Entering Ligand Dependent Displacement of Acetone from (η-C_5R_5)(AC)(CO)Fe(COMe)$^+$ by Organic Nitriles. Quantitative Analysis of Ligand Effects (QALE)

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The entering ligand displacement of acetone (AC) from the cation radicals (η-C_5R_5)(AC)(CO)Fe(COMe)$^+$ (R_5 = H_5, Me_5) by a series of organic nitriles (R′CN; R′ = $Me_xH_{3-x}C$ (x = 1–3), p-$ZPhCH_2$ (Z = H, Me, MeO, Cl), Ph_2CH, Ph_2MeC) at −41 °C has been studied using a combination of square wave and cyclic voltammetry coupled with computer simulation methods. Although the two complexes exhibit similar reactivities toward the nitriles, the Cp* complex is more reactive than the Cp complex toward all the nitriles studied. The kinetic data were correlated with various pairs of stereoelectronic parameters, and it was found that the the correlations are all similar in quality, except where E_s was used as the steric parameter, in which case the quality was significantly lower. The two complexes exhibit indistinguishably different electronic and steric sensitivities.

Introduction

The rational control of reactivity is a problem of continuing interest in organometallic chemistry.[1] In principle, the fine tuning of the properties of a complex can be achieved through systematic manipulation of the stereoelectronic properties of ancillary ligands. Most commonly this is done with phosphorus(III) ligands. Often, however, these phosphorus(III) ligands are labile,[2] and thus, the desired ligand control can be lost at a crucial stage in a reaction sequence. The families of cyclopentadienyl and substituted cyclopentadienyl ligands can also be used to control reactivity by the placement of electron-withdrawing, electron-donating, or sterically demanding substituents on the cyclopentadienyl ligand.[3] The utilization of cyclopentadienyl ligands rather than phosphorus(III) ligands to control reactivity has the advantage that the cyclopentadienyl ligands are less labile and are therefore less likely to dissociate during a multistep process. Although C_5H_5 (Cp) and C_5Me_5 (Cp*) are the most commonly encountered cyclopentadienyl ligands, we are aware, however, of only one kinetic study in which an attempt was made systematically to compare the reactivities of Cp and Cp* complexes[4] and assess the factors that control the reactivities of these complexes.

For past several years we have been interested in the chemistry surrounding the redox-promoted alkyl to acyl rearrangement and, in particular, the chemistry of the solvent coordinated cation radicals of the type η-Cp(solv)(L)FeCOMe$^+$.[5] We have found that solvent ligands such as methanol and acetone are labile, being readily displaced by acetonitrile and thioethers via entering ligand dependent reactions.[5b,f,g] Furthermore, we demonstrated that the phosphorus(III) stereoelectronic parameters[6] could be transferred to the thioethers,[5f] thereby allowing the quantitative analysis of the kinetic data in terms of these parameters. Herein, we report our study of the entering ligand dependent displacement of acetone (AC) from η-(C_5R_5)(CO)Fe(AC)(COMe)$^+$ (R_5 = H_5, Me_5) by a series of organic nitriles and the analysis of the resulting kinetic data in terms of combinations selected from a number of stereoelectronic parameters, including those for phosphorus(III) ligands. Consideration of these analyses gives insight into the nature of the transition state in this displacement reaction.

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Experimental Section

General Procedures. All manipulations and preparations were carried out under argon using standard techniques. Acetone (J. T. Baker HPLC grade) was purified by distillation from Drierite. Tetrahydrofuran was distilled from sodium benzophenone ketyl. Tetrabutylammonium hexafluorophosphate (TBAH) (Aldrich) was recrystallized from ethyl acetate and before use was heated *in vacuo* to remove residual solvent. The nitriles were purified according to literature procedures,[7] except for 2,2-diphenylpropanenitrile, which was purified by crystallization from the melt.

Preparation of η-Cp(CO)$_2$FeMe and η-Cp*(CO)$_2$FeMe. η-Cp(CO)$_2$FeMe was prepared by sodium amalgam reduction of [η-Cp(CO)$_2$Fe]$_2$ in tetrahydrofuran, followed by methylation with dimethyl sulfate.

We have found that the preparation of η-Cp*(CO)$_2$FeMe by sodium shot reduction of [η-Cp*(CO)$_2$Fe]$_2$ followed by treatment with dimethyl sulfate is superior to previously reported methods.[8] Sodium (1 g) and octane (10 mL) were added to a nitrogen-purged 100-mL three-necked flask that was equipped with a gas inlet tube and a mechanical stirrer. The octane was refluxed, and the mixture was stirred rapidly to form fine sodium shot. The flask was then cooled quickly, and 40 mL of dry THF was added along with 1 g (2.0 mmol) [η-Cp*(CO)$_2$Fe]$_2$. This mixture was stirred at room temperature until the initial maroon color changed to a deep orange (approximately 1 h). Dimethyl sulfate (4.2 mmol) was then added, and the solution was allowed to stand for 10 min. This solution was then filtered through Celite, which was washed with petroleum ether until the filtrate was lightly colored. The filtrate was then rotary evaporated until about 10 mL of a yellow-orange oil remained. The oil was then chromatographed on a 2- × 20-cm alumina column (Act I, basic washed) using petroleum ether as the eluent. The evaporation of the initial bright yellow eluate afforded (η-Cp*)(CO)$_2$FeMe as yellow crystals, which were then recrystallized from petroleum ether at −78 °C. Yields were generally greater than 75%. The material was characterized by comparison of its spectroscopic properties to literature values.[8]

Electrochemistry. Cyclic and square wave voltammetry experiments were carried out using a computer-controlled EG&G PAR Model 273 potentiostat/galvanostat. A standard three-electrode cell equipped with a platinum disk electrode and a pseudoreference platinum wire was used for all experiments. The electrodes were cleaned before each experiment by polishing with alumina. Experiments were performed on argon-purged acetone solutions at −41 °C containing 0.1 M TBAH and 2–6 mM complex.

The rate constants for the displacement of acetone by nitrile and the appropriate relative $E^{\circ\prime}$ values were obtained from square wave voltammetry experiments. The experiments were performed using a step–hold–step procedure. First, the potential was stepped for 1 s to the foot of the anodic wave for the oxidation of the η-(C$_5$R$_5$)Fe(CO)$_2$Me complex.[9] The voltage was then stepped in a negative direction for an additional 1 s to a potential insufficient to reduce the nitrile complexes, η-Cp(CO)Fe(R′CN)(COMe)$^+$. Finally, the square wave was swept toward negative potentials. The resulting voltammogram shows a new cathodic wave approximately 0.25 V positive of the cathodic wave for the reduction of η-Cp(CO)Fe(AC)(COMe)$^+$. This wave is assigned to the reduction of the nitrile complex, η-Cp(CO)Fe(R′CN)(COMe)$^+$. The characterization of one (R′ = Me) of these complexes has been previously described.[5h,i] The complex η-Cp*(CO)$_2$FeMe behaves in a similar manner. Data were collected at various scan rates which were varied by a factor of 5 within the range from 0.040 to 0.500 V s^{-1} for each concentration of nitrile. The concentrations of the nitriles were varied by a factor of 2 for a given nitrile, with the concentrations ranging between 0.30 and 1.7 M (pseudo-first-order conditions). Kinetic data for the conversion of the acetone complexes to the nitrile complexes as well as the $E^{\circ\prime}$ values for the (η-C$_5$R$_5$)(CO)Fe(R′CN)(COMe)$^{0/+}$ couples relative to the (η-C$_5$R$_5$)(CO)Fe(AC)(COMe)$^{0/+}$ couples were obtained by computer simulation of squarewave voltammetry experiments. These simulations were of a quality similar to those described earlier.[5f]

Electrochemical parameters needed for the purposes of simulation were obtained in the following manner. Heterogeneous rate constants (k_h), transfer coefficients (α), and the decomposition rate constant of the neutral acetone complex were obtained as discussed previously by means of a combination of cyclic and square wave voltammetry measurements on acetone solutions of the complex in the *absence of nitrile*.[5f,6b] The potential waveform for the cyclic voltammogram consisted of a step for 10 s to a potential on the foot of the anodic wave for η-(C$_5$R$_5$)Fe(CO)$_2$Me, followed by a step for 1 s to a potential insufficient to reduce the acetone complex and then by negative and positive sweeps. The resulting voltammograms show a new cathodic wave (approximately 1.0 V negative of the initial oxidation potential), which has been previously assigned to the reduction of η-Cp(CO)(AC)FeCOMe$^+$.[5b,g] A similar procedure was followed for the square wave voltammetry measurements.

Computer Simulation and Analysis. The simulations we used to extract kinetic (k_3) and electrochemical ($E^{\circ\prime}$) parameters from the electrochemical data are based on the following model as shown in the reaction scheme. The code, based on the Adams–Moulton method, is provided in the supplementary material. Computed results were extrapolated to zero net size.[5a] On the basis of our previous experience, we assigned the same value of α and k_h to both the acetone and the nitrile complexes. We took the decomposition rate constants for (η-C$_5$R$_5$)(CO)Fe(R′CN)(COMe)$^{+/0}$ and (η-C$_5$R$_5$)Fe(AC)(CO)COMe$^+$ to be zero at −41 °C. The rate constants for the decomposition of (η-C$_5$R$_5$)Fe(AC)(CO)COMe^0 (Cp, k_d = 1.3 s^{-1}; Cp*, k_d = 3.0 s^{-1}) were obtained by simulation of experiments in the absence of nitrile as described above. The ratio of the pseudo-first-order rate constants for the incorporation of acetone (k_1) and nitrile (k_2) by (η-C$_5$R$_5$)Fe(CO)$_2$Me$^+$ was assumed to be the same as the ratio of the concentrations of acetone and nitrile. The formation of the nitrile complex was assumed to be irreversible. (See Scheme 1).

A check on the appropriateness of the value of k_h was possible by examination of the ratio i_{min}/i_3, the height of the valley between the two peaks (i_{min}), and the peak current of the acetone complex (i_3). (See Figure 1.) This works because the computed ratio of the two peak heights (i_1/i_3) is relatively insensitive to the value of k_h, although it is sensitive to k_3; on the other hand, the i_{min}/i_3 ratio is sensitive to both k_h and k_3. Thus once k_3 is obtained through the ratio i_1/i_3, we are free to determine k_h using the ratio i_{min}/i_3. We found good agreement between the two methods of determining the value of k_h (vide supra). The k_h values for the nitriles ranged from 2.0 to 10.0 s$^{-1/2}$.

Variations of the transfer coefficients (α) for acetone and nitrile complexes together from 0.3 to 0.7 had an insignificant effect on the computed rate constants. For α outside this range the simulated CV peak shapes change markedly from the experimental peak shapes. Therefore, we used a value of 0.50 for α.

The effect of variation of the decomposition rates, k_d, of (η-C$_5$R$_5$)Fe(AC)(CO)COMe^0 was also investigated. When k_d was doubled, the resulting value of k_3 changed by less than 5%. Also, if k_d was set to 0.0, the resulting value of k_3 changed by less than 10%. Thus, knowledge of the exact value of k_d is not critical in the determination of k_3.

Although the value of the ratio k_1/k_2 is important, and given by the ratio of concentrations (acetone/nitrile) (*vide supra*), the absolute values of k_1 and k_2 did not appear to be important. k_2

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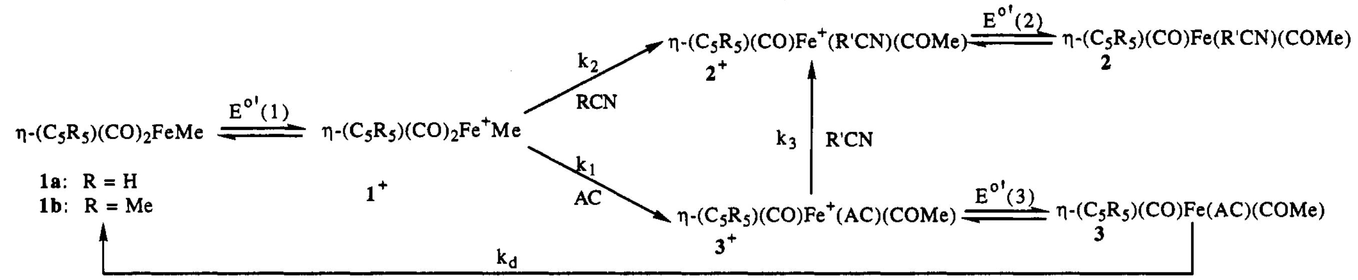
Scheme 1



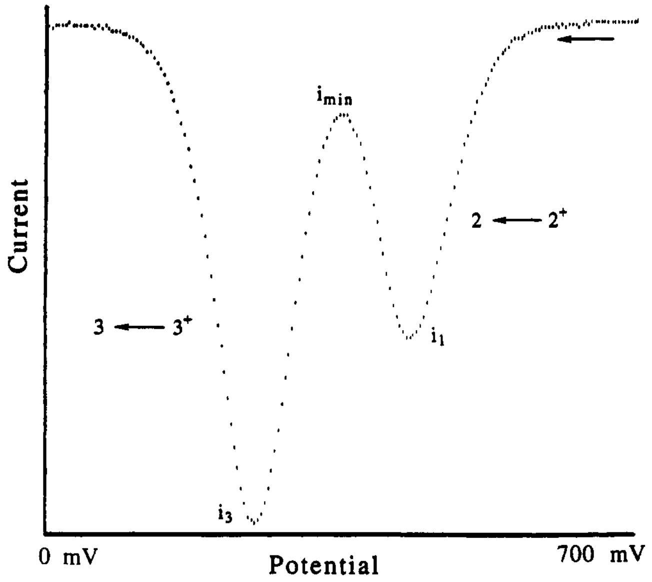


Figure 1. Example of an experimental square wave voltammogram of η-Cp(CO)$_2$FeMe in acetone at −41 °C, with 1.71 M Ph$_2$MeCCN. The potential waveform consisted of a pause of 1 s at 1400 mV, followed by a second pause at 700 mV and then a scan toward negative potentials at 0.10 V s^{-1}.

was arbitrarily set to 0.1, and the rate constant for the incorporation of acetone (k_1) was varied accordingly. If both k_1 and k_2 were increased by as much as a factor of 10, the resulting rate constant changed by less than 6%.

Results

All kinetic data were collected under pseudo-first-order conditions. Plots of k_{obs} versus [R'CN] were linear with intercepts statistically indistinguishable from zero (Figure 2). Thus, all the reactions were found to be second order, i.e. first order both in the acetone complex and in the nitrile. We found no evidence for a first-order component in the rate equation. The appropriate kinetic data along with $E°'$ values for the (η-C$_5$R$_5$)(CO)Fe(R'CN)(COMe)$^{+/0}$ couple (relative to the $E°'$ values for the (η-C$_5$R$_5$)(CO)Fe(AC)COMe)$^{+/0}$ couple) are displayed in Table 1.

The rates of reaction were found to be relatively insensitive to the stereoelectronic properties (Table 2) of the nitrile. The rate constants span a range of about 7, with acetonitrile being the most reactive and 2,2-diphenylpropanenitrile being the least reactive. η-Cp*(CO)Fe(AC)(COMe)$^+$ is more reactive than η-Cp(CO)Fe(AC)(COMe)$^+$ toward all of the nitriles studied (see Figure 3).

The rate constants as well as the relative $E°'$ values were correlated with stereoelectronic parameters selected from the following six: the phosphorus(III) stereoelectronic parameters, χ and θ; the isocyanide cone angles, θ_{iso}; and the organic substituent constants $\sum\sigma^*$, σ^*, and E_s.

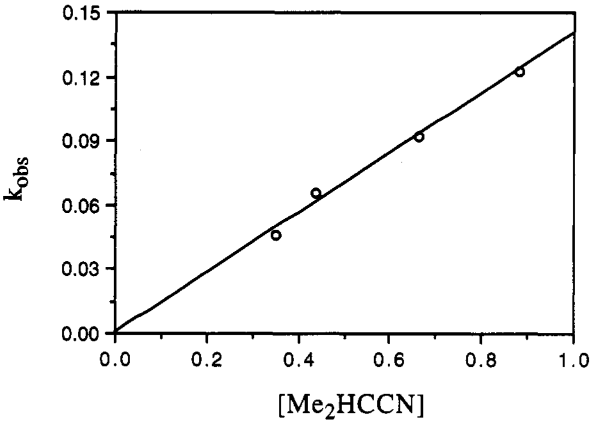


Figure 2. Plot of the observed rate constant k_3 vs [Me$_2$HCCN] (M).

Table 1. Stereoelectronic Parameters for Nitrile Ligands (R'CN)

R'	χ^a	θ^b	$\theta_{iso}{}^c$	$\sigma^{*\,d}$	$\sum\sigma^{*\,d}$	$E_s{}^d$
Me	24.5	87	48	0.00	1.47	−1.24
CH$_2$Me	19.2	97	58	−0.10	0.98	−1.31
CHMe$_2$	13.9	108	66	−0.19	0.49	−1.71
CMe$_3$	8.55	118	76	−0.30	0.00	−2.78
CH$_2$Ph	20.85	106	63	0.26	1.58	−1.62
CH$_2$(*p*-MePh)	20.2	106	63	0.17	1.43	−1.62
CH$_2$(*p*-MeOPh)	19.8	106	63	0.14	1.34	−1.62
CH$_2$(*p*-ClPh)	21.9	106	63	0.28	1.73	−1.62
CHPh$_2$	17.35	126	79	0.41	1.69	−3.00
CMePh$_2$	12.1	136	88	0.36	1.20	−4.97

[a] χ values (cm^{-1}) are taken from ref 10b or calculated from data given therein, based upon additivity. [b] Cone angles (deg) are taken from ref 10a or calculated from data given therein. [c] Isocyanide cone angles (deg) were taken from ref 10d or calculated from data given therein, based on additivity. [d] σ^*, $\sum\sigma^*$, and E_s values are taken from ref 10c.

The result of including the aryl effect parameter[6b] (E_{ar}) in the analyses did not lead to significantly different results.

For reasons we do not understand, we had difficulty obtaining consistent data for the reaction between η-Cp(CO)Fe(AC)(COMe)$^+$ and Me$_3$CCN. Inclusion of this datum in the correlation analysis gave a low r^2 (0.85, entry 1, Table 3). Deletion of this point from the analysis improved the quality of the fit (r^2 = 0.92, entry 2, Table 3) and, even more importantly, gave a statistically significant regression coefficient for χ.

Discussion

It is not surprising that the displacement of acetone from the cation radicals (η-C$_5$R$_5$)(AC)(CO)FeCOMe$^+$ is a second-order reaction depending on the concentration of both the complex and nitrile. Associative reactions appear to be quite common for 17-electron complexes, and a number of examples have been reported.[11] It is, however, surprising that η-Cp*(AC)(CO)Fe(COMe)$^+$, with its more

Table 2. Kinetic Data[a] for the Displacement of Acetone from η-Cp(CO)(AC)Fe(COMe)$^+$ and η-Cp*(CO)(AC)Fe(COMe)$^+$ and $E^{\circ\prime}$ Values[b] for the η-Cp(CO)Fe(R′CN)(COMe)$^{+/0}$ and η-Cp*(CO)Fe(R′CN)(COMe)$^{+/0}$ Couples

	η-Cp*(CO)-Fe(AC)(COMe)$^+$		η-Cp(CO)-Fe(AC)(COMe)$^+$	
R′	log k_3	$E^{\circ\prime}$	log k_3	$E^{\circ\prime}$
Me	−0.481	124	−0.553	134
CH_2Me	−0.481	132	−0.620	145
$CHMe_2$	−0.658	141	−0.770	141
CMe_3	−0.678	149	−1.092	149
CH_2Ph	−0.678	152	−1.000	159
CH_2(p-MePh)	−0.823	155	−0.886	160
CH_2(p-MeOPh)	−0.745	152	−1.000	158
CH_2(p-ClPh)	−0.770	157	−1.100	165
$CHPh_2$	−1.050	184	−1.220	184
$CMePh_2$	−1.222	190	−1.275	194

[a] The experiment was performed at −41 °C in acetone, containing 0.1 M TBAH. Second-order rate constants have units of $M^{-1}\,s^{-1}$. [b] $E^{\circ\prime}$ values (mV) for the (η-C_5R_5)(CO)(R′CN)Fe(COMe)$^{+/0}$ couple are given relative to the (η-(C_5R_5)(CO)(AC)Fe(COMe)$^{+/0}$ couple. These values were obtained through simulations of square wave voltammetry experiments.

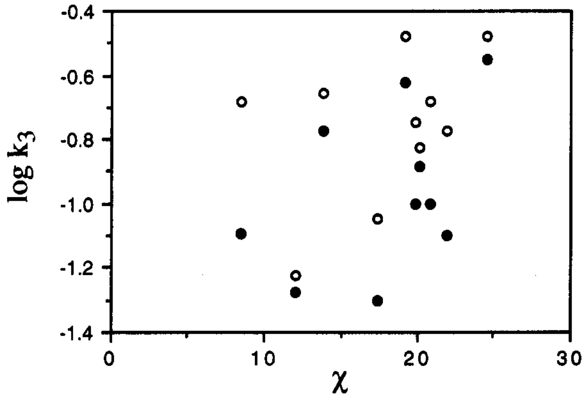


Figure 3. Comparison between the electronic profiles for the displacement of acetone from η-Cp(CO)Fe$^+$(AC)(COMe) (filled circles) and η-Cp*(CO)Fe$^+$(AC)(COMe) by organic nitriles.

sterically demanding and more electron rich Cp* ligand, is more reactive than the Cp complex in this associative nucleophilic displacement process. Although the difference between the reactivities of these two complexes and the range of rate constants are rather small (only a factor of 7 for both complexes), the fact that *all* the nitriles react more rapidly with the Cp* complex indicates that this is a statistically valid observation.

In order to gain further insight into the origins of the reactivity patterns of these complexes, we analyzed the kinetic data in terms of the stereoelectronic parameters of the nitriles using the combinations of parameters shown in Table 3, according to eq 1. Several features are to be noted. First, regardless of the combination of stereoelectronic parameters employed, the analyses show that the rate of reaction is enhanced as the electron donor capacity of the nitrile increases and that the rate of reaction decreases as the size of the nitrile increases. It is also clear that good correlations are obtained as long as a cone angle (either Tolman's cone angles or the isonitrile cone angle) is used as the steric parameter. We found no evidence for the existence of a steric threshold.

$$\log k = a(\text{electronic parameter}) + b(\text{steric parameter}) + c \quad (1)$$

The following discussion, which describes our interpretation of the ligand effect data, is based on the analysis of the kinetic data in terms of χ and θ (entries 2 and 6, Table 3). First, we find that the respective χ coefficients and θ coefficients are statistically indistinguishable for the two families of reactions. This observation suggests that the difference in reactivity of these complexes is a function of factors unrelated to the degree of nitrile–iron bonding in the transition state. These observations coupled with the observation that the Cp* complex is inherently more reactive in this reaction suggests that we are dealing with a transition state in which the leaving group, acetone, is largely dissociated and the nitrile is just entering the coordination sphere of the metal. We then view the transition state as one that resembles the transition state for a purely dissociative process; the transition state is less crowded and more electron deficient than the ground state. Hence, the more electron rich and more sterically encumbered Cp* is better able to stabilize the transition state and sterically to destabilize the ground state. Both factors would accelerate the reactions of the Cp* complex relative to the Cp complex. The similarity of the θ coefficients suggests that the steric effect that we observed is not a result of interligand repulsion. If the steric effect were a result of interligand repulsion, we would expect a more severe steric effect (larger coefficient of θ) for the reactions of the Cp* complexes. Thus, we are of the opinion that the steric effect might be a result of hindered solvation or hindered ion pairing, attributable to the increasing size of the pendant group of the nitrile. Analysis of the $E^{\circ\prime}$ values for the (η-C_5R_5)(R′CN)(CO)-FeCOMe$^{0/+}$ couple is consonant with this conclusion (*vide infra*).

The character of the k_3 step in the scheme differs dramatically from that of the displacement of acetone from η-Cp(AC)(CO)FeCOMe$^+$ by sulfides (eq 2). The displacement of acetone from η-Cp(AC)(CO)FeCOMe$^+$ by the most reactive nitrile (CH_3CN) is 300 times slower than the displacement of acetone by the most reactive sulfide,[5f,g] Me_2S, under comparable conditions, and the range of reactivities of the sulfides spans 2 orders of magnitude. It is noteworthy that preliminary results indicate that η-Cp*-(AC)(CO)FeCOMe$^+$ is at least an order of magnitude less reactive toward organic sulfides than is η-Cp(AC)(CO)-FeCOMe$^+$.[13] These results are consistent with the greater nucleophilicity of the sulfides (as compared to the nitriles)

$$\eta\text{-Cp(AC)(CO)FeCOMe}^+ + R_2S \rightarrow \eta\text{-Cp}(R_2S)\text{(CO)FeCOMe}^+ + \text{AC} \quad (2)$$

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[11] See, for example: (a) Therien, M. J.; Trogler, W. C. *J. Am. Chem. Soc.* **1987**, *109*, 5127. (b) Meng, Q.; Huang, Y.; Ryan, W. J.; Sweigart, D. A. *Inorg. Chem.* **1992**, *31*, 4051. (c) Zhang, Y.; Gosser, D. K.; Rieger, P. H.; Sweigart, D. A. *J. Am. Chem. Soc.* **1991**, *113*, 4062. (d) Watkins, W. C.; Macartney, D. H.; Baird, M. C. *J. Organomet. Chem.* **1989**, *377*, C52. (e) Hershberger, J. W.; Klingler, R. J.; Kochi, J. K. *J. Am. Chem. Soc.* **1983**, *105*, 61. (f) Zizleman, P. M.; Amatore, C.; Kochi, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 3771. (g) Kowaleski, R. M.; Basolo, F.; Trogler, W. C.; Gedridge, R. W.; Newbound, T. D.; Ernst, R. D. *J. Am. Chem. Soc.* **1987**, *109*, 4860.

[12] The isonitrile complexes show an increase in the difficulty of oxidation as the size of the isonitrile ligand increases, which is similar to our results. See: Bohling, D. A.; Evans, J. F.; Mann, K. R. *Inorg. Chem.* **1982**, *21*, 3546.

[13] Carbon cone angles (Datta, D.; Majumdar, D. *J. Phys. Org. Chem.* **1991**, *4*, 611) were also compared to the isocyanide cone angles (r^2 = 0.91). They did not work as well as either the isocyanide or Tolman cone angles in the correlations with the experimental data.

Table 3. Comparison of Analyses of log k_3 (Scheme 1) Using Various Stereoelectronic parameters, According to the Equation log k = a(Electronic Parameter) + b(Steric Parameter) + c(Standard Errors Given underneath the Coefficients)

entry	R	params	n	a	b	c	r^2
1	H	χ, θ	10	–0.019 ±0.010	–0.021 ±0.003	1.66 ±0.56	0.854
2	H	χ, θ	9^a	–0.040 ±0.012	–0.024 ±0.003	2.38 ±0.57	0.915
3	H	χ, θ_{iso}	9^a	–0.047 ±0.015	–0.031 ±0.005	2.02 ±0.57	0.898
4	H	σ^*, θ	9^a	–0.637 ±0.185	–0.009 ±0.003	0.16 ±0.27	0.922
5	H	$\sum\sigma^*, \theta$	9^a	–0.243 ±0.078	–0.015 ±0.002	1.00 ±0.25	0.913
6	H	σ^*, E_s	9^a	–0.835 ±0.252	0.067 ±0.043	–0.67 ±0.08	0.834
7	H	$\sum\sigma^*, E_s$	9^a	–0.262 ±0.145	0.151 ±0.047	–0.27 ±0.22	0.696
8	Me	χ, θ	10	–0.025 ±0.005	–0.021 ±0.001	2.00 ±0.29	0.953
9	Me	χ, θ_{iso}	10	–0.033 ±0.007	–0.028 ±0.003	1.73 ±0.31	0.938
10	Me	σ^*, θ	10	–0.372 ±0.091	–0.012 ±0.002	0.63 ±0.17	0.947
11	Me	$\sum\sigma^*, \theta$	10	–0.147 ±0.036	–0.016 ±0.001	1.13 ±0.17	0.947
12	Me	σ^*, E_s	10	–0.442 ±0.114	0.138 ±0.024	–0.42 ±0.05	0.913
13	Me	$\sum\sigma^*, E_s$	10	–0.157 ±0.057	0.181 ±0.027	–0.18 ±0.10	0.869

[a] Trimethylacetonitirle was not included in these analyses.

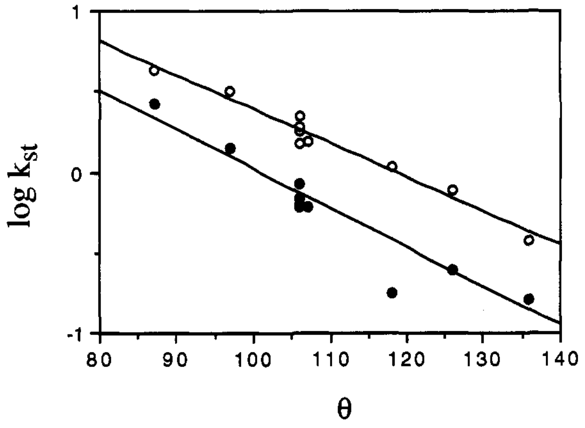

Figure 4. Comparison between the steric profiles for the displacement of acetone from η-Cp(CO)Fe$^+$(AC)(COMe) (filled circles) and η-Cp*(CO)Fe$^+$(AC)(COMe) by organic nitriles. The trimethylacetonitrile point (θ = 118) was not included in the Cp analysis. For clarity, 0.5 log unit was added to each of the Cp* values.

leading to a transition state with greater entering ligand–metal bonding and diminished breaking of the (AC)–iron bond. Hence, in reaction 2, the transition state is more crowded and more electron rich than the transition state for the nitriles. These features would tend to reduce the relative reactivity of η-Cp*(AC)(CO)FeCOMe$^+$ compared to that of η-Cp(AC)(CO)FeCOMe$^+$.

The only other ligand effect study (of which we are aware) where Cp and Cp* complexes are compared was reported by Basolo for the displacement of CO by phosphorus(III) ligands from (η-C_5R_5)Rh$(CO)_2$.[4] Even though the study of the Cp* complex was performed at higher temperature and in a different solvent, three conclusions can be drawn. First, through the quantitative analysis of the ligand effect data it appears that both complexes exhibit similar steric and electronic sensitivities.[6g] Second, it was found that the Cp* complex is less reactive by several orders of magnitude, and this was attributed to the greater steric bulk of the Cp* ligand, which translates into a smaller steric threshold for this complex. Third, the reactivity of the Cp* complex is probably diminished by enhanced Rh–CO bonding because of the greater electron density on the metal.

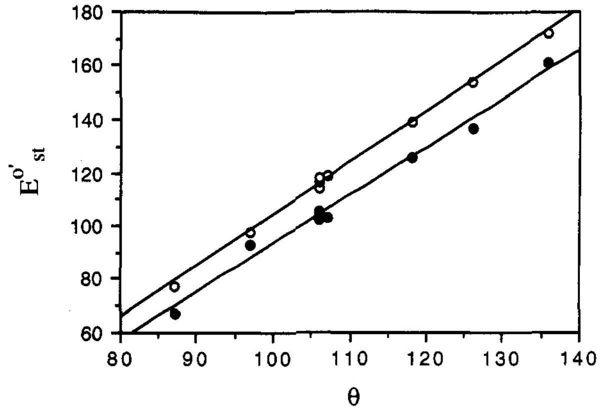

Figure 5. Comparison between steric profiles for the $E^{\circ\prime}$ values of the η-Cp(CO)Fe$^{+/0}$(R′CN)(COMe) (filled circles) and η-Cp*(CO)Fe$^{+/0}$(R′CN)(COMe). For clarity, 10 mV was added to each of the Cp* values.

$$(\eta\text{-}C_5R_5)Rh(CO)_2 + L \rightarrow (\eta\text{-}C_5R_5)Rh(CO)(L) + CO \tag{3}$$

Analysis of the Relative $E^{\circ\prime}$ Values for the (η-C_5R_5)(R′CN)(CO)FeCOMe$^{0/+}$ Couple. We analyzed the $E^{\circ\prime}$ values for the (η-C_5R_5)(R′CN)(CO)FeCOMe$^{0/+}$ couple in terms of χ and θ. For both the Cp and Cp* complexes we find excellent correlation as shown by eqs 4 and 5. There

$$E^{\circ\prime}\ (\text{mV, Cp}) = (2.7 \pm 0.3)\chi + (1.8 \pm 0.1)\theta - (88 \pm 17) \qquad r^2 = 0.98 \tag{4}$$

$$E^{\circ\prime}\ (\text{mV, Cp*}) = (2.3 \pm 0.2)\chi + (1.9 \pm 0.1)\theta - (98 \pm 8) \qquad r^2 = 0.996 \tag{5}$$

are several important features to be noted. First, the ease of oxidation is diminished by decreasing electron donor ability (increasing χ) of R′CN. Second, the ease of oxidation is diminished by increasing θ, thereby indicating that the oxidized complexes are more congested.[12] Third, the response of the $E^{\circ\prime}$ values to variations in the stereoelectronic parameters of R′CN is statistically indistinguishable for the two families of complexes. The similarity in the steric profiles for the oxidation of the two families illustrates this point. Thus, the change in steric effect on going from the reduced to oxidized state is independent of the C_5R_5 ring. This observation suggests that the steric effect is attributable to other factors such as hindered solvation of the cation or hindered ion pairing between the cation radical and the PF_6^- counterion.

A Consideration of the Stereoelectronic Parameters. When we began this research, we were not aware of any stereoelectronic parameters that had been measured specifically for organic nitriles although the cone angles (θ_{iso}) for a variety of the related isonitriles had been recently reported.[10d,e] If we were to transfer organic or organometallic stereoelectronic parameters to the nitriles, it was not evident as to which combination of parameters would be most appropriate for the analyses. Hence, we examined the transference of Taft's substituent constants, $\Sigma\sigma^*$, σ^*, and E_s for the various pendent alkyl groups attached to the nitriles. In addition, since we have found that the phosphorus(III) stereoelectronic parameters, χ and θ, are eminently transferable to other groups such as silyl ligands,[6c] alkyl ligands,[14] and thioethers,[5g] we also employed these parameters in the analysis of the kinetic data for the nitriles.

We have summarized the results of these analyses (coefficients, standard errors, and correlation coefficients, r^2) in Table 3. An examination of these data shows that good correlations are obtained when θ or θ_{iso} rather than E_s is used as the steric parameter. Since there is an excellent correlation ($r^2 = 0.996$) between θ and θ_{iso}. It is not surprising that both steric parameters work equally well in the analysis.[13]

We point out that, even though the combination of σ^* and θ gives a good correlation, the coefficients for θ are statistically and significantly different when χ and θ are used. We attribute this to the fact that σ^* probably has a steric component as we pointed out earlier.[6b] We also examined the problem with the steric parameter, E_s, which gives a poor correlation regardless of the electronic parameter employed. A comparison of E_s with θ for a variety of hydrocarbyl substituents reveals that E_s is not a linear function of θ (Figure 6). In fact, the plot resembles a steric profile with a steric threshold near 110 °C. After the threshold, there is a good linear relationship between θ and E_s. Thus it appears to us that for small hydrocarbyl groups, E_s is independent of steric factors and that it becomes a steric parameter only after the steric threshold is exceeded.

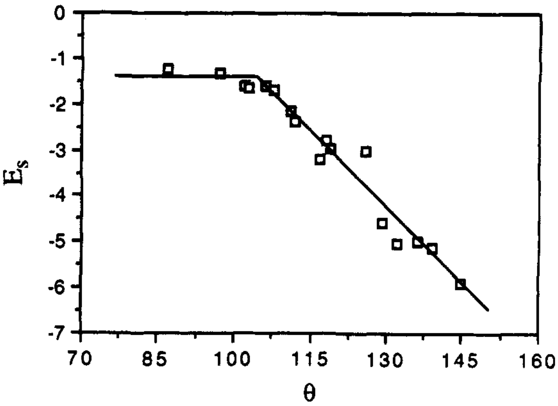

Figure 6. Plot of E_s versus θ for a series of hydrocarbyl ligands. The E_s[10c] and θ[10a] values for the ligands CH_3, CH_2Me, $CHMe_2$, CMe_3, $CH_2(p\text{-}XPh)$, $CHPh_2$, and $CMePh_2$ are given in Table 1. The other ligands in the plot are listed below followed by their E_s and θ values (E_s, θ): $CH_2{}^nPr$ (−1.63, 103), $CH_2{}^iPr$ (−2.17, 111), CHMeEt (−2.37, 112), $CHEt_2$ (−3.22, 117), $CH_2{}^tBu$ (−2.98, 119), $CHMe^tBu$ (−4.57, 129), CEt_3 (−5.04, 132), $CMe_2{}^tBu$ (−5.14, 139), CPh_3 (−5.92, 145).

Can Different Families of Ligands Be Treated in a Single Correlation? The results of this study and previous work[5,6,14] have shown that we can analyze ligand effect data for different families of ligands (phosphines, phosphites, arsines, silyl groups, nitriles, thioethers) using a common set of stereoelectronic parameters. The question now arises as to whether it is possible to treat sets of data for different families of ligands together in a unified analysis using stereoelectronic parameters unique to each family. In general, we do not believe that this possible. The central problem is that different constant terms arise from regression analysis of the separate families. These constant terms reflect chemical properties other than those expressed by the stereoelectronic parameters of the families of ligands. Even if the stereoelectronic parameters are on the same scale for each system, the fact that the constants are different precludes describing different systems with a single equation. Combining data for different families is further complicated by the possibility of a different steric threshold for each family. Different steric thresholds and steric sensitivities certainly seem reasonable since the real sizes of the families of ligands will differ as will their metal–ligand bond lengths. Thus, we are left with the opinion, at least at present, that combining the analyses for different families of ligands is not likely to be fruitful.

Conclusions

We have demonstrated that a Cp* complex can be more reactive than a Cp complex in an associative reaction. Clearly, the idea that the Cp* complexes are less reactive than Cp complexes because of steric factors needs to be investigated further. In both the displacement of acetone from $(\eta\text{-}C_5R_5)(AC)(CO)FeCOMe^+$ and the oxidation of $(\eta\text{-}C_5R_5)(R'CN)(CO)FeCOMe^0$, steric effects associated with the nitrile ligand appear to be independent of the C_5R_5 ligand. Thus, QALE reveals aspects of this chemistry that would otherwise be difficult to observe.

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Supplementary Material Available: The computer simulation code used (7 pages). Ordering information is given on any current masthead page.

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(14) Fernandez, A. L.; Prock, A.; Giering, W. P. Unpublished results.