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Assessing the stereoelectronic properties of pyrrolyl phosphines and related ligands. The quantitative analysis of ligand effects (QALE)

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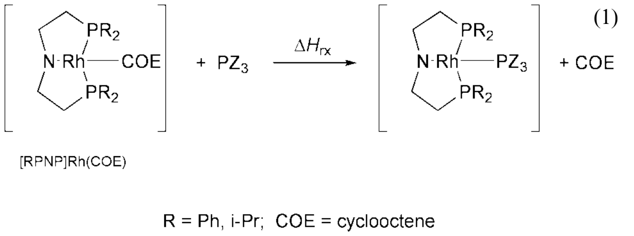
Received (in Cambridge, UK) 2nd May 2000, Accepted 4th May 2000
Published on the Web 15th June 2000

By application of the QALE model (quantitative analysis of ligand effects) to the standard reduction potentials ($E°$ values) and the standard enthalpies of reduction ($\Delta H°$) of the η-Cp(CO)(PZ$_3$)Fe(COMe)$^{+/0}$ couple (PZ$_3$ = a phosphorus(III) ligand), and ν_{CO} for η-Cp(CO)(PZ$_3$)Fe(COMe)^0, we have determined that a minimum of four parameters are necessary to describe the stereoelectronic properties of the set of ligands PPh$_i$(Pyr)$_{3-i}$ (Pyr = pyrrolyl) and P(NC$_4$H$_8$)$_3$ (NC$_4$H$_8$ = pyrrolidinyl). These parameters are χ_d, θ, E_{ar} and the π acidity parameter, π_p. The values of these parameters were determined by linear regression analysis of a set of QALE equations. The coefficients of these equations were based on the analyses of data for PR$_3$, PPh$_i$R$_{3-i}$, P(p-XC$_6$H$_4$)$_3$, P(OR)$_3$, and P(O-p-XC$_6$H$_4$)$_3$. The parameters for P(Pyr)$_3$ are $\chi_d = 31.9 \pm 0.7$, $\theta = 145 \pm 3$, $E_{ar} = 3.3 \pm 0.2$ and $\pi_p = 1.9 \pm 0.2$; and for P(NC$_4$H$_8$)$_3$ the parameters are $\chi_d = -1.2 \pm 1.4$, $\theta = 145 \pm 5$, $E_{ar} = -0.6 \pm 0.4$ and $\pi_p = 0.9 \pm 0.3$. P(Pyr)$_3$ is a poor σ donor that possesses an E_{ar} parameter comparable to P(p-XC$_6$H$_4$)$_3$ and a π acidity that is about two thirds that of P(OR)$_3$ and half that of P(O-p-XC$_6$H$_4$)$_3$. On the other hand, P(NC$_4$H$_8$)$_3$, which is one of the strongest σ donor phosphorus(III) ligands, is a weak π acid with a value for E_{ar} that is statistically indistinguishable from zero. PPh$_i$(Pyr)$_{3-i}$ and P(NC$_4$H$_8$)$_3$ appear to be isosteric to P(p-XC$_6$H$_4$)$_3$.

Introduction

There is accumulating and compelling evidence that the pyrrolyl phosphines,[1] PPh$_i$(Pyr)$_{3-i}$ (i = 0–2), are π acids. This assertion is certainly supported by Nolan and co-workers'[2] observation that the trend of $-\Delta H_{rx}$ in reaction (1) is CO ≫ P(Pyr)$_3$ > PPh(Pyr)$_2$ > PPh$_2$Pyr > PPh$_3$. This trend parallels the putative π acidity of the pyrrolyl ligands and is in opposition to their overall electron donor capacity.



(1)

Likewise, the initial formation of *cis*-Fe(CO)$_3$[P(Pyr)$_3$]$_2$ from Fe(CO)$_3$(BDA) (BDA = benzylideneacetone)[3] and the facile transformation of Rh(CO)$_4^-$ to Rh[P(Pyr)$_3$]$_4$ are consonant with the intervention of M–P π-bonding. The high ν_{CO} values of Rh(CO)(Cl)[P(Pyr)$_3$]$_2$ indicate that PPh$_i$(Pyr)$_{3-i}$ are poorer electron donors than P(OPh)$_3$, possibly because of the greater π-acidity of pyrrolyl phosphines.[1] Recently, Gonzalez-Blanco and Branchadell,[4] through a density functional study of Fe(CO)$_4$PZ$_3$ (where PZ$_3$ is a general representation of a phosphorus(III) ligand), predicted that P(Pyr)$_3$ would be a π acid comparable in strength to PF$_3$. Thus, both experimental and theoretical studies suggest that pyrrolyl phosphines can behave as π acids.

Surprisingly, however, Nolan's thermochemical studies of other substitution reactions involving pyrrolyl phosphines do not make a clear cut case for π acidity[3,5–9] especially when the heats of reaction (ΔH_{rx}) of PPh$_i$(Pyr)$_{3-i}$ are compared to those of P(p-XC$_6$H$_4$)$_3$. Qualitatively, it appears that PPh$_i$(Pyr)$_{3-i}$ behave at times as π acids and at other times they behave more like P(p-XC$_6$H$_4$)$_3$. Nolan addressed this dichotomy and suggested that the dramatic manifestation of the π acidity of PPh$_i$(Pyr)$_{3-i}$ in reaction (1) is due to the synergistic interaction between the π basic amide group and the π acidic pyrrolyl phosphine.[2] He further reasoned that the failure to observe significant π effects in $-\Delta H_{rx}$ for the formation of Rh(CO)(Cl)[PPh$_i$(Pyr)$_{3-i}$]$_2$ is a result of compensating competition between two π acidic ligands.

Central to the problem of detecting and assessing π acidity is the identification and evaluation of the stereoelectronic parameters for PPh$_i$(Pyr)$_{3-i}$. Values for the electronic parameter, χ,[10,11] and the steric parameter, θ,[11] for PPh$_i$(Pyr)$_{3-i}$ have been suggested. Based on the molecular structure of Rh(CO)(Cl)[P(Pyr)$_3$)]$_2$, Petersen and Moloy[1] concluded that PPh$_i$(Pyr)$_{3-i}$ are isosteric with P(p-XC$_6$H$_4$)$_3$ and assigned a cone angle of 145° to P(Pyr)$_3$. Nolan and co-workers[2] came to the same conclusion based on the structures of [RPNP]RhPZ$_3$ complexes.[2] (See reaction (1) for the structure of [RPNP].) Analysis of ν_{CO} for Rh(CO)(Cl)(PZ$_3$)$_2$ in terms of the electronic parameter, χ,[10,11] also led Moloy and Petersen[1] to predict that $\chi = 36$ for P(Pyr)$_3$. Through an analysis of ΔH_{rx} for the formation of Fe(CO)$_3$(PZ$_3$)$_2$, Serron and Nolan[3] arrived at a set of values: χ = 37, 29, 20 for PPh$_i$(Pyr)$_{3-i}$. These χ values are consistent with PPh$_i$(Pyr)$_{3-i}$ being poor electron donors overall, possibly because of their π acidity. However, there is a problem with using χ as a fundamental electronic parameter for π acidic ligands. We have already pointed out that χ for the π acidic ligands is a measure of their total electron donor capacity; χ, undoubtedly, has a contribution from π acidity[12,13] and possibly from E_{ar}[12] ('aryl effect'[14]). Several years ago, we introduced the χ_d parameter, which we suggested was free of π influences and therefore was a better descriptor of the σ donor

DOI: 10.1039/b003494k

Table 1 $E°/T^a$, $\Delta H°^b$, and $\Delta S°^c$ for the reduction of η-Cp(CO)(L)Fe(COMe)$^+$, and, $\nu_{CO}{}^d$ for η-Cp(CO)(L)Fe(COMe)^0

Ligand (L)	$E°/229$	$E°/252$	$E°/264$	$E°/273$	$E°/293$	$\Delta H°$	$\Delta S°$	ν_{CO}
$PPh_2(Pyr)$	-4.81×10^{-4}	-4.49×10^{-4}	-4.35×10^{-4}	-4.21×10^{-4}	-4.05×10^{-4}	7.81	−12.3	34.9
$PPh(Pyr)_2$	1.44×10^{-5}	3.16×10^{-6}	-1.14×10^{-6}	-3.29×10^{-6}	-1.35×10^{-5}	−2.74	−10.52	41.8
$P(Pyr)_3$	4.74×10^{-4}	4.30×10^{-4}	4.06×10^{-4}	3.92×10^{-4}	3.63×10^{-4}	−11.3	−3.53	49.2
$P(NC_4H_8)_3$	-2.13×10^{-3}	-1.94×10^{-3}	-1.86×10^{-3}	-1.80×10^{-3}	-1.68×10^{-3}	46.3	−4.18	13.7

[a] $E°$ (V) were measured *via* cyclic voltammetry in acetonitrile using tetrabutylammonium hexafluorophosphate as the supporting electrolyte and acetylferrocene as the internal standard. The uncertainty in $E°$ is 0.7 mV. [b] In units of kJ mol^{-1}. [c] In units of J K^{-1} mol^{-1}. [d] ν_{CO} − 1900 cm^{-1}.

Table 2 Coefficients for the plots (Fig. 2) of $E°/T$ *vs.* $1/T$, fit to the following equation: $E°/T = a'(1/T) + b'$

L	a'	b'	r^2	n
$PPh_2(Pyr)$	$-(0.081 \pm 0.003)$	$(1.3 \pm 0.1) \times 10^{-4}$	0.999	5
$PPh(Pyr)_2$	(0.028 ± 0.002)	$-(1.09 \pm 0.08) \times 10^{-4}$	0.999	5
$P(Pyr)_3$	(0.117 ± 0.002)	$-(3.7 \pm 0.7) \times 10^{-5}$	0.999	5
$P(NC_4H_8)_3$	$-(0.480 \pm 0.004)$	$-(4 \pm 2) \times 10^{-5}$	0.999	5

Table 3 Ligands (L) used in this study and their stereoelectronic properties (χ_d, θ, E_{ar}, π_p). New values are displayed in bold type

	L	$\chi_d{}^a$	$\theta^b/°$	$E_{ar}{}^c$	$\pi_p{}^d$
1	$P(OCH_2)_3CEt$	20.0	101	0.2	5.0
2	$P(OMe)_3$	17.9	107	1.0	2.8
3	$P(OEt)_3$	15.8	109	1.1	2.9
4	$P(OBu)_3$	15.9	110	1.3	2.7
5	$P(OCH_2CH_2Cl)_3$	20.3	110	0.4	3.6
6	PMe_3	8.55	118	0	0
7	P(O-i-Bu)$_3$	15.5	120?	1.4	3.0
8	$PPhMe_2$	10.5	122	1.0	0
9	P(O-*p*-MeOPh)$_3$	22.5	128	1.4	3.8
10	P(O-*p*MePh)$_3$	22.4	128	1.4	4.1
11	$P(OPh)_3$	23.6	128	1.3	4.1
12	P(O-*p*-ClPh)$_3$	27.2	128	1.3	4.0
13	P(O-*p*-CNPh)$_3$	31.7	128	1.0	3.7
14	P(O-i-Pr)$_3$	13.4	130	1.3	2.9
15	PEt_3	6.3	132	0	0
16	P(*n*-Bu)$_3$	5.25	136	0	0
17	$PPhEt_2$	8.6	136	1.1	0
18	PPh_2Me	12.6	136	2.2	0
19	PPh(*n*-Bu)$_2$	8.1	139	1.3	0
20	PPh_2Et	11.1	140	2.3	0
21	PPh_2Pr	11.2	141	1.9	0
22	PPh$_2$(*n*-Bu)	11.3	142	2.1	0
23	P(i-Bu)$_3$	5.7	143	0	0
24	**$P(Pyr)_3$**	**31.9**	**145**	**3.3**	**1.9**
25	**$PPh(Pyr)_2$**	**25.7**	**145**	**3.2**	**1.3**
26	**$PPh_2(Pyr)$**	**19.5**	**145**	**3.1**	**0.6**
27	P(*p*-Me$_2$NC$_6$H$_4$)$_3$	5.25	145	2.7	0
28	P(*p*-MeOC$_6$H$_4$)$_3$	10.5	145	2.7	0
29	P(*p*-MeC$_6$H$_4$)$_3$	11.5	145	2.7	0
30	P(C$_6$H$_5$)$_2$(*p*-MeC$_6$H$_4$)	12.1	145	2.7	0
31	$P(C_6H_5)_3$	13.25	145	2.7	0
32	P(*p*-FC$_6$H$_4$)$_3$	15.7	145	2.7	0
33	P(*p*-ClC$_6$H$_4$)$_3$	16.8	145	2.7	0
34	P(*p*-F$_3$CC$_6$H$_4$)$_3$	20.5	145	2.7	0
35	**$P(NC_4H_8)_3$**	**−1.2**	**146**	**−0.6**	**0.9**
36	P(*m*-MeC$_6$H$_4$)$_3$	11.3	148	2.7	0
37	P(*m*-ClC$_6$H$_4$)$_3$	19.6	148	2.7	0
38	PPh$_2$(i-Pr)	9.6	150	1.7	0
39	PPh_2Cy	9.1	153	1.6	0
40	PPh(i-Pr)$_2$	7.1	155	1.7	0
41	P(i-Pr)$_3$	3.45	160	0	0
42	$PPhCy_2$	5.7	162	1.6	0
43	P(*t*-Bu)(i-Pr)$_2$	2.5	167	0	0
44	PCy_3	1.4	170	0	0
45	P(*t*-Bu)Cy$_2$	0.9	174	0	0
46	P(*t*-Bu)$_3$	0	182	0	0

[a] The χ_d values for the phosphites are taken from reference 12. The χ_d values for the mixed alkylphenylphosphines are taken from reference 58. The χ_d values for PR$_3$ and P(*p*-XC$_6$H$_4$)$_3$ are taken from reference 10. [b] Tolman's cone angles are taken from reference 11. [c] E_{ar} values are taken from references 58 and 14. [d] The π_p values for the phosphites are taken from reference 12.

ability of PZ$_3$.[13] More recently, we refined our original χ_d values for the phosphites so that they are also free of 'aryl effects' as well as π effects.[12]

Herein, we combine the QALE (quantitative analysis of ligand effects) model[14–36] and the isoequilibrium behavior[37–55] of the η-Cp(CO)(PZ$_3$)Fe(COMe)$^{+/0}$ couple[12,56,57] to determine the number and values of the electronic parameters of PPh$_i$(Pyr)$_{3-i}$ and P(NC$_4$H$_8$)$_3$. We find that, indeed, like the phosphites,[12] the parameter, π_p, is required to describe PPh$_i$(Pyr)$_{3-i}$ in addition to θ, χ_d, and E_{ar}. The values for the stereoelectronic parameters for PPh$_i$(Pyr)$_{3-i}$ and P(NC$_4$H$_8$)$_3$ were determined by regression analysis of the QALE equations for a variety of physicochemical properties. The coefficients of these QALE equations are based on the analysis of data for PR$_3$, P(*p*-XC$_6$H$_4$)$_3$, P(OR)$_3$, and P(O-*p*-XC$_6$H$_4$)$_3$ and are independent of the properties of PPh$_i$(Pyr)$_{3-i}$ or P(NC$_4$H$_8$)$_3$.

Results and discussion

For the past few years, we have explored ways to determine the minimum number and values of the stereoelectronic parameters necessary to describe phosphorus(III) ligands.[12,20] One such way is based on plots of one physicochemical property *versus* another.[20] This procedure provides us with the minimum number of parameters needed to describe a ligand but not their values. To determine the minimum number of parameters, we begin our analysis of PPh$_i$(Pyr)$_{3-i}$ by examining plots (Fig. 1) of $\Delta H°$ and $E°$ (229 K) for the η-Cp(CO)(PZ$_3$)Fe(COMe)$^{+/0}$ couple [eqn. (2)] *versus* ν_{CO} for η-Cp(CO)(PZ$_3$)Fe(COMe)^0. All

$$\eta\text{-Cp(CO)(PZ}_3\text{)Fe(COMe)}^+ + e^- = \eta\text{-Cp(CO)(PZ}_3\text{)Fe(COMe)}^0 \quad (2)$$

these data were measured in our laboratory. The new $E°/T$, $\Delta H°$ and $\Delta S°$ data for the η-Cp(CO)(PZ$_3$)Fe(COMe)$^{+/0}$ couple and ν_{CO} for η-Cp(CO)(PZ$_3$)Fe(COMe)^0 (PZ$_3$ = PPh$_i$(Pyr)$_{3-i}$ and P(NC$_4$H$_8$)$_3$) are displayed in Table 1 along with the values for $\Delta H°$ and $\Delta S°$. $\Delta H°$ and $\Delta S°$ were calculated in the standard manner from the slopes and intercepts (Table 2) of the $E°/T$ *versus* $1/T$ plots. The ligands used in this study and their stereoelectronic parameters are displayed in Table 3. The sets of physicochemical data analyzed in this study are listed in Table 4.

Before we begin the analysis of the plots of one property (prop$_1$) *versus* a second property (prop$_2$) in Fig. 1, we briefly discuss the simple algebra behind these plots. In the QALE model, each physicochemical property is described by its own linear equation [*e.g.* eqns. (3) and (4)] in terms of the stereoelectronic parameters of the phosphorus(III) ligands.[12,20] In the absence of a steric threshold these equations are:

$$\text{prop}_1 = a_1\chi_d + b_1\theta + c_1E_{ar} + d_1\pi_p + e_1 \quad (3)$$

$$\text{prop}_2 = a_2\chi_d + b_2\theta + c_2E_{ar} + d_2\pi_p + e_2 \quad (4)$$

where χ_d describes the σ donor capacity,[12,13] θ is Tolman's cone angle[11] which describes the size, E_{ar} is the aryl effect parameter,[14] and π_p is a measure of the π acidity of the phospho-

Table 4 Sets of physicochemical data that were analyzed in this paper

	System	Property	Ligands[a]	Ref.
1	η-Cp(CO)(PZ$_3$)Fe(COMe)^0	$\nu_{CO} - 1900\ \text{cm}^{-1}$	1–7, 9–13, 15, 16, 24, 28, 29, 31–35, 41, 44	This paper, 12
2	Rh(acac)(CO)PZ$_3$	$\nu_{CO} - 1900\ \text{cm}^{-1}$	11, 24, 28–34, 37, 41, 44	9
3	Rh(CO)(Cl)(PZ$_3$)$_2$	$\nu_{CO} - 1900\ \text{cm}^{-1}$	2, 6, 11, 15, 24, 28, 29, 31–34, 41, 44	3, 8, 59
4	Fe(CO)$_3$(PZ$_3$)$_2$	$\nu_{CO} - 1800\ \text{cm}^{-1}$	6, 15, 16, 24, 28, 29, 31–34, 41, 44, 46	6, 60, 61, 62
5	η-Cp(CO)(PZ$_3$)Fe(COMe)$^{+/0}$	$E°$ (229 K)	1–26, 28, 29, 31–35, 38, 39, 40–42, 44	57, 56, 58
6	η-Cp(CO)(PZ$_3$)Fe(COMe)$^{+/0}$	$\Delta S°$	1–26, 28, 29, 31–35, 38, 39, 40–42, 44	56, 58, this paper
7	η-Cp(CO)(PZ$_3$)Fe(COMe)$^{+/0}$	$\Delta H°$	1–26, 28, 29, 31–35, 38, 39, 40–42, 44	56, 58, this paper
8	[(*p*-Cymene)RuCl$_2$]$_2$ + 2PZ$_3$ = 2(*p*-cymene)RuCl$_2$PZ$_3$	$-\Delta H_{rx}$	2, 6, 8, 11, 15, 18, 20, 24–26, 28, 29, 31–35, 39, 41, 42, 44	7, 63
9	[(*p*-Cymene)OsCl$_2$]$_2$ + 2 PZ$_3$ = 2(*p*-cymene)OsCl$_2$PZ$_3$	$-\Delta H_{rx}$	6, 8, 15, 18, 24, 25, 26, 28, 29, 31–35, 41, 44	64
10	[RhCl(CO)$_2$]$_2$ + 4 PZ$_3$ = 2 Rh(CO)(Cl)(PZ$_3$)$_2$ + 2CO	$-\Delta H_{rx}$	2, 6, 8, 11, 15, 18, 24, 25, 26, 28, 29, 31–34, 41, 44	3, 8
11	Rh(acac)(CO)$_2$ + PZ$_3$ = Rh(acac)(CO)PZ$_3$ + CO	$-\Delta H_{rx}$	11, 16, 20, 23, 28–35, 41, 44	9
12	Fe(CO)$_3$(BDA) + 2 PZ$_3$ = Fe(CO)$_3$(PZ$_3$)$_2$ + BDA	$-\Delta H_{rx}$	6, 8, 15, 16, 18, 20, 23, 25, 28, 29, 31–35, 39, 42, 43, 45	6, 60, 61, 62
13	PtMe$_2$(CO)$_2$ + 2 PZ$_3$ = PtMe$_2$(PZ$_3$)$_2$ + 2 CO	$-\Delta H_{rx}$	6, 8, 15, 18, 23–26, 28, 29, 31–34, 41, 44	65
14	CpRu(COD)Cl + 2 PZ$_3$ = CpRu(PZ$_3$)$_2$Cl + COD	$-\Delta H_{rx}$	1, 2, 6, 8, 11, 14–16, 18, 24, 25, 26, 28, 29, 31–35	5, 66, 67
15	Cp*Ru(COD)Cl + 2 PZ$_3$ = Cp*Ru(PZ$_3$)$_2$Cl + COD	$-\Delta H_{rx}$	1, 2, 6, 8, 11, 14–16, 18, 24, 25, 26, 28, 31–35	5, 66, 67

[a] Numbers refer to the entry numbers in Table 3.

rus(III) ligand.[12] Combining eqns. (3) and (4) we obtain eqn. (5).

$$\text{prop}_1 = \frac{a_1}{a_2}\,\text{prop}_2 + \left(b_1 - \frac{a_1 b_2}{a_2}\right)\theta + \left(c_1 - \frac{a_1 c_2}{a_2}\right)E_{ar} + \left(d_1 - \frac{a_1 d_2}{a_2}\right)\pi_p + e_1 - \frac{a_1 e_2}{a_2} \qquad (5)$$

For the properties ($\Delta H°$, $E°$ and ν_{CO} for the η-Cp(CO)(PZ$_3$)-Fe(COMe)$^{+/0}$ couple and η-Cp(CO)(PZ$_3$)Fe(COMe)^0, we can safely regard the $b_i\theta$ contributions to these plots as negligible (see the percent contributions listed in entries 1, 5, and 7 in Table 5). Therefore, eqn. (5) becomes eqn. (6).

$$\text{prop}_1 = \frac{a_1}{a_2}\,\text{prop}_2 + \left(c_1 - \frac{a_1 c_2}{a_2}\right)E_{ar} + \left(d_1 - \frac{a_1 d_2}{a_2}\right)\pi_p + e_1 - \frac{a_1 e_2}{a_2} \qquad (6)$$

For the special case of the PR$_3$ ligands, eqn. (6) simplifies to eqn. (7) because in the QALE model both E_{ar} and π_p are zero

$$\text{prop}_1 = \frac{a_1}{a_2}\,\text{prop}_2 + e_1 - \frac{a_1 e_2}{a_2} \qquad (7)$$

for this family. Thus, in a plot of prop$_1$ *versus* prop$_2$ the lines for the other ligands differ from the line defined by PR$_3$ due to the E_{ar} and/or the π_p terms [compare eqns. (6) and (7)].

In the plot of $\Delta H°$ *versus* ν_{CO} (Fig. 1A), we see a set of parallel lines. The line for P(*p*-XC$_6$H$_4$)$_3$ lies below the line for PR$_3$ because of the 'aryl effect'. (In the QALE model π_p is assumed to be zero for both PR$_3$ and P(*p*-XC$_6$H$_4$)$_3$.) The point for P(Pyr)$_3$ lies on the line for P(*p*-XC$_6$H$_4$)$_3$. This might mean that P(Pyr)$_3$ is behaving like the P(*p*-XC$_6$H$_4$)$_3$ to which it is thought to be isosteric.[1] This pattern could be described by eqn. (8),

$$\text{prop}_1 = \frac{a_1}{a_2}\,\text{prop}_2 + \left(c_1 - \frac{a_1 c_2}{a_2}\right)E_{ar} + e_1 - \frac{a_1 e_2}{a_2} \qquad (8)$$

which does not invoke a π effect. If this is the case, then the point for P(Pyr)$_3$ should always lie on the line for P(*p*-XC$_6$H$_4$)$_3$ in a property-*versus*-property plot.

In Fig. 1B, where we plot $E°$ (229 K) *versus* ν_{CO}, we observe that the point for P(Pyr)$_3$ does not lie on the line for P(*p*-XC$_6$H$_4$)$_3$ but rather it lies on the line for PR$_3$. Thus, we conclude that at least one electronic parameter in addition to χ_d and E_{ar} is required to describe P(Pyr)$_3$ and PPh$_i$(Pyr)$_{3-i}$, in general. Based on the theoretical work of Gonzalez-Blanco and Branchadell[4] and the experimental work of Moloy[1] and Nolan,[2] we believe that this parameter is π_p, which describes the π acidity of P(Pyr)$_3$.

Isoequilibrium behavior of the η-Cp(CO)[PPh$_i$(Pyr)$_{3-i}$]-Fe(COMe)$^{+/0}$ couple gives us information about the additivity of parameters for PPh$_i$(Pyr)$_{3-i}$. In Fig. 2, we display relevant plots of $E°/T$ *versus* $1/T$.

The plot of $E°/T$ *versus* $1/T$ for these complexes shows a fan shaped array of lines that intersect at a point—this is isoequilibrium behavior.[56,57] We have defined a 'family' as a set of ligands that exhibit isoequilibrium behavior.[12] Isoequilibrium behavior requires that a family of ligands respond to variation in an 'effectively single' parameter.[58] If the ligands of a family are not structurally related then this 'effectively single' parameter is a linear combination of stereoelectronic parameters (see Appendix). If the ligands of the family are structurally related such as PPh$_i$(Pyr)$_{3-i}$, then we may reasonably assume that χ, θ, E_{ar}, π_p are parametrically related and therefore additive. Thus, any one of the four parameters can play the role of the 'effectively single' parameter. Because of the additivity of parameters, we can incorporate PPh$_i$(Pyr)$_{3-i}$ into our determination of the stereoelectronic parameters of P(Pyr)$_3$ (*vide infra*).

We are now ready to determine the values of χ_d, θ, E_{ar} and π_p for P(Pyr)$_3$. We begin by obtaining the coefficients 'a_i' through to 'e_i' for the general form of eqn. (3) by means of analyses of sets of data for the σ donor ligands PR$_3$ and P(*p*-XC$_6$H$_4$)$_3$, and π acid ligands P(OR)$_3$ and P(O-*p*-XC$_6$H$_4$)$_3$. (See Table 4 for the properties that we analyzed and Table 5 for the coefficients of the resulting QALE equations.) In the QALE model these

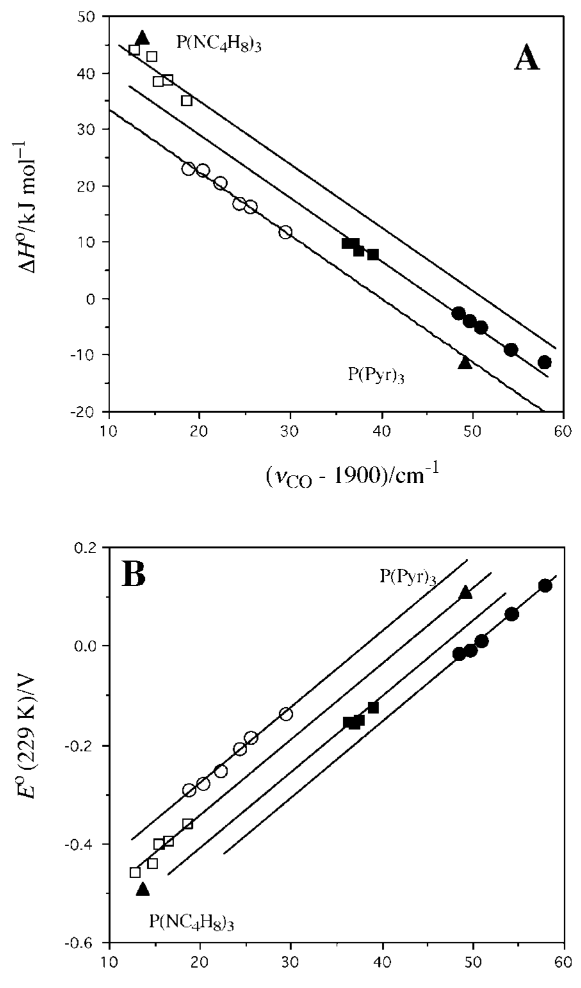


Fig. 1 (A) ΔH° *versus* ν_{CO} (minus 1900 cm^{-1}). (B) E° (229 K) *versus* ν_{CO}. The data refer to η-Cp(CO)(PZ$_3$)Fe(COMe)^0 and the η-Cp(CO)(PZ$_3$)Fe(COMe)$^{+/0}$ couple. PZ$_3$ is PR$_3$ (open squares), P(*p*-XC$_6$H$_4$)$_3$ (open circles), P(OR)$_3$ (filled squares) and P(O-*p*-XC$_6$H$_4$)$_3$ (filled circles).

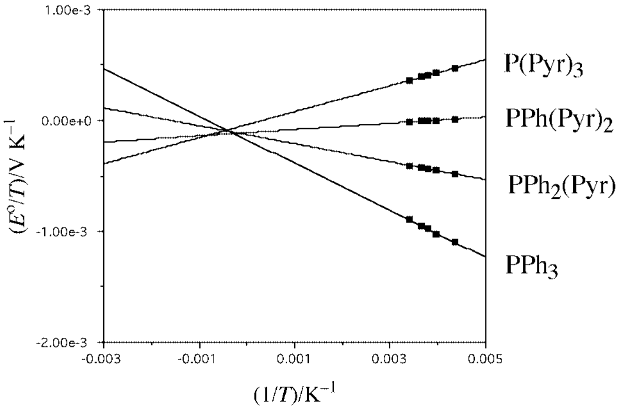


Fig. 2 Plot of E°/T *versus* $1/T$ for the reduction potentials of the η-Cp(CO)[PPh$_i$(Pyr)$_{3-i}$]Fe(COMe)$^{+/0}$ couple.

coefficients should not change as new sets of ligands are added to the individual analyses. Thus, these coefficients are appropriate for the analysis of data for P(Pyr)$_3$. We used additivity also to incorporate PPh(Pyr)$_2$ and PPh$_2$(Pyr) into the analysis of P(Pyr)$_3$. Next, we constructed a set of equations using the measured properties of PPh$_i$(Pyr)$_{3-i}$, and the known coefficients of the QALE equations describing these properties along with their unknown values of χ_d, θ, E_{ar} and π_p. This gave us 24 equations, which are identified in entry 1, Table 6. We weighted the equations and made them dimensionless by dividing each by its standard deviation, σ (see Table 5). Finally, we solved the resulting 24 equations for χ, θ, E_{ar} and π_p by linear regression; the values of these parameters along with relevant statistics are also displayed in entry 1 of Table 6.

We determined the stereoelectronic parameters of P(NC$_4$H$_8$)$_3$ in a manner similar to that described for P(Pyr)$_3$. Appropriate information and values of the parameters for P(NC$_4$H$_8$)$_3$ are also displayed in Table 6.

Comments on the stereoelectronic properties of PPh$_i$(Pyr)$_{3-i}$ and P(NC$_4$H$_8$)$_3$

Our calculated cone angle (145 ± 3°) of P(Pyr)$_3$ agrees with the value of 145° suggested by Moloy[1] and Nolan.[2] Thus, the family PPh$_i$(Pyr)$_{3-i}$ is isosteric to P(*p*-XC$_6$H$_4$)$_3$. The range of the σ donor capacity (χ_d) of PPh$_i$(Pyr)$_{3-i}$ is similar to the range of χ_d for P(O-*p*-XC$_6$H$_4$)$_3$. The aryl effect parameter (E_{ar}) of PPh$_i$(Pyr)$_{3-i}$ is similar to P(*p*-XC$_6$H$_4$)$_3$. The π acidity of P(Pyr)$_3$ is about two thirds of the π acidity of P(OR)$_3$ and less than half that of P(O-*p*-XC$_6$H$_4$)$_3$. This result, which seems reasonable intuitively, is in sharp contrast to the theoretical study[4] that predicted that P(Pyr)$_3$ would have a π acidity comparable to PF$_3$.

Our calculated value (146 ± 5°) of θ for P(NC$_4$H$_8$)$_3$ is statistically indistinguishable from that (145°) suggested by Nolan and co-workers.[2] The σ electron donor capacity is comparable to that of P(*t*-Bu)$_3$ as we had previously suggested.[58] This ligand has a small π acidity (about thirty percent as large as P(OR)$_3$) and a small (negative) aryl effect that is statistically indistinguishable from zero.

Analyses of physicochemical data

We analyzed 15 sets of spectroscopic, electrochemical, and thermochemical data that included data for PPh$_i$(Pyr)$_{3-i}$ and P(NC$_4$H$_8$)$_3$. The systems studied are listed in Table 4. The resulting analyses are listed in Table 5.

In doing QALE analyses it is necessary to identify any ligands (outliers) that for some reason do not fit the QALE model. Initially, this can be done graphically and then analytically. Graphical analyses are useful for exploring the trends within families of ligands. In the absence of change of mechanism or structure, or in the absence of a steric threshold, the data for PR$_3$, P(*p*-XC$_6$H$_4$)$_3$ and for PPh$_i$Z$_{3-i}$ should form individual straight lines when plotted *versus* χ_d. A large deviation of a point from the respective line is sufficient grounds to exclude the datum from the QALE analysis.

This graphical analysis clearly does not work when there are insufficient representatives of a family of ligands. We then use the results of a second test of the appropriateness of including ligands in the QALE analysis. This test, which we routinely apply to all analyses, is a comparison of the regression coefficients that are obtained as additional ligands are added to the analysis. If it is appropriate to include the data in the analysis then the regression coefficients should not change when these ligands are added to the data set. This is illustrated in Table 5. For most entries, we started with the regression equation for the set of ligands that contains phosphines and phosphites. We then added the PPh$_i$(Pyr)$_{3-i}$ and then P(NC$_4$H$_8$)$_3$. In all cases, the addition of PPh$_i$(Pyr)$_{3-i}$ to the data does not significantly alter the coefficients of the regression equations. The addition of P(NC$_4$H$_8$)$_3$ to the data sets is more problematic; three of the analyses (entries 4C, 9C, 15D) show significant changes when the datum for the ligand is added. Based on these criteria, a handful (13 out of a total set of 322 data) were excluded from the QALE analyses. (The excluded ligands are noted in the comments column of Table 5.)

Overall, the analyses are excellent (excluding 4C, 9C, 15D) with high correlation coefficients.

Interpretation of the analyses

Carbonyl stretching frequency (ν_{CO}). The QALE analyses of the systems shown in Table 4, clearly show that PPh$_i$(Pyr)$_{3-i}$ behave in a manner similar to the phosphites and are described by the same set of stereoelectronic parameters. The analyses of the sets of ν_{CO} data (entries 1–4 in Table 5) show that π effects account for a positive contribution of 26 to 38% in the variations of ν_{CO}. It is certainly expected that enhanced π acidity of the phosphorus(III) ligands would increase ν_{CO}.

Heats of reaction ($-\Delta H_{rx}$). The demonstration of the π acidity of the pyrrolyl phosphines is most dramatic in the heat of formation of [RPNP]Rh(PPh$_i$(Pyr)$_{3-i}$) complexes where $-\Delta H_{rx}$ is greatest for P(Pyr)$_3$ and least for PPh$_3$. Nolan and co-workers[2] ascribe this manifestation of π-effects to the synergistic interaction between the *trans* π basic amide ligand and the π acidic PPh$_i$(Pyr)$_{3-i}$. Under these conditions both the N–Rh and P–Rh π-bonds are strengthened.[2]

In analyses reported herein we find a large positive π effect is observed for the PPh$_i$(Pyr)$_{3-i}$ in the heat of formation[9] of Rh(acac)(CO)PZ$_3$, an observation that suggests that the π basicity of the ligand 'acac' is enhanced by the π acidity of PPh$_i$(Pyr)$_{3-i}$ (entry 11B, Table 5). This is in accord with Nolan and co-workers' interpretation[2] of $-\Delta H_{rx}$ for the formation of [RPNP]Rh(PPh$_i$(Pyr)$_{3-i}$). The π contribution to heat of formation of Rh(CO)(Cl)L$_2$ is smaller and actually negative (entry 10B, Table 5) even though the analyses of ν_{CO} for this complex shows a significant π effect (+26%). Having a small π effect in $-\Delta H_{rx}$ is hardly surprising. Nolan and co-workers[3,8] have already pointed out that the π acidity can be masked in $-\Delta H_{rx}$ data when the π acid ligand is competing with another π acid. In this situation, strengthening of the Rh–PZ$_3$ bond through back bonding would come at the expense of bonds to other π acidic ligands. The negative π contribution is surprising but we believe that this is real. The π contribution to $-\Delta H_{rx}$ for the formation of Fe(CO)$_3$(PZ$_3$)$_2$ (entry 12C in Table 5) is large and negative (−19%). It appears that the gain in stability attributable to Fe–P π bonding does not compensate for the loss of Fe–CO π bonding.

Conclusions

Through the analyses of property-*versus*-property plots, we have shown that a minimum of four parameters are required to describe stereoelectronic properties of PPh$_i$(Pyr)$_{3-i}$ and P(NC$_4$H$_8$)$_3$. We calculated values for these parameters. The cone angles of all four ligands are close to the values predicted based on crystallographic measurements. PPh$_i$(Pyr)$_{3-i}$ are poor electron donors; the π acidity of P(Pyr)$_3$ is approximately two thirds of the π acidity of P(OR)$_3$ and half that of P(O-*p*-XC$_6$H$_4$)$_3$. PPh$_i$(Pyr)$_{3-i}$ have values of E_{ar} that are very close to those exhibited by P(*p*-XC$_6$H$_4$)$_3$. P(NC$_4$H$_8$)$_3$ is a potent σ donor ligand comparable to P(*t*-Bu)$_3$. It is weakly π acidic and has an E_{ar} parameter of approximately zero. We found that increasing π acidity of the phosphorus ligand increases ν_{CO} substantially. The effect of M–P π bonding on $-\Delta H_{rx}$ is variable and can be large and positive or large and negative. Thus, it appears that π-effects can stabilize or destabilize the complex; in one case in the formation of Rh(acac)(CO)PZ$_3$ it appears that Rh–P π bonding enhances Rh–acac bonding leading to an overall stabilization of the complex. The large negative contribution of π effects in $-\Delta H_{rx}$ for the formation of Fe(CO)$_3$(PZ$_3$)$_2$ suggest that Fe–P π bonding leads to a disproportionate attenuation of Fe–CO π bonding thereby leading to an overall destabilization of the complex.

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$_2$O$_5$, 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)(PZ$_3$)Fe(COMe) complexes were synthesized according to literature methods.[68] The $E°$ values for the η-Cp(CO)(PZ$_3$)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 agree with the original measurements. This leads to an error of ±0.0007 V in the $E°$ values.

Acknowledgements

SPN gratefully acknowledges the support of the National Science Foundation (CHE-9631611). We also gratefully acknowledge the helpful advice of John Houlihan, Senior Consultant for Research Statistics, Office of Information Technology, Boston University.

Appendix

We can show by isoequilibrium behavior that we have a set of self consistent parameters for the π acidic phosphorus(III) ligands. We start with the assumption that the $\Delta G°$ is linearly related to the variation in the stereoelectronic properties of a set of ligands [eqn. (A1)] in terms of the four QALE parameters

$$\Delta G^\circ = a\chi_d + b\theta + cE_{ar} + d\pi_p + e \qquad \text{(A1)}$$

χ, θ, E_{ar}, and π_p, where the coefficients a, b, c, d, and e are characteristic of the system being studied. These coefficients are temperature dependent and this dependence is shown explicitly in eqn. (A2).

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \qquad \text{(A2)}$$

$\Delta S°$ and $\Delta H°$ are also related to the QALE parameters *via* eqns. (A3) and (A4).

$$\Delta H^\circ = a_1\chi_d + b_1\theta + c_1E_{ar} + d_1\pi_p + e_1 \qquad \text{(A3)}$$

$$\Delta S^\circ = a_2\chi_d + b_2\theta + c_2E_{ar} + d_2\pi_2 + e_2 \qquad \text{(A4)}$$

We assume that the coefficients of eqns. (A3) and (A4) are temperature independent over the experimental range of temperature. For a group of ligands to produce a fan shaped array of lines in the $\Delta G°/T$ *versus* $1/T$ plot, it must be true that $\Delta H°$ is linearly related to $\Delta S°$ [eqn. (A5)] for this group of ligands. This requirement can be written as eqn. (A5).

$$\Delta H^\circ = \beta\Delta S^\circ + \Delta G^\circ_\beta \qquad \text{(A5)}$$

We have defined the term 'family' to describe a group of ligands that form such a fan shaped array (*vide infra*). β is the temperature of the intersection point of the fan shaped array of lines for a given family, and is the value of $\Delta G°$ at the intersection point. On combining eqs. (A3)–(A5) and solving for θ, we get an expression in terms of the other three parameters.

Table 5 Results of regression analysis of the physicochemical properties listed in Table 4. Analyses are based on the following equation: prop = $a\chi_d + b(\theta - \theta_{st})\lambda + cE_{ar} + d\pi_p + e$, where θ_{st} in the steric threshold and λ is the switching function. Entry numbers refer to the entries in Table 4.

	n	r^2	σ	*a*	*b*	*c*	*d*	*e*	θ_{st}	Comments
1A	22	0.9993	0.1848	1.05 ± 0.03	0.036 ± 0.008	−0.9 ± 0.1	4.3 ± 0.1	5 ± 1		Ligands with C_3 symmetry without $P(Pyr)_3$
B	23	1.000	0.1781	1.04 ± 0.01	0.037 ± 0.003	−0.89 ± 0.05	4.29 ± 0.05	5.1 ± 0.4		Same as above plus $P(Pyr)_3$
C	24	1.000	0.1781	1.05 ± 0.01	0.037 ± 0.003	−0.89 ± 0.05	4.28 ± 0.04	5.0 ± 0.4		Same as above plus $P(NC_4H_8)_3$
				56%[a]	4%	6%	34%			
2A	11	0.997	0.8789	1.2 ± 0.1	0	1.7 ± 0.5	5.0 ± 0.4	56.5 ± 0.7		Ligands with C_3 symmetry without $P(Pyr)_3$
B	12	0.999	0.7416	1.22 ± 0.07	0.11 ± 0.05	2.4 ± 0.6	5.6 ± 0.5	39 ± 8		Same as above plus $P(Pyr)_3$
				47%	8%	12%	33%			
3A	12	0.997	1.595	1.6 ± 0.2	−0.25 ± 0.04	4.5 ± 0.8	6.0 ± 0.6	82 ± 6		Ligands with C_3 symmetry without $P(Pyr)_3$
B	13	0.997	1.562	1.7 ± 0.1	−0.24 ± 0.03	4.3 ± 0.7	5.8 ± 0.6	79 ± 5		Same as above plus $P(Pyr)_3$
C	14	0.993	2.442	1.5 ± 0.2	−0.23 ± 0.05	4 ± 1	6.6 ± 0.9	80 ± 8		Same as above plus $P(NC_4H_8)_3$
				46%	14%	14%	26%			
4A	12	0.9991	0.5599	1.69 ± 0.07	−0.09 ± 0.01	3.6 ± 0.3	—	67 ± 2		Ligands with C_3 symmetry without $P(Pyr)_3$. No data are available for phosphites
B	13	1.000	0.5599	1.69 ± 0.07	−0.09 ± 0.01	3.6 ± 0.3	9.2 ± 0.6	67 ± 2		Same as above plus $P(Pyr)_3$
C	14	0.998	1.077	1.5 ± 0.1	−0.11 ± 0.2	4.2 ± 0.5	11.6 ± 0.6	74 ± 3		Same as above plus $P(NC_4H_8)_3$
				37%	6%	13%	44%			
5A	35	0.999	0.003505	0.0159 ± 0.0002	0.00020 ± 0.00005	0.0110 ± 0.0009	0.0271 ± 0.0008	−0.519 ± 0.008		Ligands include PR_3, $P(p\text{-}XC_6H_4)_3$, PPh_iR_{3-i}, $P(OR)_3$, $P(O\text{-}p\text{-}XC_6H_4)_3$
B	38	0.999	0.004757	0.0161 ± 0.0002	0.00022 ± 0.00007	0.012 ± 0.001	0.027 ± 0.001	−0.52 ± 0.01		Same as above plus $PPh_i(Pyr)_{3-i}$
C	39	0.999	0.004760	0.0161 ± 0.0002	0.00023 ± 0.00007	0.012 ± 0.001	0.027 ± 0.001	−0.52 ± 0.01		Same as above plus $P(NC_4H_8)_3$
				73%	2%	6%	19%			
6A	35	0.978	1.374	1.68 ± 0.07	0.14 ± 0.02	−11.7 ± 0.4	−8.2 ± 0.3	−27 ± 3		Ligands include PR_3, $P(p\text{-}XC_6H_4)_3$, PPh_iR_{3-i}, $P(OR)_3$, $P(O\text{-}p\text{-}XC_6H_4)_3$
B	38	0.972	1.491	1.77 ± 0.08	0.14 ± 0.02	−11.7 ± 0.4	−8.4 ± 0.3	−29 ± 3		Same as above plus $PPh_i(Pyr)_{3-i}$
C	39	0.962	1.734	1.71 ± 0.08	0.16 ± 0.03	−11.7 ± 0.5	−8.2 ± 0.4	−30 ± 4		Same as above plus $P(NC_4H_8)_3$
				36%	7%	26%				
					31%					
7A	35	0.999	0.4628	−1.16 ± 0.02	0.013 ± 0.007	−3.7 ± 0.1	−4.8 ± 0.1	44 ± 1		Ligands include PR_3, $P(p\text{-}XC_6H_4)_3$, PPh_iR_{3-i}, $P(OR)_3$, $P(O\text{-}p\text{-}XC_6H_4)_3$
B	38	0.999	0.5143	−1.15 ± 0.02	0.013 ± 0.008	−3.8 ± 0.1	−4.45 ± 0.1	44 ± 1		Same as above plus $PPh_i(Pyr)_{3-i}$
C	39	0.999	0.5291	−1.16 ± 0.02	0.015 ± 0.008	−3.8 ± 0.1	−4.4 ± 0.1	44 ± 1		Same as above plus $P(NC_4H_8)_3$
				51%	1%	20%	28%			
8A	16	0.969	1.443	−0.77 ± 0.08	−0.57 ± 0.03	0	−1.0 ± 0.4	63 ± 1	121	All ligands except $P(i\text{-}Bu)_3$ and PPh_2Cy
B	18	0.962	1.582	−0.66 ± 0.07	−0.55 ± 0.02	0	−1.2 ± 0.4	61 ± 1	121	Same as above plus PPh_2Pyr and $PPh(Pyr)_2$. $P(Pyr)_3$ was excluded
C	19	0.958	1.621	−0.61 ± 0.06	−0.55 ± 0.3	0	−1.3 ± 0.5	60 ± 1	121	Same as above plus $P(NC_4H_8)_3$
				37%	50%	0%	13%			
9A	12	0.955	1.728	−0.7 ± 0.2	−0.42 ± 0.05	−1.5 ± 0.8	0	67 ± 2	125	Only phosphines were analyzed, data are not available for phosphites
B	14	0.965	1.629	−0.7 ± 0.2	−0.42 ± 0.04	−1.5 ± 0.8	1 ± 2	67 ± 2	125	Same as above plus $PPh_i(Pyr)_{3-i}$
				48%[b]	39%	13%	0%			
C	15	0.929	2.215	−0.3 ± 0.2	−0.38 ± 0.06	−2 ± 1	−3 ± 2	63 ± 2	125	Same as above plus $P(NC_4H_8)_3$
10A	14	0.991	1.397	−1.5 ± 0.2	−0.42 ± 0.03	−2.2 ± 0.7	−1.3 ± 0.6	140 ± 5		Phosphines and phosphites
B	16	0.998	1.501	−1.4 ± 0.1	−0.40 ± 0.03	−2.5 ± 0.7	−1.5 ± 0.6	136 ± 5		Same as above plus $PPh_i(Pyr)_{3-i}$ except for $P(Pyr)_3$
				51%	30%	11%	8%			

11A	9	0.983	0.4634	−0.39 ± 0.08	−0.26 ± 0.07	−2.5 ± 0.5	—	53 ± 11		Phosphines, $P(OC_6H_5)_3$ and $P(p\text{-}CF_3C_6H_4)_3$ were excluded
B	12	0.981	0.4449	−0.40 ± 0.08	−0.24 ± 0.06	−2.4 ± 0.5	4.2 ± 0.8	52 ± 10		Same as above plus $PPh_i(Pyr)_{3-i}$
				21%	28%	16%	35%			
12A	16	0.983	0.8712	−0.77 ± 0.09	−0.45 ± 0.03	−1.5 ± 0.4	—	46.6 ± 0.8	134	Phosphines, data are not available for phosphites
B	19	0.990	0.9304	−0.8 ± 0.1	−0.45 ± 0.03	−1.4 ± 0.5	−1.4 ± 0.9	46.6 ± 0.8	135	Same as above plus $PPh_i(Pyr)_{3-i}$
C	20	0.991	0.8994	−0.78 ± 0.07	−0.45 ± 0.02	−1.4 ± 0.3	−1.3 ± 0.6	46.7 ± 0.5	135	Same as above plus $P(NC_4H_8)_3$
				48%	29%	11%	12%			
13A	12	0.978	0.9022	−0.21 ± 0.11	−0.42 ± 0.03	−1.0 ± 0.4	—	36 ± 1	129	Phosphines, P(i-Bu)$_3$ were excluded. Data are not available for phosphites
B	15	0.977	0.8874	−0.2 ± 0.1	−0.42 ± 0.03	−1.0 ± 0.4	0.5 ± 0.9	35.8 ± 0.9	129	Same as above plus $PPh_i(Pyr)_{3-i}$
				42%	32%	26%	0%			
14A	13	0.975	1.011	0	−0.9 ± 0.1	−1.1 ± 0.5	0	36.4 ± 0.5	135	Phosphines and phosphites, $P(OMe)_3$ and $P(C_6H_5)_3$ were excluded
B	16	0.961	1.190	0	−0.9 ± 0.1	−0.7 ± 0.5	0	36.1 ± 0.6	135	Same as above plus $PPh_i(Pyr)_{3-i}$
C	17	0.961	1.153	0	−0.89 ± 0.07	−0.9 ± 0.3	0	36.2 ± 0.5	135	Same as above plus $P(NC_4H_8)_3$
				0%	90%	10%	0%			
15A	12	0.972	1.00	−0.2 ± 0.1	−0.74 ± 0.08	1.9 ± 0.6	0.5 ± 0.3	33 ± 1	127	Phosphines and phosphites, $P(OMe)_3$ and $P(C_6H_5)_3$ were excluded
B	12	0.969	1.050	−0.1 ± 0.1	−0.73 ± 0.09	1.5 ± 0.7	0.3 ± 1	33 ± 1	128	Phosphines plus $PPh_i(Pyr)_{3-i}$. Phosphites and $P(C_6H_5)_3$ were excluded
C	15	0.970	0.9920	−0.15 ± 0.08	−0.73 ± 0.08	1.7 ± 0.5	0.3 ± 0.3	32.7 ± 0.7	127	Phosphines, phosphites and $PPh_i(Pyr)_{3-i}$. $P(OMe)_3$ and $P(C_6H_5)_3$ were excluded
D	16	0.949	1.248	−0.22 ± 0.09	−0.57 ± 0.06	1.0 ± 0.6	0.7 ± 0.3	33.0 ± 0.8	127	Same as above plus $P(NC_4H_8)_3$
				18%	62%	11%	9%			

[a] The percent contribution of a parameter to the property. This was determined by multiplying the coefficient of the parameter by the range of the parameter. The result is divided by the sum of all the products of coefficient and range. [b] Percent contributions are based on line 9B since the addition of $P(NC_4H_8)_3$ to the analysis caused large changes in the values of the coefficients, *i.e.* it is an outlier.

We substitute this expression for π_p into eqns. (A3) and (A4). On collecting terms in χ, E_{ar}, and π_p, we get the following expressions for $\Delta H°$ and $\Delta S°$, where z_4 (the subscript '4' refers

$$\Delta H° = \beta A z_4 + B \qquad (A6)$$

$$\Delta S° = A z_4 + C \qquad (A7)$$

to the fact that z_4 is derived for a four parameter system) is the effectively single variable given in eqn. (A8), and q is given in eqn. (A9).

$$z_4 = \chi_d + q\pi_p + rE_{ar} \qquad (A8)$$

$$q = \frac{d_2b_1 - d_1b_2}{a_2b_1 - a_1b_2} \qquad (A9)$$

We see that, in general, both $\Delta S°$ and $\Delta H°$ for a family are expressible in terms of a single variable z_4, which is a linear combination of χ, E_{ar}, and π_p. Thus, for a given family of ligands we should obtain a linear plot of $\Delta S°$ *versus* z_4 [eqn. (A7)]. From the coefficients presented in entries 6A and 7A in Table 5 we obtain the following values of 'q' and 'r': $q = 2.90$ and $r = 2.05$. The values of χ_d, 'q' and 'r' were used to calculate z_4 and the plot of $\Delta S°$ *versus* z_4 is shown in Fig. A1.

We found two families of ligands containing at least four ligands each by means of a plot (not shown) of $\Delta H°$ *versus* $\Delta S°$. Members of a family lie on a straight line in the $\Delta H°$ *versus* $\Delta S°$ plot and must exhibit isoequilibrium behavior as is verified in the plots of $E°/T$ *versus* $1/T$ (Figs. A1-B and A1-C). The plot of $\Delta S°$ *versus* z_4 for each family is indeed linear as is seen in Figs. A1-D, and A1-E. For comparison, we have also shown plots of $\Delta S°$ *versus* χ_d only for each family. These points do not fall on a straight line and simply provide a visual estimate of the contribution of the terms $q\pi_p$ and rE_{ar} to the value of z_4.

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Table 6 A listing of the methods of the determination of the stereoelectronic parameters of P(Pyr)$_3$ and P(NC$_4$H$_8$)$_3$ and the regression analyses

	Ligand	Equations used[a]	χ	θ	E_{ar}	π_p	n	r^2
1	P(Pyr)$_3$	1A[P(Pyr)3], 2A[P(Pyr)$_3$], 3A[P(Pyr)$_3$], 5A[PPh$_i$(Pyr)$_{3-i}$], 6A[PPh$_i$(Pyr)$_{3-i}$], 7A[PPh$_i$(Pyr)$_{3-i}$], 8A[PPh$_i$(Pyr)$_{3-i}$], 10A[PPh$_i$(Pyr)$_{3-i}$], 14A[PPh$_i$(Pyr)$_{3-i}$], 15A[PPh$_i$(Pyr)$_{3-i}$]	31.9 ± 0.7	145 ± 3	3.3 ± 0.2	1.9 ± 0.2	24	0.999
2	P(NC$_4$H$_8$)$_3$	1A,3A,5A,6A,7A,8A,14A,15A	−1.2 ± 1.4	146 ± 5	−0.6 ± 0.4	0.9 ± 3	8	0.998

[a] The numbers refer to entries in Table 5. Designations such as 1A[PPh$_i$(Pyr)$_{3-i}$] indicate that the data for these ligands were incorporated into the P(Pyr)$_3$ parameter calculation by taking advantage of the additivity of the parameters for PPh$_i$(Pyr)$_{3-i}$.

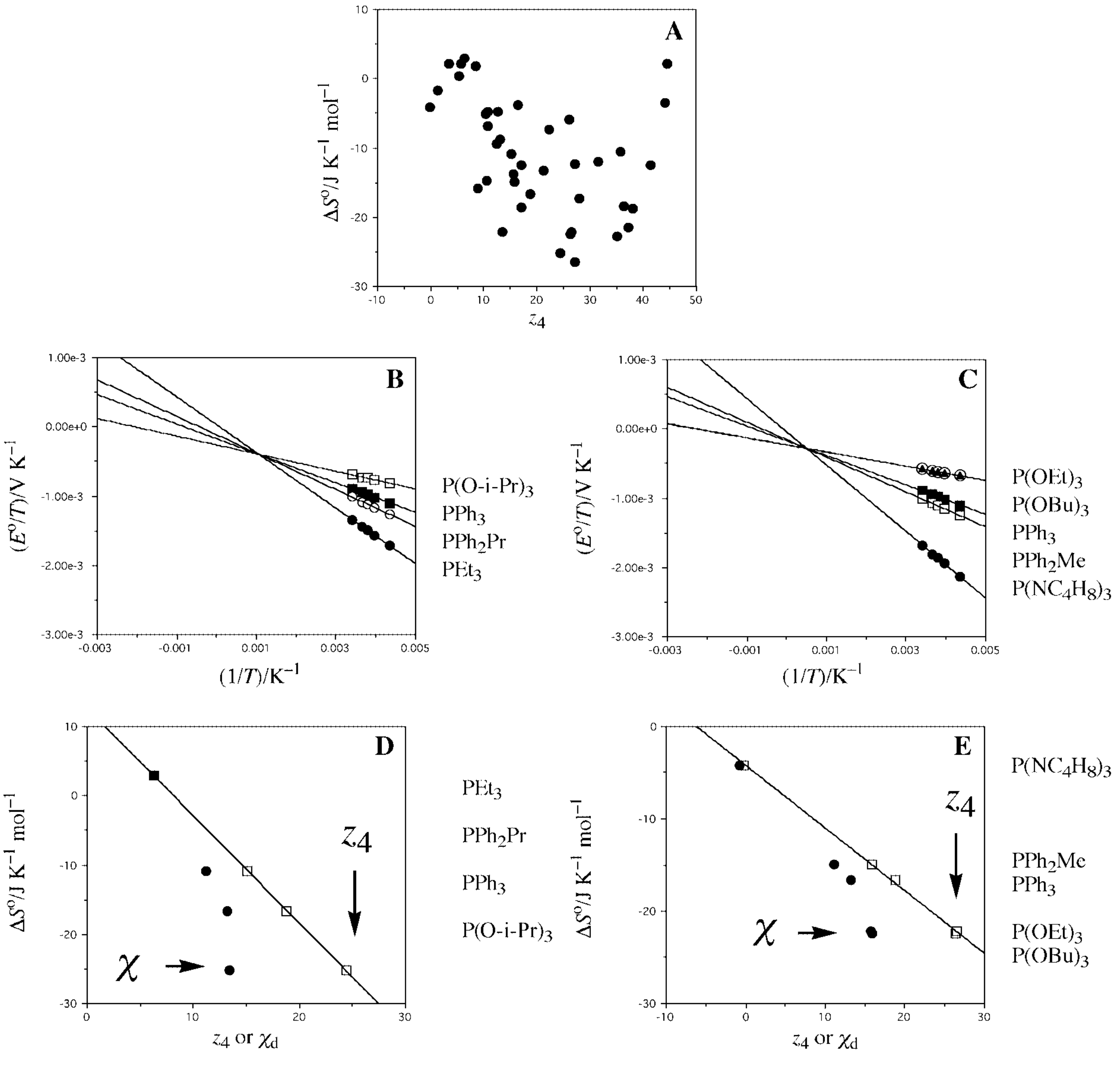

Fig. A1 Data for this figure are taken from measurements on the η-Cp(CO)(PZ$_3$)Fe(COMe)$^{+/0}$ couple. (A) Plot of $\Delta S°$ *versus* z_4 for all the ligands in Table 3. (B) Plot of $E°/T$ *versus* $1/T$ for the family comprised of PZ$_3$ = P(O-iPr)$_3$, P(C$_6$H$_5$)$_3$, PPh$_2$Pr, PEt$_3$. (C) Plot of $E°/T$ *versus* $1/T$ for the family comprised of PZ$_3$ = P(OEt)$_3$, P(OBu)$_3$, P(C$_6$H$_5$)$_3$, PPh$_2$Me, P(NC$_4$H$_8$)$_3$. (D) Plot of $\Delta S°$ *versus* z_4 and χ_d for PZ$_3$ = P(O-iPr)$_3$, P(C$_6$H$_5$)$_3$, PPh$_2$Pr, PEt$_3$. (E) Plot of $\Delta S°$ *versus* z_4 or χ_d for PZ$_3$ = P(OEt)$_3$, P(OBu)$_3$, P(C$_6$H$_5$)$_3$, PPh$_2$Me, P(NC$_4$H$_8$)$_3$.

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