Reactivity of Phosphorus Donors

Steven Joerg,* Russell S. Drago,[†] and Joaquim Sales[‡]

Department of Chemistry, University of Florida, Gainesville, Florida 32611-7200

Received September 8, 1997

A greatly expanded database has led to a revised set of E_B and C_B basicity parameters for the analysis of the reactivity of phosphorus donors with the ECW model. Reactivity and spectral shift analyses are reported for 79 acceptors. General patterns for the reactivity of phosphorus donors emerge, for example, π-back-bond acceptor tendencies are shown to decrease as the σ basicity increases. Steric effects are encountered with a few acceptors, and a procedure is offered that uses an extension of ECW to quantitatively confirm steric repulsions. Very different interpretations of reactivity result from ECW compared to those from analyses that use one-parameter electronic basicities, χ, and cone angles, θ. When donor orders reverse with acceptor softness (covalency), one-parameter electronic basicity scales cannot accommodate the reversals. It will be shown that the cone angle is used inappropriately to compensate for changing softness in the χ and θ correlations. Attempting to compensate for softness using θ leads to an exaggeration of the steric contributions and to unprecedented interpretations of reactivity trends when the parameters for different acceptors are compared. The meaning of the correlations is questioned. Donors for which θ does not correlate to E_B and C_B parallel those that require extra parameters, e.g., E_{ar}, to obtain good fits with the QALE procedures. It is also shown that the extra QALE terms provide parameters that enable one to correlate systems which demonstrate nonlinear free-energy behavior, clouding even further the meaning of QALE correlations.

Introduction

The ECW model[1] was developed at about the same time that chemists began to recognize the need for at least two independent effects to define basicity. These effects have been called hard/soft, Class A/B, charge/frontier, nucleophilicity/basicity, and electrostatic/covalent. The ECW model, eq 1, uses the enthalpies of adduct formation measured in poorly solvating solvents to derive quantitative parameters for a scale of σ donor, B, basicity and a scale of σ-acceptor, A, acidity.[1] Two

$$-\Delta H = E_A E_B + C_A C_B + W \qquad (1)$$

effects are needed to fit the data. The magnitudes of the parameters for these two effects parallel qualitative hard−soft, etc., reactivity trends. The electrostatic, E, and covalent, C, model was selected *to name* the parameters E_A, E_B, C_A, and C_B.

The enthalpy basis for ECW provides parameters that are related to donor−acceptor bond strength and are free of complications from solvation or entropic effects. Omission of systems with π-back-bonding contributions and steric effects provide parameters free of these

influences. In enthalpy analyses of new systems where these effects exist, the parameters provide estimates of the magnitudes of steric strain and π-back-bonding.[1]

The E_B and C_B parameters provide a σ basicity scale that can be used with eq 2 in correlations to determine if physicochemical measurements, χ, are controlled by the same factors that influence bond strengths. χ can

$$\chi = E_A{}^* E_B + C_A{}^* C_B + W \qquad (2)$$

be a spectral shift, rate constant, activation enthalpy, redox potential, or any measurement that is expressed in energy units. Free energies can be interpreted with these enthalpy-based parameters because the goal of established *linear free-energy* scales is to derive *enthalpy-related* parameters in order to interpret the correlation in terms of electronic effects. This is an important point that has been overlooked in the organometallic literature. Parameter derivation must use enthalpies or employ systems in which the enthalpies vary linearly with the entropy to be meaningful. If the desire were to predict and understand entropies in nonlinear free-energy systems, a separate entropy scale would be needed.

In analyzing χ's for new systems where entropies do not vary in a linear manner with enthalpies, frequencies are not linear with force constants, or NMR chemical shifts contain neighbor anisotropic contributions, the correlations of these χ's to ECW or meaningful linear free-energy parameters *should* fail. In failed correlations, the ECW or linear free-energy models have not failed, but rather χ has contributions from effects not related to bond strength. Thus, the model provides an

* To whom correspondence should be addressed. Phone: (352) 392-5263. Fax: (352) 392-4658.
† Deceased Dec 5, 1997.
‡ Department de Química Inorgànica, Universitat de Barcelona, Barcelona, Spain.

(1) (a) Drago, R. S. *Applications of Electrostatic-Covalent Models in Chemistry*; Surfside Scientific Publishers: Gainesville, FL, 1994. (b) Drago, R. S. *Coord. Chem. Rev.* **1980**, *33*, 251. (c) Drago, R. S. *Organometallics* **1995**, *14*, 3408. (d) Drago, R. S. *Inorg. Chem.* **1995**, *34*, 3453. (e) Drago, R. S. *Inorg. Chim. Acta* **1996**, *250*, 265. (f) Drago, R. S.; Vogel, G. C. *J. Am. Chem. Soc.* **1992**, *114*, 9527. (g) Drago, R. S. *Inorg. Chem.* **1990**, *29*, 1379. (h) Drago, R. S.; Vogel, G. C.; Needham, T. *J. Am. Chem. Soc.* **1971**, *93*, 6018 and references therein.

understanding of reactivity and spectroscopy even when poor correlations result.

In recent work,[2] the ECW model has been extended to phosphorus donors. Only a few adduct-formation enthalpies have been measured for phosphorus donors reacting with σ-acceptors in the ECW correlation. In addition, there is limited data for acceptors studied with both phosphorus donors and other donors in the ECW correlation. This lack of overlapping data required a departure from the standard way[1a] of adding new donors to the correlation (see Calculations). The addition of new systems in this article gives new phosphorus donor parameters that are different than those reported earlier[2] but are better connected to the other donor parameters.

An important conclusion about π-back-bonding to phosphorus donors resulted from the earlier ECW analyses.[2] Acceptors in which π-back-bonding is expected (e.g., spectral shifts of $Ni(CO)_3PX_3$) gave good correlations using the same phosphorus donor parameters as those for acceptors in which only σ-bond interactions are involved (e.g., enthalpies of reaction of donors with CF_3SO_3H and $Al_2(CH_3)_6$). The data fits for acceptors that can π-back-bond are restricted to phosphorus donors, while those with acceptors that only σ-bond may include phosphines, phosphites, sulfides, amines, pyridines, ethers, etc. Equations were derived[2] to show that such a result is possible if the π-acceptor properties of the phosphines and phosphites, $E_A{}^\pi$ and $C_A{}^\pi$, decrease proportionately with increasing σ-donor strength, E_B and C_B. Equations 3 and 4, where k and k' are proportionality constants, give such a relationship.

$$E_A{}^\pi = E_A{}^{\pi\circ} - kE_B \qquad (3)$$

$$C_A{}^\pi = C_A{}^{\pi\circ} - k'C_B \qquad (4)$$

The $E_A{}^{\pi\circ}$ and $C_A{}^{\pi\circ}$ terms refer to the π-acceptor contributions of a phosphorus donor with no σ-donor strength. When eq 1 or 2 is fit to a data set that contains a π-back-bonding contribution, the resulting parameters, $E_A{}^{*FIT}$, $C_A{}^{*FIT}$, and W^{FIT} for the π-back-bonding acceptors are given[2] by eqs 5, 6, and 7. The

$$E_A{}^{*FIT} = E_A{}^* - kE_B{}^{\pi M} \qquad (5)$$

$$C_A{}^{*FIT} = C_A{}^* - k'C_B{}^{\pi M} \qquad (6)$$

$$W^{FIT} = W + E_A{}^{\pi\circ}E_B{}^{\pi M} + C_A{}^{\pi\circ}C_B{}^{\pi M} \qquad (7)$$

$E_B{}^{\pi M}$ and $C_B{}^{\pi M}$ terms represent the electrostatic and covalent back-bond-forming tendencies of the metal. The correlation parameters $E_A{}^{*FIT}$, $C_A{}^{*FIT}$, and W^{FIT} are difficult to interpret because the separate contributions from π- and σ-effects in eqs 5–7 cannot be separated. In these instances, the value of the correlation of the physicochemical property is to detect donor contributions other than σ-bond strength.

A good data fit to eq 2 will result for acceptors that π-back-bond as long as the same proportionality constants in eqs 3 and 4 apply to all the donors studied. This is the case for all the phosphines and phosphites

studied. However, different constants are needed for other families of donors, e.g., pyridines. Thus, when data for other families are combined with phosphorus donors, good fits to eq 2 will result for acceptors that only σ-bond but not for acceptors that also π-back-bond.

The ECW model is unique in terms of its generality. No other set of reactivity parameters encompasses the variety of donors and acceptors used in this model. This is a very important point for any multiparameter correlation. In the study of new acceptors, the E_A and C_A parameters used to correlate reactivity arise by solving simultaneous equations of the form of eq 2. These equations must be independent and show a low correlation to each other in order to obtain a definitive fit. In acceptor correlations, we have emphasized that the C_B/E_B ratio for the donors must vary in order to define the E_A and C_A parameters accurately.[1a,b] Unfortunately, in studies limited to phosphorus donors, the C_B/E_B ratios of the donors selected are often similar. When this is the case, good data fits can result but the acceptor correlation parameters are without meaning.[1] Enthalpies cannot be predicted for any donor whose C_B/E_B ratio lies outside the C_B/E_B range used, and correlated systems may contain reactivity effects that are not related to bond strength. The only reliable conclusion from the correlation of such a data set is to spot a deviant system and to then proceed to investigate the causes for its deviation. Acceptor parameters from such analyses should be considered tentative.

There is widespread acceptance of the dual nature of donor−acceptor bond strength in electrostatic/covalent, hard/soft, or charge/frontier descriptions. With the exception of the ECW model and early work by Edwards,[3] literature correlation analyses of reactivity have not employed parameters related to these quantities as measures of substituent effects or basicity. Derivations are reported[1d] that show that each acceptor, with a significantly different softness, requires a different one-parameter basicity scale. As a result, use of a one parameter scale to define basicity and substituent constant effects has led to a proliferation of scales, each with limited utility.

This article reports improved phosphorus donor parameters which are better connected to the other donors in the ECW model. Many new acceptors are analyzed, and reported systems[2] are reanalyzed. The ECW approach and its interpretations of reactivity are contrasted with the reported unprecedented conclusions from correlations using cone angles and one-parameter basicity scales.

Calculations

Master Fit for Determining E_B and C_B for Phosphines. The measured physicochemical properties for all donors (Table 1) and all the acceptors (Table 2) are substituted into eq 1, leading to a series of simultaneous equations. In most instances, each equation has five unknowns. When the E_A and C_A values are known from earlier studies,[2] these are entered into the equation and held constant. When donors from the E and C correlation other than phosphines are used in the study of a reaction or spectral shift, their E_B and C_B values[1a] are also entered into the equation and fixed in the data fit. The best set of unknown parameters are determined by a least-

(2) Drago, R. S.; Joerg, S. *J. Am. Chem. Soc.* **1996**, *118*, 2654.

(3) Edwards, J. O. *J. Am. Chem. Soc.* **1954**, *76*, 1540.

Table 1. E_B and C_B Parameters for Phosphines

no.	phosphine	wt[a]	E_B	C_B	C_B/E_B	θ[b]
1	P(CH₃)₃	1.0	0.31	5.15	17	118
2	P(C₂H₅)₃	1.0	0.28	5.53	20	132
3	P(n-C₃H₇)₃	0.5	0.37	5.16	14	132
4	P(i-C₃H₇)₃	0.7	0.36	5.46	15	160
5	P(n-C₄H₉)₃	1.0	0.32	5.36	17	132
6	P(i-C₄H₉)₃	0.7	0.48	4.60	10	143
7	P(t-C₄H₉)₃	0.5	0.25	6.08	24	182
8	P(c-C₆H₁₁)₃	1.0	0.41	5.35	13	170
9	P(CH₂CH₂CN)₃	0.5	0.95	1.50	1.6	132
10	P(CH₂C₆H₅)₃	0.2	0.63	3.32	5.3	165
11	P(OCH₃)₃	1.0	0.50	3.32	6.6	107
12	P(OC₂H₅)₃	1.0	0.56	3.17	5.7	109
13	P(O-i-C₃H₇)₃	0.7	0.53	3.59	6.8	130
14	P(OC₄H₉)₃	0.5	0.45	3.86	8.6	110
15	P(OC₆H₅)₃	1.0	0.71	1.69	2.4	128
16	P(OCH₂)₃R	0.7	0.09	4.85	54	101
17	P[N(CH₃)₂]₃	0.3	0.38	5.11	13	c
18	P(CH₂CH=CH₂)₃	0.2	0.64	3.61	5.6	c
19	P(C₆H₅)₃	1.0	0.70	3.05	4.4	145
20	P(4-CH₃C₆H₄)₃	1.0	0.65	3.41	5.2	145
21	P(4-OCH₃C₆H₄)₃	1.0	0.62	3.57	5.8	145
22	P(4-FC₆H₄)₃	1.0	0.74	2.70	3.6	145
23	P(4-ClC₆H₄)₃	1.0	0.82	2.35	2.9	145
24	P(4-CF₃C₆H₄)₃	1.0	0.91	1.52	1.7	145
25	P(4-NMe₂C₆H₄)₃	0.5	0.05	6.90	140	145
26	P(3-CH₃C₆H₄)₃	1.0	0.55	3.83	7.0	145
27	PCl₃	0.2	0.70	0.18	0.26	124
28	P(CH₃)₂C₆H₅	1.0	0.44	4.49	10	122
29	P(C₂H₅)₂C₆H₅	1.0	0.39	4.91	13	136
30	P(OCH₃)₂C₆H₅	0.5	0.59	3.39	5.7	120
31	P(Cl)₂C₆H₅	0.2	0.92	0.25	0.27	131
32	P(C₆H₅)₂CH₃	1.0	0.57	3.74	6.6	136
33	P(C₆H₅)₂C₂H₅	1.0	0.55	3.83	4.4	140
34	P(C₆H₅)₂n-C₄H₉	0.5	0.58	3.80	6.6	140
35	P(C₆H₅)₂OCH₃	1.0	0.59	3.39	5.7	132
36	P(C₆H₅)₂Cl	0.5	0.66	2.35	3.6	138
37	P(C₆H₁₁)₂H	0.2	0.49	4.51	9.2	143
38	AsPh₃	0.2	0.90	2.16	2.4	141

[a] If more than 12 systems are studied, a weight (wt) value of 1 is assigned, 12−10 studied a value of 0.7, 9−7 studied a value of 0.5, less than 7 studied a value of 0.3. If all of the acceptors studied for a donor have C_A/E_A ratios that do not differ by more than 1.0 or if a given phosphine has not been studied with at least one acceptor that also has measurements with donors other than phosphines, 0.1 is subtracted. [b] Cone angles are from refs 6b−d. [c] No cone angle is reported in refs 6b−d.

squares minimization[1a] for the entire set of weighted simultaneous equations. This is referred to as the master fit.

In using the master fit to determine phosphine σ-donor parameters, it is essential to eliminate contributions from both enthalpic and entropic steric effects from the data set. These concerns led to an assignment of less weight to rate and equilibrium data and more to enthalpic, spectroscopic, and electrochemical data than in the earlier fit.[2] This and the appearance of new data in the literature led to an expansion of the 43 acceptor physicochemical properties used in the first fit to 79 in this study. Since the connection between the phosphine parameters and those of other donors is critically dependent on systems such as CF₃SO₃H, C₆H₅OH, and Al₂(CH₃)₆, which are measured with different families of donors, an increased weight was given to these acceptors in the new fit. In general, enthalpies are assigned weight values of 1, ¹³C NMR shifts a value of 1, redox potentials a value of 2 (in view of the small range of values that are accurately known), and infrared shifts, Δν, a value of 0.1 (because the values span a large range) in the data fit. The logs of rate constants are assigned weights of between 0.6 and 0.2 depending on the estimated severity of the steric contributions. Acceptors with bulky donors, for which preliminary fits indicate that steric repulsions do exist, are omitted. With acceptors that π-back-bond, donors other than phosphorus donors are not included, vide infra.

As a result of the new data and weights, substantial changes in the values have occurred in the new, improved phosphine parameters. The refined set of E_B and C_B parameters for phosphorus donors is reported in Table 1. Also given in Table 1 are the weights that reflect their relative certainty based on the number and type of different acceptors used to determine the parameters. Several of the phosphines were studied with few physicochemical measurements. The reported parameters for these systems are given low weights in Table 1, and the parameters should be redetermined as more data become available.

Most of the $E_A{}^*$, $C_A{}^*$, and W parameters (Table 2) have changed for the systems studied earlier because of the revised phosphorus donor parameters, but for the most part, the interpretations of steric and π-bonding contributions to reactivity have not changed. In the footnotes, statistics for each acceptor system are presented. The average deviation, x, and the % fit, which is the average deviation divided by the range of experimental values times 100, have been discussed earlier.[1a,f]

ECW Analysis of New Acceptors. The donor parameters from the master fit described above can be used to analyze measurements of reactivity and spectroscopy for a new acceptor. A good definition of the parameters in any fit requires that the donors and acceptors be selected in which there is a large variation in the relative importance of the components of the reactivity scale. In ECW fits, the C_B/E_B ratio of the donors employed should vary. Each measurement with the new acceptor produces an equation in the series with the form of eq 1. The weighted series can then be solved by least-squares minimization routines for the parameters $E_A{}^*$, $C_A{}^*$, and W. A good fit for a wide range of donor types indicates that the acceptor property is dominated by the same electronic factors that influence σ-bond strength. If donors other than phosphorus donors are included and a poor fit results, these other donors are omitted. A good fit of the remaining phosphines and phosphites suggests a π-back-bonding acceptor.

A poor fit of only the phosphorus donors indicates added complexity in the reaction. Donors that deviate by 2.5 times the average deviation are omitted and the fit is redetermined. A good fit usually results, and one looks for patterns (steric effects, incomplete complexation, etc.) in the donors that were omitted to reveal the complicating factor. The fit is again redetermined, omitting those donors expected to have contributions from the suspected effect. A good fit at this point leads to a tentative assignment of the complication. Omitted donors that are fit well (less than 2.5 times the deviation) in this last fit are added back into the final fit.

Systems were selected to show how steric effects can be parametrized in the ECW model. This is done with an enthalpy of reaction or activation by first running a correlation of all available data using eq 1. If steric effects are operative in the system, a poor correlation will result. Donors with the largest cone angles are then removed one at a time, and the correlations are redone until a good fit of the remaining donors results. Using this fit, the deviations are calculated for the donors that have been removed. These deviations are plotted versus their cone angles, and a least-squares regression is done. The slope of the line, s, will give the severity of the steric effect, while the intercept divided by s will give θ_{ON}, the cone angle above which steric repulsion becomes operative in the system.

Results and Discussion

ECW Donor−Acceptor Parameters and Their Use. The E_B and C_B parameters in Table 1 can be substituted into eq 2 to analyze a new physicochemical property as a function of base variation using the guidelines in the Calculations section. In designing an experiment, the maximum amount of information can

Table 2. E_A*, C_A*, and W Parameters for Acceptor Systems

acceptor property	wt[a]	E_A*	C_A*	W	C_A*/E_A*
$-\Delta H$ (CF$_3$SO$_3$H)[b]	1.2	4.51	5.70	0.84	1.26
$-\Delta H$ (B(CH$_3$)$_3$)[c]	0.4	3.57	2.97	0	0.83
$-\Delta H$ (Al(CH$_3$)$_3$)[d]	1.2	8.28	3.23	−8.46	0.39
$-\Delta H$ (CpIr(CO)PR$_3$)[e]	0.5	1.16	1.52	24.8	1.31
$-\Delta H$ (Cp*Ir(CO)PR$_3$)[f]	0.1	36.68	7.11	−10.18	0.19
ΔH (Ti(C$_7$H$_{11}$)$_2$PX$_3$)[g]	0.4	−9.10	0.83	13.13	−0.09
$-\Delta H$ (HgCl$_2$)[h]	0.1	9.94	6.75	−9.46	0.68
$-\Delta H$ (HgBr$_2$)[h]	0.1	21.13	8.01	−20.88	0.38
$-\Delta H$ ([Ni(η-C$_5$H$_7$)CH$_3$]$_2$)[i]	0.8	−72.6	−11.7	111.5	0.16
$-\Delta H$ (CpMo(CO)$_3$CH$_3$)[j]	0.1	−30.57	−1.75	38.49	0.06
$-\Delta H$ (CpMo(CO)$_3$C$_2$H$_5$)[j]	0.1	−23.08	−0.97	34.55	0.04
$\Delta H^{\ddagger}$ (CoNO(CO)$_3$)[k]	0.1	1.44	−2.88	22.83	−2.0
$\Delta H^{\ddagger}$ (Ru(CO)$_4$PX$_3$(Dis 1))[l]	0.1	3.97	0.77	26.4	0.19
$\Delta H^{\ddagger}$ (V(CO)$_6$ (S$_N$2))[m]	0.1	−8.16	−2.44	22.98	0.30
$\Delta H^{\ddagger}$ (Ru(CO)$_3$PX$_3$(SiCl$_3$)$_2$)[n]	0.8	−0.68	0.47	26.02	−0.69
$\Delta H^{\ddagger}$ (Rh$_2$(OAc)$_4$)[o]	0.1	4.79	0.78	5.65	0.16
$\Delta H^{\ddagger}$ (Ru$_6$C(CO)$_{17}$)[p]	0.1	−1.64	−3.21	19.15	1.96
$\Delta H^{\ddagger}$ (Cp(CO$_2$Me)Co(CO)$_2$)[q]	0.1	−11.02	−0.79	22.00	0.07
^{13}C (Ni(CO)$_3$L)[r]	0.8	8.27	1.95	−7.47	0.24
^{13}C (Cr(CO)$_5$L)[s]	1.2	8.87	1.84	−6.67	0.21
^{13}C (Mo(CO)$_5$PX$_3$)[t]	0.8	7.90	1.63	−5.82	0.21
^{13}C (W(CO)$_5$L)[u]	0.1	13.74	2.36	180.1	0.17
^{13}C (CpMn(CO)$_2$L)[v]	0.1	−22.11	−3.01	−208.1	0.14
^{13}C (PtPh$_2$(CO)L)[w]	0.5	21.76	3.90	154.3	0.18
^{1}H (CpMo(CO)$_2$LMe)[x]	0.3	0.63	0.71	3.73	1.13
^{1}H (CpMo(CO)$_2$LCOMe)[y]	0.3	1.66	0.28	3.04	0.17
^{1}H ((CpCO$_2$Me)Co)[z]	0.8	−1.04	−0.11	4.58	0.11
^{1}H ((MePAr$_3$)Br)[aa]	0.1	−4.60	−1.05	9.67	0.23
ν (Ni(CO)$_3$PX$_3$)[bb]	0.4	−52.4	−12.2	2143	0.23
ν (Ru(CO)$_3$L)[cc]	0.4	−72.2	−14.7	2164	0.20
ν (CH$_3$CpMn(CO)$_2$PX$_3$)[dd]	0.4	−15.0	−4.9	1967	0.33
ν (η-CpFe(CO)(COMe)PX$_3$)[ee]	0.4	−114.9	−21.7	2069	0.19
ν (η-Cp′Fe(CO)(COMe)PX$_3$)[ee]	0.4	−114.1	−21.6	2063	0.19
ν (Rh(OAc)$_4$L)[ff]	0.1	−7.64	−1.57	42.96	0.21
ν [(Fe(CO)$_3$(PR$_3$)C$_7$H$_9$)$^+$][gg]	0.4	−10.63	−3.60	2074	0.34
ν (PtPh$_2$(CO)L)[hh]	0.4	−86.6	−17.2	2177	0.20
ν ((CpCO$_2$Me)Co)[ii]	0.4	−60.8	−16.8	2034	0.28
ν (Ru(CO)$_3$PX$_3$(SiCl$_3$)$_2$)[jj]	0.4	−72.2	−14.7	2164	0.20
$E_{1/2}$ (Cp′Mn(CH$_2$Cl$_2$))[kk]	1.7	−0.37	−0.12	1.16	0.32
$E_{1/2}$ (Cp′Mn(CH$_3$CN))[ll]	1.7	−1.10	−0.25	2.05	0.23
$E_{1/2}$ [(Ru(bpy)$_2$PX$_3$)$^{2+}$(CH$_3$CN)][mm]	1.3	0.30	−0.03	1.20	−0.10
$E_{1/2}$ [(Ru(bpy)$_2$PX$_3$)$^{2+}$(4Ac-py)][mm]	0.1	0.11	−0.06	1.43	−0.55
$E_{1/2}$ [(Ru(bpy)$_2$PX$_3$)$^{2+}$(Cl$^-$)][mm]	0.1	0.28	−0.03	1.24	−0.11
$E_{1/2}$ (η-CpFe(CO)(COMe)PX$_3$)[nn]	1.3	−0.89	−0.19	1.53	0.21
$E_{1/2}$ (η-Cp′Fe(CO)(COMe)PX$_3$)[nn]	1.3	−0.85	−0.19	1.47	0.22
log K (CF$_3$C$_6$H$_4$OH)[oo]	0.6	1.69	0.26	−1.49	0.15
log K (CpMo(CO)$_2$LCOMe)[pp]	0.1	28.26	3.84	−34.55	0.14
log K_1 (Rh$_2$(OAc)$_4$L)[qq]	0.1	4.76	1.30	−2.15	0.28
log K (W(CO)$_5$(aniline))[rr]	0.1	0.30	0.43	−0.20	1.43
log K (W(CO)$_5$(p-Br-aniline))[rr]	0.1	−1.64	−0.01	2.64	0.01
log k (Co(NO)(CO)$_3$(S$_N$2))[ss]	0.5	4.98	1.51	−10.71	0.30
log k (V(CO)$_6$(S$_N$2))[tt]	0.3	0.60	1.37	−5.10	2.28
log k (Ru(CO)$_4$L)[uu]	0.8	2.77	0.41	−6.42	0.15
log k (MoBr$_2$(CO)$_3$(PX$_3$)$_2$)[vv]	0.1	−17.47	−3.36	26.33	0.19
log k (Cp$_2$Fe$_2$(CO)$_4$)[ww]	0.3	−1.28	−0.66	8.38	0.52
log k (CpMn(py))[xx]	0.1	−13.75	−0.01	10.81	0.001
log k (Ru(bpy)$_2$PX$_3$(H$_2$O)$^{2+}$)[yy]	0.5	12.24	2.40	−18.14	0.20
log k (Co−C$_6$H$_5$CH$_2$Br)[zz]	0.9	−4.38	0.43	−0.05	−0.13
log k (Co′−C$_6$H$_5$CH$_2$Br)[zz]	0.4	−3.58	0.13	0.46	−0.04
log k (Fe(CO)$_2$Cp(ethene)$^+$)[aaa]	0.1	24.34	5.01	−30.49	0.21
log k (η^5-Me$_5$CpRh(CO)$_2$)[bbb]	0.1	−7.38	−0.23	0.90	0.03
log k (Mn(CO)$_2$(NO)(6-C$_6$H$_6$))[ccc]	0.1	0.26	0.99	−2.75	3.81
log k (CpIr(CO)PX$_3$)[ddd]	0.3	5.32	1.58	−10.08	0.30
log k (Cp*Ir(CO)PX$_3$)[ddd]	0.1	−1.94	0.46	−0.18	−0.24
log k (C$_2$H$_5$I)[eee]	0.5	−0.63	0.46	−5.05	−0.73
log k (η^5-Me$_5$CpCo(CO)$_2$)[fff]	0.3	−5.22	0.15	−1.88	−0.03
log k (η-CpMo(CO)$_2$LCOMe)[ggg]	0.3	10.60	1.56	−17.11	0.15
log k (Fe(η-Cp)(CO)LMe$^+$)[hhh]	0.8	−3.67	−0.72	3.61	0.20
log k (Fe(η-Cp)(CO)LMeAN)[iii]	0.8	18.71	3.29	−23.03	0.18
log k_2 (Ru$_6$C(CO)$_{17}$)[jjj]	0.3	−13.93	−0.87	11.55	0.06
log k_2 (Mo$_2$(CO)$_8$)[kkk]	0.1	−2.53	−0.57	−0.41	0.23
log k (Fe(CO)$_3$(C$_7$H$_9$)$^+$)[lll]	0.1	16.30	3.53	−19.96	0.22
log k (PtPh$_2$CO(5-AQ))[mmm]	0.8	−22.81	−3.33	26.24	0.15
log k (Os$_3$H$_2$(CO)$_{10}$)[nnn]	0.5	−2.92	0.59	2.01	−0.20

Table 2 (Continued)

acceptor property	wt[a]	E_A*	C_A*	W	C_A*/E_A*
log T_1 [Re(CO)$_3$Cl(PPh$_3$)$_2$]ax[ooo]	0.1	1.98	0.39	−1.78	0.20
log T_1 [Re(CO)$_3$Cl(PPh$_3$)$_2$]equil[ooo]	0.1	0.49	0.27	−1.22	0.55
pK_A[ppp]	0.8	22.03	5.81	−29.87	0.26

[a] The weight (w) value is to be used in future correlations with this physicochemical property to determine new donor E_B and C_B. If more than 12 donors give satisfactory data fits, a wt of 1 is assigned, 10−12 a value of 0.7, 7−9 a value of 0.5, and less than 7 a value of 0.2. If donors other than phosphines are fit, 0.2 is added. If not, 0.2 is subtracted. In view of the small magnitude, 0.5 is added to $E_{1/2}$ values. A value of 0.4 is assigned to IR shifts because of their large magnitude. Smaller weights should be assigned to free energies (other than $E_{1/2}$) for substituents where entropic factors can contribute. The weight in a fit is related to n used in articles before 1996 by wt = $^1/_5 n$. [b] −ΔH for the reaction of CF$_3$SO$_3$H with bases in 1,2-dichloroethane solvent. $x = 0.07$, % fit = 0.3. Data from ref 4. [c] Gas phase −ΔH of adduct formation. $x = 0.32$, % fit = 7. Data from ref 1h. [d] −ΔH for the reaction of [Al(CH$_3$)$_3$] with donors in hexane solvent. $x = 0.26$, % fit = 2. Data from ref 5 with Et$_2$O and Et$_3$N omitted. [e] −ΔH of protonation of CpIr(CO)PX$_3$ with CF$_3$SO$_3$H in 1,2-dichloroethane. $x = 0.26$, % fit = 5. Data from ref 4b and 7 with P(c-hx)$_3$ omitted. [f] −ΔH of protonation of Cp*Ir(CO)PX$_3$ with CF$_3$SO$_3$H in 1,2-dichloroethane. $x = 0.22$, % fit = 5. Data from ref 7b. [g] Endothermic ΔH for PX$_3$ dissociation from bis(2,4-dimethylpentadienyl)titanium in THF solvent. $x = 0.04$, % fit = 0.7. Data from ref 8 with PEt$_3$ omitted. [h] −ΔH of 1:1 adduct formation in benzene. For HgCl$_2$, $x = 1.10$, % fit = 8. For HgBr$_2$, $x = 0.61$, % fit = 5. Data from ref 9 with P(c-hx)$_3$, benzene, pyridine, and THF omitted. [i] Heat evolved corrected for the heat of solution of the base in kcal mol^{-1} when a 1.0 M solution of the donor is added to 0.05 M di-μ-methylbis[1-methyl-1-η^3-(2-butenyl)] dinickel in tetralin. $x = 0.06$, % fit = 0.4. Data from ref 10 with P(OPh)$_3$ and PPh$_3$ omitted. [j] Enthalpy for the insertion of CO in the Mo−R bond of CpMo(CO)$_3$R, where R = Me or Et, and coordination of PR$_3$ to form CpMo(CO)$_2$(PR$_3$)RC(O). For R = Me, $x = 0.08$, % fit = 2. For R = Et, $x = 0.21$, % fit = 3. Data from ref 11. [k] Activation enthalpy for the second-order substitution of CO by phosphines for Co(NO)(CO)$_3$ in toluene. $x = 0.04$, % fit = 1. Data from ref 12. [l] Activation enthalpy for the first-order dissociative substitution of CO in Ru(CO)$_4$PX$_3$ by P(OEt)$_3$ in hexane and decalin. $x = 0.4$, $r^2 = 0.92$. A steric onset of 128° and an s of −0.12 is needed. Data from ref 13. [m] Activation enthalpy for second-order substitution of CO by phosphines in V(CO)$_6$ in hexane. $x = 0.22$, % fit = 7. Data from ref 14. [n] Activation enthalpy for the first-order dissociative substitution of CO in Ru(CO)$_3$PX$_3$(SiCl$_3$)$_2$ by P(OMe)$_3$ or P(t-C$_4$H$_9$)$_3$. $x = 0.23$, % fit = 7. Data from ref 15. [o] Activation enthalpy for the substitution of solvent with phosphines in dirhodium(II) tetraacetate in CH$_3$CN. $x = 0.20$, % fit = 17. Data from ref 16 with P(OPh)$_3$ and P(benzyl)$_3$ omitted. [p] Activation enthalpy for the second-order reaction of Ru$_6$C(CO)$_{17}$ with nucleophiles in heptane. $x = 0.30$, % fit = 5. Data from ref 17. [q] Activation enthalpy for the second-order substitution of CO with ligands in (η^5-C$_5$H$_4$CO$_2$Me)Co(CO)$_2$. $x = 0.13$, % fit = 9. Data from ref 18 with all donors omitted that have two or more phenyl substituents and P(OPh)$_3$. [r] ^{13}C chemical shift of Ni(CO)$_3$PX$_3$ relative to Ni(CO)$_4$ in CDCl$_3$. $x = 0.12$, % fit = 2. Data from ref 19. [s] ^{13}C chemical shift of the *cis*-carbonyl in Cr(CO)$_5$L relative to Cr(CO)$_6$ in CDCl$_3$. $x = 0.12$, % fit = 2. Data from ref 19 with pyridine omitted. [t] ^{13}C chemical shift of the *cis*-carbonyl in Mo(CO)$_5$PX$_3$ relative to Mo(CO)$_6$ in CDCl$_3$. $x = 0.14$, % fit = 2. Data from ref 19. [u] ^{13}C chemical shift of the *cis*-carbonyl in W(CO)$_5$PX$_3$ downfield from TMS in CDCl$_3$. $x = 0.22$, % fit = 6. Data from ref 20 with 4-methylpyridine omitted. [v] ^{13}C chemical shift for the CO in CpMn(CO)$_2$PR$_3$ relative to TMS in CDCl$_3$. $x = 0.26$, % fit = 6. Data from ref 21. [w] ^{13}C chemical shift for *cis*-[PtPh$_2$(CO)$_2$L] relative to TMS. $x = 0.17$, % fit = 25. Data from ref 22 with P(i-Pr)$_3$, P(t-Bu)$_3$, and P(c-hx)$_3$ omitted. [x] ^{1}H chemical shift for the Cp group in CpMo(CO)$_2$LMe relative to TMS. $x = 0.04$, % fit = 20. Data from ref 23. [y] ^{1}H chemical shift for the Cp group in CpMo(CO)$_2$LCOMe relative to TMS. $x = 0.04$, % fit = 16. Data from ref 23. [z] ^{1}H chemical shift for the CO$_2$Me group in (η^5-CpCO$_2$Me)Co(CO)L relative to TMS in CDCl$_3$. $x = 0.05$, % fit = 22. Data from ref 18 with P(c-Hx)$_3$ omitted. [aa] ^{1}H chemical shift for the methyl group in [MePAr$_3$]Br relative to TMS. $x = 0.02$, % fit = 2. Data from ref 24. [bb] A$_1$, CO stretching frequency (cm^{-1}) of Ni(CO)$_3$PX$_3$ in CH$_2$Cl$_2$. $x = 1.26$, % fit = 3. Data from ref 25 with P(OCH$_2$)$_3$CR and P(O−i-Pr)$_3$ omitted. [cc] ν1(ax), CO stretching frequency of Ru(CO)$_4$L in heptane or hexane. $x = 1.18$, % fit = 7. Data from ref 13 with AsPh$_3$ omitted. [dd] Higher energy CO stretching frequency (cm^{-1}) of η^5-MeCpMn(CO)$_2$PX$_3$ in heptane. $x = 1.31$, % fit = 19. Data from ref 26 with nitrogen donors and PPhEt$_2$ omitted. [ee] CO stretching frequency of η^5-CpFe(CO)COCH$_3$PX$_3$ in cyclohexane. for Cp, $x = 0.89$, % fit = 2. For Cp*, $x = 0.87$, % fit = 4. Data from ref 27. [ff] Electronic absorption maximum in 10^{-3} cm^{-1} for Rh$_2$(OAc)$_4$(CH$_3$CN)L. $x = 0.39$, % fit = 18. Data from ref 16 with AsPh$_3$. [gg] Higher energy CO stretching frequency (cm^{-1}) for [Fe(CO)$_3$(1-4-η−R$_3$P·C$_7$H$_9$)]$^+$ adducts. $x = 0.35$, % fit = 9. Data from ref 28. [hh] CO stretching frequency for *cis*-[PtPh$_2$(CO)L]. $x = 0.82$, % fit = 3. Data from ref 22 with P(i-Pr)$_3$, P(t-Bu)$_3$, and P(c-hx)$_3$ omitted. [ii] CO stretching frequency of (η^5-CpCO$_2$Me)Co(CO)L. $x = 0.93$, % fit = 3. Data from ref 18 with P(c-hx)$_3$ omitted. [jj] CO stretching frequency of Ru(CO)$_3$L(SiCl$_3$)$_2$. $x = 0.82$, % fit = 3. Data from ref 15 with P(OPh)$_3$ and P(benzyl)$_3$ omitted. [kk] Standard oxidation potential in volts of CH$_3$CpMn(CO)$_2$L in CH$_2$Cl$_2$. $x = 0.02$, % fit = 5. Data from ref 26a. [ll] Same as kk, but in CH$_3$CN. $x = 0.02$, % fit = 3. Data from ref 26b. [mm] Redox potential for [Ru(H$_2$O)(bpy)$_2$PX$_3$]$^{2+/3+}$ in CH$_2$Cl$_2$ vs SCE with an incoming group of CH$_3$CN, 4-Ac-pyridine, or Cl$^-$. For CH$_3$CN, $x = 0.02$, % fit = 4. For 4-Ac-py, $x = 0.02$, % fit = 4. For Cl$^-$, $x = 0.01$, % fit = 3. Data from ref 30. [nn] Redox potential for η^5-Cp and η^5-Cp*Fe(CO)(COCH$_3$)PX$_3$ in CH$_3$CN (0.2 M LiClO$_4$) vs SCE. For Cp, $x = 0.01$, % fit = 3. For Cp′, $x = 0.01$, % fit = 3. Data from ref 27. [oo] Log of the equilibrium constant for PX$_3$ hydrogen bonding to 4-CF$_3$-C$_6$H$_4$OH in CS$_2$ at 25 °C. $x = 0.07$, % fit = 3. Data from ref 31 with P(Ph-p-OCH$_3$)$_3$ omitted. [pp] Log of the equilibrium constant for ligand dissociation from CpMo(CO)$_2$LCOCH$_3$. $x = 0.14$, % fit = 5. Data from ref 23 with PBu3 omitted. [qq] Log of the equilibrium constant for ligand addition to Rh$_2$(OAc)$_4$(CH$_3$CN)$_2$. $x = 0.73$, % fit = 23. Data from ref 16 with AsPh$_3$ omitted. [rr] Log of the equilibrium constant for substitution of either aniline of p-Br-aniline with a ligand on W(CO)$_5$L. For aniline, $x = 0.09$, % fit = 6. For p-Br-aniline, $x = 0.13$, % fit = 13. Data from ref 32 with AsPh$_3$ omitted. [ss] Log rate constant for the second-order displacement of CO by phosphines from Co(NO)(CO)$_3$ in toluene. $x = 0.26$, % fit = 6. Data from ref 12 with nitrogen donors, P(c-hx)$_3$, and P(NMe$_2$)$_3$. [tt] Log rate constant for the second-order displacement of CO from V(CO)$_6$ by PX$_3$ at 25 °C in hexane. $x = 0.22$, % fit = 6. Data from ref 14 with P(i-Pr)$_3$, PBu$_3$, and AsPh$_3$ omitted. [uu] Log of the rate constant for the first dissociative substitution of CO from Ru(CO)$_4$ L by another L to form Ru(CO)$_3$L$_2$ in heptane at 60 °C. $x = 0.19$, % fit = 12. Data from ref 13 with PEt$_3$, PBu$_3$, and P(c-hx)$_3$ omitted. [vv] Log of the bimolecular rate constant for Mo(CO)$_2$(PR$_3$)Br$_2$ generated by flash photolysis with CO in 1,2-dichloroethane. $x = 0.08$, % fit = 9. Data from ref 33 with PEt$_3$, PPhEt$_2$, and PPh$_2$Et omitted. [ww] Log of the rate constant for the second-order addition of PX$_3$ to Cp$_2$Fe$_2$(CO)$_3$ in hexane at 25 °C. $x = 0.05$, % fit = 3. Data from ref 34 with P(OPh)$_3$, PBu$_3$, and CH$_3$CN omitted. [xx] Log rate constant for the second-order substitution of 4-NO$_2$C$_5$H$_5$N in the electrochemically generated cation MeCpMn(CO)$_2$·4-NO$_2$C$_5$H$_5$N$^+$ by phosphine and other donor ligands in CH$_2$Cl$_2$. $x = 0.06$, % fit = 3. Data from ref 26a with PEt$_3$, PPhEt$_2$, PPh$_2$Et, and PPh$_2$Bu. [yy] Log second-order rate constant for exchange of H$_2$O by CH$_3$CN in Ru^{II}(bpy)$_2$(PX$_3$)(H$_2$O)$^{2+}$ in o-dichlorobenzene. $x = 0.18$, % fit = 12. Data from ref 30 with PEt$_3$, PPr$_3$, and PBu$_3$ omitted. [zz] Log rate constants for the reactions of Co(bis(dioximato)cobalt(II)−L) and Co′(bis-(1,2-cyclohexanedionedioximato)cobalt(II)L) with C$_6$H$_5$CH$_2$Br in benzene. For Co, $x = 0.20$, % fit = 8. For Co′, $x = 0.13$, % fit = 7. Data from ref 35 with PEt$_3$ and PBu$_3$ omitted. [aaa] Log of the second-order rate constant for phosphorus nucleophiles toward [CpFe(CO)$_2$(η-C$_2$H$_4$)]$^+$. $x = 0.26$, % fit = 9. Data from ref 36 with P(CH$_2$CH$_2$CN)$_3$ omitted. [bbb] Log of the second-order rate constant for CO substitution by a ligand in Rh(η^5-C$_5$Me$_5$)(CO)$_2$ in toluene. $x = 0.18$, % fit = 7. Data from ref 37 with PBu$_3$ and P(i-Bu)$_3$ omitted. [ccc] Log of the second-order rate constant for nucleophilic addition in Mn(CO)$_2$(NO)(6-MeC$_6$H$_6$)$^+$ in CH$_3$CN. $x = 0.09$, % fit = 4. Data from ref 38 with nitrogen donors omitted. [ddd] Log of the second-order rate constant of CpIr complexes with CH$_3$I in CD$_2$Cl$_2$ at 25 °C. For Cp, $x = 0.07$, % fit = 3. For Cp*, $x = 0.17$, % fit = 6. Data from ref 7b with PEt$_3$ and P(c-hx)$_3$ omitted. [eee] Log of the second-order rate constant between phosphine and C$_2$H$_5$I in acetone. $x = 0.15$, % fit = 9. Data from ref 39 with pyridine omitted. [fff] Same as bbb except with Co(η^5-C$_5$Me$_5$)(CO)$_2$. $x = 0.11$, % fit = 7. Data from ref 37 with PBu$_3$ and P(i-Bu)$_3$ omitted. [ggg] Log of the rate constant for CO dissociation from CpMo(CO)$_2$L(COMe) in CH$_3$CN. $x = 0.10$, % fit = 9. Data from ref 23. [hhh] Log of the second-order rate constant

Table 2 (Continued)

for CO insertion for $(\eta\text{-Cp})\text{Fe(CO)LMe}^+$ in CH_2Cl_2 $x = 0.10$, % fit = 11. Data from ref 40 with PEt_3 omitted. [iii] Log of the second-order rate constant for the substitution of CO for CH_3CN in $CpFe(COMe)L(CH_3CN)$. $x = 0.36$, % fit = 20. Data from ref 41 with PEt_3, $P(i\text{-Pr})_3$, $P(i\text{-Bu})_3$, and $P(c\text{-hx})_3$ omitted. [jjj] Log of the second-order rate constant for reaction of $Ru_6C(CO)_{17}$ with nucleophiles in chlorobenzene. $x = 0.35$, % fit = 7. Data from ref 17 with $P(O-i\text{-Pr})_3$ and PBu_3 omitted. [kkk] Log of the first-order rate constant of the dissociation of a ligand in $[(CO)_4Mo(\mu\text{-PEt}_2)_2Mo(CO)_3L]$ in decalin. $x = 0.13$, % fit = 21. Data from ref 42 with PBu_3 omitted. [lll] Log of the second-order rate constant for the addition of phosphorus nucleophiles to $Fe(CO)_3(C_7H_9)^+$ in acetone at 20 °C. $x = 0.35$, % fit = 9. Data from ref 28. [mmm] Log of the second-order rate constant for the substitution of 5-aminoquinoline with ligand in $[PtPh_2CO(5\text{-AQ})]$ in toluene at 25 °C. $x = 0.36$, % fit = 12. Data from ref 22 with $P(i\text{-Pr})_3$ and $P(t\text{-Bu})_3$ omitted. [nnn] Log of the second-order rate constant for the addition of nucleophiles to $(\mu_2\text{-H})_2Os_3(CO)_{10}$ in heptane at 30 °C. $x = 0.27$, % fit = 8. Data from ref 43 with $P(OPh)_3$, $P(NMe_2)_3$, $P(t\text{-Bu})_3$, $P(c\text{-hx})_3$, $P(benzyl)_3$, and $AsPh_3$ omitted. [ooo] Log of the axial and equatorial ^{31}P relaxation times in CD_2Cl_2. For axial, $x = 0.02$, % fit = 5. For equatorial, $x = 0.02$, % fit = 4. Data from ref 44. [ppp] pK_A values. $x = 0.66$, % fit = 6. Data from ref 45 with PMe_3 omitted.

be obtained by using a variety of donors including well-defined phosphorus donors with different C_B/E_B ratios and different steric requirements.

Acceptors studied only with phosphorus donors may have parameters with a π-back-bonding component. These parameters are difficult to interpret, and incorrect predictions are likely when these parameters are used on donors other than phosphines or phosphites. When a W value for an extensive data set appears unreasonable in terms of the expected behavior for a system with no base attached, π-back-bonding contributions are probably involved, vide infra.

A limited number of the acceptors in Table 2 will be discussed in detail to illustrate the understanding that results from ECW analyses. Slightly different correlation parameters and statistics than those given in Table 2 result when the phosphine parameters in Table 1 are used for regression analyses of the individual acceptors. In this and subsequent discussions, when individual fits are carried out those parameters are reported. The reader can investigate acceptors that are not discussed below in more detail by referring to the references given in Table 2, carrying out a regression analysis of the reported data omitting the systems described in the footnotes.

ECW Interpretation of Phosphine Enthalpies. Several enthalpy changes of reactions and enthalpies of activation have been reported for phosphorus donors. Since a linear free-energy assumption is not required for enthalpy data, enthalpies provide the critical test of ECW or linear free-energy models. The enthalpies of formation for $Al_2(CH_3)_6$ adducts[5] are important data for they include 17 phosphorus, sulfur, oxygen, and nitrogen donors. The observed enthalpies corrected for the enthalpy of solution of the base are used in this correlation. The resulting W value is endothermic ($-\Delta H = -8.5$ kcal mol^{-1}) and corresponds to one-half of the enthalpy of dissociation of the dimer in solution. Steric effects are evident in the Et_2O and Et_3N adducts. The correlation is illustrated graphically in Figure 1a.

The enthalpies of *dissociation* of phosphorus donors from bis(2,4-dimethylpentadienyl)titanium,[8a] Cp'_2Ti, are fit very well to $E_A^* = -9.10$, $C_A^* = 0.83$, $W = 13.13$ ($r^2 = 0.99$, $F = 4440$) of eq 2. χ is a *positive* ΔH, and as a result, a positive parameter is endothermic. Contrary to our earlier interpretation,[8b] W has the wrong sign for association of THF after the phosphorus ligand is displaced. The W sign arises from changes upon pro-
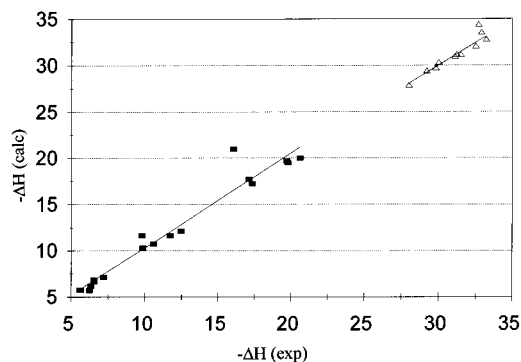

Figure 1. Calculated and experimental enthalpies of reaction for (a) $[Al(CH_3)_3]_2$ (■), with Et_2O and Et_3N deviating, and (b) the protonation of $CpIr(CO)PR_3$ (△), with $P(c\text{-hex})_3$ deviating.

tonation of the metal–phosphorus ligand $E_A^{\pi\circ}E_B^{\pi M}$ and $C_A^{\pi\circ}C_B^{\pi M}$ terms of eq 7 and indicates a π-back-bonding contribution. Triethylphosphine, the largest cone-angle phosphine studied, deviates and is omitted from the correlation because of an enthalpic steric effect.

Enthalpies for a wide range of donors (phosphines, pyridines, and $(C_2H_5)_3N$) reacting with CF_3SO_3H were measured[7] using 1,2-dichloroethane as the solvent. This is the first system treated by ECW where the products are ionic; leading to an intimate ion pair in this solvent. All donors fit very well ($r^2 = 0.99$, $F = 25\,000$) with an average deviation of 0.07 kcal mol^{-1}. The small W value (1 kcal mol^{-1}) could result from a constant, minor difference in the solvation of the ion-paired product and the reactants.

Enthalpies of protonation of $CpIr(CO)PX_3$ by CF_3-SO_3H in 1,2-dichloroethane were fit earlier for five reported[4b,7a] phosphines. Subsequently, the number of phosphines has increased[7b] to 11. ECW analysis of the larger data set still gives an excellent fit ($r^2 = 0.9$), as illustrated in Figure 1b. $P(c\text{-hex})_3$ was omitted and gave a predicted value that is 1.7 kcal mol^{-1} too large. This deviation is attributed to larger enthalpic steric repulsion of the phosphine ligands in the protonated complex than that in the neutral complex or to a steric effect that weakens the ion-pairing energy to $CF_3SO_3^-$ in the product. The large exothermic W value is not anticipated in view of the CF_3SO_3H/phosphine fit. In this

(4) (a) Bush, R. C.; Angelici, R. J. *Inorg. Chem.* **1988**, *27*, 681. (b) Angelici, R. J. *Acc. Chem. Res.* **1995**, *28*, 51.

(5) (a) Hendrickson, C. H.; Eyman, D. P. *Inorg. Chem.* **1967**, *6*, 1461. (b) Hendrickson, C. H.; Duffy, D.; Eyman, P. C. *Inorg. Chem.* **1968**, *7*, 1047.
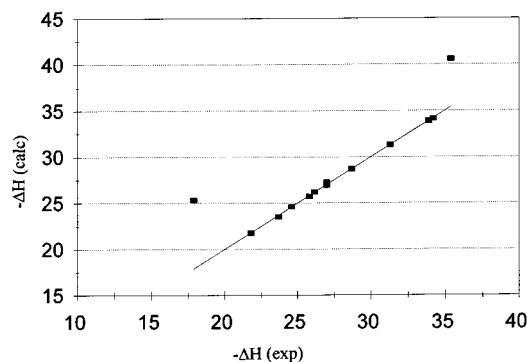
(6) (a) Manzer, L. E.; Tolman, C. A. *J. Am. Chem. Soc.* **1975**, *97*, 1955. (b) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313. (c) Brown, T. L. *Inorg. Chem.* **1992**, *31*, 1286. (d) Chen, L.; Poë, A. J. *Coord. Chem. Rev.* **1995**, *143*, 265.

(7) (a) Sowa, J. R., Jr.; Zanotti, V.; Facchin, G.; Angelici, R. J. *J. Am. Chem. Soc.* **1991**, *113*, 9185. (b) Wang, D.; Angelici, R. J. *Inorg. Chem.* **1996**, *35*, 1321.

(8) (a) Stahl, L.; Ernst, R. D. *J. Am. Chem. Soc.* **1987**, *109*, 5673. (b) Stahl, L.; Trakarnpruk, W.; Freeman, J. W.; Arif, A. M.; Ernst, R. D. *Inorg. Chem.* **1995**, *34*, 1810.

Figure 2. Calculated and experimental enthalpies of reaction of $[Ni(\eta\text{-}C_5H_7)CH_3]_2$ (■), with PPh_3 and $P(OPh)_3$ deviating.

Figure 3. Calculated and experimental activation enthalpies for (a) $Ru_6C(CO)_{17}$ (■) and (b) $CoNO(CO)_3$ (△).

Figure 4. Activation enthalpies (△) and $(2034 - \nu_{CO})/10$ (■) for $Cp(CO_2Me)Co(CO)_2$. The W value is 2034 cm^{-1}.

case, W corresponds to the $E_A{}^{\pi\circ}E_B{}^{\pi M}$ and $C_A{}^{\pi\circ}C_B{}^{\pi M}$ terms of eq 7. The enthalpies[7b] for the protonation of $Cp^*Ir(CO)PX_3$ give a very good fit ($r^2 = 0.98$, $x = 0.23$), with very different parameters from those calculated above for the Cp complex. Only five phosphines with a narrow range of C_B/E_B ratios were used with the Cp* complex, so these acceptor parameters are tentative.

Enthalpies of formation for 1:1 adducts of $[(\eta\text{-}C_5H_7)\text{-}Ni(CH_3)]_2$ have been determined by adding excess base to a solution of the complex in tetralin.[10] The correlation is very good with $E_A = -74.1$, $C_A = -11.8$, $W = 113.1$, $r^2 = 0.99$, and $x = 0.21$, as shown in Figure 2. Earlier analysis of this system required the removal of PPh_2Et and $P(benzyl)_3$, whose improved parameters now fit. Both $P(C_6H_5)_3$ and $P(OPh)_3$ had enthalpies smaller than those predicted by ECW and were omitted from the fit. Bulky phosphines such as $P(i\text{-}Pr)_3$ with a cone angle of 160° are well behaved. The experimental enthalpies are based on the assumption that the limiting reagent is fully coordinated. The two omitted donors are the weakest studied, they probably do not completely complex all of the nickel, and their reported enthalpies would be too small. In the absence of π-back-bonding, the W value for this system is expected to correspond to the endothermic cleavage of the dimer but W is large and exothermic. This result is attributed to an extensive π-back-bond stabilization contribution in this system, i.e., W includes the $E_A{}^{\pi\circ}E_B{}^{\pi M}$ and $C_A{}^{\pi\circ}C_B{}^{\pi M}$ terms of eq 7.

The average deviation of the calculated and experimental enthalpies in all of the enthalpy correlations in Table 2 is 0.2 kcal mol^{-1} or less. When large % fits (see the footnotes to Table 2) arise, the range of enthalpies measured is small. The few donors removed from the correlations are invariably the bulkiest donors which cause enthalpic steric effects. In phosphorus donors, steric effects usually involve $P(t\text{-}Bu)_3$ and to a lesser extent $P(i\text{-}Pr)_3$ and $P(c\text{-}hex)_3$. The adduct formation enthalpies leave little doubt about the applicability of ECW to phosphorus donors and the need for a dual-parameter scale to describe their basicity.

Enthalpies of activation are reported for associative and dissociative substitution reactions of several metal complexes with phosphines. Those in the former cat-
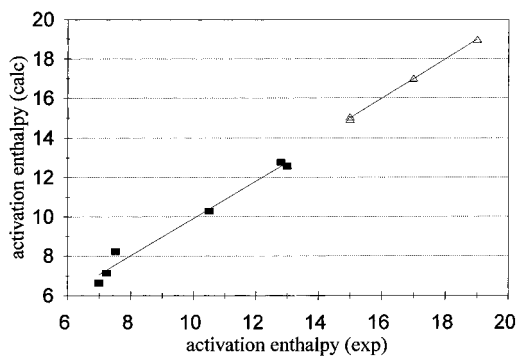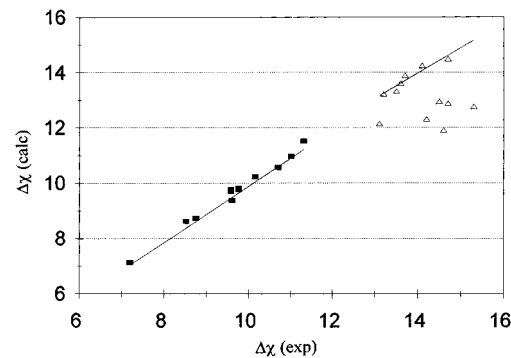
egory provide excellent correlation statistics, but the number of phosphines studied are limited. The results of typical associative reaction correlations are shown in Figure 3 and include $Co(NO)(CO)_3$ ($r^2 = 0.99$, $F = 824$), $V(CO)_6$ ($r^2 = 0.96$, $F = 26.8$), and $Ru_6C(CO)_{17}$ ($r^2 = 0.98$, $F = 65.5$).

The enthalpies of activation for displacing CO with a phosphine in toluene solvent by a mechanism that is first order in $Co(\eta^5\text{-}C_5H_4CO_2Me)(CO)_2$ and phosphine are reported[18] for 12 phosphines. Large deviations occur for the six phosphines that contain two or more aromatic substituents. While these ligands have large cone angles, steric effects are not indicated in this system because $P(c\text{-}hex)_3$ is well behaved in the correlation (Figure 4) when aromatic phosphines are omitted ($r^2 = 0.92$, $F = 44.3$). Aromatic solvents are known[1] to undergo π-complexation with aromatic donors, and loss of this interaction in the transition state would account for the observed increase in activation energy above that predicted. The reported frequencies, ν_{CO}, for the ($\eta^5\text{-}C_5H_4CO_2Me)Co(CO)L$ adducts of all of the phosphines studied give the excellent correlation shown in Figure 4 ($r^2 = 0.99$, $F = 280$). This is a meaningful result

(9) Gallagher, M. J.; Graddon, D. P.; Sheikh, A. R. *Aust. J. Chem.* **1976**, *29*, 759.
(10) Schenkluhn, H.; Scheidt, W.; Weimann, B.; Zähres, M. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 401.

(11) (a) Nolan, S. P.; López de la Vega, R.; Mukerjee, S. L.; Hoff, C. D. *Inorg. Chem.* **1986**, *25*, 1160. (b) Nolan, S. P.; López de la Vega, R.; Mukerjee, S. L.; Gonzalez, A. A.; Zhang, K.; Hoff, C. D. *Tetrahedron* **1988**, *7*, 1491.
(12) Thorsteinson, E. M.; Basolo, F. *J. Am. Chem. Soc.* **1966**, *88*, 3929.
(13) Chen, L.; Poë, A. J. *Inorg. Chem.* **1989**, *28*, 3641 and references therein.
(14) Shi, Q.-Z.; Richmond, T. G.; Trogler, W. C.; Basolo, F. *J. Am. Chem. Soc.* **1984**, *106*, 71.
(15) Chalk, K. C.; Pomeroy, R. K. *Inorg. Chem.* **1984**, *23*, 444.
(16) Aquino, M. A. S.; Macartney, D. H. *Inorg. Chem.* **1987**, *26*, 2696.
(17) Poë, A. J.; Farrar, D. H.; Zheng, Y. *J. Am. Chem. Soc.* **1992**, *114*, 5146.

because if π solvent interactions are the cause of the activation enthalpy deviations, they are not expected to have a significant effect on ν_{CO}.

For an associative mechanism, the W value contains the energy needed to dissociate a carbonyl when a phosphine with no basicity is involved in the transition state. The transition-state stabilization during nucleophilic attack should lead to a W value that is larger (more endothermic) than the $\Delta H^{\ddagger}$ value with any donor. This is found in all four systems. The fit and interpretations of these systems are the same as those reported earlier. The activation enthalpies for the CO dissociation from $Ru(CO)_4PX_3$ for seven phosphorus ligands are poorly fit ($r^2 = 0.39$) with an average deviation of 1.80 kcal mol^{-1}. The fit still was not satisfactory with the bulky $P(t\text{-Bu})_3$ removed, and this acceptor will be discussed further below.

ECW Parametrization of Steric Effects. The poor correlation of the enthalpy of activation of $Ru(CO)_4PX_3$ to ECW suggests that this data set could be used to test the addition of a steric term. The literature and data fit of $B(CH_3)_3$ enthalpies to ECW[1a] indicate steric repulsion is absent with ammonia and primary amine donors, marginal with secondary amines, and appreciable with tertiary amines. This pattern suggests that the enthalpic steric term should have the form $s(\theta - \theta_{ON})\delta$ where θ is the donor cone angle, θ_{ON} the cone angle for the onset of repulsion, and s is the coefficient indicating the severity of the effect. The Kronecker delta, δ, is zero when $\theta < \theta_{ON}$ and is one otherwise. This term differs from the linear steric term of QALE and has the same form as their nonlinear component of the steric effect.[47] The three smallest cone angle ligands for $Ru(CO)_4PX_3$ are fit to ECW. Adding any other fourth
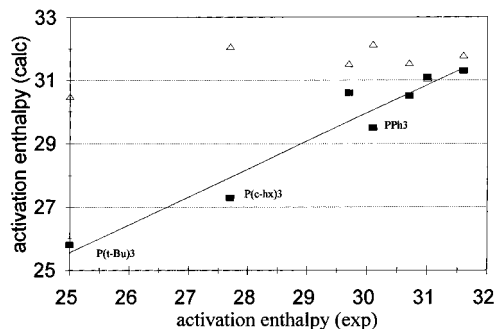

Figure 5. ECW (■) and ECW + cone angle fits (△) for the first-order dissociative activation enthalpy of CO from $Ru(CO)_4PX_3$.

ligand gives an unsatisfactory fit. The plot of the deviations of the excluded donors from the three phosphorus donor fit gives an intercept whose magnitude is $s\theta_{ON}$ (dev = $s\theta - s\theta_{ON} = s\theta$ − intercept). A θ_{ON} value of 128° results from the slope and intercept. This value is substituted into eq 8, and the acceptor coefficients obtained from a least-squares data fit are $E_A^* = 3.97$, $C_A^* = 0.77$, $s = -0.12$, and $W = 26.4$ with $r^2 = 0.92$ and an average deviation of 0.46 kcal mol^{-1} for all seven phosphines. One line of Figure 5 shows the fit of the

$$\Delta\chi = E_A^* E_B + C_A^* C_B + W + s(\theta - \theta_{ON})\delta \qquad (8)$$

calculated activation enthalpy from the E, C, and steric term correlation to the experimental values, and the other line is a plot of the E, C contribution to the enthalpy. The ratio of unknown parameters to data is large, but the conclusion that steric strain is relieved in the transition state is valid. This system illustrates the use of a steric term that is compatible with the integrity of the parameters in the ECW model. It should be emphasized that we are not advocating a four-parameter analysis of data. Instead, when ECW gives a poor correlation for bulky acceptors, we are offering a method to determine quantitatively if an enthalpic steric explanation is reasonable. For most of the acceptors in this article, too few of the donors studied deviate to provide this check.

Poor correlation of the enthalpies of adduct formation in $trans\text{-}(CH_3Pt[P(CH_3)_2C_6H_5]_2L)^+(PF_6)^-$ complexes[6a] to ECW were obtained in this and the earlier study. After removal of the nitrogen donors and bulky phosphines ($\theta > 160°$), r^2 in the master fit is 0.42, with an average deviation of 0.94 kcal mol^{-1}. Large misses are seen with bulky phosphines, but adding a steric term, eq 8, does not produce a satisfactory fit even with θ_{ON} equal to zero. Large contributions from steric effects are evident, but other complications exist in these data.

Interpretation of Redox Potentials and Spectral Shifts. Fits of the reduction potentials for series of

(18) Moreno, C.; Macazaga, M. J.; Delgado, S. *Organometallics* **1991**, *10*, 1124.
(19) Bodner, G. M.; May, M. P.; McKinney, L. E. *Inorg. Chem.* **1980**, *19*, 1951.
(20) Woodward, S. J.; Angelici, R. J.; Dombek, B. D. *Inorg. Chem.* **1978**, *17*, 1951.
(21) Bodner, G. M. *Inorg. Chem.* **1974**, *13*, 2564.
(22) Romeo, R.; Arena, G.; Scolaro, L. M. *Inorg. Chem.* **1992**, *31*, 4879.
(23) Barnett, K. W.; Pollmann, T. G. *J. Organomet. Chem.* **1974**, *69*, 413.
(24) Grim, S. O.; Yankowsky, A. W. *J. Org. Chem.* **1977**, *42*, 1236.
(25) Tolman, C. *J. Am. Chem. Soc.* **1970**, *92*, 2953.
(26) (a) Zizelman, P. M.; Amatore, C.; Kochi, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 3771. (b) Hershberger, J. W.; Klingler, R. J.; Kochi, J. K. *J. Am. Chem. Soc.* **1983**, *105*, 61.
(27) Rahman, M. M.; Lui, H.-Y.; Ericks, K.; Prock, A.; Giering, W. P. *Organometallics* **1989**, *8*, 1.
(28) Evans, S. G.; Gilmore, K.; Kane-Maguire, L. A. P. *J. Chem. Soc., Dalton Trans.* **1988**, 2009.
(29) Chatt, J.; Kan, C. T.; Leigh, G. J.; Pickett, C. J.; Stanley, D. R. *J. Chem. Soc., Dalton Trans.* **1980**, 2032.
(30) Leising, R. A.; Ohman, J. S.; Takeuchi, K. J. *Inorg. Chem.* **1988**, *27*, 3804.
(31) Hopkins, H. P., Jr.; Rhee, H. S.; Sears, C. T.; Nainan, K. C.; Thompson, W. H. *Inorg. Chem.* **1977**, *16*, 2884.
(32) Angelici, R. J.; Ingemanson, C. M. *Inorg. Chem.* **1969**, *8*, 83.
(33) Herrick, R. S.; Peters, C. H.; Duff, R. R. *Inorg. Chem.* **1988**, *27*, 2214.
(34) Zhang, S.; Brown, T. L. *Organometallics* **1992**, *11*, 4166.
(35) Halpern, J.; Phelan, P. F. *J. Am. Chem. Soc.* **1972**, *94*, 1881.
(36) Chapman, S.; Kane-Maguire, L. A. P. *J. Chem. Soc., Dalton Trans.* **1995**, 2021.
(37) Rerek, M. E.; Basolo, F. *Organometallics* **1983**, *2*, 372.
(38) Kane-Maguire, L. A. P.; Honig, E. D.; Sweigart, D. A. *Chem. Rev.* **1984**, *84*, 525.
(39) Henderson, W. A., Jr.; Buckler, S. A. *J. Am. Chem. Soc.* **1960**, *82*, 5794.
(40) Prock, A.; Giering, W. P.; Green, J. E.; Meirowitz, R. E.; Hoffman, S. L.; Woska, D. L.; Wilson, M. L.; Chang, R.; Chen, J.; Magnuson, R. H.; Eriks, K. *Organometallics* **1991**, *10*, 3479.

(41) Woska, D. C.; Bartholomew, J.; Greene, J. E.; Eriks, K.; Prock, A.; Giering, W. P. *Organometallics* **1993**, *12*, 304.
(42) Basato, M. *J. Chem. Soc., Dalton Trans.* **1986**, 217.
(43) Hudson, R. H. E.; Poë, A. J. *Organometallics* **1995**, *14*, 3238.
(44) Beringhelli, T.; D'Alfonso, G.; Freni, M.; Minoja, A. P. *Inorg. Chem.* **1996**, *35*, 2393.
(45) (a) Henderson, W. A., Jr.; Streuli, C. A. *J. Am. Chem. Soc.* **1960**, *82*, 5791. (b) Allman, T.; Goel, R. G. *Can. J. Chem.* **1982**, *60*, 716.
(46) Courtright, R. L.; Drago, R. S.; Nusz, J. A.; Nozari, M. S. *Inorg. Chem.* **1973**, *12*, 2809.
(47) Fernandez, A.; Reyes, C.; Wilson, M. R.; Woska, D. C.; Prock, A.; Giering, W. P. *Organometallics* **1997**, *16*, 342, and references therein.

M−L complexes in which L is varied measure the free energy of interaction of L with M in the oxidized and reduced forms of the complex. The magnitudes of the parameters would be influenced by π-back-bonding if the interaction differs in the two oxidation states. Steric effects would cause deviations in the data fit to ECW only to the extent that they differ in the two oxidation states. Average deviations of 0.02 or better are obtained for all systems studied.

The interpretations of the spectral shifts reported earlier remain essentially unchanged. The correlation of ν_{CO} for adducts of $(\eta\text{-Cp})(CO)(L)Fe(CO)Me$ to ECW is excellent. Only two of the 18 systems deviate by more than 2 cm^{-1}, and the average deviation of the fit is 0.9 cm^{-1}. With frequencies correlated, instead of the bond-strength related force constants, this is as good a correlation as can be expected. Our earlier fit of ν_{CO} for these adducts gave similar results, so it is inconceiveable that these data indicate[47] "something is amiss with the E/C model".

Interpretation of Reaction Rates. In general, reaction rates are poorly correlated to ECW, and as in the earlier study, good correlations require omission of phosphorus donors with long chain substituents. In contrast to our earlier report, the improved phosphine parameters show the rates of reaction[35] of benzyl bromide with Co(DMGH)L in benzene have a significant π-back-bonding contribution. This is consistent with a reported analysis of enthalpies in an analogous system.[46]

The analysis of free energies of reaction with parameters related to bond strength requires a linear free-energy assumption. This assumption is less likely to be valid on complex inorganic and organometallic systems than on the structurally similar organic systems treated with Hammett or Taft parameters. Six of the acceptors in Table 2 for which both free energies and enthalpies are reported show unacceptable linear free-energy relations, i.e., entropy changes are not linear with enthalpy changes. Our earlier analysis[2] suggested an entropic steric effect in rate and free-energy data from the reorganization of substituents on donors causing a breakdown in the linear free-energy assumption. This entropic contribution occurs with n-alkyl substituents longer then methyl that have small cone angles. Thus, in contrast to front strain, entropic strain is not related to the cone angle, θ. When enthalpies and entropies are reported, these systems lead to nonlinear enthalpy−entropy plots. Thus, it is encouraging that the logs of the rate constants are often poorly fit by ECW because they are nonlinear free-energy systems. The ECW difficulty with rates is in contrast to the good ECW data fits obtained on the same acceptor for enthalpies of activation, spectral shifts, and $E_{1/2}$ values. If one desires to correlate nonlinear entropic effects, terms would have to be added to eq 2 to accommodate each effect. Clearly, entropic and enthalpic steric effects would require different parameters. Rather than trying to parametrize entropic effects, it has been our philosophy to use ECW to detect complications in these systems that are not related to donor−acceptor bond strength and to use other measurements to confirm the cause of deviations.

Comparison of ECW and Literature Analyses of Phosphine Reactivity. Typically, phosphorus donor

reactivity has been analyzed with a one-parameter basicity scale, χ, and a linear steric contribution, $b\theta$. These are linear free-energy, bond-strength related parameters whose meaning is different than the parameters of the ECW model. A χ scale, based on the ^{13}C or C−O frequency shift of Ni(CO)$_3$L, is a one-parameter, basicity scale that applies to electrostatic acceptors with a C_A/E_A of 0.2 (see Table 2). If the θ term paralleled covalency, χ/θ would fit phosphorus donor reactivity as well as E/C. A recent "examination" of the ECW parameters with QALE claimed[47] that E_B and C_B are linear combinations of χ and θ with a small contribution from E_{ar}, "a phenyl effect, whose origins are poorly understood". Such a result would have profound implications for it would suggest, for phosphorus donors at least, that hard/soft, covalent/electrostatic, and charge/frontier control are in effect hard/steric, electrostatic/steric, or charge/steric for any donor without a phenyl group. We would not know if covalency, softness, or frontier control are in reality a linear steric effect.

The claim[47] that E_B and C_B are linear combinations of mostly χ and θ parameters will be tested using enthalpies of reaction and activation. Enthalpies best measure bond strengths and avoid a linear free-energy assumption.[1a] For enthalpic systems, ECW uses only two parameters to fit the measurements so the two QALE parameters χ and θ were used in the comparison with the "minor E_{ar}" contribution[47] omitted. Enthalpies of reaction for phosphorus donors with CF$_3$SO$_3$H, enthalpies of protonation of CpIr(CO)PX$_3$, enthalpies of adduct formation with Cp'$_2$Ti and $[\eta\text{-}C_5H_7Ni(CH_3)]_2$, and enthalpies of activation for associative CO substitution by phosphorus donors in CpCO$_2$MeCo(CO)$_2$ were fit to χ and θ to test their "equivalency" to the ECW fits described above. To afford a direct comparison, those donors eliminated from the ECW fit because of steric effects were also omitted in the QALE(χ,θ) fits. The enthalpies of protonation of phosphines by CF$_3$SO$_3$H are fit[48] with an r^2 of 0.98 using QALE(χ,θ). A poor χ/θ fit results for $[\eta\text{-}C_5H_7Ni(CH_3)]_2$ ($r^2 = 0.81$ with $c_\chi = 0.41$, $c_\theta = -0.068$, and intercept = 32.0). The Cp'$_2$Ti fit is not much better ($r^2 = 0.86$ with $c_\chi = -0.52$, $c_\theta = -0.39$, and intercept = 65.7). The protonation of CpIr(CO)-PX$_3$ fits very well ($r^2 = 0.98$ with $c_\chi = -0.31$, $c_\theta = -0.056$, and intercept = 42.4). The (χ,θ) fit of the enthalpies of activation for CO substitution by phosphine in Co(η^5-C$_5$H$_4$CO$_2$Me)(CO)$_2$ give a poor fit ($r^2 = 0.72$ with $c_\chi = -0.082$, $c_\theta = -0.035$, and intercept = 19.2). ECW correlated all of these measurements to at least an r^2 of 0.9. Clearly, the two parameter sets are not equivalent, and the success of ECW indicates that the θ term is added to χ in an inadequate attempt to compensate for changes in the covalency of the acceptor from that of the one-parameter χ scale.

Our earlier reports detailing the inadequacy of one-parameter basicity scales[1g] predicts that the next step to be taken to improve data fits is to divide the data set into subsets that limit the C_B/E_B ratios of the donors.

---

(48) In eq 15 of a recent QALE article,[47] an incorrect ECW fit of the enthalpies of reaction of only phosphine donors with CF$_3$SO$_3$H is reported. The correct fit parameters using the previously reported E_B and C_B values for phosphines should have been $E_A^* = 7.83$, $C_A^* = 6.17$, and $W = -6.22$, and $r^2 = 1.0$. The current phosphine parameters give slightly different values.

As mentioned above, this leads to great correlations with poorly defined parameters.[1d,e] When χ/θ gives poor correlations, this subdivision of the data is accomplished in QALE by a variety of procedures: eliminate phosphites, treat phenyl-substituted phosphines separately, divide the set according to θ, and treat only C_{3v} phosphines.[49,50] The deviating systems become "effects" that are then parametrized empirically and used as needed in subsequent QALE analyses. It is not surprising that one can derive parameters, e.g., the aryl effect,[40] E_{ar}, and steric thresholds,[41] to make these subsets conform and fit phosphine reactivity trends for many acceptors.[50]

ECW is criticized[47] with the obvious claim that no two parameters will correlate all phosphine reactivity. It is emphasized[1] that when eq 2 is used to analyze data, the conclusion is that the property either does or does not parallel bond strength. No claim has ever been made to fit every property. The parametrization that leads to the extra QALE parameters give better fits of free energies than ECW. However, what does it all mean? The aryl-effect parameter is not defined, and its existence cannot be determined apriori. To quote[40] "we do not understand the nature of the aryl effect" and "the contributions of E_{ar} relative to χ change from system to system and even change sign". Adding a steric threshold suggests that there are two kinds of enthalpic steric effects. What do presumably electronic parameters mean when they are able to fit nonlinear free energies? One is also prompted to ask, why are phosphorus donors so different from other donors where these effects are not used? Another question seldom addressed in QALE is "do the added parameters produce acceptor coefficients from the analyses that make sense when different acceptors are compared"?

The meaning is clear in the ECW interpretation of the reactivity in these systems. The parameters describe varying electrostatic and covalent contributions with a few deviations attributed to steric effects. Explanations of this sort have precedence in the qualitative explanations of reactivity. In QALE analyses, steric effects dominate phosphine reactivity, with the $c_\theta\theta$ steric term usually required in the analyses. The QALE fit of $-\Delta H$ for CF_3SO_3H to phosphorus donors is excellent, giving fit parameters[47] of $\chi = -1.05$, $\theta = -.088$, and $E_{ar} = -1.21$ with an intercept of 51.3. Keeping in mind that θ is usually 10 times larger than χ, a substantial steric effect, $(c_\theta\theta)$ is involved for the enthalpies of protonation by CF_3SO_3H according to these coefficients. The steric *enthalpy* component for PMe_3, for example, is 10 kcal mol^{-1}. It is hard to imagine a contemporary view of reactivity to account for a repulsive enthalpy term of this magnitude toward the proton that is not present in $Ni(CO)_3PMe_3$. Front strain steric effects in Bronsted acids are without literature precedent, and the QALE conclusion[47] that the coefficients from χ/θ analy-
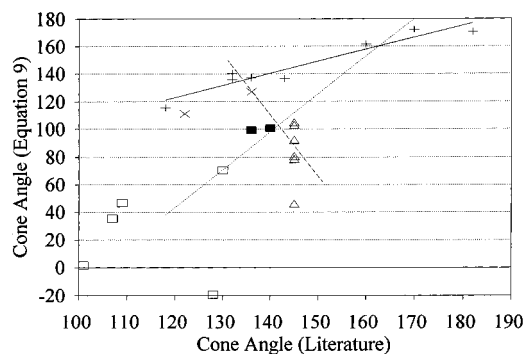
(49) Golovin, M. N.; Rahman, M. M.; Belmonte, J. E.; Giering, W. P. *Organometallics* **1985**, *4*, 1981.

(50) Bartholomew, J.; Fernandez, A. L.; Lorsbach, B. A.; Wilson, M. R.; Prock, A.; Giering, W. P. *Organometallics* **1996**, *15*, 295. In some correlations, graphical procedures are employed by QALE on limited data sets to, in effect, introduce assumptions that enable one to separate highly correlated parameters for small subsets. This procedure often involves extrapolation to phosphines with χ values an equal distance outside of the range of points plotted. Good fits result and correlation statistics improve when correlated parameters are estimated, but this unprecedented statistical procedure causes all meaning to be lost.

Figure 6. Donor choices for which the cone angle, θ, is linear with E_B and C_B. The solid line is a fit of the aliphatic-substituted phosphines to eq 9. Phosphines on the line will fit data to χ and θ as well as to E_B and C_B. Points marked with + are aliphatic-substituted phosphines, those with × are for phosphines with one aromatic group, those with ■ are for phosphines with two aromatic groups, those with △ are phosphines with three aromatic groups, and those with □ are for phosphites. The dashed lines represent arbitrary donor selections that would also be linear to E_B and C_B.

ses are "consonant with the contemporary views" is not supported by this system. The contribution of this steric component is not changed significantly when all the QALE parameters are used.

With decreasing values of χ for increasing basicity and increasing values of θ for increasing steric repulsion, the ratio of the coefficients for fitting the enthalpies of reactions should be positive with the signs on each depending on the intercept. QALE parameters often are not consistent with these signs, e.g., for $[(\eta\text{-}C_5H_7)Ni(CH_3)]_2$, and apparently have an unexplained meaning that is different than the contemporary view. These unaddressed[47,49] questions and the inconsistencies described above must be answered to accept the claim that the "QALE conclusions are consistent with contemporary views of chemical trends".

How does ECW explain the good fits that sometimes result if the QALE model is using incorrect basicity parameters? For all phosphines and phosphites in Table 1 whose weights are 0.7 or more, an excellent correlation of χ to E_B and C_B is found ($r^2 = 0.98$, $F = 606$, and $x = 1.0$). This is expected because ECW gives an excellent fit to the frequency shifts used to determine the χ parameters. The C/E ratio for the χ fit is 0.20, and that for ν $Ni(CO)_3L$ is 0.23. Any acceptor with a C_A/E_A ratio of 0.2 will correlate to ECW and to χ without need for a linear steric term, even for different size acceptors. Next, the θ term was fit to E_B and C_B. When all of the donors used in the χ fit were correlated, an r^2 of 0.61 resulted. Fits were attempted with only phosphites removed and another with only aromatic phosphines removed. The r^2 values showed insignificant improvement. Thus, there is no combination of E_B and C_B that will be equivalent to θ for these combinations of donors. The omission of all but alkyl-substituted phosphines in the θ fit led to the excellent correlation (r^2 of 0.93) given in eq 9. The θ values calculated using

$$\theta_{Calc} = 399.7E_B + 85.1C_B - 446.9 \qquad (9)$$

eq 9 are plotted vs literature values in Figure 6 with the solid line drawn for the alkyl phosphines. When

only alkyl phosphines are studied, χ and θ will fit data as well as E_B and C_B but parameter meaning will differ. The points in Figure 6 for other phosphines are not intended to give revised θ values but to show what the value of the cone angle would have to be to correlate to E and C. For some donors, a conceptually impossible negative θ would be needed. Since the cone angles are fixed, QALE adds new effects to bring the deviant points to the solid line and to do the job E_B and C_B do. As shown in Figure 6, compounds containing a phenyl group show negative deviations. With the $PhPR_2$ deviating slightly, Ph_2PR deviating to a greater extent, and the average of the triphenyl-substituted phosphines deviating the most, the plot suggests that the "electronic aryl effect"[40] is just an added empirical parameter to compensate θ for its improper estimate of covalency in aromatic phosphines. Data can be fit with this compensation, but it is not surprising that meaning is lost.

Phosphites were not included in the recent comparison[47] of QALE and ECW. Figure 6 suggests that when a large number of donors are studied, another effect, the phosphite effect proposed in earlier QALE reports,[27] will be needed to adjust for the inadequacy of the cone angle to compensate for covalency in correlations of these donors to acceptors that have a C/E ratio different than that of χ. ECW recommends the use of phosphites in all reactivity studies for they have a different C_B/E_B ratio than alkyl phosphines.

Finally, Figure 6 provides the E/C explanation of why good QALE fits result when a limited number of phosphorus donors are selected for study. If the donors selected can have a line drawn through them in Figure 6, an equation similar to eq 9 can be derived to relate θ to E_B and C_B. A good fit to QALE(χ,θ) will result for this set of donors, with the correlation coefficients adjusting to incorporate the new line slope. The resulting coefficients will be without meaning. Two of the many possible donor selections that can have a line drawn through them are illustrated by the dashed lines in Figure 6. For these selections, good fits to χ and θ can result, and if deviations occur for a few of the selected phosphorus donors that are not on the line, the misses can be accommodated by using the extra QALE terms. The signs and magnitudes of these terms will not have meaning and will vary with donor selection to compensate for the θ deficiency. The line drawn with large dashes will not require a phenyl effect but will need a θ_{ON} for large cone angles. Figure 6 should be used in phosphorus donor selection to probe the steric contribution and can explain the need for extra QALE terms to make up for covalency in data fits that are correlated by ECW with only two parameters.

Conclusions

ECW analyses of the reactivity and spectroscopy of substituted phosphines have shown that spectral shifts, enthalpies of reaction and activation, and redox potentials are primarily dominated by the donor strength of the phosphines and phosphites. Over 500 of these physicochemical measurements are correlated to within experimental error with just two sets of E_B and C_B parameters for phosphorus donors. Only in crowded acceptors with bulky phosphines are enthalpic steric effects evident. An extension of ECW is offered using cone angles to verify the magnitude and onset of steric effects.

Rate constants for complex organometallic systems often do not exhibit linear free-energy behavior and thus should not be expected to correlate to enthalpic bond strength parameters. Deviations are attributed to entropic steric contributions that result from changes in substituent chain organization in the transition state or intermediate that are not cone-angle-related. These deviations are found in rate data but not in redox potential, frequency shift, or enthalpy data analyses of the same acceptor.

Analyses of phosphorus donor data with QALE procedures provides a very different interpretation of reactivity than ECW. With QALE, steric effects are ubiquitous and no account is made for changes in covalency or softness of the acceptors. Hard/soft, electrostatic/covalent, or charge/frontier are replaced by hard/steric, electrostatic/steric, or charge/steric. In ECW, the importance of covalency is found to vary with the acceptor, and a linear steric contribution is not observed in most systems. Using the two QALE χ and θ parameters, it is shown by using data fits that these parameters are not "the same as E_B and C_B except for a *minor* E_{ar} contribution".[47] It is also shown that additional empirical QALE parameters are used to obtain good fits of individual data sets at the expense of meaning. This is evident in seldom-made comparisons of the parameters for different acceptors.

QALE has been parametrized to correlate phosphine reactivity and will fit many properties, but in using the parameters, one must be careful not to confuse correlation and meaning. For example, what meaning can be inferred from the parameters when the QALE linear free-energy parameters fit nonlinear free energy data sets? Is there meaning in an unprecedented 10 kcal mol^{-1} steric repulsion contribution toward the proton of CF_3SO_3H when there is none for $Ni(CO)_3L$? Other examples are given to show that the meaning of the QALE coefficients do not represent contemporary views of reactivity. If more attention is paid to the interpretation of the coefficients from QALE fits and comparison of these coefficients for different acceptors, more questions will arise about the procedure. Finally, an ECW analysis of θ indicates that the meaning of the extra terms of QALE are to compensate for the failed attempt of θ to accommodate the widely accepted differences in covalency (softness) that exist in different acceptors.[1]

In the larger scheme of understanding the factors that influence reactivity, the test of any set of multiple scale reactivity parameters is not in slight differences in good data fits. A more important concern is the consistency of the interpretation of the fit coefficients when patterns for donor reactivity are compared for different acceptors. This consistency affords understanding in the context of the model, leads to significant generalizations of reactivity principles, and inspires new experimentation. Lack of consistency, e.g., the E_{ar} parameter, suggests meaningless correlations with only limited value for use in interpolative predictions.