Exploring Ligand Effects through Isoequilibrium Phenomena: The Quantitative Analysis of Ligand Effects

Anthony Fernandez, Clementina Reyes, Alfred Prock,* and Warren P. Giering*

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

Received November 25, 1997

Analysis of the $E°$ values of the η-Cp(CO)(L)Fe(COMe)$^{+/o}$ couple (measured via cyclic voltammetry at 229, 252, 264, 273, and 293 K in acetonitrile/0.1 M TBAH) has revealed different isoequilibrium behavior for $P(p\text{-}XC_6H_4)_3$ and PR_3. We classify ligands as a family when they exhibit a single isoequilibrium point. A family of ligands affects a property via variation of a single, or effectively single, parameter. Thus, through isoequilibrium behavior, we have an unambiguous way to identify families, which in quantitative analysis of ligand effects (QALE), must be treated separately in the preliminary graphical analysis of data that leads to the full regression analysis. The QALE model predicts that there is an isoequilibrium temperature associated with each stereoelectronic parameter; i.e., for each parameter, there is a specific temperature where the effect disappears. The fan-shaped arrays of lines that result when $E°/T$ is plotted versus either $1/T$ or the stereoelectronic parameter χ gives insight into the nature of and the number of stereoelectronic parameters necessary to describe the system and the partitioning of steric effects between enthalpy and entropy. In this particular system, steric effects are almost entirely an entropic phenomenon.

Introduction

Building on the work of Linert,[1−11] Exner,[12−17] and Krug[18] and the earlier work of Grunwald and Leffler[19] concerning isoequilibrium phenomenon, we show that the multiparameter QALE (quantitative analysis of ligand effects)[20−42] model is consistent with the isoequilibrium behavior of the reduction potentials of the η-Cp(CO)(L)Fe(COMe)$^{+/o}$ couple (L = phosphorus(III) ligands).

It has been found that variations in a number of physiochemical properties are related via eq 1[20−42] to the stereoelectronic properties of phosphine ligands.

$$\text{property} = a\chi + b\theta + b'(\theta - \theta_{st})\lambda + cE_{ar} + d \quad (1)$$

Equation 1 is a general form of the QALE equation for systems that exhibit no more than one observable steric

---

[1] Linert, W. *Aust. J. Chem.* **1986**, *39*, 199.
[2] Linert, W.; Jameson, R. F. *Chem. Soc. Rev.* **1989**, *18*, 477.
[3] Linert, W.; Sapunov, V. N. *Chem. Phys.* **1988**, *119*, 265.
[4] Linert, W.; Schmid, R.; Kudrjawtsev, A. B. *Aust. J. Chem.* **1985**, *38*, 677.
[5] Linert, W.; Han, L. *Chem. Phys.* **1989**, *139*, 441.
[6] Linert, W. *Chem. Phys.* **1987**, *116*, 381.
[7] Kreuzer, H. J.; March, N. H. *Theor. Chim. Acta* **1988**, *74*, 339.
[8] Linert, W. *Inorg. Chim. Acta* **1988**, *141*, 233.
[9] Linert, W.; Kudrjawtsev, A. B. *Aust. J. Chem.* **1984**, *37*, 1139.
[10] Linert, W.; Kudrjawtsev, A. B.; Schmid, R. *Aust. J. Chem.* **1983**, *36*, 1903.
[11] Linert, W. *Chem. Soc. Rev.* **1994**, 429.
[12] Exner, O. *Prog. Phys. Org. Chem.* **1973**, *10*, 411.
[13] Exner, O. *Collect. Cxech. Chem. Commun.* **1972**, *37*, 1425.
[14] Exner, O.; Beranek, V. *Collect. Cxech. Chem. Commun.* **1973**, *38*, 781.
[15] Exner, O. *Collect. Cxech. Chem. Commun.* **1973**, *38*, 799.
[16] Wold, S.; Exner, O. *Chem. Scr.* **1973**, *3*, 5.
[17] Exner, O. *Collect. Cxech. Chem. Commun.* **1975**, *40*, 2762.
[18] Krug, R. R.; Hunter, W. G.; Grieger, R. A. *J. Phys. Chem.* **1976**, *80*, 2335.
[19] Leffler, J. E.; Grunwald, E. *Rates and Equilibria of Organic Reactions*; John Wiley: New York, 1963.
[20] Wilson, M. R.; Woska, D. C.; Prock, A.; Giering, W. P. *Organometallics* **1993**, *12*, 1742.
[21] Wilson, M. R.; Liu, H.; Prock, A.; Giering, W. P. *Organometallics* **1993**, *12*, 2044.
[22] Tracey, A. A.; Eriks, K.; Prock, A.; Giering, W. P. *Organometallics* **1990**, *9*, 1399.
[23] Panek, J.; Prock, A.; Eriks, K.; Giering, W. P. *Organometallics* **1990**, *9*, 2175.
[24] Lorsbach, B. A.; Prock, A.; Giering, W. P. *Organometallics* **1995**, *14*, 1694.
[25] Lorsbach, B. A.; Bennett, D. M.; Prock, A.; Giering, W. P. *Organometallics* **1995**, *14*, 869.
[26] Fernandez, A.; Reyes, C.; Wilson, M. R.; Woska, D. C.; Prock, A.; Giering, W. P. *Organometallics* **1997**, *16*, 342.
[27] Fernandez, A. L.; Prock, A.; Giering, W. P. *Organometallics* **1996**, *15*, 2784.
[28] Fernandez, A. L.; Prock, A.; Giering, W. P. *Organometallics* **1994**, *13*, 2767.
[29] Bartholomew, J.; Fernandez, A. L.; Lorsbach, B. A.; Wilson, M. R.; Prock, A.; Giering, W. P. *Organometallics* **1996**, *15*, 295.
[30] Poë, A. J.; Hudson, R. H. E. *Organometallics* **1995**, *14*, 3238.
[31] Poë, A. J.; Farrar, D. H.; Zheng *J. Am. Chem. Soc.* **1992**, *114*, 5146.
[32] Neubrand, A.; Poë, A. J.; van Eldik, R. *Organometallics* **1995**, *14*, 3249.
[33] Farrar, D. H.; Poë, A. J.; Zhang, Y. *J. Am. Chem. Soc.* **1994**, *116*, 6252.
[34] Chen, L.; Poë, A. J. *Coord. Chem. Rev.* **1995**, *143*, 265.
[35] Brodie, N. M. J.; Poë, A. J. *Can. J. Chem.* **1995**, *73*, 1187.
[36] Romeo, R.; Arena, G.; Scolaro, L. M. *Inorg. Chem.* **1992**, *31*, 4879.
[37] Luo, X.; Kubas, G. J.; Burns, C. J.; Bryan, J. C.; Unkefer, C. J. *J. Am. Chem. Soc.* **1995**, *117*, 1159.
[38] Bessel, C. A.; Margarucci, J. A.; Acquaye, J. H.; Rubino, R. S.; Crandall, J.; Jircitano, A. J.; Takeuchi, K. J. *Inorg. Chem.* **1993**, *32*, 5779.
[39] Moreno, C.; Delgado, S.; Macazaga, M. J. *Organometallics* **1991**, *10*, 1124.
[40] Herrick, R. S.; Duff, R. R., Jr.; Frederick, A. B. *J. Coord. Chem.* **1994**, *32*, 103.
[41] Farrar, D. H.; Hao, J.; Poë, A. J.; Stromnova, T. A. *Orgnaometallics* **1997**, *16*, 2827.
[42] Romeo, R.; Alibrandi G. *Inorg. Chem.* **1997**, *36*, 4822.

S0276-7333(97)01041-8 CCC: $15.00
Publication on Web 05/08/1998

Table 1. Stereoelectronic Parameters for Phosphorus (III) Ligands

ligand	χ^a	θ^b	$E_{ar}{}^c$
PMe_3	8.55	118	0
PEt_3	6.3	132	0
P(n-Bu)$_3$	5.25	136	0
P(i-Bu)$_3$	5.7	143	0
P(*p*-MeOC$_6$H$_4$)$_3$	10.5	145	2.7
P(*p*-MeC$_6$H$_4$)$_3$	11.5	145	2.7
P(*p*-C$_6$H$_5$)$_3$	13.25	145	2.7
P(*p*-FC$_6$H$_4$)$_3$	15.7	145	2.7
P(*p*-ClC$_6$H$_4$)$_3$	16.8	145	2.7
P(*p*-CF$_3$C$_6$H$_4$)$_3$	20.5	145	2.7
P(i-Pr)$_3$	3.45	160	0
PCy_3	1.4	170	0

[a] The χ values (cm^{-1}) are taken from ref 43. [b] The cone angles (deg) are taken from ref 44. [c] The E_{ar} values are taken from ref 20.

threshold (χ is related to the A_1 ν_{CO} stretching frequency of $LNi(CO)_3$,[43] θ is Tolman's cone angle,[44] and E_{ar}[20] is the aryl effect parameter).[29] The stereoelectronic parameters are presented in Table 1.

Via eq 1, we and others have found excellent correlations of over 200 sets of data (for example, see refs 26, 29, 34, 36−40). These properties include kinetic and stereoselectivity data, thermodynamic data (pK_a values, $E°$ values, heats of reaction, equilibrium constants), bond lengths, and spectroscopic data (IR, NMR, UV−vis, and photoelectron data). In addition, we have found that the QALE parameters (χ, θ, E_{ar}) are transferable to other groups and ligands including silyls,[23,24] arsines,[45] alkyls,[45] nitriles,[28] amines,[45] and thioethers.[22,27]

Recently, we showed that by the comparisons of physiochemical properties of phosphine complexes it is possible to identify the minimum number and nature of the stereoelectronic parameters necessary to describe a phosphine ligand.[29] A further test of the QALE model is how well it accounts for the temperature dependence of a property. This idea has led us to consider isokinetic and isoequilibrium behavior[1−11,19] in terms of the QALE model.

For the reactions of a set of complexes in which the structure of a ligand is varied, "isoequilibrium behavior" describes the case where plots of $\Delta G°/T$ versus $1/T$ show a common point of intersection (i.e., isoequilibrium point). At this point, this set of compounds displays a common equilibrium property, i.e., one that is independent of the ligand that is being modified.

Results and Discussion

The η-Cp(CO)(L)(COMe)Fe$^+$/η-Cp(CO)(L)(COMe)Fe° (L = phosphorus(III) ligand) couple is a remarkably well-behaved system suitable for systematic and quantitative studies of ligand effects. The stereoelectronic properties of phosphorus(III) ligands are almost continuously variable. More over, the system is chemically reversible and electrochemically quasi reversible, eq 2.

$$\eta\text{-Cp(CO)(L)Fe(COMe)}^+ + e^- \rightleftharpoons \eta\text{-Cp(CO)(L)Fe(COMe)} \quad (2)$$

Table 2. Electrochemical Data for (η-Cp)(CO)(L)Fe(COMe) Complexes

	$E°$(V)^a				
L	229 K	252 K	264 K	273 K	293 K
PMe_3	−0.3593	−0.3579	−0.3579	−0.3577	−0.3584
PEt_3	−0.3941	−0.3946	−0.3923	−0.3935	−0.3922
P(n-Bu)$_3$	−0.3994	−0.3980	−0.4000	−0.3986	−0.3990
P(i-Bu)$_3$	−0.3939	−0.3916	−0.3926	−0.3921	−0.3925
P(*p*-MeOC$_6$H$_4$)$_3$	−0.2918	−0.2969	−0.2992	−0.3017	−0.3067
P(*p*-MeC$_6$H$_4$)$_3$	−0.2790	−0.2815	−0.2848	−0.2869	−0.2912
P(*p*-C$_6$H$_5$)$_3$	−0.2515	−0.2569	−0.2570	−0.2590	−0.2630
P(*p*-FC$_6$H$_4$)$_3$	−0.2068	−0.2091	−0.2118	−0.2132	−0.2151
P(*p*-ClC$_6$H$_4$)$_3$	−0.1858	−0.1862	−0.1873	−0.1882	−0.1910
P(*p*-CF$_3$C$_6$H$_4$)$_3$	−0.1367	−0.1359	−0.1380	−0.1385	−0.1407
P(i-Pr)$_3$	−0.4406	−0.4399	−0.4398	−0.4393	−0.4393
PCy_3	−0.4597	−0.4607	−0.4612	−0.4615	−0.4604

[a] These values refer to the (η-Cp)(CO)(L)Fe(COMe)$^{+/o}$ redox couple relative to the (η-Cp)(η^5-C$_5$H$_4$COMe)Fe$^{+/o}$ redox couple. Each value listed has an error of ±0.0007 V.

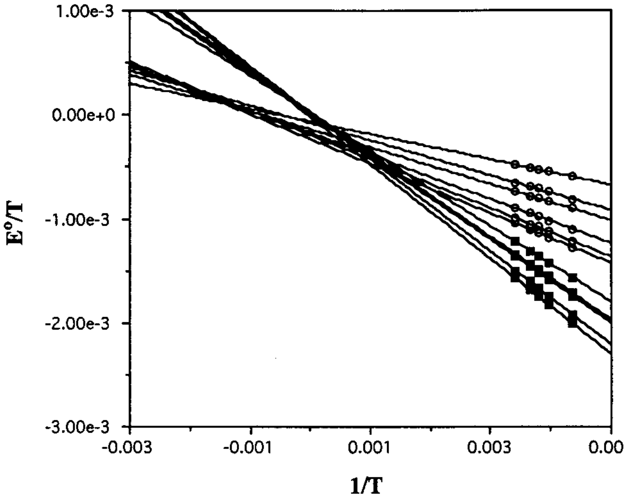

Figure 1. Plot of $E°/T$ versus $1/T$ for PR_3 (■) and P(*p*-XC$_6$H$_4$)$_3$ (○). Going from top to bottom, the order of the lines is as follows: P(*p*-CF$_3$C$_6$H$_4$)$_3$, P(*p*-ClC$_6$H$_4$)$_3$, P(*p*-FC$_6$H$_4$)$_3$, P(*p*-C$_6$H$_5$)$_3$, P(*p*-MeC$_6$H$_4$)$_3$, P(*p*-MeOC$_6$H$_4$)$_3$, PMe_3, PEt_3, P(i-Bu)$_3$, P(n-Bu)$_3$, P(i-Pr)$_3$, PCy_3. The lines for PEt_3, P(i-Bu)$_3$, and P(n-Bu)$_3$ all fall very close to each other and are difficult to distinguish.

Accordingly, we have been able to measure accurately and precisely $E°$ values for this system relative to the acetylferrocinium/acetylferrocene couple at five temperatures over a range of 60 K for a large number of phosphorus(III) ligands. The measurements were repeated 5−10 times; the error in our measurements is less than 0.0007 V, which is more than sufficient for our studies. The data are displayed in Table 2.

The plots of $E°/T$ versus $1/T$ tell us about the number and nature of the stereoelectronic parameters necessary to describe the system, whereas the plots of $E°/T$ versus χ tell us about the distribution of steric effects between enthalpy and entropy of reaction (vide infra).

Analysis of $E°/T$ versus $1/T$ Plots. We begin our analyses of the $E°$ data by examining the plot $E°/T$ versus $1/T$, Figure 1. We note that PR_3 and P(*p*-XC$_6$H$_4$)$_3$ form two fan-shaped arrays of lines, each of which comes together in a small region. On the basis of the statistical treatment developed by Exner,[12] Linert has proposed statistical tests (based upon two applications of the F-test)[11,46] to answer the question of whether a point of intersection exists that could simultaneously be a

---

(43) Bartik, T.; Himmler, T.; Schulte, H.; Seevogel, K. J. *J. Organomet. Chem.* **1984**, *272*, 29.

(44) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

(45) Bartholomew, J.; Bennett, D. M.; Chakar, F.; Fernandez, A. L.; Giering, W. P.; Lorsbach, B. A.; Prock, A.; Wilson, M. R. Unpublished results.

Table 3. Coefficients for the Plots[a] of $E°/T$ vs $1/T$, Fit to $E°/T = a(1/T) + b$

L	a	b	r^2	n
PMe_3	$-(0.363 \pm 0.003)$	$(2.30 \pm 0.07) \times 10^{-4}$	0.99	5
PEt_3	$-(0.402 \pm 0.005)$	$(3.10 \pm 1.80) \times 10^{-5}$	0.99	5
$P(n\text{-}Bu)_3$	$-(0.400 \pm 0.005)$	$(3.54 \pm 18.4) \times 10^{-6}$	0.99	5
$P(i\text{-}Bu)_3$	$-(0.398 \pm 0.005)$	$(2.23 \pm 1.83) \times 10^{-5}$	0.99	5
$P(p\text{-}MeOC_6H_4)_3$	$-(0.239 \pm 0.002)$	$-(2.30 \pm 0.07) \times 10^{-4}$	0.99	5
$P(p\text{-}MeC_6H_4)_3$	$-(0.234 \pm 0.006)$	$-(1.92 \pm 0.19) \times 10^{-4}$	0.99	5
$P(p\text{-}C_6H_5)_3$	$-(0.212 \pm 0.005)$	$-(1.72 \pm 0.18) \times 10^{-4}$	0.99	5
$P(p\text{-}FC_6H_4)_3$	$-(0.175 \pm 0.003)$	$-(1.37 \pm 0.12) \times 10^{-4}$	0.99	5
$P(p\text{-}ClC_6H_4)_3$	$-(0.168 \pm 0.005)$	$-(7.61 \pm 1.76) \times 10^{-5}$	0.99	5
$P(p\text{-}CF_3C_6H_4)_3$	$-(0.122 \pm 0.006)$	$-(6.20 \pm 2.26) \times 10^{-5}$	0.99	5
$P(i\text{-}Pr)_3$	$-(0.446 \pm 0.001)$	$-(2.21 \pm 0.40) \times 10^{-5}$	0.99	5
PCy_3	$-(0.456 \pm 0.004)$	$-(1.85 \pm 1.40) \times 10^{-5}$	0.99	5

member of each line in a single array. The second F-test is extremely rigorous, and few systems pass both of them. Nevertheless, Linert maintains that passage of the first F-test is very good evidence that the point of intersection exists.[8] The two fan-shaped arrays easily pass the first test, and we take this as sufficient evidence for a point of intersection, i.e., an isoequilibrium point. In Figure 1, it is obvious that the isoequilibrium points are different for PR_3 and $P(p\text{-}XC_6H_4)_3$.

Isoequilibrium behavior can only occur when a property responds to variations in one parameter. Linert and Jameson showed the connection between a one-parameter linear free energy relationship and isoequilibrium behavior.[2] In the multiparameter QALE model, isoequilibrium behavior will also only occur when the property is responding to changes in a single parameter but this parameter might be an effectively single parameter comprised of a linear combination of stereoelectronic parameters. (A complete algebraic treatment of the connection between the QALE model and isoequilibrium behavior is presented in the Appendix.)

Since the two sets of ligands give different isoequilibrium points, they must be responding to different stereoelectronic parameters. In the QALE model, isoequilibrium behavior is expected for $P(p\text{-}XC_6H_4)_3$, since the only variable for this set of ligands is the electronic parameter, χ; the cone angle (θ) and the aryl effect parameter (E_{ar}) are constant, see eq A7 (Appendix). The PR_3 ligands, for which both χ and θ are variables, respond linearly to an effectively single parameter because χ and θ are linearly related[29] and E_{ar} is zero, see eqs A13 and A17. We define a *family* of ligands as those ligands that exhibit a single isoequilibrium point. This definition of family is independent of the set of stereoelectronic parameters used to describe the ligands.

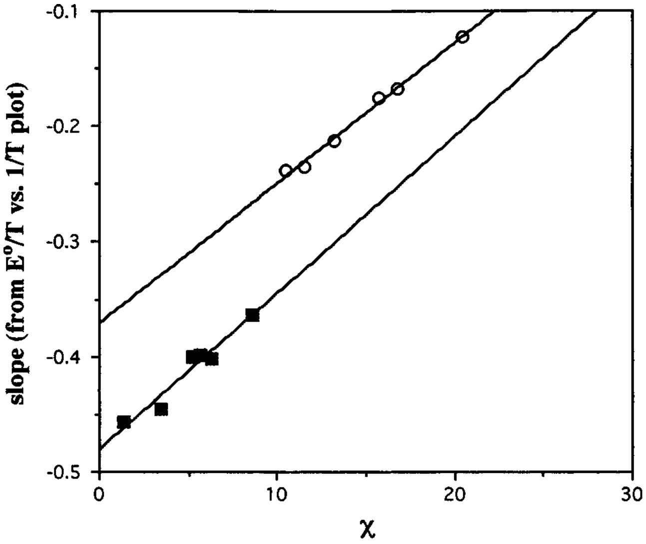

Figure 2. Plot of the slopes (from $E°/T$ versus $1/T$ plots from Figure 1) versus χ for PR_3 (■) and $P(p\text{-}XC_6H_4)_3$ (○).

Two parameters would be sufficient to account for the two isoequilibrium points if for each family there were a different linear relationship between the two parameters, i.e., the two combinations give rise to two different effectively single parameters. However, consideration of the relative positions of the isoequilibrium points (Figure 1) provides evidence that a third parameter is needed in this particular system. Let us consider the situation when only the stereoelectronic parameters χ and θ describe the properties of our two families of ligands. First, we need to note that according to eqs A7 and A17, the slopes (proportional to $\Delta H°$, Table 3) of the lines in Figure 1 are predicted and found to be linearly related to χ (eqs 3 and 4 and Figure 2). Because

$$\text{slope (aryl, } 1/T) = (0.0121 \pm 0.0005)\chi - (0.370 \pm 0.007) \quad (3)$$

$$r^2 = 0.994$$

$$\text{slope (alkyl, } 1/T) = (0.0136 \pm 0.0016)\chi - (0.480 \pm 0.009) \quad (4)$$

$$r^2 = 0.945$$

of the linear relationship between χ and θ[20] for PR_3, we predict that a hypothetical PR_3 ligand with a cone angle of 145° should have a χ value equal to 4.8. Since the slopes of the lines for PR_3 in Figure 1 are linearly correlated to χ (Figure 2) and must pass through the isoequilibrium point for PR_3 (Figure 1), we can predict where this line should fall in Figure 1—between the lines for PBu_3 and $P(i\text{-}Pr)_3$. In this two-parameter world, θ equal to 145° would make the PR_3 ligand with a χ value of 4.8 a member of the $P(p\text{-}XC_6H_4)_3$ family also. Since the slopes of the lines for $P(p\text{-}XC_6H_4)_3$ in Figure 1 are linearly correlated to χ (Figure 2) and must pass through the isoequilibrium point for $P(p\text{-}XC_6H_4)_3$ (Figure 1), we can also predict where this line should fall in Figure 1—just below the line for $P(p\text{-}MeOC_6H_4)_3$. In this two-parameter world, the lines for the PR_3 and $P(p\text{-}XC_6H_4)_3$ with $\chi = 4.8$ and $\theta = 145°$ should be coincident and should pass through the isoequilibrium points for both families. A glance at Figure 1 shows that this is impossible; hence, another parameter is needed to distinguish between the two families. In the QALE model, this is the aryl effect parameter (E_{ar}).

Analysis of $E°/T$ versus χ Plots. We begin this analysis using the information about family membership obtained from the $1/T$ plot (Figure 1). Thus, in the plot of $E°/T$ versus χ, we now treat the two families separately. Equations A6 and A14 predict that the plots of $E°/T$ versus χ for $P(p\text{-}XC_6H_4)_3$ and PR_3 will form two fan-shaped arrays of lines with different points of intersection. Indeed, these plots, which are displayed in Figure 3, show the expected behavior. The values of

---

(46) Linert, W.; Soukup, R. W.; Schmid, R. *Comput. Chem.* **1982**, *6*, 47.

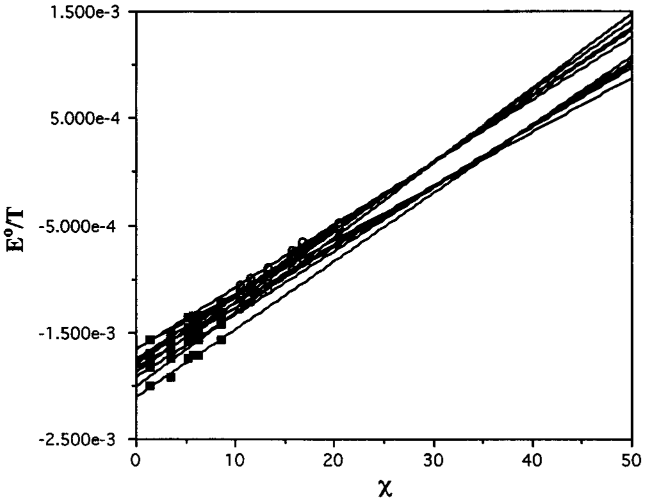

Figure 3. Plot of $E°/T$ versus χ for PR_3 (■) and $P(p\text{-}XC_6H_4)_3$ (○). For the lines for each family, the temperature increases from bottom to top (229, 252 264, 273, 293 K).

the isoequilibrium points ($E°/\beta_{\mathrm{alk}}$ (1.41e-4 V K^{-1}) and $E°/\beta_\chi$ (1.23e-4 V K^{-1}) and $1/\beta_{\mathrm{alk}}$ (−3.57e-4 K^{-1}) and $1/\beta_\chi$ (1.40e-3 K^{-1})) obtained from the plots of $E°/T$ versus χ are the same as the values obtained from the $1/T$ plots. β_{alk} and β_χ are the temperatures at the isoequilibrium points for the two families in Figure 1. According to eqs A6 and A14, the slopes of these lines are proportional to $1/T$. Values for β_{alk} and β_χ are the temperatures where the slopes of the lines in Figure 3 become zero.

Analysis of the slopes of the lines in Figure 3 gives us information about the contribution of steric effects to $\Delta H°$ and $\Delta S°$. $\Delta H°$ and $\Delta S°$ are assumed to be temperature independent within our experimental temperature range; thus, the plots of the slopes of the lines of $E°/T$ versus χ are predicted to be linearly related to $1/T$ by eqs A6 and A14. Indeed, the high values of r^2 for the plots in Figure 4, where we have plotted slope(aryl or alkyl) versus $1/T$, indicate the appropriateness of this assumption, see eqs 5 and 6, which are derived from A6 and A14. The slopes of the two lines in Figure 4 are predicted to be same as the slopes of the lines in Figure 2. Indeed, this is the case, as shown by a comparison of eqs 3−6.

$$(nF)\text{slope (aryl)} = -\frac{a_1}{nF}\left(\frac{1}{T}\right) + \frac{a_2}{nF} = -(0.0136 \pm 0.0008)\left(\frac{1}{T}\right) + (4.84 \pm 3.09) \times 10^{-6} \quad (5)$$

$$r^2 = 0.996$$

$$(nF)\text{slope (alkyl)} = -\frac{a_1 + \alpha b_1}{nF}\left(\frac{1}{T}\right) + \frac{a_2 + \alpha b_2}{nF} = -(0.0123 \pm 0.0004)\left(\frac{1}{T}\right) + (1.75 \pm 0.17) \times 10^{-6} \quad (6)$$

$$r^2 = 0.990$$

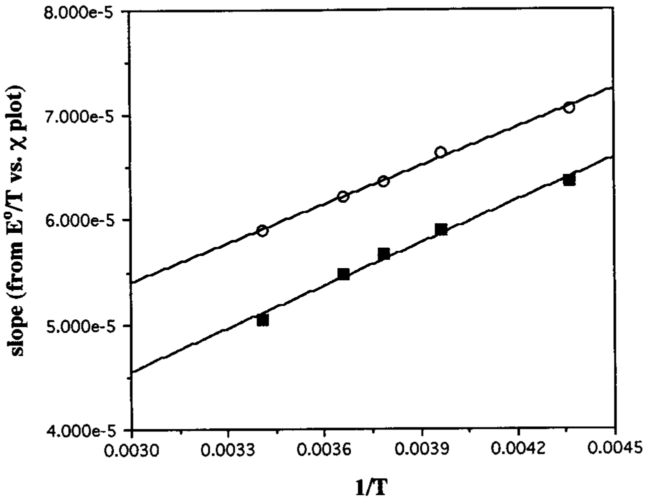

Figure 4. Plot of the slopes (from $E°/T$ versus χ plots) versus $1/T$ for PR_3 (■) and $P(p\text{-}XC_6H_4)_3$ (○).

From the plots in Figure 4 and eqs 5 and 6 we can make some interesting predictions: If the steric effect resides in both $\Delta H°$ and $\Delta S°$ ($b_1 \neq b_2 \neq 0$), then the plots of the slopes of the lines in Figure 3 versus $1/T$ will exhibit different slopes and intercepts. If the steric effect resides only in $\Delta H°$ ($b_2 = 0$), then the plots of slopes versus $1/T$ will exhibit different slopes but the same intercept. In other words, the lines will cross at $1/T = 0$. If the steric effect resides only in $\Delta S°$ ($b_1 = 0$), then two parallel lines will be observed (see Figure 4). Finally, if there are no steric effects ($b_1 = b_2 = 0$), then the two lines will be coincident.

The results of the regression analysis (eqs 5 and 6) show that the two separate lines in Figure 4 are close to being parallel. Thus, a steric effect is operative, and this effect is mostly an entropic phenomenon. This is consistent with our analysis of $\Delta H°$ and $\Delta S°$ (vide infra).

Although plots of $E°/T$ versus χ contain the same information as the plots of $E°/T$ versus $1/T$, there is a major pitfall that must be avoided. **We observe an excellent linear relationship between $E°/229$ and χ (Figure 5A, $r^2 = 0.99$) for all of the ligands.** When we plot the data against a single parameter, we are implying that the ligands belong to a single family. When all of the data ($E°/T$) measured at the five temperatures are plotted versus χ (Figure 5B) and the regression lines are drawn, a point of convergence is observed. This analysis is incorrect, for as we have seen in Figure 1, PR_3 and $P(p\text{-}XC_6H_4)_3$ are two separate families of ligands and they must be treated separately. Inspection of Figure 5B shows that the value of $(E°/T)_{\mathrm{iso}}$ (at the point of intersection) is negative and is very different from the values of ($E°/\beta_{\mathrm{alk}}$) and ($E°/\beta_\chi$) for PR_3 and $P(p\text{-}XC_6H_4)_3$ observed in Figure 1. Furthermore, the value of $(1/T)_{\mathrm{iso}}$ determined from an analysis of the slopes and intercepts of the lines in Figure 5B does not correspond to either of the values of ($1/\beta_{\mathrm{alk}}$) and ($1/\beta_\chi$) for PR_3 or $P(p\text{-}XC_6H_4)_3$. Thus, an excellent linear relationship does not necessarily imply a correct analysis unless family membership has been established.

In Figure 5C, we illustrate a rather curious and counterintuitive result; in plots of sets of free energy data measured precisely at different temperatures versus any parameter, *even a set of random numbers* will always give fan-shaped arrays of *linear regression* lines. In Figure 5C, we have plotted the data versus a set of random numbers instead of χ. For any temperature the fit is terrible; however, the set of lines obtained by *linear regression* still intersect at a point; the slopes

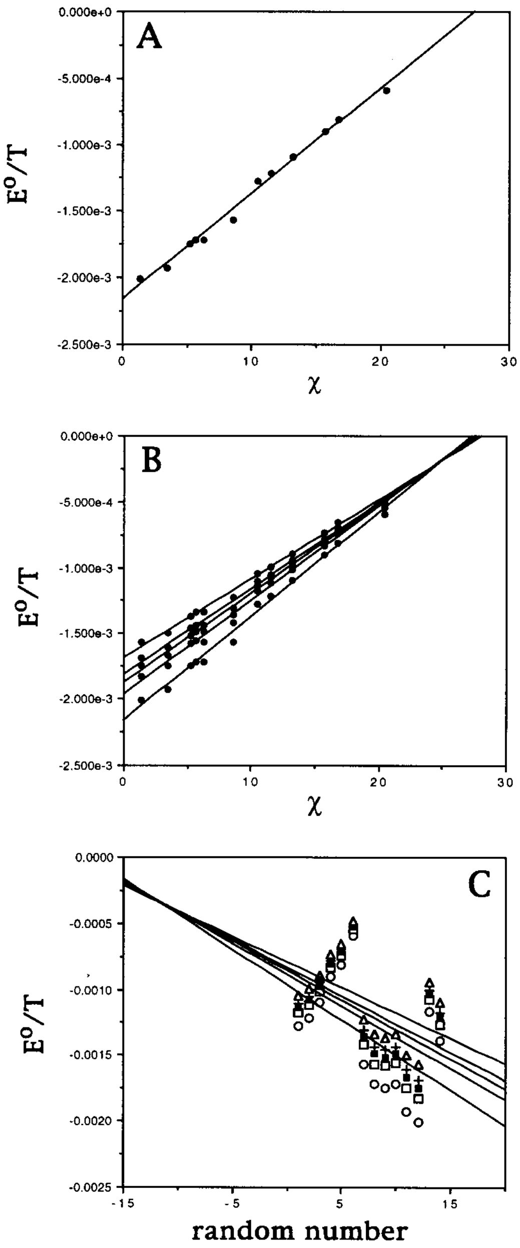

Figure 5. (A) Plot of $E°/T$ (T = 229 K) for PR$_3$ and P(p-XC$_6$H$_4$)$_3$ versus χ. r^2 is 0.991 for the regression line. (B) Plot of $E°/T$ (T = 229, 253, 264, 273, 293 K) versus χ. (C) Plot of $E°/T$ (T = 229, 253, 264, 273, 293 K) versus a random number.

of these lines are still proportional to 1/T. Nothing fundamental can be gleaned from such a plot.

Analysis of Δ*H*° and Δ*S*°. ΔH° and ΔS° of reduction of η-Cp(CO)(L)FeCOMe$^+$ (measured relative to the reduction of acetylferricinium) were calculated from the slopes and intercepts of the $E°/T$ versus 1/T plots in the standard manner (eq A5). These values are displayed in Table 4.

We begin the analysis of ΔH° and ΔS° by plotting these values versus χ. The plots of ΔH° versus χ, which is equivalent to the data displayed in Figure 2, show two lines for PR$_3$ and P(p-XC$_6$H$_4$)$_3$ that are not quite parallel. This observation indicates that there is a small steric contribution to ΔH°. Furthermore, there appears to be no steric threshold. The separation of the lines in Figure 2 indicates that there is a small but significant aryl effect.

Table 4. Thermodynamic Data for the Reduction of (η^5-C$_5$H$_5$)(CO)(L)Fe(COMe) Complexes[a]

L	ΔH° (kJ mol^{-1})	ΔS° (J K^{-1} mol^{-1})
PMe$_3$	35.0	1.8
PEt$_3$	38.7	3.0
P(n-Bu)$_3$	38.6	0.3
P(i-Bu)$_3$	38.5	2.2
P(p-MeOC$_6$H$_4$)$_3$	23.1	−22.2
P(p-MeC$_6$H$_4$)$_3$	22.6	−18.5
P(p-C$_6$H$_5$)$_3$	20.5	−16.6
P(p-FC$_6$H$_4$)$_3$	16.9	−13.2
P(p-ClC$_6$H$_4$)$_3$	16.2	−7.3
P(p-CF$_3$C$_6$H$_4$)$_3$	11.7	−6.0
P(i-Pr)$_3$	43.0	2.1
PCy$_3$	44.0	−1.8

[a] The ΔH° and ΔS° values are relative to acetylferrocene. The errors in ΔH° and ΔS° are reflected in the errors in the slopes and intercepts given in Table 3.

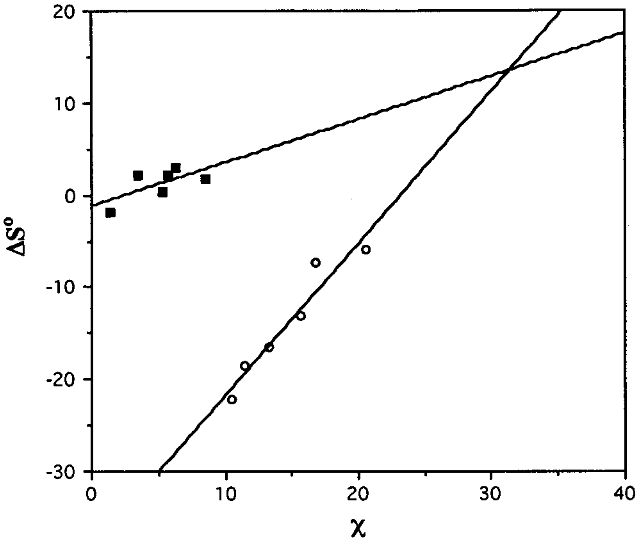

Figure 6. Plot of ΔS°(J/mol K) versus χ for PR$_3$ (■) and P(p-XC$_6$H$_4$)$_3$ (○).

The plots of ΔS° versus χ (Figure 6) show two nonparallel lines that intersect at a position far removed from χ = 4.8 (vide supra)—the point of intersection that is expected if there were no aryl effect. Thus, there are significant aryl and steric effects. There is no apparent steric threshold.

The regression analysis of ΔH° was done using the three-parameter QALE equation (eq A2); the results are shown in eq 7.

$$\Delta H° = -(1.14 \pm 0.08)\chi + (0.023 \pm 0.016)\theta - (3.84 \pm 0.30)E_{\rm ar} + (42.2 \pm 2.5) \quad (7)$$

$$n = 16 \qquad r^2 = 0.997$$

ΔS° was analyzed analogously (eq A3). The analysis shows statistically significant aryl and steric effects (eq 8)—a result that was predicted graphically (vide supra).

$$\Delta S° = (1.71 \pm 0.19)\chi + (0.174 \pm 0.040)\theta - (11.9 \pm 0.8)E_{\rm ar} - (32.7 \pm 6.3) \quad (8)$$

$$n = 16 \qquad r^2 = 0.969$$

The χ dependence of ΔH° is reasonable in that the increasing electron-withdrawing capacity of the ligand is associated with greater exothermicity of the reduction. The small dependence of $\Delta H°$ on θ indicates (1) that either enthalpic steric effects are significant and nearly equivalent in both oxidation states or (2) that there are small enthalpic steric effects in either state. Because of the large number of effects that can influence $\Delta H°$, the lack of a significant steric effect might be fortuitous. A larger value of E_{ar} makes $\Delta H°$ become more negative. $\Delta S°$ becomes more positive as the ligands become larger and better electron-withdrawing groups. Increasing size increases $\Delta S°$, while the aryl effect diminishes $\Delta S°$ as the number of aryl groups increases.

Conclusion

The QALE model accounts for all of the experimental observations described herein; this supports the validity of the model. An analysis of isoequilibrium behavior of the reduction of η-Cp(CO)(L)Fe(COMe)$^+$ has allowed the classification of the phosphine ligands by family. By defining a family by a common point of intersection in an $E°/T$ versus $1/T$ plot, we identify families of ligands (for a particular system) in an unambiguous and unbiased manner. This assignment by family is intuitively reasonable and in agreement with the QALE model. Furthermore, theory tells us that a family will influence a property by variations in a single, or effectively single, parameter. Thus, interpretations of data that involve a single family of ligands are of limited utility since the effects of the stereoelectronic parameters cannot be separated. Analysis of plots of $E°/T$ versus χ gives information about the partitioning of steric effects between enthalpy and entropy as long as families of ligands are recognized appropriately. In contrast, analysis of $E°/T$ versus $1/T$ gives values for $\Delta H°$ and $\Delta S°$ as well as revealing the minimum number and nature of the stereoelectronic parameters necessary to describe the system. In the present case, three parameters are required. The theory presented herein shows that the effect of the stereoelectronic parameters on free energy can be turned off at temperatures that are specific for each parameter. It is satisfying to see how these isoequilibrium studies demonstrate the fully self-consistent nature of the QALE model. This methodology should have ramifications in all applications of structure−reactivity relationships.

Experimental Section

General Procedures. All manipulations and preparations were carried out under argon using standard techniques. Acetonitrile (J. T. Baker HPLC grade), which was purified by distillation from P_2O_5, was then kept refluxing over CaH_2 and distilled immediately prior to use. Tetrabutylammonium hexafluorophosphate (TBAH) (Aldrich) was recrystallized from warm ethyl acetate, before use it was heated in vacuo to remove residual solvent. The phosphines (Aldrich, Lancaster, and Strem) were used as received. The η-Cp(CO)(L)Fe(COMe) complexes were synthesized according to literature methods.[47]

The $E°$ values for the η-Cp(CO)(L)Fe(COMe)$^{+/o}$ couple were obtained via cyclic voltammetry and measured relative to acetylferrocene. Since there was no significant decomposition of the electrochemically generated species, the $E°$ values could be obtained by averaging the voltage of the peak potentials of the cyclic voltammogram. Each measurement was taken between 5 and 10 times. The measurements were then repeated with a fresh sample and found to agree with the original measurements. This leads to an error of ±0.0007 V in the $E°$ values.

Acknowledgment. We gratefully acknowledge the helpful comments of the reviewers.

Appendix

The QALE Model and Isoequilibrium Behavior. In the following analyses, we consider a property (related to free energy) where there is no steric threshold. Thus, eq 1 reduces to

$$\Delta G° = a\chi + b\theta + cE_{ar} + d \qquad \text{(A1)}$$

Since the QALE equation can be applied at different temperatures (vide infra), it follows that eq A1 can be applied to the analysis of $\Delta H°$ and $\Delta S°$ individually (eqs A2 and A3). Hence,

$$\Delta H° = a_1\chi + b_1\theta + c_1E_{ar} + d_1 \qquad \text{(A2)}$$

$$\Delta S° = a_2\chi + b_2\theta + c_2E_{ar} + d_2 \qquad \text{(A3)}$$

In what follows, we assume that $\Delta H°$ and $\Delta S°$ are independent of temperature over the temperature range of the measurements. Combining eqs A2 and A3 with the expression relating $\Delta G°$ with reduction potential, $E°$, leads to eq A4 and its variant (eq A5), where the β's represent temperatures (isoequilibrium temperatures) at which the corresponding parameters, χ, θ, or E_{ar}, have no observable effect. Thus, a regression analysis performed at such a temperature would show no contribution from the particular parameter.

$$\frac{E°}{T} = -\frac{a_1}{nF}\left(\frac{1}{T} - \frac{1}{\beta_\chi}\right)\chi - \frac{b_1}{nF}\left(\frac{1}{T} - \frac{1}{\beta_\theta}\right)\theta - \frac{c_1}{nF}\left(\frac{1}{T} - \frac{1}{\beta_{E_{ar}}}\right)E_{ar} - \frac{d_1}{nF}\left(\frac{1}{T} - \frac{1}{\beta}\right) \qquad \text{(A4)}$$

$$\beta_\chi \equiv \frac{a_1}{a_2} \qquad \beta_\theta \equiv \frac{b_1}{b_2} \qquad \beta_{E_{ar}} \equiv \frac{c_1}{c_2} \qquad \beta \equiv \frac{d_1}{d_2}$$

$$\frac{E°}{T} = -\frac{a_1\chi + b_1\theta + c_1E_{ar} + d_1}{nF}\left(\frac{1}{T}\right) + \frac{a_2\chi + b_2\theta + c_2E_{ar} + d_2}{nF} \qquad \text{(A5)}$$

In eq A4, we group terms according to the stereoelectronic parameters, whereas in eq A5, we group the terms according to $1/T$. Equation A4 will be useful when interpreting plots of $E°/T$ versus χ, and eq A5 will be useful when interpreting plots of $E°/T$ versus $1/T$.

To have isoequilibrium behavior, $\Delta H°$ and $\Delta S°$ (which are proportional to the slope and intercept of eq A5) must be linearly related. To be linearly related $\Delta H°$ and $\Delta S°$ must depend linearly on a single parameter or an effectively single parameter (vide infra). (The parameter can then be eliminated between $\Delta H°$ and $\Delta S°$.)

We now consider the P(p-XC$_6$H$_4$)$_3$ and PR$_3$ ligands. For the first family (see text), the variations in the

---

[47] Rahman, M. M.; Liu, H.; Eriks, K.; Prock, A.; Giering, W. P. *Organometallics* **1989**, *8*, 1.

property depend on a single parameter (χ), and for the second family, the property depends on two linearly related parameters (χ and θ).

Case 1. Variations in $\Delta G°$ Depend on a Single Parameter (χ). Consider the family of para-substituted triaryl phosphines, P(p-XC$_6$H$_4$)$_3$, whose effects on a property are described by the variations of a single parameter, χ. Here, $\theta = 145°$ and $E_{\mathrm{ar}} = 2.7$. Thus, eq A4 becomes eq A6 and eq A5 becomes equation A7.

$$\frac{E°}{T} = -\frac{a_1}{nF}\left(\frac{1}{T} - \frac{1}{\beta_\chi}\right)\chi - \frac{b_1}{nF}\left(\frac{1}{T} - \frac{1}{\beta_\theta}\right)(145) - \frac{c_1}{nF}\left(\frac{1}{T} - \frac{1}{\beta_{E_{\mathrm{ar}}}}\right)(2.7) - \frac{d_1}{nF}\left(\frac{1}{T} - \frac{1}{\beta}\right) \quad \text{(A6)}$$

$$\frac{E°}{T} = -\frac{a_1\chi + b_1(145) + c_1(2.7) + d_1}{nF}\left(\frac{1}{T}\right) + \frac{a_2\chi + b_2(145) + c_2(2.7) + d_2}{nF} \quad \text{(A7)}$$

Equation A6 shows that when $1/T = 1/\beta_\chi$ then $E°/T$ is independent of χ (the only variable parameter in this case); thus, the QALE model predicts that a fan-shaped array of lines will result when $E°/T$ is plotted versus $1/T$. The coordinates ($1/\beta_\chi$ and $E°/\beta_\chi$) of the isoequilibrium point (point of intersection) are given by eqs A8 and A9. It is important to note that $1/\beta_\chi$ is dependent only on the coefficients of χ in eqs A2 and A3, whereas $E°/\beta_\chi$ is dependent on all of the coefficients from eqs A2 and A3 as well as the particular values of θ and E_{ar} (vide infra).

$$\frac{1}{\beta_\chi} = \frac{a_2}{a_1} \quad \text{(A8)}$$

$$\frac{E°}{\beta_\chi} = -\frac{b_1}{nF}\left(\frac{1}{\beta_\chi} - \frac{1}{\beta_\theta}\right)(145) - \frac{c_1}{nF}\left(\frac{1}{\beta_\chi} - \frac{1}{\beta_{E_{\mathrm{ar}}}}\right)(2.7) - \frac{d_1}{nF}\left(\frac{1}{\beta_\chi} - \frac{1}{\beta}\right) \quad \text{(A9)}$$

From eq A7, we see that the slope [$-\Delta H°/(nF)$] and intercept [$\Delta S°/(nF)$] of the $1/T$ plots are given by eqs A10 and A11. Notice that the slope of the plot of $E°/T$ versus $1/T$ should be linearly related to the electronic parameter χ (eq A10), with a proportionality constant of $-a_1/nF$. Notice also that the slope of the plot of $E°/T$ versus χ (eq A6) should be linearly related to $1/T$, with the same proportionality constant, $-a_1/nF$.

$$\text{slope} = -\frac{a_1\chi + b_1(145) + c_1(2.7) + d_1}{nF} = -\frac{\Delta H°}{nF} \quad \text{(A10)}$$

$$\text{intercept} = \frac{a_2\chi + b_2(145) + c_2(2.7) + d_2}{nF} = \frac{\Delta S°}{nF} \quad \text{(A11)}$$

According to eq A7, there exists a χ value that removes the temperature dependence of $E°/T$; thus, the plot of $E°/T$ versus χ is also expected to yield a fan-shaped array of lines. In principle, the same information is encoded in the plots of $E°/T$ versus $1/T$ as in the plots of $E°/T$ versus χ. Linert and Jameson[2] concluded that this is a necessary relationship between linear free energy relationships and isoequilibrium behavior. The coordinates of the point of intersection are given by eqs A9 and A12.

$$\chi_{\mathrm{iso}} = -\frac{b_1(145) + c_1(2.7) + d_1}{a_1} \quad \text{(A12)}$$

Case 2. $\Delta G°$ Depends on Two Parameters That Are Linearly Related. For our second example, we consider PR$_3$ ligands where $\Delta G°$ depends on two linearly related parameters (effectively one parameter). Thus, these ligands constitute a family. This might be a selection of PR$_3$ whose cone angles, θ, are linearly related to χ (eq A13). On substituting eq A13 into eq A5, we get eq A14 ($E_{\mathrm{ar}} = 0$ for this family). Equation A14 describes a fan-shaped array of lines whose intersection is given by the coordinates $1/\beta_{\mathrm{alk}}$ and $E°/\beta_{\mathrm{alk}}$ (eqs A15 and A16).

$$\theta = \alpha\chi + \gamma \quad \text{(A13)}$$

$$\frac{E°}{T} = -\frac{a_1 + \alpha b_1}{nF}\left(\frac{1}{T} - \frac{1}{\beta_{\mathrm{alk}}}\right)\chi - \frac{\gamma b_1 + d_1}{nF}\left(\frac{1}{T} - \frac{1}{\beta'}\right) \quad \text{(A14)}$$

$$\beta_{\mathrm{alk}} \equiv \frac{a_1 + \alpha b_1}{a_2 + \alpha b_2} \qquad \beta' \equiv \frac{\gamma b_1 + d_1}{\gamma b_2 + d_2}$$

$$\frac{1}{\beta_{\mathrm{alk}}} = \frac{a_2 + \alpha b_2}{a_1 + \alpha b_1} \quad \text{(A15)}$$

$$\frac{E°}{\beta_{\mathrm{alk}}} = -\frac{\gamma b_1 + d_1}{nF}\left(\frac{1}{\beta_{\mathrm{alk}}} - \frac{1}{\beta'}\right) \quad \text{(A16)}$$

Incorporation of eq A13 into eq A6 gives eq A17. The measured slope of the $E°/T$ versus $1/T$ plot (eq A17) when plotted against χ should have a slope of $-(a_1 + \alpha b_1)/nF$. Similarly, the measured slope of the $E°/T$ versus χ plot (eq A14) when plotted against $1/T$ should have the same slope, $-(a_1 + \alpha b_1)/nF$. The coordinates of the point of intersection of the fan-shaped array (eq A14) are given by eqs A18 and A19. Equation A19 also follows from eq A17 with $\chi = \chi_{\mathrm{iso}}$. *Note that the isoequilibrium points for PR$_3$ and P(p-XC$_6$H$_4$)$_3$ are predicted to be different.*

$$\frac{E°}{T} = -\frac{(a_1 + \alpha b_1)\chi + \gamma b_1 + d_1}{nF}\left(\frac{1}{T}\right) + \frac{(a_2 + \alpha b_2)\chi + \gamma b_2 + d_2}{nF} \quad \text{(A17)}$$

$$\chi_{\mathrm{iso}} = -\frac{\gamma b_1 + d_1}{a_1 + \alpha b_1} \quad \text{(A18)}$$

$$\frac{E°}{\beta_{\mathrm{alk}}} = -\frac{\gamma b_1 + d_1}{nF}\left(\frac{1}{\beta_{\mathrm{alk}}} - \frac{1}{\beta'}\right) \quad \text{(A19)}$$

OM971041F