2784 *Organometallics* **1996,** *15,* 2784−2789

Displacement of Acetone from η-(C_5R_5)(CO)Fe(AC)(COMe)$^+$ by Thioethers. Application of the Quantitative Analysis of Ligand Effects (QALE)

A. L. Fernandez, A. Prock,* and W. P. Giering*

Department of Chemistry, Metcalf Science and Engineering Center, Boston University, Boston, Massachusetts 02215

Received October 19, 1995[⊗]

The displacement of acetone (AC) from η-(C_5R_5)(CO)Fe(AC)(COMe)$^+$ (R = H, Me) by thioethers {SMe_2, SMeEt, SEt_2, S(n-Bu_2), SMe(t-Bu), S(i-Pr)$_2$,S(t-Bu)$_2$, SPh_2, SMe(p-XC_6H_4) (X = H, Me, MeO, Cl), and SEtPh} at −41 °C was studied using square-wave voltammetry. Rate constants were extracted from the square-wave voltammograms using computer simulation methods and were found to be sensitive to the stereoelectronic properties of the nucleophiles. The Cp (C_5H_5) complex is more reactive toward the smaller thioethers than the Cp* (C_5Me_5) complex, but there is an inversion of reactivity for the large thioethers. The rate constants were analyzed in terms of the electronic parameters (χ and E_{ar}) and one of the steric parameters θ, E_R, or Ω_s. The best correlation is found using χ, θ, and E_{ar}. Of the two families of complexes, the rates of reaction of the Cp* complex with the thioethers are *less* dependent on the stereoelectronic properties of the nucleophiles. This leads to a model of the transition states for the Cp* complex that is more flexible than that for the Cp complex, thereby allowing the reactions with the larger thioethers.

Introduction

The η-C_5Me_5 (Cp*) ligand has at times been treated as a “magic” ligand that imparts solubility, stability, and enhanced steric and electronic properties to a metal center.[1] Many studies have focused on the electronic effect of the Cp* ligand on the metal center. Greater basicity and the lower ionization potentials of Cp* complexes (relative to the analogous Cp complexes) suggest an enhanced electron donor capacity of the Cp* ligand,[2] although some argue that this effect is negligible.[3] The Cp* ligand is also thought to impart greater steric congestion about the metal as compared to the Cp ligand.[4] The differences in the reactivities of Cp and Cp* complexes have also been discussed in terms of ring slippage,[5] where compared to Cp, which readily undergoes this conversion, Cp* is less likely to accept an electron pair from the metal and slip into an η^3-coordination mode. Despite all of the attention that these ligands have been given, there are relatively few studies that compare systematically and quantitatively the reactivities of these two types of complexes.[5,6]

Our group is studying solvent-coordinated cation radicals of the type η-(C_5R_5)(solvent)(CO)Fe(COMe)$^+$ (R = H, Me), where the solvent ligand is readily displaced by nucleophiles such as nitriles and thioethers.[6−8] In the displacement of the solvent ligand acetone by nitriles, the Cp* complex is more reactive than the Cp complex toward all of the nitriles studied.[6] The QALE (Quantitative Analysis of Ligand Effects)[9,10] analysis of

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[⊗] Abstract published in *Advance ACS Abstracts,* May 15, 1996.

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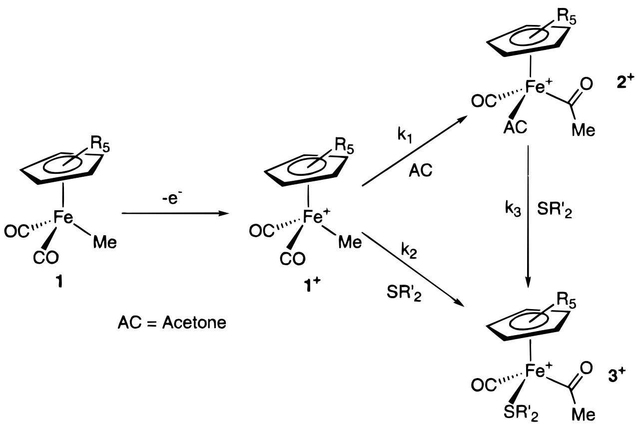
S0276-7333(95)00829-6 CCC: $12.00

Scheme 1



the kinetic data showed that the steric and electronic properties of the nitriles had little effect on the rate of the reaction and that these effects for the Cp and Cp* complexes were indistinguishable. In contrast, the rate of displacement of acetone from η-Cp(AC)(CO)Fe(COMe)$^+$ by thioethers is sensitive to the steric and electronic properties of the thioether ligands.[7] Since the thioethers are more nucleophilic than the nitriles and their steric bulk is concentrated on the ligating atom, it is easy to understand why the thioethers have a greater influence on the rate of reaction than do the nitriles. We now report the displacement of acetone from η-Cp*(AC)(CO)Fe(COMe)$^+$ (AC = acetone) by thioethers and then compare the results of this study with the previous study of the reaction between η-Cp(AC)(CO)Fe(COMe)$^+$ and thioethers.[7] The final results give us insight into the manner in which the Cp and Cp* ligands influence the reactivities of metal complexes.

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 (nonindicating). Tetrabutylammonium hexafluorophosphate (TBAH) (Aldrich) was recrystallized from warm ethyl acetate and before use was heated *in vacuo* to remove residual solvent. The thioethers (Aldrich and Lancaster) were used as received. In our earlier study we demonstrated that further purification of the thioethers had no effect on the kinetic data.[7]

The electrochemical experiments were performed at −41 °C (acetonitrile slush) in acetone containing 0.1 M tetrabutylammonium hexafluorophosphate. Computer simulation methods were similar to those described earlier,[6,7] and the simulations were based on the reactions in Scheme 1. In this study, we collected all of the data for the reactions of thioethers with η-Cp*(AC)(CO)Fe(COMe)$^+$ and augmented a previous data set[7] with the following points: SMeEt and SMe(p-XC$_6$H$_4$) (X = H, Me, MeO, Cl).

Results

All of the reactions were found to be second order overall: first order in complex and first order in thioether. All kinetic data were collected in triplicate at −41 °C under pseudo-first-order conditions using a greater than a 20-fold excess of thioether. Plots of k_{obs} versus [SR$'_2$] were linear with intercepts statistically indistinguishable from zero (Figure 1). The second-order rate constants (M^{-1} s^{-1}) were obtained from the slopes of these graphs. The average rate constants along with the $E^{\circ\prime}$ values are displayed in Table 1.

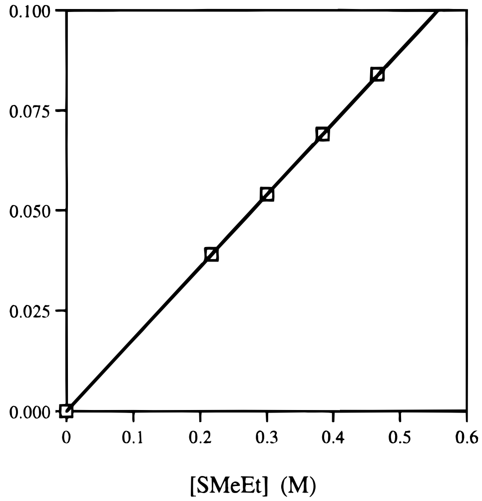


Figure 1. Plot of the observed rate constant, k_{obs}, vs [SMeEt] (M).

Table 1. Kinetic Data (log k_3) for the Reaction of Thioethers with η-(C$_5$R$_5$)(AC)(CO)Fe(COMe)$^+$ and $E^{\circ\prime}$ Values for the η-(C$_5$R$_5$)(SR$'_2$)(CO)Fe(COMe)$^{+/0}$ couples

	log k_3[a]		$E^{\circ\prime}$ (V)[b]	
thioether	Cp	Cp*	Cp	Cp*
SMe$_2$[c]	0.987	−0.620	0.120	−0.04
SMeEt	0.916	−0.678	0.119	−0.02
SEt$_2$[c]	0.104	−0.959	0.125	−0.01
SMePh[c]	−0.851	−0.854	0.157	0.00
SMe(p-ClPh)	*d*	−1.108	0.172	0.03
SMe(p-MeOPh)	−0.366	*e*	0.144	0.00
SMe(p-MePh)	−0.578	−0.796	0.136	0.00
S(n-Bu)$_2$[c]	−0.051	−1.222	0.122	−0.03
SEtPh[c]	−1.155	−1.071	0.146	0.01
SPh$_2$[c]	no rxn	no rxn	0.204[f]	*g*
SMe(t-Bu)[c]	−0.947	−1.119	0.126	−0.03
S(i-Pr)$_2$[c]	no rxn	−1.319	0.116	−0.03
S(t-Bu)$_2$[c]	no rxn	−1.569	*g*	−0.02

[a] The second-order rate constants have units of M^{-1} s^{-1}. The error in these values is ±7%. [b] The $E^{\circ\prime}$ values for the Cp complexes were obtained by analysis of cyclic voltammetry data using the ferrocene/ferrocenium couple (0.307 V) as an internal standard. The $E^{\circ\prime}$ values for the Cp* complexes could not be measured accurately because of the instability of the iron(II) complexes, and the values for the quasi-reversible waves were obtained using computer simulation methods. The values reported here are those values that give best fit of simulated data to experimental data. The simulations were relatively insensitive to the value of $E^{\circ\prime}$. [c] The data for the reactions of these thioethers with η-Cp(CO)Fe(AC)(COMe)$^+$ were previously reported in ref 7. [d] We could not simulate the square-wave voltammograms. [e] We could not obtain a reliable rate constant for the reaction of this thioether with η-Cp*(CO)Fe(AC)(COMe)$^+$ due to the limited solubility of SMe(p-MeOPh). [f] In spite of the lack of a reaction between the Fe(III) complex and this thioether, the value could be obtained because the thioether does react with the Fe(II) complex. [g] These values could not be obtained because the thioether did not react with the Fe(II) or Fe(III) complex.

The rates of these reactions were obtained by computer simulation of square-wave voltammetry experiments in the following manner. The cation radical, η-(C$_5$R$_5$)(CO)$_2$FeMe$^+$ (**1**$^+$) (see Scheme 1) was generated by setting the potential at the foot on the anodic wave for the η-(C$_5$R$_5$)(CO)$_2$FeMe$^{0/+}$ couple for 5 s. (Traversing this wave leads to the formation of unidentified secondary products.) The potential was then lowered but kept above the reduction potentials of η-(C$_5$R$_5$)(AC)(CO)Fe-

$(COMe)^+$ and η-$(C_5R_5)(SR'_2)(CO)Fe(COMe)^+$ and held then for 1 s. The potential was then swept in a negative direction, and the reduction waves for the acetone and thioether complexes were observed. These voltammograms were done at several scan rates ranging from 60 to 500 mV s^{-1}. Kinetic data were extracted from these experiments by means of previously described computer simulation techniques.[6,7]

The rate constants for the reactions of the thioethers toward η-Cp*(AC)(CO)Fe(COMe)$^+$ (Scheme 1) span 1 order of magnitude (0.24−0.05 M^{-1} s^{-1}), whereas the rate constants for the reactions toward η-Cp(AC)(CO)Fe(COMe)$^+$ span 2 orders of magnitude (9.7−0.070 M^{-1} s^{-1}). Dimethyl sulfide was the most reactive thioether toward both the Cp and Cp* complexes. Diphenyl sulfide and di-*tert*-butyl sulfide were unreactive toward both complexes. Although diisopropyl sulfide was reactive toward the Cp* complex, it was unreactive toward the Cp complex. Of the thioethers that reacted, the ethyl phenyl sulfide was the least reactive toward the Cp complex and the diisopropyl sulfide was the least reactive toward the Cp* complex. We could not obtain a rate constant for the reaction of $SMe(p\text{-}MeOC_6H_4)$ with η^5-Cp*(CO)Fe(AC)(COMe)$^+$ due to solubility problems. These solubility problems were not encountered with the Cp complex because a lower concentration of thioether produces an observable reaction. Also, the square-wave voltammograms of the reaction of η^5-Cp(CO)Fe(AC)(COMe)$^+$ with $SMe(p\text{-}ClC_6H_4)$ could not be simulated

We were not able to extract accurate rate constants for the displacement of acetone from the iron(II) complexes η^5-Cp*(CO)Fe(AC)(COMe)^0. The simulations of the electrochemical experiments are, however, insensitive to the rates of the substitution reactions in the iron(II) state thereby allowing us to get accurate data for the iron(III) state. A similar situation has been encountered and discussed in ref 6.

The second-order rate constants (log k_3) were correlated with stereoelectronic parameters via eq 1 since

$$\log k_3 = a\,(\text{electronic parameter}) + b\,(\text{steric parameter}) + c\,(\text{aryl effect parameter}) + d \qquad (1)$$

we found no evidence for a steric threshold in the data (*vide infra*). The electronic parameters are χ[11] and E_{ar},[10b] which are derived from the phosphorus(III) electronic parameters. The steric parameters were chosen from the following: θ[12] (derived from phosphorus(III) cone angles), E_R[13] (ligand repulsive energies for thioethers), and Ω_S[13,14] (solid angles for thioethers). The values of the stereoelectronic parameters are listed in Table 2.

Table 2. Stereoelectronic Parameters for Thioether Ligands

thioether	$\chi^{a,b}$	$\theta^{a,c}$	$E_R{}^d$	$\Omega_s{}^d$
SMe_2	5.7	78	42	0.190
SMeEt	4.95	83	51	0.227
SEt_2	4.2	88	59	0.258
SMePh	7.3	88	48	0.207
SMe(p-ClPh)	8.45	88	47	0.208
SMe(p-MeOPh)	6.35	88	48	0.203
SMe(p-MePh)	6.68	88	49	0.208
$S(n\text{-}Bu)_2$	3.5	91	63	0.325
SEtPh	6.5	92	44	0.224
SPh_2	8.8	97	45	0.230
SMe(t-Bu)	2.85	100	57	0.249
$S(i\text{-}Pr)_2$	2.3	107	71	0.286
$S(t\text{-}Bu)_2$	0.0	121	79	0.303

[a] These are fractional values calculated from the phosphorous(III) values. See ref 7. [b] χ values (cm^{-1}) were taken from ref 11. [c] θ values (deg) were taken from ref 12. [d] Most E_R (ligand repulsive energies, kcal mol^{-1}) and Ω_s (solid angles, steradians) values were taken from ref 13. The values for the aryl-substituted thioethers were obtained through personal communication with Dr. D. White and Prof. T. L. Brown, University of Illinois at Urbana-Champaign.

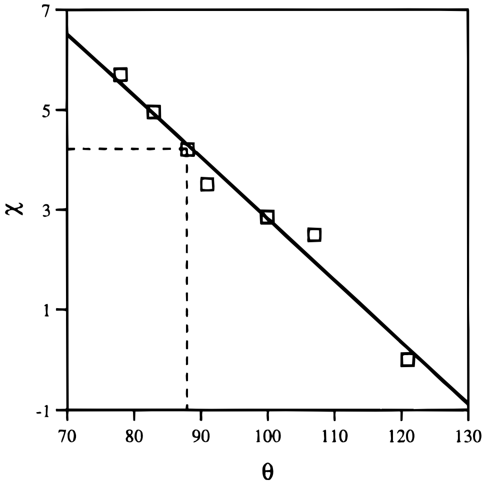


Figure 2. Plot of χ versus θ for the alkyl thioethers. In the absence of an aryl effect, a hypothetical $SMe(p\text{-}XC_6H_4)$ ligand (θ = 88°) should behave as a dialkyl thioether with a χ value of 4.2. This is shown by the dashed lines, and the importance of this point is explained in the text.

QALE Treatment of Data

We begin with a graphical analysis of the data in order to uncover the presence of a steric threshold and to examine steric effects and the magnitude of the contribution of the aryl effect and to identify rogue points. This protocol is described in ref 9. The analysis of the data for the dialkyl thioethers (SR'_2) allows us to determine the position of the steric threshold if one is present. We note that for this set of thioethers $E_{ar} = 0$ and that there is a linear relationship between θ and χ (Figure 2). Thus, if a plot of log k_3 versus θ shows a break, then we can ascribe this break to a steric threshold since in the QALE model electronic effects are taken to be linear.[10] Since a plot of log k_3 versus θ (Figure 3A) shows no break, we conclude that there is no steric threshold. Thus, eq 1 is the appropriate form of the QALE eq to be used in the regression analysis of the total set of data. We also note that the datum for $S(n\text{-}Bu)_2$ lies significantly and reproducibly off the line in Figure 3A; we have treated it as a rogue point. (There might be a system-specific interaction between the long-chain butyl groups of the thioether and the methyl groups of the Cp* ligand that diminishes the reactivity of this thioether.) Indeed, the quality of the regression analysis improves upon removal of this point.

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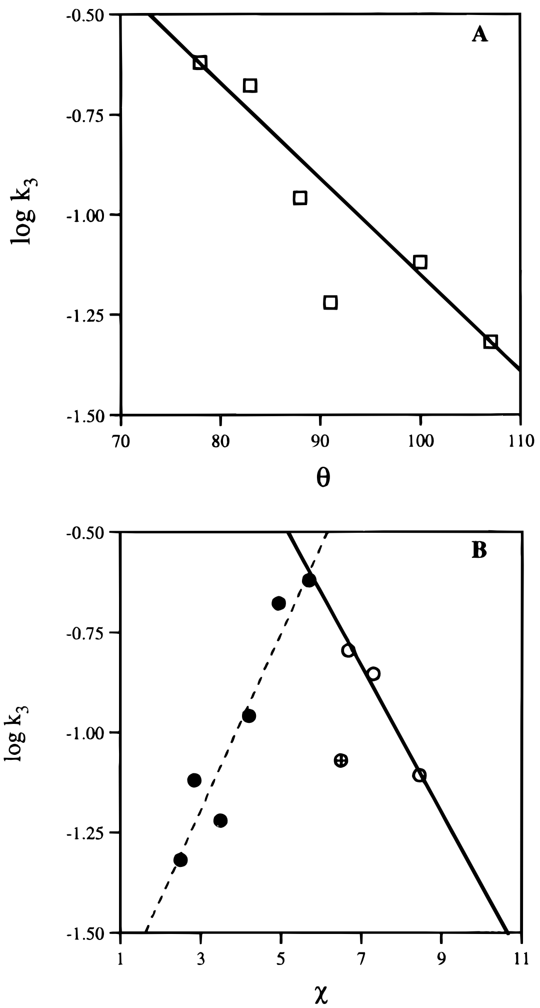

Figure 3. Graphical analysis of the log k_3 for the reaction of thioethers with η^5-Cp*(CO)Fe(AC)(COMe)$^+$: (A) Plot of log k_3 versus θ for the dialkyl thioethers; (B) plot of log k_3 versus χ. The data for the dialkyl thioethers are represented by filled circles, and the data for S(Me)(p-XC_6H_4) are represented by open circles. The datum for SEtPh is represented by the circle with a cross.

Insight into the importance of aryl and steric effects can be obtained through plots of the data of SR'_2 and the data for S(Me)(p-XC_6H_4) versus the electronic parameter χ. Thus, a plot of log k_3 for S(Me)(p-XC_6H_4) versus χ (Figure 3B, open circles) affords an estimate (-0.18 ± 0.03) of the coefficient of χ in eq 1 because for this subset of ligands θ and E_{ar} are constant. Since the lines for the SR'_2 and S(Me)(p-XC_6H_4) data have coefficients with opposite signs (Figure 3B), we can conclude that there is a dominant and inhibitory steric effect. Finally, the intersection of the lines for SR'_2 and S(Me)-(p-XC_6H_4) at $\chi = 6.2$ rather than $\chi = 4.2$ indicates a significant aryl effect (Figure 3B). (A hypothetical thioether, S(Me)(p-XC_6H_4), with $\theta = 88°$ and $\chi = 4.2$ would behave like a SR'_2 ligand if there were no aryl effect (Figure 2).)

In summary, we find that inhibitory steric effects are linearly operative for the entire set of ligands, that the rate of reaction is enhanced with increased electron donor capacity of the thioethers, and that there is a significant aryl effect that enhances the reactivity of the aryl thioethers.

A regression analysis of log k_3 using eq 1 affords eq 2. The large standard errors are not due to a poor fit

$$\log k_3 = -(0.13 \pm 0.06)\chi - (0.040 \pm 0.008)\theta + (0.33 \pm 0.19)E_{\mathrm{ar}} + (3.3 \pm 1.0) \quad (2)$$

$$n = 9 \qquad r^2 = 0.92$$

but reflect a high degree of linear correlation among the parameters (χ with θ and E_{ar}, $r^2 = 0.94$). In order to obtain meaningful coefficients that allow us to compare this system with others, we pursued a different approach to the regression analysis.

We apply a fundamental tenet of the QALE model: the coefficient of χ determined from the regression analysis (eq 3) of log k_3 for S(Me)(p-XC_6H_4) must be the

$$\log k_3 \text{ (for S(Me)(p-XC}_6\text{H}_4\text{))} = -(0.18 \pm 0.03)\chi + (0.44 \pm 0.24) \quad (3)$$

$$n = 3 \qquad r^2 = 0.97$$

coefficient of χ in eq 1. The coefficient of χ in eq 3 is then used to calculate the χ contribution to the rate constant for the full set of ligands. This contribution is subtracted from the experimental data to yield a log $k(\theta,E_{ar})$ for each thioether. Now we can proceed in two different ways, one being graphical.

Graphically we can obtain the coefficient of E_{ar}. log $k(\theta,E_{ar})$ is plotted versus E_{ar} (Figure 2C) for the isosteric ligands (θ = 88), which include all of the para-substituted thioanisoles ($E_{ar} = 1$) and the diethyl sulfide ($E_{ar} = 0$). The slope of the line is the coefficient of E_{ar} term. This contribution in turn can be removed from log $k(\theta,E_{ar})$ to yield log $k(\theta)$ (or, as we usually call it, log k_{st}). This can then be plotted versus θ to yield a steric profile. This steric profile is a pictorial representation of the analysis, including all of the error, and thereby serves as a visual check of the quality of the analysis.

An alternate way of treating log $k(\theta,E_{ar})$ is through a two-parameter linear regression, which will yield the coefficients of θ and E_{ar}. The regression analysis yields the following eq:

$$\log k(\theta,E_{\mathrm{ar}}) = -(0.045 \pm 0.003)\theta + (0.46 \pm 0.06)E_{\mathrm{ar}} + (3.88 \pm 0.32) \quad (4)$$

$$r^2 = 0.98$$

The standard errors given in this eq do not reflect error in the χ coefficient. In order to get an estimate of the true standard errors, we calculate log $k(\theta,E_{ar})$ using the two extreme values (value of the coefficient with the standard error added and subtracted) of the χ coefficient in eq 3. Each set of results is reanalyzed, and the total range of each coefficient obtained in this manner represents twice the standard error. We have validated this method by application to large sets of data, where the parameters are not correlated and the full regression analysis gives meaningful results. The final result of this analysis is eq 5, which can be used for comparison with others set of data.

$$\log k_3(\mathrm{Cp}^*) = -(0.18 \pm 0.03)\chi - (0.045 \pm 0.007)\theta + (0.46 \pm 0.15)E_{\mathrm{ar}} + (4.34 \pm 1.0) \quad (5)$$

$$n = 9 \qquad r^2 = 0.90$$

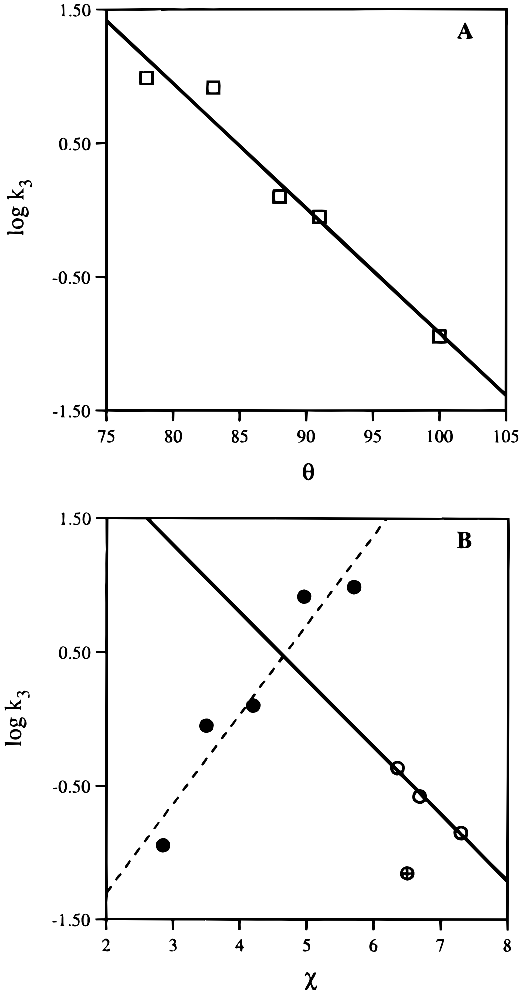

Figure 4. Graphical analysis of the log k_3 for the reaction of thioethers with η^5-Cp(CO)Fe(AC)(COMe)$^+$: (A) Plot of log k_3 versus θ for the dialkyl thioethers; (B) plot of log k_3 versus χ. The data for the dialkyl thioethers are represented by filled circles, and the data for S(Me)(p-XC_6H_4) are represented by open circles. The datum for SEtPh is represented by the circle with a cross.

The original kinetic data[7] for the reaction of thioethers with η^5-Cp(CO)Fe(AC)(COMe)$^+$ has been supplemented and then analyzed in the same manner (Figure 4, eq 6).

$$\log k_3(\mathrm{Cp}) = -(0.50 \pm 0.05)\chi - (0.16 \pm 0.02)\theta + (0.46 \pm 0.24)E_{\mathrm{ar}} + (16.5 \pm 1.6) \quad (6)$$

$$n = 9 \qquad r^2 = 0.97$$

Discussion

It is commonly thought that Cp* complexes are less reactive then Cp complexes in associative reactions because of enhanced congestion in the transition state. Therefore, it was not surprising that the smaller thioethers, such as SMe_2, are more reactive toward the Cp complex. It is quite surprising, however, that the large thioethers, such as S(i-Pr)$_2$, are more reactive toward the Cp* complex. Clearly, more than congestion in the transition state is controlling the reactivity pattern of these complexes.

When discussing steric factors, we must consider steric thresholds and steric sensitivity. In a transition metal complex a certain volume of the coordination sphere is allocated to each ligand. Until the size of the ligand reaches the size of the coordination site, there are no steric effects. When the size of the ligand matches the size of the coordination site (steric threshold), steric effects begin. The magnitude of the steric threshold is a measure of congestion at the coordination site. The coefficient of the θ term (steric sensitivity) in the QALE eq 1 is a measure of the flexibility of the transition state. A larger steric sensitivity indicates a more rigid state.

We can see from eqs 5 and 6 that the signs of the coefficients are characteristic of entering ligand-dependent substitution reactions. Thus, the negative coefficients of χ indicate that the rates of reaction are enhanced as the thioethers become better electron donors (smaller χ). Likewise, the negative coefficients of θ indicate that the rates of reaction are diminished as the size of the thioether increases. Interestingly, the positive sign of the E_{ar} coefficient suggests that replacing an alkyl group with an aryl group enhances the nucleophilicity of the thioether and, thereby, the rate of reaction.

The relative magnitudes of the coefficients give insight into the nature of the transition states of these reactions. By comparing eqs 5 and 6, we can see that η^5-Cp(CO)Fe(AC)(COMe)$^+$ is more sensitive to two of the stereoelectronic properties, χ and θ, of the thioethers. (In Figure 5, we display the χ, E_{ar}, and θ profiles for the two families of reactions.) Since the χ coefficient is greater for the Cp complex, we conclude that there is greater iron−sulfur interaction in its transition state than in the Cp* transition state. Since we do not observe a steric threshold for either reaction, we cannot comment on the relative congestion of the two transition states. The greater steric sensitivity (coefficient of θ) of the Cp reaction suggests a more rigid transition state for this complex. These observations lead to the following models of the two transition states.

In entering ligand-dependent substitution reactions, there is a continuum of transition states that range from associative to dissociative. On the basis of the QALE analysis, we believe that the transition state of the Cp complex is more associative in nature, whereas the transition state of the Cp* complex is more dissociative in nature. A transition state that involves significant dissociation of the acetone and relatively little sulfur−iron bonding leaves an electron deficient iron center. Since this transition state contains two loosely bound ligands, we would expect the transition state to be more flexible. Because of its electron richness, the Cp* ligand would be expected to favor this type of transition state. In a primarily associative reaction, there is significant bonding to both the leaving group and the entering ligand, thereby enhancing the rigidity of the transition state and the electron density on the metal center. Both features suggest that the Cp ligand would favor a more associative transition state. The QALE analyses supports these two models.

We have also correlated the data using E_{R} or Ω_{s} values (in place of θ as the steric parameter) which have been derived specifically for the thioethers. The results are given in eqs 7 and 8. These analyses show a poorer

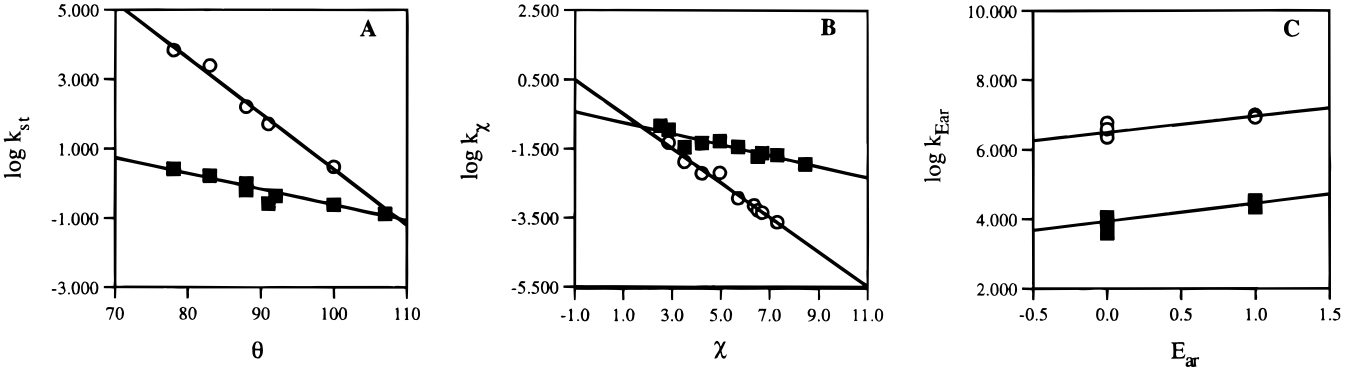

Figure 5. Comparison of the θ (A), χ (B), and E_{ar} (C) profiles for the Cp (open circles) and Cp* (filled squares) complexes.

correlation than is obtained when using θ as the steric parameter.

$$\log k_3 = -(0.047 \pm 0.085)\chi - (0.018 \pm 0.012)E_R - (0.33 \pm 0.23)E_{ar} - (0.11 \pm 0.97) \quad (7)$$

$$n = 9 \qquad r^2 = 0.63$$

$$\log k_3 = -(0.008 \pm 0.082)\chi - (7.9 \pm 3.5)\Omega_s - (0.23 \pm 0.21)E_{ar} + (0.99 \pm 1.1) \quad (8)$$

$$n = 9 \qquad r^2 = 0.74$$

Conclusions

η^5-Cp*(CO)Fe(AC)(COMe)$^+$ exhibits a different reactivity pattern from the Cp complex in the ligand substitution reaction involving thioethers. The QALE analysis shows that the Cp* transition state in more dissociative in nature. The striking inversion of reactivity of the Cp and Cp* complexes when going from smaller (SMe_2) to larger ($S(i\text{-}Pr)_2$) thioethers points out that when discussing steric effects we need to consider not only congestion but also the flexibility of the transition state.

Because we have successfully transferred the phosphorus(III) stereoelectronic parameters to silyl groups, nitriles, and thioethers, it appears to us that these parameters are measures of the stereoelectronic properties of the pendant groups and are independent of the ligating atoms. Therefore χ, θ, and E_{ar} may very well be the stereoelectronic descriptors for a wide variety of AR_3 and AR_2 ligands.

Acknowledgment. We thank Professor T. L. Brown and Dr. D. White for calculating E_R values for the aryl-substituted thioethers.

OM9508290