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The stereoelectronic parameters of phosphites. The quantitative analysis of ligand effects (QALE)

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Through an analysis of pK_a values for HPZ_3^+, ionization potentials (IP) for PZ_3, ν_{CO} for η-Cp(CO)(PZ_3)Fe(COMe)^0, and $E°$ (229 K) and $\Delta H°$ for the η-Cp(CO)(PZ_3)Fe(COMe)$^{+/0}$ couple, we determined the values of the three electronic parameters, χ_d, E_{ar} and π_p that are needed to describe the stereoelectronic properties of phosphites. The phenomenon we call the 'aryl effect', which is described by the parameter E_{ar}, is apparently not restricted to phosphines bearing pendant aryl groups but applies to the phosphites. π_p is a new parameter related to the π acidity of the phosphites. The phosphites studied are listed in terms of increasing π acidity: $P(OMe)_3 \approx P(OEt)_3 \approx P(OBu)_3 \approx P(O\text{-}i\text{-}Bu)_3 \approx P(O\text{-}i\text{-}Pr)_3 < P(OCH_2CH_2Cl)_3 < P(O\text{-}p\text{-}XC_6H_4)_3 < P(OCH_2)_3CEt$ (X = MeO, Me, H, Cl, CN). Using these electronic parameters, along with Tolman's cone angle, we have now incorporated the phosphites into the QALE (quantitative analysis of ligand effects) model and analyzed 32 sets of spectroscopic, thermodynamic, and kinetic data mostly taken from the literature. The analyses give a median r^2 value of 0.982.

Introduction

Because of the importance of transition metal–phosphorus(III) compounds in catalytic and stoichiometric reactions,[1,2] there is a long standing interest in metal–phosphorus bonding.[1–19] Currently, metal–phosphorus bonding is viewed as being comprised of σ-donation from phosphorus to metal and back donation *via* π-bonding between a filled metal d-orbital and a ligand orbital of appropriate symmetry.[20–25] Theoretical studies are not in agreement about the importance of M–P π bonding. For example, one study suggested that all phosphorus(III) ligands including the PR_3 are good π-acids.[17] Another found that phosphines are poor π-acids whereas $P(OR)_3$ and particularly PF_3 are good π-acids.[24]

The validation of the theoretical models has remained elusive. The separation of the σ and π components, which is central to understanding M–P bonding, has been attempted empirically[9,10,22,26–39] but the results are not conclusive, although the NMR approach suggested by Alyea[22,26,29–31] might prove fruitful.

Several electronic parameters have been suggested for the phosphorus(III) ligands.[22,26] The pK_a values[40–43] of HPZ_3^+ are attractive since they are free of the influences of M–P π bonding. The pK_a values are however, sensitive to the size[44,45] of the phosphorus(III) compounds and are, of course, limited to those PZ_3 which are sufficiently basic that such measurement is possible. Others have proposed spectroscopic properties (NMR[46–50] or IR[51,52]) that are undoubtedly influenced by both the σ-donor and π-acceptor capacity of the ligands.

For the past fifteen years we have been studying linear free energy relationships involving phosphorus(III) compounds *via* the QALE model (quantitative analysis of ligand effects[53–74]). In our original work, we included organophosphites as well as the alkyl and aryl phosphines. Shortly thereafter, we noted that the spectroscopically derived and commonly used electronic parameter, χ, cannot be used as a measure of σ-donicity for the phosphites since there is no evidence that χ is free of π influences. At the time, we introduced the χ_d parameter[45] (based on the pK_a values HPZ_3^+) which we believed was a measure of the σ-donor capacity of these ligands. Unfortunately, we had not yet discovered the 'aryl effect'[53] and were unaware that, as we show herein, at least four parameters (χ_d, θ, E_{ar}, and the π acidity parameter, π_p) are needed to describe the properties of the phosphites. (We find E_{ar} is not restricted to the $P(p\text{-}XC_6H_4)_3$ ligands and should probably be renamed.) Accordingly these 'old' χ_d parameters might have been free of π effects but they are not free of 'aryl effects'. Herein, we introduce a new set of χ_d parameters that we believe are free of both π and aryl effects, and indeed describe the σ-donor capacity of the phosphorus(III) ligands. As in the past, we use the Bartik–Tolman χ values[51,52] as the χ_d values of the PR_3 and $P(p\text{-}XC_6H_4)_3$, and we continue to assume the absence of M–P π bonding (*i.e.* $\pi_p = 0$) for these phosphines.

Results and discussion

There is apparently little doubt that phosphites are stronger π-acids than alkyl and aryl phosphines. In the QALE model we assume that PR_3 and $P(p\text{-}XC_6H_4)_3$ have no appreciable π-acidity. We do question, however, whether it is only π acidity that distinguishes phosphites from PR_3.

To gain insight into the number and nature of parameters needed to describe phosphite ligands, we turn to property *versus* property plots.[62] In the QALE model, each physiochemical property is described by its own equation in terms of the stereoelectronic parameters of the phosphorus(III) ligands. In order to lead the reader through the analysis, we anticipate our results from this paper and give the appropriate form of the QALE equations for two properties ($prop_1$ and $prop_2$) in the absence of a steric threshold [eqns. (1) and (2)].

$$\mathrm{prop}_1 = a_1\chi_d + b_1\theta + c_1E_{ar} + d_1\pi_p + e_1 \qquad (1)$$

$$\mathrm{prop}_2 = a_2\chi_d + b_2\theta + c_2E_{ar} + d_2\pi_p + e_2 \qquad (2)$$

In these equations χ_d describes the σ donor capacity, θ is Tolman's cone angle which describes the size,[75] E_{ar} is the aryl effect parameter, and π_p is a measure of the π acidity of the phosphorus(III) ligand. We eliminate χ_d between eqns. (1) and (2) and obtain eqn. (3).

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$$\mathrm{prop}_1 = \frac{a_1}{a_2}\mathrm{prop}_2 + \left(b_1 - \frac{a_1b_2}{a_2}\right)\theta + \left(c_1 - \frac{a_1c_2}{a_2}\right)E_{\mathrm{ar}} + \left(d_1 - \frac{a_1d_2}{a_2}\right)\pi_{\mathrm{p}} + e_1 - \frac{a_1e_2}{a_2} \tag{3}$$

For the properties we consider, we can safely take the θ contributions to these plots to be small and negligible. Therefore, eqn. (3) becomes eqn. (4).

$$\mathrm{prop}_1 = \frac{a_1}{a_2}\mathrm{prop}_2 + \left(c_1 - \frac{a_1c_2}{a_2}\right)E_{\mathrm{ar}} + \left(d_1 - \frac{a_1d_2}{a_2}\right)\pi_{\mathrm{p}} + e_1 - \frac{a_1e_2}{a_2} \tag{4}$$

For the special case of the PR_3 ligands, eqn. (4) simplifies to eqn. (5) because both E_{ar} and π_{p} are zero for this family. Thus,

$$\mathrm{prop}_1 = \frac{a_1}{a_2}\mathrm{prop}_2 + e_1 - \frac{a_1e_2}{a_2} \tag{5}$$

the other ligands differ from PR_3 due to the E_{ar} and/or the π_{p} terms [compare eqns. (4) and (5)].

In the following example, we use as our properties ν_{CO} for η-Cp(CO)(L)Fe(COMe)^0, and $\Delta H°$ and $E°$ (229 K) for the Cp(CO)(L)Fe(COMe)$^{+/0}$ couple, all of which have been measured in our laboratories. The appropriate data are displayed in Tables 1 and 2. In the plot of ν_{CO} *versus* $E°$ (229 K) (Fig. 1A), we see a set of parallel lines. The parallel nature of the lines indicates that both properties are responding to a single variable parameter that is common to all the ligands. In the QALE model this parameter is χ_{d}. Although the lines have the same slopes they have different intercepts which demands that the remaining parameters differ from family to family by a constant value. For example, in Fig. 1A, the line for P(p-XC_6H_4)$_3$ lies below the line for PR_3 because of the 'aryl effect' which is constant (2.7) for P(p-XC_6H_4)$_3$ and zero for PR_3. (π_{p} is assumed to be zero for both P(p-XC_6H_4)$_3$ and PR_3.) Notice that the P(OR)$_3$ and P(O-p-XC_6H_4)$_3$ lie on two lines on the **other side** of the PR_3 line and the point for P(OCH$_2$)$_3$CEt lies above all the lines. This pattern of lines could be described by eqn. (6) without invoking

$$\mathrm{prop}_1 = \frac{a_1}{a_2}\mathrm{prop}_2 + \left(c_1 - \frac{a_1c_2}{a_2}\right)E_{\mathrm{ar}} + e_1 - \frac{a_1e_2}{a_2} \tag{6}$$

a π effect provided that the phosphites possess negative values of the 'aryl effect' parameter, E_{ar}. If this be the case, then the lines for the phosphites and P(p-XC_6H_4)$_3$ should always lie on opposite sides of the PR_3 line in the absence of a steric effect.

However, we observe a different ordering of the lines, when we plot ν_{CO} *versus* $\Delta H°$. In this case **all the lines lie below** the PR_3 line. Thus, the deviation of the phosphite data from the PR_3 lines is not explainable in terms of eqn. (6) along with a negative aryl effect for the phosphites. Let us see if the deviation of the phosphites is explainable in terms of a new π parameter, π_{p}, only [eqn. (7)].

$$\mathrm{prop}_1 = \frac{a_1}{a_2}\mathrm{prop}_2 + \left(d_1 - \frac{a_1d_2}{a_2}\right)\pi_{\mathrm{p}} + e_1 - \frac{a_1e_2}{a_2} \tag{7}$$

Thus according to eqn. (7), the deviation of the lines for the phosphites (Fig. 1A) from the PR_3 line would be attributable to π effects. This same pattern of lines (PR_3, P(OR)$_3$, P(O-p-XC_6H_4)$_3$, P(OCH$_2$)$_3$CEt) must then be observed for each property *versus* property plot. In Fig. 1B, we see that this is not the case, the point for P(OCH$_2$)$_3$CEt lies on the PR_3 line and the points for P(OR)$_3$ and P(O-p-XC_6H_4)$_3$ lie on a single line below the line for PR_3. Thus, we conclude that at least two parameters, in addition to χ_{d} and θ, are required to describe the phosphites.

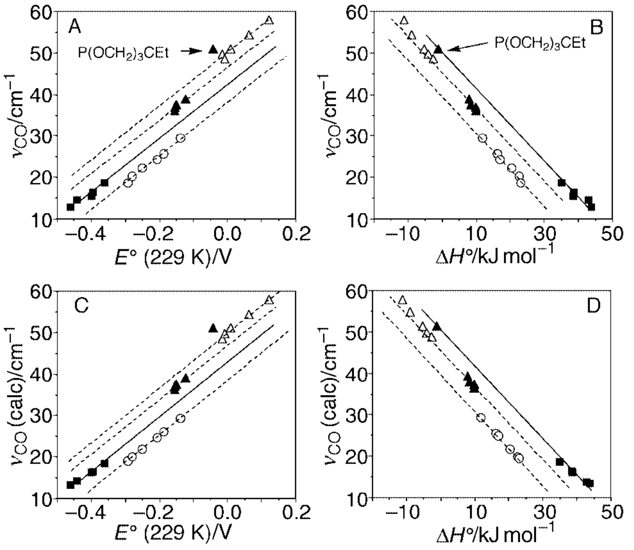

Fig. 1 (A) ν_{CO} (-1900 cm^{-1}) *versus* $E°$ (229 K), (B) ν_{CO} (-1900 cm^{-1}) *versus* $\Delta H°$, (C) ν_{CO} (calc) *versus* $E°$ (229 K), and (D) ν_{CO} (calc) *versus* $\Delta H°$. Values of ν_{CO}, $E°$ (229 K), and $\Delta H°$ are taken from Tables 1 and 2. ν_{CO} (calc) were calculated *via* regression analysis using the E_{ar} and π_{p} parameters presented in Table 1 *via* eqn. (4) where prop$_2$ is $E°$ (229 K) (Fig. 1C) or $\Delta H°$ (Fig. 1D). The sets of ligands are represented in the following way: PR_3 (filled squares), P(p-XC_6H_4)$_3$ (open circles), P(OR)$_3$ (filled triangles) and P(O-p-XC_6H_4)$_3$ (open triangles). P(OCH$_2$CH$_2$Cl)$_3$ is not included in this analysis.

Applying Occam's razor, we make the assumption that the first additional parameter for the phosphites is E_{ar} which apparently describes a property not restricted to aryl phosphines. For historical reasons and the sake of continuity we will retain the symbol E_{ar} to describe this effect. The second additional parameter (π_{p}) is then attributed to a π interaction between the phosphites and the metal to which they are attached. As pointed out above, the parallel lines in Figs. 1A and 1B require that E_{ar} and π_{p} be virtually constant for each family.

We are now ready to determine the values of E_{ar} and π_{p} for the phosphites. In eqn. (1), we can obtain the coefficients 'a', 'b', 'c' and 'e' through analysis of the data for the PR_3 and P(p-XC_6H_4)$_3$, alone. Since in the QALE model these coefficients should not change as new sets of ligands are added to the analysis, these coefficients are appropriate for the analysis of data for the phosphites; however, we do not know the values of χ_{d}, E_{ar}, nor π_{p} and its coefficient 'd' in eqn. (1). We now present a way to determine χ_{d} and E_{ar} values of the phosphites.

We make use of two properties that can be reasonably assumed to be independent of metal–phosphorus π-bonding. These properties are pK_{a} values of HPZ_3^+, and the ionization potential of PZ_3 as determined by photoelectron spectroscopy. Since π-bonding is not involved, the regression equations that describe these properties in terms of χ_{d}, θ, and E_{ar} for the phosphines (entries 1 and 2 in Table 3) must also be applicable to the phosphites as well. Using the experimental values and Tolman's cone angles for the P(OMe)$_3$ and P(OCH$_2$)$_3$CEt, we solved the two simultaneous equations (entries 1 and 2 in Table 3) to obtain initial values of χ_{d} (17.7 and 20.0 respectively) and E_{ar} (1.0 and 0.12, respectively). These initial values are used in an iterative process to arrive at the final values of χ_{d} and E_{ar} for these ligands.

The next step is to get an estimate of the π parameters for P(OMe)$_3$ and P(OCH$_2$)$_3$CEt. From the analysis of $\Delta S°$ and $\Delta H°$ for the η-Cp(CO)(L)Fe(COMe)$^{+/0}$ couple we know that the aryl effect in $\Delta G°$ vanishes at 320 K (the E_{ar} isoequilibrium temperature[83–86]). Thus, we calculated $\Delta G°$ (320 K) and analyzed the data for the phosphines in terms of χ_{d} and θ only (entry 6, Table 3). We then subtracted $b\theta$ from the calculated $\Delta G°$ (320 K) for the phosphines as well as P(OMe)$_3$ and P(OCH$_2$)$_3$CEt and plotted the difference *versus* χ_{d} (Fig. 2). The

Table 1 Ligands (PZ_3) used in this study, ν_{CO} for η-Cp(CO)(PZ_3)Fe(COMe)^0 where PZ_3 has formally C_3 symmetry, and stereoelectronic parameters (χ_d, θ, E_{ar}, π_p) of the phosphorus(III) ligands considered in this paper. The values of parameters shown in italics were determined by a least squares analysis as described in the text and the footnotes to this table

	PZ_3	$\nu_{CO} - 1900^a$/cm^{-1}	$\chi_d{}^b$	θ^c/°	$E_{ar}{}^d$	$\pi_p{}^e$
1	$P(OCH_2)_3CEt$	51.0	20.2	101	0.2	5.0
	[f]		*20.0*		*0.15*	*5.1*
2	$P(OMe)_3$	39.0	17.9	107	1.0	2.8
	[f]		*17.6*		*1.05*	*2.9*
3	$P(OEt)_3$	36.9	15.8	109	1.1	2.9
	[g]		*16.3*		*1.1*	*2.8*
4	$P(OBu)_3$	36.2	15.9	110	1.3	2.7
	[h]		*12.0*		*1.5*	*3.6*
5	$P(OCH_2CH_2Cl)_3$	45.6	20.3	110	0.4	3.6
	[h]		*20.5*		*0.45*	*3.6*
6	PMe_3	18.6	8.55	118	0	0
7	P(O-i-Bu)$_3$	37.5	15.5	120?	1.4	3.0
8	$PPhMe_2$		10.5	122	1.0	0
9	P(O-*p*-MeOC$_6$H$_4$)$_3$	48.5	22.5	128	1.4	3.8
10	P(O-*p*-MeC$_6$H$_4$)$_3$	49.7	22.4	128	1.4	4.1
11	P(O-C$_6$H$_5$)$_3$	50.9	23.6	128	1.3	4.1
	[i]		*23.6*		*1.4*	*4.2*
12	P(O-*p*-ClC$_6$H$_4$)$_3$	54.3	27.2	128	1.3	4 .0
13	P(O-*p*-CNC$_6$H$_4$)$_3$	57.9	31.7	128	1.0	3.7
14	P(O-i-Pr)$_3$	[j]	13.4	130	1.3	2.9
	[k]		*13.2*		*1.7*	*2.7*
15	PEt_3	16.5	6.3	132	0	0
16	P(*n*-Bu)$_3$	15.5	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)$_3$	[j]	5.7	143	0	0
24	P(*p*-Me$_2$NC$_6$H$_4$)$_3$		5.25	145	2.7	0
25	P(*p*-MeOC$_6$H$_4$)$_3$	18.7	10.5	145	2.7	0
26	P(*p*-MeC$_6$H$_4$)$_3$	20.3	11.5	145	2.7	0
27	$P(C_6H_5)_3$	22.3	13.25	145	2.7	0
28	P(*p*-FC$_6$H$_4$)$_3$	24.3	15.7	145	2.7	0
29	P(*p*-ClC$_6$H$_4$)$_3$	25.6	16.8	145	2.7	0
30	P(*p*-F$_3$CC$_6$H$_4$)$_3$	29.4	20.5	145	2.7	0
31	P(*m*-MeC$_6$H$_4$)$_3$		11.3	148	2.7	0
32	P(*m*-ClC$_6$H$_4$)$_3$		19.6	148	2.7	0
33	PPh$_2$(i-Pr)		9.6	150	1.7	0
34	PPh_2Cy		9.1	153	1.6	0
35	PPh(i-Pr)$_2$		7.1	155	1.7	0
36	P(i-Pr)$_3$	14.7	3.45	160	0	0
37	$PPhCy_2$		5.7e	162	1.6	0
38	P(*t*-Bu)(i-Pr)$_2$		2.5	167	0	0
39	PCy_3	12.8	1.4	170	0	0
40	P(*t*-Bu)Cy$_2$		0.9	174	0	0
41	P(*t*-Bu)$_3$		0	182	0	0
42	P(C$_6$H$_5$)$_2$(*p*-MeC$_6$H$_4$)		12.1	145	2.7	0

[a] ν_{CO} (cm^{-1}) values were measured in cyclohexane. The error is estimated to be ±0.2 cm^{-1}. [b] The χ_d values for the phosphites are reported in this paper. The χ_d values for the mixed alkyl phenyl phosphines are taken from ref. 83. The χ_d values for PR_3 and P(*p*-XC$_6$H$_4$)$_3$ are taken from ref. 52. [c] Tolman's cone angles are taken from ref. 51. [d] E_{ar} values are taken from refs. 53 and 83. [e] The π_p values for the phosphites are reported in this paper. [f] The least squares analyses were carried out in the following manner. First, the '*d*' coefficients were determined by regression analysis [*via* eqn. (1)] of sets of data ($\Delta H°$, $E°$ (229), ν_{CO}, Bodner's δ values, pK_a, and IP) comprised of the phosphines plus $P(OMe)_3$ and $P(OCH_2)_3CEt$. Employing Tolman's cone angles and using a least squares program, we then found the best fit values for χ_d, E_{ar}, and π_p for the phosphites. Combinations selected from these six sets of equations were used in the least squares analyses for the other phosphites as described below. [g] Regression equations for $\Delta H°$, $E°$ (229), ν_{CO}, Bodner's δ values, pK_a, and IP were used in the least squares analysis. [h] Regression equations for $\Delta H°$, $E°$ (229), ν_{CO} and Bodner's δ values were used in the least squares analysis. [i] Regression equations for $\Delta H°$, $E°$ (229), ν_{CO}, Bodner's δ values and pK_a were used in the least squares analysis. [j] Multiple ν_{CO} were observed. [k] Regression equations for $\Delta H°$, $E°$ (229), Bodner's δ values and pK_a were used in the least squares analysis.

deviation of the phosphite data from the line determined by the phosphines is a measure of the π acidity (and therefore π_p) of the phosphites. We arbitrarily set $\pi_p = 3.0$ for $P(OMe)_3$ and then calculated a value of $\pi_p = 5.0$ for $P(OCH_2)_3CEt$.

We still need the values of '*d*' (equations 1 and 2) for a given property. In the QALE model the addition of a new parameter (*i.e.* π_p) should not change significantly the coefficients of the other parameters. Thus, incorporation of the data for $P(OMe)_3$ and $P(OCH_2)_3CEt$ along with PR_3 and P(*p*-XC$_6$H$_4$)$_3$ into analysis of the aforementioned $\Delta H°$, ν_{CO}, and $E°$ (229) should leave the coefficients '*a*', '*b*', '*c*' and '*e*' unchanged and give an estimate of the respective '*d*' coefficients. Examination of entries 3, 6, 9 (phosphines only) and 4, 7, 10 (phosphines, $P(OMe)_3$ and $P(OCH_2)_3CEt$) in Table 3 shows that indeed this is very nearly the case. We now generate the first iteration of the QALE equations (entries 5, 8, and 11 in Table 3) for $\Delta H°$, $E°$ (229 K) and ν_{CO} by taking entries 3, 6 and 9 and adding to them the respective $d\pi_p$ term from entries 4, 7, and 10.

We now solve simultaneously the three QALE equations (entries 5, 8, and 11 in Table 3) for $P(OMe)_3$ and $P(OCH_2)_3CEt$ in terms of the parameters χ_d, E_{ar}, and π_p. This gives values (which we use in subsequent analyses) for $P(OMe)_3$ ($\chi_d = 17.9$,

Table 2 Standard reduction potentials,[a] and standard entropies and enthalpies of reduction for η-Cp(CO)(L)Fe(COMe)$^{+/0}$ couple

Ligand[b]	$\Delta S°$/J deg^{-1} mol^{-1}	$\Delta H°$/kJ mol^{-1}	$E°$/V (229 K)	$E°$/V (252 K)	$E°$/V (264 K)	$E°$/V (273 K)	$E°$/V (293 K)
1	−22.7 ± 2.1	−1.10 ± 0.62	−0.0418	−0.0493	−0.0504	−0.0535	−0.0567
2	−17.3 ± 1.6	7.97 ± 0.41	−0.1235	−0.1271	−0.1309	−0.1318	−0.1344
3	−22.2 ± 0.9	9.92 ± 0.20	−0.1551	−0.1612	−0.1633	−0.1658	−0.1697
4	−22.4 ± 0.8	9.81 ± 0.22	−0.1548	−0.1601	−0.1630	−0.1656	−0.1693
5	−12.0 ± 1.6	4.00 ± 0.42	−0.0703	−0.0716	−0.0746	−0.0750	−0.0782
7	−26.5 ± 1.9	8.41 ± 0.49	−0.1494	−0.157	−0.1607	−0.1621	−0.1667
9	−18.4 ± 1.1	−2.69 ± 0.30	−0.0159	−0.0198	−0.0231	−0.0247	−0.0277
10	−21.5 ± 1.4	−4.00 ± 0.36	−0.0090	−0.0153	−0.0165	−0.0186	−0.0237
11	−18.7 ± 0.4	−5.21 ± 0.11	0.0094	0.0050	0.0028	0.0012	−0.0032
12	−12.4 ± 0.8	−9.01 ± 0.21	0.0637	0.0611	0.0598	0.0577	0.0556
13	2.07 ± 0.38	−11.3 ± 0.10	0.1221	0.1223	0.1229	0.1228	0.1235
14	−25.2 ± 1.2	12.2 ± 1.30	−0.1867	−0.1926	−0.1955	−0.1991	−0.2030

[a] Errors are ±0.0007 V. [b] The numbers refer to the entries in Table 1.

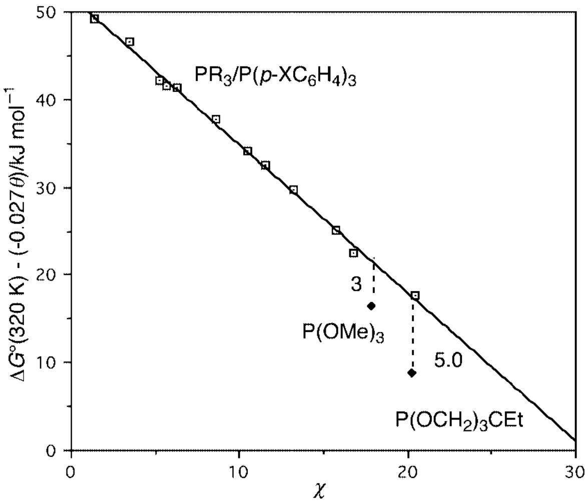

Fig. 2 A plot of $\Delta G°$ (320 K) − (−0.027θ) *versus* χ_d for PR$_3$ and P(p-XC$_6$H$_4$)$_3$. The deviation of the points for P(OMe)$_3$ and P(OCH$_2$)$_3$CEt from the line is a measure of their π acidity (π_p).

E_{ar} = 1.0, π_p = 2.8) and P(OCH$_2$)$_3$CEt (χ_d = 20.2, E_{ar} = 0.2, π_p = 5.0). These values are quite similar to what we estimated initially and give us confidence that we can determine the parameters for the other phosphites by solving the same set of simultaneous equations using the appropriate experimental data. (We had to substitute the pK_a eqn. (entry 1 in Table 3) for the ν_{CO} equation for P(O-i-Pr)$_3$ since three ν_{CO} were observed for η-Cp(CO)[P(O-i-Pr)$_3$]FeCOMe.) The calculated parameters are displayed in Table 1.

We point out that the results are not particularly sensitive to the value of θ used in the simultaneous equations. For example, we show in Table 4 the calculated values of χ, E_{ar}, and π_p using different values of θ. The results, which are shown in Table 4 for P(OMe)$_3$ and P(O-i-Bu)$_3$, reveal minor changes in the parameters over a range of 20° in θ.

We checked the validity of the phosphite parameters by using a linear regression analysis of combinations of six sets of data ($\Delta H°$, $E°$ (229 K), ν_{CO}, Bodner's δ values, pK_a values of HPZ$_3^+$, and IP of PZ$_3$). We did the analysis in the following manner. Using the experimental data and the parameters for the phosphines and P(OMe)$_3$ and P(OCH$_2$)$_3$CEt (our standard phosphites) we performed the regression analyses on each of the six properties in order to establish the 'd' coefficients for each of the regression equations. We then took the six regression equations and did a least squares analysis to determine the best fit values of χ_d, E_{ar}, and π_p for P(OMe)$_3$ and P(OCH$_2$)$_3$CEt. Not surprisingly, the least squares analysis gave values for P(OMe)$_3$ and P(OCH$_2$)$_3$CEt (presented in italics in Table 1) in excellent agreement with the original parameters. We then performed the least squares analyses on combinations of these properties (see footnotes for Table 1) for other phosphites (P(OEt)$_3$, P(OBu)$_3$, P(OCH$_2$CH$_2$Cl)$_3$, P(O-C$_6$H$_5$)$_3$, and P(O-i-Pr)$_3$) where we have sufficient data. The values of the parameters thereby obtained, are in excellent agreement with the parameters obtained *via* the simultaneous equations. The one exception is P(OBu)$_3$ where the linear regression analysis gives results that are quite different from the parameters for P(OEt)$_3$. Normally, P(OBu)$_3$ and P(OEt)$_3$ behave similarly—therefore we believe that Bodner's δ value for P(OBu)$_3$ is anomalous.

An examination of the χ_d and π_p parameters for the phosphites is insightful. The χ_d values of the P(OR)$_3$ indicate that their σ donor capacities are as good as those for P(p-XC$_6$H$_4$)$_3$. This observation is consonant with the similarity of the pK_a values of P(OR)$_3$ and P(p-XC$_6$H$_4$)$_3$. The π acidity of the P(OR)$_3$ is almost invariant, ranging between 2.7 and 3.0. This is in agreement with our analysis of Fig. 1. There are two exceptions: P(OCH$_2$CH$_2$Cl)$_3$, which displays an enhanced π acidity, π_p = 3.6, and P(OCH$_2$)$_3$CEt, which is a reasonably good electron donor (χ_d = 20.2) (not much different than P(OMe)$_3$, (χ_d = 17.9) and a strong π acid (π_p = 5.0).

P(O-p-XC$_6$H$_4$)$_3$ are poorer σ donors than P(OR)$_3$. Their σ donor capacity is influenced by the *para* substituent in the expected manner with P(O-p-MeOC$_6$H$_4$)$_3$ and P(O-p-MeC$_6$H$_4$)$_3$ being the best σ donors and P(O-p-NCC$_6$H$_4$)$_3$ being the poorest. It is noteworthy that the π-acidity of the aryl phosphites appears to be almost invariant with π_p ranging between 3.7 and 4.2 again in agreement with the analysis of Fig. 1.

P(O-p-XC$_6$H$_4$)$_3$ and most P(OR)$_3$ exhibit significant 'aryl effects' that are relatively invariant, with E_{ar} values between 1.0 and 1.4. The smallest aryl effects are observed for P(OCH$_2$)$_3$CEt and P(OCH$_2$CH$_2$Cl)$_3$ (E_{ar} = 0.2 and 0.4 respectively).

We used the parameters in Table 1 and eqn. (4) to calculate the data necessary to simulate property *versus* property plots shown Figs. 1A and 1B. The results, which are displayed in Figs. 1C and 1D, are virtually identical to Figs. 1A and 1B.

We recently described another diagnostic test for adequacy of a set of stereoelectronic parameters.[86] If a set of parameters adequately describes the stereoelectronic properties of phosphorus(III) ligands, then the regression equations resulting from the use of these parameters in the analysis of $\Delta H°$, $\Delta S°$ and/or $E°$ must be able to reproduce the experimental graph of $E°/T$ *versus* $1/T$. Although the parameters for the phosphites are in part based on $\Delta H°$ and $\Delta S°$ (this would lead to circular reasoning if this were the only input), they also have input from ν_{CO}, pK_a, and IP (as described earlier), which are independent of $\Delta H°$ and $\Delta S°$. In Fig. 3, we compare the plots of experimental and calculated $E°/T$ *versus* $1/T$. Clearly, they are virtually the same; thus, we conclude that the parameters are valid descriptors.

We used these new phosphite parameters to analyze (*via* eqn. 8, where θ_{st} is the steric threshold and λ is the switching

$$\text{prop} = a\chi + b(\theta - \theta_{st})\lambda + cE_{ar} + d\pi_p + e \qquad (8)$$

Table 3 Results of the regression analyses of the properties indicated below. The data for PR_3, PPh_iR_{3-i}, and $P(p\text{-}XC_6H_4)_3$ were used in the analyses of pK_a and IP. Only the data for PR_3 and $P(p\text{-}XC_6H_4)_3$ were used in the analyses of entries 3–7

	Property	*n*	r^2	*a*	*b*	*c*	*d*	*e*	PZ_3[e]
1	pK_a[a]	16	0.980	−0.58 ± 0.06	−0.036 ± 0.011	−0.41 ± 0.25	—	17.1 ± 1.9	6, 8, 15–18, 20, 23, 25, 30, 39, 41
2	IP[a]	14	0.962	0.115 ± 0.007	—	−0.49 ± 0.03	—	7.64 ± 0.06	6, 8, 15, 16, 18, 24–30, 36, 41
3	$\Delta H°$/kJ mol^{-1}[b]	12	0.998	−1.16 ± 0.08	0.023 ± 0.018	−3.7 ± 0.3	—	42.3 ± 2.8	6, 15, 16, 23, 25–30, 36, 39
4	$\Delta H°$/kJ mol^{-1}[b]	14	0.999	−1.17 ± 0.08	0.02 ± 0.02	−3.7 ± 0.3	−4.4 ± 0.2	42.9 ± 2.7	1, 2, 6, 15, 16, 23, 25–30, 36, 39
5	$\Delta H°$/kJ mol^{-1}[b]			−1.16	0.023	−3.7	−4.4	42.3	
6	$E°$/V (229 K)[b]	12	0.998	0.0159 ± 0.0007	0.00014 ± 0.00016	0.011 ± 0.003		−0.51 ± 0.02	6, 15, 16, 23, 25–30, 36, 39
7	$E°$/V (229 K)[b]	14	0.999	0.0159 ± 0.0006	0.0001 ± 0.0001	0.011 ± 0.003	0.027 ± 0.002	−0.51 ± 0.02	1, 2, 6, 15, 16, 23, 25–30, 36, 39
8	$E°$/V (229 K)[b]			0.0159	0.00014	0.011	0.027	−0.51	
9	ν_{CO}[c]/cm^{-1}	11	0.998	1.04 ± 0.03	0.034 ± 0.007	−0.87 ± 0.12		5.5 ± 1.1	6, 15, 16, 25–30, 36, 39
10	ν_{CO}[c]/cm^{-1}	13	0.999	1.05 ± 0.05	0.040 ± 0.010	−0.92 ± 0.19	4.3 ± 0.1	4.7 ± 1.6	1, 2, 6, 15, 16, 25–30, 36, 39
11	ν_{CO}[c]/cm^{-1}			1.04	0.034	−0.87	4.3	5.5	
12	$\Delta G°$ (320 K)[d]/kJ mol^{-1}	12	0.997	−1.69 ± 0.03	−0.027 ± 0.013	—		52 ± 2	6, 15, 16, 23, 25–30, 36, 39

[a] The datum for $P(p\text{-}Me_2NC_6H_4)_3$ was not included in the analysis. [b] From electrochemical measurements reported herein. [c] Data reported herein. [d] Calculated from the $\Delta H°$ and $\Delta S°$ values reported in ref. 76. [e] The numbers refer to the entries in Table 1.

Table 4 Values of χ, E_{ar}, π_p for selected values of θ determined by solving simultaneously three variations of eqn. (1) whose coefficients are listed in entries 5, 8 and 11 in Table 3. The appropriate experimental data are listed in Table 1. The values of the parameters used in the analyses shown later in this paper are in bold

	L	θ	χ	E_{ar}	π_p
1	$P(OMe)_3$	97	18.1	0.9	2.8
2	$P(OMe)_3$	**107**	**17.9**	**1**	**2.8**
3	$P(OMe)_3$	117	17.8	1.1	2.8
4	$P(O\text{-}i\text{-}Bu)_3$	110	15.6	1.3	3.1
5	$P(O\text{-}i\text{-}Bu)_3$	**120**	**15.5**	**1.4**	**3.0**
6	$P(O\text{-}i\text{-}Bu)_3$	130	15.3	1.6	3.0

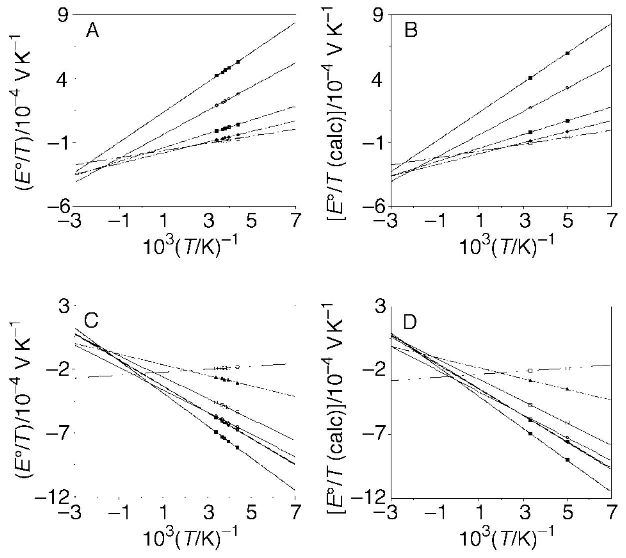

Fig. 3 Plots of $E°/T$ *versus* $1/T$. (A) Experimental values for $P(O\text{-}P\text{-}XC_6H_4)_3$. (B) Calculated values (from entries 18 and 19 in Table 6) for $P(O\text{-}p\text{-}XC_6H_4)_3$. (C) Experimental values for $P(OR)_3$. (D) Calculated values (from entries 18 and 19 in Table 6) for $P(OR)_3$.

function) 32 sets of data that are large enough to support a four parameter analysis (or a five parameter analysis if a steric threshold were present). We used all the parameters in each analysis even though in some cases the contribution of one or more parameters is statistically indistinguishable from zero. The results of these analyses are presented in Table 6. We note that out of nearly 600 data, we found only twelve outliers. There is an excellent fit of the QALE model to each set of data with a median r^2 of 0.980.

These analyses give chemically reasonable results (see Table 5 and Table 6). ν_{CO} increases as the π acidity of the phosphorus(III) ligand increases, and decreases as the σ donicity increases. ν_{CO} is relatively insensitive to steric effects. $\Delta S°$ and $\Delta H°$ for the reduction of η-Cp(CO)(L)Fe(COMe)$^+$ both become more negative as the π acidity of the phosphorus(III) ligand increases (entries 19 and 20). These observations suggest that π acidity is more important in the Fe(II) state than in the Fe(III) state and that the enhanced π bonding increases the rigidity of the Fe(II) complex. The dissociation of CO from ruthenium complexes is dominated by steric factors which accelerate the reaction as the size of the ancillary phosphorus(III) ligand increases (entries 27 and 28). The entering ligand dependent substitution reactions (entries 29–32) are all accelerated as the σ donicity of the phosphorus(III) ligand increases and inhibited as the size of the entering ligand increases. There is virtually no statistically significant evidence for a π effect in these reactions.

The one surprising result is that the rate of addition of PZ_3 to $(\eta^5\text{-}C_6H_7)Fe(CO)_3^+$ shows a large inhibition because of π-effects. On the other hand, the rate is enhanced by increasing σ donicity and inhibited by increasing size as expected.

Table 5 Sets of physiochemical data that were analyzed in this paper

	System	Property	Ligands[a]	Ref.
1	η-Cp(CO)(L)Fe(COMe)^0	ν_{CO}–1900 cm^{-1}	1–7, 9–13, 15, 16, 25–30, 36, 39	This paper
2	η-Cp(CO)$_2$(L)Mn^0	ν_{CO}–1800 cm^{-1}	2–6, 10, 11, 15, 16, 26, 27, 36, 39	87
3	η-Cp(CO)$_3$(L)V^0	ν_{CO}–1900 cm^{-1}	2–6, 10, 11, 15, 16, 26, 27, 36, 39	87
4	[1,4-(MeO$_2$)$_2$(C$_6$H$_4$)]Cr(CO)$_2$L	ν_{CO}–1900 cm^{-1}	2–6, 10, 11, 15, 16, 27, 36, 39	87
5	1,3,5-Me$_3$(C$_6$H$_3$)Cr(CO)$_2$L	ν_{CO}–1800 cm^{-1}	2–6, 10, 11, 15, 16, 27, 39	87
6	(CO)$_3$NiL	ν_{CO}–2000 cm^{-1}	1–7, 9–13, 15, 16, 25–30, 36, 39	51
7	(CO)$_4$RuL	ν_{CO}–2000 cm^{-1}	1–3, 6, 11, 15, 16, 25–27, 29, 39, 41	88, 89
8	η-(C$_5$H$_4$CO$_2$Me)Co(CO)L	ν_{CO}–1900 cm^{-1}	2, 3, 6, 11, 16, 25–27, 31, 39	71
9	[OsCl$_2$(cymene)]L	^{187}Os chemical shift +2000 ppm	2–4, 6, 8, 11, 14, 16, 18, 27, 31, 36, 39	90
10	(CO)$_3$NiL	^{13}CO chemical shift	1–6, 8, 11, 12, 14–20, 22–29, 36, 39, 41	47
11	(CO)$_5$CrL	^{13}CO (*cis*) chemical shift	1–3, 5, 6, 8, 11, 12, 14–18, 20, 23, 27, 34, 39	47
12	(CO)$_5$CrL	^{13}CO (*trans*) chemical shift	1–3, 5, 8, 11, 12, 14–18, 20, 23, 27, 34, 39	47
13	(CO)$_5$MoL	^{13}CO (*cis*) chemical shift	1–3, 5, 8, 11, 15–18, 20, 27, 39, 41	47
14	(CO)$_5$MoL	^{13}CO (*trans*) chemical shift	1–3, 5, 8, 11, 15–18, 20, 27, 39, 41	47
15	(dmg)$_2$(Me)CoL	$J_{H,P}$	2, 6, 8, 11–17, 20, 24–29, 33, 36, 39	91
16	η-Cp(CO)(L)Fe(COMe)$^{+/0}$	$E°$ (229 K)	1–23, 25–30, 33–37, 39	83, 84, 86
17	η-Cp(CO)$_2$MnL$^{+/0}$	$E°$	1–3, 6, 8, 11, 14–18, 20, 22, 25–30, 39	92
18	PZ$_3$	Ionization potential (IP)	1–3, 6, 8, 15, 16, 18, 24–30, 36, 41	93–100
19	η-Cp(CO)(L)Fe(COMe)$^{+/0}$	$\Delta S°$	1–23, 25–30, 33–37, 39	83, 84, this paper
20	η-Cp(CO)(L)Fe(COMe)$^{+/0}$	$\Delta H°$	1–23, 25–30, 33–37, 39	83, 84, this paper
21	HPZ$_3^+$	pK_a	1–3, 6, 8, 11, 14–18, 20, 23, 24–30, 39, 41	40–43
22	η-CpRu(COD)Cl + 2L = η-CpRuL$_2$Cl + COD	$-\Delta H_{rx}$	1, 6, 8, 11, 14–16, 18, 25, 26, 28–30	101, 102
23	η-Cp*Ru(COD)Cl + 2L = η-Cp*RuL$_2$Cl + COD	$-\Delta H_{rx}$	1, 6, 8, 11, 14–16, 18, 25, 26, 28–30	101, 103
24	[MePt(PhMe$_2$)(THF)]$^+$ + L = [MePt(PhMe$_2$)L]$^+$ + THF	$-\Delta H_{rx}$	1–3, 5, 6, 9, 11, 13–15, 18, 27, 36, 41	104
25	[(η^3-pentenyl)NiMe]$_2$ + 2L = 2(η^3-pentenyl)Ni(Me)L	$-\Delta H_{rx}$	3, 4, 6, 8, 11, 14–17, 20, 27, 36, 38, 40	105
26	(η^5-C$_6$H$_7$)Fe(CO)$_3^+$ + L = η^4-(5-LC$_6$H$_7$)Fe(CO)$_3^+$	log ($k/k_{P(OPh)_3)}$	2–4, 11, 16, 17, 25–29, 39, 42	106
27	Ru(CO)$_4$L + L′ = Ru(CO)$_3$LL′ + CO	log k	1, 3, 6, 11, 15, 16, 20, 25–29, 39, 41	88, 89
28	Ru(CO)$_3$(L)(SiCl$_3$)$_2$ + L′ = Ru(CO)$_2$(L)(L′)(SiCl$_3$)$_2$ + CO	log k	2, 4, 8, 11, 12, 16, 18, 25–29, 31–33	107
29	Ru$_6$C(CO)$_{17}$ + L = Ru$_6$C(CO)$_{16}$L + CO	log k	1–3, 11, 14, 16, 25–30, 39	63
30	η-(C$_5$H$_4$CO$_2$Me)Co(CO)$_2$ + L = η-(C$_5$H$_4$CO$_2$Me)Co(CO)L + CO	log k	2, 3, 6, 8, 11, 16, 18, 25–27, 31, 39	71
31	(μ-H)$_2$Os$_3$(CO)$_{10}$ + L = (μ-H)(H)Os$_3$(CO)$_{10}$L	log k	1, 3, 11, 14, 15, 25–31, 39, 41	44
32	Co(CO)$_3$(NO) + L = Co(CO)$_2$(NO)L + CO	log k	2, 3, 11, 15–17, 20, 22, 27, 39	108

[a] Numbers refer to the entry numbers in Table 1.

Table 6 Results of regression analyses [*via* eqn. (8)] of the physiochemcial properties listed in Table 5. Entry numbers refer to the entries in Table 5

	n	r^2	*a*	*b*	*c*	*d*	*e*	θ_{st}	Ligands excluded from the analyses
1	22	0.9993	1.05 ± 0.03 (58%)[a]	0.036 ± 0.008 (5%)	−0.90 ± 0.14 (5%)	4.3 ± 0.1 (32%)	5 ± 1		Ligands without C_3 symmetry
2	13	0.988	1.8 ± 0.3 (67%)	0.17 ± 0.04 (17%)	−1.6 ± 1.0 (7%)	1.3 ± 1.0 (9%)	96 ± 6		Ligands without C_3 symmetry
3	13	0.994	0.9 ± 0.2 (65%)	0.01 ± 0.02 (2%)	0.4 ±0.5 (4%)	2.2 ± 0.5 (29%)	43 ± 4		Ligands without C_3 symmetry
4	12	0.982	1.1 ± 0.3 (77%)	0.03 ± 0.04 (6%)	0.5 ± 1.0 (4%)	1 ± 1 (13%)	11 ± 6		Ligands without C_3 symmetry
5	11	0.974	2.0 ± 0.5 (74%)	0.15 ± .06 (16%)	−2 ± 2 (8%)	0.4 ± 1.6 (2%)	44 ± 10		Ligands without C_3 symmetry
6	22	0.999	0.94 ± 0.03 (68%)	−0.018 ± 0.008 (3%)	0.1 ± 0.1 (5%)	2.6 ± 0.1 (24%)	3 ± 1		Ligands without C_3 symmetry
7	12	0.994	1.1 ± 0.1 (63%)	0.06 ± 0.02 (11%)	−2.4 ± 0.4 (15%)	0.9 ± 0.3 (11%)	45 ± 3		Ligands without C_3 symmetry, $P(OC_6H_5)_3$
8	12	0.989	1.7 ± 0.2 (73%)	0.09 ± 0.04 (13%)	0.5 ± 0.7 (1%)	2.0 ± 0.7 (13%)	0 ± 7		
9	13	0.972	−20 ± 6 (37%)	10 ±1 (33%)	74 ± 20 (16%)	42 ± 16 (14%)	−37 ± 50	130	
10	27	0.985	−0.18 ± 0.01 (80%)	−0.005 ±0.003 (7%)	−0.03 ± 0.05 (1%)	−0.14 ± 0.05 (12%)	7.4 ± 0.4		
11	18	0.990	−0.17 ± 0.01 (80%)	0.005 ± 0.003 (6%)	0.12 ± 0.07 (5%)	−0.07 ± 0.05 (9%)	6.3 ± 0.4		$PPhCy_2$ and P(*t*-Bu)$_3$
12	17	0.978	−0.22 ± 0.02 (69%)	−0.010 ± 0.005 (6%)	0.70 ± 0.10 (25%)	0 ± 0.08 (0%)	12.4 ± 0.7		$PPhCy_2$ and P(*t*-Bu)$_3$
13	14	0.973	−0.23 ± 0.04 (69%)	−0.007 ± 0.006 (8%)	0.3 ± 0.2 (10%)	0.2 ± 0.1 (13%)	7.7 ± 0.9		
14	14	0.93	−0.25 ± 0.07 (56%)	−0.015 ± 0.009 (11%)	0.9 ± 0.3 (23%)	0.20 ± 0.20 (10%)	12 ± 2		
15	18	0.965	0.14 ± 0.02 (43%)	0.063 ± 0.005 (42%)	0.11 ± 0.06 (4%)	−0.19 ± 0.06 (11%)	136.0 ± 0.2	122	
16	35	0.999	0.0159 ± 0.0002 (73%)	0.00020 ± 0.00005 (2%)	0.0110 ± 0.0009 (5%)	0.0271 ± 0.0008 (20%)	−0.519 ± 0.008		
17	18	0.992	0.018 ± 0.001 (63%)	0.0007 ± 0.0003 (6%)	0.002 ± 0.006 (2%)	0.042 ± 0.004 (29%)	0.17 ± 0.04		$P(OCH_2)_3CEt$
18	17	0.981	0.112 ± 0.009 (64%)	0 ± 0.002 (0%)	−0.47 ± 0.04 (33%)	0.02 ± 0.03 (3%)	7.7 ± 0.4		
19	35	0.972	1.71 ± 0.08 (39%)	0.15 ± 0.02 (7%)	−11.7 ± 0.4 (24%)	−8.2 ± 0.3 (30%)	−29 ± 3		
20	35	0.999	−1.16 ± 0.02 (51%)	0.013 ± 0.007 (1%)	−3.7 ±0.1 (15%)	−4.5 ± 0.1 (33%)	43 ± 1		
21	22	0.984	−0.62 ± 0.04 (79%)	−0.041 ± 0.008 (16%)	−0.2 ± 0.2 (3%)	0.07 ± 0.12 (2%)	18 ± 1		
22	13	0.975	−0.0 ± 0.1 (0%)	−0.9 ± 0.1 (68%)	−1.1 ± 0.6 (24%)	−0.1 ± 0.4 (8%)	37 ± 1	135	$P(C_6H_5)_3$ and $P(OMe)_3$
23	12	0.972	−0.2 ± 0.1 (15%)	−0.75 ± 0.08 (57%)	1.8 ± 0.6 (20%)	0.4 ± 0.3 (8%)	33 ± 1	127	$P(C_6H_5)_3$ and $P(OMe)_3$
24	14	0.977	−0.35 ± 0.08 (27%)	−0.41 ± 0.02 (61%)	1.1 ± 0.4 (7%)	0.4 ± 0.3 (5%)	30 ± 1	121	PCy_3
25	15	0.953	0.2 ± 0.2 (16%)	−0.17 ± 0.03 (40%)	−2.0 ± 0.8 (20%)	1.6 ± 0.6 (24%)	48 ± 6		
26	13	0.995	−0.26 ± 0.03 (35%)	−0.129 ± 0.007 (32%)	0.6 ± 0.1 (10%)	−0.95 ± 0.09 (23%)	9.4 ± 0.2	128	
27	14	0.986	0.02 ± 0.02 (10%)	0.139 ± 0.008 (67%)	0.16 ± 0.06 (9%)	−0.12 ± 0.06 (14%)	−3.8 ± 0.1	160	
28	15	0.976	−0.00 ± 0.02 (0%)	0.064 ± 0.007 (71%)	0.10 ± 0.08 (11%)	−0.07 ± 0.07 (18%)	−4.9 ± 0.2	120	$P(OCH_2)_3CEt$
29	13	0.985	−0.23 ± 0.04 (31%)	−0.20 ± 0.01 (59%)	−0.4 ± 0.2 (7%)	0.1 ± 0.1 (3%)	7.5 ± 0.5	122	
30	12	0.952	−0.09 ± 0.02 (40%)	−0.043 ± 0.005 (44%)	0.06 ± 0.07 (3%)	−0.17 ± 0.08 (13%)	2.7 ± 0.2	120	
31	14	0.988	−0.27 ± 0.02 (44%)	−0.28 ± 0.01 (48%)	−0.24 ± 0.09 (4%)	0.11 ± 0.06 (4%)	6.1 ± 0.2	156	
32	10	0.995	−0.19 ± 0.03 (63%)	−0.052 ± 0.004 (34%)	0.03 ± 0.09 (1%)	−0.03 ± 0.09 (2%)	0.7 ± 0.2	122	

[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 times range.

Conclusions

We have determined values for χ_d, E_{ar}, and π_p of phosphite ligands. χ_d for $P(OR)_3$ depends on the nature of the pendent alkoxy group whereas the π acidity is relatively invariant except for $P(OCH_2CH_2Cl)_3$ and $P(OCH_2)_3CEt$; the latter ligand is the most π acidic ligand considered in this study. χ_d for $P(O\text{-}p\text{-}XC_6H_4)_3$ is dependent on the *para* substituent whereas π_p appears to be invariant and independent of the *para* substituent. With identification of the parameters needed to describe the stereoelectronic properties of the phosphite ligands, and the determination of their values, we have incorporated the phosphites into the QALE model. Thus, QALE now accommodates PR_3 (including the large ligands such as PCy_3), $P(p\text{-}XC_6H_4)_3$, PPh_iR_{3-i}, and the π acidic ligands $P(OR)_3$ and $P(O\text{-}p\text{-}XC_6H_4)_3$. We point out that the QALE model is general and applicable to the analysis of kinetic, spectroscopic and thermodynamic properties including entropy. We report the QALE analyses (median $r^2 = 0.982$) of 32 sets of data.

We are currently extending these studies to other π acidic ligands.

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.[43]

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 agree with the original measurements. This leads to an error of ±0.0007 V in the $E°$ values.

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