A thermodynamic method based on isoequilibrium behavior to determine the values of stereoelectronic parameters of phosphines

Anthony L. Fernandez,[a] Tsung Ying Lee,[a] Clementina Reyes,[a] Alfred Prock,*[a] Warren P. Giering,*[a] Christopher M. Haar[b] and Steven P. Nolan[b]

[a] *Department of Chemistry, Metcalf Science and Engineering Center, Boston University, Boston MA 02215, USA*
[b] *Department of Chemistry, University of New Orleans, New Orleans, LA 70148, USA*

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Isoequilibrium behavior provides a method of determining stereoelectronic parameters, for use in linear free energy relationships. This method is based on thermodynamics and is different from the usual ways of assigning values to these parameters. Analysis of isoequilibrium behavior is done in terms of the three parameter QALE (quantitative analysis of ligand effects) model, with parameters χ, θ and E_{ar}. We use this method to interpret new $E°/T$ values of the η-Cp(CO)(L)Fe(COMe)$^{+/0}$ couple (Cp = cyclopentadienyl, L = PPh_iR_{3-i}) and establish a way to calculate χ and E_{ar} values for PPh_iR_{3-i}. In support of the validity of the method, we find that these calculated χ values agree well, except for PPh_2Pr^i, with the values previously reported by Bartik. We also calculated a value for χ equal to 0.4 for $P(NC_4H_8)_3$ for which a χ value had not been reported previously.

Introduction

Isoequilibrium behavior[1–19] for a process involving a set of compounds occurs when a plot of $\Delta G°/T$ *versus* $1/T$ shows a fan-shaped array of lines with a single point of intersection [equivalently, $\Delta H°$ (slope) is linearly related to $\Delta S°$ (intercept)]. In principle, at this point, called the isoequilibrium point, the variations of $\Delta G°$ become independent of the stereoelectronic properties of the substituents or ligands. The isoequilibrium point simply arises from the linear extrapolation of the experimental data and reflects the linear relationship between $\Delta S°$ and $\Delta H°$ over an experimental range of temperature where both $\Delta H°$ and $\Delta S°$ may be treated as constant. This point often occurs outside the experimental range and even occurs at negative temperatures. The observation of isoequilibrium or isokinetic behavior for a set of related compounds is believed to indicate that a system is responding to variations in a single stereoelectronic parameter "although the physical meaning of this parameter might not be known".[2] In this study, we identify this single parameter and show that in the general case for an n parameter system, this parameter is comprised of a linear combination of a maximum of $n - 1$ parameters. We will show in this study that we can use isoequilibrium behavior to determine χ values (*vide infra*) for PPh_iR_{3-i} in a manner very different from the spectroscopic methods that have been used previously.[20]

We have been working on combining isoequilibrium behavior[21,22] and the QALE model (quantitative analysis of ligand effects) of phosphorus(III) ligand effects.[23–45] In the QALE model a physiochemical property is related to the QALE parameters *via* eqn. (1),

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

where χ is a measure of the electron donor capacity.[20] [We define χ for ligand L, beginning with the A_1 carbonyl stretching frequency (ν_{CO} in units of cm^{-1}) for $LNi(CO)_3$ minus the constant value, 2056.1 cm^{-1}. Then we divide this difference by 1 cm^{-1} in order to produce a dimensionless χ value.] θ is the cone angle of the phosphine,[46] θ_{st} is the steric threshold[47] (the cone angle at which there is a change in the steric effect), λ is a switching function that turns on the second steric effect after θ exceeds θ_{st}, and E_{ar} is the aryl effect parameter,[23] which depends only on the number of aryl groups attached to the phosphine. Using eqn. (1), we have correlated (median $r^2 = 0.975$) over two hundred sets of thermodynamic data (pK_a values, equilibrium constants, $\Delta H°$ and $\Delta S°$, $E°$ values), kinetic (log k, $\Delta H^\ddagger$ and $\Delta S^\ddagger$, product distributions, stereoselectivities), spectroscopic (IR, UV/VIS, NMR, ionization potentials) and structural (bond lengths) data.[29,32,37,39–43,48] In addition, we have found that the QALE parameters (χ, θ, E_{ar}) are transferable to other groups and ligands including silyl,[26,27] arsines,[49] alkyl,[49] nitriles,[31] amines[49] and thioethers.[25,30]

Recently, we have been studying the isoequilibrium behavior of the formal reduction potentials ($E°$ values) of the η-Cp(CO)(L)Fe(COMe)$^{+/0}$ [Cp = cyclopentadienyl, L = PR_3 and $P(p\text{-}XC_6H_4)_3$] couple. These $E°$ values can be measured easily, accurately, and precisely over a large range of temperature. We have focused on the variation of the structure of the very common and important ancillary phosphine ligands since these ligands have almost continuously variable stereoelectronic properties. In our initial paper[21] on isoequilibrium behavior, we reported that these $E°/T$ data (equivalent to $\Delta G°/T$) exhibit distinct isoequilibrium behavior for PR_3 and $P(p\text{-}XC_6H_4)_3$ ligands. (We take this behavior to define a family of ligands or substituents.) Since the observation of isoequilibrium behavior indicates that the property is responding to a single stereoelectronic parameter then the $E°$ values for PR_3 and $P(p\text{-}XC_6H_4)_3$ must be responding to different parameters. This is understandable in terms of the QALE model:[21,22] Variations of $\Delta G°$ for $P(p\text{-}XC_6H_4)_3$ depend only on single parameter, χ, since the other QALE parameters, θ and E_{ar}, are constant. $\Delta G°$ for PR_3 depends on both χ and θ but these two parameters are linearly related so that in effect $\Delta G°$ can appear to depend on either χ or θ alone.

These results led us to the realization that with a large enough set of $\Delta H°$ and $\Delta S°$ values, it would be possible to choose numerous families of ligands that exhibit isoequilibrium behavior. There is no reason why the ligands in a family need to possess any particular structural relationship. The question then arises as to how the QALE model would account for these families of ligands in general, and what fundamental information can be gleaned from analysis of these families. Accordingly, we enlarged the set of $E°/T$ data for the η-Cp(CO)(L)Fe(COMe)$^{+/0}$ couple to include data for eleven complexes containing the mixed alkyl phenyl phosphines, PPh_iR_{3-i} ($i = 1$,

Table 1 List of E°/T values for the η-Cp(CO)(L)Fe(COMe)$^{+/0}$ couple and ΔS° and ΔH° of reduction. Data in italics are taken from ref. 52. Remaining data are reported for the first time in this paper. The standard errors of ΔS° and ΔH° are shown

	Ligand	ΔS°/ J K^{-1} mol^{-1}	ΔH°/ kJ mol^{-1}	$(-E^\circ/T)/10^{-3}$ V K$^{-1\,a}$				
				229 K	252 K	264 K	273 K	293 K
1	*PMe_3*	*1.8 ± 0.1*	*35.0 ± 0.3*	*1.568*	*1.419*	*1.355*	*1.310*	*1.223*
2	$PPhMe_2$	−4.7 ± 1.2	29.5 ± 0.3	1.383	1.262	1.208	1.172	1.090
3	*PEt_3*	*3.0 ± 1.7*	*38.7 ± 0.5*	*1.720*	*1.565*	*1.485*	*1.441*	*1.338*
4	*PBu_3*	*0.3 ± 1.6*	*38.6 ± 0.5*	*1.743*	*1.578*	*1.514*	*1.459*	*1.361*
5	PPh_2Me	−12.4 ± 3.3	23.0 ± 0.1	1.167	1.072	1.030	1.001	0.940
6	$PPhEt_2$	−6.9 ± 1.1	31.5 ± 0.3	1.495	1.364	1.309	1.267	1.183
7	$PPhBu_2$	−4.7 ± 1.2	32.7 ± 0.3	1.524	1.394	1.331	1.289	1.201
8	PPh_2Et	−14.9 ± 0.6	24.2 ± 0.1	1.253	1.155	1.108	1.076	1.014
9	PPh_2Pr	−10.9 ± 0.6	25.5 ± 0.2	1.266	1.162	1.114	1.081	1.014
10	PPh_2Bu	−13.8 ± 0.1	24.7 ± 0.4	1.258	1.155	1.111	1.082	1.017
11	*$PBu^i{}_3$*	*2.2 ± 1.8*	*38.5 ± 0.5*	*1.719*	*1.553*	*1.486*	*1.436*	*1.339*
12	*$P(p\text{-}MeOC_6H_4)_3$*	*−22.2 ± 0.7*	*23.1 ± 0.2*	*1.273*	*1.178*	*1.133*	*1.105*	*1.105*
13	*$P(p\text{-}Me_6H_4)_3$*	*−18.5 ± 1.8*	*22.6 ± 0.6*	*1.217*	*1.116*	*1.078*	*1.050*	*0.9934*
14	*PPh_3*	*−16.6 ± 1.7*	*20.5 ± 0.5*	*1.098*	*1.019*	*0.9729*	*0.9482*	*0.8972*
15	*$P(p\text{-}FC_6H_4)_3$*	*−13.2 ± 1.2*	*16.9 ± 0.3*	*0.9025*	*0.8293*	*0.8018*	*0.7805*	*0.7338*
16	*$P(p\text{-}ClC_6H_4)_3$*	*−7.3 ± 1.7*	*16.2 ± 0.5*	*0.8108*	*0.7385*	*0.7091*	*0.6890*	*0.6515*
17	*$P(P\text{-}F_3CC_6H_4)_3$*	*−6.0 ± 2.2*	*11.7 ± 0.6*	*0.5966*	*0.5390*	*0.5224*	*0.5071*	*0.4800*
18	$P(NC_4H_8)_3$	−4.18 ± 1.5	46.3 ± 0.1	2.136	1.947	1.858	1.803	1.677
19	PPh_2Pr^i	−8.8 ± 0.1	28.5 ± 0.2	1.380	1.263	1.208	1.171	1.100
20	PPh_2Cy	−9.4 ± 1.1	29.1 ± 0.3	1.417	1.294	1.239	1.206	1.128
21	$PPhPr^i{}_2$	−14.2 ± 0.7	31.1 ± 0.2	1.557	1.427	1.369	1.330	1.251
22	*$PPr^i{}_3$*	*2.1 ± 0.8*	*43.0 ± 0.2*	*1.917*	*1.742*	*1.662*	*1.606*	*1.495*
23	$PPhCy_2$	−14.7 ± 1.4	32.9 ± 0.4	1.637	1.505	1.443	1.402	1.314
24	*PCy_3*	*−1.8 ± 1.4*	*44.0 ± 0.4*	*2.006*	*1.827*	*1.746*	*1.690*	*1.571*

[a] E° measured by cyclic voltammetry relative to the acetylferrocenium/acetylferrocene couple in acetonitrile. The error in E° is estimated to be 0.7 mV.

2; R = Me, Et, Pr (i = 2 only), Bu, Pr^i, Cy). This set of data when combined with the previously reported data for PR_3 and $P(p\text{-}XC_6H_4)_3$ does indeed show many families of ligands that exhibit isoequilibrium behavior.

In this paper, we show that isoequilibrium (and isokinetic) behavior may result from a system responding not to a single stereoelectronic parameter but to a linear combination of $n - 1$ stereoelectronic parameters where n is the total number of fundamental parameters needed to describe the system. We then present a methodology based on isoequilibrium behavior for $n = 3$ that allows us to determine this linear combination of two stereoelectronic properties and to evaluate them individually. We then test this methodology by calculating the χ values of PPh_iR_{3-i}. Since Bartik[20] has already reported χ values for a number of PPh_iR_{3-i}, we have a set of values with which to compare our results. We extended this study to the (previously unreported) stereoelectronic properties of tris(pyrrolidinyl)phosphine, $P(NC_4H_8)_3$. This strong electron donor ligand is considered to be isosteric with $P(p\text{-}XC_6H_4)_3$, so that determination of its χ and E_{ar} values would make it useful for ligand effect studies.[50]

Results and discussion

The η-Cp(CO)(L)(COMe)Fe$^{+/0}$ couple is a remarkably well-behaved system suitable for systematic and quantitative studies of ligand effects. The complexes are readily prepared[51] and the stereoelectronic properties of phosphorus(III) ligands are almost continuously variable.[46]

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

The system is chemically reversible and electrochemically quasi-reversible. We have been able to measure accurately and precisely E°/T values for this system relative to the acetylferrocinium/acetylferrocene couple at five temperatures over a range of 60 K. These data are listed in Table 1. Each measurement was repeated five to ten times at each of the five temperatures. The error in our measurements is less than 0.7 mV, which is more than adequate for our studies. We established the validity of the reported E° value by computer simulation methods. There is no evidence of any follow-up reactions, there is no deposition on the electrodes and finally the plots of E°/T *versus* $1/T$ are linear ($r^2 = 0.999$) over a range of 60 °C. From the slopes and intercepts of the plots of E°/T *versus* $1/T$ we obtained the ΔH° and ΔS° of reduction, which are displayed in Table 1. The errors in ΔH° and ΔS° are presented in Table 1.

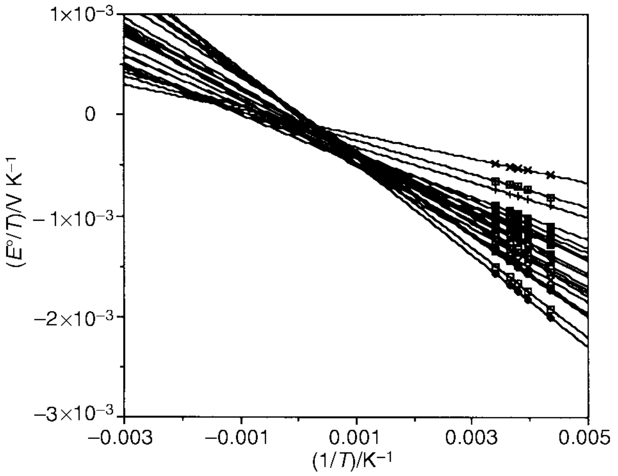

Fig. 1 Plot of E°/T *versus* χ for all the ligands displayed in Table 1.

We summarize the results of our study in a plot of E°/T *versus* $1/T$ (Fig. 1) for all the ligands displayed in Table 1. Although there are several families of ligands (sets of ligands that exhibit isoequilibrium behavior) buried in this plot [*e.g.* PR_3 and $P(p\text{-}XC_6H_4)_3$], these points of intersection are obscured by the complexity of the graph.

To clarify the situation, we turn to the corresponding plot of ΔH° *versus* ΔS° and look for any series of three or more points that lie on a straight line (Fig. 2). For these ligands, ΔH° is

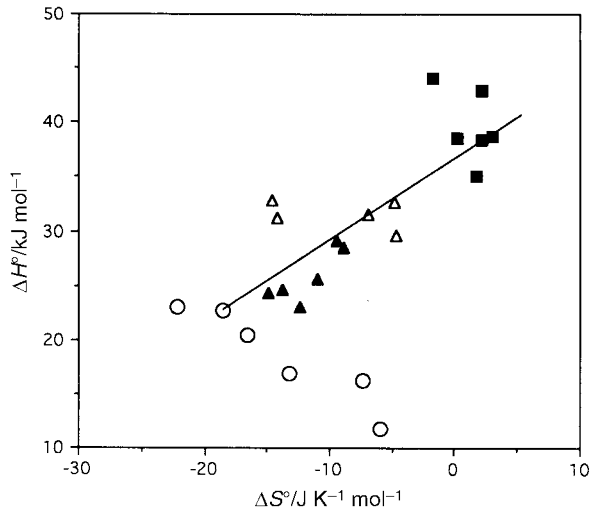

Fig. 2 A plot of $\Delta H°$ *versus* $\Delta S°$ for the reduction of η-Cp(CO)(L)Fe(COMe)$^+$. The solid line is drawn through the points for P(p-MeC$_6$H$_4$)$_3$, PPh$_2$Cy, PPhEt$_2$, PPhBu$_2$, PBu$^i_3$ and PEt$_3$.

linearly related to $\Delta S°$, a necessary condition that the ligands form a family. In Fig. 2, a family [P(p-MeC$_6$H$_4$)$_3$, PPh$_2$Cy, PPhEt$_2$, PPhBu$_2$, PBu$^i_3$, and PEt$_3$] is identified and in Fig. 3 this family membership is confirmed by the observation of a fan shaped array of lines in the $E°/T$ *versus* $1/T$ plot. This set of data passes Linert's first F test[11,53] but not the second. 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] Other families are readily found.

The set of ligands that form the family shown in Fig. 3 do not have any special structural relationship other than being phosphines. The question arises as to how they can form a family if $E°/T$ must respond to only a single parameter. As we will see the $E°/T$ values for this family do respond to an 'effectively single' parameter but this parameter is a linear combination of two QALE parameters.

In the following discussion, we show the general requirement for a set of ligands to form a family, *i.e.* they exhibit isoequilibrium behavior. We start with the assumption that $\Delta G°$ is linearly related to the variation in the stereoelectronic properties of a set of ligands [eqn. (3)]. We restrict our attention to a

$$\Delta G° = a\chi + b\theta + cE_{\mathrm{ar}} + d \qquad (3)$$

three parameter system with no steric threshold. For convenience we use the three QALE parameters χ, θ and E_{ar}, where the coefficients a, b and c are characteristic of the system being studied. These coefficients are temperature dependent and this dependence is shown explicitly in eqn. (4).

$$\Delta G° = \Delta H° - T\Delta S° \qquad (4)$$

Since $\Delta G°$ can be expressed in terms of a linear combination of parameters [eqn. (3)] then its components, $\Delta S°$ and $\Delta H°$, must also be related to the same QALE parameters *via* eqns. (5) and (6).

$$\Delta H° = a_1\chi + b_1\theta + c_1E_{\mathrm{ar}} + d_1 \qquad (5)$$

$$\Delta S° = a_2\chi + b_2\theta + c_2E_{\mathrm{ar}} + d_2 \qquad (6)$$

We assume that the coefficients of eqns. (5) and (6) are temperature independent over the experimental range of temperature. We conclude that $\Delta H°$ is linearly related to $\Delta S°$ since the plot of $\Delta G°/T$ *versus* $1/T$ is fan shaped [eqn. (7)]. β is the temperature of the intersection point of the fan-shaped array of lines for a given family, and ΔG°_β is the value of $\Delta G°$ at the intersection point. On combining eqns. (5)–(7) and solving for E_{ar}, we get eqn. (8).

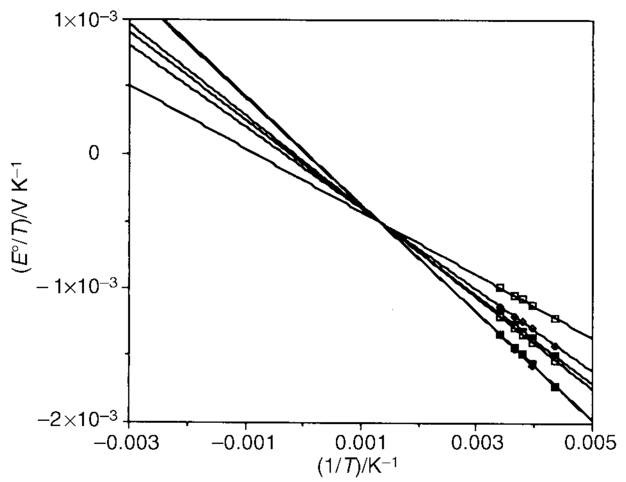

Fig. 3 A plot of $E°/T$ *versus* $1/T$ for the ligands P(p-MeC$_6$H$_4$)$_3$, PPh$_2$Cy, PPhEt$_2$, PPhBu$_2$, PBu$^i_3$ and PEt$_3$ (in descending order on the right side of the plot).

$$\Delta H° = \beta\Delta S° + \Delta G^\circ_\beta \qquad (7)$$

$$E_{\mathrm{ar}} = \frac{(\beta a_2 - a_1)\chi + (\beta b_2 - b_1)\theta + (\Delta G^\circ_\beta + \beta d_2 - d_1)}{c_1 - \beta c_2} \qquad (8)$$

We substitute this expression for E_{ar} into eqns. (5) and (6). On collecting terms in χ and θ, we get expressions for $\Delta H°$ and $\Delta S°$ [eqns. (9) and (10)]. where p, A, B and C are given by eqns. (11)–(14).

$$\Delta H° = \beta A(\chi + p\theta) + B \qquad (9)$$

$$\Delta S° = A(\chi + p\theta) + C \qquad (10)$$

$$p = \frac{b_2c_1 - b_1c_2}{a_2c_1 - a_1c_2} \qquad (11)$$

$$A = \frac{a_2c_1 - a_1c_2}{c_1 - \beta c_2} \qquad (12)$$

$$B = \frac{\beta(d_2c_1 - d_1c_2) + c_1\Delta G_\beta^\circ}{a_2c_1 - a_1c_2} \qquad (13)$$

$$C = \frac{d_2c_1 - d_1c_2 + c_2\Delta G_\beta^\circ}{a_2c_1 - a_1c_2} \qquad (14)$$

A and B depend on the isoequilibrium temperature β, thus, are constant within a family but vary from family to family. Thus, we see that, in general, both $\Delta S°$ and $\Delta H°$ for a family are expressible in terms of a single variable z_3 [eqn. (15)], which is a

$$z_3 = \chi + p\theta \qquad (15)$$

composite of χ and θ. The symbol z_3 designates that this composite parameter is derived for a *three* parameter model. Or put another way, $\Delta H°$ and $\Delta S°$ for a family must each be linearly related to z_3, which is not one of the three fundamental stereoelectronic parameters in the model. Thus, the observation of isoequilibrium (or isokinetic) behavior does not necessarily mean that $\Delta G°$ is responding to variations in a single fundamental stereoelectronic parameter. Because of the single relationship [eqn. (7)] relating $\Delta H°$ and $\Delta S°$ for a fan-shaped array of lines, we see that for an 'n' parameter system the 'effect-

Table 2 Values of z_3 and χ_z calculated as described in the text using the ligands listed under the heading 'Source'. We estimate that the standard error in χ_z is ±1.0

	Ligand	z_3	χ_z [a]	Source
1	$\mathrm{PPhMe_2}$	13.9	10.5	$\mathrm{P(C_6H_5)_3}$ and $\mathrm{PMe_3}$
2	$\mathrm{PPhMe_2}$	13.8	10.4	$\mathrm{P(\mathit{p}\text{-}ClC_6H_4)_3}$, $\mathrm{PCy_3}$
3	$\mathrm{PPh_2Me}$	16.4	12.6	$\mathrm{P(C_6H_5)_3}$ and $\mathrm{PMe_3}$
4	$\mathrm{PPh_2Me}$	16.4	12.6	$\mathrm{P(\mathit{p}\text{-}ClC_6H_4)_3}$, $\mathrm{PPh_2Bu}$
5	$\mathrm{PPhEt_2}$	12.4	8.6	$\mathrm{P(\mathit{p}\text{-}FC_6H_4)_3}$, $\mathrm{PCy_3}$
6	$\mathrm{PPhEt_2}$	12.5	8.7	$\mathrm{P(\mathit{p}\text{-}MeC_6H_4)_3}$, $\mathrm{PEt_3}$
7	$\mathrm{PPhEt_2}$	12.4	8.6	$\mathrm{P(\mathit{p}\text{-}MeC_6H_4)_3}$, $\mathrm{PEt_3}$, $\mathrm{PBu^i_3}$
8	$\mathrm{PPhBu_2}$	11.8	7.9	$\mathrm{PPh_3}$, $\mathrm{PCy_3}$
9	$\mathrm{PPhBu_2}$	11.8	7.9	$\mathrm{PPh_2Me}$, $\mathrm{PBu_3}$
10	$\mathrm{PPhBu_2}$	12.2	8.3	$\mathrm{PPh_2Et}$, $\mathrm{PEt_3}$
11	$\mathrm{PPhBu_2}$	12.1	8.2	$\mathrm{P(\mathit{p}\text{-}MeOC_6H_4)_3}$, $\mathrm{PPhEt_2}$
12	$\mathrm{PPhBu_2}$	11.9	8.0	$\mathrm{P(\mathit{p}\text{-}MeC_6H_4)_3}$, $\mathrm{PPh_2Cy}$
13	$\mathrm{PPhBu_2}$	12.0	8.2	$\mathrm{P(\mathit{p}\text{-}F_3CC_6H_4)_3}$, $\mathrm{PPhMe_2}$
14	$\mathrm{PPh_2Et}$	14.9	10.9	$\mathrm{PPh_2Cy}$, $\mathrm{PPhEt_2}$
15	$\mathrm{PPh_2Et}$	15.0	11.1	$\mathrm{PPh_2Pr^i}$, $\mathrm{PMe_3}$
16	$\mathrm{PPh_2Et}$	15.2	11.2	$\mathrm{P(\mathit{p}\text{-}MeC_6H_4)_3}$, $\mathrm{PPhMe_2}$
17	$\mathrm{PPh_2Pr}$	15.2	11.2	$\mathrm{PPh_2Me}$, $\mathrm{PBu_3}$
18	$\mathrm{PPh_2Pr}$	15.2	11.2	$\mathrm{PPh_2Pr^i}$, $\mathrm{PPhEt_2}$
19	$\mathrm{PPh_2Bu}$	15.3	11.3	$\mathrm{PPh_3}$, $\mathrm{PCy_3}$
20	$\mathrm{PPh_2Bu}$	15.3	11.3	$\mathrm{PPh_2Cy}$, $\mathrm{PPhEt_2}$, $\mathrm{PBu_3}$
21	$\mathrm{PPh_2Pr^i}$	13.8	9.6	$\mathrm{P(\mathit{p}\text{-}MeC_6H_4)_3}$, $\mathrm{PMe_3}$
22	$\mathrm{PPh_2Pr^i}$	13.8	9.6	$\mathrm{PPh_2Me}$, $\mathrm{PPh_2Pr}$
23	$\mathrm{PPh_2Cy}$	13.2	8.9	$\mathrm{P(\mathit{p}\text{-}MeC_6H_4)_3}$, $\mathrm{PEt_3}$, $\mathrm{PBu^i_3}$
24	$\mathrm{PPh_2Cy}$	13.4	9.1	$\mathrm{PPh_2Me}$, $\mathrm{PCy_3}$
25	$\mathrm{PPh_2Cy}$	13.7	9.4	$\mathrm{PPh_3}$, $\mathrm{PPr^i_3}$
26	$\mathrm{PPh_2Cy}$	13.2	8.9	$\mathrm{P(\mathit{p}\text{-}MeOC_6H_4)_3}$, $\mathrm{PMe_3}$
27	$\mathrm{PPhPr^i_2}$	11.3	7.0	$\mathrm{P(\mathit{p}\text{-}MeOC_6H_4)_3}$, $\mathrm{PCy_3}$
28	$\mathrm{PPhPr^i_2}$	11.6	7.2	$\mathrm{P(\mathit{p}\text{-}FC_6H_4)_2}$, $\mathrm{PPh_2Bu}$
29	$\mathrm{PPhCy_2}$	10.6	6.1	$\mathrm{P(\mathit{p}\text{-}FC_6H_4)_3}$, $\mathrm{PPh_2Bu}$
30	$\mathrm{P(NC_4H_8)_3}$	4.5	0.4	$\mathrm{PPh_2Me}$, $\mathrm{PPh_2Pr}$, $\mathrm{PPh_2Cy}$, $\mathrm{P(\mathit{p}\text{-}FC_6H_4)_3}$
31	$\mathrm{P(NC_4H_8)_3}$	4.5	0.4	$\mathrm{PEt_3}$, $\mathrm{PCy_3}$

[a] We treat the χ and χ_z values as dimensionless parameters defined by $\chi(\mathrm{exp})/1\ \mathrm{cm^{-1}}$.

ively single' parameter can be made up of a linear combination of a maximum of $n - 1$ parameters.

Eqns. (9) and (15) give us a way to determine values of χ and E_{ar} for $\mathrm{PPh}_i\mathrm{R}_{3-i}$ that is very different from previous methods. We show that for this particular system the values of z_3 are not very sensitive to the actual value of the cone angle, θ. Furthermore, evaluation of z_3 is independent of the actual values of E_{ar} for the individual $\mathrm{PPh}_i\mathrm{R}_{3-i}$. To calculate the χ values for $\mathrm{PPh}_i\mathrm{R}_{3-i}$ we need the values of the coefficients a_1 through d_2 in eqns. (5) and (6). For this purpose, we used the ligands $\mathrm{PR_3}$ and $\mathrm{P(\mathit{p}\text{-}XC_6H_4)_3}$, whose QALE parameters (Table 2) are known. We then analyzed their $\Delta H°$ and $\Delta S°$ (Table 1) values *via* regression analysis using eqns. (5) and (6). We note for $\Delta H°$ that there is a negligible contribution from θ, which is statistically indistinguishable from zero [eqn. (16)]. (The percent contribution of

$$\Delta H° = -(1.16 \pm 0.08)\chi + (0.023 \pm 0.018)\theta - (3.72 \pm 0.31)E_{\mathrm{ar}} + 42 \pm 2.8 \quad (16)$$
$$n = 12 \quad r^2 = 0.998$$
$$\chi = 66\% \quad \theta = 4\% \quad E_{\mathrm{ar}} = 30\%$$

a parameter to the property was determined by first multiplying the absolute value of the coefficient of the parameter by the range of the parameter. Then the result was divided by the sum of all the products of coefficient times range.) Hence, we performed the analysis of $\Delta H°$ in terms of χ and E_{ar} only [eqn. (17)]. (Note that here is a case where *removal* of a

$$\Delta H° = -(1.21 \pm 0.07)\chi - (3.51 \pm 0.28)E_{\mathrm{ar}} + 45.8 \pm 0.4 \quad (17)$$
$$n = 12 \quad r^2 = 0.997$$

parameter leads to *better* statistics in terms of smaller standard errors.) Eqn. (17) gives the values of a_1 and c_1 that we will use in calculating 'p' in eqn. (11).

The values of a_2, b_2 and c_2 needed for the calculation of 'p' come from the regression analysis of $\Delta S°$ for the 12 $\mathrm{PR_3}$ and $\mathrm{P(\mathit{p}\text{-}XC_6H_4)_3}$ [eqn. (18)].

$$\Delta S° = (1.65 \pm 0.20)\chi + (0.16 \pm 0.05)\theta - (11.6 \pm 0.8)E_{\mathrm{ar}} - 29.8 \pm 7.2 \quad (18)$$
$$n = 12 \quad r^2 = 0.976$$

Using the appropriate values of the coefficients we get a value for 'p' [eqn. (19)]. We note that the contribution of $p\theta$ to z_3 is

$$p = 0.028 \pm 0.013 \quad (19)$$

small. For example, in the $\mathrm{PPh}_i\mathrm{Me}_{3-i}$ family (*vide infra*), the variation of $p\theta$ is around 14% of the variation of z_3.

In the following examples we show how we determine the χ and E_{ar} values for $\mathrm{PPh}_i\mathrm{R}_{3-i}$. One might expect family membership to be shown by a set of ligands, $\mathrm{PPh}_i\mathrm{R}_{3-i}$ ($i = 1, 2, 3$) on the basis of their structural relationships. In other words, we might assume that χ, θ and E_{ar} would be linear functions of the index 'i'. Formally, one would then describe these stereoelectronic parameters as being parametrically related or simply as showing the property of additivity. More generally, the label 'i' can be left out of the picture and the parametric (family) relationship would arise from θ, and E_{ar}, being linear functions of χ. In either case, a plot of $E°/T$ *versus* $1/T$ for the set $\mathrm{PPh}_i\mathrm{R}_{3-i}$ is expected to form a fan-shaped array of four lines. Fig. 4 shows such plots for R = Me, Et, Bu, $\mathrm{Pr^i}$ and Cy. Indeed, we see for the first three sets the expected fan-shaped arrays. The last two sets form a fan-shaped array with three of their members, but the fourth turns out not to be a member of the family. As pointed earlier, all of these experimental results have been checked five to ten times with freshly prepared materials and found to be reproducible. We believe that these results indicate, first, that our method is capable of good accuracy; second, that the deviant ligands in the last two sets are truly not family members of their sets, but they might be (and are) members of families that show no particular structural relationships among their members. Recall that family membership requires only that $\Delta H°$ and $\Delta S°$ are expressible in terms of an effectively single parameter. In contrast to structurally related families, this parameter for a structurally unrelated family is not a single fundamental stereoelectronic parameter, but rather is a linear combination of one fewer stereoelectronic parameters than the number required to describe the total group of ligands under study (*vide supra*). In the present study, three parameters (χ, θ and E_{ar}) are required, thus the general effectively single variable is a linear combination of any pair of these; we have chosen the pair to be χ and θ. We note that for a special case of a structurally related family, the effectively single parameter is still valid, it merely collapses to a single fundamental stereoelectronic parameter.

We are now ready to calculate the values of χ for $\mathrm{PPh}_i\mathrm{R}_{3-i}$ based on their isoequilibrium behavior. We know the values of χ and θ for $\mathrm{PMe_3}$ and $\mathrm{PPh_3}$, thus, we know their values of z_3. We make a plot of z_3 *versus* $\Delta H°$ for these two ligands and use this plot as a calibration curve to determine the z_3 values of the $\mathrm{PPh_2Me}$ and $\mathrm{PPhMe_2}$ whose $\Delta H°$ values are known (Table 1). Using eqn. (15) we convert the z_3 values back to χ_z (the subscript 'z' to designate that these χ values are derived from z_3). In a similar manner, we find other families that contain at least one $\mathrm{PPh}_i\mathrm{R}_{3-i}$, $\mathrm{PR_3}$ and $\mathrm{P(\mathit{p}\text{-}XC_6H_4)_3}$ ligand. For each family we calculate the z_3 values of a particular $\mathrm{PPh}_i\mathrm{R}_{3-i}$ ligand. For a few ligands (*e.g.* $\mathrm{PPhCy_2}$) that do not fall on lines that connect $\mathrm{PR_3}$ and $\mathrm{P(\mathit{p}\text{-}XC_6H_4)_3}$, we found that these ligands form families with other $\mathrm{PPh}_i\mathrm{R}_{3-i}$ whose z_3 values were determined previously.

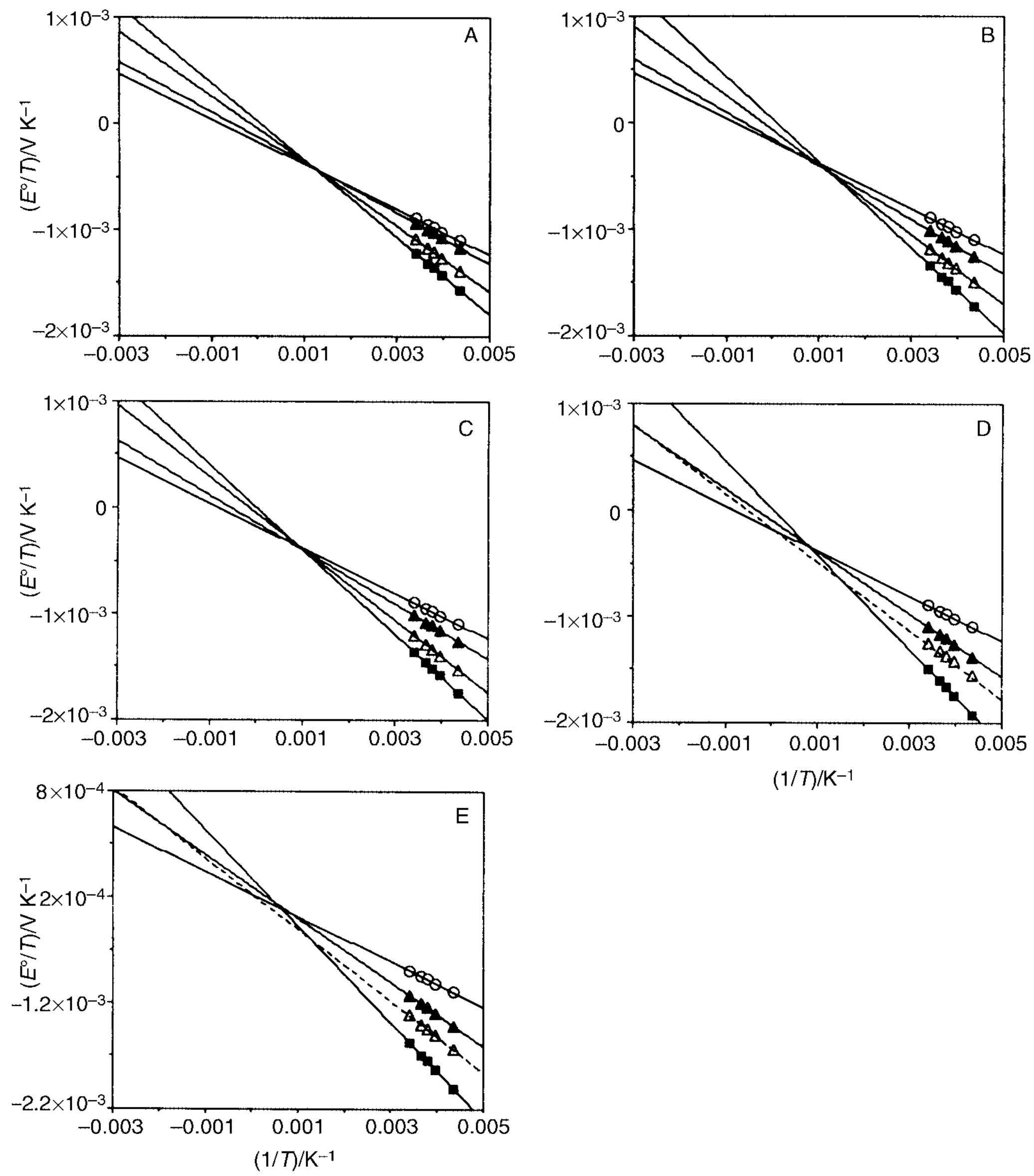

Fig. 4 Plots of $E°/T$ *versus* $1/T$ for (A) PPh_iMe_{3-i}, (B) PPh_iEt_{3-i}, (C) PPh_iBu_{3-i}, (D) $PPh_iPr^i_{3-i}$, (E) PPh_iCy_{3-i}. The observation of isoequilibrium confirms family membership for (A)–(C). Thus, plots of $\Delta H°$ or $S°$ *versus* z_3 for this family should be linear. In (D) and (E), the dashed lines correspond to the data for $PPhPr^i_2$ and $PPhCy_2$, respectively.

We illustrate this protocol in Fig. 5 where we show the families to which PPh_2Cy belongs. We also show the $E°/T$ *versus* $1/T$ plots which we use to confirm the family membership. In Table 2, we present the z_3 values, calculated using different sets of ligands, for PPh_iR_{3-i} and their corresponding calculated χ_z values. We present in Table 3 the average values of z_3 and χ_z. We estimate that the error in χ_z is ±1.0.

We noted earlier that $\Delta H°$ and $\Delta S°$ are both linearly related to z_3 for a family of ligands. In Fig. 6, we illustrate that this is indeed the case for the family of ligands presented in Figs. 2 and 3.

We note that the χ_z values that we calculate, in general, do not deviate greatly from the Bartik χ values (Table 2, Fig. 7). The one exception is PPh_2Pr^i for which our calculated χ_z value is 9.6 in comparison to the Bartik[20] value of 10.85. Our value is closer to the additive value of 10.0. (Bartik did not report χ values for $PPhCy_2$ or PPh_2Cy.)

We next examine the E_{ar} values for PPh_iR_{3-i}. A plot of $\Delta H°$ *versus* χ (either the new values reported herein or Bartik's values) show considerable scatter for PPh_iR_{3-i} (Fig. 8). This is unexpected if the E_{ar} values of PPh_iR_{3-i} were 1 and 2 for $i = 1$ and 2, respectively. In this case the expected plot should show three nearly equally spaced parallel lines for PR_3, $PPhR_2$, and PPh_2R. We interpret this to mean that one of the stereoelectronic parameters is incorrectly defined. The problem cannot be θ since $\Delta H°$ is not very sensitive to θ. We can also eliminate χ since this parameter was calculated in a manner that did not depend on E_{ar} of the mixed alkyl phenyl ligands and only weakly on θ through eqn. (15) (θ would have to vary over an unrealistic range to produce this scatter). In addition, our calculated χ values agree well with Bartik's values. Therefore, the problem resides in E_{ar}.

Values of E_{ar} for PPh_iR_{3-i} are readily calculated *via* eqn. (17) once we have the χ values. These calculated E_{ar} values are listed in Table 3. We estimate that the error is ±0.30 in the E_{ar} values. In the QALE model, we made the approximation that E_{ar} depended only on 'i' for a PPh_iR_{3-i}. Thus when $i = 2$, $E_{ar} = 2$ and when $i = 1$, $E_{ar} = 1$. The calculated values of E_{ar} are within statistical error of 2.0 for PPh_2R with the exception of the isopropyl and cyclohexyl derivatives, whose E_{ar} values (1.5 and 1.6, respectively) are significantly less than 2. Similarly, we find that the E_{ar} values for $i = 1$ are close to 1.0, with the exception of the isopropyl and cyclohexyl derivatives, whose E_{ar} values (1.7 and 1.6, respectively) are significantly larger than 1.0. These observations *suggest* that the E_{ar} values are significantly altered by large alkyl groups. We do not yet know if this deviation of the

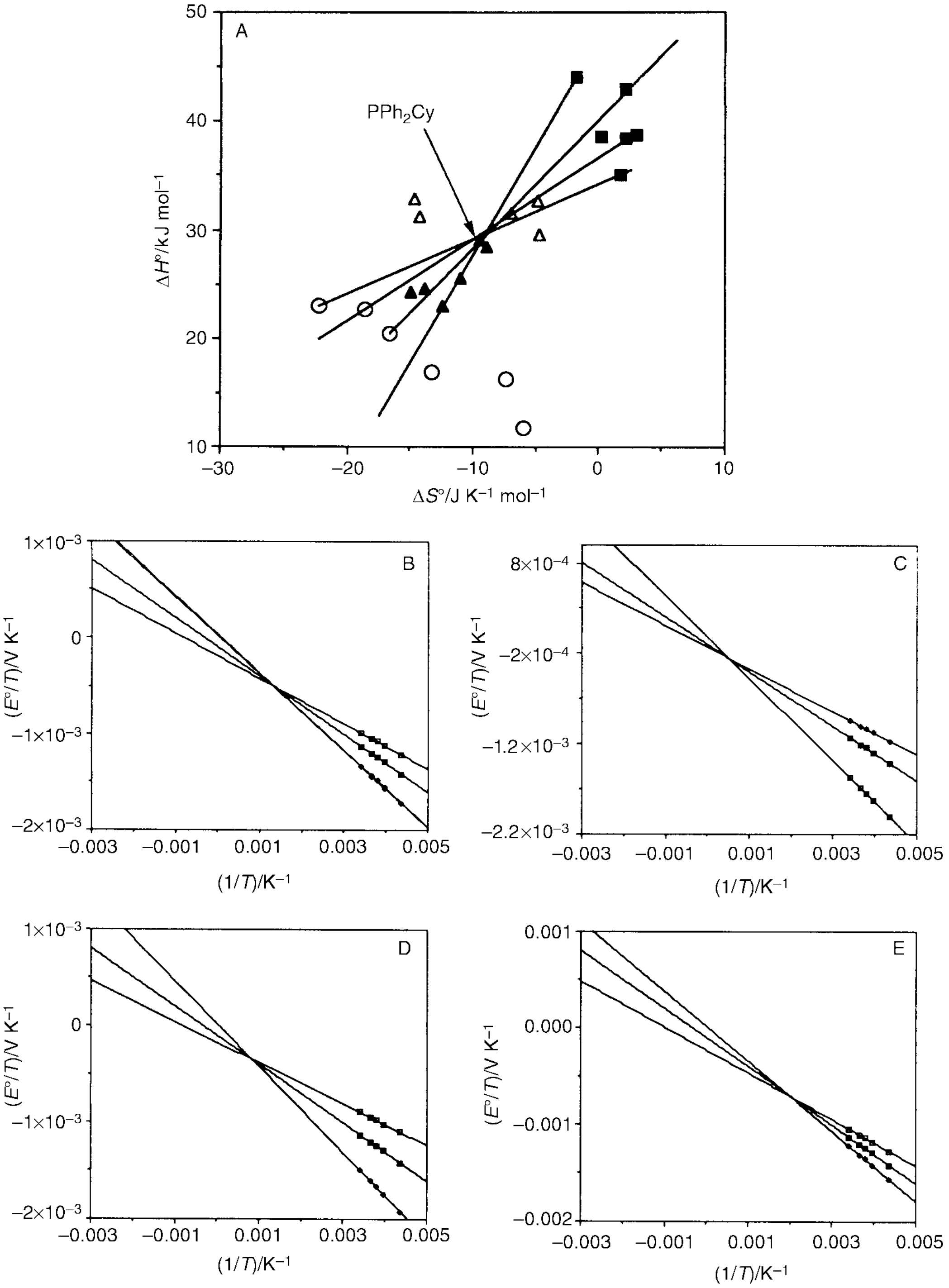

Fig. 5 A plot (A) of $\Delta H°$ *versus* $\Delta S°$. The lines show the families to which PPh_2Cy belongs. The confirmation of family membership is shown in the plots [(B)–(E)] of $E°/T$ *versus* $1/T$ where isoequilibrium behavior is observed for each of the four families. The families of ligands are (B) $P(p\text{-}MeC_6H_4)_3$, PEt_3, PBu^i_3 (lines for PEt_3 and PBu^i_3 overlap), PPh_2Cy; (C) PPh_2Me, PCy_3, PPh_2Cy; (D) PPh_3, PPr^i_3, PPh_2Cy; (E) $P(p\text{-}MeOC_6H_4)_3$, PMe_3, PPh_2Cy.

E_{ar} values from the values of 1 or 2 is system-dependent. This situation is perplexing; its resolution might shed light on the nature of the aryl effect.

Evaluation of the stereoelectronic parameters of $P(NC_4H_8)_3$ [54]

We have used the methodology described herein to determine the χ value for $P(NC_4H_8)_3$ based on the assumption that the stereochemical properties are adequately described by χ, θ and E_{ar}. The appropriate data are displayed in entries 30 and 31 in Table 2. We use 145° for θ as reported by Moloy and Petersen.[50] We find that $\chi = 0.4 \pm 1.0$ for this ligand making it second only to PBu^t_3 in electron donor capacity. As we will show, $E_{ar} = 0$ for this ligand (*vide infra*).

Because of the particular nature of the stereoelectronic properties of $P(NC_4H_8)_3$, it will behave at times as a PR_3, a $P(p\text{-}XC_6H_4)_3$, or neither depending on the nature of the system. We illustrate this behavior in the next three examples. It is important to note that with $\chi = 0.4$ and $\theta = 145°$, this ligand does not share the same parametric relationship between χ and θ that is exhibited by the common PR_3. Consequently, the datum for $P(NC_4H_8)_3$ will fall along the line determined by PR_3 in a 'χ' plot (Fig. 9) only when *steric effects are not operative* and either the aryl effect is not operative, or E_{ar} is zero for this ligand. Steric effects are not operative for $\Delta H°$ of reduction of the $\eta\text{-}Cp(CO)(L)Fe(COMe)^{+/0}$ couple (*vide supra*), thus $P(NC_4H_8)_3$ behaves like a PR_3 ligand and lies along the line defined by the PR_3 ligands (Fig. 9A). Since the 'aryl effect' is

Table 3 Literature parameters and parameters calculated as described in this paper

	Ligand	θ^a	χ^b	$E_{ar}{}^c$	z_3 (calc)^d	z_3 (ave)^e	χ_z (ave)^e	E_{ar} (z)^e
1	PMe_3	118	8.55	0	11.9			
2	$PPhMe_2$	122	10.6	1		13.9	10.5	1.0
3	PEt_3	132	6.3	0	10.0			
4	PBu_3	136	5.25	0	9.1			
5	PPh_2Me	136	12.1	2		16.4	12.6	2.2
6	$PPhEt_2$	136	9.3	1		12.4	8.6	1.1
7	$PPhBu_2$	139	8.6	1		12.0	8.1	1.3
8	PPh_2Et	140	11.3	2		15.1	11.1	2.3
9	PPh_2Pr	141	11.2	2		15.2	11.2	1.9
10	PPh_2Bu	142	11.1	2		15.3	11.3	2.1
11	$PBu^i{}_3$	143	5.7	0	9.7			
12	$P(p\text{-}MeOC_6H_4)_3$	145	10.5	2.7	14.6			
13	$P(p\text{-}MeC_6H_4)_3$	145	11.5^f	2.7	15.6			
14	PPh_3	145	13.25	2.7	17.3			
15	$P(p\text{-}FC_6H_4)_3$	145	15.7	2.7	19.8			
16	$P(p\text{-}ClC_6H_4)_3$	145	16.8	2.7	20.9			
17	$P(p\text{-}F_3CC_6H_4)_3$	145	20.5^e	2.7	24.6			
18	$P(NC_4H_8)_3$	145		0		3.8	0.4	0
19	PPh_2Pr^i	150	10.9	2		13.8	9.6	1.5
20	PPh_2Cy	153	9.3^g	2		13.4	9.1	1.6
21	$PPhPr^i{}_2$	155	7.5	1		11.5	7.1	1.7
22	$PPr^i{}_3$	160	3.45	0	7.9			
23	$PPhCy_2$	161	5.35^g	1		10.2	5.7	1.6
24	PCy_3	170	1.4	0	6.2			

[a] Data are taken from ref. 46. [b] Data are taken from ref. 20. [c] Data are taken from ref. 23. [d] Calculated *via* eqn. (15). [e] Data were calculated as described in this paper. [f] Data are taken from ref. 47. [g] Estimated based on additivity.

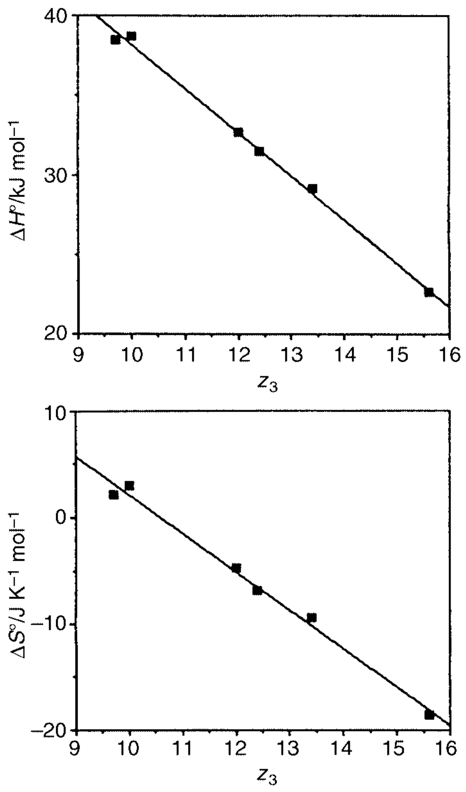

Fig. 6 Plots of $\Delta H°$ and $\Delta S°$ *versus* z_3 for the family of ligands $P(p\text{-}MeC_6H_4)_3$, PPh_2Cy, $PPhEt_2$, $PPhBu_2$, $PBu^i{}_3$, and PEt_3. The r^2 values are 0.996 and 0.991 for the two plots, respectively.

operative (as shown by the separation of lines in Fig. 9A) and since the datum for $P(NC_4H_8)_3$ lies on the PR_3 line, it follows that $E_{ar} = 0$ for $P(NC_4H_8)_3$.

Since $P(NC_4H_8)_3$ is isosteric to $P(p\text{-}XC_6H_4)_3$ but has $E_{ar} = 0$, its datum will fall along the line determined by $P(p\text{-}XC_6H_4)_3$ only if the aryl effect is not operative. Even when steric effects are operative this is true. The analysis of the heats of reaction for the formation of η-Cp*RuL₂Cl from η-Cp*Ru(cod)Cl[55] is an example of this case (Fig. 9B). (The datum for PPh₃ appears to be an outlier.) (Note that absence of the aryl effect is indicated by a crossing of PR_3 and $P(p\text{-}XC_6H_4)_3$ lines at $\chi = 4.8$.[23]).

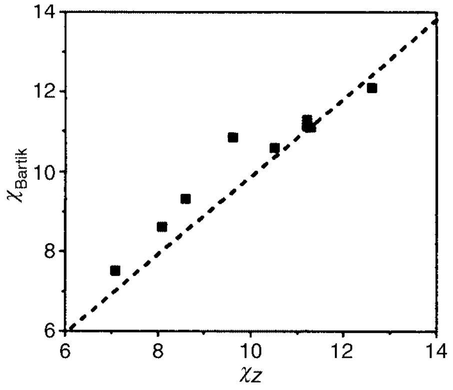

Fig. 7 A plot of χ values for PPh_iR_{3-i} reported by Bartik[20] and the χ_z values reported in this paper.

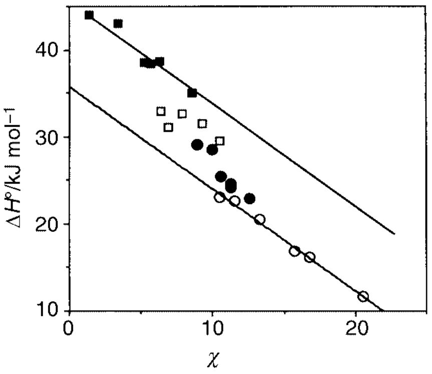

Fig. 8 A plot of $\Delta H°$ *versus* χ values. The χ values for PPh_iR_{3-i} were calculated as described in this paper.

Finally, if both steric effects and the aryl effect are operative then the datum for $P(NC_4H_8)_3$ will not fall along the lines determined by either the PR_3 or $P(p\text{-}XC_6H_4)_3$ families of ligands. The point, however, will fall along the line that would

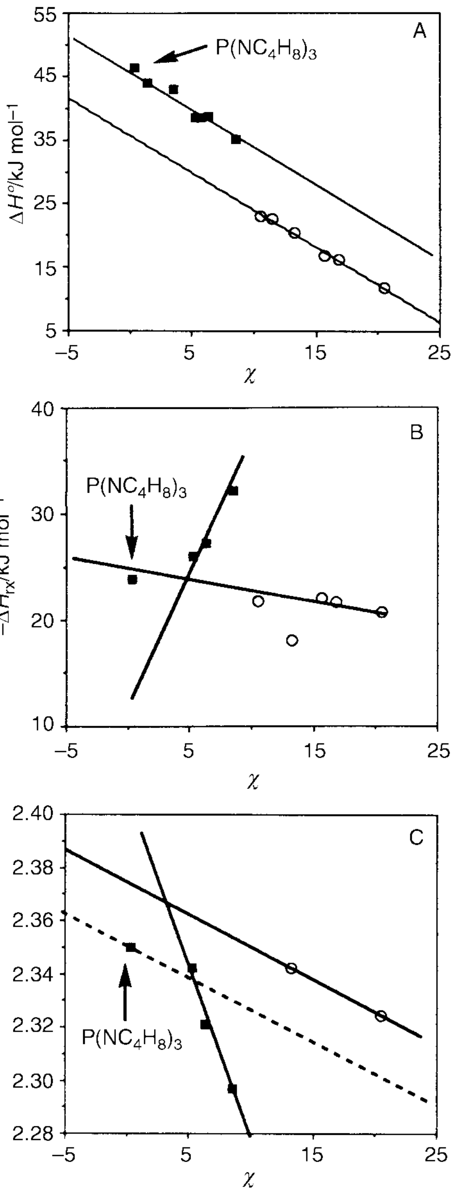

Fig. 9 Plots of physicochemical data for $P(NC_4H_8)_3$ and PR_3 (■), and $P(p\text{-}XC_6H_4)_3$ (○) *versus* the electronic parameter χ. (A) Since there is no significant steric effect in $\Delta H°$ for the reduction of η-Cp(CO)(L)Fe(COMe)$^+$ and since $E_{ar} = 0$ for $P(NC_4H_8)_3$, the datum for $P(NC_4H_8)_3$ lies along the line defined by PR_3. (B) Since there is no significant 'aryl effect' in $-\Delta H_{rx}$ for the transformation of η-Cp*Ru(cod)Cl into η-Cp*RuL$_2$Cl and since $P(NC_4H_8)_3$ is isosteric with $P(p\text{-}XC_6H_4)_3$, the datum for $P(NC_4H_8)_3$ lies along the line defined by $P(p\text{-}XC_6H_4)_3$. (The point for PPh_3 appears to be an outlier.) (C) The average Ru–P bond length for η-Cp*RuL$_2$Cl depends on both steric effects and the 'aryl effect', hence, the datum for $P(NC_4H_8)_3$ is not on either line. The point is, however, on the hypothetical (dashed) line that would be determined by $P(p\text{-}XC_6H_4)_3$ if there were no aryl effect. (The dashed line intersects the PR_3 line at $\chi = 4.8$.)

have been determined by $P(p\text{-}XC_6H_4)_3$ if there were no aryl effect. The analysis of the average Ru–P bond lengths in η-Cp*RuL$_2$Cl[55,56] illustrates this case (Fig. 9C). Based on these results, we believe that $\chi = 0.4$ is a reasonable value for $P(NC_4H_8)_3$ and that this ligand behaves more like a trialkylphosphine.

Conclusions

It had been previously suggested that the observation of isoequilibrium (or isokinetic) behavior indicated that the free energy of a process was responding to a single stereoelectronic parameter. Herein, we have shown rigorously for a three parameter model that the general case is that isoequilibrium behavior is observed when $\Delta G°$ responds to a linear combination of two of the parameters. We call this combination z_3. Furthermore, these two parameters do not have to be related. $\Delta H°$ and $\Delta S°$ also respond linearly to z_3 for a family of ligands. We showed how to use the linear relationship between $\Delta H°$ and z_3 to calculate values of χ and E_{ar} for PPh_iR_{3-i}. With one exception, the values of χ that we obtained do not differ greatly from the values obtained by Bartik *via* analysis of the ν_{CO} values of $Ni(CO)_3L$. The E_{ar} values appear to be sensitive to the nature of R in PPh_iR_{3-i}. For R = isopropyl and cyclohexyl, E_{ar} values deviate significantly from the previously assigned values of 1 and 2. Thus, we have used isoequilibrium behavior to determine the stereoelectronic parameters of ligands relative to a standard set of PR_3 and $P(p\text{-}XC_6H_4)_3$ ligands. Using this methodology, we calculated $\chi = 0.4 \pm 1.0$ and $E_{ar} = 0$ for $P(NC_4H_8)_3$, values that had not been reported previously.

Experimental

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.[57]

The $E°$ values for the η-Cp(CO)(L)Fe(COMe)$^{+/0}$ couple were obtained *via* cyclic voltammetry, and were 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 agreed with the original measurements. This leads to an error of ±0.0007 V in the $E°$ values.

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