Phosphine E_B and C_B Values

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Abstract: This article presents a scale of σ donor strengths for phosphines. The phosphine parameters, E_B and C_B, can be used in combination with previously reported parameters for oxygen, nitrogen, and sulfur donors to measure σ-basicity. The advantages of combining donors from more than one family to analyze reactivity are demonstrated. When substituents are changed in a family of donors, the change in the C_B/E_B ratio is small and this is shown to lead to limitations in the conclusions that can be drawn from substituent constant correlations. QALE analyses also treat only single families and are subject to the same limitations. The dual parameter E_B, C_B basicity scale is less reliant upon steric effects than QALE analyses to rationalize trends in the reactivity of phosphines. This leads to an alternative interpretation of a large body of phosphine chemistry. A model is presented to support the idea that the π-acceptor properties of the phosphines decrease regularly as their σ basicity increases. It is shown that the phosphine σ donor, E_B and C_B parameters inappropriately can correlate reactivity toward acceptors that π-back-bond when a data set involves only phosphines. In order to obtain reliable acceptor parameters and to detect a π-back-bond component in donor−acceptor interactions, donors from families other than phosphines have to be studied with the π-donor.

Introduction

Research from this laboratory has shown[1] the widespread utility of eq 1 in analyzing chemical reactivity

$$\Delta\chi = E_AE_B + C_AC_B + W \qquad (1)$$

$\Delta\chi$ is the measured property determined when the acceptor, A, is held constant as a series of donors, B, is varied or as the donor, B, is held constant as a series of acceptors is varied. In the former experiment, reported E_B and C_B values for each $\Delta\chi$ are substituted into eq 1 and the series of equations (one for each base) is solved for E_A*, C_A*, and W. In effect, E_B and C_B are a dual parameter, enthalpy based, basicity scale that can be used to determine donor strength influence on $\Delta\chi$. An asterisk is placed on E and C when they refer to a physicochemical property other than a solvation minimized enthalpy. The parameters contain the conversion units to express eq 1 in the units of $\Delta\chi$.

It should be clear that if the C_B/E_B ratios of the series of donors studied are the same, the set of simultaneous equations corresponding to eq 1 cannot be solved for the unknowns C_A*, E_A*, and W. An infinite number of combinations of E_A*, C_A*, and W would fit the data. Accordingly, these parameters and the relative importance of covalency in the interaction are best defined when the different equations in the set involve donors with different C_B/E_B ratios. This idea is essential to the discussion that follows. The terms donor and acceptor are reversed in the above discussion when the donor is held constant and the acceptor is varied in the series of experiments.

The reported E_B and C_B values for donors and E_A and C_A values for acceptors are empirically derived, mainly from solvation minimized enthalpies. The E values parallel the tendency of the reactant to undergo electrostatic or charged controlled interactions and the C values parallel the tendency of the reactant to undergo covalency or frontier controlled interactions. The parameters are derived from adducts devoid of steric problems or π-back-bond contributions. As a result, the parameters can be used to detect these effects in the analysis of new systems when the experiments are properly designed.

Recently,[2] a dual parameter *substituent constant equation* (eq 2) was reported to analyze the reactivity *of families of compounds* whose E and C values are not known. In eq 2,

$$\Delta\chi^X = d^E\Delta E^X + d^C\Delta C^X + \Delta\chi^H \qquad (2)$$

$\Delta\chi^X$ is the measured property for the molecule containing substituent, X, $\Delta\chi^H$ is the value for the parent hydrogen compound, ΔE^X and ΔC^X give the proportional change in the E and C values of the parent compound induced by the substituent, and d^E and d^C gauge the sensitivity of the reaction to substituent change. The ΔE^X and ΔC^X values are the dual parameter analogues of the Hammett σ-values while d^E and d^C are the dual parameter analogues of ρ. It is reported[2] that the set of dual substituent parameters correlates data that previously required different sets of substituent constants for analysis.

The d-values of eq 2 are related to the E and C values of eq 1 by:

$$d_A{}^E = s_B{}^E E_A^* \qquad (3)$$

$$d_A{}^C = s_B{}^C C_A^* \qquad (4)$$

Equations 3 and 4 are written for an analysis in which a family of donors is studied and the acceptor is held constant. The subscripts are changed when the donor is kept constant and a family of acceptors studied. In eqs 3 and 4, the $d_A{}^E$ of eq 2 and E_A* of eq 1 are related by the family dependent proportion-

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ally constant s_B^E which measures the sensitivity of the E values of the family of donors to the substituent change. The proportionality constant s_B^C, which relates d_A^C to C_A*, measures the sensitivity of the C values of the family of donors to substituent change relative to setting $s_B^E = 1$ and $s_B^C = 1$ for pyridine. Thus, an s_B value >1 indicates the family has a greater basicity response to the substituent than pyridine, while $s_B < 1$ indicates the substituent effect is transmitted less effectively.

It has been further shown[2] that the E_B or C_B values of the X-substituted donor E_B^X and C_B^X are given by

$$E_B^X = s_B^E \Delta E^X + E_B^H \tag{5}$$

$$C_B^X = s_B^C \Delta C^X + C_B^H \tag{6}$$

where E_B^H and C_B^H are the E and C values for the parent hydrogen compound. The implications of eqs 5 and 6 are profound for they greatly expand the number of donors that can be analyzed with eq 1. For example, with $s_B^E = 1$ and $s_B^C = 1$ for substituted pyridines, E_B^X and C_B^X values for seventy-seven 3- and 4-monosubstituted pyridines can be calculated with eqs 5 and 6 from reported[2d] ΔE^X and ΔC^X values. In a similar fashion, with reported[2d] values of $s_A^E = -0.83$ and $s_A^C = -0.23$, the E_A^X and C_A^X values of seventy-seven 3- and 4-substituted phenols can be calculated. Substituting the resulting E^X and C^X values for pyridines and phenols into eq 1 permits the calculation of 6084 enthalpies of interaction of various pyridines with various phenols. Calculations can also be made for the reaction of all of these pyridines with all the acceptors whose E_A and C_A values are reported and for the reactions of all these phenols with all the donors whose E_B and C_B are reported.[1a]

It has been emphasized, that in using eq 1 to solve for E_A* and C_A* to characterize a new reaction, one should use donors with very different C_B/E_B ratios. When this is not done, a shallow minimum exists in the data fit and the uncertainty in the parameters exceeds the errors determined from goodness-of-fit criteria. This is a very significant problem in the interpretation of the d^E and d^C parameters of eq 2. By definition a substituent constant analysis restricts the study of a reaction to a single family of donors (or acceptors). This restriction usually leads to a small variation in the C_B/E_B ratio of the data set. Thus, if the E_B and C_B values are available, eq 1 should be used to characterize an acid property and instead of restricting measurements to a single family, different donors with a wide range of C_B/E_B values should be studied. Increasing the range provides more accurate values of E_A* and C_A* whose interpretation is more reliable than that of d^E and d^C.

The reactivities of phosphines have been analyzed[2d] with eq 2 by summing the ΔE and ΔC values of the substituents attached to phosphorus. In this article, the E_B and C_B values of trisubstituted phosphines will be determined directly. This is particularly significant because of the importance of phosphines in organometallic and catalytic chemistry. At present, only tentative E_B and C_B values are reported[1a] for two phosphines. Determination of E_B and C_B will permit an evaluation of the validity of the substituent summation used[2d] in the phosphine analyses and by providing more accurate E_A* and C_A* values for several physicochemical properties lead to a more meaningful interpretation of the influence of electronic, steric, and π-back-bonding effects in the reactions these compounds undergo with acceptors.

Results and Discussion

Results from the Data Fit. In order to incorporate a new donor into the E and C model, enthalpies or physicochemical properties are measured for reactions of this donor with acceptors in the correlation. A series of simultaneous equations like eq 1 is written, one for each measured property, whose E_A and C_A are known. The equations are solved for E_B and C_B. A satisfactory fit indicates the model can be extended to this new donor. The reactions of phosphines with most of the acceptors in the E and C correlation have not been included in this work because the phosphine adducts often are expected to have appreciable contributions from π-back-bonding and most of the reported studies of phosphines do not include donors in the E and C model.

Table 1

no.	phosphine	wt[a]	E_B	C_B	C_B/E_B	θ[b]
1	$P(CH_3)_3$	1.0	0.247	5.81	23.5	118
2	$P(C_2H_5)_3$	1.0	0.274	6.11	22.3	132
3	$P(n\text{-}C_3H_7)_3$	0.5	0.310	5.78	18.6	132
4	$P(n\text{-}C_4H_9)_3$	1.0	0.294	5.90	20.1	132
5	$P(i\text{-}C_3H_7)_3$	0.5	0.352	5.91	16.8	160
6	$P(i\text{-}C_4H_9)_3$	0.5	0.312	5.55	17.8	143
7	$P(c\text{-}C_6H_{11})_3$	1.0	0.374	5.91	15.8	170
8	$P(t\text{-}C_4H_9)_3$	0.7	0.331	6.52	19.7	182
9	$P(CH_2C_6H_5)_3$	0.2	0.307	3.77		165
10	$P(OCH_3)_3$	1.0	0.131	4.83	36.9	107
11	$P(OC_2H_5)_3$	1.0	0.173	4.65	26.9	109
12	$P(O\text{-}i\text{-}C_3H_7)_3$	0.7	0.211	4.59	21.8	130
13	$P(OC_6H_5)_3$	1.0	0.090	3.36	37.3	128
14	$P(OCH_2)_3R$	0.7	0.037	5.24	142	101
15	$P[N(CH_3)_2]_3$	0.3	0.313	5.70	18	
16	$P(CH{=}CH_2)_3$	0.2	0.426	2.28		
17	$P(C_6H_5)_3$	1.0	0.301	4.07	13.5	c
18	$P(4\text{-}CH_3C_6H_4)_3$	1.0	0.308	4.37	14.2	c
19	$P(4\text{-}CH_3OC_6H_4)_3$	1.0	0.307	4.52	14.7	c
20	$P(4\text{-}FC_6H_4)_3$	0.6	0.288	3.81	13.2	c
21	$P(4\text{-}ClC_6H_4)_3$	1.0	0.282	3.55	12.6	c
22	$P(4\text{-}CF_3C_6H_4)_3$	0.4	0.280	2.85	10.2	c
23	$P(4\text{-}NMe_2C_6H_4)_3$	0.4	0.342	5.05	14.8	c
24	PCl_3	0.2	0.056	0.073		
25	$P(CH_3)_2C_6H_5$	1.0	0.273	5.27	19.3	122
26	$P(C_2H_5)_2C_6H_5$	1.0	0.288	5.43	18.9	136
27	$P(OCH_3)_2C_6H_5$	0.4	0.197	4.09	20.8	120
28	$P(Cl)_2C_6H_5$	0.2	0.167	1.08		
29	$P(C_6H_5)_2\ CH_3$	1.0	0.276	4.67	16.9	136
30	$P(C_6H_5)_2\ C_2H_5$	1.0	0.274	4.85	17.7	140
31	$P(C_6H_5)_2\ n\text{-}C_4H_9$	0.5	0.310	4.69	15	140
32	$P(C_6H_5)_2OCH_3$	0.4	0.260	4.11	15.8	132
33	$P(C_6H_5)_2Cl$	0.4	0.220	2.80	12.7	
34	$P(C_6H_{11})_2H$	0.2	0.303	5.46		143
35	$As(C_6H_5)_3$	0.2	0.339	3.54		141

[a] If 12 or more systems are studied, a weight (wt) value of 1 is assigned, 12−10 a value of 0.7, 9 to 7 a value of 0.5, less than 7 a value of 0.3. If all 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 ref 3. [c] The reported value is 145, but 140 has been empirically found to provide better fits in our correlations.

The above difficulties are circumvented, and a set of E_B and C_B values for phosphines are obtained by carrying out a master fit on data for over forty-five spectrochemical probes and reactions of substituted phosphines. A master fit involves solving a series of equations of the form of eq 1 for all five parameters. In order to connect this master fit to reported parameters, it is crucial to include physicochemical properties that include both phosphines and donors or acceptors already in the ECW model. The reported[1a] E_B and C_B values for the donors and the reported E_A and C_A values for the acceptors are entered into the corresponding simultaneous equations for these systems. (See calculation section.)

The E_B and C_B values for phosphines obtained from the data fit are listed in Table 1. The resulting E_A^* and C_A^* values for the reactions and spectral probes are reported in Table 2. The

Table 2. E_A* and C_A* for Spectral Shifts and Reactions[a]

shift or reactant	wt	E_A*	C_A*	W	C_A*/E_A*	no. of phosphines (others) [omitted]
$-\Delta H$ (CF_3SO_3H)[e]	1.2	7.69	6.17	−6.15	0.80	12 (3) [0]
log k(C_2H_5I (S_N2))[f]	0.9	−0.789	0.823	−7.40	−1.0	10 (1) [1]
$-\Delta H$ ($B(CH_3)_3$)[b,g]	0.4	4.03	2.71	0	0.65	2 (4) [0]
$-\Delta H$ ($Al(CH_3)_3$)[b,h]	1.2	8.06	2.33	5.63	0.29	3 (14) [2]
$-\Delta H$ ($Ga(C_2H_5)_3$)[i]	0.4	6.16	2.18	0	0.35	1 (4) [0]
ΔH ($CH_3Pt(PR_3)_2THF^+$)[b,j]	1.2	−7.16	1.43	19.7	−0.20	15 (4) [6]
ΔH ($CpIr(CO)PR_3$)[d,k]	0.1	1.39	1.82	22.4	1.3	5 (0) [0]
ΔH ($Ti(C_7H_{11})_2PX_3$)[l]	0.4	−1.44	3.47	−5.22	−2.4	5 (1) [1]
ΔH ($HgCl_2$)[m]	0.1	−15.8	6.32	−3.11	−0.4	6 (0) [0]
ΔH ($HgBr_2$)[m]	0.1	28.1	5.94	−14.3	0.2	6 (0) [0]
ΔH ([Ni η-$C_5H_7)CH_3]_2$)[n]	0.3	−66.8	−0.089	45.8	0.00	9 (0) [4]
$\Delta H^‡$ ($CoNO(CO)_3$)[o]	0.1	−17.4	−0.514	22.3	0.30	4 (0) [0]
$\Delta H^‡$ ($Ru(CO)_4PX_3$(Dis 1))[b,p]	0.1	−11.6	−0.71	36.4	0.06	6 (0) [1]
$\Delta H^‡$ ($V(CO)_6$(S_N2))[q]	0.1	−12.3	−1.51	19.7	0.12	5 (0) [0]
$\Delta H^‡$ ($Ru(CO)_3PX_3(SiCl_3)_2$)[r]	0.8	−1.29	0.612	25.0	−0.47	14 (0) [0]
^{13}C ($Ni(CO)_3PX_3$)[s]	0.8	9.57	0.779	−1.8	0.08	33 (0) [0]
^{13}C ($Cr(CO)_5L$)[t]	1.2	9.94	0.612	−0.445	0.06	24 (1) [1]
^{13}C ($Mo(CO)_5PX_3$)[u]	0.8	9.48	0.514	−0.277	0.05	17 (0) [0]
^{13}C ($W(CO)_5L$)[v]	0.4	13.7	0.237	191.8	0.02	5 (1) [1]
ν ($Ni(CO)_3PX_3$)[w]	0.4	−65.8	−3.97	2100	0.06	28 (0) [1]
ν ($CH_3CpMn(CO)_2PX_3$)[x]	0.4	−5.57	−2.75	1954	0.49	9 (5) [2]
ν (η-CpFe(CO)(COMe)PX_3)[y]	0.4	−125	−4.02	1975	0.03	18 (0) [0]
ν (η-Cp′Fe(CO)(COMe)PX_3)[z]	0.4	−123	−4.09	1971	0.03	18 (0) [0]
ν ($Ru(CO)_4L$)[aa]	0.4	−60.9	−1.53	2086	−0.18	17 (0) [0]
$E_{1/2}$ (Cp′Mn(CH_2Cl_2))[bb]	1.7	−0.307	−0.057	0.827	0.19	9 (9) [0]
$E_{1/2}$ (Cp′Mn(CH_3CN))[cc]	1.7	−0.738	−0.116	1.27	0.16	18 (1) [0]
Ep (Cp′Mn[$(CH_3)_2CO$])[dd]	0.9	−0.276	−0.013	0.599	0.05	2 (4) [1]
$E_{1/2}$ ($Cr(CO)_5L$)[ee]	0.9	−1.09	−0.032	1.85	0.03	3 (3) [3]
$E_{1/2}$ ($Ru(bpy)_2^{2+}(H_2O)PX_3^{2+}$)[ff]	1.3	0.098	−0.081	1.63	−0.83	13 (0) [0]
$E_{1/2}$ (η-Cp Fe(CO)(COMe)PX_3)[gg]	1.3	−1.01	−0.068	0.904	0.07	18 (0) [0]
$E_{1/2}$ (η-Cp′ Fe(CO)(COMe)PX_3)[hh]	1.3	−0.993	−0.072	0.894	0.07	18 (0) [0]
log k ($CF_3C_6H_4OH$)[ii,c]	0.6	1.35	−0.033	0.236	−0.02	4 (1) [1]
log k (Co $NO(CO)_3$ (S_N2))[jj]	1.2	−0.15	1.36	−8.91	−1.4	12 (3) [0]
log k ($V(CO)_6$ (S_N2))[kk]	0.1	5.53	1.69	−9.03	0.31	8 (0) [2]
log k ($Ru(CO)_4L$)[ll]	0.8	3.60	−0.19	−3.50	−0.05	15 (0) [1]
log k ($MoBr_2(CO)_3(PX_3)_2$)[mm]	0.1	−59.9	0.89	18.0	0.00	8 (0) [2]
log k (Cp_2 $Fe_2(CO)_4$)[nn]	0.4	−2.50	−0.68	9.19	2.7	8 (1) [3]
log k ($CoCp^*(CO)_2$)[oo]	0.3	−1.18	1.31	−10.1	−1.1	8 (0) [0]
log k_1 (CpMn(py))[pp]	0.3	−26.5	1.63	2.74	−0.06	9 (0) [1]
log k ($Ru(bpy)_2(H_2O)PX_3^{2+}$)[qq]	0.5	30.1	0.04	−11.6	0.00	11 (0) [0]
log k (Co-$C_6H_5CH_2Br$)[rr]	0.9	0.80	0.89	−5.49	1.1	7 (4) [1]
log k (Co′-$C_6H_5CH_2Br$)[rr]	0.4	0.67	0.88	−5.33	1.3	4 (2) [0]
pK_A[ss]	0.8	14.8	3.19	−14.5	0.22	14 (0) [0]

[a] In the far right column, the first entry gives the number of phosphines fit, the number of other types of donors included, and the number of phosphines with known E_B and C_B that were omitted. The reported fit includes both the phosphines and other donors. The wt (weight) value is to be used in future correlations with this physicochemical property to determine a new donor E_B and C_B. If more than 12 donors give satisfactory data fits a wt of 1 is assigned, 12−10 a value of 0.7, 9−7 a value of 0.5, less than 7 a value of 0.2. If donors other than phosphines are fit, 0.2 is added and if not, 0.2 is subtracted. In view of the small magnitude, 0.5 is added for $E_{1/2}$ values. A value of 0.4 is assigned to IR shifts because of their large magnitude. Smaller wt values 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 earlier articles by wt = 1/5n. [b] Steric problems are common in this probe. [c] Phosphines with potential donor substituents, e.g. OR, are excluded. [d] Redetermined parameters using weighted phosphine parameters. [e] $-\Delta H$ for the reaction of CF_3SO_3H with bases in 1,2-dichloroethane solvent. In addition to phosphines, C_5H_5N, 3-BrC_5H_4N, and $(C_2H_5)_3N$ were included. $\bar{x} = 0.04$ and % fit = 0.1. Reference 4. [f] log rate constant for the S_N2 nucleophilic attack of phosphines on C_2H_5I in acetone at 35.0 °C. $\bar{x} = 0.2$ and % fit = 9. Reference 5. [g] Gas phase $-\Delta H$. $\bar{x} = 0.4$ and % fit = 10. Reference 6. [h] −ΔH reaction of $[Al(CH_3)_3]_2$ with donors in hexane solvent. $\bar{x} = 0.7$ and % fit = 5. Reference 7. [i] Gas phase −ΔH; $\bar{x} = 1$ and % fit = 20. Reference 8. [j] Heat evolved/complex concentration when 10 equiv of base are added to 0.001 M $CH_3Pt[P(CH_3)_2C_6H_5]_2(PF_6)$ in THF solvent. $\bar{x} = 1$ and % fit = 6. Reference 9. [k] $-\Delta H$ protonation $CpIr(CO)PX_3$ with CF_3SO_3H in 1,2 dichloroethane: $\bar{x} = 0.1$; % fit = 3. References 4a and 10. [l] ΔH for dissociation of PX_3 from bis(2,4-dimethylpentadienyl) titanium in THF determined by NMR. $\bar{x} = 0.1$ and % fit = 0.6. Reference 11. [m] Enthalpy $-\Delta H$ of 1:1 adduct formation in benzene. For $HgCl_2$ $\bar{x} = 0.1$ and % fit = 1. For $HgBr_2$ $\bar{x} = 0.7$ and % fit = 6. Reference 12. [n] Heat evolved corrected for heat of solution of the base in kcal mol^{-1} when a 1.0 M solution of the donor is added to 0.05M di-M-methylbis[1-methyl-1-n^3-(2-butenyl)]dinickel in tetralin. $\bar{x} = 0.06$ and % fit = 0.5. Reference 13. [o] Activation enthalpy for the second order substitution of CO by phosphines for $Co(NO)(CO)_3$ in toluene. $\bar{x} = 0.03$ and % fit = 0.7. Reference 14. [p] $\Delta H^‡$ for first order dissociative substitution of CO in $Ru(CO)_4PX_3$ by $P(OEt)_3$ in hexane and decalin. $\bar{x} = 0.7$ and % fit = 17. Reference 15. [q] $\Delta H^‡$ for second order dissociative substitution of CO by phosphines in $V(CO)_6$ in hexane. $\bar{x} = 0.3$ and % fit = 9. Reference 16. [r] $\Delta H^‡$ for first order dissociative substitution of CO in $Ru(CO)_3PX_3(SiCl_3)_2$ by $P(OMe)_3$ or $P(tC_4H_9)_3$ in toluene. $\bar{x} = 0.3$ and % fit = 8. Reference 17. [s] ^{13}C chemical shift of $Ni(CO)_3PX_3$ relative to $Ni(CO)_4$ in $CDCl_3$ solvent. $\bar{x} = 0.09$; % fit = 1. Reference 18. [t] ^{13}C chemical shift of the *cis*-carbonyl in $Cr(CO)_5PX_3$ relative to $Cr(CO)_6$ in $CDCl_3$. $\bar{x} = 0.1$ and % fit = 2. Reference 18. [u] ^{13}C chemical shift of the *cis*-carbonyl in $Mo(CO)_5PX_3$ relative to $Mo(CO)_6$ in $CDCl_3$. $\bar{x} = 0.1$ and % fit = 2. Reference 18. [v] ^{13}C chemical shift of the *cis*-carbonyl in $W(CO)_5PX_3$ downfield from $Si(CH_3)_4$ in $CDCl_3$. $\bar{x} = 0.07$ and % Fit = 2. Reference 19. [w] A_1, CO stretching frequency (cm^{-1}) of $Ni(CO)_3PX_3$ in CH_2Cl_2. $\bar{x} = 1$ and % fit = 3. Reference 20. [x] Higher energy CO stretching frequency (cm^{-1}) of η^5-$CH_3CpMn(CO)_2PX_3$ in C_7H_{16}. $\bar{x} = 2$ and % fit = 13. Reference 21.[y] CO stretching frequency of η^5-$CpFe(CO)COCH_3PX_3$ in cyclohexane. $\bar{x} = 0.06$ and % fit = 1. Reference 22. [z] CO stretching frequency of η^5-$CH_3CpFeCOCH_3PX_3$ in cyclohexane. $\bar{x} = 0.07$ and % fit = 2. Reference 22. [aa] ν_1(ax), CO stretching frequency of $Ru(CO)_4L$ in heptane or hexane. $\bar{x} = 1$ and % fit = 5. Reference 15. [bb] Standard oxidation potential in V of $CH_3CpMn(CO)_2L$ vs SCE in CH_2Cl_2 (0.1 MTBAP). $\bar{x} = 0.02$ and % fit = 4. Reference 21a. [cc] Same as *bb* except in CH_3CN. $\bar{x} = 0.04$ and % fit = 7. Reference 21b. [dd] Same as *bb* except in $(CH_3)_2CO$. $\bar{x} = 0.04$ and % fit = 9. Reference 21b. [ee] Reduction potential for $Cr(CO)_5L$. $\bar{x} = 0.01$ and % fit = 17. Reference 24. [ff] Redox potential for

Table 2 (Continued)

$[Ru(H_2O)(bpy)_2PX_3]^{2+/3+}$ in CH_2Cl_2 vs SCE. $\bar{x} = 0.04$ and % fit = 8. Reference 22. [gg] Redox potential for η^5-$CpFe(CO)(COCH_3)PX_3$ in CH_3CN (0.2 M $LiClO_4$) vs SCE. $\bar{x} = 0.01$ and % fit = 3. Reference 22. [hh] Redox potential for η^5- $CH_3CpFe(CO)(COCH_3)PX_3CH_3CN$ (0.2 M $LiClO_4$) vs SCE. $\bar{x} = 0.01$ and % fit = 2. Reference 22. [ii] log equilibrium constant for PX_3 hydrogen bonding to 4-$CF_3C_6H_4OH$ in CS_2 at 25 °C. $\bar{x} = 0.7$ and % fit = 3. Reference 25. [jj] log rate constant for the second order displacement of CO from $Co(NO)(CO)_3$ in toluene. $\bar{x} = 0.6$ and % fit = 14. Reference 14. [kk] log rate constant for the second order displacement of CO from $V(CO)_6$ by PX_3 at 25 °C in hexane. $\bar{x} = 0.1$ and % fit = 3. Reference 16. [ll] log rate constant for the first dissociative substitution of CO from $Ru(CO)_4$ PX_3 by $P(OEt)_3$ in heptane at 60 °C. $\bar{x} = 0.01$ and % fit = 16. Reference 15. [mm] log bimolecular rate constant for $Mo(CO)_2(PR_3)_2Br_2$ generated by flash photolysis with CO in 1,2-dichloroethane. $\bar{x} = 0.2$ and % fit = 9. Reference 26. $(C_2H_5)_3P$ is omitted. [nn] log rate constant for the second order addition of PX_3 to $Cp_2Fe_2(m\text{-}CO)_3$ in hexane at 25 °C. $\bar{x} = 0.3$ and % fit = 16. Reference 27. [oo] log rate constant for the second order displacement of CO by PX_3 in η^5-$(CH_3)_5$ $CpCo(CO)_2$ at 70 °C in toluene. $\bar{x} = 0.5$ and % fit = 18. Reference 28. [pp] log rate constant for the second order substitution of 4-$NO_2C_5H_5N$ in the electrochemically generated cation $MeCpMn(CO)_2$4-$NO_2C_5H_4N^+$ by phosphine and other donor ligands in CH_2Cl_2. $\bar{x} = 0.4$ and % fit = 14. Reference 21a. [qq] log second-order rate constant for exchange of H_2O by CH_3CN in $Ru^{II}(bpy)_2(PX_3)(H_2O)^{2+}$ in *o*-dichlorobenzene. $\bar{x} = 0.2$ and % fit = 6. Reference 29. [rr] log rate constants for the reactions of Co(bis(dioximato)cobaltII-L) and Co′(bis(1,2-cyclohexanedionedioximato)cobalt(II)L) with $C_6H_5CH_2Br$ in benzene at 25 °C. $\bar{x} = 0.1$ and % fit = 6 and $\bar{x} = 0.1$ and % fit = 6.5, respectively. Reference 30. [ss] pK_A values. $\bar{x} = 0.3$ and % fit = 3. Reference 31. $(CH_3)_3P$ and $C_6H_5P(C_2H_5)_2$ were omitted and deviate by 1.0 and 0.8 pK_A units.

weight values of Table 1 are determined from the number and types of acceptors studied with a given phosphine. The smaller the weight, the more uncertain the parameters. Correlations involving phosphines should use these weights in data fits. The column to the far right of Table 2 indicates the number of phosphine donors studied, the number of the other type donors studied, and the number of phosphines omitted from the fit for each physicochemical property. This information also can be utilized to judge the reliability of the parameters resulting from the correlation, vide infra. The values of $\bar{x}$ in the footnotes are average deviations and % fit is 100 times the $\bar{x}$ divided by the range of values in the measurement. In general, percent fits of 2 correspond to R^2 values of 0.99, 8 to an R^2 of 0.95, 10 to an R^2 of 0.8, and 13 to and R^2 of 0.7.

Insights about Phosphine Donor Strength. The objective of the ECW model is not merely to fit data, but also to provide understanding about trends in reactivity.[1] The chemist has available a myriad of bonding concepts that can be utilized qualitatively to rationalize almost any series of measurements. Quantitative analysis of the data puts constraints on what is deemed unusual, thereby making the rationalizations more meaningful. This is particularly important in the area of phosphine reactivity where π-back-bonding and steric effects are often present and more often invoked to rationalize perceived surprises. The many literature attempts[4,5,9,13,18,20,21,23,32−34] to find quantitative models to analyze phosphine reactivity are indications of a general appreciation for the need of a quantitative reactivity scale. All the reported scales utilize one parameter to measure donor strength. This is contrary to the two-term hard−soft, charged-frontier or electrostatic-covalent descriptions of bond strength. The problems that arise with one-parameter donor scales have been discussed.[35]

The dual scale E_B and C_B parameters in Table 1 are presented as a relative measure of the σ bond strength of the donor in terms of its tendency to undergo covalent and electrostatic bonding. The C/E ratios of the alkylphosphines are larger than those of typical donors in the model (ratios vary from 0.2 to 16) and this establishes the phosphines as a unique family of donors.

Because of entropic complications, enthalpies instead of free energies have provided the basis for the ECW model. The model will fail if it does not fit systems that are devoid of steric effects, π-back-bond contributions, and entropy contributions that do not parallel bond strength. As a result, in the extension of the model to the phosphine series, reactions that are expected to provide a good measure of σ basicity are particularly important tests. These include $-\Delta H$ (CF_3SO_3H), log K($CF_3C_6H_4$-OH), and $-\Delta H$ for $B(CH_3)_3$, $[Al(CH_3)_3]_2$, $Ga(C_2H_5)_3$, *m*-FC_6H_4-OH, and $HCCl_3$. As reported earlier[1a] for $B(CH_3)_3$, steric effects are operative for this acceptor and similar problems are found for $[Al(CH_3)_3]_2$ with large donor molecules, vide infra. With these exceptions, excellent fits of these acceptors result and most of them have been studied with donors from families whose C_B/E_B ratios differ from those of phosphines. This result is the basis for the claim that the phosphine E_B and C_B parameters in Table 1 are a valid scale of σ basicity whose values are compatible with the reported[1a] parameters for other donors in the $E-C$ model.

The phosphine pK_A's have been used[21] and questioned[32] as a scale of phosphine σ donor strength. The E_B and C_B parameters fit the phosphine pK_A's, $\bar{x} = 0.3$ and % fit = 3 for 14 phosphines[4a] producing a $C_A{}^*/E_A{}^*$ ratio of 0.2.

***EC* vs Substituent Constant Correlations.** The E_B and C_B parameters from this data fit can be compared to those estimated by summing the substituent constants by substituting these quantities into eqs 5 and 6 and solving for $s_B{}^E$ and $s_B{}^C$. A poor fit results with R^2 values of 0.64 and 0.60 for eqs 5 and 6, respectively. The prediction of E_B and C_B by the summation of substituent constants does not produce as accurate a measure of basicity as solving for E_B and C_B with a data set that contains phosphines and other donors. Problems could arise with substituents saturating the inductive properties, *i.e.* three-electron withdrawing alkoxy substituents do not cause incremental changes for each substituent added. It is also possible that the influence of the substituent is conformation dependent and bulky substituents are locked into certain conformations when reaction occurs making the substituent constant estimate of C_B unreliable.

Why do good fits result[2d] when the ΔE^X and ΔC^X substituents were used to analyze the phosphine systems of Table 2? Good fits result because only phosphine donors are used in substituent constant correlations. The small range of C_B/E_B values enables the fit to compensate for the small but significant deviations in additivity by adjusting the d^E and d^C values of the acceptors. This makes interpretation of the d^E and d^C values difficult, but does not impact on the use of substituent constants to spot irregularities (e.g. entropic and enthalpic steric effects) in the chemistry of a series of phosphine donors.

The similarity in the C_B/E_B ratios is a serious problem for substituent constant correlations in general. Unless phenyl, alkyl, and alkoxy substituents are studied to afford the maximum variation in the C_B/E_B ratios of the family, an apparently good correlation can be meaningless.

The above conclusions regarding the need to vary the C_B/E_B ratio in a data fit also apply to fits to eq 1 or to any basicity scale. As can be seen from the data in Table 1, many of the phosphines have a C_B/E_B ratio of 18 ± 2. When only phosphines with a similar ratio are used to characterize a reaction or spectral change of an acceptor, a very shallow minimum exists in the data set leading to a wide range in the magnitude of $E_A{}^*$ and $C_A{}^*$ values that provide good data fits. Considerable error could result in the $C_A{}^*$ and $E_A{}^*$ values that the least-squares routine selects as the best fit parameters. At best, these parameters can only be used to predict properties for other phosphines with similar C_B/E_B ratios. At worst, if bonding contributions from effects other than σ bond formation are accommodated in determining the minimum, the resulting E_A* and C_A* parameters are meaningless.[36]

Determining the Existence of π-Back-bonding. The surprising aspect of the data fit to eq 1 is the ability of σ donor phosphine parameters to predict physicochemical properties of a series of phosphine donors bonding to acceptors in which π-back-bonding is sure to exist. When both σ donation and π-acceptance of the ligand are important for a physical property, $\Delta\chi$, terms for the latter contribution should be added to eq 1. For simplicity this discussion will be illustrated for the C_AC_B term realizing the same arguments could apply to the E_AE_B term. Consider the case first where increased π-back-bonding and increased σ bonding have the same influence on the magnitude of the measured property, e.g. $-\Delta H$ gets larger as σ- and π-back-bonding increase. For this case, the covalent term of eq 1 is given by:

$$C_AC_B + C_A{}^PC_B{}^M \tag{7}$$

where C_AC_B describes the σ donation of the phosphine to the metal acceptor (A), $C_B{}^M$ describes the metal π-donor properties, and $C_A{}^P$ describes the phosphine π-acceptor tendency. As substituents make the phosphine more basic, C_B increases, but $C_A{}^P$ would decrease because the phosphine empty acceptor orbitals would be higher in energy. One possible relationship that could reproduce this trend is given by:

$$C_A{}^P = C_A{}^{PX} - kC_B \tag{8}$$

where $C_A{}^{PX}$ could be a constant π-back-bond parameter for a hypothetical π-acceptor phosphine with $C_B = 0$. The $C_A{}^{PX}$ value is decreased by the kC_B term so that donors with substituents that lead to a larger C_B have a smaller $C_A{}^P$. A positive proportionally constant k is predicted from energy match of the nickel and phosphorus orbitals, but a negative contribution to k could result from overlap considerations, *i.e.*, a stronger donor leads to a shorter bond and better overlap. The magnitude of k is the net of the energy match and overlap which is expected to be positive. Substituting (8) into (7) leads to:

$$C_AC_B + (C_A{}^{PX} - kC_B{}^P)C_B{}^M \tag{9}$$

Rearranging produces eq 10:

$$C_AC_B + C_A{}^{PX}C_B{}^M - kC_BC_B{}^M \tag{10}$$

The $C_A{}^{PX}C_B{}^M$ term represents a positive π-back-bond contribution that is reduced in magnitude in proportion to kC_B by the last term. The second term of eq 10 is a constant when the phosphine is varied and the metal is not changed. This constant is absorbed into W when a data set in which π-back-bonding exists is fit to eq 1. Combining the C_B dependent terms of eq 10 gives $C_B(C_A - kC_B{}^M)$. Thus, the C_A* from the fit of a data set in which π-back-bonding exists is in fact $C_A - kC_B{}^M$ and includes both σ and π effects. When only phosphines are utilized and the metal can π-back-bond, E_A*, C_A*, and W include contributions from both effects and cannot be interpreted in terms of electrostatic and covalent acceptor properties.

Several of the expected π-back-bonding acceptors in Table 2 provide good data fits to a single C_A* and $E_A{}^*$ supporting eq 8 and its E_A* counterpart. Equation 8 also illustrates the difficulty in separating or even detecting σ and π effects in a study of only phosphine donors. When π-acceptor donors other than phosphines and donors without low energy vacant π-orbitals are included in a data set, a different k for eq 8 is expected ($k = 0$ for σ only donors) and the data set will give a poor fit to eq 1 if π-back-bonding exists. This lack of correlation in systems where donors other than phosphines are used enables one to detect contributions from π-back-bonding.

Next, consider the case where increased phosphine π-back-bonding and increased σ bonding have the opposite influence on the measured property, e.g. log k values, eq 7 becomes

$$C_A{}^MC_B{}^P - C_A{}^PC_B{}^M \tag{11}$$

and eq 9 becomes

$$C_B(C_A{}^M + kC_B{}^M) - C_A{}^XC_B{}^M \tag{12}$$

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The C_A* from the data fit is $C_A + kC_B^M$ and the σ bonding C_B parameters for phosphines again will fit a phosphine only data set.

Interpretation of Reaction Enthalpies. Enthalpies provide the basis for the $E-C$ model and also provide the basis for testing its applicability to phosphine donors. The enthalpy data sets will be discussed in detail.

A substantial variation in the C_B/E_B ratio of the donors was employed in the measurement of the enthalpies of reaction of bases with CF_3SO_3H in 1,2-dichloroethane. In addition to phosphines, pyridine, 3-bromopyridine, and triethylamine are included providing a range of $C_B/\ E_B$ values from 1.5 to 23. All of the donors studied provide an excellent fit with an average deviation of 0.04 kcal mol^{-1}. The reaction has significant contributions from the covalent bond forming tendencies of the donors giving a C_A*/E_A* ratio of 0.8 compared to 0.5 for the enthalpy of hydrogen bonding to phenol. The negative *W* value indicates that an endothermic contribution accompanies all reactions.

The well-defined E_A and C_A values for $CHCl_3$ and *m*-FC_6H_4-OH were held fixed in the data fit. The gas-phase enthalpies of all reported donors toward $B(CH_3)_3$ and $Ga(C_2H_5)_3$ and solution enthalpies for $[Al(CH_3)_3]_2$ were entered to refine the tentative E_A and C_A parameters previously reported.[1a] The values used in the fit of $Al(CH_3)_3$ were corrected for the gas-phase heat of dissociation of the dimer. The positive *W* value would suggest that the gas-phase correction is too large and the dissociation of the dimer in solution is ~5 kcal mol^{-1} less endothermic than in the gas phase. In the case of $[Al(CH_3)_3]_2$, a steric effect was detected in diethyl ether and triethylamine.

The enthalpy of dissociation of a phosphine from bis(2,4-dimethylpentadienyl)titanium in THF solvent is fit very well. Triethylphosphine, the bulkiest phosphine studied ($\theta = 132$), showed evidence of an enthalpic steric effect of ~6 kcal mol^{-1} and was omitted from the fit. Though a limited number of phosphines were studied, a fair range of C_B/E_B ratios was employed. The same E_A*, C_A*, and *W* parameters correspond to a positive ΔH of dissociation or a $-\Delta H$ of formation. In the former interpretation, *W* is exothermic corresponding to THF coordination after dissociation, and when interpreted as a $-\Delta H$, *W* is endothermic corresponding to THF displacement. If one calculates $-\Delta H$ for THF coordination using E_A* and C_A* from the data fit (with $W = 0$) and reported values of E_B and C_B for THF, a value of 5.2 results in agreement with the *W* value. This internal consistency for THF, a donor not expected to π-back-bond, indicates reliable E_A*, C_A*, and *W* parameters and the absence of a significant π-back-bond component in the phosphine interaction.

Enthalpies have been reported for the protonation of CpIr-(CO)PX_3 by CF_3SO_3H in 1,2-dichloroethane. Only five phosphines were studied in this series. An excellent data fit resulted ($\bar{x} = 0.1$, % fit = 3). Enthalpies of protonation of other metal complexes have been reported[4a] but two or more phosphines are changed in each complex. Equation 1 may not apply to these systems because coordination of the first phosphine changes E_A* and C_A* for coordination of the second, etc.

The enthalpies of adduct formation to $CH_3PtPC_6H_5(CH_3)_2^+$ have been used to support the assignment of cone angles to phosphines. While the *E* and *C* fit leads to deviations for bulky phosphines, the *ECW* analysis indicates that this reaction is considerably more complex than thought. If the *W* value corresponded to THF displacement, it should be equal in magnitude and opposite in sign to the value calculated using E_A* and C_A* ($W = 0$) along with E_B and C_B for THF. *W* is very different from the calculated value. Furthermore, the change in sign of E_A and C_A is not expected for an enthalpy. These complications could arise because significant variation in the extent of ion pairing exists as the size, donor strength, and solvating properties of the base vary. Although a good data fit results for small phosphines, it is not possible to interpret the E_A*, C_A*, and *W* acceptor parameters from the data fit.

If one accepts a potential error of 2−3 kcal mol^{-1} in the data fit (experimental error is 1.0 kcal mol^{-1}) from ion-pairing complications, larger deviations can suggest steric effects. The following order of decreasing steric repulsion results from the magnitude of the deviation in the fit: $(t\text{-}C_4H_9)_3P > (i\text{-}C_3H_7)_3P > (\text{cyhex})_3P > (C_6H_5)_3P > (C_6H_5)_2PCH_3 \sim (C_2H_5)_3P$. The reported cone angles are 182, 160, 170, 145, 136, and 132°, respectively. The remaining phosphines in the data set have reported cone angles below 135°, and no information concerning the relative steric requirements of these phosphines can be obtained from this measurement.

Limited data sets are available for the enthalpies of 1:1 adduct formation of $HgCl_2$ and $HgBr_2$ in benzene solution. An excellent data fit results. It was necessary to omit $(c\text{-}C_6H_{11})_3P$ from the data fit for $HgBr_2$ apparently because of steric problems. In view of the similarity in the C_B/E_B ratio (17 ± 3) and the limited number of donors studied, not much confidence can be placed in the values of the E_A and C_A parameters for these two acceptors.

Enthalpies for cleaving $[\eta\text{-}C_5H_7Ni(CH_3)]_2$ to form 1:1 adducts have been determined by adding excess base to a solution in tetralin.[13] Those compounds whose E_B and C_B are known were analyzed with eq 1. There is no evidence of a steric effect even with a phosphine as large as $(i\text{-}C_3H_7)_3P$ ($\theta = 160$). However, the $(C_6H_5)_3P$, $(C_6H_5)_2PC_2H_5$, $(C_6H_5CH_2)_3P$, and $(C_6H_5O)_3P$ adducts all had enthalpies that are too small and had to be omitted to obtain a good fit. Since the reported enthalpies assume complete complexation of the nickel complex, lower than expected enthalpies would be measured if incomplete complexation occurred because *K* was small. This is the proposed cause of the observed deviations.

The *W* value for this system is expected to correspond to the endothermic cleavage of the dimer. Instead, a large exothermic value results. This is indicative of extensive π-back-bond stabilization with eq 9 applying.

Enthalpies of activation are reported for reactions of Co(NO)-$(CO)_3$, $V(CO)_6$, $Ru(CO)_4PX_3$, and $Ru(CO)_3PX_3(SiCl_3)_2$. The first two reactions are S_N2 displacements. Good fits result with the limited number of phosphines studied. There is no indication of any enthalpic steric repulsion in the transition state, but the largest cone angle studied is 145°. The *W* values from the data fits are informative concerning π-back-bonding. The *W* value corresponds to the energy to dissociate a carbonyl without any donor−acceptor stabilization of the transition state, *i.e.* by a donor−acceptor interaction with $E_B = C_B = 0$. For both Co-(NO)$(CO)_3$ and $V(CO)_6$, *W* is larger than the $\Delta H^{\ddagger}$ value of any of the donors studied as expected for stabilization of the transition state by nucleophilic attack. Accordingly, *W* does not contain significant π-contributions (eq 10), suggesting that the metal−phosphine interaction involves mainly σ-donation. The CO dissociation energy (*W*) is slightly larger for cobalt than vanadium, and the donor−acceptor interactions in the transition state, which facilitate the displacement, are comparable for the two metals.

The latter two sets of activation enthalpies correspond to reactions that are first-order dissociative. The poor fit of Ru-$(CO)_3(SiCl_3)_2PX_3$ suggests some factor other than the donor properties of the phosphines is operative. Even though in most of the systems the largest cone angle studied is 148°, the large $SiCl_3$ groups are expected to cause steric problems.

The six reported[15] activation enthalpies for the first-order substitution of CO by PX_3 in $Ru(CO)_4PX_3$ are poorly fit. Omission of any single phosphine does not produce a satisfactory fit. The reported results are obtained when $(n\text{-}C_4H_9)_3P$ and $(t\text{-}C_4H_9)_3P$ are omitted ($\bar{x} = 0.1$) leaving only four phosphines. The data fit very well for all six phosphines when a $c\theta$ term is added [(with $\theta = 140$) for $(C_6H_5)_3P$)]. The resulting parameters are $E_A^* = 30.28$, $C_A^* = 0.29$, $c = -0.16$, and $W = 41.61$. The parameters suggest that the activation enthalpy is lowered by release of strain in the transition state. However, these phosphines are well behaved in the ν_{CO} fit of $Ru(CO)_4L$ without a $c\theta$ term. More donors are needed in the data set to understand this chemistry.

Interpretation of Spectral Shifts. The ^{13}C chemical shifts of $Ni(CO)_3PX_3$ relative to $Ni(CO)_4$ and the CO stretching frequencies of these adducts are fit very well with E_B and C_B ($\bar{x} = 0.09$ and 1, respectively). Decreasing the formal charge on nickel by a more basic σ bonding phosphine increases Ni−CO π-back-bonding which in turn decreases the C−O stretching frequency. On the other hand, π-back-bonding from nickel into the phosphine decreases electron density on nickel and increases the C−O frequency. The zero-valent nickel atom is expected to be involved in π-back-bonding to the phosphines. The excellent data fit supports compensating σ- and π-effects in the complexes, eq 8. As expected, W, the shift for a donor with $E_B = C_B = 0$ is larger than any phosphine adduct frequency. However, expected π-back-bonding makes interpretation of E_A^*, C_A^*, and W difficult and limits their application to phosphines.

The qualitative interpretation of the trends in $\delta^{13}C$ of $Ni(CO)_3$-PX_3 is complicated by changes in the ^{13}C electron population from σ and π effects as well as the influence of those effects on ground and excited state energies.[18] The more basic phosphine gives rise to a larger ^{13}C shift. The excellent data fit again indicates that compensating π and σ changes exist, i.e. eq 8 applies. This compensation permits the use of $\delta^{13}C$ of $Ni(CO)_3PX_3$ as a one-parameter scale of phosphine σ-basicity for physicochemical properties with a C_A^*/E_A^* ratio of ~ 0.1.

The same trends as in $Ni(CO)_3PX_3$ are also noted in the fit of the ^{13}C chemical shifts of $Cr(CO)_5PX_3$,$W(CO)_5PX_3$, and $Mo(CO)_5PX_3$ adducts. The ^{13}C shift has been reported for $Cr(CO)_5py$ and $W(CO)_5$4-CH_3py. In both instances, the pyridine donor had to be omitted from the fit because the ^{13}C calculated from E_A^*, C_A^*, and W is considerably larger (~ 5 ppm) than measured. This deviation provides strong support for π-back-bond contributions to the shifts and, as one would expect, indicates that the same k cannot be used in eq 8 for both phosphines and pyridines.

The CO stretching frequencies for $Ru(CO)_4PX_3$, η^5-Cp, and η^5-Cp′ $Fe(CO)(COCH_3)PX_3$ fit very well and there is no indication of a steric contribution in any of the compounds. Large cone angle phosphines were not studied with the latter two systems, but were with the nickel and ruthenium complexes. None of the spectral shifts show any indication of steric strain in the ground states of the complexes studied.

Interpretation of Redox Potentials. The change in reduction potential for a series of M−L complexes in which L is varied is amenable to an *EC* analysis. When only L is varied, the potential change can be viewed as a measure of the free energy of interaction of L with M in the oxidized and reduced forms of the complex. The value of W indicates what this potential difference would be if a ligand with $E_B = C_B = 0$ were attached. Steric effects would cause deviations in the data fit to *ECW* and π-back-bonding would influence the parameters to the extent that these contributions differ in the two oxidation states of the complex. Steric problems are expected to be larger and π-back-bonding less effective in the higher oxidation state complex.

The potentials for $Ru(bpy)_2(H_2O)(PX_3)^{2+}$, η^5-Cp, and η^5-Cp′$FeCO(COCH_3)PX_3$ have been reported only with phosphine ligands. An excellent data fit results, but compensating π and σ interactions (eq 8) are expected for the ruthenium (II) complex and are uncertain for the iron(II) complex. Potentials for Cp′$Mn(CO)_2L$ complexes have been measured with phosphines, pyridines, nitriles, and THF as ligands. Excellent data fits suggest that π-back-bonding into any of these ligands is not appreciable in this system. There is no indication of a cone angle steric effect influencing $E_{1/2}$ in any of the four complexes. The largest cone angle employed in the iron complexes was 145, but $(c\text{-}C_6H_{11})_3P$ with a cone angle of 170 and $(i\text{-}C_3H_7)_3P$ ($\theta = 160$) were well behaved in the ruthenium complex.

The $E_{1/2}$ values for $Cr(CO)_5L$ are not fit very well even with a small data set that consists of L = $P(CH_3)_3$, $P(C_2H_5)_3$, $P(C_6H_5)_3$, NH_3, CH_3CN, and pyridine. Variations in the relative importance of π-back-bonding and σ bonding (*i.e.* failure of a single k in eq 8 to apply) are causing the poor data fit.

Interpretation of Reaction Rates. In contrast to the good data fits for most of the systems which involve enthalpies of adduct formation, enthalpies of activation, spectral shifts, and $E_{1/2}$, the logs of the rate constants are often poorly fit. Usually certain phosphines must be omitted from the analysis. In the substituent constant analysis of phosphine reactivity,[2d] deviations were also found in the rate data that were not found in $E_{1/2}$, spectral shift, and enthalpy analyses of the same complexes. Two types of steric effects were suggested.[2d] The first is a cone angle, front strain effect that is manifested in both the enthalpy and free energy of interaction. The second was an entropic steric effect, often found in ethyl and longer alkyl chain phosphines, that involved loss of rotational freedom in the chain in the course of forming the transition state. These same patterns are found in the E_B and C_B fit of rate data for most of the systems in Table 2 and the reader is referred to the earlier literature[2d] for a discussion of the specific systems. In future analyses of free energy data, a percent fit of greater than 6 (if experimental error warrants a better fit) would suggest assigning less weight to the longer chain phosphine or adding a $c\theta$ term to determine the influence of entropic and enthalpic steric effects, respectively, on the measurement. If these effects are not operative, the data fit will not be improved by the omission of all long chain phosphines or addition of a $c\theta$ term.

A linear free energy assumption is inherent in any substituent constant analysis or analyses involving eq 1 ($\Delta G \propto \Delta H$). The chances of this occurring are much better for substituents in the meta and para positions of a benzene ring than for those close to a reactive center. Thus, it comes as no surprise that many of the reaction rates in Table 2 fail to fit demonstrated bond strength related parameters. When eq 1 gives a poor data fit, the *ECW* model has not failed, but it has led to the important conclusion that the measurements are not dominated by bond strengths. The objective of *ECW* analyses is to gain chemical insight about reactivity and not to fit every system. Indeed, the most interesting result is a poor correlation followed by experiments designed to show the cause.

Rate constants[30] for the reaction of benzyl bromide with Co-(DMGH)L in benzene at 25 °C comprise one of the few systems studied with both nitrogen (4) and phosphorus (7) donors. This set of rate data is also significant because of the similarity in the geometry of the transition state $[Co-^{\delta-}Br\text{--}CH_2C_6H_5]$ for all adducts. Except for $(CH_3)_3P$, the data give an excellent fit to eq 1 ($\bar{x} = 0.1$ and % fit = 6) with $E_A{}^* = 0.80$, $C_A{}^* = 0.89$, and $W = -5.49$. The good fit encompasses the σ-only donors, *N*-methylimidazole and piperdine as well as pyridine, 4-methylpyridine, phosphites, and alkyl- and arylphosphines. The fit of this wide range of donors indicates domination of the cobalt reactivity by the σ interaction of the ligand L with cobalt. The *C/E* ratio of 1.0 indicates that the covalent bond forming properties of L make the more important contribution to the reaction. This behavior results in spite of the known π-back-bond stabilization in the Co−L bond when L is phosphine. Apparently, the energy of the d_{z^2} orbital involved in the reaction is relatively insensitive to π-back-bonding into the phosphine. Adding $(CH_3)_3P$ to the data set and adding a $c\theta$ term to the fit does not produce as good a fit as that with both $(CH_3)_3P$ and $c\theta$ omitted.

The literature analysis of these data[30] omits $(CH_3O)_3P$ and reports a linear plot of log *k* vs θ, claiming that steric rather than electronic factors dominate the correlated phosphine donor properties. Using the θ values in Table 1, an R^2 of 0.83 was obtained for this correlation even with $(CH_3O)_3P$ omitted. The *ECW* analysis suggests that ligand σ-donor properties determine the chemistry and steric properties make no contribution for the phosphines used in this study.

The benzyl bromide reaction was studied under the same conditions except the cobalt complexes were derived from 1,2-cyclohexanedione dioxime. An excellent data fit results with $E_A{}^* = 0.67$, $C_A{}^* = 0.88$, and $W = -5.32$. In this study, tricyclohexylphosphine was employed and had to be omitted from the data fit. The calculated value of −0.12 compared to an experimental value of −2.6 corresponds to a much slower measured rate. This is expected from a front strain type of steric effect in the ligand bonding to cobalt.

Comparison of *EC* Based and Literature Interpretations of Phosphine Reactivity. The *EC* analyses are not offered to fit data better, but to provide bond strength based data interpretation. The EC conclusions about π-bonding, steric, etc. effects differ considerably from those offered in the literature for most of the systems in Table 2. A few examples were given above and more offered here. The value of conflicting interpretations is to provide motivation for design of further experiments to resolve the ambiguity and gain a more complete understanding of the measurement.

The importance of a wide variation in the C_B/E_B ratio of the bases studied can be illustrated with the data for Co(DMGH)L. If only the six phosphines are used in the analysis with eq 1, a good fit results ($R^2 = 0.98$), but the parameters are quite different ($E_A{}^* = -0.94$, $C_A{}^* = 0.943$, $W = -5.2$). The *W* value for the phosphine only fit is reasonable suggesting little or no contribution from π-back-bonding. However, the $E_A{}^*$ and $C_A{}^*$ values are very different from those of the full data set and when E_B and C_B for the nitrogen donors are used with the $E_A{}^*$ and $C_A{}^*$ values from the phosphine only fit in eq 1, the calculated values for the pyridine donors deviate from the experimental values by ~3 kcal mol^{-1}.

This discussion emphasizes the necessity of studying donors from other families along with phosphines. When this is not the case for the systems in Table 2, the resulting parameters are tentative, their meaning uncertain, and their use for predictive purposes should be limited to phosphines. These limitations are recognized in the above discussion and do not affect the conclusions drawn in this article.

The need for including donors from more than one family in any data fit is a problem for analyses of phosphine reactivity with methods that employ one term for electronic effects and a second steric term:

$$\Delta\chi = a\text{El} + c(\theta - \theta_T) + I \qquad (13)$$

where El is a one parameter measure of the electronic effect (basicity), θ is the cone angle, θ_T the threshold angle at which steric effects become operative, *I* an intercept, and *a* and *c* parameters that weigh the importance of the factors involved. No other scale is reported besides *ECW* which provides an internally consistent set of electronic parameters that permit analyses of data sets that combine nitrogen, phosphorus, and sulfur donors. Analyses using eq 13 are generally carried out one family at a time, and as a result, the reactivity parameters (*a, c, I*) suffer from the uncertainty demonstrated above with Co(DMGH)L.

Equation 13 has provided some excellent fits to experimental data. The question to be addressed is: Are these fortuitous and, thus, without meaning? For systems in which only electronic effects are operative, correlations to ν_{CO}, ^{13}C, and pK_a provide scales of varying C_B/E_B ratios and good fits of $\Delta\chi$ to these quantities are compatible with *ECW* fits. Incompatibility arises when a $(\theta - \theta_T)$ term is significant in eq 13, but steric effects are not evident in *ECW*. For the two approaches to be compatible, E_B would have to measure electronic basicity and C_B would have to include the steric component. Reported cone angles were substituted for $\Delta\chi$ in eq 1, and fit to the E_B and C_B values of the phosphines. A correlation between these quantities would suggest that cone angle related steric effects could be included in a data fit when the phosphine E_B and C_B values are used to analyze reactivity. The correlation is poor as shown by an R^2 value of 0.6. Figure 1 is a plot of C_B versus cone angle. By properly omitting phosphines, several straight lines could be constructed through the points of this plot. Thus, with restricted phosphine data sets, $c\theta$ could be compensating for an electronic parameter without proper covalency in a fit to eq 13 or C_B could be compensating for a $c\theta$ steric effect in an *ECW* fit. Phosphines should be selected for study that are not connected by any of the many lines that can be drawn through Figure 1. For this reason, interpretation of limited data sets is uncertain. This uncertainty is manifested in the ECW conclusion used above: there is no evidence for a steric effect in contrast to there is no steric effect.

The log rate constants for the second order phosphine substitution of L in η^5-$CH_3CpMn(CO)_2L^+$ were correlated[21] to:

$$\log k_1 = 17 - 0.15pK_A{}^L + 0.28pK_A{}^P - 0.12[\theta] \quad (14)$$

The $pK_A{}^L$ accounts for electronic properties of the leaving ligand L and $pK_A{}^P$ accounts for electronic properties of the phosphine. This interpretation suggests that each phosphine has a significant component of the rate (0.12 θ) from steric effects. No attempt

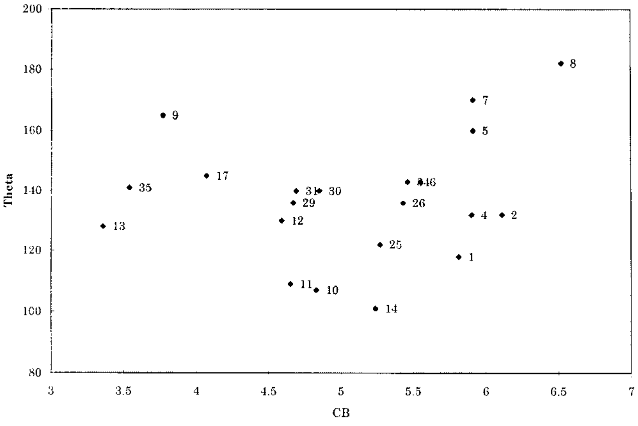

Figure 1. Plot of θ vs. C_B.

was made[21] to correlate $E_{1/2}$ to an equation of the form of eq 14 and it is reported that $E_{1/2}$ does not correlate with log k ($R^2 = 0.22$).

In contrast, the *ECW* analysis fits the combined $E_{1/2}$ data of phosphines and pyridines very well, indicating no steric or π-back-bonding contribution in the ground states of these complexes. The potentials are dominated by the electrostatic bond forming tendencies of the donor with covalency making a smaller contribution. The log k for the bimolecular displacement of L is poorly fit. When certain phosphines are omitted systematically to improve the fit, a pattern revealing a cone angle related steric effect is not found. An entropic steric effect unrelated to cone angle exists in the displacement of L as indicated by omission of $P(C_2H_5)_3$, $C_6H_5P(C_2H_5)_2$, $(C_6H_5)_2PC_2H_5$, and $(C_6H_5)_2PC_4H_9$ to get a reasonable fit. This entropic effect corresponds to loss of rotational degrees of freedom in the alkyl chain in the transition state. Such an effect would not contribute to $E_{1/2}$ and, as a result, these phosphines are well behaved in the $E_{1/2}$ correlation. Supporting an entropic steric effect, triphenylphosphine is fit well with a cone angle of 145 while the largest entropically deviant system has a cone angle of only 140. The deviations caused by this entropic effect are ~1 kcal mol^{-1} for $(C_2H_5)_3P$, $C_6H_5P(C_2H_5)_2$, and $(C_6H_5)_2PC_2H_5$. The systems that fit log k give a C_A^*/E_A^* ratio of -0.06 compared to 0.16 ± 0.02 for $E_{1/2}$. Thus, differences in covalency would lead to a non-linear plot of the two quantities[35] for well-behaved rates. In contrast to the literature analysis, there is no indication of contributions from cone angle related steric effects in the rate data and the $E_{1/2}$ values correlate with the electronic E_B and C_B basicity parameters.

Giering et al.[32] have published extensively on the QALE analysis of phosphine reactivity. They propose an equation of the form

$$\Delta\chi = a(pK_A) + bE_\pi + c(\theta - \theta_T) + I \qquad (15)$$

where pK_a measures the phosphine σ-basicity, E_π is a measure of π acidity and is obtained from $E_{1/2}$ values, θ is the cone angle, θ_T is the threshold value, and I is an intercept. The authors do not use linear regression to fit the entire data set to eq 15 because they propose distinct onsets of π-electronic effects. Thus, the data set is broken up into smaller sets where σ-donor/π-donor (Class I), σ-donor (Class II), and σ-donor/π-acceptor (Class III) effects exist. Plots of the data for various classes produce profiles to indicate which terms in eq 15 are relevant in the data sets.

Though we agree with the idea of a steric threshold, our analyses reject a threshold for π-back-bonding in favor of a continuous change. Equation 15 usually leads to a very different interpretation of phosphine reactivity than *ECW*. The differences are best illustrated with the analyses of ν_{CO} and $E_{1/2}$ data for η-Cp′Fe(CO)(COCH$_3$)PX$_3$ and $-\Delta H$ for $[\eta\text{-}C_5H_7NiCH_3]_2$ adducts. The QALE analysis plots ν_{CO} versus $E_{1/2}$ to divide the ligands into pure σ-donor ligands with no π-acceptor character and a second group of ligands, which include P(OR)$_3$, that are π-acceptor ligands. The two groups require different a, b, and I constants for eq 15. The donors $(c\text{-}C_6H_{11})_2PH$, $(C_6H_5)_2PCH_3$, and $(C_6H_5)_2PC_2H_5$ deviated from the correlation and were omitted.

The $E°$ values[22] and ν_{CO} values[22] of Cp and CH$_3$CpFe(CO)(CH$_3$CO)PX$_3$ for eighteen phosphines are fit extremely well to eq 1. The W values are reasonable for a system in which π-back-bonding is small or non-existent. It would be necessary to have data for donors other than phosphines to determine the magnitude of a π-contribution. If π-back-bonding does exist, there is no threshold for it, but the contribution must decrease regularly with increased σ basicity in order to fit eq 1. This opposite trend in the phosphine σ donation and π-acceptance makes it impossible to separate π-back-bonding when only phosphines are studied.

The C_A^*/E_A^* ratios of $E_{1/2}$ and ν_{CO} differ, so differences in covalency lead to a nonlinear plot of these two quantities.[35] There is no evidence for the existence of a steric effect in any of the 72 measurements analyzed. The *ECW* analysis constitutes a very different, greatly simplified interpretation of this chemistry. If an entire data set is fit by one set of parameters, but this set must be divided into classes to fit an alternate model, the former is the accepted result.

Different interpretations of the enthalpies of adduct formation of $[\eta\text{-}C_5H_7Ni(CH_3)]_2$ with phosphines have been offered.[13,32a] QALE analysis concludes that all but four of the ligands are π-acceptors and fit eq 15 with $c\theta$ omitted. The remaining four phosphines are fit separately generating a new correlation with a different intercept.

The interpretation by Schenkluhn[13] is based on the equation:

$$-\Delta H = 172.0 + 1.65\chi_j + 0.56\theta \qquad (16)$$

where ΔH is in kilojoules, θ is the cone angle, and χ_j is the electronic parameter based on the CO stretching frequency of LNi(CO)$_3$. The phosphines $(C_6H_5)_3P$, $(C_6H_5)_2PC_2H_5$, and $(C_6H_5CH_2)_3P$ were omitted from the fit. There is a steric component of 0.56θ in all adducts with a 60:40 ratio of electronic to steric contribution over the range of phosphines studied. The equation becomes meaningless for a small ligand with no basicity. The *ECW* analysis shows no evidence of a steric effect and the same three phosphines are omitted because of incomplete complexation.

Interpretation of a More Complex Reaction. The solution enthalpies for coordinating phosphine to RMo(CO)$_3$Cp forming RCO Mo(CO)$_2$Cp have been measured[37] in THF solution. The fit of $-\Delta H$ to eq 1 for R = CH$_3$ produced $E_A^* = -16.0$, $C_A^* = 4.19$, and $W = -0.68$, while R = C$_2$H$_5$ gave $E_A^* = -10.4$, $C_A^* = 3.56$, and $W = 4.09$. The W value is expected to give the enthalpy of inserting CO into the R−Mo bond to form CpMo(RCO)(CO)$_2$ and E_A^* and C_A^* the acceptor properties of this acid. A W of ~−15 kcal mol^{-1} is expected from the endothermic contribution expected for CO insertion. The very different values obtained for W indicate that the parameters are compensating for a substantial π-back-bond stabilization (see eq 10).

Summary

The extension of the *ECW* model to phosphines is demonstrated producing E_B and C_B parameters that permit their use with other donors and acceptors in the model. Equations are derived and data evaluated to show that systems in which π-back-bonding exists would be inappropriately fit by eq 1 if donors other than phosphines are not studied. The fit of acceptors that are π-donors to eq 1 results because the tendency of a phosphine to behave as a π-acceptor decreases regularly as its σ-basicity increases. The same proportionality constant does not apply to other families of donors.

The E_B and C_B parameters fit enthalpies of adduct formation, activation enthalpies, and $E_{1/2}$ values very well. Though instances are found in which cone angle, front strain steric effects are operative, the number of cases is much less than suggested by QALE analyses. With a proper selection of phosphines (Figure 1), $c\theta$ could compensate for an improper estimate of covalency in the electronic parameter and be confused as a steric effect. The *ECW* analysis suggests that

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(37) Nolan, S. P.; de la Vega, R. L.; Mukerje, S. L.; Hoff, C. O. *Inorg. Chem.* **1986**, *25*, 1160.

rate data for many of the systems in Table 2 do not obey linear free energy relations and contain entropic steric contributions that are not cone angle related. Some of the most interesting applications of the *ECW* model are those in which exceptions to the correlations are found, for the exceptions suggest additional experiments to detect unusual effects.

The limitations of substituent constant and QALE analyses are convincingly demonstrated. By definition, a substituent constant analysis is limited to a single family and the C_B/E_B ratios of the family do not vary much. QALE analyses generally treat reactions of one family at a time. Whether one is solving eqs 1, 2, 15, or 16, if the donors all have similar C_B/E_B ratios, one cannot obtain meaningful coefficients from a data fit. Unusual effects can be accommodated in a substituent constant or QALE analysis because the C_B/E_B ratios of the donors measured are similar. The most meaningful result from a substituent constant analysis is a poor fit which indicates something unusual is going on. If one accepts the hard−soft, frontier-charge control or electrostatic−covalent models of bond strength, then one must accept that it is essential to study a physicochemical property with more than a single family to understand the property.

Calculations

The measured physicochemical properties for the systems in Table 2 are substituted into eq 1 leading to a series of simultaneous equations. In most instances the equations have five unknowns. When the E_A and C_A values or E_A^* and C_A^* values are known from earlier studies, these are entered into the equation and kept constant in the data fit. When donors from the *E* and *C* correlation are used in the study of a reaction or spectral shift, these E_B and C_B values are also entered into the equation and fixed in the data fit.

The different physicochemical properties are given different weights in the data fit. In general, enthalpies are assigned weight values of 1, ^{13}C a value of 1, $E_{1/2}$ a value of 2 (in view of its small range of values that are accurately known) and $\Delta\nu$ a value of 0.1 (large range of values). The log *k* values are assigned weights of 0.6 for C_2H_5I to 0.2 for rates in which several phosphines are found to deviate. A least-squares minimization[1b] is used to find the best fit set of parameters for the sets of simultaneous equations.

Several of the phosphines were studied with a very limited number of physicochemical properties. The reported parameters for these systems are given low weights in Table 1 and the parameters should be redetermined as more data become available. For those systems with a weight of 0.2, the *E* value was estimated with eq 5 and used as one of the simultaneous equations in the data fit with a weight of 0.4.

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