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A Thermodynamically Based and Definitive Demonstration of the Inadequacy of the ECW Model for Phosphorus(III) Ligands

Anthony L. Fernandez, Tsung Ying Lee, Clementina Reyes, Alfred Prock,* and Warren P. Giering*

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

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Isoequilibrium behavior arising from the temperature dependence of $\Delta G°$ of families of complexes containing phosphorus(III) ligands provides a diagnostic method for evaluating a model (used to describe ligand effects) and the associated set of stereoelectronic parameters. This evaluation is based not on the quality of a linear free energy relationship, but rather on the results of a thermodynamic argument. Studies of the temperature dependence of $E°/T$ values for the η-Cp(CO)(L)Fe(COMe)$^+$/η-Cp(CO)(L)Fe(COMe)^0 couple, where L is a phosphorus(III) ligand, provide isoequilibrium data to test the ECW model for analysis of ligand effects. The ECW model fails this test. Therefore, we conclude that the ECW model is, in general, inadequate to describe the stereoelectronic properties of phosphorus(III) ligands.

Introduction

Proponents of the ECW model[1−4] for analyzing ligand-effect data have been critical of the QALE model (quantitative analysis of ligand effects).[5−31] It has been noted that QALE uses a graphical analysis of data, which is called an "unprecedented statistical procedure [that] causes all meaning to be lost"; QALE supposedly over relies on steric arguments; does not address hard/soft acidity and basicity; uses "invented" parameters to make up for these deficiencies; and although QALE gives good correlations, the results are "without meaning".[1] In contrast, the ECW model supposedly avoids all of the above problems.

In our opinion, there are clear problems with the ECW model. In the latest version[1] of the 1995[3] and 1996[2] papers not only do the parameters change in magnitude but for one set of ligands (i.e., E_B for P(p-XC$_6$H$_4$)$_3$), the ordering is reversed! Such a reversal of order raises concern for the trustworthiness of the interpretation of ECW analyses. In this same paper,[1] ECW is used to analyze 79 sets of data for phosphorus ligands, suggesting the general applicability of the ECW methodology. A closer inspection of these analyses reveals, however, that by the standards of the proponents of the ECW model,[4] one-half the analyses are poor and only a few are excellent. In addition, ligands are often deleted (outliers) from the analyses. The nature of these outliers supposedly reveals fundamental information about the system such as the involvement of "entropic steric effects", π-bonding or "nonlinear free energy relationships". However, outliers can also result from inappropriately assigned parameters.

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Table 1. $\Delta H°$, $\Delta S°$, and $E°$ Values for the η-(Cp)(CO)(L)Fe(COMe)$^{+/0}$ Couple

L	$\Delta H°$ [a]	$\Delta S°$ [a]	$E°$ (V)[b]				
			229 K	252 K	264 K	273 K	293 K
$P(p\text{-MeOC}_6H_4)_3$	23.1	−22.2	−0.2918	−0.2969	−0.2992	−0.3017	−0.3067
$P(p\text{-MeC}_6H_4)_3$	22.6	−18.5	−0.2790	−0.2815	−0.2848	−0.2869	−0.2912
$P(C_6H_5)_3$	20.5	−16.6	−0.2515	−0.2569	−0.2570	−0.2590	−0.2630
$P(p\text{-FC}_6H_4)_3$	16.9	−13.2	−0.2068	−0.2091	−0.2118	−0.2132	−0.2151
$P(p\text{-ClC}_6H_4)_3$	16.2	−7.3	−0.1858	−0.1862	−0.1873	−0.1882	−0.1910
$P(p\text{-CF}_3C_6H_4)_3$	11.7	−6.0	−0.1367	−0.1359	−0.1380	−0.1385	−0.1407
PMe_3	35.0	1.8	−0.3593	−0.3579	−0.3579	−0.3577	−0.3584
PEt_3	38.7	3.0	−0.3941	−0.3946	−0.3923	−0.3935	−0.3922
$P(n\text{-Bu})_3$	38.6	0.34	−0.3994	−0.3980	−0.4000	−0.3986	−0.3990
$P(i\text{-Bu})_3$	38.5	2.2	−0.3939	−0.3916	−0.3926	−0.3921	−0.3925
$P(i\text{-Pr})_3$	43.0	2.1	−0.4406	−0.4399	−0.4398	−0.4393	−0.4393
PCy_3	44.0	−1.8	−0.4597	−0.4607	−0.4612	−0.4615	−0.4604
PMe_2Ph	29.5	−4.7	−0.3170	−0.3182	−0.3191	−0.3202	−0.3196
$PMePh_2$	23.0	−12.4	−0.2674	−0.2704	−0.2721	−0.2733	−0.2755
PEt_2Ph	31.5	−6.9	−0.3426	−0.3438	−0.3457	−0.3462	−0.3467
$PEtPh_2$	24.3	−14.9	−0.2871	−0.2912	−0.2927	−0.2939	−0.2971
$P(OCH_2)_3CEt$	−1.1	−22.7	−0.0418	−0.0493	−0.0504	−0.0535	−0.0567
$P(OMe)_3$	8.0	−17.3	−0.1235	−0.1271	−0.1309	−0.1318	−0.1344
$P(OEt)_3$	9.9	−22.2	−0.1551	−0.1612	−0.1633	−0.1658	−0.1697
$P(OBu)_3$	9.8	−22.4	−0.1548	−0.1601	−0.1634	−0.1656	−0.1693
$P(O\text{-i-Pr})_3$	12.2	−25.2	−0.1867	−0.1926	−0.1955	−0.1991	−0.2030
$P(OC_6H_5)_3$	−5.2	−18.7	0.0094	0.0050	0.0028	0.0012	−0.0032

[a] $\Delta H°$ values are in kJ mol^{-1}, and $\Delta S°$ values are in J K^{-1} mol^{-1}. The $\Delta H°$ and $\Delta S°$ values are relative to the reduction of acetylferrocene (see ref 32). [b] These values refer to the (η-Cp)(CO)(L)Fe(COMe)$^{+/0}$ redox couple relative to the (η-Cp)(η-C$_5$H$_4$COMe)Fe$^{+/0}$ redox couple. Each value listed has an error of ±0.0007 V.

Table 2. ECW[a] and QALE[b] Parameters for Phosphorus(III) Ligands

ligand	E_B	C_B	χ	θ	E_{ar}
$P(p\text{-MeOC}_6H_4)_3$	0.62	3.57	10.5	145	2.7
$P(p\text{-MeC}_6H_4)_3$	0.65	3.41	11.5	145	2.7
$P(C_6H_5)_3$	0.70	3.05	13.25	145	2.7
$P(p\text{-FC}_6H_4)_3$	0.74	2.70	15.7	145	2.7
$P(p\text{-ClC}_6H_4)_3$	0.82	2.35	16.8	145	2.7
$P(p\text{-CF}_3C_6H_4)_3$	0.91	1.52	20.5	145	2.7
PMe_3	0.31	5.15	8.55	118	0
PEt_3	0.28	5.53	6.3	132	0
$P(n\text{-Bu})_3$	0.32	5.36	5.25	136	0
$P(i\text{-Bu})_3$	0.48	4.60	5.7	143	0
$P(i\text{-Pr})_3$	0.36	5.46	3.45	160	0
PCy_3	0.41	5.35	1.4	170	0
PMe_2Ph	0.44	4.49			
$PMePh_2$	0.57	3.74			
PEt_2Ph	0.39	4.91			
$PEtPh_2$	0.55	3.83			
$P(OCH_2)_3CEt$	0.09	4.85			
$P(OMe)_3$	0.50	3.32			
$P(OEt)_3$	0.56	3.17			
$P(OBu)_3$	0.45	3.86			
$P(O\text{-i-Pr})_3$	0.53	3.59			
$P(OC_6H_5)_3$	0.71	1.69			

[a] Parameters are taken from ref 1. [b] Parameters are taken from ref 5. Quale parameters are given only for those ligands included in the regression analysis shown in parts B and D of Figure 1.

The ECW model forces physiochemical properties to be described by only two parameters that supposedly reflect the electrostatic/covalent or hard/soft acid/base ideas of chemical bonding. Only recently, the idea of the steric threshold (or steric onset in their parlance) has been incorporated into the ECW model;[1] they even appear to take ownership of the idea even though the concept was introduced by Poë[31] et al. and us[6] in the mid 1980s. Recently, we showed how to determine the minimum number and nature of stereoelectronic parameters necessary to describe variations in a physiochemical property caused by changes in the structure of phosphine ligands.[12] We revealed that two parameters are insufficient to describe the stereoelectronic properties of phosphorus(III) ligands; thus, we concluded that any two-parameter model, including the ECW model, cannot be adequate.

Herein, we show in a thermodynamically based and definitive manner that the ECW model is inadequate. We do this via an analysis of the isoequilibrium behavior of the standard reduction potentials ($E°$ values) for the η-Cp(CO)(L)(COMe)Fe$^+$/η-Cp(CO)(L)(COMe)Fe^0 couple (L = phosphorus(III) ligand). Correlations of $E°$ and $\Delta H°$ are supposedly handled well by the ECW model.[1−4] In fact, as we will see, the ECW model, indeed, gives excellent correlations at all of the temperatures studied, but this is not sufficient—isoequilibrium behavior places additional and defining requirements on a model of analysis of $\Delta G°$. The ECW model does not, in general, meet these requirements.

Results and Discussion

The η-Cp(CO)(L)(COMe)Fe$^+$/η-Cp(CO)(L)(COMe)Fe^0 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. Furthermore, the system is chemically reversible and electrochemically quasi reversible, eq 1. Accordingly, we have been able

$$\eta\text{-Cp(CO)(L)Fe(COMe)}^+ + e^- \rightleftharpoons \eta\text{-Cp(CO)(L)Fe(COMe)} \quad (1)$$

to measure $E°$ values accurately and precisely 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. Each measurement for the 22 ligands was repeated 5−10 times at each of the five temperatures. The error in our measurements is less than 0.0007 V, which is more than adequate for our studies. The data are displayed in Table 1. The appropriate ECW parameters are displayed in Table 2.

Table 3. Values of E_A* and C_A* Obtained from the Regression Analysis of $E°$ Values for PR_3 and $P(p\text{-}XC_6H_4)_3$[a] in Terms of the ECW Parameters[b]

temp (K)	E_A*	C_A*	W	r^2
229	$-(2.93 \pm 0.45) \times 10^{-3}$	$-(7.68 \pm 0.70) \times 10^{-4}$	$(3.31 \pm 0.52) \times 10^{-3}$	0.990
252	$-(2.72 \pm 0.40) \times 10^{-3}$	$-(7.03 \pm 0.62) \times 10^{-4}$	$(3.05 \pm 0.47) \times 10^{-3}$	0.990
264	$-(2.62 \pm 0.40) \times 10^{-3}$	$-(6.73 \pm 0.61) \times 10^{-4}$	$(2.93 \pm 0.46) \times 10^{-3}$	0.990
273	$-(2.54 \pm 0.39) \times 10^{-3}$	$-(6.50 \pm 0.59) \times 10^{-4}$	$(2.83 \pm 0.45) \times 10^{-3}$	0.990
293	$-(2.37 \pm 0.38) \times 10^{-3}$	$-(6.02 \pm 0.58) \times 10^{-4}$	$(2.62 \pm 0.44) \times 10^{-3}$	0.990

[a] At each temperature, the data set consisted of 12 points. [b] The $E°$ values were fit to eq 2.

Isoequilibrium Behavior. Isoequilibrium behavior allows us to apply two tests to the ECW model and it's stereoelectronic parameters (E_B and C_B). (1) How well is the temperature dependence of the experimental data reproduced by the linear regression equations that connect the parameters to the physiochemical property? Do we see the appropriate isoequilibrium behavior in the calculated data? (2) Are the two parameters of the ECW model linearly related for each set of ligands that forms a fan-shaped array of lines in a plot of $E°/T$ versus $1/T$? (The ligands that give a fan-shaped array of lines define a family.) In a two-parameter world, this linear relationship between parameters is required if multiple families are observed.[32,33]

A plot of the experimental $E°/T$ data (equivalent to $\Delta G°/T$) versus $1/T$ for PR_3 and $P(p\text{-}XC_6H_4)_3$ appears to reveal the existence of two isoequilibrium points, one for PR_3 and one for $P(p\text{-}XC_6H_4)_3$ (Figure 1A). Regression analysis of the individual lines in Figure 1A gives an average r^2 value of 0.99. The observation of these two isoequilibrium points, which is key to this study and our following arguments, is supported by statistical analyses. Figure 1B shows a map of 90% confidence limits for the intersections of the two arrays of lines in Figure 1A. We present the methodology of obtaining this map in the Appendix. The regions of the 90% confidence limits do not overlap and clearly indicate the existence of two statistically distinguishable isoequilibrium points. In another statistical approach, we found, via the method of minimum residuals, that there is no single point of intersection for the all the lines in Figure 1A that passes either of Linert's F tests.[34,35] Thus, it is clear that we are dealing with a system that exhibits at least two isoequilibrium points; any valid model of ligand effects must reproduce this behavior.

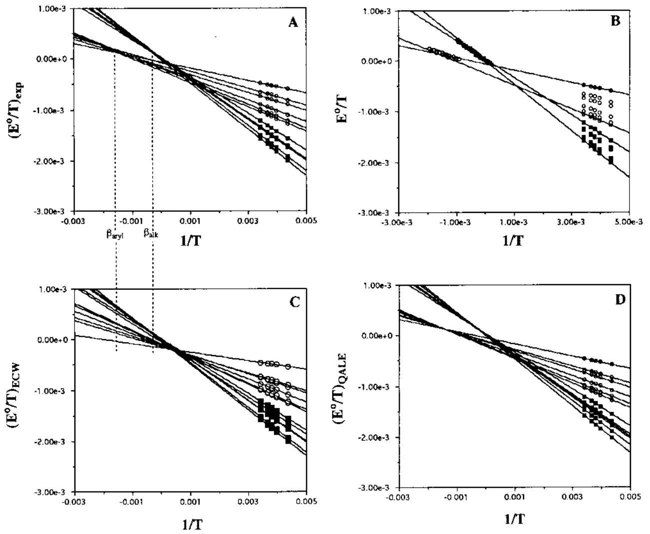

Figure 1. Plot of $E°/T$ versus $1/T$ for PR_3 (■) and $P(p\text{-}XC_6H_4)_3$ (○). (A) Plot of experimental data versus $1/T$. Going from top to bottom on the right side, the order of the lines is as follows: $P(p\text{-}CF_3C_6H_4)_3$, $P(p\text{-}ClC_6H_4)_3$, $P(p\text{-}FC_6H_4)_3$, $P(C_6H_5)_3$, $P(p\text{-}MeC_6H_4)_3$, $P(p\text{-}MeOC_6H_4)_3$, 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. The vertical dashed lines indicate the position of the experimental isoequilibrium temperatures, β_{alk} and β_{aryl}. The lines are extended from Figure 1A to 1C to illustrate the deviation of the apparent single isoequilibrium point in Figure 1C from the experimental values. (B) Map of 90% confidence limits for the intersection points of the two arrays of lines representing PR_3 and $P(p\text{-}XC_6H_4)_3$. The map shows that the regions of 90% confidence (defined by the collections of points in upper left portion of the plot) do not overlap, thereby excluding the possibility that there is a common point of intersection for both families. Only two lines are drawn per family for the sake of clarity. (C) Plot of $(E°/T)_{ECW}$ (calculated from eq 2 and the information provided in Table 2) versus $1/T$. (D) Plot of $(E°/T)_{QALE}$ (calculated from eq 3 and the information provided in Table 2) versus $1/T$.

We begin our analysis of the ECW model by examining (via eq 2) the $E°$ data for 12 ligands of the type PR_3 and $P(p\text{-}XC_6H_4)_3$ at the five temperatures employed in this study. There is a statistically excellent fit of the

$$E°/T = E_A{}^*E_B + C_A{}^*C_B + W \qquad (2)$$

ECW model ($r^2 = 0.990$ for each temperature). There is no reason to exclude any of these ligands as outliers; even the large PR_3 cannot be excluded as is often done in ECW analyses.[1] The coefficients of eq 2 and appropriate statistical data are presented in Table 3. We use the data in Table 3 to calculate a set of $E°/T$ values ($(E°/T)_{ECW}$) at the five temperatures. We then compare $(E°/T)_{ECW}$ with experimental $E°/T$ values via $1/T$ plots (see Figures 1A and C).

If the ECW analysis were adequate, then a plot (Figure 1C) of $(E°/T)_{ECW}$ versus $1/T$ should reproduce the plot shown in Figure 1A. It is obvious that the plots are different. The experimental plot shows two isoequilibrium points, which we have indicated by their isoequilibrium temperatures (β_{alk} and β_{aryl}). In Figure 1C, we see that $(E°/T)_{ECW}$ gives, in essence, a single isoequilibrium point. Thus, there is something missing from the ECW analysis. We can understand why a single

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(33) There is a special case where a linear relationship between the two stereoelectronic parameters is not required for a family of ligands. A family of ligands is defined as those ligands that produce a fan-shaped array of lines when $\Delta G°/T$ is plotted versus $1/T$. This case is where the β values are the same for the two parameters. If the β values were the same, the set of 22 ligands would constitute a single family. This is not the case here since we observe multiple families. See refs 15 and 32.

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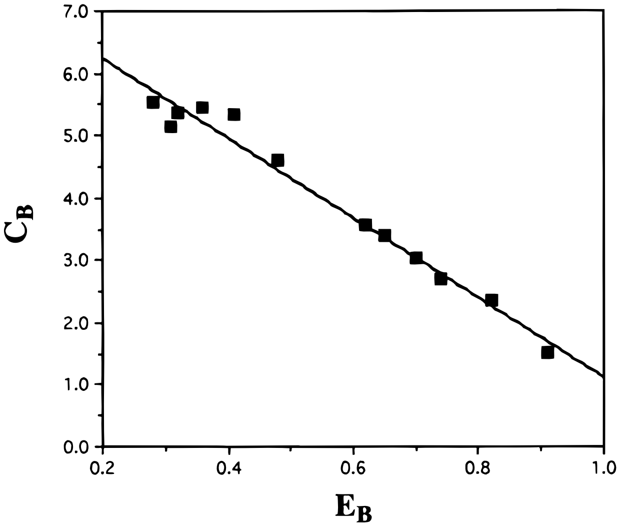

Figure 2. A plot of E_B versus C_B for PR_3 and $P(p\text{-}XC_6H_4)_3$, which shows an excellent linear relationship between the two parameters.

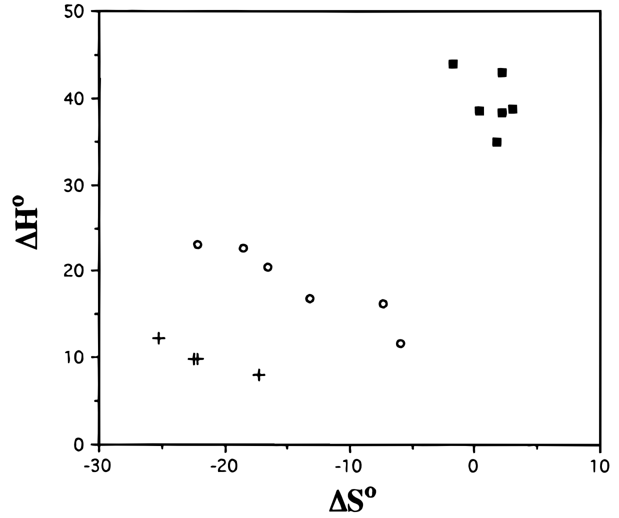

Figure 3. Plot of $\Delta H°$ versus $\Delta S°$ for $P(p\text{-}XC_6H_4)_3$ (○), PR_3 (■), and $P(OR)_3$ (+). $\Delta H°$ and $\Delta S°$ are taken from Table 1. The negative slopes indicate negative isoequilibrium temperatures.

isoequilibrium point is observed with the calculated data. A plot of E_B versus C_B for the 12 phosphines shows an excellent linear relationship ($r^2 = 0.976$) between the two parameters (Figure 2). Thus, in the ECW model there is only one effective parameter for this group (PR_3 and $P(p\text{-}XC_6H_4)_3$) of ligands, and therefore, there can only be one isoequilibrium point in the ECW model.[32]

There is still another problem. Not only does the ECW model give a single isoequilibrium point for the PR_3 and $P(p\text{-}XC_6H_4)_3$ ligands, but this point occurs at a positive temperature. The actual isoequilibrium temperature for $P(p\text{-}XC_6H_4)_3$ is shown in Figure 1A to be negative. This negative temperature is in agreement with the plot of $\Delta H°$ versus $\Delta S°$, as shown in Figure 3. Clearly, the ECW model incorrectly describes the number and position of the isoequilibrium points.

In Figure 1D, we display the plot of $(E°/T)_{QALE}$ versus $1/T$. The $(E°/T)_{QALE}$ values were calculated from eq 3 and the information provided in Table 4. It is obvious

$$E°/T = a\chi + b\theta + cE_{ar} + d \qquad (3)$$

that the QALE analysis reproduces for PR_3 and $P(p\text{-}XC_6H_4)_3$ the two isoequilibrium points which occur at negative temperatures.

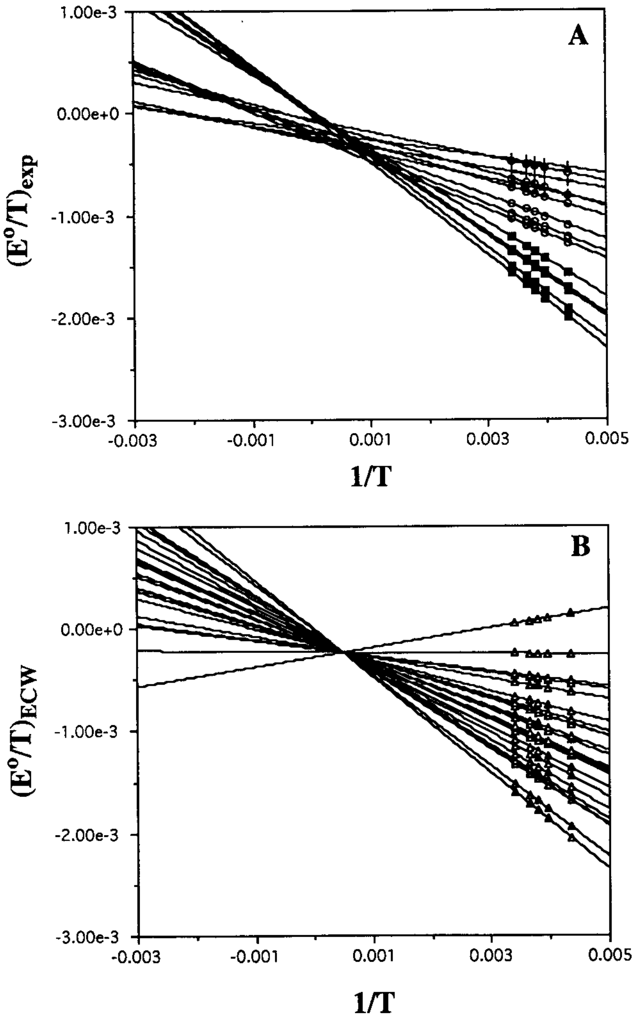

Figure 4. (A) Plot of $E°/T$ (exp) versus $1/T$ for PR_3 (■), $P(p\text{-}XC_6H_4)_3$ (○), and $P(OR)_3$ (+), omitting the data for $P(OCH_2)_3CEt$, $P(OPh)_3$, and the mixed alkyl aryl phosphines. (B) Plot of $(E°/T)_{ECW}$ versus $1/T$ for all of the ligands listed in Table 1.

We now consider all the ligands in Table 1. The ECW model gives excellent statistics for fitting the data for the 22 ligands to eq 2; once again, there appear to be no outliers. We illustrate this for the analysis of $E°/293$. The remaining analyses are equally as good statistically, eq 4.

$$E°/293 = -(0.00315 \pm 0.0001)E_B - (0.00071 \pm 0.00002)C_B + (0.00348 \pm 0.00014) \qquad (4)$$

$$n = 22 \quad r^2 = 0.99$$

Despite the excellent statistics, the same problems still exist. When we plot $(E°/T)_{ECW}$ (for the 22 ligands) versus $1/T$ (Figure 4B), we observe a sharp isoequilib-

Table 4. Results of Linear Regression Analysis of $E°$ Values for PR_3 and $P(p\text{-}XC_6H_4)_3$[a] in Terms of QALE Parameters[b]

temp (K)	a	b	c	d	r^2
229 K	$(6.93 \pm 0.29) \times 10^{-5}$	$(5.97 \pm 6.90) \times 10^{-7}$	$(4.82 \pm 1.19) \times 10^{-5}$	$-(2.22 \pm 0.11) \times 10^{-3}$	0.998
252 K	$(6.53 \pm 0.24) \times 10^{-5}$	$(7.08 \pm 6.90) \times 10^{-7}$	$(3.09 \pm 1.19) \times 10^{-5}$	$-(2.05 \pm 0.10) \times 10^{-3}$	0.997
264 K	$(6.25 \pm 0.25) \times 10^{-5}$	$(6.55 \pm 5.90) \times 10^{-7}$	$(2.63 \pm 1.02) \times 10^{-5}$	$-(1.95 \pm 0.09) \times 10^{-3}$	0.998
273 K	$(6.12 \pm 0.26) \times 10^{-5}$	$(7.21 \pm 6.00) \times 10^{-7}$	$(2.05 \pm 1.04) \times 10^{-5}$	$-(1.91 \pm 0.09) \times 10^{-3}$	0.998
293 K	$(5.79 \pm 0.24) \times 10^{-5}$	$(8.58 \pm 5.70) \times 10^{-7}$	$(1.12 \pm 0.98) \times 10^{-5}$	$-(1.81 \pm 0.09) \times 10^{-3}$	0.998

[a] At each temperature, the data set consisted of 12 points. The $E°$ values were fit to eq 4.

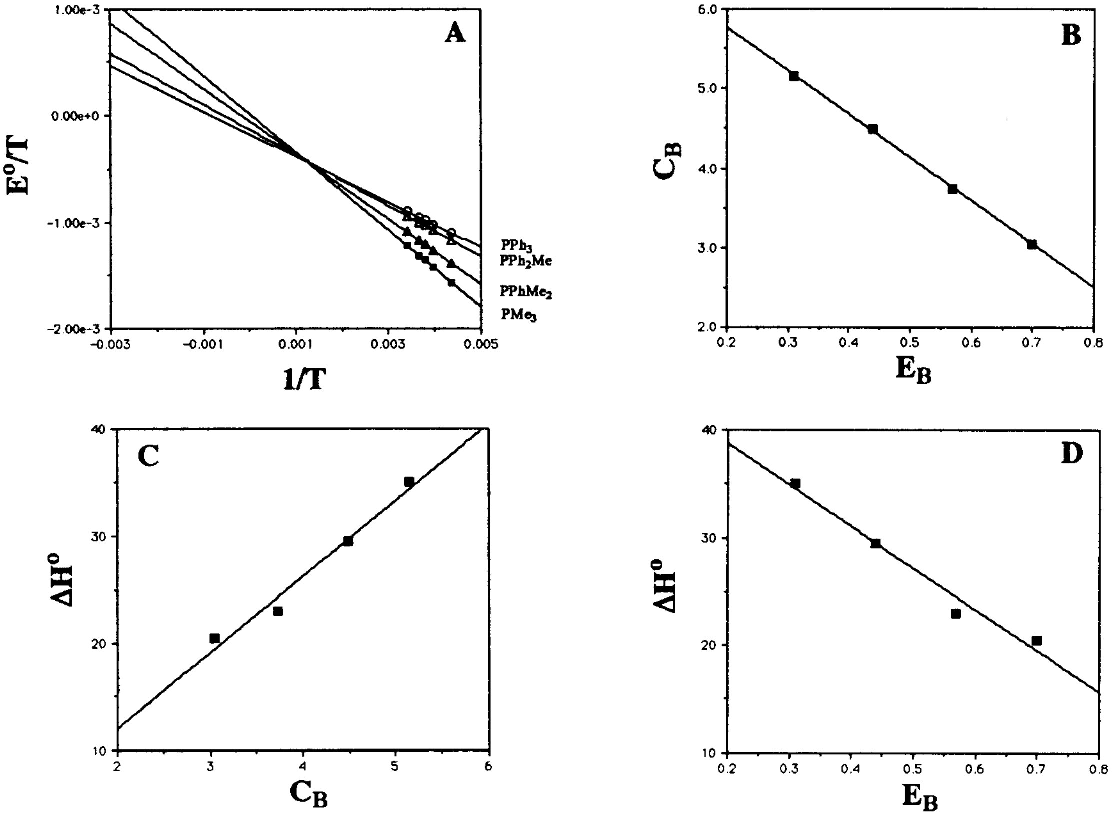

Figure 5. (A) Plot of $E°/T$ versus $1/T$ for $PPh_{3-x}Me_x$, which shows their family membership and resulting isoequilibrium behavior. (B) Plot of E_B versus C_B for $PPh_{3-x}Me_x$, showing the required linear relationship. (C and D) Plots of $\Delta H°$ versus C_B and E_B, respectively, again showing the required linear relationship.

rium point that again occurs at a positive temperature. There are clearly multiple isoequilibrium points. For example, Figures 3 and 4A show that the trialkyl phosphites, excluding $P(OCH_2)_3CEt$, form a family that also exhibits a negative isoequilibrium temperature. The plots of $(E°/T)_{ECW}$ and $(E°/T)_{exp}$ versus $1/T$ (Figure 4) are certainly very different. Thus, despite the excellent statistics, the ECW analysis is fundamentally flawed.

Next, we apply the second test to the ECW model by addressing the question of correlation of parameters for families of ligands. In this set of 22 ligands, there are subsets that form families, in addition to PR_3, $P(OR)_3$, and $P(p\text{-}XC_6H_4)_3$. Examination of the relationship between the E_B and C_B parameters for the families of ligands provides a further test of the ECW model. We note again that a family of ligands is a set of ligands that exhibits isoequilibrium behavior. The variations in the properties of a family of ligands must be described by a single or effectively single parameter. Thus, the test is that $E°$ (or $\Delta G°$), $\Delta H°$, and $\Delta S°$ must be linearly related to a single parameter for a family of ligands.[32] Then, in the two-parameter world of ECW, (1) the E_B and C_B parameters for a family of ligands must be linearly related or (2) only one parameter can be operative.[33] We know from eq 3 that the contributions of both E_B and C_B are statistically significant in the analysis of the data for all 22 ligands. Therefore, if the ECW model were valid, then E_B and C_B must be linearly related for a family of ligands.

The set of ligands, $PPh_{3-x}Me_x$, form a family as is evident from the isoequilibrium behavior shown in Figure 5A. The ECW model passes the second test for this family of phosphines. Figure 5, indeed, shows the required linear relationship between E_B and C_B. As expected, $\Delta H°$ (and $\Delta S°$ and $E°$, which we do not show) is linearly related to both parameters. Clearly the ECW model works well here.

To be valid, however, the ECW model has to work for all families of ligands that it purports to cover. The $E°/T$ versus $1/T$ plot (Figure 6) shows the family behavior of another set of ligands $P(i\text{-}Pr)_3$, PBu_3, $PPhMe_2$, $P(p\text{-}FC_6H_4)_3$, $P(OMe)_3$, and $P(OCH_2)_3CEt$. If the ECW model were adequate, then for this family E_B and C_B would be linearly related and $\Delta H°$ would be linearly related to both E_B and C_B. The appropriate plots are shown in Figure 6. Clearly these conditions are NOT met. In Figure 7, we show another example for a family of ligands. Again, the conditions are not met.

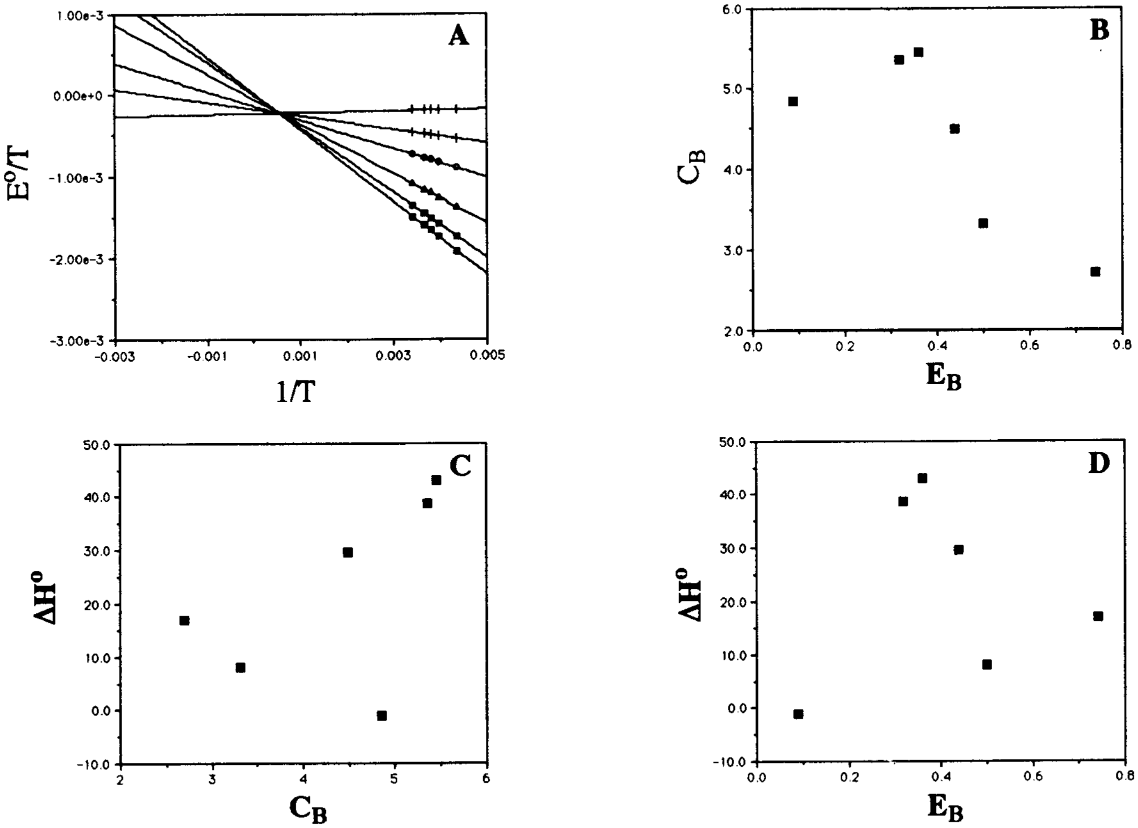

Figure 6. (A) Plot of $E°/T$ versus $1/T$ for the family of ligands $P(i\text{-}Pr)_3$, PBu_3, $PPhMe_2$, $P(p\text{-}FC_6H_4)_3$, $P(OMe)_3$, and $P(OCH_2CH_2)_3CEt$. (B) Plot of E_B versus C_B for this family of ligands, showing the lack of correlation between parameters. (C and D) Plots of $\Delta H°$ versus C_B and E_B, respectively, again showing lack of correlation between the parameters and $\Delta H°$.

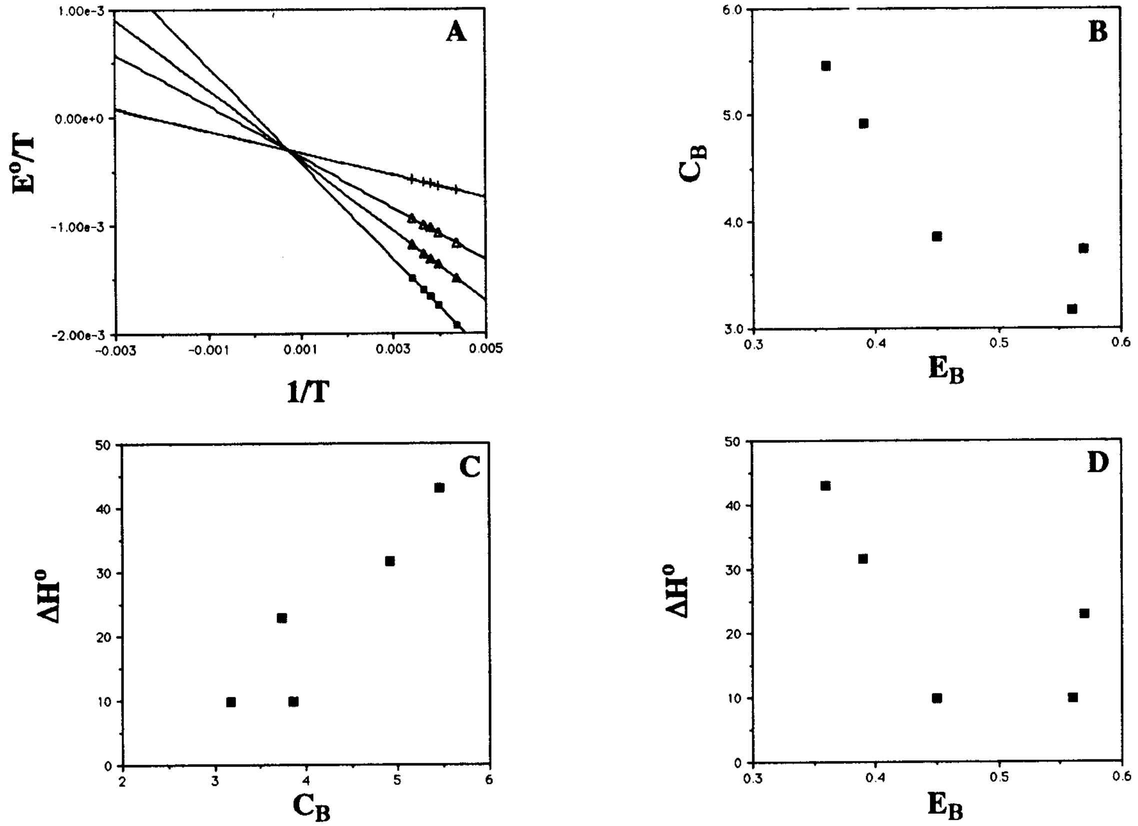

Figure 7. (A) Plot of $E°/T$ versus $1/T$ for the family of ligands $P(i\text{-}Pr)_3$, $PPhEt_2$, PPh_2Me, $P(OEt)_3$, and $P(OBu)_3$. (B) Plot of E_B versus C_B for this family of ligands, showing the lack of correlation between parameters. (C and D) Plots of $\Delta H°$ versus C_B and E_B, respectively, again showing lack of correlation between the parameters and $\Delta H°$.

Any model of ligand or substituent effects, including QALE, must pass the two tests presented above. QALE passes the tests when only hydrocarbyl phosphines are considered. We are currently developing parameters that will allow the incorporation of phosphites and pyrrolyl phosphines into the QALE model.

Conclusions

Isoequilibrium behavior provides a method to unambiguously evaluate models of ligand effects and the validity of the associated stereoelectronic parameters. A good fit of the data to the parameters is, of course, a requirement that must be met by any set of acceptable parameters, but passing this requirement alone is not sufficient to validate a model of ligand effects. The resulting analyses must also meet the additional requirement of reproducing the isoequilibrium behavior of families of ligands. Furthermore, the parameters for a family of ligands must be linearly related for a system that shows multiple families (such as the $E°/T$ values of the η-Cp(CO)(L)(COMe)Fe$^+$/η-Cp(CO)(L)(COMe)Fe^0 couple). In general, the ECW model fails these tests. The conclusions are obvious: the ECW model is inadequate, in agreement with our earlier assessment.[12] These conclusions are definitive and based on thermodynamic considerations—not on goodness-of-fit of regression equations.

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.[6]

The $E°$ values for the η-Cp(CO)(L)Fe(COMe)$^{+/0}$ couple were obtained via cyclic voltammetry and measured relative to acetylferrocene. Each measurement was taken 5 −10 times. The measurements were then repeated with a fresh sample and found to agreed with the original measurements. This leads to an error of ±0.0007 V in the $E°$ values.

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Appendix

The map of 90% confidence limits (Figure 1B) was determined via computer simulation. We began with two sets of perfect fake data derived from the linear regression fits of $E°/T$ versus $1/T$ for the data for PR_3 and $P(p\text{-}XC_6H_4)_3$. These fits included the two isoequilibrium points, which had been determined from the experimental data by the method of minimum sum of residuals. Then to each set of fake data a set of normally distributed random numbers was added and the new isoequilibrium point along with the sum of residuals was determined. The computation was repeated many times with the appropriately chosen standard deviation of the set of random numbers that produced an average minimum sum of residuals identical to that derived from the experimental data. The results were collected, and the outlying 10% were removed to produce the map of 90% confidence limits. The map shows that the regions of 90% confidence are rather narrow and that there is clearly no statistical justification to claim that there is a single point of intersection for all of the data.

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