have structures similar to $(\eta$-Cp$')(CO)LFeCOMe^+$.

The electrochemistry of $(\eta\text{-Cp})(CO)_2FeCH_2CH_2OMe$[6] provides additional support for the assignment of the acyl structures to the species formed upon oxidation of the iron complexes in the oxygen solvents. The CV of $(\eta\text{-Cp})$-$(CO)_2FeCH_2CH_2OMe$ shows the formation of a new species upon oxidation. This new species shows a quasi-reversible couple at 0.016 V. Because of the entropically favored
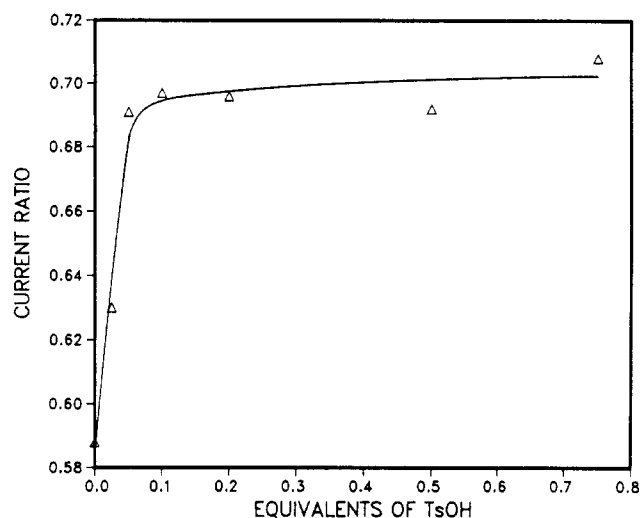
Figure 1. A plot of the anodic/cathodic current ratios for the $(\eta\text{-Cp}')(CO)(MeOH)FeCOMe^{0,+}$ couple vs. the number of equivalents of p-toluene sulfonic acid added to the electrolyte at -45 °C. $(\eta\text{-Cp}')(CO)(MeOH)FeCOMe^+$ was generated by the potential step and sweep method described in the Results.

coordination of the methoxy group to the iron, we assign the structure $(\eta\text{-Cp})(CO)FeCOCH_2CH_2OMe^+$ to this oxidation product. Since the electrochemical properties of the methoxy complex[7] are similar to those observed for the transient that gives rise to the -0.07 V couple (vide supra), we believe that both complexes possess similar structures with iron–oxygen linkages.

$(\eta\text{-Cp}')(CO)(MeOH)FeCOMe^+$ is rather stable at -45 °C and persists for more than 30 min after chemical generation. The cyclic voltammograms of $(\eta\text{-Cp}')(CO)(MeOH)$-$FeCOMe^+$ (generated electrochemically or by chemical oxidation with Ce(IV)) show that the reduction of the cation is not completely reversible chemically—the neutral partner $((\eta\text{-Cp}')(CO)(MeOH)FeCOMe^0)$ of the couple is considerably less stable. In addition, the stability of the $(\eta\text{-Cp}')(CO)(MeOH)FeCOMe^0$ is acid-dependent. Thus, the addition of acid increased the value of $(E_{pa} + E_{pc})/2$ from -0.07 V to a limiting value of -0.009 V. Both the peak potential and current of the cathodic wave are invariant while the peak potential for the anodic wave shifts slightly in a positive direction (attributable to uncompensated internal resistance) and the anodic current increases to a maximum $i_a/i_c = 0.71$ (Figure 1) as the concentration of acid increases. Computer analysis of the CV of $(\eta\text{-Cp}')$-$(CO)(MeOH)FeCOMe^+$ (generated by the potential step and sweep method, vide infra) provides a current ratio of 0.77 in the absence of decomposition of either member of the couple. Therefore, $(\eta\text{-Cp}')(CO)(MeOH)FeCOMe^0$ decomposes by both acid-dependent and -independent pathways. We calculate a first-order rate constant of $k = 0.08$ s^{-1} for the decomposition of $(\eta\text{-Cp}')(CO)(MeOH)Fe$-$COMe^0$ in the absence of added external acid.

The addition of acetonitrile to solutions of $(\eta\text{-Cp}')$-$(CO)(MeOH)FeCOMe^+$ in methanol results in CV's that are temperature and scan rate dependent. At -78 °C, the CV of $(\eta\text{-Cp}')(CO)_2FeMe$ in methanol containing up to 10 mol % acetonitrile exhibits new couples ($E° = +0.10$ and -0.07 V) upon repetitive scanning. The relative currents ($i_{AN}/i_{MeOH} = 0.13$, 10 mol % AN) of the cathodic waves of the couples, which are assigned to the reduction $(\eta$-Cp$)(CO)(AN)FeCOMe^+$ and $(\eta\text{-Cp})(CO)(MeOH)Fe$-$COMe^+$, respectively, are scan rate independent and reflect

(5) Unpublished results.
(6) Lennon, P.; Madhavarao, M.; Rosan, A.; Rosenblum, M. *J. Organomet. Chem.* **1976**, *108*, 93.

(7) Connelly, N. G.; Kitchen, M. D. *J. Chem. Soc., Dalton Trans.* **1977**, 931.
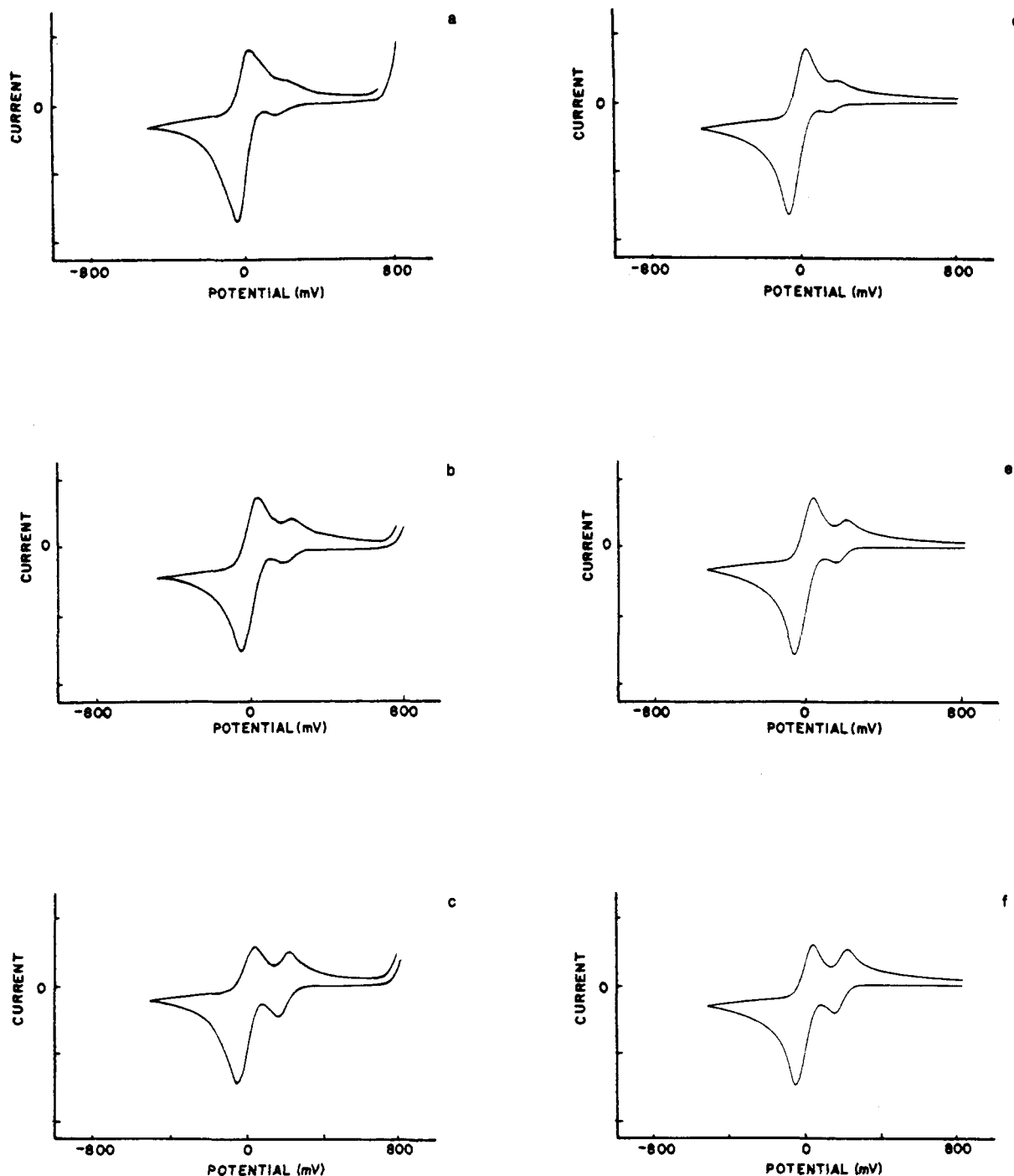
Figure 2. Experimental cyclic voltammograms obtained on mixtures of (η-Cp′)(CO)(MeOH)FeCOMe$^+$ and (η-Cp′)(CO)(AN)FeCOMe$^+$ generated electrochemically by a potential step and sweep method (described in the Results) at –45 °C in an electrolyte containing 0.2 M LiClO$_4$. Data were collected at 200 mV s^{-1} on solutions containing (a) 2.5, (b) 5.0, and (c) 10.0 mol % acetonitrile in methanol. Capacitive current has been substracted from the experimental cyclic voltammograms. The simulated cyclic voltammogram are displayed in (d) 2.5, (e) 5.0, and (f) 10.0 mol %.

the relative concentrations of the two solvents (1:9). In similar experiments at higher temperatures, the current ratio of the cathodic waves increased and became scan rate dependent, thereby demonstrating an increasingly facile interconversion of these complexes on the CV time scale.

The interconversion of (η-Cp′)(CO)(AN)FeCOMe$^+$ and (η-Cp′)(CO)(MeOH)FeCOMe$^+$ was readily followed at –45 °C by reverse pulse voltammetry (RPV)[8] monitoring of a methanol solution of (η-Cp′)(CO)$_2$FeMe that had been preoxidized with Ce(IV). It was necessary to allow the

irreversible wave at 0.47 V to decay before the addition of acetonitrile. This usually required about 15 min after which an aliquot of acetonitrile was added to the reaction mixture. The formation of the acetonitrile complex was followed by observing the growth of the waves at $E^{\circ\prime}$ = 0.10 V and a concomitant attenuation of the couple at $E^{\circ\prime}$ = –0.07 V ((η-Cp′)(CO)(MeOH)FeCOMe$^+$). The kinetic data were treated as a pseudo-first-order approach to equilibrium since the concentration of acetonitrile in all experiments was at least 20 times that of the initial concentration of (η-Cp′)(CO)$_2$FeMe. The plots of log (i_{AN}) vs. time are linear over 2.5 half-lives. A plot of log k_{obsd} versus log [AN] is linear with a slope of unity and affords a second-order

(8) Hermolin, J.; Kirowa-Eisner, E.; Kosower, E. M. *J. Am. Chem. Soc.* 1981, 1591.

rate constant of k_{23} = 0.005 M^{-1} s^{-1} (Scheme I). An average value of the equilibrium constant (K_{eq} = 60 ± 8) for reaction 4 (Scheme I) was determined by using five different mole ratios of acetonitrile and methanol. This value for the equilibrium constant was used in subsequent calculations. An equilibrium constant of 41 was estimated at −38 °C, but at yet higher temperatures the equilibrium constant could not be measured because of rapid decomposition of the equilibrating species. The equilibration of (η-Cp$'$)(CO)(AN)FeCOMe$^+$ and (η-Cp$'$)(CO)(MeOH)Fe-COMe$^+$ is too slow to be measured by RPV at −65 °C.

The dynamics of the interconversion of (η-Cp$'$)(CO)-(AN)FeCOMe$^+$ and (η-Cp$'$)(CO)(MeOH)FeCOMe$^+$ were also analyzed by computer simulation of cyclic voltammetry experiments. These simulations confirm the RPV results and afford new information concerning the chemistry of (η-Cp$'$)(CO)(MeOH)FeCOMe^0.

Scheme I

$$(\eta\text{-Cp}')(\text{CO})_2\text{FeMe} \underset{}{\overset{E^{0\prime}(1/1^+)}{\rightleftharpoons}} (\eta\text{-Cp}')(\text{CO})_2\text{FeMe}^+ \quad (1)$$
$$\mathbf{1} \qquad\qquad\qquad\qquad\qquad \mathbf{1^+}$$

$$(\eta\text{-Cp}')(\text{CO})_2\text{FeMe}^+ \xrightarrow{k_{12}[\text{MeOH}]}$$
$$\mathbf{1^+}$$
$$(\eta\text{-Cp}')(\text{CO})(\text{MeOH})\text{FeCOMe}^+ \quad (2)$$
$$\mathbf{2^+}$$

$$\eta\text{-Cp}')(\text{CO})_2\text{FeMe}^+ \xrightarrow{k_{13}[\text{AN}]} (\eta\text{-Cp}')(\text{CO})(\text{AN})\text{FeCOMe}^+$$
$$\mathbf{1^+} \qquad\qquad\qquad\qquad\qquad\qquad \mathbf{3^+}$$
$$(3)$$

$$(\eta\text{-Cp}')(\text{CO})(\text{MeOH})\text{FeCOMe}^+ \underset{k_{32}[\text{MeOH}]}{\overset{k_{23}[\text{AN}]}{\rightleftharpoons}}$$
$$\mathbf{2^+}$$
$$(\eta\text{-Cp}')(\text{CO})(\text{AN})\text{FeCOMe}^+ \quad (4)$$
$$\mathbf{3^+}$$

$$(\eta\text{-Cp}')(\text{CO})(\text{MeOH})\text{FeCOMe}^+ \overset{E^{0\prime}(2/2^+)}{\rightleftharpoons}$$
$$\mathbf{2^+}$$
$$(\eta\text{-Cp}')(\text{CO})(\text{MeOH})\text{FeCOMe}^0 \quad (5)$$
$$\mathbf{2}$$

$$(\eta\text{-Cp}')(\text{CO})(\text{AN})\text{FeCOMe}^+ \overset{E^{0\prime}(3/3^+)}{\rightleftharpoons}$$
$$\mathbf{3^+}$$
$$(\eta\text{-Cp}')(\text{CO})(\text{AN})\text{FeCOMe}^0 \quad (6)$$
$$\mathbf{3}$$

$$(\eta\text{-Cp}')(\text{CO})(\text{MeOH})\text{FeCOMe}^0 \xrightarrow{k_4}$$
$$\mathbf{2}$$
$$\text{decomposition (H}^+ \text{ dependent) } (7)$$

$$(\eta\text{-Cp}')(\text{CO})(\text{MeOH})\text{FeCOMe}^0 \xrightarrow{k_5}$$
$$\mathbf{2}$$
$$\text{decomposition (H}^+ \text{ independent) } (8)$$

The experiment being simulated is a combination of a potential step and linear sweep voltammetry. The system is described in Scheme I. Initially, complex 1, only, is present in solution. Potential is stepped to a point on the foot of the initial anodic wave so as to effect the oxidation of 1 to 1$^+$ and held there for 5 s. The potential is then swept linearly in the negative direction and finally is returned at the same sweep rate to the initial potential. With the inclusion of a small resistance term in the expression for electrode potential we find that we can treat all of the electron-transfer steps as Nernstian. In the step and hold part of the simulation, 1$^+$ is generated and converts into 2$^+$ and 3$^+$ which interconvert as shown in Scheme I. These concentration profiles at the end of the step and hold part, which are computed in a subprogram, are used as the

initial condition for the linear sweep portion of the simulation. Equal and large (>1.4 M^{-1} s^{-1}) values of the rate constants (k_{12} and k_{13}) of formation of 2$^+$ and 3$^+$ from 1$^+$ were used. (This is justified by the observations that at −65 °C the CV's show no return wave for the reduction of (η-Cp$'$)(CO)$_2$FeMe$^+$ and that CV's are scan rate invariant with 2$^+$ and 3$^+$ being formed in concentrations reflecting the mole ratio of methanol to acetonitrile.) We note that values of k_{12} in excess of 1.4 M^{-1} s^{-1} produce invariant results. A common diffusion coefficient was used for all species.

The main program describes the linear sweep portion and computes the concentration profiles of 2$^+$ and 3$^+$ as a function of time. After each time interval, current is computed as proportional to the sum of concentration gradients of these species at the solution/electrode interface. The final picture of current vs. applied potential is obtained through iteration. Effective damping of oscillations is readily achieved by suitably averaging the output of a cycle with its previous value. (Equally weighted averaging and 15 iterations produced convergence to four significant figures.) The code is provided in supplementary material.

The rate constant k_d (0.08 s^{-1} = k_4 + k_5) for the sum of the acid-dependent and acid-independent decomposition of (η-Cp$'$)(CO)(MeOH)FeCOMe^0 was determined on samples of (η-Cp$'$)(CO)(MeOH)FeCOMe$^+$ in the absence of acetonitrile (vide supra). The equilibrium constant (K_{eq} = 60) determined by RPV was used for step 3. The kinetic parameters were then varied until the simulated CV's matched the experimental CV's. We found that when the second-order rate constant k_{23} = 0.007 M^{-1} s^{-1}, the peak to peak separations and current ratios of the experimental and simulated CV's matched well for three different scan rates (Figure 2). This value of k_{23} is in good agreement with that obtained via the RPV method (0.005 M^{-1} s^{-1}).

Discussion

The susceptibility of odd-electron organometallic complexes to entering ligand-dependent substitution reactions[9] certainly suggests that the alkyl to acyl migratory insertion reaction of the complex (η-Cp$'$)(CO)$_2$FeMe$^+$ also may be solvent assisted in a manner similar to that observed for the complexes (η-Cp)(CO)$_3$MoR.[10] This proposal is attractive since it avoids invoking a 15-electron species ((η-Cp$'$)(CO)FeCOMe$^+$) which would be generated in the absence of participation by a nucleophile. However, another way to avoid a 15-electron species is to postulate dihapto coordination of the acyl ligand—a reasonable and precedented alternative.[11]

(9) (a) Schroder, N. C.; Angelici, R. J. *J. Am. Chem. Soc.* **1986**, *108*, 3688. (b) Downard, A. J.; Robinson, B. H.; Simpson, J. *Organometallics* **1986**, *5*, 1140. (c) Bagchi, R. N.; Bond, A. M.; Colton, R.; Luscombe, D. L.; Moir, J. E. *J. Am. Chem. Soc.* **1986**, *108*, 3352. (d) Bond, A. M.; Colton, R.; McGregor, K. *Inorg. Chem.* **1986**, *25*, 2378. (e) Therien, M. J.; Ni, C. L.; Anson, F. C.; Osteryoung, J. G.; Trogler, W. C. *J. Am. Chem. Soc.* **1986**, *108*, 4037. (f) Kruisic, P. J.; Briere, R.; Rey, P. *Organometallics* **1985**, *4*, 801. (g) Zizelman, P. M.; Amatore, C.; Kochi, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 3771. (h) Narayanan, B. A.; Kochi, J. K. *J. Organomet. Chem.* **1984**, *272*, C49. (i) Herschberger, J. W.; Kochi, J. K. *J. Chem. Soc., Chem. Commun.* **1982**, 212. (j) Hershberger, J. W.; Klinger, R. J.; Kochi, J. K. *J. Am. Chem. Soc.* **1982**, *104*, 3034. (k) Shi, Q.-Z.; Richmond, T. G.; Trogler, W. C.; Basolo, F. *J. Am. Chem. Soc.* **1982**, *104*, 71. (l) Richmond, T. G.; Shi, Q.-Z.; Trogler, W. C.; Basolo, F. *J. Am. Chem. Soc.* **1982**, *104*, 76.

(10) (a) Webb, S. L.; Giandomenico, C. M.; Halpern, J. *J. Am. Chem. Soc.* **1986**, *108*, 345. (b) Wax, M. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 7028.

(11) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*; Wiley: New York, 1980; p 1131. Carmona, E. J.; Sanchez, L.; Marin, J. M.; Poveda, M. L.; Atwood, J. L.; Priester, R. D.; Rogers, R. D. *J. Am. Chem. Soc.* **1984**, *106*, 3214 and references therein.

The results of our studies demonstrate that the product distribution resulting from the oxidation of (η-Cp')(CO)$_2$FeMe is kinetically determined and involves a highly reactive species. Thus, at −65 °C, where the interconversion of (η-Cp')(CO)(MeOH)FeCOMe$^+$ and (η-Cp')(CO)(AN)FeCOMe$^+$ is quenched, the distribution ratio of the acetonitrile to methanol complexes reflects the solvent ratio (0.13); however, predicated on an estimated equilibrium constant of $K = 10^2$, this ratio should be approximately 10. We conclude that the formations of (η-Cp')(CO)(MeOH)FeCOMe$^+$ and (η-Cp')(CO)(AN)FeCOMe$^+$ from (η-Cp')(CO)$_2$FeMe$^+$ occur with nearly the same rate constants. Further strong evidence for the equality of k_{12} and k_{13} comes from the matching of the computer simulation to the experimental CV results at −45 °C at different scan rates. The simulated results are sensitive to the *ratio* k_{12}/k_{13}; a ratio of unity coupled with a value $k_{23} = 0.007$ M^{-1} s^{-1} (which is in excellent agreement with $k_{23} = 0.005$ M^{-1} s^{-1} obtained via RPV) reproduces the experimental CV's. The failure to observe a return wave for the oxidation of (η-Cp')(CO)$_2$FeMe at −78 °C in mixtures of acetonitrile and methanol demonstrates that k_{12} and k_{13} are large even at this temperature. Therefore, the transition state of the rate-determining step of the transformation of (η-Cp')(CO)$_2$FeMe$^+$ to (η-Cp')(CO)(MeOH)FeCOMe$^+$ or (η-Cp')(CO)(AN)FeCOMe$^+$ involves little, if any, iron–acetonitrile or iron–methanol bonding. It appears that we are dealing with a highly reactive and electron-deficient species reminiscent of the carbocations of organic chemistry.[12] The evidence is consonant with the involvement of the η^2-acyl complex (η-Cp')(CO)Fe–η^2-COMe$^+$ (or the coordinatively unsaturated acyl complex (η-Cp')(CO)FeCOMe$^+$).

The involvement of the η^2-acyl complex seems reasonable in view of the increasing oxophilic character of iron in the higher oxidation states. This increased oxophilic

character is manifest in a comparison of the equilibrium constants for the (η-Cp')(CO)(MeOH)FeCOMe^0/(η-Cp')(CO)(AN)FeCOMe^0 and (η-Cp')(CO)(MeOH)FeCOMe$^+$/(η-Cp')(CO)(AN)FeCOMe$^+$ interconversions. (The latter interconversion proceeds via a ligand-dependent pathway with no evidence for a first order component.) Using the equilibrium constant ($K_{eq} = 60$) for the interconversion in the iron(III) state and the E^0 values for the (η-Cp')(CO)(AN)FeCOMe$^{0,+}$ and (η-Cp')(CO)(MeOH)FeCOMe$^{0,+}$ couples (vide supra), we obtain an equilibrium constant of K_{eq}(II) $= 3.5 \times 10^5$ in the iron(II) state; in the iron(II) state the acetonitrile complex is some 5.7 kcal/mol more favored than the methanol complex. However, in the iron(III) state the energy difference (1.8 kcal/mol) is diminished. This is undoubtedly attributable to the increased affinity of the iron(III) for the harder base methanol.

Experimental Section

Electrochemistry. Cyclic voltammetry and reverse pulse voltammetry experiments were carried out on an EG&G Parr 174A polarographic analyzer using a two-compartment cell with a three-electrode configuration. The cell was designed so that the reference electrode compartment, which was kept at 22 °C, was connected via a Luggin capillary to the working electrode compartment which could be dipped in appropriate slush baths. Either a platinum disk or bead electrode was used as a working electrode. All potentials are reported vs. an aqueous SCE electrode with ferrocene set to 0.31 V as a standard. The electrolyte was 0.2 M in lithium perchlorate and approximately 1 mM in complex. Acetonitrile was distilled from phosphorus pentoxide, and methanol was distilled from sodium before use. Data were routinely collected at −78, −65, −45, −22, and 0 °C.

Registry No. (η-Cp')(CO)$_2$FeMe, 64023-11-6; (η-Cp')(CO)(MeOH)FeCOMe$^+$, 110173-59-6; (η-Cp')(CO)(AN)FeCOMe$^+$, 110173-60-9.

Supplementary Material Available: The code for the program describing the linear sweep portion and computing the concentration profiles of **2**$^+$ and **3**$^+$, as a function of time (2 pages). Ordering information is given on any current masthead page.

(12) Carey, F. A.; Sunberg, R. J. *Advanced Organic Chemistry*, 2nd ed.; Plenum: New York, 1985; Part A.