The Quantitative Analysis of Ligand Effects (QALE). The Aryl Effect

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It has been found that the electronic parameter χ is insufficient to describe the total electron-donor capacity of arylphosphines. There is an additional electronic effect, the aryl effect (described by E_{ar}), which appears to be dependent only on the number of aryl groups attached to the central phosphorus atom and not on the para substituents of the aryl groups. An evaluation of E_{ar} was made by correlating the phosphorus(III) stereoelectronic parameters, χ, with θ and Taft's polar substituent constants $\sum\sigma^*$. The values of E_{ar} are 0, 1.0, 2.0, and 2.7 for phosphines bearing no, one, two, and three aryl groups, respectively. The problem of correlation of stereoelectronic parameters is addressed. A protocol for the quantitative analysis of ligand effects (QALE) is described in detail and illustrated by application to the set of kinetic data for the carbonylation of (η-Cp)(CO)(L)FeMe$^+$ in methylene chloride. By including E_{ar} as one of the stereoelectronic parameters along with χ and θ, it is possible to analyze disparate sets of data which could not be analyzed satisfactorily in terms of χ and θ alone. These sets include the first vertical ionization potentials of phosphines, $\sum\sigma^{Ph}$ values of Kabachnik, the equilibration of the cis and trans isomers of the carbene complexes $(CO)_4(PR_3)Cr[C(OMe)Me]$, and kinetic data for the reactions between phosphines and iodoethane and between (*p*-MeOPh)(Ph)CH$^+$ and $HSiR_3$.

Introduction

For more than 25 years organometallic chemists have been intrigued by the idea that the variations in the properties of transition-metal complexes can be quantified in terms of the stereoelectronic properties of the ancillary ligands.[1] In principle, such quantification would be useful as a probe of mechanism and for predicting and controlling the reactivity, stereochemistry, and regiochemistry of stoichiometric and catalytic reactions involving phosphines, phosphine complexes, and other related ligands. Building on the earlier work of Basolo,[2] Tolman,[3] Schlenkcluhn,[4] Trogler,[5] Marzilli,[5] Cotton,[6] and Kochi,[7] we[8] proposed, concurrently with Poë,[9] that steric effects in entering-ligand-dependent substitution reactions (with phosphorus(III) compounds as the entering ligands) appear to be discontinuous and that the rates of these reactions are related by eq 1a to the steric parameter (Tolman's

$$\log k = a\chi + b(\theta - \theta_{st})\lambda + d \qquad (1a)$$

cone angle,[3] θ) and an electronic parameter (pK_a, χ, or χ_d).[10] We view the term containing θ in eq 1a as a measure of the steric interaction between the phosphorus(III) ligand and the metal-containing fragment to which it is attached. θ_{st} is the steric threshold for the reaction; for phosphorus(III) ligands with cone angles less than θ_{st}, there is no steric effect and the switching function, λ (eq 1a), is zero. When $\theta > \theta_{st}$, λ is unity and sterics are operative. Equation 1a has been applied satisfactorily to a large body of kinetic data for entering-ligand-dependent substitution reactions.[11] The apparent generality of this approach lends credence to the concept of the steric threshold.

The situation is more complicated, both electronically and sterically, when the phosphorus(III) compounds are spectator ligands (present in both the ground and transition states, or reactant and product states of a reaction). This is especially true when different families of phosphorus(III) compounds are considered together.[12] For example, phosphites appear to mimic the behavior of phosphines in entering-ligand-dependent substitution reactions; the reactivity of the phosphines and phosphites as a group is readily accommodated by eq 1a.[8,11] In contrast, other spectroscopic, thermodynamic, and structural data for other systems (but not all) suggest that phosphites can behave as π acids.[12] These observations led us to speculate that in species containing long M-P bonds (e.g. the transition states for entering-ligand-dependent substitution reactions) π-bonding is negligible and that π-bonding becomes particularly important for sterically unencumbered complexes containing phosphites. In our earlier studies,[12] we attempted to accommodate

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(2) Thorsteinson, E. M.; Basolo, F. *J. Am. Chem. Soc.* **1966**, *88*, 3929.
(3) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.
(4) Schenkluhn, H.; Scheidt, W.; Weimann, B.; Zahres, M. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 401 and references therein.
(5) Trogler, W. C.; Marzilli, L. *J. Am. Chem. Soc.* **1974**, *96*, 7589.
(6) Cotton, F. A.; Darensbourg, D. J.; Kolthammer, B. *Inorg. Chem.* **1981**, *20*, 4440.
(7) Zizelman, P. M.; Amatore, C.; Kochi, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 3771-84.
(8) Golovin, M. N.; Rahman, M. M.; Belmonte, J. E.; Giering, W. P. *Organometallics* **1985**, *4*, 1981-91.
(9) Dahlinger, K.; Falcone, F.; Poë, A. J. *Inorg. Chem.* **1986**, *25*, 2654-8.
(10) Liu, H.-Y.; Eriks, E.; Prock, A.; Giering, W. P. *Organometallics* **1990**, *9*, 1758.
(11) Poë, A. J.; Farrar, D. H.; Zheng, Y. *J. Am. Chem. Soc.* **1992**, *114*, 5146.
(12) Rahman, M. M.; Liu, H.-Y.; Prock, A.; Giering, W. P. *Organometallics* **1987**, *6*, 650.

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these ideas (along with π-basicity for certain phosphines) in our analysis of ligand effect data.

Steric effects also are more complicated for spectator ligands.[13] In the former case of entering-ligand-dependent substitution reactions, the phosphorus(III) ligand is present in the transition state but absent in the ground state of the complex; hence, steric effects (because of phosphorus–metal interactions) are only operative in the transition state. Thus, there can be only one steric threshold. However, as a spectator ligand, the phosphorus(III) ligand is found in both states and there can be two steric thresholds (one for each state). Thus, reactions involving spectator ligands might exhibit regions of no steric effects, steric inhibition, and steric acceleration depending on the nature of the reaction.[13]

We found that analysis of data for spectator ligands that contained phosphines, phosphites, and related compounds became very cumbersome, requiring an increasing number of parameters, which in turn required large data sets. For this reason we have narrowed our focus to the chemistry of phosphines with the expectation that π-effects would be least important for this class of compounds. We have since put aside the idea that phosphines behave as π-bases, since we have found no further corroborating evidence for such a phenomenon.

We have found that many organometallic processes involving phosphines are correlated with the two stereoelectronic parameters χ and $(\theta - \theta_{st})\lambda$. We have analyzed such systems either via eq 1a or by constructing graphically electronic and steric profiles.[8,12-14] The electronic profile is a plot of the data (e.g. log k) versus an electronic parameter. The deviations (log k_{st}) of the data in the electronic profile from the line determined by small ligands that show no steric effects or from the line determined by a set of isosteric ligands (most commonly P(p-XPh)$_3$) are assumed to be a measure of the steric effect. Alternatively, we can determine log k_{st} by first fitting the data to eq 1a (or eq 1b, vide infra) and then subtracting all the terms of this equation except for the θ term from the experimental data. The plot of log k_{st} versus θ gives the steric profile of the reaction. For many systems, where sufficient data are available, the steric profiles are intuitively reasonable and their interpretation is insightful.

There are systems where this analysis does not afford satisfactory results. For example, several years ago we showed that the stereoelectronic parameters (pK_a and θ) for phosphines are not sufficient to describe the variations in the rates of addition of methyl iodide to the iridium complexes, Ir(CO)(Cl)L$_2$.[8] These results have led us to speculate that there is an additional electronic effect associated with the arylphosphine ligands.

In this paper, we report on the quantification of this additional electronic effect, which we call the aryl effect, with its corresponding parameter E_{ar}. In addition, we discuss the problem of correlation of parameters and then present a protocol for analyzing ligand effect data. Using χ, θ, and E_{ar}, we go on to analyze sets of data via eq 1b, for which we could not obtain satisfactory correlations with χ and θ alone.

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

(13) Eriks, K.; Giering, W. P.; Liu, H.-Y.; Prock, A. *Inorg. Chem.* **1989**, *28*, 1759.

(14) Prock, A.; Giering, W. P.; Green, J. E.; Meirowitz, R. E.; Hoffman, S. L.; Woska, D. C.; Wilson, M.; Chang, R.; Chen, J.; Magnuson, R. H.; Eriks, K. *Organometallics* **1991**, *10*, 3479.

Determination of the Values of E_{ar}

We are reinvestigating the kinetics of the addition of small molecules to Ir(CO)(Cl)L$_2$ and find that the arylphosphines behave as much stronger electron donors in these reactions than is predicted by their χ values. In addition, we observe that the families of complexes PR$_x$Ph$_{3-x}$ (x = 0–2) fall along parallel lines in the steric profile of the reaction. The line to which each data point belongs is determined by the number of phenyl groups attached to the phosphorus. The separation of the steric profile into these parallel lines indicates to us that the phenyl groups are exerting an electronic effect additional to that described by χ. The results of this study will be reported in a future paper.

The pattern observed in the aforementioned steric profile is also observed in the correlation of Taft's polar substituent constants $\sum\sigma^*$[15] with χ and θ. It is from this correlation that we determine the values of the E_{ar} parameter. We treated $\sum\sigma^*$ as the dependent variable and constructed a steric profile. This was accomplished by plotting $\sum\sigma^*$ versus χ for P(p-XPh)$_3$ (Figure 1a) and calculating the deviations of the other data from the resulting line. The plot (Figure 1b, steric profile) of these deviations versus θ shows that the data fall around three parallel lines with a separate cluster for P(p-XPh)$_3$. Clearly, the number of aryl groups attached to the phosphorus affects its electron-donor capacity in an incremental manner. The four families of compounds differ by the number of aryl groups attached to the phosphorus. The spacing between lines c (two phenyl groups) and a (no phenyl groups) is about twice that between lines b (one phenyl group) and a. Accordingly, we defined E_{ar} as 0 for trialkylphosphines (line a) and 1.0 and 2.0 for phosphines containing one and two phenyl groups, respectively. The value 2.7 for E_{ar} for PAr$_3$ is the one which maximizes r^2 for the entire set of data according to eq 1b, with θ_{st} = 0. This leads to eq 2. Note that

$$\sum\sigma^* = (0.158 \pm 0.005)\chi + (0.0077 \pm 0.001)\theta + (0.289 \pm 0.023)E_{ar} - (2.32 \pm 0.22) \qquad (2)$$

$$n = 21;\ r^2 = 0.996;\ r^2(\chi/\theta,E_{ar}) = 0.71;\ r^2(\chi/E_{ar}) = 0.56,\ r^2(\chi/\theta) = 0.20;\ \chi\ (72\%),\ \theta\ (11\%),\ E_{ar}\ (17\%)$$

underneath the appropriate linear regression equations we show the number (n) of data used in the analysis, the square of the correlation coefficient (r^2) for the equation, the squares of the correlation coefficients for the indicated parameters (e.g. $r^2(\chi/\theta,E_{ar})$), and the percentage of the contribution (e.g. χ (72%)) of each parameter to the quantity being analyzed over the range of the parameter.

(15) Hansch, C.; Leo, A. *Substituent Constants for Correlation Analysis in Chemistry and Biology*; Wiley: New York, 1979.

(16) Bartik, T.; Himmler, T.; Schulte, H.-G.; Seevogel, K. *J. Organomet. Chem.* **1984**, *272*, 29.

(17) Data are taken from the following references: (a) Schafer, W.; Schweig, A. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 836. (b) Lappert, M. F.; Pedley, J. B.; Wilkins, B. T.; Stelzer, O.; Unger, E. *J. Chem. Soc., Dalton Trans.* **1975**, 1207. (c) Debies, T. P.; Rablais, J. W.; *Inorg. Chem.* **1974**, *13*, 308. (d) Weiner, M. A.; Lattman, M.; Grim, S. O. *J. Org. Chem.* **1975**, *40*, 1292. (e) Bock, H. *Pure Appl. Chem.* **1975**, *44*, 343. (f) Ikuta, S.; Kebarle, P.; Bancroft, G. M.; Chan, T.; Puddephatt, R. J. *J. Am. Chem. Soc.* **1982**, *104*, 3699. (g) Stelzer, O.; Unger, E. *Chem. Ber.* **1975**, *108*, 1246. (h) Puddephatt, R. J.; Dignard-Bailey, L.; Bancroft, G. M. *Inorg. Chim. Acta* **1985**, *96*, L91.

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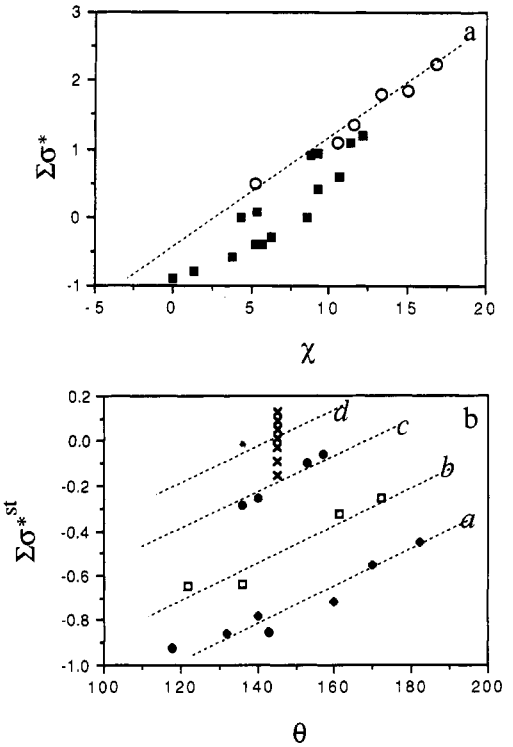

Figure 1. (a) Plot of $\sum\sigma^*$ versus χ. The best-fit line is drawn through the data for P(*p*-XPh)$_3$, shown as open circles. (b) Plot of the deviations of the data from the line in Figure 1a versus θ. Lines are drawn through families of phosphines: (a) PR_3; (b) PR_2Ph; (c) $PRPh_2$; (d) P(*p*-XPh)$_3$. Data are taken from Table I.

The E_{ar}[19] values along with the other stereoelectronic parameters are displayed in Table I.

Later in the paper we will analyze a number of systems that could not be dealt with in terms of χ and θ alone but which are satisfactorily analyzed in terms of χ, θ, and E_{ar}. The involvement of E_{ar} in the analysis of ligand-effect data complicates QALE because of the accidental correlation of parameters. Before we address this issue, we turn to the question of the interrelationships among the three stereoelectronic parameters, χ, θ, and E_{ar}.

Does χ Possess a Steric Component? The lines in the steric profile (Figure 1b) exhibit a nonzero slope, suggesting that in addition to the extra electronic effect, E_{ar}, there is a statistically significant steric effect present in one or both of the electronic parameters. This steric contribution is quite small, however, and contributes only 11% to $\sum\sigma^*$ (eq 2). Even though $\sum\sigma^*$[15] and χ[3] are believed by some to be free of steric effects, we suspect that the small steric dependence resides in $\sum\sigma^*$ rather than χ. We base this statement on the following arguments.

χ is based on the totally symmetric terminal carbonyl stretching frequency of $LNi(CO)_3$.[3] These tetrahedral complexes are about as sterically unencumbered as can be envisioned for an organometallic complex. Thus, intuitively it seems reasonable that there would be little dependence of χ on θ. Some experimental support for χ being free of steric influences comes from the observation that the χ values of P(*p*-MePh)$_3$ and P(*o*-MePh)$_3$ are very similar,[3] even though the ligands differ in cone angle by 49°.

(19) We have also calculated these E_{ar} values by using $\sum\sigma^*_{RCH_2}$ in place of $\sum\sigma^*$. We obtained values of E_{ar} that are proportional to the ones derived from $\sum\sigma^*$.

Strong evidence for χ being free of steric influences comes from analysis of the first vertical ionization potentials (IP) of the phosphines as determined in the gas phase by photoelectron spectroscopy (Table I). It has been argued that the first ionization potential is a measure of the intrinsic electron-donor ability of the phosphine.[20] As expected within a family, the phosphine bearing the most electron-rich pendant groups exhibits the smallest ionization potential. For example, within the trialkylphosphines, P(*t*-Bu)$_3$ has a smaller IP (7.7 eV) than PMe_3 (8.65 eV). Likewise, for the para-substituted triarylphosphines, P(*p*-Me_2NPh)$_3$ has a significantly smaller IP (6.9 eV) than P(*p*-ClPh)$_3$ (8.18 eV). The problem arises that PPh_3, with its supposedly more electronegative phenyl groups, is more easily ionized (IP = 7.92 eV) than PMe_3. A similar observation was also made by Puddephatt,[20] who found that the IP of $(PPh_3)W(CO)_5$ is smaller than that for $(PMe_3)W(CO)_5$. These observations led Puddephatt[20] to assert provocatively that PPh_3 is a better electron donor than PMe_3—a conclusion that appears to fly in the face of conventional wisdom. We will see that Puddephatt's interpretation is correct under certain circumstances—PPh_3 can be a better electron donor than PMe_3, but it depends on the environment of the phosphine. We believe that this inversion of the expected electron-donor ability is a manifestation of the aryl effect.

We analyzed the IP's of 21 phosphines reported in the literature. The set of phosphines includes PR_3, P(*p*-XPh)$_3$, mixed alkylarylphosphines, and several compounds of the type $PH_{3-x}R_x$. In Figure 2 we plot the data for the trialkyl- and triarylphosphines versus the electronic parameter χ. There are three points to be made on the basis of Figure 2. First, the triarylphosphines, as a family, are more easily ionized than the trialkylphosphines. Second, the isosteric triarylphosphines fall on a line parallel to that for the trialkylphosphines (eqs 3a and 3b, respectively). This

$$\text{IP} = (0.114 \pm 0.004)\chi + (6.30 \pm 0.06) \quad (3a)$$

$$n = 6,\ r^2 = 0.993$$

$$\text{IP} = (0.106 \pm 0.012)\chi + (7.66 \pm 0.07)$$

$$n = 5,\ r^2 = 0.957 \quad (3b)$$

suggests that there is no steric effect. Third, there is no simple collective relationship between IP and χ and θ for the two families of phosphines.

Linear regression analysis of the entire set of data using χ, θ, and E_{ar} gives an excellent correlation, described by eq 3c. Note that the coefficients of χ are the virtually the

$$\text{IP} = (0.105 \pm 0.009)\chi - (0.0009 \pm 0.002)\theta - (0.451 \pm 0.038)E_{ar} + (7.78 \pm 0.46) \quad (3c)$$

$$n = 21;\ r^2 = 0.967;\ r^2(\chi/\theta,E_{ar}) = 0.68;\ r^2(\chi/E_{ar}) = 0.05,\ r^2(\chi/\theta) = 0.46;\ \chi\ (69\%),\ \theta\ (0\%),\ E_{ar}\ (31\%)$$

same in eqs 3a–c (vide infra). In contrast, analysis without E_{ar} gives a poor correlation, as shown in eq 3d. In addition, we note that the coefficients of χ are statistically different

(20) Bancroft, G. M.; Dignard-Bailey, L.; Puddephatt, R. *J. Inorg. Chem.* **1986**, *25*, 3675.

Table I. Electronic (χ, $\Sigma\sigma^*$, and $\Sigma\sigma^{Ph}$) and Steric (Cone Angle, θ) Parameters and Ionization Potentials (IP) of Phosphines

entry no.	phosphine	χ[a]	θ[b]	E_{ar}[c]	$\Sigma\sigma^*$[d]	IP[e]	$\Sigma\sigma^{Ph}$[f]
1	PH_3[g]	24.5	87	0	1.49	10.58	−0.00
2	PH_2Me	18.9	97	0	0.98	9.70	−0.96
3	PH_2Ph	20.9	106	1.0	1.58	9.07	−0.48
4	$PHMe_2$	13.7	107	0	0.49	9.1	−1.92
5	PMe_3	8.55	118	0	0.00	8.65	−2.88
6	PH_2-*t*-Bu	16.7	119	0	0.68	9.30	−1.55
7	$PHBu_2$	11.7	120	0			
8	$PH(octyl)_2$[h]	11.5	120	0			
9	PMe_2Ph	10.6	122	1.0	0.600	8.45	−2.40
10	$PEtMe_2$	7.8	123	0			
11	$PH(i\text{-}Bu)_2$	12.0	124	0			
12	$PHPh_2$	17.35	126	2.0	1.69	8.40	−0.96
13	PEt_2Me	7.05	127	0			
14	PEt_3	6.3	132	0	−0.30	8.31	−3.30
15	PPr_3^i	5.4	134	0			
16	PEt_2Ph	9.3	136	1.0	0.40		−2.68
17	$PMePh_2$	12.1	136	2.0	1.20	8.28	−1.92
18	PBu_3[h]	5.25	136	0	−0.39	8.11	−3.66
19	$P(pentyl)_3$[h]	5.0	136	0			
20	$P(octyl)_3$[h]	5.0	136	0			
21	$PEtPh_2$	11.3	140	2.0	1.10		−2.06
22	$P(i\text{-}Bu)_3$	5.7	143	0	−0.39		−3.90
23	$P(p\text{-}Me_2NPh)_3$	5.25	145	2.7	0.48	6.9	−2.73
24	$P(p\text{-}MeOPh)_3$	10.5	145	2.7	1.08	7.48	−2.22
25	$P(p\text{-}MePh)_3$	11.5	145	2.7	1.36	7.60	−1.65
26	PPh_3	13.25	145	2.7	1.80	7.92	−1.44
27	$P(p\text{-}FPh)_3$	15.7	145	2.7	1.86	8.12	−1.13
28	$P(p\text{-}ClPh)_3$	16.8	145	2.7	2.25	8.18	−0.87
29	$P(p\text{-}CF_3Ph)_3$	20.5	145	2.7	2.88	8.65	−0.25
30	$PH(t\text{-}Bu)_2$	8.2	150	0	−0.11	8.35	−3.10
31	$PCyPh_2$	9.3	153	2.0	0.94		−2.17
32	$P(t\text{-}Bu)Ph_2$	8.8	157	2.0	0.90		−2.51
33	$P(i\text{-}Pr)_3$	3.45	160	0	−0.57	8.05	−3.90
34	PCy_2Ph	5.35	161	1.0	0.08		−2.86
35	PCy_3	1.4	170	0	−0.78		−4.35
36	$P(t\text{-}Bu)_3$	0	182	0	−0.900	7.70	−4.65

[a] χ is defined as the difference between the A_1 ν_{CO} absorption of $LNi(CO)_3$ and the A_1 ν_{CO} absorption for $((t\text{-}Bu)_3PNi(CO)_3$. Data are taken from or calculated from the data presented in refs 3 and 16. [b] Cone angle (θ) data (deg) are taken from ref 3. [c] Values for the aryl-effect parameter, E_{ar}, are calculated as described in the text. [d] $\Sigma\sigma^*$ values are calculated from σ^* values given in ref 15. [e] Data (eV) taken from ref 17. [f] Data taken or calculated from data presented in ref 18. [g] The value of χ is estimated on the basis of the values of χ for PPh_3, $PHPh_2$, and PH_2Ph. [h] The fractional χ values for $P(hexyl)_3$ were used for the octyl groups. Although Tolman reports a cone angle of 132° for PBu_3, we have found that 136° in general gives a better correlation. We have also used a cone angle or fractional cone angles based on 136° to estimate the cone angles of pentyl-, hexyl-, and octylphosphines. [i] A cone angle of 134° is based on the average of the cone angles for PEt_3 and PBu_3.

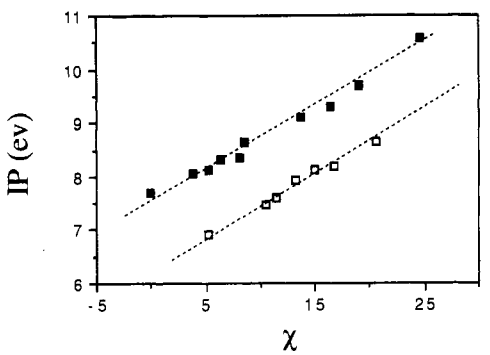

Figure 2. Plots of the first vertical ionization potentials of five trialkylphosphines and several other alkylphosphines containing P–H bonds (solid squares) and $P(p\text{-}XPh)_3$ (open squares) versus the electronic parameter χ. Data are taken from Table I.

in eqs 3a and 3d (vide infra). Equation 3c shows us, indeed, that the IP decreases as the electron-donor ability of the

$$IP = (0.033 \pm 0.022)\chi - (0.023 \pm 0.006)\theta + (11.11 \pm 1.06) \quad (3d)$$

$$r^2 = 0.70$$

phosphines increases (smaller χ). Secondly, and importantly, there is no statistically significant steric effect. Finally, there is a very significant aryl effect that accounts for 31% of the total variation of the IP.

There are two reasonable explanations for the absence of observable steric effects in the correlation of the IP with χ, θ, and E_{ar}. This could occur if, first, both IP and χ exhibit similar steric effects or, second, if neither IP nor χ exhibits steric effects. The first explanation seems unlikely, since the two properties have different origins and involve different compounds ($R_3PNi(CO)_3$ versus R_3P). The second explanation appears to us to be more reasonable.

Thus, predicated on (a) the method of determining χ values, (b) the observation that the χ values of $P(o\text{-}MePh)_3$ and $P(p\text{-}MePh)_3$ are similar, and (c) results for the analysis of the IP's of the phosphines, we believe that χ is free of steric influences.

Does χ Have an E_{ar} Component? We believe that χ has an E_{ar} component on the basis of our analyses of the carbonyl stretching frequencies of $Ir(CO)(Cl)L_2$ and $LCr(CO)_5$ (trans CO), as well as $LNi(CO)_3$. In Figure 3, we plot the three sets of infrared data versus χ. For the iridium complexes, we observe that the data for $P(p\text{-}XPh)_3$ lie above the data for PR_3, indicating that as a family $P(p\text{-}XPh)_3$ species are poorer electron-donor ligands toward iridium than PR_3. In the chromium complexes we see the opposite situation; the data for $P(p\text{-}XPh)_3$ lie below those for PR_3, thereby indicating that as a family $P(p\text{-}XPh)_3$

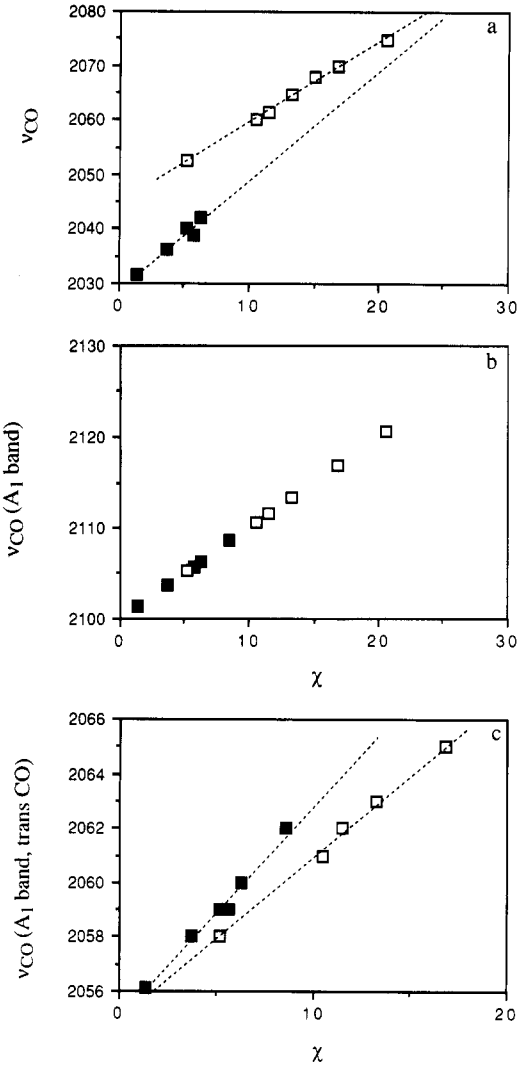

Figure 3. Plots of the carbonyl stretching frequencies for $Ir(CO)(Cl)L_2$ (a), $LNi(CO)_3$ (b), and $LCr(CO)_5$ (c) versus the electronic parameter χ. Data for the complexes containing $P(p\text{-}XPh)_3$ are displayed as open squares, and the data for PR_3 are displayed as solid squares. Data for the nickel complexes are taken from ref 16. Data for the iridium (in methylene chloride) and chromium (in cyclohexane) complexes were measured in our laboratories.

groups are better electron donors toward the $Cr(CO)_5$ fragment than PR_3. For the nickel complexes $LNi(CO)_3$, both sets of phosphines fall on the same line because χ is derived from the infrared data for $LNi(CO)_3$. Thus, the aryl effect clearly is different for all three metal centers, which suggests that it could be present in all three complexes.[21]

We must assume that χ contains an electronic component related to E_{ar}. This means that if a set of data can be correlated without using E_{ar}, then the phosphines are behaving as they do toward $Ni(CO)_3$. It does not mean that there is no aryl effect. If E_{ar} is necessary in the analysis, then it represents the deviation in behavior from the $Ni(CO)_3$ standard.

(21) The difference in the slopes of the plots of the data for $P(p\text{-}XPh)_3$ and PR_3 in parts a and c of Figures 3 suggests a steric effect. Steric effects, as discussed by Brown,[22] can be attractive or repulsive. A repulsive steric effect would be expected to lengthen the M–P bond and thereby decrease the electron-donor ability of the phosphine ligand as the size of the phosphine increases. However, we observe the opposite. On the other hand, attractive dispersion forces between the metal fragment and the phosphine might enhance the electron-donor ability of the phosphine.

(22) (a) Caffery, M.; Brown, T. L. *Inorg. Chem.* **1991**, *30*, 3907. (b) Lee, K. J.; Brown, T. L. *Inorg. Chem.* **1992**, *31*, 289.

Performing Analyses Using χ, θ, and E_{ar}

General Considerations. In order to correlate kinetic or thermodynamic data with stereoelectronic parameters, one wants the parameters to be uncorrelated. However, in many cases the parameters are found to be accidentally correlated as a result of the particular selection of ligands chosen for the experiment. In fact, for all the systems that we studied involving phosphines, the value of r^2 among the parameters is not very close to zero. How serious is the effect of this correlation on our studies? It turns out that a fair amount of correlation can be tolerated, particularly if r^2 for the correlation of the data with the parameters is very high.

Consider, as an example, a set of eight PR_3 ligands (Table I, entries 5, 14, 15, 18, 22, 33, 35, and 36). The correlation between χ and θ is rather high: $r^2(\chi/\theta) = 0.95$. Consider a particular correlation of some hypothetical rate data ($\log k'$) where the parameters are of about equal importance (i.e. contribute about 50% each to the range of $\log k'$), where steric effects are continuously operative, and where $r^2(\log k'/\chi,\theta) = 0.90$. It turns out that the 90% confidence limit for the errors in the coefficients of χ and θ are 42% and 36%, respectively, a somewhat large uncertainty but still a useful result for some purposes. On the other hand, suppose that a steric threshold (θ_{st} = 140°) had been present with four of these ligands having cone angles above θ_{st}. Now we find that the 90% confidence limit for the errors in the coefficients of χ and θ are reduced to 23% and 24%. (For a fuller discussion of the uncertainty involving θ_{st}, see below.)

Even in the absence of a steric threshold, if we consider a group of 10 ligands, including some phosphorus(III) hydrides (Table I, entries 5, 7, 8, 10, 11, 13–15, 18, and 19), we find that $r^2(\chi/\theta)$ decreases to 0.69. Again, for some hypothetical rate data where the value of $r^2(\log k'/\chi,\theta) = 0.90$, we find the 90% confidence limits for the coefficients of χ and θ to be 28% and 24%, respectively.

How does uncertainty in the value of θ_{st} affect the 90% confidence limits of the coefficients of χ and θ as determined by linear regression analysis? The question arises because the presence of θ_{st} and the switching function makes the problem into a nonlinear regression problem. In practice, the regression is handled as a linear two-parameter problem where θ_{st} is determined as the value that maximizes r^2 (equivalently, minimizes the standard deviation). To address this concern, we find it useful to perform model computations which allow us a direct view of the statistics.

For example, again consider the hypothetical data set ($\log k'$) for the eight PR_3 ligands (Table I, entries 5, 14, 15, 18, 22, 33, 35, and 36), which by the maximization procedure mentioned above yields the result

$$\log k' = (1.17 \pm 0.15)\chi + (0.182 \pm 0.025)(\theta - 140)\lambda + \text{constant} \quad (4a)$$

$$r^2 = 0.92,\ \sigma = 0.336$$

We begin with this expression and add a noise term to get

$$\log k' = 1.17\chi + 0.182(\theta - 140)\lambda + c(r_n) \quad (4b)$$

where r_n is a normally distributed pseudo random number

with zero mean and unity standard deviation. With this equation, using the parameters of the eight PR_3 ligands, along with eight random numbers, we generate a set of "experimental data". Then using linear regression analysis of this data set (including the aforementioned maximization procedure), we obtain θ_{st} and the coefficients of the χ and θ terms. We repeat the computations many times with a fixed value of c and different sets of random numbers, looking for a value of c that produces an average value of σ (within a narrow range) which agrees with the original set of experimental data. For this particular value of c, the coefficients obtained from a large number of repeated analyses are sorted and the 90% confidence limits are readily obtained. In this way we find that the 90% confidence limits of the coefficients of χ and θ are 23% and 24%, when θ_{st} is assumed to be known a priori and it increases to 26% and 30%, respectively, with a corresponding 90% confidence limit for θ_{st} of ±5° when the procedure for maximizing r^2 described above is used. For a corresponding case where $r^2(\log k'/\chi,\theta)$ is larger (0.95), we find, as expected, the standard errors are smaller as is the uncertainty in θ_{st}. Furthermore, we find that when we have unequal distribution of ligands around θ_{st} (e.g. 3 below and 5 above θ_{st}) we obtain virtually the same results as for an equal distribution. This result is intuitively reasonable. The present results demonstrate that when we include the uncertainty of θ_{st} we find that the true 90% confidence limits are not far removed from those estimated on the basis of the simpler two-parameter linear regression analysis where θ_{st} is obtained by the maximization procedure (vide supra). The case of a three-parameter fit is discussed below in the section where we consider reaction 11. (The codes for these statistical calculations (two- and three-parameter fits) are included in the supplementary material.)

Protocol for QALE When the Set of Ligands Is Restricted to PR_xPh_{x-3} and $P(p\text{-}XPh)_3$

In order to illustrate the protocol that we believe is appropriate for the analysis of phosphine ligand effect data, we consider the correlation between the stereoelectronic parameters of different families of phosphines and then investigate how the analysis of real data is affected. We will show how eq 1a (and its modified form eq 1b), which was originally developed for entering-ligand-dependent substitution reactions, can be applied to reactions involving spectator ligands with one observable steric threshold. (The case of two observable steric thresholds will not be considered.) We will first consider the analysis of data for separate families of phosphines and then the analysis of a complete set of data that includes $P(p\text{-}XPh)_3$, PR_3, and $PR_{3-x}Ph_x$.

Estimation of the Coefficient of χ. Analysis of the Data for $P(p\text{-}XPh)_3$. First and foremost in our model for treating ligand effect data, we take both E_{ar} and θ to be constant for $P(p\text{-}XPh)_3$. Thus, a plot of the appropriate data (e.g. $\log k$) versus χ for this set of ligands affords an estimate of the coefficient of χ in the equation that relates the total set of experimental data to the three stereoelectronic parameters. Then, we look for this coefficient of χ to be similar to that obtained by regression analysis of the total set. This serves as a check on the analysis.

Determination of the Presence of a Steric Threshold. Analysis of the Data for PR_3. When the data are restricted to the trialkylphosphines, the coefficients of χ and θ might contain large errors (vide supra) because of the high degree of correlation between χ and θ. (E_{ar} is zero by definition for this set of phosphines.) We can obtain, however, a value of the steric threshold if it is observable. The presence of a steric threshold (θ_{st}) makes the new steric parameter $(\theta-\theta_{st})\lambda$ (eq 1a). As pointed out above, with sufficient points above and below the threshold, the original correlation between χ and the steric parameter is reduced. This threshold is readily apparent when eq 1a is used to analyze the data. (In fact, θ_{st} might be observable when the data are plotted versus θ because of the high correlation between χ and θ.) The value of θ_{st} is meaningful and will be obtained no manner how the analysis is performed (vide infra).

The coefficients obtained via eq 1a for the PR_3 data with a steric threshold are reliable for entering-ligand-dependent reactions but are not necessarily reliable for reactions involving spectator ligands. The slope of the steric profile below the steric threshold is zero by construction (eq 1a). This does not necessarily mean that the real slope is zero for reactions involving spectator ligands. The reason it is possible to impose a zero slope is because χ and θ are closely correlated within this region. Thus, with data limited to the trialkylphosphines, the absolute slopes of the two portions of the steric profile are unknown. The difference in the slopes of the two portions of the steric profile is, however, informative.

Analysis of the Data for $PR_{3-x}Ph_x$. In the past, in order to overcome the problem of good correlation between χ and θ, the mixed alkylphenylphosphines were included along with the trialkylphosphines. Thus, for this larger group there is a poor correlation between χ and θ (r^2 = 0.429). However, when we include E_{ar}, we find an excellent correlation of χ with θ and E_{ar} (r^2 = 0.990). Hence, when E_{ar} is included, this set of phosphines correlates like PR_3 as described above in the absence of a steric threshold. The presence of a steric threshold again reduces the correlation between the stereoelectronic parameters, but the analysis still suffers from the limitations described for PR_3.

Determination of the Actual Slopes of the Steric Profile. Only when the isosteric ligands $P(p\text{-}XPh)_3$ are included in the analysis is the correlation reduced between the three parameters even in the absence of a steric threshold. In the presence of a steric threshold, the correlation between parameters is reduced even further. The slopes of the steric profile can be obtained in the following manner. We apply eq 1b to the set of ligands, either above or below the steric threshold (determined as described above), that contains $P(p\text{-}XPh)_3$. For this subset of ligands there is no steric threshold. Equation 1b will then give both the electronic coefficient (applicable to the entire set of ligands) and the steric coefficient for this subset. The steric profile for the data is then obtained by subtracting the electronic portion of eq 1b as well as the constant term from the experimental data and then plotting the difference versus θ. The slope of the other part of the steric profile can then be determined graphically.

Analysis of Data for an Entering-Ligand-Dependent Reaction. The situation is less complicated when the phosphine (or other incipient ligand) is an entering ligand than when it is a spectator ligand. When it is an entering ligand, there are steric effects only in the transition state and the coefficient of the steric term is truly zero for

Table II. Kinetic and Thermodynamic Data for Reactions 5, 9, and 11

entry no.[a]	phosphine	log k_5[b]	log(c/t)[c]	log k_{11}[d]
5	PMe_3	−1.17	0.474	−2.65
7	$PHBu_2$			−4.09
8	$PH(octyl)_2$			−4.34
9	PMe_2Ph	−1.15		−3.12
10	$PEtMe_2$			−2.09
11	$PH(i\text{-}Bu)_2$			−4.42
13	PEt_2Me			−2.37
14	PEt_3	−2.30	0.288	−2.81
15	PPr_3			−2.86
16	PEt_2Ph	−1.39	0.522	−3.32
17	$PMePh_2$	−1.23		
18	PBu_3		0.265	−2.79
19	$P(pentyl)_3$			−2.80
20	$P(octyl)_3$		0.250	
21	$PEtPh_2$	−1.40	0.602	−3.95
22	$P(i\text{-}Bu)_3$			−3.72
24	$P(p\text{-}MeOPh)_3$	−1.38		−3.56
25	$P(p\text{-}MePh)_3$	−1.32	0.713	
26	PPh_3	−1.17	0.661	−4.42
27	$P(p\text{-}FPh)_3$	−1.10	0.502	
28	$P(p\text{-}ClPh_3)$	−0.74		
31	$PCyPh_2$	−1.70		
32	$P(t\text{-}Bu)Ph_2$	−1.40		
33	$P(i\text{-}Pr)_3$	−1.67	−0.229	
34	PCy_2Ph	−1.57		
35	PCy_3	−1.63	−0.260	−2.68

[a] Entry numbers correspond to those listed in Table I. [b] Data are taken from ref 14. [c] Data are taken from ref 23. [d] Data are taken from ref 24.

$\theta < \theta_{st}$. If there is a steric threshold, then eq 1b is valid *regardless of the nature of the phosphines, and the coefficients are meaningful.* If a steric threshold is not observed, then the data for $P(p\text{-}XPh)_3$ must be included (vide supra). Analysis of the data for $P(p\text{-}XPh)_3$ alone in terms of χ should give an estimate of the value of the coefficient of the χ term in eq 1b ($\theta_{st} = 0$). Analysis of the entire set of data should also give the same coefficient of χ.

Illustrative Example of an Analysis of Kinetic Data in Terms of χ, θ, and E_{ar} for a Reaction Involving Spectator Ligands

In order to show how be believe an analysis should be done, we have reanalyzed a set of our own kinetic data[14] (Table II) for the rate of carbonylation (eq 5) of $(\eta\text{-Cp})(CO)(L)FeMe^+$ in CH_2Cl_2 containing 0.1 M tetrabutylammonium hexafluorophosphate at 0 °C. It turns out that E_{ar} is of marginal importance here, but the example serves as a good illustration of our protocol.

$$(\eta\text{-Cp})(CO)(L)FeMe^+ + CO \xrightarrow{k_5} (\eta\text{-Cp})(CO)(L)FeCOMe^+ \quad (5)$$

Our original analysis used χ and θ, but not E_{ar}. The resulting steric profile (Figure 4a) was generated by plotting the deviations (log k_5^{st}) of the data from the line (eq 6) determined by the complexes containing the isosteric

$$\log k_5 = (0.087 \pm 0.02)\chi - (2.32 \pm 0.28) \quad (6)$$

$$n = 5; r^2 = 0.86$$

ligands $P(p\text{-}XPh)_3$. The resulting steric profile shows regions of steric inhibition and a steric threshold near 150° followed by a region of steric acceleration. log k_5^{st} values for the $P(p\text{-}XPh)_3$ groups were located slightly above the steric profile, and the data point for PEt_3 was inexplicably located significantly below the steric profile. (The $P(i\text{-}Bu)_3$ complex reacted too slowly to measure.) As we will see, the shape of the steric profile is essentially correct and there is only one observable steric threshold.

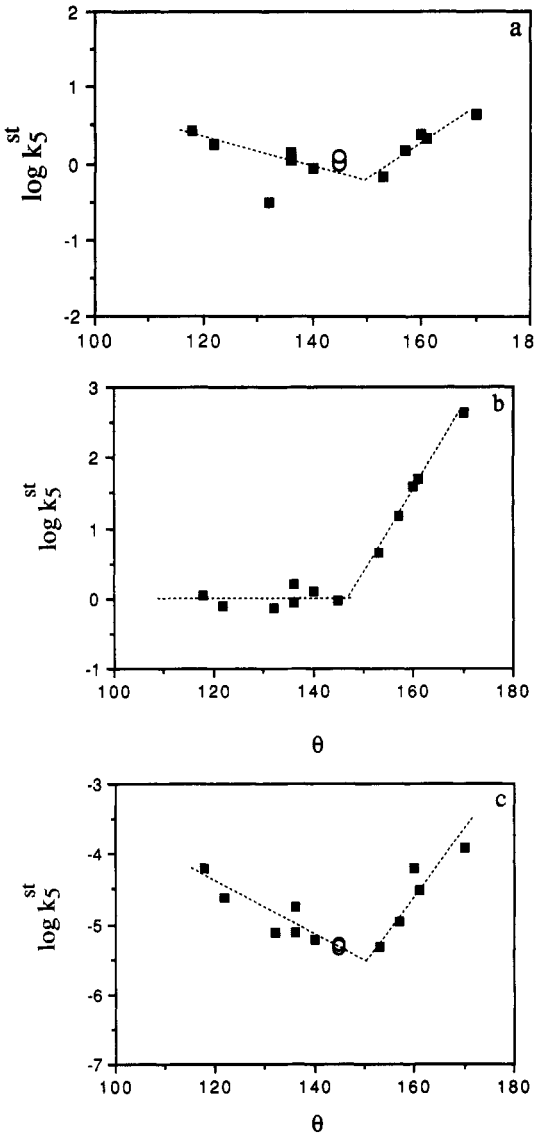

Figure 4. Steric profiles for the carbonylation of $(\eta\text{-Cp})(CO)(L)FeMe^+$ in CH_2Cl_2 containing 0.1 M tetrabutylammonium hexafluorophosphate. Each steric profile is based on a different mode of analysis. Profile a was constructed graphically by the deviations of the data from the line (eq 6) determined by the data for the complexes containing the ligands $P(p\text{-}XPh)_3$. Profile b was generated from eq 7. The data for the $P(p\text{-}XPh)_3$ ligands were not included in the analysis. Profile c was generated from eq 8, which was based on analysis of the data for the complexes containing ligands with $\theta < 147°$.

We will now perform the analysis following the protocol that we outlined earlier. From the analysis of the data for the complexes containing $P(p\text{-}XPh)_3$, we get an estimate of the coefficient of χ (eq 6) for the entire set of data.

The steric threshold that we originally observed can also be seen when the analysis is performed on the set containing only the trialkylphosphines, mixed alkylphenylphosphines, and PPh_3 but excluding other $P(p\text{-}XPh)_3$ ligands. This limited set of ligands is commonly used in ligand-effect studies. We know for $PR_{3-x}Ph_x$ that there is good correlation between χ and the other two stereo-

electronic parameters in the absence of a steric threshold (vide supra). Analysis according to eq 1b affords a good fit of the data to the three parameters, with a steric threshold near 150° (eq 7). However, it is important to

$$\log k_5 = (0.404 \pm 0.060)\chi + (0.111 \pm 0.016) \times (\theta - 147°)\lambda - (0.693 \pm 0.129)E_{ar} - (4.79 \pm 0.042) \quad (7)$$

$$n = 12;\ r^2 = 0.88;\ r^2(\chi/(\theta - \theta_{st})\lambda, E_{ar}) = 0.966$$

note that the coefficients of χ in eqs 6 and 7, which should be similar if eq 7 were correct, actually differ dramatically. This indicates that something is amiss with eq 7. In Figure 4b, we show the steric profile that results from eq 7. An important feature about the steric profile is that the data point for the PEt_3 complex, which was an outlier in Figure 4a, now correlates with the rest of the data in this set. Note that the section below 147° exhibits zero slope, suggesting incorrectly that steric effects are not operative in this region. As mentioned above, the problem is that, in either segment of the steric profile, there is correlation among the variables and therefore θ can be expressed as a linear combination of the two electronic parameters. Thus, forcing the coefficient of θ to be zero for ligands below the steric threshold results in the steric dependence being absorbed in the coefficients of the electronic terms, χ and E_{ar}. Above the steric threshold there is still correlation among the three parameters but with a different dependence of the data on the stereoelectronic parameters. Since the coefficients of the electronic parameters are set by eq 7, the new functional dependence properly shows up as a change in the coefficient of the steric term. This leads to a nonzero slope for the steric profile above the steric threshold. This illustrates the problem arising from the correlation of the parameters. Thus, the absolute values of the coefficients in eq 7 convey little information. On the basis of eq 7, we can only say that there is indeed a threshold near 150° and that above 150° there appears to be *relative* steric acceleration compared to the region below the steric threshold.

Additional information about the real coefficients of the stereoelectronic terms is obtained as outlined in the protocol (vide supra). We note that $P(p\text{-}XPh)_3$ groups have cone angles (145°) which lie in the region below the steric threshold. Accordingly, we can obtain a meaningful analysis for the subset of ligands with θ less than 147° because the parameters correlate poorly there (vide supra). (If the steric threshold were less than 145°, we would perform the analysis on the data for $P(p\text{-}XPh)_3$ and larger ligands and proceed as shown below.) Analysis using χ, θ, and E_{ar} gives eq 8, which we used to generate the steric

$$\log k_5 = (0.094 \pm 0.032)\chi - (0.0380 \pm 0.012)\theta + (0.27 \pm 0.15)E_{ar} - (2.32 \pm 1.65) \quad (8)$$

$$n = 11;\ r^2 = 0.85;\ r^2(\chi/\theta, E_{ar}) = 0.68,\ r^2(\chi/E_{ar}) = 0.64,\ r^2(\chi/\theta) = 0.37$$

profile (Figure 4c) for *all* the data. In this final result E_{ar} has marginal significance. In other examples we will see that E_{ar} is significant.

Importantly, we see in eqs 6 and 8 that the coefficients of χ are virtually the same, as demanded by our model. In the steric profile (figure 4c) generated from eq 8, we see the steric threshold at 147° which also appears in eq 7. The first segment now, however, has a negative slope (steric inhibition) and is followed by a region of steric acceleration. Since eq 8 determines the coefficients of the electronic parameters for all the data, the slope of the right side of the steric profile is meaningful even though the stereoelectronic parameters for this group are correlated. It is satisfying that the data for the PEt_3 and the $P(p\text{-}XPh)_3$ complexes now fall on or close to the steric profile.

In conclusion, these analyses illustrate the need for a set of appropriate phosphines (or ligands) in order to obtain a complete analysis of the data. Even with a limited set, however, one can see qualitatively major features of the dependence of the data on the stereoelectronic properties of the phosphines.

Other Examples of Analyses Involving E_{ar}

In this part of the paper, we utilize the three stereoelectronic parameters (χ, θ, and E_{ar}) to analyze several disparate sets of data for which we could not obtain satisfactory analyses with χ and θ alone. These analyses provide further support for the involvement of the additional electronic effect described by E_{ar} and test the transferability of the parameters.

Equilibration of the Cis and Trans Isomers of the Carbene Complexes $(CO)_4(L)Cr[C(OMe)Me]$. Nearly 20 years ago Fischer[23] reported this study of the equilibration of the cis and trans isomers of $(CO)_4(L)Cr[C(OMe)Me]$:

$$cis\text{-}(CO)_4(L)Cr[C(OMe)Me] \rightleftarrows trans\text{-}(CO)_4(L)Cr[C(OMe)Me] \quad (9)$$

Data for a wide variety of alkyl-, mixed alkylaryl-, and arylphosphines were presented (Table II). Several trends are evident. First, the cis/trans ratio (c/t) decreases as the electron-donor capacity of $P(p\text{-}XPh)_3$ decreases. Second, c/t decreases as the size of the trialkylphosphines increases. A unified analysis of the total set of data was not attempted.

We have analyzed the c/t ratios according to our protocol. We used the entire set of data except that for the complex containing the $P(m\text{-}FPh)_3$ ligand, for which we do not have a value for θ. Analysis of the data for the three complexes containing $P(p\text{-}XPh)_3$ gave eq 10a. Analysis of the

$$\log(c/t) = -(0.051 \pm 0.009)\chi + (1.32 \pm 0.13) \quad (10a)$$

$$n = 3;\ r^2 = 0.964$$

complexes containing $PR_{3-x}Ph_x$ did not show the presence of a steric threshold. Hence, we analyzed the entire set of data according to eq 1b and obtained eq 10b. (Note

$$\log(c/t) = -(0.052 \pm 0.013)\chi - (0.022 \pm 0.001)\theta + (0.370 \pm 0.045)E_{ar} + (3.54 \pm 0.33) \quad (10b)$$

$$n = 11;\ r^2 = 0.987,\ r^2(\chi/\theta, E_{ar}) = 0.954;\ r^2(\chi/E_{ar}) = 0.80,\ r^2(\chi/\theta) = 0.10;\ \chi\ (25\%),\ \theta\ (40\%),\ E_{ar}\ (35\%)$$

that although $r^2(\chi/\theta, E_{ar}) = 0.954$ we still obtain a useful correlation between the data and the parameters because r^2 is close to unity (vide supra).) Importantly, the

(23) Fischer, E. O.; Fischer, H. *Chem. Ber.* **1974**, *107*, 657.

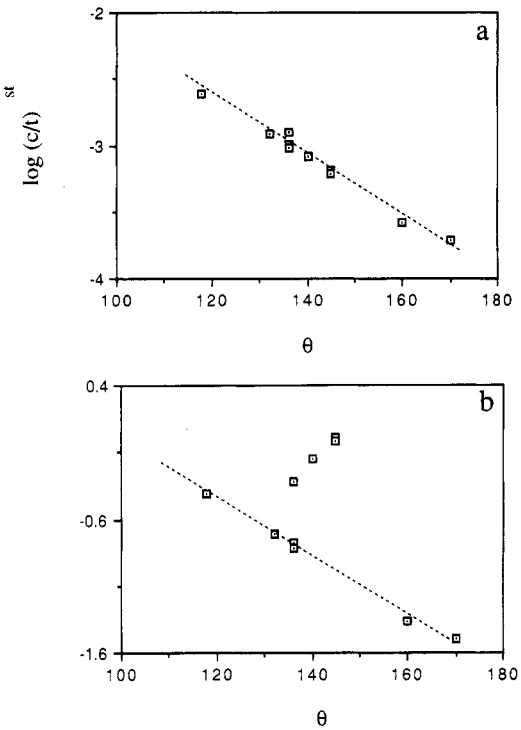

Figure 5. Steric profiles for reaction 9. Figure 5a was generated from eq 10b, whereas Figure 5b was generated on the basis of a graphical analysis involving only χ and θ as described in the text.

coefficients of χ in eqs 10a and 10b are virtually the same, as demanded by our method. Figure 5a shows the steric profile for reaction 9. The lack of scatter in the steric profile is striking, considering that the method of generating these profiles includes all the error in the analysis.

The importance of E_{ar} is readily seen when the analysis of the data is done graphically in terms of χ and θ only or by regression analysis without E_{ar} (eq 10c). Equation 10c

$$\log(c/t) = (0.055 \pm 0.010)\chi - (0.0090 \pm 0.003)\theta + (1.17 \pm 0.51) \quad (10c)$$

$$r^2 = 0.859$$

shows a significantly poorer fit, but most importantly the coefficients of χ are different in eqs 10a and 10c; in fact, they have opposite signs. In graphical analysis, we subtracted the data from the line determined by eq 10a for the complexes containing P(*p*-XPh)$_3$ and plotted the deviations versus θ to obtain the steric profile shown in Figure 5b. It is clear that the data for the ligands containing the aryl groups deviate systematically from the line drawn through the trialkylphosphine complexes.

The S_N2 Reaction between Iodoethane and Phosphines. In their classic study of the S_N2 reaction between phosphines and iodoethane (eq 11), Henderson and Buckler[24] made some important observations. First, the

$$PR_3 + EtI \xrightarrow{k_{11}} EtPR_3^+ + I^- \quad (11)$$

order of reactivity of the ethylmethylphosphines was $PMe_2Et > PMeEt_2 > PMe_3 > PEt_3$, which correlated neither with $\sum\sigma^*$ nor with size. Second, PCy_3 appeared

(24) Henderson, W. A.; Buckler, S. A. *J. Am. Chem. Soc.* **1960**, *82*, 5794.

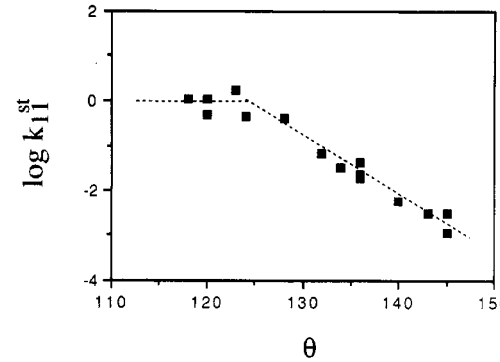

Figure 6. Steric profile for the S_N2 reaction between phosphines and iodoethane (eq 11).

to correlate as a "normal" phosphine, whereas the smaller P(*i*-Bu)$_3$ was "unusually" unreactive. Correlation of the data for the entire set of phosphines with $\sum\sigma^*$ afforded a scatter diagram.

We have analyzed the kinetic data (log k_{11}, Table II) in terms of χ, θ, and E_{ar}. We treated this substitution reaction in the same manner as the entering-ligand-dependent substitution reactions (vide supra); i.e., we applied eq 1b directly to the data. We used all the data presented in the paper except the points for PMe_2Ph, PCy_3 (which we think is unusually reactive), and P(EtCN)$_3$. This gave a total of 15 points. Regression analysis gave eq 12a. We also

$$\log k_{11} = -(0.457 \pm 0.034)\chi - (0.124 \pm 0.013) \times (\theta - 123°)\lambda + (1.10 \pm 0.13)E_{ar} + (1.23 \pm 0.35) \quad (12a)$$

$$n = 15;\ r^2 = 0.951;\ r^2(\chi/(\theta - \theta_{st})\lambda, E_{ar}) = 0.73;$$
$$r^2(\chi/E_{ar}) = 0.31,\ r^2(\chi/(\theta - \theta_{st})\lambda) = 0.015;$$
$$\chi\ (40\%),\ (\theta - \theta_{st})\lambda\ (29\%),\ E_{ar}\ (31\%)$$

analyzed the data using the statistical method based on variable θ_{st} (vide supra). The 90% confidence limits for χ, θ, E_{ar}, and θ_{st} were ±14%, ±22%, ±22%, and ±2°, respectively. The first three numbers are to be compared to the respective 90% confidence limits of ±13%, ±19%, and ±19% from the analysis leading to eq 12a with θ_{st} taken as fixed, a priori.

The importance of the aryl effect is shown by doing the analysis without E_{ar}, which results in a poor correlation, as shown in eq 12b.

$$\log k_{11} = -(0.216 \pm 0.046)\chi - (0.024 \pm 0.015)(\theta - 123)\lambda - (1.24 \pm 0.46) \quad (12b)$$

$$n = 15;\ r^2 = 0.66$$

Since data for only two triarylphosphines were reported, we do not believe that a meaningful comparison can be made of the coefficients of χ for the triarylphosphines with that of the entire set. Even though the condition of similarity of the coefficients of χ cannot be tested, the results are intuitively reasonable (eq 12a). The rate of reaction increases as the electron-donor ability of the phosphine increases and diminishes as the size of the phosphine increases. Importantly, there is a steric threshold at 123°. It is the turning on of the steric effect at this point that diminishes the reactivity of the larger members of the $PMe_{3-x}Et_x$ family and leads to the unusual reactivity pattern for these four compounds. In addition, on the

basis of this analysis, P(*i*-Bu)$_3$ behaves normally. It contrast, PCy$_3$ is more reactive than predicated by eq 12a. We are uncertain as to the origin of this enhanced reactivity. It is also noteworthy that the nucleophilicity of the arylphosphines is significantly enhanced (10^3) by the aryl effect.

Analysis of Kabachnik's σ^{Ph} Constants. One of the most widely used sets of substituent constants for describing the electronic effects of phosphorus groups is σ^{Ph}, which was introduced by Kabachnik in 1956.[18] The constants are based on the pK_a values of the phosphonic acids RR′P(O)OH. In a manner analogous to the treatment of $\sum\sigma^*$ described earlier in this paper, we correlated $\sum\sigma^{Ph}$ with χ, θ, and E_{ar}. We used data for a set of 28 phosphines comprised of trialkyl-, triaryl-, and mixed alkylarylphosphines (Table I). The coefficients of χ determined for the set of P(*p*-XPh)$_3$ ligands (eq 13a) and

$$\sum\sigma^{Ph} = (0.168 \pm 0.012)\chi - (3.70 \pm 0.17) \quad (13a)$$

$$n = 7;\ r^2 = 0.974$$

$$\sum\sigma^{Ph} = (0.174 \pm 0.009)\chi - (0.003 \pm 0.002)\theta + (0.265 \pm 0.036)E_{ar} - (4.08 \pm 0.45) \quad (13b)$$

$$n = 28;\ r^2 = 0.985;\ r^2(\chi/\theta,E_{ar}) = 0.73,\ r^2(\chi/E_{ar}) = 0.05,\ r^2(\chi/\theta) = 0.53;\ \chi\ (83\%),\ \theta\ (0\%),\ E_{ar}\ (17\%)$$

for the complete set of compounds (eq 13b) were similar, in accordance with our model. The results show that, indeed, steric effects do not appear to be statistically significant. There is an important χ electronic effect, and the aryl effect is small but statistically significant.

When E_{ar} is not included in the analysis (eq 13c), the 90% confidence limits for the coefficients of χ for the seven compounds (*p*-XPh)$_2$P(O)OH and for the full set do not overlap; therefore, the coefficients are statistically different, which is unacceptable according to our model. In addition, the omission of E_{ar} (eq 13c) leads to a steric effect (19%), whereas proper inclusion of E_{ar} leads to no steric effect.

$$\sum\sigma^{Ph} = (0.222 \pm 0.013)\chi + (0.011 \pm 0.003)\theta - (6.15 \pm 0.64) \quad (13c)$$

$$n = 28;\ r^2 = 0.949$$

Hydride Transfer from Silanes to Carbenium Ions. A few years ago we reported[25] that kinetic data for the addition of the carbenium ion (*p*-MeOPh)(Ph)CH$^+$ to allylsilanes (eq 14), as reported by Mayr,[26] gives an excellent correlation when we use the stereoelectronic parameters χ and θ for analogous phosphorus(III) compounds. This was the first indication that the phosphorus(III) parameters could be transferred to silyl groups. Since then, Brown[27] and Yang[28] have successfully used the phosphorus(III) parameters to analyze kinetic and thermodynamic data for the interaction of silanes with organometallic complexes:

$$(p\text{-MeOPh})(\text{Ph})\text{CH}^+ + \text{CH}_2{=}\text{CHCH}_2\text{SiR}_3 \rightarrow (p\text{-MeOPh})(\text{Ph})\text{CHCH}_2{-}{}^+\text{CHCH}_2\text{SiR}_3 \quad (14)$$

Recently Mayr[29] reported a new set of kinetic data (Table III) for the abstraction of hydride from organosilanes by the same carbenium ion (*p*-MeOPh)(Ph)CH$^+$ (eq 15).

$$(p\text{-MeOPh})(\text{Ph})\text{CH}^+ + \text{HSiR}_3 \xrightarrow{k_{15}} (p\text{-MeOPh})(\text{Ph})\text{CH}_2 + {}^+\text{SiR}_3 \quad (15)$$

Mayr's observation that HSi(*i*-Pr)$_3$ is 6 times less reactive than HSiPr$_3$ suggested steric inhibition of the reaction. Comparison of the rate data with Taft's σ_I constants indicated that the reaction was enhanced by better electron-donor groups on the silicon. We reanalyzed this set of data in terms of the phosphorus(III) stereoelectronic parameters. (Data for the silanes bearing chloro, alkoxy, and benzyl groups attached to the silicon were excluded from the analysis.) Unlike the analysis of reaction 14, we were unable to correlate satisfactorily the rate data for eq 15 with χ and θ alone (eq 16a). We then included E_{ar} and

$$\log k_{15} = -(0.242 \pm 0.040)\chi - (0.014 \pm 0.015)\theta + (5.81 \pm 218) \quad (16a)$$

$$n = 19;\ r^2 = 0.76$$

repeated the analysis according to our protocol (vide supra). Analysis (eq 16b) of the four data for the silanes containing SiMe$_2$(*p*-XPh) yields a coefficient for χ in agreement with that found (eq 16c) for the analysis of the full set of data. The result of the analysis (eq 16c) is as one might expect for a reaction where positive charge is developing on the silyl group in the transition state. The rate of reaction is dominated by electronic effects, with the better electron-donor groups being more reactive.

Table III. Stereoelectronic Parameters (χ, θ, and E_{ar}) for the Silyl Groups and Kinetic Data for the Transference of Hydride from Silanes to (*p*-MeOPh)(Ph)CH$^+$ (Eq 15)

entry no.	silyl group	χ^a	θ^a	E_{ar}	log $k_{15}{}^b$
1	SiH$_2$(hexyl)	18.0	103	0	−1.320
2	SiH$_2$Ph	20.9	106	1.0	−1.157
3	SiHMePh	15.4	117	1.0	0.727
4	SiMe$_3$	8.55	118	0	1.804
5	SiH(hexyl)$_2$	11.7	120	0	0.871
6	SiMe$_2$(*p*-MeOPh)	9.2	122	1.0	2.940
7	SiMe$_2$(*p*-MePh)	9.5	122	1.0	2.519
8	SiMe$_2$Ph	10.6	122	1.0	2.173
9	SiMe$_2$(*p*-ClPh)	11.3	122	1.0	1.695
10	SiMe$_2$Et	7.8	123	0	1.954
11	SiHPh$_2$	17.3	126	2.0	0.079
12	SiMeEt$_2$	7.05	127	0	2.064
13	SiEt$_3$	6.3	132	0	2.093
14	SiPr$_3$	5.4	134	0	2.342
15	Si(hexyl)$_3$	5.0	136	0	2.577
16	SiBu$_3$	5.25	136	0	2.585
17	SiMePh$_2$	12.1	136	2.0	1.350
18	SiPh$_3$	13.25	145	2.7	0.918
19	Si(*i*-Pr)$_3$	3.75	160	0	1.565

[a] The stereoelectronic parameters, χ (cm) and θ (deg), for the silyl group are transferred directly from the isostructural phosphines. [b] Kinetic data are taken from ref 30.

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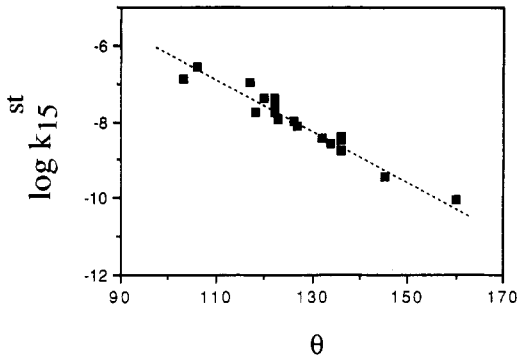

Figure 7. Steric profile for reaction 15.

There is a smaller inhibitory steric effect with no observable steric threshold. (The steric profile for reaction 15 is displayed in Figure 7.) The aryl effect is significant and enhances the rate of reaction by up to a factor of about 10^3.

$$\log k_{15} = -(0.527 \pm 0.086)\chi + (7.69 \pm 0.88) \quad (16b)$$

$$n = 4; r^2 = 0.949$$

$$\log k_{15} = -(0.431 \pm 0.027)\chi - (0.066 \pm 0.008)\theta + (1.05 \pm 0.12)E_{ar} + (13.6 \pm 1.3) \quad (16c)$$

$$n = 19; r^2 = 0.961; r^2(\chi/\theta,E_{ar}) = 0.83; r^2(\chi/E_{ar}) = 0.28, r^2(\chi/\theta) = 0.42; \chi\ (54\%), \theta\ (22\%), E_{ar}\ (24\%)$$

Conclusions

Although we do not understand the nature of the aryl effect (E_{ar}), we believe that the analyses described herein clearly demonstrate the existence of this electronic effect for phosphine ligands and silyl groups. It appears that this effect is dependent only on the number of aryl groups attached to the ligating atom. Since we have correlated in terms of χ, E_{ar}, and θ disparate sets of kinetic and thermodynamic data for transition-metal complexes, main-group-metal compounds, and phosphorus(V) compounds, it appears that these stereoelectronic parameters might be the descriptors for a very wide body of chemical information.

It is important to note that the contributions of E_{ar} relative to χ vary from system to system and even change in relative sign. This means in a most general sense that at least two electronic parameters are required and that a single electronic parameter (pK_a, χ, δ, $\sum\sigma^*$, $\sum\sigma^{Ph}$, etc.) cannot be generally applied to the analysis of ligand-effect data.

We also note that there might be other potential problems in the analysis of ligand effect data. For example, it seems reasonable that there might be a corresponding effect associated with other pendant groups (alkoxy and halo groups) of phosphorus(III) ligands. If this is the case, then correlation (χ and θ, or pK_a and θ) of data from a set of ligands containing phosphites and phosphines might not be appropriate, since the aryl effect as well as the analogous effect for the alkoxy- and halophosphines has not been considered. We are currently measuring sets of new kinetic data that should shed light on this problem.

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Supplementary Material Available: IBM 7090 computer programs used in the statistical analyses described in the text (16 pages). Ordering information is given on any current masthead page.

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