Examination of Drago's E_B and C_B Parameters for Phosphines through the Quantitative Analysis of Ligand Effects (QALE)

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Comparison of pairs of physiochemical properties of phosphines and their complexes demonstrates that, in general, *at least* four independent stereoelectronic parameters are in general required to describe the variations in these properties. Consequently, any two-parameter model such as Drago's *E*/*C* model will have limited use in correlation analyses involving phosphines. The QALE analysis of E_B and C_B shows that these parameters are linear combinations of the QALE parameters χ and θ, with a small contribution from E_{ar}. Thus, successful application of the *E*/*C* model will be restricted to the situation where the property being analyzed depends primarily on χ and θ.

Introduction

Drago has used his electrostatic/covalent (*E*/*C*) model to analyze ligand effect data for various physiochemical properties of phosphines and phosphine complexes.[1−3] This model supposedly differs in a very fundamental way from the model we call the Quantitative Analysis of Ligand Effects (QALE).[4,5] In his model, Drago asserts that two parameters are necessary to describe physiochemical properties of ligands and their complexes.[6] One of these parameters corresponds to the portion of their bonding that can be ascribed to an electrostatic (E_A/E_B) interaction and the other to the covalent (C_A/C_B) interaction between the Lewis base (e.g. phosphines) and a Lewis acid. These parameters have been assigned to a large number of Lewis acids and bases.[2] Physiochemical properties can then be predicted or new parameters can be determined by analyzing appropriate sets of data using the *E*/*C* equation (1). Deviations of the properties

$$\text{property} = E_AE_B + C_AC_B + W \qquad (1)$$

of ligands from the behavior predicted by the *E*/*C* analysis is interpreted as an indication of the intervention of steric effects and/or π-acidity.[3] The *E*/*C* model is thought to be able to accommodate data from disparate families of ligands (e.g. phosphines and pyridines) into a single analysis. In fact, it is argued that reliable analyses of ligand effect data can only be obtained when disparate families of ligands are mixed because of the high correlation between the E and C parameters within a single family.[3] Drago notes that the *E*/*C* model is most successful in the analyses of enthalpies of reaction, enthalpies of activation, spectral properties, and *E*° values. log *k* is often poorly accommodated by the *E*/*C* model.[3]

On the other hand, the QALE model[4,5] builds on the idea that there is an electronic parameter (χ[7,8]) that describes the intrinsic electron donor capacity of a ligand and a steric parameter (cone angle θ[8]) that describes the size of the ligand. Novel features of the QALE model are (a) provisions for a steric threshold via the parameter $(\theta - \theta_{st})\lambda$, at which point the nature of the steric effect abruptly changes,[9] and (b) the inclusion of the aryl effect parameter (E_{ar}), which is related to the number of pendent aryl groups but not their para substituents.[10] The QALE equation (2) expresses the

$$\text{property} = a\chi + b\theta + c(\theta - \theta_{st})\lambda + dE_{ar} + e \qquad (2)$$

relationship between a physiochemical property and these parameters.[4] QALE has been used in studies involving ligands of the type AR_3, where R may be any mix of alkyl, aryl, or hydrogen and A can be C,[11−13] N,[13] P,[4,5,13] As,[13] and Si.[13,14] QALE has even been extended to thioethers, SR_2.[13,15,16] Nearly 200 sets of thermodynamic, kinetic, spectroscopic, and structural data have been analyzed; the median r^2 value is around 0.975 for these analyses.[13] In the current version there is no

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provision for π-acidity or for handling collectively data for distinctly different families of ligands.

Drago suggested that in the QALE model there is an overreliance on steric factors and wonders if the good correlations obtained via the QALE analyses are fortuitous and therefore meaningless.[3] The observation that, in several instances,[3,13] both the *E*/*C* and QALE models give excellent results when applied to the same sets of data suggested to us that there must be some connection between the two models. In this paper, we show that, in the general case, at least four parameters are needed to describe the stereoelectronic properties of phosphine ligands. Furthermore, we go on to show that E_B and C_B values for phosphines are linear combinations of primarily χ and θ with a smaller contribution from E_{ar}. Therefore, properties that are best described by the *E*/*C* model are those that depend primarily on χ and/or θ.

Results and Discussion

What is the Minimum Number of Parameters and the Forms of These Parameters That Are Necessary To Describe the Variations of Physiochemical Properties of Phosphines and Phosphine Complexes? The answer to this question lies at the center of the study of ligand effects. In general, we can determine the minimum number of ligand stereoelectronic parameters that are necessary to describe the variations in physiochemical properties by examining a series of plots of one property versus another property for the same families of ligands. These properties may be for the free or complexed ligand. To simplify our arguments, we restrict our discussion to two families of phosphine ligands, namely the para-substituted triarylphosphines, PAr_3, and the trialkylphosphines, PR_3. The only assumption that we make is that the variations in the two properties ($prop_1$ and $prop_2$) are linearly related to a set of parameters (x_1, x_2, x_3, ..., x_n) of unknown dimensions (eqs 3 and 4) and that

$$\mathrm{prop}_1 = ax_1 + bx_2 + cx_3 + \ldots C \tag{3}$$

$$\mathrm{prop}_2 = a'x_1 + b'x_2 + c'x_3 + \ldots C' \tag{4}$$

these equations are different: We relate $prop_1$ to $prop_2$ by eliminating x_1 between them, and we get eq 5.

$$\mathrm{prop}_1 = (a/a')\mathrm{prop}_2 + (b - ab'/a')x_2 + (c - ac'/a')x_3 + \ldots (C - C'/a') \tag{5}$$

For the two properties ($prop_1$ and $prop_2$) to be linearly related, eq 5 must reduce to

$$\mathrm{prop}_1 = A(\mathrm{prop}_2) + \mathrm{const} \tag{6}$$

For this to occur, one of the following must be true.

(a) Each property depends on one and the same parameter. This is the simplest situation.

(b) Each property depends on a number of parameters, but only one varies while the others are constant.

(c) Each property depends on the same group of parameters, and the coefficients of each parameter are in the same ratio ($a_1/a_2 = b_1/b_2$...). In this case all the coefficients in eq 5 become zero except a/a' for the first term.

(d) There is sufficient correlation between all of the parameters to effectively reduce the number of parameters to 1.

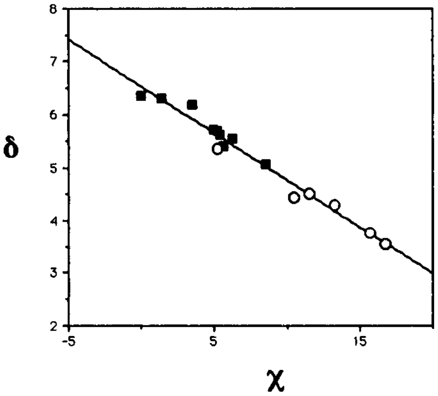

Figure 1. Plot of Bodner's δ values versus χ. The linear relationship indicates that the minimum number of stereoelectronic parameters necessary to describe the stereoelectronic properties of the ligands is 1. The data for PAr_3 are shown as open circles, and the data for PR_3 are shown as filled squares.

We start our search for the number and form of the parameters by looking at the trivial case where a plot of one property versus another yields the same line for both families of phosphines. Such a case is the relationship between Bodner's δ values[17] (the relative ^{13}C chemical shift of the CO ligands in $LNi(CO)_3$) and the χ values,[4,7,8] which are related to A_1 ν_{CO} of $LNi(CO)_3$ (Figure 1). (All stereoelectronic parameters and physiochemical data discussed in this paper are displayed in Table 1.) The linear plot between χ and δ indicates that the *minimum* number of parameters needed to describe each property is 1. Furthermore, since a single linear relationship is observed for both families, x_1 must be a continuous (as opposed to discrete) parameter. In the QALE model, we set the electronic parameter χ to be x_1.

In the next example, we plot the $E°$ values of the η-Cp(CO)Fe(L)(COMe)$^{0/+}$ couple versus the position of ν_{CO} for (η-Cp)(CO)Fe(L)(COMe)^0 (Figure 2).[19,20] We observe in this plot that the data for PAr_3 and PR_3 fall on two separate but parallel lines. A second parameter is needed and consideration of eq 7 allows us to establish

$$E° = (a/a')\nu_{CO} + (b - ab'/a')x_2 + (C - C'/a') \tag{7}$$

the form of this parameter. In eq 7, the terms a/a', $b - ab'/a'$, $C - C'/a'$, are the same for both PR_3 and PAr_3. *Thus, to get two parallel lines, x_2 must have different values for PR_3 and PAr_3 and be constant within each family.* In our QALE model, x_2 is the aryl effect parameter, E_{ar},[10] which is 2.7 for PAr_3 and 0 for PR_3.

In the third example, we plot (Figure 3A) log *k* for the second-order addition of MeI to $Ir(CO)(Cl)L_2$[18] versus ν_{CO}.[18] In Figure 3B we plot A_1 ν_{CO} for $LCr(CO)_5$[21] versus χ, which is just another property of the phosphines. In Figure 3A we see that the data for PAr_3 and PR_3 lie along lines with very different slopes. In Figure 3B, again we see lines with different slopes. So far, we have identified x_1 as a variable parameter (χ) and x_2 as a parameter (E_{ar}) that differs for PR_3 and PAr_3 but

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Table 1. Stereoelectronic Parameters of Phosphines and Physiochemical Properties of the Phosphines and Phosphine Complexes Discussed in This Paper

phosphine	E_B[a]	C_B[a]	E_{ar}[b]	χ[b]	θ[b]	δ[c]	$E°$[d]	ν_{CO}[e]	log k[f]	ν_{CO}[g]	ν_{CO}[h]	log k[i]	IP[j]	log k[k]	$-\Delta H$[l]
PMe_3	0.247	5.81	0	8.55	118	5.05	0.184	1918.6			2062.0	−3.77	8.65	−4.509	31.6
PMe_2Ph	0.273	5.27	1	10.6	122						2063.0		8.45		28.4
PEt_3	0.274	6.11	0	6.3	132	5.54	0.154	1916.5	−1.638	1942.0	2060.0	−3.77	8.31	−3.699	33.7
PPr_3	0.310	5.78	0	5.4	134	5.62								−3.292	
PBu_3	0.294	5.9	0	5.25	136	5.69	0.143	1915.5		1940.1	2059.0	−3.60	8.11	−3.149	
$P(pentyl)_3$			0	5.0	136	5.7									
$P(hexyl)_3$			0	5.0	136	5.7									
$PMePh_2$	0.276	4.67	2	12.1	136				−1.752		2065.0		8.28		24.7
PEt_2Ph				9.3	136				−1.939			−3.33			
$PEtPh_2$			2	11.3	140				−1.866		2063.0	−3.16			
$P(i\text{-}Bu)_3$	0.312	5.55	0	5.7	143	5.4			−3.26	1938.9	2059.0				
$P(p\text{-}Me_2NC_6H_4)_3$	0.342	5.05	2.7	5.25	145	5.35				1952.7	2058.0		6.9		
$P(p\text{-}MeOC_6H_4)_3$	0.307	4.52	2.7	10.5	145	4.43	0.244	1918.7	−1.597	1960.6	2061.0	−3.25	7.48	−2.824	24.1
$P(p\text{-}MeC_6H_4)_3$	0.308	4.37	2.7	11.5	145	4.50	0.257	1920.3	−1.879	1961.5	2062.0	−3.17	7.60	−2.699	23.2
PPh_3	0.301	4.07	2.7	13.25	145	4.3	0.287	1922.3	−2.44	1964.7	2063.0	−3.12	7.92	−2.959	21.2
$P(p\text{-}FC_6H_4)_3$	0.288	3.81	2.7	15.7	145	3.77	0.334	1924.3	−4.069	1968.0			8.12	−3.367	19.6
$P(p\text{-}ClC_6H_4)_3$	0.282	3.55	2.7	16.8	145	3.54	0.357	1925.6	−4.842		2065.0	−3.14	8.18		17.9
$P(p\text{-}CF_3C_6H_4)_3$	0.280	2.85	2.7	20.5	145		0.409	1929.4		1974.9	2067.3		8.65		13.6
$P(t\text{-}Bu)Ph_2$			2	8.8	157				−3.745		2058.0				
$P(i\text{-}Pr)_3$	0.352	5.91	0	3.45	160	6.2	0.105	1914.7	−3.721	1936.3	2058.0			−1.523	
PCy_3	0.374	5.91	0	1.4	170	6.32	0.086	1912.8	−3.509	1931.7	2056.1	−2.38	8.05	−1.004	33.2
$P(t\text{-}Bu)_3$	0.331	6.52	0	0	182	6.37						−0.737	7.70		36.6

[a] Data are taken from ref 3. [b] Data are taken from ref 18. [c] ^{13}C chemical shift of the CO ligands in $LNi(CO)_3$ measured relative to $Ni(CO)_4$. Data are taken from ref 17. [d] $E°$ (V relative to the ferrocene/ferrocenium couple) for the (η-Cp)(CO)(L)$FeCOMe^{0/+}$ couple as measured by cyclic voltammetry in 0.1 M tetrabutylammonium hexafluorophosphate/acetonitrile at 0 °C. Data are taken from ref 19. [e] ν_{CO} (cm^{-1}) in cyclohexane for (η-Cp)(CO)(L)FeCOMe. Data are taken from refs 19 and 20. [f] log k for the second-order reaction between MeI and $Ir(CO)(Cl)L_2$ in benzene. Data are taken from ref 18. [g] ν_{CO} (cm^{-1}) in CH_2Cl_2 for $Ir(CO)(Cl)L_2$. Data are taken from ref 18. [h] A_1 ν_{CO} (cm^{-1}) for $Cr(CO)_5$ in cyclohexane. Data are taken from ref 21. [i] log k for the first-order reaction between $LRu(CO)_4$ and L′. Data are taken from refs 22 and 23. [j] First vertical ionization potentials (eV). Data taken from refs 24–31. [k] log k for the first-order reaction between $[Ru(H_2O)(byp)(trpy)]^{2+}$ and acetonitrile. Data are taken from ref 32. [l] Heats of protonation of phosphines by trifluoromethanesulfonic acid. Data are taken from refs 33 and 34.

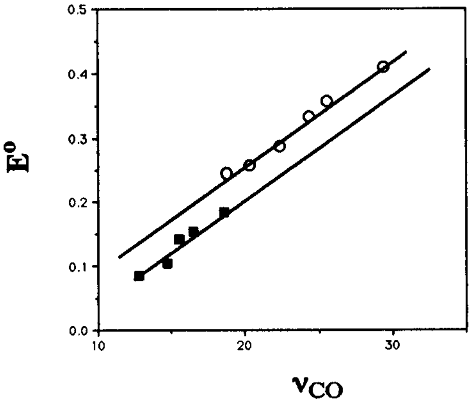

Figure 2. Plot of the $E°$ values for (η-Cp)(CO)Fe(L)-$(COMe)^{0/+}$ versus ν_{CO} of (η-Cp)(CO)Fe(L)$(COMe)^0$ (cyclohexane). The observation of two parallel lines indicates that at least two stereoelectronic parameters are operative, one that determines the slopes and one that determines the separation between the lines. The data for PAr_3 are shown as open circles, and the data for PR_3 are shown as filled squares.

is constant within each family of ligands. These two parameters alone are insufficient to account for any difference in slope of the lines for the two families. Thus, a third parameter, x_3, is required to distinguish between the behavior of the two families of ligands. Since the relationships within each family are still linear, x_3 must be either constant for one family and variable for the other, or x_3 must be variable for both families. In addition, if x_3 is variable, then it must be linearly correlated with x_1 and have a different correlation for the two families of ligands. In the QALE model, x_3 is the steric parameter, θ, which is linearly correlated with χ for PR_3 but is constant at 145° for PAr_3. (For some PR_3 species the linear relationship between χ and θ does not hold, e.g. $P(i\text{-}Bu)_3$. These ligands are excluded from the graphical analysis but would be included in a full regression analysis.) Thus, the slope of the PAr_3 line is determined by the coefficients of χ, whereas the slope of the PR_3 line is determined by the a combination of the coefficients of the correlated χ and θ parameters.

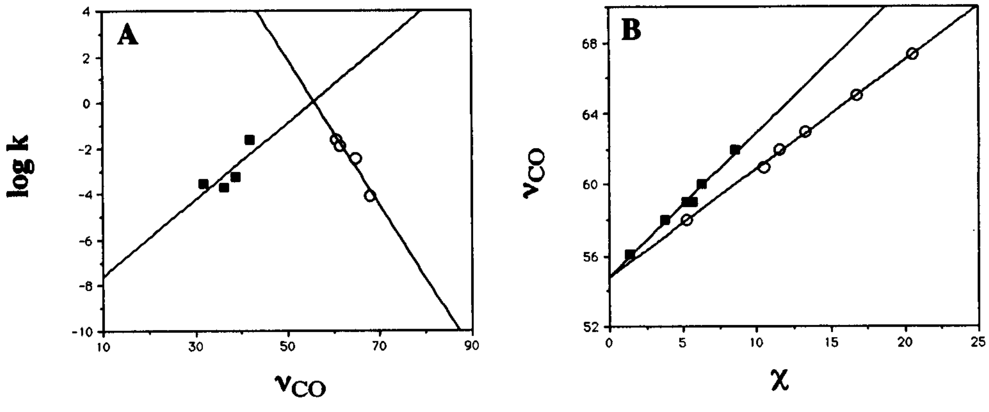

Figure 3. (A) Plot of log k for the addition of MeI to $Ir(CO)(Cl)L_2$ versus ν_{CO} of $Ir(CO)(Cl)L_2$. (B) Plot of A_1 ν_{CO} of $LCr(CO)_5$ versus χ. The differences in the slopes of the lines indicates the need for a third parameter. The data for PAr_3 are shown as open circles, and the data for PR_3 are shown as filled squares.

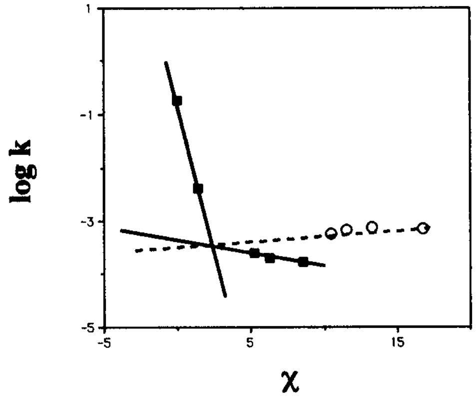

Figure 4. Plot of log *k* for the dissociation of CO from LRu-$(CO)_4$ versus χ. The break in the line for PR_3 demonstrates the need for a fourth stereoelectronic parameter. The data for PAr_3 are shown as open circles, and the data for PR_3 are shown as filled circles.

Finally, to show that still a fourth parameter is needed, we take as one property log *k* for the dissociation of CO from $LRu(CO)_4$[22,23] and let χ be the other property. In Figure 4, we show this plot of log *k* versus χ. We observe that the data for PAr_3 lie along a single line but that there is a break in the line for the PR_3 data. Hence, we need a fourth parameter (x_4) that breaks the trialkyl ligands into two groups. In the QALE model, x_4 is the steric parameter $(\theta - \theta_{st})\lambda$.

Thus, we can see that at least four parameters are generally needed to describe the stereoelectronic properties of phosphines. This conclusion is based on simple linear algebra and is not dependent on any particular model.

A consequence of this analysis is that a two-parameter model, such as the *E*/*C* model or the QALE model using only χ and θ, is not sufficient, in general, for analysis of phosphine data.

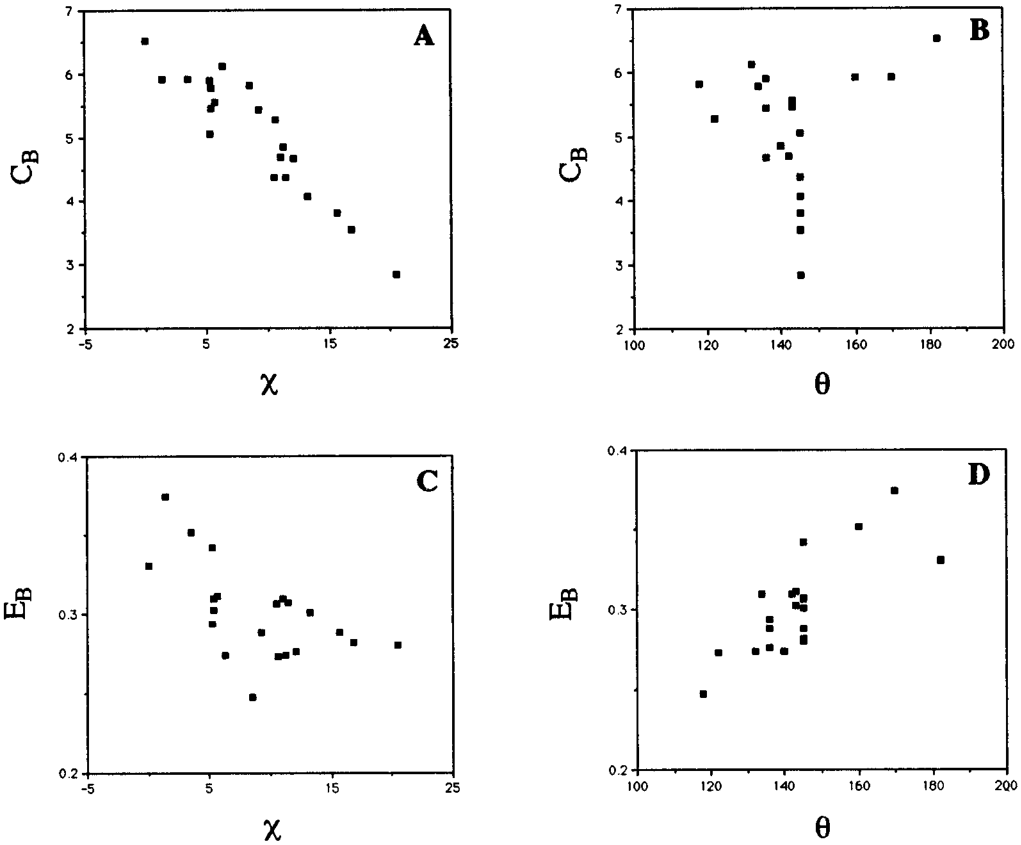

Figure 5. Plots of Drago's E_B and C_B parameters versus the phosphine stereoelectronic parameters χ and θ for all the phosphine ligands found in Table 1.

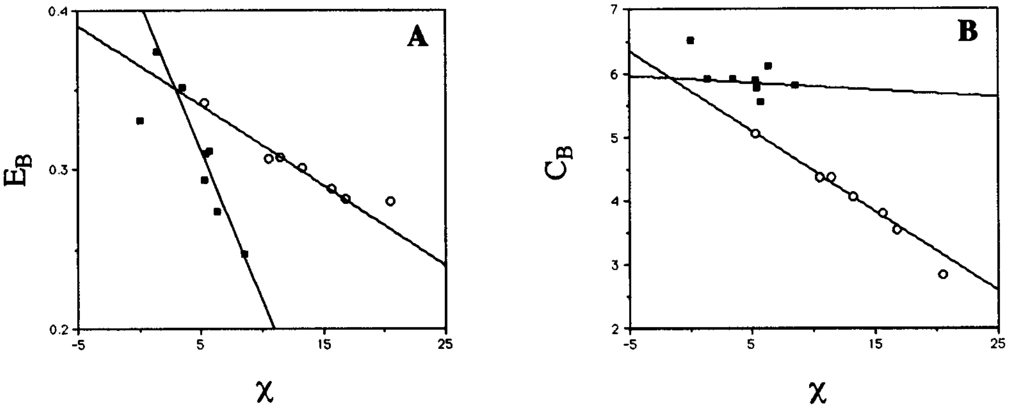

Figure 6. Plots of E_B and C_B versus χ for PR_3 and PAr_3. The data for PAr_3 are shown as open circles, and the data for PR_3 are shown as filled squares. The points at $\chi = 0$, which are significantly off the lines, correspond to $P(t\text{-Bu})_3$.

QALE Analysis of Drago's E_B and C_B Parameters for Phosphines. The question now arises as to why the *E*/*C* model succeeds in correlating some phosphine data and fails with other sets.[3] The answer to this question lies in the nature of the relationship between the *E*/*C* parameters (E_B and C_B) and the QALE parameters (χ, θ, and E_{ar}). We start our QALE analysis of E_B and C_B by examining graphically these parameters in terms of χ and θ, as is shown in Figure 5. (This protocol was described recently.[4]) Drago correctly pointed out that there appears to be little correlation between C_B and θ (Figure 5B).[3] We find, however, that there is a definite correlation between C_B and χ (Figure 5A). In contrast, E_B shows relatively poor correlations with either χ or θ, individually (Figure 5C,D).

Graphical analysis of E_B and C_B values of PAr_3 and PR_3 reveals important information about their relationship to the QALE parameters. The plots of these limited sets of data versus χ are shown in Figure 6. First, the data for PR_3 and PAr_3 lie along two lines with different slopes. Only the data points for P(*t*-Bu)$_3$ lies significantly off the lines. There can be little doubt that the E_B and C_B parameters of P(*t*-Bu)$_3$ reflect the disproportionately large steric effects that complexes of this ligand experience. Accordingly, we dropped this ligand from the regression analysis of E_B and C_B (vide infra). Second, since the lines in both plots differ in slope, steric effects are important in determining the values of E_B and C_B. Third, the intersection of the two lines in the plot for E_B is near $\chi = 4.8$, which indicates that the aryl effect is playing a minor role[4] in E_B. For C_B, the aryl effect appears to play a somewhat larger role. Since the E_B and C_B values are obtained by analyzing many sets of data, and since the aryl effect can enhance or diminish the electron donor capacity of the phosphines, it is not surprising that the aryl effect almost averages out.

In order to quantify the relationship between *E*/*C* and the QALE parameters, we performed regression analyses on the data for PR_3 and PAr_3, and then on the full sets of ligands shown in Table 1. The results are shown below. Underneath each equation we show the number of data used in the analysis, r^2 for the analysis, and the percent contribution of each parameter.

For PR_3 and PAr_3 only:

$$\begin{array}{lllll} C_B = -0.141\chi & -\ 0.017\theta & -\ 0.219E_{ar} & +\ 8.92 \\ \quad \pm 0.014 & \quad -0.004 & \quad \pm 0.056 & \quad \pm 0.65 \end{array} \tag{8}$$

$$n = 15,\ r^2 = 0.979;\ \chi\ (65\%),\ \theta\ (21\%),\ E_{ar}\ (14\%)$$

$$\begin{array}{lllll} E_B = -0.0042\chi & +\ 0.0019\theta & +\ 0.008E_{ar} & +\ 0.064 \\ \quad \pm 0.0007 & \quad \pm 0.0002 & \quad \pm 0.002 & \quad \pm 0.030 \end{array} \tag{9}$$

$$n = 15,\ r^2 = 0.951;\ \chi\ (40\%),\ \theta\ (49\%),\ E_{ar}\ (11\%)$$

For all phosphine ligands listed in Table 1:

$$\begin{array}{lllll} C_B = -0.14\chi & -\ 0.0192\theta & -\ 0.21E_{ar} & +\ 9.3 \\ \quad \pm 0.02 & \quad \pm -0.004 & \quad \pm 0.06 & \quad \pm 0.6 \end{array} \tag{10}$$

$$n = 20,\ r^2 = 0.967;\ \chi\ (65\%),\ \theta\ (22\%),\ E_{ar}\ (13\%)$$

$$\begin{array}{lllll} E_B = -0.0042\chi & +\ 0.0018\theta & +\ 0.008E_{ar} & +\ 0.08 \\ \quad \pm 0.0008 & \quad \pm -0.0002 & \quad \pm 0.003 & \quad \pm 0.03 \end{array} \tag{11}$$

$$n = 20,\ r^2 = 0.907;\ \chi\ (43\%),\ \theta\ (47\%),\ E_{ar}\ (10\%)$$

These analyses show good to excellent correlation between E_B and C_B and the QALE parameters. The regression analyses are also consistent with the graphical analyses in that the coefficients of χ determined by analysis of the PAr_3 data only (−0.141 for C_B and −0.0042 for E_B) are indistinguishable from the coefficients obtained by regression analysis for entire sets of data. Furthermore, the contribution of E_{ar} to either E_B or C_B is small, 10% and 13%, respectively, as predicted by the graphical analyses. We can conclude then that E_B and C_B will be most successful in the analysis of a property that depends primarily on χ and/or θ. The *E*/*C* model will fail in the analysis of a property that depends significantly on E_{ar} and/or $(\theta - \theta_{st})\lambda$.

Comparison of QALE and *E*/*C* Analyses for Several Sets of Physiochemical Properties of Phosphines and Phosphine Complexes. We start this section by examining sets of data that give good results by both the *E*/*C* and QALE methods. We show QALE analyses (eqs 12 and 14) for log *k* for the displacement of H_2O from $[Ru(H_2O)(bpy)_2(PR_3)]^{2+}$ by acetonitrile[32] and the heats of protonation ($-\Delta H$) of phosphines by trifluoromethanesulfonic acid.[33,34] Each of these analyses reveals that the property is largely dependent on χ and θ with only small (12% and 11%, respectively) contributions from E_{ar} and no steric threshold. Thus, as expected, *E*/*C* analyses (eqs 13 and 15) are also very good.

Log *k* for displacement of H_2O from $[Ru(H_2O)(bpy)_2(PR_3)]^{2+}$ by acetonitrile:

QALE analysis

$$\begin{array}{lllll} \log k = -0.112\chi & +\ 0.055\theta & +\ 0.21E_{ar} & -\ 10.1 \\ \quad \pm 0.032 & \quad \pm 0.005 & \quad \pm 0.10 & \quad \pm 0.8 \end{array} \tag{12}$$

$$n = 10,\ r^2 = 0.989;\ \chi\ (31\%),\ \theta\ (57\%),\ E_{ar}\ (12\%)$$

E/*C* analysis

$$\begin{array}{llll} \log k = 27.6E_B & -\ 0.026C_B & -\ 11.2 \\ \quad \pm 2.1 & \quad \pm 0.085 & \quad \pm 0.7 \end{array} \tag{13}$$

$$n = 10,\ r^2 = 0.968$$

$-\Delta H$ for the protonation of PR_3 by F_3CSO_3H:

QALE analysis

$$\begin{array}{lllll} -\Delta H = -1.05\chi & -\ 0.088\theta & -\ 1.21E_{ar} & +\ 51.3 \\ \quad \pm 0.10 & \quad \pm 0.019 & \quad \pm 0.41 & \quad \pm 3.1 \end{array} \tag{14}$$

$$n = 12,\ r^2 = 0.990;\ \chi\ (70\%),\ \theta\ (19\%),\ E_{ar}\ (11\%)$$

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E/*C* analysis

$$-\Delta H = \underset{\pm 8}{-112E_{\mathrm{B}}} - \underset{\pm 0.7}{3.1C_{\mathrm{B}}} - \underset{\pm 4}{69} \qquad (15)$$

$$n = 12,\ r^2 = 0.949$$

The signs of the coefficients of the QALE equations (eqs 12 and 14) are consonant with the contemporary views of these reactions. Thus, according to eq 12, the rate of dissociation of H_2O from $[Ru(H_2O)(bpy)_2(PR_3)]^{2+}$ is sterically accelerated and facilitated by better electron donor ligands. Equation 14 reveals that the heat of protonation increases as the electron donor capacity of the phosphine increases but decreases as θ increases; this is consonant with steric inhibition of solvation.

We now give three examples where the *E*/*C* model (eqs 17, 20, and 23) does not give good results. The first example is the analysis of the vertical ionization potentials (IP)[24−31] of phosphines; the second and third examples are the analyses of log *k* for the dissociation of CO from $LRu(CO)_4$[22,23] and the log *k* values for the addition of MeI to $Ir(CO)(Cl)L_2$.[18] The QALE analyses of the IP (eq 16) and log *k* for the addition of MeI to $Ir(CO)(Cl)L_2$ (eq 22) show a significant dependence on E_{ar}. The QALE analysis (eq 19) of the dissociation of CO from $LRu(CO)_4$ shows a sharp steric threshold. Thus, each of these sets of data depend not only on χ and θ but also on E_{ar} and/or $(\theta - \theta_{\mathrm{st}})\lambda$. Thus, it is expected and it is found that the *E*/*C* model does not accommodate these properties (eqs 17, 29, and 23). Since E_{B} and C_{B} are primarily linear combinations of χ and θ, the inclusion of E_{ar} and $(\theta - \theta_{\mathrm{st}})\lambda$ into *E*/*C* analysis would be expected to give highly improved correlations. This is what we observe, and these hybrid analyses are shown in eqs 18, 21, and 24.

The first vertical ionization potentials (IP) of phosphines:

QALE analysis

$$\mathrm{IP} = \underset{\pm 0.008}{0.115\chi} - \underset{\pm 0.002}{0.00025\theta} - \underset{\pm 0.034}{0.484E_{\mathrm{ar}}} + \underset{\pm 0.32}{7.67} \qquad (16)$$

$$n = 14,\ r^2 = 0.967;\ \chi\ (64\%),\ \theta\ (0\%),\ E_{\mathrm{ar}}\ (36\%)$$

E/*C* analysis

$$\mathrm{IP} = \underset{\pm 3.6}{-12.9E_{\mathrm{B}}} + \underset{\pm 0.10}{0.02C_{\mathrm{B}}} + \underset{\pm 1.1}{11.7} \qquad (17)$$

$$n = 14,\ r^2 = 0.562$$

E/*C* analysis with E_{ar}

$$\mathrm{IP} = \underset{\pm 1.48}{-7.01E_{\mathrm{B}}} - \underset{\pm 0.085}{-0.575C_{\mathrm{B}}} - \underset{\pm 0.070}{0.548E_{\mathrm{ar}}} + \underset{\pm 0.47}{13.78} \qquad (18)$$

$$n = 14,\ r^2 = 0.941;\ E_{\mathrm{B}}\ (17\%),\ C_{\mathrm{B}}\ (49\%),\ E_{\mathrm{ar}}\ (34\%)$$

log *k* for the first-order dissociation of CO from $LRu(CO)_4$:

QALE analysis

$$\log k = \underset{\pm 0.018}{-0.015\chi} + \underset{\pm 0.0045}{0.011\theta} + \underset{\pm 0.012}{0.128(\theta - 163)\lambda} + \underset{\pm 0.06}{0.09E_{\mathrm{ar}}} - \underset{\pm 0.67}{5.20} \qquad (19)$$

$$n = 11,\ r^2 = 0.994;\ \chi\ (7\%),\ \theta\ (19\%),\ (\theta - \theta_{\mathrm{st}})\lambda\ (67\%),\ E_{\mathrm{ar}}\ (7\%)$$

E/*C* analysis

$$\log k = \underset{\pm 7}{16E_{\mathrm{B}}} + \underset{\pm 0.2}{0.2C_{\mathrm{B}}} - \underset{\pm 2.1}{8.7} \qquad (20)$$

$$n = 11,\ r^2 = 0.469$$

E/*C* analysis with E_{ar} and $(\theta - \theta_{\mathrm{st}})\lambda$

$$\log k = \underset{\pm 1.24}{+1.22E_{\mathrm{B}}} - \underset{\pm 0.112}{0.026C_{\mathrm{B}}} + \underset{\pm 0.008}{0.143(\theta - 162)\lambda} + \underset{\pm 0.082}{0.163E_{\mathrm{ar}}} - \underset{\pm 0.80}{3.83} \qquad (21)$$

$$n = 14,\ r^2 = 0.991;\ E_{\mathrm{B}}\ (4\%),\ C_{\mathrm{B}}\ (2\%),\ (\theta - \theta_{\mathrm{st}})\lambda\ (81\%),\ E_{\mathrm{ar}}\ (13\%)$$

log *k* for the second-order addition of MeI to $Ir(CO)(Cl)L_2$:

QALE analysis

$$\log k = \underset{\pm 0.06}{-0.55\chi} - \underset{\pm 0.013}{0.126\theta} + \underset{\pm 0.21}{1.63E_{\mathrm{ar}}} + \underset{\pm 2.1}{18.4} \qquad (22)$$

$$n = 12,\ r^2 = 0.935;\ \chi\ (48\%),\ \theta\ (27\%),\ E_{\mathrm{ar}}\ (25\%)$$

E/*C* analysis

$$\log k = \underset{\pm 10.6}{-7.0E_{\mathrm{B}}} + \underset{\pm 0.44}{0.41C_{\mathrm{B}}} - \underset{\pm 3.2}{2.5} \qquad (23)$$

$$n = 12,\ r^2 = 0.099$$

E/*C* analysis with E_{ar}

$$\log k = \underset{\pm 4.45}{-9.66E_{\mathrm{B}}} + \underset{\pm 0.52}{3.63C_{\mathrm{B}}} + \underset{\pm 0.36}{2.37E_{\mathrm{ar}}} - \underset{\pm 3.1}{21.1} \qquad (24)$$

$$n = 12,\ r^2 = 0.86;\ E_{\mathrm{B}}\ (6\%),\ C_{\mathrm{B}}\ (56\%),\ E_{\mathrm{ar}}\ (38\%)$$

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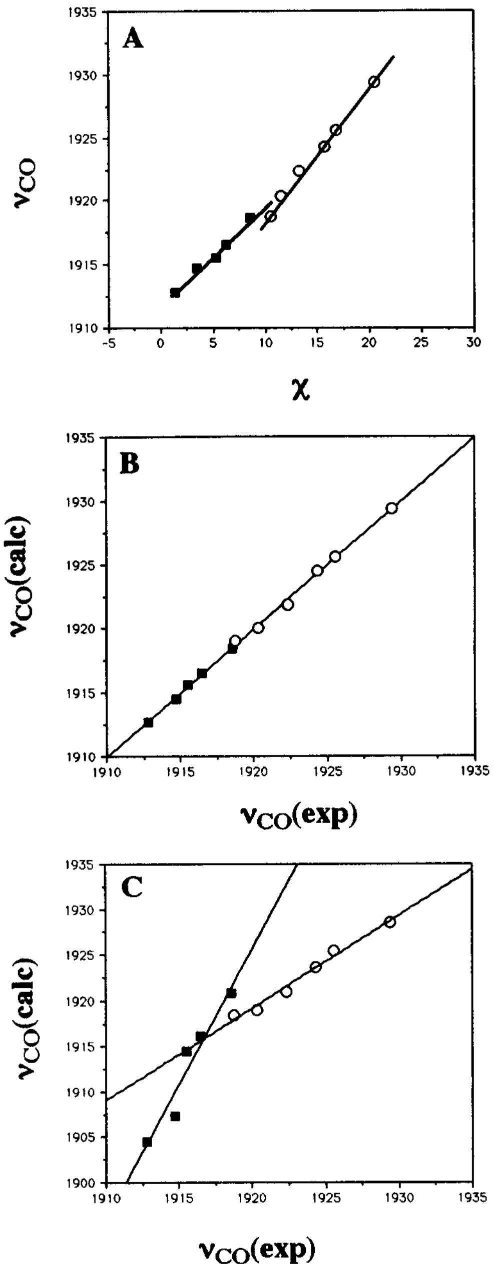

Figure 7. (A) Plot of ν_{CO} for (η-Cp)(CO)(L)FeCOMe versus χ. (B) Plot of ν_{CO} for (η-Cp)(CO)(L)FeCOMe calculated by QALE (eq 25) versus the experimental values of ν_{CO}. (C) Plot of ν_{CO} for (η-Cp)(CO)(L)FeCOMe calculated by the *E*/*C* method, using literature values of E_B, E_A, C_B, and C_A, versus the experimental values of ν_{CO}. The data for PAr_3 and PR_3 are shown as open circles and filled squares, respectively.

Importance of Examining Graphically the Results of a Regression Analysis. Even when a model gives a statistically excellent fit, it is imperative that the results be examined graphically to check the validity of the fit. If the model is correct, then a plot of the calculated data versus the experimental data should display a single line and not a series of lines corresponding to different families of ligands (i.e. PR_3 and PAr_3). Furthermore, the slope of this line should be close to 1. The *E*/*C* analysis gives statistically an excellent fit to ν_{CO} for (η-Cp)(CO)(L)FeCOMe,[3] where L = phosphines and phosphites. We have examined graphically ν_{CO} for just the phosphines. Thus, in Figure 7A, we plot ν_{CO} versus χ. *Importantly, the data for PR_3 fall on a single line, which indicates that there is no steric threshold within the range of θ spanned by these ligands.* We do see for the two families, however, two slightly separated, slightly nonparallel lines, which indicates a small aryl effect and a small continuous steric effect.[4] Equation 25 shows the QALE analysis of the data obtained by linear regression.

$$\nu_{CO} = \underset{\pm 0.01}{+1.04\chi} + \underset{\pm 0.03}{0.034\theta} - \underset{\pm 0.12}{0.87E_{ar}} + \underset{\pm 1.1}{1905.5} \tag{25}$$

$$n = 11,\ r^2 = 0.998;\ \chi\ (83\%),\ \theta\ (7\%),\ E_{ar}\ (10\%)$$

In Figure 7B we show the plot of ν_{CO} (calculated via eq 25) versus the experimental ν_{CO} for the iron complex. The points for PAr_3 and PR_3 lie along a single line with a slope of 1. Figure 7B is to be contrasted with Figure 7C. In Figure 7C we plot the calculated ν_{CO} (via the *E*/*C* method) for the phosphines versus the experimental ν_{CO}. We used values for E_B and C_B and the appropriate values of E_A and C_A *taken directly from ref 3.* (The values of E_A and C_A were obtained by Drago through the analysis of the combined data for the phosphines and phosphites.)

At first glance it would appear that the data fall along a single line (Figure 7C), with the exception of the data for P(*i*-Pr)$_3$ and PCy$_3$. In the *E*/*C* model this deviant behavior might be indicative of steric problems for these large ligands. If this be true, then in the *E*/*C* model a steric threshold parameter in addition to E_B and C_B[3] is needed to complete the description of P(*i*-Pr)$_3$ and PCy$_3$ for the iron complex. This is inconsistent, however, with the linear plot of ν_{CO} (L = PR_3, (η-Cp)(CO)(L)FeCOMe) versus χ in Figure 7A. In the *E*/*C* model, χ is only dependent on E_B and C_B and is free of steric effects.[1,3] If the analysis of the iron data required a steric threshold for P(*i*-Pr)$_3$ and PCy$_3$, then a linear plot with χ (Figure 7A) cannot result. What we see in Figure 7C is actually two intersecting lines: one for PAr_3 with a slope of about 1, and one for PR_3 with a slope of about 3! Clearly, something is amiss in the *E*/*C* model.

Conclusions

There can be no doubt that at least four parameters for phosphines are required, in general, to describe variations in the physiochemical properties of phosphines and phosphine complexes. These results in no way invalidate the *E*/*C* parameters but simply indicate that any two-parameter model (e.g. the *E*/*C* model, or using the QALE model with only χ and θ) is insufficient. Since the *E*/*C* parameters are linear combinations of χ and θ with only a small contribution from E_{ar}, the *E*/*C* model will fit satisfactorily properties that depend on χ and θ but will not fit properties that depend significantly on E_{ar} or $(\theta - \theta_{st})\lambda$ as well as on χ and θ. On the other hand, when we include E_{ar} and/or $(\theta - \theta_{st})\lambda$ into the *E*/*C* analysis we, indeed, obtain good correlations in those situations where *E*/*C* analyses do not give satisfactory results.

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