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In the introduction to his Reflections on the Psalms, C.S. Lewis wrote: “It often happens that two schoolboys can solve difficulties in their work for one another better than the master can. . . . The fellow-pupil can help more than the master because he knows less. The difficulty we want him to explain is one he has recently met. The expert met it so long ago that he has forgotten.” This has been my experience so many times throughout graduate school. Students help students in their work, and then we turn to the expert for final confirmation. We learn by solving our own problems. Many have helped me to do this during my time here.

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# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>ACKNOWLEDGMENTS</th>
<th>page</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ii</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>ABSTRACT</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ix</td>
</tr>
</tbody>
</table>

## CHAPTERS

### 1 INTRODUCTION
- Single Parameter Models                                                      | 1    |
- Dual Parameter Models                                                           | 3    |
- One Parameter Plots in a Two-Parameter World                                   | 14   |
- Multiple Parameter Approaches                                                  | 18   |
- Solvatochromism                                                                | 22   |
- Models Used to Quantify Solvent Effects                                        | 24   |

### 2 REACTIVITY OF PHOSPHORUS DONORS
- Introduction                                                                   | 31   |
- Calculations                                                                   | 37   |
- Results and Discussion                                                         | 46   |
- Conclusions                                                                    | 71   |

### 3 EXTENSION OF THE ELECTROSTATIC-COVALENT MODEL TO 2:1 ADDUCTS
- Introduction                                                                   | 74   |
- Calculations                                                                   | 78   |
- Results and Discussion                                                         | 80   |
- Conclusions                                                                    | 104  |

### 4 DONOR-ACCEPTOR AND POLARITY PARAMETERS FOR HYDROGEN BONDING SOLVENTS       |      |
- Introduction                                                                   | 106  |
- Experimental and Calculations                                                  | 108  |
- Results and Discussion                                                         | 112  |
<table>
<thead>
<tr>
<th>Chapter/Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conclusions</td>
<td>135</td>
</tr>
<tr>
<td>5 MESITYL OXIDE AS A PROBE OF SOLVENT POLARITY AND ACIDITY.</td>
<td>136</td>
</tr>
<tr>
<td>Introduction</td>
<td>136</td>
</tr>
<tr>
<td>Experimental</td>
<td>138</td>
</tr>
<tr>
<td>Calculations</td>
<td>138</td>
</tr>
<tr>
<td>Results and Discussion</td>
<td>144</td>
</tr>
<tr>
<td>Conclusions</td>
<td>150</td>
</tr>
<tr>
<td>REFERENCES</td>
<td>151</td>
</tr>
<tr>
<td>BIOGRAPHICAL SKETCH</td>
<td>163</td>
</tr>
</tbody>
</table>
EXTENSIONS OF THE ELECTROSTATIC-COVALENT AND UNIFIED SOLVATION MODELS TO INCLUDE PHOSPHINE BASICITY AND HYDROGEN BONDING SOLVENT POLARITY AND ACIDITY

By

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The understanding of how molecules interact is a fundamental step toward creating more efficient chemical processes. Many models have been developed that characterize molecules as donors and acceptors. These models usually calculate empirical parameters for donors and acceptors based on their interaction with each other. If a particular model is effective, using these parameters, one can then make predictions about how a given donor and acceptor will interact without actually running the experiment.

One highly successful means of correlating donor-acceptor chemistry is the Electrostatic-Covalent (ECW) model. This particular model assigns parameters to each donor and acceptor based on the degree to which the molecule interacts electrostatically and covalently. This research has brought a very important class of donors, the phosphines, into the ECW model. Because phosphines are widely used as ligands in
organometallic chemistry, prediction of their reactivities is extremely important. This research also examines the role that steric effects play in phosphine reactivity. Different attempts to correlate the chemistry of phosphines are examined in detail.

Reactions are often affected by the solvent in which they are run. Very often the solvent itself is a donor or acceptor, and a competition may occur between the reaction of interest and the solvent. The Electrostatic-Covalent model correlates data only in poorly solvating solvents, and one extension (the Unified Solvation Model, USM) has included the addition of a term to take into account a solvent that interacts. The data used to create many other scales of solvent polarity are all correlated with the USM, thus making only one scale necessary. This research correlates the reactivity of many probe solute molecules in solvents, including those that hydrogen bond. The USM is able to separate specific and non-specific contributions to reactivity, something not possible with other models. The reactivity of one particular solute, mesityl oxide, is studied in detail because it has the potential for use as a probe of solid acid reactivity.
CHAPTER 1

INTRODUCTION

Many methods have been proposed in the literature\textsuperscript{1-9} for the correlation of acid-base and solvation chemistry. Each method has its basis in a set of fundamental assumptions. Some of the more common approaches will be discussed below with attention paid to those assumptions. Criticisms are outlined for each of the models presented, and conclusions are drawn about the effectiveness of each. This dissertation is concerned with extensions of the Electrostatic-Covalent Model (ECW) of donor-acceptor chemistry and the Unified Solvation Model (USM).

**Single Parameter Models**

There have been many attempts in the literature to create scales of acidity or basicity based on a single physical property or measurement with one particular acid or base. For the most part, these have been successful for a specific case. These methods assume that there is an inherent scale of acidity or basicity. (For example, a given base is always stronger than another given base toward all acids.) This is a poor assumption, and a graphical method for showing this will be presented.

A few of the more common one parameter examples will be presented here, and then later in this introduction, reasons will be given for their limited success. These one parameter plots are being done in a two parameter world, and under certain conditions,
good results are found. However, their use is not recommended because many assumptions are made and the presence of two different contributions to σ bonding is ignored.

Gutmann’s scale\textsuperscript{1} of Donor Numbers (DN) is a classic example of a one-parameter plot. It is defined as the enthalpy of reaction of a dilute solutions of base and SbCl\textsubscript{3} in 1,2-dichloroethane. With this scale established, one can plot the enthalpy of interaction of a base with any other acid versus the Donor Number. The results are usually linear. Several assumptions\textsuperscript{2} are made with this method. The major assumption is that the scale of acidity with any acid will be the same as that established with SbCl\textsubscript{3}, that is, that there is one inherent scale of acidity (the one found with SbCl\textsubscript{3}). Despite this faulty assumption, the DN scale has met with great success\textsuperscript{9} in areas such as predicting NMR chemical shifts, variation in O-H bond length through infrared measurements, ligand substitution reaction rates and a wide range of other acid-base enthalpies.

Mayer, Gutmann, and Gerger\textsuperscript{2} have also introduced a scale of acidity called Acceptor Numbers (AN). This scale is based on the \textsuperscript{31}P chemical shift of (C\textsubscript{2}H\textsubscript{5})\textsubscript{3}PO (TEPO) when it forms an adduct with a given acid. (C\textsubscript{2}H\textsubscript{5})\textsubscript{3}PO has also been used as a probe of specific and non-specific interactions with various solvents. TEPO is a good reference base for many reasons. The ethyl groups are large enough to shield any alternate coordination sites, but too small to sterically hinder coordination of acidic solvents.\textsuperscript{9} As with donor numbers, the assumption is made that the scale created with this reference base will be the same regardless of the base studied. This scale will be discussed in Chapter 4.
Many other one-parameter scales are seen in the literature. One of the most
common is to plot an enthalpy or spectral shift versus the pKₐ of a series of acids or bases.
One other scale that has been proposed,³ similar to the Donor Numbers, is the enthalpy for
coordination of a base to BF₃ in methylene chloride solution. Although these one-
parameter plots are widely used (and frequently work well), they are limited by the
assumption that inherent scales of acidity and basicity exist. Several two-parameter scales
have been developed to take into account the different aspects of σ bonding.

Dual Parameter Models

The Edwards Equation

Edwards began his study of two parameter models with the correlation of
equilibrium constant and rate data for nucleophilic displacement reactions.⁴ He correlated
the data to Equations (1-1) and (1-2), where Eₙ is a nucleophilic constant characteristic of

\[
\log \left( \frac{K_n}{K_{ref}} \right) \text{ or } \log \left( \frac{k_n}{k_{ref}} \right) = \alpha E_n + \beta H_n
\]

\[
\log \left( \frac{K_n}{K_{ref}} \right) \text{ or } \log \left( \frac{k_n}{k_{ref}} \right) = \alpha P_n + \beta H_n
\]

an electron donor, Hₙ is the basicity of the donor relative to the proton, Pₙ is the
polarizability of the donor [calculated as log (Rₜₙ/Rₜₜₜ), where R is the refractive index],
and \( \alpha \) and \( \beta \) are substrate constants. The reference used is water (which is assigned \( E_n = 0 \)
and \( H_n = 0 \) values). The \( H_n \) values are defined as 1.74 + pKₐ of base \( B_n \), and the \( E_n \) is
defined as 2.6 + E°ₜₜₜ for base \( B_n \). Edwards and Pearson⁵ concluded that nucleophiles and
substrates tended to sort into two categories: those whose displacement reactions
correlated well with the pKₐ of the nucleophile and those correlating well with \( E_n \) or \( P_n \) of
the nucleophile.⁵
About this same time, Ahrland, Chatt, and Davies\textsuperscript{6} recognized that metal ions could be divided into classes depending upon whether they formed their most stable complexes with the first ligand atom of each group (class a) or whether they formed their most stable complexes with the second or subsequent member of each group (class b). Class (a) metal ions include alkali metal, alkaline earth metals, and lighter transition metals in high oxidation states. Class (b) metal ions are mostly heavier transition metals in low oxidation states.\textsuperscript{7}

**Hard/Soft Acid/Base Theory (HSAB)**

Pearson\textsuperscript{8} recognized consistency in this classification system and began to classify potential acceptors as “hard” [class (a)] and “soft” [class (b)]. He expanded these designations to include a wide variety of Lewis acids. He proposed that donors also have this quality of “softness” to varying degrees. Hardness and softness are related to the polarizability of the acid or base. Thus, those acids or bases with small size, high positive charge, and no easily distorted or removed electrons are called “hard.” Those acids or bases with large size, small positive charge, and easily distorted electron clouds are termed “soft.”\textsuperscript{9} The general rule is that hard acids tend to prefer hard bases, and soft acids prefer soft bases. This is observed from experimental evidence. Pearson refers to the hard-soft principle as “... a simple, but imprecise, law with a wide range of applicability.”\textsuperscript{8c} Many physical properties and reactivity patterns have been explained using hard/soft principles. These include geometry trends, organic nucleophilic-electrophilic reactivity, selection of organic catalysts, and solubility rules for inorganic salts. References to these and many other chemical phenomena using hard/soft explanations are given in reference 5.
As one example, the solubility of salts is predicted fairly well with hard/soft principles. Generally speaking, insoluble salts will be those that are combinations of ions that are hard-hard or soft-soft. For example, AgI, a soft cation (acid) combined with a soft anion (base), is very insoluble ($K_{sp} = 9 \times 10^{-17}$). The principle is not absolute, however. The chloride ion is classified as a hard base, thus making the prediction that AgCl would be soluble. It is, in fact, insoluble. Also it is observed experimentally that AgCl is soluble in an ammonia solution forming Ag(NH$_3$)$_2^+$. Thus, the soft silver ion gives up a borderline to hard base (Cl$^-$) in favor of a hard base (NH$_3$). Another example is Ag$_2$SO$_4$, the combination of a soft cation with a hard anion. This should be a soluble salt, but it observed to be only slightly soluble ($K_{sp} = 1 \times 10^{-5}$).

Exceptions to the hard/soft rules are observed when one does not consider the relative strength of the acids and bases. Pearson began his studies looking at one-parameter scales of acidity and basicity, but he knew “that reactivity of a Lewis acid or base depend[s] on something more than a single monotonic scale of relative strengths” (p. 17).$^5$ Here he began a more systematic study of the phenomena of “softness.” Following a suggestion by D.H. Busch, Pearson called it the “hard/soft parameter,” with soft corresponding to a large value of the parameter and hard to a small value.$^5$ This nomenclature is imprecise, simply because these words are normally used as opposites, but in this case, they refer to the same property, but to different degrees.

Pearson introduced Equation (1-3) to show the contributions of strength ($S_A$ and $S_B$) and softness ($\sigma_A\sigma_B$) to the overall equilibrium constant.

$$\log K = S_A S_B + \sigma_A \sigma_B$$

(1-3)
This equation is not meant to be used quantitatively, but it is given merely to show the different contributions. The hard-hard and soft-soft rules work well when hard species are also strong and when soft species are weak.\(^5\) Equation (1-3) is very similar to the equations proposed by Edwards. Yingst and McDaniel\(^{10}\) observed that acids classified as “hard” in general have low \( \alpha \) values, meaning they are sensitive to nucleophilic ligand character or polarizability, and high \( \beta \) values. Acids classified as “soft” tend to have the opposite (larger \( \alpha \), smaller \( \beta \)) values. They propose the use of the absolute value of \((\alpha/\beta)\) to assign “hard” or “soft” designations. Pearson\(^8c\) equates the \( \beta H_a \) term with his \( S_A S_B \) term and \( \alpha E_a \) term with his \( \sigma_A \sigma_B \) term, but admits that Edwards’ equation is not the only one that might be related to Equation (1-3).

Molecular orbital theory can be applied to hard and soft acids and bases. Soft species are characterized by a high density of low-lying empty orbitals and/or by a high-lying HOMO. Hard species are characterized by isolated ground states and/or by a low-lying HOMO.\(^5\) The base HOMO and acid LUMO are closer in energy in a soft-soft interaction, and the stability gained from the HOMO-LUMO interaction brings the bonding molecular orbital to a lower energy than the acid HOMO. This is characteristic of a covalent (electron-sharing) interaction. In the hard-hard interaction, the acid LUMO and base HOMO are more spread apart in energy, and the stabilization gained brings the bonding molecular orbital to a higher energy than the acid HOMO. This is a more electrostatic interaction, and the acid and base must react by means of any net charges or permanent dipoles they happen to possess.\(^5\)
Criticisms of HSAB

Many criticisms of hard-soft acid-base theory have been published. Myers\textsuperscript{11} questions Pearson's use of polarizability in defining hardness and softness. In general, Pearson describes something as "soft" if it is polarizable and "hard" if it is not. He has been careful to point out that that polarizability is not the only factor which influences softness. Myers gives many examples of metal ions that are supposed to be hard that actually have larger polarizabilities than ions that are soft. He believes the terms "hard" and "soft" are inadequate and that the relationship between class (a) and class (b) metal ions needs to be re-examined to find an effect other than polarizability which distinguishes them.

Perhaps the most vocal criticisms of HSAB have come from Drago.\textsuperscript{12} His primary criticism is that HSAB defines hardness and softness as opposite properties, meaning that something that is hard cannot be soft. This is illustrated by the binding of (CH\textsubscript{3})\textsubscript{3}N, (CH\textsubscript{3})\textsubscript{2}O, and (CH\textsubscript{3})\textsubscript{2}S to phenol (hard acid) and I\textsubscript{2} (soft acid).\textsuperscript{12a} Toward phenol, the enthalpies would be expected to follow this trend: (CH\textsubscript{3})\textsubscript{2}O > (CH\textsubscript{3})\textsubscript{3}N > (CH\textsubscript{3})\textsubscript{2}S (hardest base binding with the highest enthalpy). Toward I\textsubscript{2} the opposite trend is expected (softest base binding with the highest enthalpy). However, in measuring these enthalpies, only four of the six are correctly ordered. Toward I\textsubscript{2} the nitrogen donor is "softer" than the sulfur donor, and toward phenol, the nitrogen donor is "harder" than the oxygen donor. Clearly, something cannot be both soft and hard at the same time.\textsuperscript{12a}

Purcell and Kotz\textsuperscript{13} have analyzed around 37,000 donor-acceptor pairs, trying to predict which ones would form stable adducts. They based their prediction on the similarity in hardness or softness (using Drago's C/E ratio, \textit{vide infra}) of the donors and
acceptors. They found that they made the correct prediction only 40% of the time. It is surprising that HSAB seems to work so well given these findings.

The Electrostatic-Covalent Model (E and C)

In 1965, Drago and Wayland\(^ {14}\) proposed a four-parameter equation [Equation (1-4)] for predicting enthalpies of adduct formation in the gas phase or in poorly solvating solvents (e.g., CCl\(_4\) or cyclohexane). In the equation, \(E_A\) and \(E_B\) are defined as the susceptibility of the acid and base, respectively, to undergo electrostatic bonding. \(C_A\) and \(C_B\) are the susceptibility of the acid and base, respectively, to undergo covalent bonding.

Mulliken's work\(^ {15}\) on the covalent-electrostatic nature of the adduct bond is the theoretical basis for the Electrostatic-Covalent model. In brief, Equation (1-5) gives the

\[
\psi_G(A,B) = a\psi_0(AB) + b\psi_1(A^+B^-) \tag{1-5}
\]

Mulliken charge-transfer or valence bond model for a donor-acceptor interaction, where the total ground-state wave function for the complex \(AB\) is given by \(\psi_G\). The wave function \(\psi_0\) describes the interactions in the complex in which classical intermolecular forces such as ion-dipole, dipole-dipole, and London dispersion forces are involved. The function \(\psi_1\) arises from the overlap of the filled base orbital with the empty acceptor orbital.\(^ {15}\) The coefficients \(a\) and \(b\) indicate the relative importance of electrostatic and covalent bonding.

Drago and Wayland's initial method\(^ {14}\) of determining electrostatic and covalent parameters for acids and bases differs greatly from the method currently employed (\textit{vide infra}). They arbitrarily assigned \(E_A=1.00\) and \(C_A=1.00\) to the acid I\(_2\). The parameters for
four amines [NH$_3$, CH$_3$NH$_2$, (CH$_3$)$_2$NH, and (CH$_3$)$_3$N] were the first to be determined. They postulated that the $E_B$ for each base should be proportional to the molecule’s dipole moment ($\mu$), and the $C_B$ for each base is proportional to the total distortion polarization of the molecule ($R_B$). Using four simultaneous equations in the form of Equation (1-6), they estimated the relative contributions of electrostatic and covalent bonding [coefficients $a$ and $b$ from Equation (1-5)] to the enthalpy of adduct formation. Because $E_A$ and $C_A$ were assigned to be 1.00 for I$_2$, the sum of the $E_B$ and $C_B$ parameters ($E_B = a\mu$ and $C_B = bR_B$) will be the adduct formation [see Equation (1-4)].

After these amine donor parameters were determined, more typical methods of determining acid parameters were then used. Several simultaneous equations in the form of Equation (1-4) could be written, and keeping the $E_B$ and $C_B$ parameters constant, one can calculate $E_A$ and $C_A$ for any acid for which enthalpies of adduct formation are known. Currently, master-fit programs are used, with which one can enter enthalpies for hundreds of adduct formations. The program will then determine the best acceptor and donor parameters that will fit the enthalpies. Further information on this program will be included in Chapter 2, where it is used to study phosphine reactivity.

The $E$ and $C$ equation underwent a minor change with the work of Guidry and Drago.\textsuperscript{16a} They used previously measured enthalpies of adduct formation between 1,1,1,3,3,3-hexafluoro-2-propanol, HFIP, and a series of Lewis bases. When trying to correlate the enthalpies to Equation (1-4) (fixing known $E_B$ and $C_B$ parameters for the donors), a poor fit resulted. They attributed the source of the problem to intramolecular
hydrogen bonding between the hydroxyl proton and fluorines on the -CF₃ groups. It was
determined (vide infra) that upon adduct formation, this intramolecular hydrogen bond
was broken, at the cost of approximately 1.1 kcal mol⁻¹. This constant contribution to the
measured enthalpy does not depend upon the base added and must be expended before
adduct formation can take place. The measured enthalpies were then 1.1 kcal mol⁻¹ less
exothermic because this amount was needed to break the hydrogen bond.

Guidry and Drago proposed an extension to the E and C equation similar to
Equation (1-7), where W is any constant contribution to an enthalpy that is not associated
\[ -\Delta H = E_A E_B + C_A C_B + W \]  
with the specific donor-acceptor interaction. As in this case, some change needed to be
made to the acceptor before it could react with the donor. Other examples of this type of
constant contribution would include breaking a dimer, in order for the monomers to react
as acceptors. An endothermic W is entered as a negative number into Equation (1-7),
to decrease the magnitude of the calculated -\(\Delta H\).

Using Equation (1-7), the enthalpies of adduct formation, and the known \(E_B\) and
\(C_B\) parameters for the donors, Guidry and Drago solved a series of simultaneous equations
for the best \(E_A\), \(C_A\), and \(W\) to fit the data. The \(W\) value was 1.1 kcal mol⁻¹, the energy
needed to break the hydrogen bond. Thus, Equation (1-7) provides an indirect method for
calculating the energy needed to break the hydrogen bond or, in other cases, a dimer.

In the case of a dimer, the \(W\) value is actually one-half the enthalpy of dimerization
because all -\(\Delta H\) values are for formation of a mole of adduct (which uses one monomer,
not two). These enthalpies cannot be obtained by other methods, so this calculation becomes very valuable.

An alternate form of Equation (1-7) may also be used to correlate any physicochemical property such as spectral shifts (e.g., UV/Vis, NMR, or IR), reaction rates, and equilibrium constants. This form is given in Equation (1-8), where $\Delta \chi$ is the

$$\Delta \chi = E_A^*E_B + C_A^*C_B + W$$

value of the physicochemical property (with units of energy), and $W$ is the value of $\Delta \chi$ when $E_B=0$. The asterisks on the acceptor parameters indicate that changes in $\Delta \chi$ are being measured with a constant acceptor and a series of donors. The asterisks also indicate that these parameters are not based on enthalpies and have different units incorporating conversion units to give $\Delta \chi$ in the units of the measured property. When correlating reaction rates or equilibrium constants, one must take the log of the value in order to meet the energy unit requirement.

The most current set of donor and acceptor parameters\(^\text{17}\) was created by fixing the iodine $E_A$ and $C_A$ parameters at 0.50 and 2.00, respectively. Also fixed were the $E_B$ parameter for N,N-dimethylacetamide (DMA) at 2.35 and the $C_B$ parameter for (C\(_2\)H\(_5\))\(_2\)S at 3.92. Over 500 enthalpies of adduct formation for reactions of about 50 bases and 43 acids were solved simultaneously to give a unique solution. Fixing the parameters described above at different values would bring about another unique solution.

Many insights can be gained through an ECW analysis of a data set. The model is designed to predict the normal $\sigma$ bonding energy for adducts. When a particular system does not fit the model, it is because factors other than $\sigma$ bonding are operative. These
deviations should be used to design new experiments to help elucidate all factors that contribute to an enthalpy or spectral shift.

Several specific effects can be observed through ECW analysis. The most common effect that is observed is an enthalpic steric effect. This effect can be assigned when the enthalpy predicted by the model is more exothermic than the experimentally measured enthalpy. The steric bulkiness in the donor-acceptor interaction does not allow optimal orbital overlap. The difference between the experimentally measured and predicted enthalpies is the strain energy, a value that cannot be directly measured.

The existence of π-back-bond stabilization can also be observed with the ECW analysis. This effect is assigned when the predicted enthalpy is smaller than the experimental enthalpy. Because ECW only models σ interactions, the predicted enthalpy will be smaller. Experimentally both σ and π bonds are being formed. Chapters 2 and 3 will present a model showing how these π effects can be incorporated into the σ-only acceptor parameters, with good results. Unfortunately, when this occurs, the parameters are difficult to interpret because the contributions from the two types of bonding cannot be separated.

**Criticisms of the ECW Approach**

The early criticisms of the ECW approach have been treated with extensions to the original form of the model. The more noteworthy extensions resulted because experimenters wanted to treat systems with strongly solvating solvents. Equations (1-4) and (1-7) were developed using data in poorly solvating solvents, such as cyclohexane. A later section of this introduction will deal with an extension to Equation (1-7) to include...
wide range of solvent polarity. This extension is termed the Unified Solvation Model (USM).

Other areas that were criticized for not correlating to the ECW approach include systems having large amounts of charge transfer or those having ions as reactants instead of only discrete, neutral species. Another extension of the ECW Model, Equation (1-9),

\[- \Delta H = E_A E_B + C_A C_B + R_A T_B \]  

(1-9)

has been proposed for just these types of reactivity. In Equation (1-9), \( R_A \) is used to indicate that the acid is the acceptor in the electron transfer interaction, and \( T_B \) indicated that the base is the transmitter. These parameters are available for use, and another correlation of homolytic bond energies (using terminology such as “catimers” and “animers”) should also be examined for further insight into the use of Equation (1-9).

One general criticism that is discussed relates to the arbitrary nature of fixing four parameters initially. While this is needed in order to find a unique solution of the parameters for all acids and bases involved, deciding which parameters to fix initially is arbitrary, and changing these will give a different set of parameters. Jensen writes, “... its use of purely empirical numbers disguises any relationship between Lewis acid-base reactivity and chemical periodicity” (p.20). While this is a drawback, ECW appears to be able to correlate a wide range of donor-acceptor interactions. As described above, its extensions help to fill in areas that the original equation was unable to correlate, thus increasing its usefulness.
One-Parameter Plots in a Two-Parameter World

As discussed above, one of the major assumptions that is made with one-parameter plots is that there is an inherent scale of acidity or basicity. This means, for instance, that one particular acid is always a better acid than another regardless of the base. Drago’s E and C approach shows that it is possible for a given acid to interact better electrostatically, but not covalently, than another acid. This allows for a varying scale of acidity or basicity. Cramer and Bopp have shown how the scales can change depending upon which acid and base are interacting. (The reader should note that Cramer and Bopp’s article was written before the most current set of E and C parameters were calculated. Present use of their model requires the use of the new parameters). They present a graphical representation using Equation (1-10).

\[
\frac{-\Delta H}{(C_A + E_A)} = \frac{C_A + E_A}{2} + \frac{(C_B + E_B)}{2} \frac{(C_A - E_A)}{(C_A + E_A)}
\]  

(1-10)

Figure 1-1 is an example of the type of graph that can be created. The x-axis is the quantity \((C_A - E_A) / (C_A + E_A)\), thus showing acids moving from less covalent in nature to more covalent (as one goes from negative x to positive x). The y-axis represents \(-\Delta H / (C_A - E_A)\). Therefore, if one knows the \(E_A\) and \(C_A\) parameters for a particular acid, the enthalpy of interaction can be calculated from the value on the y-axis.

It should be noted that the slopes of the line presented in Figure 1-1 are based on the enthalpies of interaction of the donors with two acceptors, phenol and iodine. Other slopes varying slightly could be obtained using the enthalpies of interaction with other acids. This graph indeed shows the danger of assuming that one donor is always stronger...
than another. When one asks which of two donors is stronger, the next question should be when interacting with which acceptor? The degree of covalency is extremely important when predicting enthalpies of interaction, and this is largely ignored in the literature when one-parameter plots are made.

![Diagram showing the relationship between electrostatic and covalent interactions](image-url)

Figure 1-1. Five donors interacting with acids of varying C_A/E_A ratios

Drago\textsuperscript{12a,19a} has outlined the reasons that one-parameter plots often appear to give good correlations. A modified version of ECW is given [Equation (1-11)] by

\[ \frac{-\Delta H}{E_A} = \frac{C_A}{E_A} \frac{C_B}{E_B} + E_B \]  

(1-11)
dividing both sides by $E_A$. If the entire right side of Equation (1-11) is called $B_i$, where $i$ represents the $C_A/E_A$ ratio of the acceptor, Equations (1-12) and (1-13) result.

$$-\Delta H = E_A B_i$$  \hspace{1cm} (1-12)

$$B_i = E_B + iC_B$$  \hspace{1cm} (1-13)

If, for example, one uses $i = 0.2$ (i.e., some acceptor property has a $C_A/E_A$ value of 0.2), an order of donor strength can be calculated using Equation (1-13) and the $E_B$ and $C_B$ values of the donors involved. Table 1-1 shows Drago's calculated\textsuperscript{12a} $B_{0.6}$ and $B_{0.2}$ values for several donors along with their $E_B$ and $C_B$ values. The examples of $C_A/E_A$ ratios of 0.6 and 0.2 are given here because they represent very common ratios for physicochemical properties. This table is another way of viewing Figure 1-1. Notice the difference in donor strength order that is found depending upon the $C_A/E_A$ ratio of the acceptor studied.

Successful one parameter correlations can be made when one plots their physicochemical property (e.g., a measured enthalpy or chemical shift) versus $B_{0.6}$, $B_{0.2}$, or any similarly prepared scale if the new property has the same $C_A/E_A$ ratio as that used to make the scale. The most common example of this is seen when plots of experimental data are made versus $pK_A$ or $pK_B$. Drago reports\textsuperscript{12a} that the $C_A/E_A$ ratio for $pK_B$ values is 0.2. Therefore, any physicochemical property that also has a $C_A/E_A$ ratio of 0.2 will plot linearly with $pK_B$. As stated earlier, 0.2 and 0.6 are very common $C_A/E_A$ ratios, and linear plots will often result.

It would also be possible to find a nearly linear plot to $pK_B$ with experimental data that have a $C_A/E_A$ ratio of 0.6. Many of the points will fall on the best fit line, and a few may deviate. Explanations are given for the misses that are encountered with these points.
Table 1-1. $E_B$, $C_B$, $B_{0.6}$, and $B_{0.2}$ values for several donors

<table>
<thead>
<tr>
<th>Donor</th>
<th>$E_B$</th>
<th>$C_B$</th>
<th>$B_{0.6}$</th>
<th>$B_{0.2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C_5H_5N</td>
<td>1.78</td>
<td>3.54</td>
<td>3.90</td>
<td>2.49</td>
</tr>
<tr>
<td>CH_3C(O)N(CH_3)_2</td>
<td>2.35</td>
<td>1.31</td>
<td>3.14</td>
<td>2.61</td>
</tr>
<tr>
<td>(CH_2)_4O</td>
<td>1.64</td>
<td>2.18</td>
<td>2.95</td>
<td>2.08</td>
</tr>
<tr>
<td>(C_2H_5)_2O</td>
<td>1.80</td>
<td>1.63</td>
<td>2.89</td>
<td>2.22</td>
</tr>
<tr>
<td>(C_2H_5)_2S</td>
<td>0.24</td>
<td>3.92</td>
<td>2.59</td>
<td>1.02</td>
</tr>
<tr>
<td>CH_3C(O)OCH_3</td>
<td>1.63</td>
<td>0.95</td>
<td>2.50</td>
<td>1.99</td>
</tr>
<tr>
<td>CH_3CN</td>
<td>1.64</td>
<td>0.71</td>
<td>2.07</td>
<td>1.78</td>
</tr>
</tbody>
</table>
Drago believes that these explanations are often incorrect and do not credit the amount of covalency involved in the interaction. He also warns about the dangers of not using a series of very different donors (with differing $C_B/E_B$ ratios) in an analysis. Without a wide range of donors, potentially outlying points may be not be observed, and a good correlation could be determined incorrectly. Unfortunately, a majority of experimental data found in the literature use donors (or acceptors) from within a single family (e.g., all pyridines or all phenols). Drago has written\(^\text{21}\) about the limitations of such analyses.

**Multiple Parameter Approaches**

Giering and coworkers\(^\text{22}\) have developed a multiple parameter equation for the correlation of physicochemical properties. It takes the general form of Equation (1-14),

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

(1-14)

where \(\chi\) is an electronic parameter that describes the intrinsic electron donor capacity of a ligand (\textit{vide infra}); \(\theta\) is a steric parameter, the Tolman\(^\text{23}\) cone angle (\textit{vide infra}); \((\theta - \theta_{st})\lambda\) is the “steric threshold” term, with \(\theta_{st}\) the cone angle above which abrupt changes in steric effects occur; \(\lambda\) is a switching factor, either 0 or 1 depending on whether or not the particular ligand has a cone angle larger than \(\theta_{st}\) for that system; and \(E_{ar}\) is the “aryl effect” parameter (\textit{vide infra}). This equation (known as the Quantitative Analysis of Ligand Effects or QALE) has been used successfully to correlate thermodynamic, kinetic, spectroscopic, and structural data of carbon, nitrogen, phosphorus, arsenic, and silicon complexes.\(^\text{22}\)

Early QALE studies\(^\text{24}\) included ligands with aryl, alkyl, and alkoxy substituents and focused on the development of three classes of phosphorus donors, depending upon their
ability to act as a σ-donor and π-donor (class I), only a σ-donor (class II), or as a σ-donor and π-acceptor (class III). These classes have not been emphasized in the more recent literature. Giering’s attempts to calculate the relative contributions of σ and π bonding have been examined and found to be unsatisfactory.

Ligands with P-O (e.g., phosphites) and P-F bonds were studied in the early literature together with alkyl and aryl-substituted ligands. These were believed to belong to class I, ligands having both σ- and π-donor abilities. Phosphites often missed in the correlations, and these deviations have been attributed to the π-donating ability of the ligands. Poor correlations resulted because of the χ parameter, which is defined as the difference between the A₁ terminal carbonyl band of LNi(CO)₃ and 2056.1 cm⁻¹ [the A₁ band for (t-Bu)₃PNi(CO)₃]. It was found that χ must be modified for those donors that could also have a π-donor contribution to bonding. A new parameter, χ₄, based upon pKₐ and Tolman’s cone angle, is proposed that will allow better correlations. Despite this new parameter, phosphites are still not studied with other ligands in the QALE analyses.

**The Aryl Effect**

Upon examination of several systems using only their χ and θ terms, Wilson and coworkers found unsatisfactory results. They found that the inclusion of an additional electronic parameter, E₄, improved the correlations. The E₄ parameter values are dependent only on the number of aryl groups present on a ligand and not on the substitution of those aryl groups. The E₄ parameter takes values of 0, 1, 2, and 2.7 for ligands with no, one, two, and three aryl groups, respectively. These values were
determined using plots of Taft’s polar substituent constant, \( \Sigma \sigma^* \), versus \( \chi \) and \( \theta \).\textsuperscript{27} It was observed that the phosphorus donors were separated into three parallel linear regions, corresponding to no, one, or two aryl groups on the ligand. The spacings between the linear regions were about the same, so these \( E_{ar} \) values were assigned one unit apart. For the triarylphosphines (all with \( \theta = 145 \)), no parallel line could be found on the plot of \( \Sigma \sigma^* \) versus \( \theta \). The \( E_{ar} \) value was assigned to be 2.7 as this optimized the \( r^2 \) values of the systems being studied.

The \( E_{ar} \) parameter indeed improves correlation coefficients. The reason behind this improvement remains a mystery to those that use \( E_{ar} \).\textsuperscript{27,28} It has been suggested that “... the aryl effect is a consequence of incipient \( \pi \)-stacking interactions ... contributing to the stabilisation of the transition state. These interactions would be dependent on the number of aryl groups and independent of the nature and position of the substituents on the ring” (p. 232).\textsuperscript{28b} Further thoughts (from the perspective of ECW) on the nature of the aryl effect will be given in Chapter 2.

**Steric Effects**

There has been some concern in the literature about the use of the Tolman cone angle in correlations such as these. Brown and Lee\textsuperscript{29} list several assumptions (also discussed by Tolman\textsuperscript{23}) that must be made if one is to use this parameter. One assumption is the choice of the actual cone angle because the ligand’s substituents can have varying conformations. Tolman always chose the conformation that would give the smallest cone angle. Depending upon the particular complex (i.e., considering other ligands on the metal center) that is formed, this may or may not be the “actual” cone angle of that ligand.
Drago\textsuperscript{30} has discussed the need for rearrangement of an alkyl substituent chain in the formation of the transition state. Conformational degrees of freedom may be lost during this rearrangement, and he terms this an “entropic steric effect.” H.C. Brown and coworkers\textsuperscript{31} have also reported this effect.

Another possible difficulty with the use of cone angles is that “... substituent ligands bound to the same metal center can sometimes mesh with one another, permitting closer packing of ligands than would be expected based on cone angle values” (p. 92).\textsuperscript{29} Brown and Lee write: “It is too much to expect that a single set of ligand parameters will reflect accurately the relative steric requirements of ligands in markedly different situations ... Each ligand has not one, but a range of steric requirement values, depending on the reaction or structural context” (p.104).\textsuperscript{29} They also caution the use of parameters without knowing their precision. White and Coville\textsuperscript{32} report that cone angles are good to within 2°. Brown and Lee\textsuperscript{29} give many examples of the ranges of cone angles that have been reported for phosphorus donors in various complexes.

Prior to the studies of Giering and coworkers, Tolman\textsuperscript{23} proposed the “steric/electronic box,” noting that both steric and electronic effects contribute to reactivity. Giering’s model is similar in form to the one used by Tolman, Equation (1-15).

\begin{equation}
    z = a\theta + bv + c
\end{equation}

Here, $\theta$ is the cone angle, $v$ is the $A_1$ stretching frequency for Ni(CO)$_3$L (where Giering uses $\chi$ as the difference in frequency from a standard), and $z$ is any physicochemical property. The coefficients $a$ and $b$ give the relative contributions from electronic and steric factors.
Three excellent reviews\textsuperscript{29,32,33} examine the new attempts to get a grasp on the concept of cone angles and the steric requirements of ligands in general. Some of the ideas include modeling solid angles, ligand radial profiles, and development of ligand repulsive energy parameters, $E_R$.

**Solvatochromism**

**General theory**

It is experimentally observed that many molecules have solvatochromic behavior, meaning that their UV/Vis, IR, or NMR spectra are affected by the solvent used in the measurement. These effects can be related to both specific and non-specific solvation. Specific interactions are those that are related to acid-base interactions using specific orbitals, including donor solute molecules in acceptor solvents and vice versa. Non-specific effects cover a broader range including interactions of a solute dipole (permanent or induced) with both the internal dielectric of the solvent cavity and the dielectric of the bulk solvent.\textsuperscript{12a}

**Solvent Effects on Electronic Spectra**

An explanation often used\textsuperscript{12a,34} for changes in electronic spectra due to solvent effects is based on the polarity of the ground and excited states of a probe molecule. Figure 1-2 shows the changes in the transition energy of a molecule from its gas phase to its introduction into a polar solvent. Figure 1-2a shows the case for a molecule whose ground state is more polar than its excited state. In the polar solvent, the ground state is
Changes in transition energies in moving from the gas phase to a polar solvent. Two examples are possible: (a) the blue shift and (b) the red shift.

stabilized, and the excited state is destabilized, thus creating a larger ("blue-shifted") transition energy. Figure 1-2b shows the case for a molecule whose excited state is more polar than the ground state. Its excited state is stabilized in the polar solvent, creating a smaller ("red-shifted") transition energy. Reichardt\textsuperscript{34b} discusses the various combinations of polar and nonpolar solutes and solvents in detail listing various minor contributions to red and blue shifts.

This type of behavior is predicted by the Franck-Condon principle,\textsuperscript{34b,35} which states that because electronic transitions occur at a much faster rate than vibrations, the nuclei of the chromophore are not changed during the electronic transition. Therefore, when the excited state is formed, the solvent cage does not have a chance to rearrange. If the molecule becomes more polar upon moving into the excited state, there is an overall stabilization (in a polar solvent). If the molecule is less polar in the excited state, there will be a destabilization because the solvent cannot rearrange during the electronic transition.
Solvent Effects on NMR spectra

NMR spectra are affected by solvents in two ways. Differences in the bulk magnetic susceptibility ($\chi_m$) between solute and solvent is the first way. Normally the bulk susceptibility differences are accounted for with the use of an internal standard, thereby having the solute and standard each in a similarly shaped container. Another method that is used to account for the bulk susceptibility differences is to take measurements as several solute concentrations and extrapolate to infinite dilution, thus giving the chemical shift under volume susceptibility conditions of the pure solvent. If an external standard is used, corrections can be made using Equation (1-16), where $\delta_{\text{exp}}$ is the experimentally observed chemical shift, $\delta_{\text{corr}}$ is the corrected chemical shift, and $\Delta \chi_m$ is the difference between the magnetic susceptibilities of the reference and the solution.

The second way that chemical shifts are affected in the NMR experiment is through interactions (both specific and non-specific) of the solute and solvent. Non-specific interactions typically do not affect chemical shifts nearly as much as specific interactions. Examples of the effect of solvent on NMR chemical shifts are given in Chapters 4 and 5.

Models Used to Quantify Solvent Effects

Kirkwood Approach to Non-specific Solvation

Kirkwood and Onsager developed a model to calculate the solvation energy of a solute in a given solvent. Their expression takes the form of Equation (1-17), where $\varepsilon$ is...
the bulk solvent dielectric constant, $\epsilon_i$ is the internal dielectric constant of the solvent cavity, $\mu$ is the solute dipole moment, and $b$ is the radius of the molecular cavity.

$$E_{\text{sol}} = \frac{1}{2} \cdot \left[ \frac{(\epsilon_i - \epsilon)/(2\epsilon + \epsilon_i)}{2} \right] \cdot \left( \frac{\mu^2}{b^2} \right) \tag{1-17}$$

There are difficulties in estimating the internal dielectric constant of the solvent cavity and the radius of the molecular cavity. Without the use of approximations for these values, the model is not especially practical quantitatively. For this reason, efforts have been made to develop empirical models of specific and non-specific solvation using various probe molecules. While some of the more popular models will be discussed in detail in Chapter 4, a brief introduction to them will be given here. An excellent review tabulates the parameters used in these various models.

**Empirical Models Using Probe Molecules**

One of the first scales that was developed was Kosower’s Z-value. It is based on the transition energy for the longest wavelength band observed in 1-ethyl-4-methoxycarbonylpyridinium iodide (pyridinium iodide 214) in a wide range of solvents. Alternate derivatives of this probe are used for non-polar solvents. Griffiths and Pugh have expanded Kosower’s original work to include 43 more solvents. They have suggested some changes in the use of the Z-value.

Perhaps the most widely used scale of solvent polarity is based on the negative solvatochromism of the pyridinium N-phenolate betaine dye 36 of Reichardt. This probe molecule’s $\pi \rightarrow \pi^*$ absorption band has been measured in over 350 solvents. This probe is not soluble in some non-polar solvents, so an alternate probe, with t-butyl
substituents, is used. This probe is often used in the literature to correlate physicochemical data. Taft, Kamlet, and co-workers have developed and modified a scale that covers both specific and non-specific contributions to solvation. Their model takes the form of Equation (1-18), where $XYZ$ is any physicochemical property, $\pi^*$ is a measure of solvent dipolarity/polarizability, $\alpha$ is a measure of hydrogen bond donating ability, and $\beta$ is a measure of hydrogen bond accepting ability. Later versions of the model have included an $\delta(\pi^2)$ term using Hildebrand's solubility parameter as a measure of the contributions of creating a cavity in the solvent to accommodate a solute, and a $\delta$ term (with $\delta$ here being a polarizability correction term). Instead of using a single probe molecule, Taft and Kamlet chose seven molecules, mostly substituted nitro-anilines and phenols, as the basis for their scale. It was their original belief that using several probes would help to average spectral anomalies that might be found in any single probe. Later analyses of the $\pi^*$ model find that this averaging actually “... blurs very important, physically meaningful contributions” (p. 5808). These authors suggest using only 4-nitroanisole and N,N-dimethylaniline as the basis for a revised and extended $\pi^*$ model. As with $E_T(30)$, the $\pi^*$ model has been used extensively in the literature to correlate data. Drago has expressed concern over the use of the $\beta-\pi^*$ scale and has compared its use to $E_T(30)$ and his Unified Solvation Model (vide infra).
The Unified Solvation Model (USM)

Drago and coworkers\textsuperscript{45} have proposed an extension of the Electrostatic-Covalent model of acid-base chemistry to include non-specific solvation. Equation (1-19) shows

\[ \Delta \chi = PS' + W \]  

(1-19)

the extension, where \( \Delta \chi \) is any physicochemical property, \( S' \) is the non-specific solvent parameter, \( P \) is the susceptibility of a solute probe molecule to solvation, and \( W \) is the value of the physicochemical property when \( S' = 0 \). In the earliest work,\textsuperscript{45b} 162 spectral shifts (e.g., UV, IR, NMR) for thirty probes in thirty-one solvents were correlated with Equation (1-19). A master-fitting program was used so that all unknown variables (\( P, S', \) and \( W \)) could be allowed to float. Probes and solvents were chosen carefully so that only non-specific interactions would be present between solute and solvent. \( S' \) values for solvents and \( P \) and \( W \) values for probes were calculated.

Use of the term "probe" in this dissertation refers not only to the actual probe molecule, but more often to a particular physicochemical property of that molecule. For instance, if a molecule is chosen to be a "probe" of solvent polarity, it is actually a particular property such as an electronic absorption or chemical shift that is the true probe that is studied to gain the desired information. As stated above, probes have \( P \) and \( W \) values. The sign of the \( P \) value gives important information. Probes with negative \( P \) values exhibit red shifts in more polar solvents, and those with positive \( P \) values exhibit blue shifts.

Later additions to the USM\textsuperscript{45c} increased the number of probes to forty-one and the number of solvents to forty-six (using 366 spectral shifts). With the additional probes and
solvents, the P, S', and W parameters were recalculated. This work also examined specific interactions with the use of hydrogen bonding solvents. Equation (1-20) gives the combination of specific and non-specific interactions to $\Delta \chi$, combining Equations (1-8) and (1-19). Using the master-fitting program and the known P and W values for the probe molecules, $E_A^*$, $C_A^*$, and $S'$ were calculated for the hydrogen bonding solvents and $E_B$ and $C_B$ were calculated for the probe molecules. Chapters 4 and 5 will present further extensions to the USM using more probe molecules and hydrogen bonding solvents.

A graphical method is proposed for separation of specific and non-specific contributions to an electronic transition. Drago and coworkers studied Reichardt's betaine and $E_T(30)$ scale in various mixtures of o-dichlorobenzene and hydrogen bonding solvent. They began in pure o-dichlorobenzene and added small aliquots of alcohol. After each addition, the electronic transition $[E_T(30)]$ was measured in the UV/Vis. For the first several additions, $E_T(30)$ increased rapidly due to the specific interaction between betaine and the alcohol. After the majority of probe had been specifically complexed, the $E_T(30)$ values began to level out and not increase so rapidly, now as a result of non-specific solvation. The plot of measured $E_T(30)$ value versus concentration of alcohol added to the system resembles a type I adsorption isotherm (see Figure 1-2). A straight line can be drawn through the flattened region at high alcohol concentrations. This line can be extrapolated to $E_T(30)$ at zero alcohol concentration. The difference between this value and the $E_T(30)$ value in the pure alcohol is labeled the non-specific contribution of the alcohol to solvation. The difference between the first point of

$$\Delta \chi = E_A^*E_B + C_A^*C_B + PS' + W$$  \hspace{1cm} (1-20)
alcohol addition and this newly extrapolated point is the specific contribution of the alcohol to solvation. The rest of the isotherm [from \( E_r(30) = 0 \) to the first point in pure o-dichlorobenzene] is the non-specific contribution due to o-dichlorobenzene.

**The Unified Solvation Cavity Model (USCM)**

Recently introduced,\(^4\) USCM is an extension to the USM that includes a term for formation of a cavity within the solvent to accommodate a solute molecule. Equation (1-21) gives the USCM, where all variables have similar meanings as in Equation (1-20).

\[
\Delta \chi = Q S^{-2} + P S^{-1} + E_A E_B + C_A C_B + W \tag{1-21}
\]

Here \( Q \) is the solute contribution to cavity formation and \( S^{-2} \) is the square of the non-specific solvent parameter, and represents the solvent contribution to cavity formation.
S'\textsuperscript{2} was chosen as the solvent contribution because of the work of Taft and others\textsuperscript{42e,f} discussed earlier, which uses Hildebrand’s solubility parameter (δ_h\textsuperscript{2}) in the cavity term. Bustamante and Drago\textsuperscript{46} have shown a correlation between S' and δ_h, and thus have chosen S'\textsuperscript{2} as their solvent-dependent cavity term parameter. They find very good correlations of solubilities and enthalpies of solution to Equation (1-21) using donor and non-polar solvents with non-polar solutes. Bustamante and Drago found only a small contribution from the E and C (specific) terms of Equation (1-21).
CHAPTER 2

REACTIVITY OF PHOSPHORUS DONORS

Introduction

The ECW model\textsuperscript{12a,21,30,47} 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, Equation (2-1), 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.

\[-\Delta H = E_A E_B + C_A C_B + W \] (2-1)

Two effects are needed to fit the data. The magnitudes of the parameters for these two effects parallel quantitative 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 the complications from solvation or entropic effects. Omission of systems with π-back-bonding contributions and steric effects provides 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.\textsuperscript{12a}
Recently,\textsuperscript{30,48} a dual parameter substituent constant equation [Equation (2-2)] was reported to analyze the reactivity of families of compounds whose E and C values are not known.

\[ \Delta \chi^X = d^E \Delta E^X + d^C \Delta C^X + \Delta \chi^H \] (2-2)

In Equation (2-2), \( \Delta \chi^X \) is the measured property for the molecule containing substituent \( X \), \( \Delta \chi^H \), the value for the parent hydrogen compound, \( \Delta E^X \) and \( \Delta C^X \) 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 \( \Delta E^X \) and \( \Delta C^X \) values are the dual parameter analogues of the Hammett \( \alpha \)-values while \( d^E \) and \( d^C \) are the dual parameter analogues of \( \rho \). It is reported\textsuperscript{30,48} that the set of dual substituent parameters correlates data that previously required different sets of substituent constants for analysis.

The \( d \)-values of Equation (2-2) are related to the E and C values of Equation (2-1) by

\[ d_A^E = s_{BE} E_A^* \] (2-3)
\[ d_A^C = s_{BC} C_A^* \] (2-4)

Equations (2-3) and (2-4) 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 Equations (2-3) and (2-4), the \( d_A^E \) of Equation (2-2) and \( E_A^* \) of Equation (2-1) are related by the family dependent proportionality constant \( s_{BE}^E \) which measures the sensitivity of the E values of the family of donors to the substituent change. The proportionality constant \( s_{BC}^C \), 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\textsuperscript{30,48} that the $E_B$ or $C_B$ values of the $X$-substituted donor $E_B^X$ and $C_B^X$, are given by where $E_B^H$ and $C_B^H$ are the $E$ and $C$ values for the parent hydrogen compound.

\begin{align}
E_B^X &= s_B^E \Delta E^X + E_B^H \\
C_B^X &= s_B^C \Delta C^X + C_B^H
\end{align}

(2-5) \hspace{1cm} (2-6)

The implications of Equations (2-5) and (2-6) are profound for they greatly expand the number of donors that can be analyzed with Equation (2-1). 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-mono substituted pyridines can be calculated with Equations (2-5) and (2-6) from reported\textsuperscript{2d} $\Delta E^X$ and $\Delta C^X$ values. In a similar fashion, with reported values of $s_A^E = -0.817$ and $s_A^C = -0.225$ (see Chapter 4), 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 Equation (2-1) permits the calculation of 6,084 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.\textsuperscript{12a}

It has been emphasized, that in using Equation (2-1) 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 exceed 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 Equation (2-2). 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, Equation (2-1) 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\textsuperscript{30} with Equation (2-2) by summing the $\Delta E$ and $\Delta C$ values of the substituents attached to phosphorus. In this chapter, 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\textsuperscript{12a} for two phosphines. Determination of $E_B$ and $C_B$ will permit an evaluation of the validity of the substituent summation used\textsuperscript{30} 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 $\pi$-backbonding effects in the reactions these compounds undergo with acceptors.

The $E_B$ and $C_B$ parameters provide a $\sigma$ basicity scale that can be used with Equation (2-7) in correlations to determine if physicochemical measurements, $\chi$, are controlled by the same factors that influence bond strengths. $\chi$ can be a spectral shift, rate
constant, activation enthalpy, redox potential or any measurement that is expressed in energy units.

\[ \chi = E_A * E_B + C_A * C_B + W \]  \hspace{1cm} (2-7)

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 non-linear free energy systems, a separate entropy scale would be needed.

In analyzing \( \chi \)'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 \( \chi \)'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 \( \chi \) has contributions from effects not related to bond strength. Thus, the model provides an understanding of reactivity and spectroscopy even when poor correlations result.

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 Equation (2-7). 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.\textsuperscript{12a,47a} 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.\textsuperscript{12a} 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 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,\textsuperscript{4} literature correlation analyses of reactivity have not employed parameters related to these quantities as measures of substituent effects or basicity. Derivations are reported\textsuperscript{47b} 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 chapter reports phosphorus donor parameters which are well connected to the other donors in ECW. A model is presented to support the idea that the $\pi$-acceptor properties of the phosphines decrease regularly as their $\sigma$ basicity increases. It is shown that the phosphine $\sigma$ donor, $E_B$ and $C_B$, parameters inappropriately can correlate reactivity toward acceptors that $\pi$-back-bond when a data set involves only phosphines. 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 2-1) and all the acceptors (Table 2-2) are substituted into Equation (2-7) 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, 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 are also entered into the equation and fixed in the data fit. The best set of unknown parameters are determined by a least squares minimization for the entire set of weighted simultaneous equations. This is referred to as the master fit.

In using the master fit to determine phosphine $\sigma$-donor parameters, it is essential to eliminate contributions from both enthalpic and entropic steric effects from the data set.

Since the connection between the phosphine parameters and those of other donors is critically dependent on systems like CF$_3$SO$_3$H, C$_6$H$_5$OH, and Al$_2$(CH$_3$)$_6$, which are measured with different families of donors, a large weight was given to these acceptors in the master fit. In general, enthalpies are assigned weight values of 1, $^{13}$C 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, $\Delta v$ 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
Table 2-1. $E_B$ and $C_B$ Parameters for Phosphines

<table>
<thead>
<tr>
<th>no.</th>
<th>phosphine</th>
<th>wt*</th>
<th>$E_B$</th>
<th>$C_B$</th>
<th>$C_B/E_B$</th>
<th>$\theta^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>P(CH$_3$)$_3$</td>
<td>1.0</td>
<td>0.31</td>
<td>5.15</td>
<td>17</td>
<td>118</td>
</tr>
<tr>
<td>2</td>
<td>P(C$_2$H$_5$)$_3$</td>
<td>1.0</td>
<td>0.28</td>
<td>5.53</td>
<td>20</td>
<td>132</td>
</tr>
<tr>
<td>3</td>
<td>P(n-C$_3$H$_7$)$_3$</td>
<td>0.5</td>
<td>0.37</td>
<td>5.16</td>
<td>14</td>
<td>132</td>
</tr>
<tr>
<td>4</td>
<td>P(i-C$_3$H$_7$)$_3$</td>
<td>0.7</td>
<td>0.36</td>
<td>5.46</td>
<td>15</td>
<td>160</td>
</tr>
<tr>
<td>5</td>
<td>P(n-C$_4$H$_9$)$_3$</td>
<td>1.0</td>
<td>0.32</td>
<td>5.36</td>
<td>17</td>
<td>132</td>
</tr>
<tr>
<td>6</td>
<td>P(i-C$_4$H$_9$)$_3$</td>
<td>0.7</td>
<td>0.48</td>
<td>4.60</td>
<td>10</td>
<td>143</td>
</tr>
<tr>
<td>7</td>
<td>P(t-C$_4$H$_9$)$_3$</td>
<td>0.5</td>
<td>0.25</td>
<td>6.08</td>
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<td>182</td>
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<tr>
<td>8</td>
<td>P(c-C$_6$H$_5$)$_3$</td>
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<td>5.35</td>
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<td>170</td>
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<td>1.50</td>
<td>1.6</td>
<td>132</td>
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<tr>
<td>10</td>
<td>P(CH$_2$C$_6$H$_5$)$_3$</td>
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<td>0.63</td>
<td>3.32</td>
<td>5.3</td>
<td>165</td>
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<tr>
<td>11</td>
<td>P(OCH$_3$)$_3$</td>
<td>1.0</td>
<td>0.50</td>
<td>3.32</td>
<td>6.6</td>
<td>107</td>
</tr>
<tr>
<td>12</td>
<td>P(OCH$_3$)$_3$</td>
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<td>0.56</td>
<td>3.17</td>
<td>5.7</td>
<td>109</td>
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<td>13</td>
<td>P(O-i-C$_3$H$_7$)$_3$</td>
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<td>3.59</td>
<td>6.8</td>
<td>130</td>
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<td>0.71</td>
<td>1.69</td>
<td>2.4</td>
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<td>16</td>
<td>P(OCH$_3$)$_3$R</td>
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<td>101</td>
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<td>P[N(CH$_3$)$_2$]$_3$</td>
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<td>0.38</td>
<td>5.11</td>
<td>13</td>
<td>152</td>
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<td>18</td>
<td>P(CH$_2$CH=CH$_2$)$_3$</td>
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<td>0.64</td>
<td>3.61</td>
<td>5.6</td>
<td>c</td>
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<td>P(C$_6$H$_5$)$_3$</td>
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<td>0.70</td>
<td>3.05</td>
<td>4.4</td>
<td>145</td>
</tr>
<tr>
<td>20</td>
<td>P(4-CH$_3$C$_6$H$_4$)$_3$</td>
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<td>0.65</td>
<td>3.41</td>
<td>5.2</td>
<td>145</td>
</tr>
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<td>0.62</td>
<td>3.57</td>
<td>5.8</td>
<td>145</td>
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<td>22</td>
<td>P(4-ClC$_6$H$_4$)$_3$</td>
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<td>2.70</td>
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<td>145</td>
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<tr>
<td>23</td>
<td>P(4-ClC$_6$H$_4$)$_3$</td>
<td>1.0</td>
<td>0.82</td>
<td>2.35</td>
<td>2.9</td>
<td>145</td>
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<td>24</td>
<td>P(4-BrC$_6$H$_4$)$_3$</td>
<td>1.0</td>
<td>0.91</td>
<td>1.52</td>
<td>1.7</td>
<td>145</td>
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<td>25</td>
<td>P(4-NMe$_2$C$_6$H$_4$)$_3$</td>
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<td>0.05</td>
<td>6.90</td>
<td>140</td>
<td>145</td>
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<td>26</td>
<td>P(3-CH$_3$C$_6$H$_4$)$_3$</td>
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<td>0.55</td>
<td>3.83</td>
<td>7.0</td>
<td>145</td>
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<tr>
<td>27</td>
<td>PCl$_3$</td>
<td>0.2</td>
<td>0.70</td>
<td>0.18</td>
<td>0.26</td>
<td>124</td>
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<tr>
<td>28</td>
<td>P(CH$_3$)$_2$C$_6$H$_5$</td>
<td>1.0</td>
<td>0.44</td>
<td>4.49</td>
<td>10</td>
<td>122</td>
</tr>
<tr>
<td>29</td>
<td>P(C$_2$H$_5$)$_2$C$_6$H$_5$</td>
<td>1.0</td>
<td>0.39</td>
<td>4.91</td>
<td>13</td>
<td>136</td>
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<tr>
<td>30</td>
<td>P(OCH$_3$)$_2$C$_6$H$_5$</td>
<td>0.5</td>
<td>0.59</td>
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<td>5.7</td>
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<td>P(Cl)$_2$C$_6$H$_5$</td>
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<td>0.25</td>
<td>0.27</td>
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<td>0.57</td>
<td>3.74</td>
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<td>P(C$_6$H$_5$)$_2$C$_2$H$_5$</td>
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<td>0.55</td>
<td>3.83</td>
<td>4.4</td>
<td>140</td>
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<td>34</td>
<td>P(C$_6$H$_5$)$_2$n-C$_6$H$_9$</td>
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<td>0.58</td>
<td>3.80</td>
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<tr>
<td>35</td>
<td>P(C$_6$H$_5$)$_2$OCH$_3$</td>
<td>1.0</td>
<td>0.59</td>
<td>3.39</td>
<td>5.7</td>
<td>132</td>
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<tr>
<td>36</td>
<td>P(C$_6$H$_5$)$_2$Cl</td>
<td>0.5</td>
<td>0.66</td>
<td>2.35</td>
<td>3.6</td>
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<tr>
<td>37</td>
<td>P(C$_6$H$_5$)$_2$H</td>
<td>0.2</td>
<td>0.49</td>
<td>4.51</td>
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<td>38</td>
<td>AsPh$_3$</td>
<td>0.2</td>
<td>0.90</td>
<td>2.16</td>
<td>2.4</td>
<td>141</td>
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</tbody>
</table>

(a) If more than 12 systems are studied, a weight (wt) value of 1 is assigned, 12-10 a
value of 0.7, 9-7 a value of 0.5, less than 7 a value of 0.3. 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 refs. 23, 29, 32, and 49.

(c) No cone angle is reported in refs. 23, 29, 32, or 49.
Table 2-2. $E_A^*$, $C_A^*$, and $W$ Parameters for Acceptor Systems

<table>
<thead>
<tr>
<th>Acceptor Property</th>
<th>wt. *</th>
<th>$E_A^*$</th>
<th>$C_A^*$</th>
<th>$W$</th>
<th>$C_A^<em>$/$E_A^</em>$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$-\Delta H$ (CF$_3$SO$_3$H) $^b$</td>
<td>1.2</td>
<td>4.51</td>
<td>5.70</td>
<td>0.84</td>
<td>1.26</td>
</tr>
<tr>
<td>$-\Delta H$ (B(CH$_3$)$_3$) $^c$</td>
<td>0.4</td>
<td>3.57</td>
<td>2.97</td>
<td>0</td>
<td>0.83</td>
</tr>
<tr>
<td>$-\Delta H$ (Al(CH$_3$)$_3$) $^d$</td>
<td>1.2</td>
<td>8.28</td>
<td>3.23</td>
<td>-8.46</td>
<td>0.39</td>
</tr>
<tr>
<td>$-\Delta H$ (CpIr(CO)PR$_3$) $^e$</td>
<td>0.5</td>
<td>1.16</td>
<td>1.52</td>
<td>24.8</td>
<td>1.31</td>
</tr>
<tr>
<td>$-\Delta H$ (Cp*Ir(CO)PR$_3$) $^f$</td>
<td>0.1</td>
<td>36.68</td>
<td>7.11</td>
<td>-10.18</td>
<td>0.19</td>
</tr>
<tr>
<td>$\Delta H$ (Ti(C$_2$H$_5$)$_2$PX$_3$) $^g$</td>
<td>0.4</td>
<td>-9.10</td>
<td>0.83</td>
<td>13.13</td>
<td>-0.09</td>
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<tr>
<td>$-\Delta H$ (HgCl$_2$) $^h$</td>
<td>0.1</td>
<td>9.94</td>
<td>6.75</td>
<td>-9.46</td>
<td>0.68</td>
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<tr>
<td>$-\Delta H$ (HgBr$_2$) $^h$</td>
<td>0.1</td>
<td>21.13</td>
<td>8.01</td>
<td>-20.88</td>
<td>0.38</td>
</tr>
<tr>
<td>$-\Delta H$ ([Ni $\eta_5$-C$_5$H$_5$]CH$_3$)$_2$ $^i$</td>
<td>0.8</td>
<td>-72.6</td>
<td>-11.7</td>
<td>111.5</td>
<td>0.16</td>
</tr>
<tr>
<td>$-\Delta H$ (CpMo(CO)$_3$CH$_3$) $^j$</td>
<td>0.1</td>
<td>-30.57</td>
<td>-1.75</td>
<td>38.49</td>
<td>0.06</td>
</tr>
<tr>
<td>$-\Delta H$ (CpMo(CO)$_3$C$_2$H$_5$) $^j$</td>
<td>0.1</td>
<td>-23.08</td>
<td>-0.97</td>
<td>34.55</td>
<td>0.04</td>
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<tr>
<td>$\Delta H^2$ (CoNO(CO)$_3$) $^k$</td>
<td>0.1</td>
<td>1.44</td>
<td>-2.88</td>
<td>22.83</td>
<td>-2.0</td>
</tr>
<tr>
<td>$\Delta H^2$ (Ru(CO)$_3$PX$_3$(Dis 1)) $^l$</td>
<td>0.1</td>
<td>3.97</td>
<td>0.77</td>
<td>26.4</td>
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<tr>
<td>$\Delta H^2$ (V(CO)$_6$ (Sn$_2$)) $^m$</td>
<td>0.1</td>
<td>-8.16</td>
<td>-2.44</td>
<td>22.98</td>
<td>0.30</td>
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<td>$\Delta H^2$ (Ru(CO)$_3$PX$_3$(SiCl$_3$)$_2$) $^a$</td>
<td>0.8</td>
<td>-0.68</td>
<td>0.47</td>
<td>26.02</td>
<td>-0.69</td>
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<td>$\Delta H^2$ (Rh$_2$(OAc)$_4$) $^o$</td>
<td>0.1</td>
<td>4.79</td>
<td>0.78</td>
<td>5.65</td>
<td>0.16</td>
</tr>
<tr>
<td>$\Delta H^2$ (Ru$<em>6$C(CO)$</em>{17}$) $^p$</td>
<td>0.1</td>
<td>-1.64</td>
<td>-3.21</td>
<td>19.15</td>
<td>1.96</td>
</tr>
<tr>
<td>$\Delta H^2$ (Cp(CO$_2$Me)Co(CO)$_2$) $^q$</td>
<td>0.1</td>
<td>-11.02</td>
<td>-0.79</td>
<td>22.00</td>
<td>0.07</td>
</tr>
<tr>
<td>$^{13}$C (Ni(CO)$_3$L) $^r$</td>
<td>0.8</td>
<td>8.27</td>
<td>1.95</td>
<td>-7.47</td>
<td>0.24</td>
</tr>
<tr>
<td>$^{13}$C (Cr(CO)$_3$L) $^s$</td>
<td>1.2</td>
<td>8.87</td>
<td>1.84</td>
<td>-6.67</td>
<td>0.21</td>
</tr>
<tr>
<td>$^{13}$C (Mo(CO)$_5$PX$_3$) $^t$</td>
<td>0.8</td>
<td>7.90</td>
<td>1.63</td>
<td>-5.82</td>
<td>0.21</td>
</tr>
<tr>
<td>$^{13}$C (W(CO)$_3$L) $^u$</td>
<td>0.1</td>
<td>13.74</td>
<td>2.36</td>
<td>180.1</td>
<td>0.17</td>
</tr>
<tr>
<td>$^{13}$C (CpMn(CO)$_2$L) $^v$</td>
<td>0.1</td>
<td>-22.11</td>
<td>-3.01</td>
<td>-208.1</td>
<td>0.14</td>
</tr>
<tr>
<td>$^{13}$C (PtPh$_2$(CO)L) $^w$</td>
<td>0.5</td>
<td>21.76</td>
<td>3.90</td>
<td>154.3</td>
<td>0.18</td>
</tr>
<tr>
<td>$^{1}H$ (CpMo(CO)$_2$LMe) $^x$</td>
<td>0.3</td>
<td>0.63</td>
<td>0.71</td>
<td>3.73</td>
<td>1.13</td>
</tr>
<tr>
<td>$^{1}H$ (CpMo(CO)$_2$LCOMe) $^y$</td>
<td>0.3</td>
<td>1.66</td>
<td>0.28</td>
<td>3.04</td>
<td>0.17</td>
</tr>
<tr>
<td>$^{1}H$ ((CpCO$_2$Me)Co)$_2$ $^z$</td>
<td>0.8</td>
<td>-1.04</td>
<td>-0.11</td>
<td>4.58</td>
<td>0.11</td>
</tr>
<tr>
<td>$^{1}H$ ((MePAr$_3$)Br) $^{aa}$</td>
<td>0.1</td>
<td>-4.60</td>
<td>-1.05</td>
<td>9.67</td>
<td>0.23</td>
</tr>
<tr>
<td>$\nu$ (Ni(CO)$_3$PX$_3$) $^{bb}$</td>
<td>0.4</td>
<td>-52.4</td>
<td>-12.2</td>
<td>2143</td>
<td>0.23</td>
</tr>
<tr>
<td>$\nu$ (Ru(CO)$_3$L) $^{cc}$</td>
<td>0.4</td>
<td>-72.2</td>
<td>-14.7</td>
<td>2164</td>
<td>0.20</td>
</tr>
<tr>
<td>$\nu$ (CH$_3$CpMn(CO)$_2$PX$_3$) $^{dd}$</td>
<td>0.4</td>
<td>-15.0</td>
<td>-4.9</td>
<td>1967</td>
<td>0.33</td>
</tr>
<tr>
<td>$\nu$ ([Fe(CO)$_3$(PR$_3$)C$_2$H$_5$]) $^{ee}$</td>
<td>0.4</td>
<td>-114.9</td>
<td>-21.7</td>
<td>2069</td>
<td>0.19</td>
</tr>
<tr>
<td>$\nu$ (CpCO$_2$Me)Co $^{ii}$</td>
<td>0.4</td>
<td>-60.8</td>
<td>-16.8</td>
<td>2034</td>
<td>0.28</td>
</tr>
<tr>
<td>$\nu$ (Ru(CO)$_3$PX$_3$(SiCl$_3$)$_2$) $^{jj}$</td>
<td>0.4</td>
<td>-72.2</td>
<td>-14.7</td>
<td>2164</td>
<td>0.20</td>
</tr>
<tr>
<td>Acceptor Property</td>
<td>wt.</td>
<td>$E*_A$</td>
<td>$C*_A$</td>
<td>W</td>
<td>$C<em>_A/E</em>_A$</td>
</tr>
<tr>
<td>-------------------</td>
<td>-----</td>
<td>--------</td>
<td>--------</td>
<td>---</td>
<td>-------------</td>
</tr>
<tr>
<td>$E_{1/2}$(Cp'Mn(CH₂Cl₂))⁴</td>
<td>1.7</td>
<td>-0.37</td>
<td>-0.12</td>
<td>1.16</td>
<td>0.32</td>
</tr>
<tr>
<td>$E_{1/2}$(Cp'Mn(CH₂CN))⁵</td>
<td>1.7</td>
<td>-1.10</td>
<td>-0.25</td>
<td>2.05</td>
<td>0.23</td>
</tr>
<tr>
<td>$E_{1/2}[(Ru(bpy)₂PX₃)²⁺(CH₂CN)]$⁶</td>
<td>1.3</td>
<td>0.30</td>
<td>-0.03</td>
<td>1.20</td>
<td>-0.10</td>
</tr>
<tr>
<td>$E_{1/2}[(Ru(bpy)₂PX₃)²⁺(4Ac-py)]$⁶</td>
<td>0.1</td>
<td>0.11</td>
<td>-0.06</td>
<td>1.43</td>
<td>-0.55</td>
</tr>
<tr>
<td>$E_{1/2}[(Ru(bpy)₂PX₃)²⁺(Cl)]$⁶</td>
<td>0.1</td>
<td>0.28</td>
<td>-0.03</td>
<td>1.24</td>
<td>-0.11</td>
</tr>
<tr>
<td>$E_{1/2}(η-CpFe(CO)(COMe)PX₃)$⁷</td>
<td>1.3</td>
<td>-0.89</td>
<td>-0.19</td>
<td>1.53</td>
<td>0.21</td>
</tr>
<tr>
<td>$E_{1/2}(η-Cp'Fe(CO)(COMe)PX₃)$⁷</td>
<td>1.3</td>
<td>-0.85</td>
<td>-0.19</td>
<td>1.47</td>
<td>0.22</td>
</tr>
<tr>
<td>log K (CF₃C₂H₂OHH)⁸</td>
<td>0.6</td>
<td>1.69</td>
<td>0.26</td>
<td>-1.49</td>
<td>0.15</td>
</tr>
<tr>
<td>log K (CpMo(CO)₂LCOMe)⁹</td>
<td>0.1</td>
<td>28.26</td>
<td>3.84</td>
<td>-34.55</td>
<td>0.14</td>
</tr>
<tr>
<td>log K₁(Rh₂(OAc)₄L)¹⁰</td>
<td>0.1</td>
<td>4.76</td>
<td>1.30</td>
<td>-2.15</td>
<td>0.28</td>
</tr>
<tr>
<td>log K (V(CO)₆(SN₂))¹¹</td>
<td>0.3</td>
<td>0.60</td>
<td>1.37</td>
<td>-5.10</td>
<td>2.28</td>
</tr>
<tr>
<td>log K (Ru(CO)₄L)¹²</td>
<td>0.8</td>
<td>2.77</td>
<td>0.41</td>
<td>-6.42</td>
<td>0.15</td>
</tr>
<tr>
<td>log K (Cp₂Fe₂(CO)₄)¹³</td>
<td>0.3</td>
<td>-1.28</td>
<td>-0.66</td>
<td>8.38</td>
<td>0.52</td>
</tr>
<tr>
<td>log K (CpMn(py))¹⁴</td>
<td>0.1</td>
<td>-13.75</td>
<td>-0.01</td>
<td>10.81</td>
<td>0.001</td>
</tr>
<tr>
<td>log K (Ru(bpy)₂PX₃(H₂O)²⁺)¹⁵</td>
<td>0.5</td>
<td>12.24</td>
<td>2.40</td>
<td>-18.14</td>
<td>0.20</td>
</tr>
<tr>
<td>log K (Co-C₆H₅CH₂Br)¹⁶</td>
<td>0.9</td>
<td>-4.38</td>
<td>0.43</td>
<td>-0.05</td>
<td>-0.13</td>
</tr>
<tr>
<td>log K (Co-C₆H₅CH₂Br)¹⁷</td>
<td>0.4</td>
<td>-3.58</td>
<td>0.13</td>
<td>0.46</td>
<td>-0.04</td>
</tr>
<tr>
<td>log K (Fe(CO)₂Cp(ethene)⁺)¹⁸</td>
<td>0.1</td>
<td>24.34</td>
<td>5.01</td>
<td>-30.49</td>
<td>0.21</td>
</tr>
<tr>
<td>log K (η₅-Me₅CpRh(CO)₂)¹⁹</td>
<td>0.1</td>
<td>-7.38</td>
<td>-0.23</td>
<td>0.90</td>
<td>0.03</td>
</tr>
<tr>
<td>log K (Mn(CO)₂(NO)(6-C₆H₅)₂)²⁰</td>
<td>0.1</td>
<td>0.26</td>
<td>0.99</td>
<td>-2.75</td>
<td>3.81</td>
</tr>
<tr>
<td>log K (CpIr(CO)PX₃)²¹</td>
<td>0.3</td>
<td>5.32</td>
<td>1.58</td>
<td>-10.08</td>
<td>0.30</td>
</tr>
<tr>
<td>log K (Cp*Ir(CO)PX₃)²²</td>
<td>0.1</td>
<td>-1.94</td>
<td>0.46</td>
<td>-0.18</td>
<td>-0.24</td>
</tr>
<tr>
<td>log K (C₂H₅I)²³</td>
<td>0.5</td>
<td>-0.63</td>
<td>0.46</td>
<td>-5.05</td>
<td>-0.73</td>
</tr>
<tr>
<td>log K (η₅-Me₅CpCo(CO)₂)²⁴</td>
<td>0.3</td>
<td>-5.22</td>
<td>0.15</td>
<td>-1.88</td>
<td>-0.03</td>
</tr>
<tr>
<td>log K (η-CpMo(CO)₂LCOMe)²⁵</td>
<td>0.3</td>
<td>10.60</td>
<td>1.56</td>
<td>-17.11</td>
<td>0.15</td>
</tr>
<tr>
<td>log K (Fe(η-Cp)(CO)LMMe⁺)²⁶</td>
<td>0.8</td>
<td>-3.67</td>
<td>-0.72</td>
<td>3.61</td>
<td>0.20</td>
</tr>
<tr>
<td>log K (Fe(η-Cp)(CO)LMMeAN)²⁷</td>
<td>0.8</td>
<td>18.71</td>
<td>3.29</td>
<td>-23.03</td>
<td>0.18</td>
</tr>
<tr>
<td>pKₐ</td>
<td>0.8</td>
<td>22.03</td>
<td>5.81</td>
<td>-29.87</td>
<td>0.26</td>
</tr>
</tbody>
</table>
(a) The wt (weight) 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_{12} values. A value of 0.4 is assigned to IR shifts because of their large magnitude. Smaller wts. should be assigned to free energies (other than E_{12}) for substituents where entropic factors can contribute. The weight in a fit is related to n used in articles before 1996 by wt=1/5n.

(b) -ΔH for the reaction of CF₃SO₃H with bases in 1,2 dichloroethane solvent. x=0.07, % fit=0.3. Data from ref. 50.

(c) Gas phase -ΔH of adduct formation. x=0.32, % fit=7. Data from ref. 51.

(d) -ΔH for the reaction of [Al(CH₃)₃] with donors in hexane solvent. x=0.26, % fit=2. Data from ref. 52 with Et₂O and Et₃N omitted.

(e) -ΔH of protonation of CpIr(CO)PX₃ with CF₃SO₃H in 1,2 dichloroethane. x=0.26, % fit=5. Data from ref. 50b, 53 with P(c-hex)₃ omitted.

(f) -ΔH of protonation of Cp*Ir(CO)PX₃ with CF₃SO₃H in 1,2 dichloroethane. x=0.22, % fit=5. Data from ref. 53b.

(g) Endothermic ΔH for PX₃ dissociation from bis(2,4dimethylpentadienyl)titanium in THF solvent. x=0.04, % fit=0.7. Data from ref. 54 with PEt₃ omitted.

(h) -ΔH of 1:1 adduct formation in benzene. For HgCl₂, x=1.10, % fit=8. For HgBr₂, x=0.61, % fit=5. Data from ref. 55 with P(c-hex)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-η³-(2-buteryl)] dinickel in tetralin. x=0.06, % fit=0.4. Data from ref. 56 with P(OPh)₃ and PPH₃ omitted.

(j) Enthalpy for the insertion of CO in the Mo-R bond of CpMo(CO)₂R, where R=Me or Et and coordination of PR₃ to form CpMo(CO)₂(PR₃)RC(O). For R=Me, x=0.08, % fit=2. For R=Et, x=0.21, % fit=3. Data from ref. 57.

(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. 58.

(l) Activation enthalpy for the first order dissociative substitution of CO in Ru(CO)₄PX₃ by P(OEt)₃ in hexane and decalin. x=0.4, r²=0.92. A steric onset of 128° and an s of -0.12 is needed. Data from ref. 59.

(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. 60.

(n) Activation enthalpy for the first order dissociative substitution of CO in Ru(CO)₃PX₃(SiCl₃)₂ by P(OMe)₃ or P(t-C₄H₉)₃. x=0.23, % fit=7. Data from ref. 61.

(o) Activation enthalpy for the substitution of solvent with phosphines in dirhodium (II) tetraacetate in CH₃CN. x=0.20, % fit=17. Data from ref. 62 with P(OPh)₃ and P(benzyl)₃ omitted.

(p) Activation enthalpy for the second order reaction of Ru₆C(CO)₁₇ with nucleophiles in heptane. x=0.30, % fit=5. Data from ref. 63.
(q) Activation enthalpy for the second order substitution of CO with ligands in ($\eta^5$-C$_5$H$_4$CO$_2$Me)Co(CO)$_2$. x=0.13, % fit=9. Data from ref. 64 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$_3$. Data from ref. 65.

(s) $^{13}$C chemical shift of the cis-carbonyl in Cr(CO)$_3$L relative to Cr(CO)$_6$ in CDCl$_3$. x=0.12, % fit=2. Data from ref. 65 with pyridine omitted.

(t) $^{13}$C chemical shift of the cis-carbonyl in Mo(CO)$_3$PX$_3$ relative to Mo(CO)$_6$ in CDCl$_3$. x=0.14, % fit=2. Data from ref. 65.

(u) $^{13}$C chemical shift of the cis-carbonyl in W(CO)$_3$PX$_3$ downfield from TMS in CDCl$_3$. x=0.22, % fit=6. Data from ref. 66 with 4-methylpyridine omitted.

(v) $^{13}$C chemical shift for the CO in CpMn(CO)$_2$PR$_3$ relative to TMS. x=0.26, % fit=6. Data from ref. 67.

(w) $^{13}$C chemical shift of Ni(CO)$_3$PX$_3$ relative to Ni(CO)$_4$ in CH$_2$Cl$_2$. x=1.26, % fit=3. Data from ref. 71 with P(OCH$_2$)$_3$CR and P(O-i-Pr)$_3$ 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. 69.

(y) $^3$H chemical shift for the Cp group in CpMo(CO)$_2$LCOCH$_3$ relative to TMS. x=0.04, % fit=16. Data from ref. 69.

(z) $^1$H chemical shift for the CO$_2$Me group in ($\eta^5$-CpCO$_2$Me)Co(CO)L relative to TMS in CDCl$_3$. x=0.05, % fit=22. Data from ref. 64 with P(c-hex)$_3$ 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. 70.

(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. 71 with P(OCH$_2$)$_3$CR and P(O-i-Pr)$_3$ omitted.

(cc) $v_1$(ax), CO stretching frequency of Ru(CO)$_4$L in heptane or hexane. x=1.18, % fit=7. Data from ref. 59 with AsPh$_3$ omitted.

(dd) Higher energy CO stretching frequency (cm$^{-1}$) of $\eta^5$-MeCpMn(CO)$_2$PX$_3$ in heptane. x=1.31, % fit=19. Data from ref. 72 with nitrogen donors and PPhEt$_2$ omitted.

(ee) CO stretching frequency of $\eta^5$-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. 73.

(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. 62 with AsPh$_3$.

(gg) Higher energy CO stretching frequency (cm$^{-1}$) for [Fe(CO)$_3$(1-4-$\eta$-R$_3$P*C$_7$H$_9$)]$^+$ adducts. x=0.35, % fit=9. Data from ref. 74.

(hh) CO stretching frequency for cis-[PtPh$_2$(CO)L]. x=0.82, % fit=3. Data from ref. 68 with P(i-Pr)$_3$, P(t-Bu)$_3$, and P(c-hex)$_3$ omitted.

(ii) CO stretching frequency of ($\eta^5$-CpCO$_2$Me)Co(CO)L. x=0.93, % fit=3. Data from ref. 64 with P(c-hex)$_3$ omitted.

(jj) CO stretching frequency of Ru(CO)$_3$L(SiCl)$_3$. x=0.82, % fit=3. Data from ref. 61 with P(OPh)$_3$ and P(benzyl)$_3$ omitted.

(kk) Standard oxidation potential in V of CH$_3$CpMn(CO)$_2$L in CH$_2$Cl$_2$. x=0.02, % fit=5. Data from ref. 72a.

(ll) Same as (kk), but in CH$_3$CN. x=0.02, % fit=3. Data from ref. 72b.
(mm) Redox potential for [Ru(H2O)(bpy)2PX3]2+/3+ in CH2Cl2 vs. SCE. with an incoming group of CH3CN, 4-Ac-pyridine or Cl-. for CH3CN, x=0.02, % fit=4. for 4-Ac-py, x=0.02, % fit=6. for Cl-, x=0.01, % fit=3. Data from ref. 75.

(nn) Redox potential for η5-Cp and η5-Cp*Fe(CO)(COCH3)PX3 in CH3CN (0.2 M LiClO4) vs. SCE. for Cp, x=0.01, % fit=3. for Cp', x=0.01, % fit=3. Data from ref. 73.

(oo) Log of the equilibrium constant for PX3 hydrogen bonding to 4-CF3-C6H4OH in CS2 at 25°C. x=0.07, % fit=3. Data from ref. 76 with P(Ph-p-OCH3)3 omitted.

(pp) Log of the equilibrium constant for ligand dissociation from CpMo(CO)2LCOCH3. x=0.14, % fit=5. Data from ref. 73.

(qq) Log of the equilibrium constant for ligand addition to Rh2(OAc)4(CH3CN)2. x=0.73, % fit=23. Data from ref. 77 with AsPh3 omitted.

(rr) Log of the equilibrium constant for substitution of either aniline of p-Br-aniline with a ligand on W(CO)L for aniline, x=0.09, % fit=6. for p-Br-aniline, x=0.13, % fit=13. Data from ref. 77 with AsPh3 omitted.

(ss) Log rate constant for the second order displacement of CO by phosphines from Co(NO)(CO)L in toluene. x=0.26, % fit=6. Data from ref. 58 with nitrogen donors, P(c-hex)3, and P(NMe2)3.

(tt) Log rate constant for the second order displacement of CO from V(CO)6 by PX3 at 25°C in hexane. x=0.22, % fit=6. Data from ref. 60 with P(i-Pr)3, PBu3, and AsPh3 omitted.

(uu) Log rate constant for the first dissociative substitution of CO from Ru(CO)L by another L to form Ru(CO)2L2 in heptane at 60°C. x=0.19, % fit=12. Data from ref. 59 with PEt3, PBu3, and P(c-hex)3 omitted.

(vv) Log rate constant for the second order addition of PX3 to Cp2Fe2(CO)3 in hexane at 25°C. x=0.05, % fit=3. Data from ref. 79 with P(OPh)3, PBu3, and CH3CN omitted.

(ww) Log second order rate constant for exchange of H2O by CH3CN in Ru(η4-bpy)2(PX3)(H2O)2+ in o-dichlorobenzene. x=0.18, % fit=12. Data from ref. 75 with PEt3, Pr, and PBu3 omitted.

(yy) Log rate constants for the reactions of Co(bis(dioximato)cobalt(II)-L) and Co'(bis-(1,2-cyclohexanedionedioximato)cobalt(II)L) with C6H5CH2Br in benzene. for Co, x=0.20, % fit=8. for Co', x=0.13, % fit=7. Data from ref. 80 with PEt3 and PBu3 omitted.

.zz) Log of the second order rate constant for phosphorus nucleophiles toward [CpFe(CO)2(η-C2H4)]+. x=0.26, % fit=9. Data from ref. 81 with P(CH2CH2CN)3 omitted.

(aaa) Log of the second order rate constant for CO substitution by a ligand in Rh(η4-C5Me5)(CO)2 in toluene. x=0.18, % fit=7. Data from ref. 82 with PBu3 and P(i-Bu)3 omitted.
(bbb) Log of the second order rate constant for nucleophilic addition in Mn(CO)3(NO)(6-MeC6H4)⁺ in CH3CN. x=0.09, % fit=4. Data from ref. 83 with nitrogen donors omitted.

(ccc) Log of the second order rate constant of CpIr complexes with CH3I in CD₂Cl₂ at 25°C. For Cp, x=0.07, % fit=3. for Cp⁺, x=0.17, % fit=6. Data from ref. 7b with PEt₃ and P(c-hex)₃ omitted.

(ddd) Log of the second order rate constant between phosphine and C₂H₂I in acetone. x=0.15, % fit=9. Data from ref. 84 with pyridine omitted.

(eee) Same as (bbb), except with Co(η⁵-C₅Me₃)(CO)₂. x=0.11, % fit=7. Data from ref. 82 with PBu₃ and P(i-Bu)₃ omitted.

(fff) Log rate constant for CO dissociation from CpMo(CO)₂L(COMe) in CH₃CN. x=0.10, % fit=9. Data from ref. 69.

(ggg) Log of the second order rate constant for CO insertion for (η-Cp)Fe(CO)LMe⁺ in CH₂Cl₂. x=0.10, % fit=11. Data from ref. 85 with PEt₃ omitted.

(hhh) Log of the second order rate constant for the substitution of CO for CH₃CN in CpFe(COMe)L(CH₃CN). x=0.36, % fit=20. Data from ref. 86 with PEt₃, P(i-Pr)₃, P(i-Bu)₃, and P(c-hex)₃ omitted.

(iii) Log of the second order rate constant for reaction of Ru₆C(CO)₁₇ with nucleophiles in chlorobenzene. x=0.35, % fit=7. Data from ref. 63 with P(O-i-Pr)₃ and PBu₃ omitted.

(jj) Log of the first order rate constant of the dissociation of a ligand in [(CO)₄Mo(µ-PET₂)₂Mo(CO)₃L] in decalin. x=0.13, % fit=21. Data from ref. 87 with PBu₃ omitted.

(kkk) Log of the second order rate constant for the addition of phosphorus nucleophiles to Fe(CO)₃(C₇H₈)⁺ in acetone at 20°C. x=0.35, % fit=9. Data from ref. 74.

(lll) Log of the second order rate constant for the substitution of 5-aminoquinoline with ligand in [PtPh₂CO(5-AQ)] in toluene at 25°C. x=0.36, % fit=12. Data from ref. 68 with P(i-Pr)₃ and P(t-Bu)₃ omitted.

(mmm) Log of the second order rate constant for the addition of nucleophiles to (µ₂-H)₂Os₃(CO)₁₀ in heptane at 30°C. x=0.27, % fit=8. Data from ref. 88 with P(OPh)₃, P(NMe₂)₃, P(t-Bu)₃, P(c-hex)₃, P(benzyl)₃, and AsPh₃ omitted.

(nn) Log of the axial and equatorial ³¹P relaxation times in CD₂Cl₂. For axial, x=0.02, % fit=5. for equatorial, x=0.02, % fit=4. Data from ref. 89.

(ooo) pKₐ values. x=0.66, % fit=6. Data from ref. 90 with PMe₃ omitted.
0.2 depending on the estimated severity of steric contributions. Acceptors with bulky
donors, for which preliminary fits indicate that steric repulsions do exist, are omitted.
With acceptors that \(\pi\)-backbond, donors other than phosphorus donors are not included
\textit{(vide infra)}.

The \(E_B\) and \(C_B\) parameters for phosphorus donors are reported in Table 2-1. Also
given in Table 2-1 are the weights that reflect their relative certainty based on the number
and type of different acceptor used to determine the parameters. Several of the
phosphines were studied with a very limited number of physicochemical measurements.
The reported parameters for these systems are given low weights in Table 2-1, and the
parameters should be redetermined as more data become available.

\textbf{Results and Discussion}

\textbf{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
parameters in any fit requires that 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 Equation (2-7). 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 \(\sigma\)-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-backbonding acceptor.

A poor fit of only 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 Equation (2-7). 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 correlation 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 θon, the cone angle above which steric repulsion becomes operative in the system.
ECW 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 Equations (2-5) and (2-6) 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 Equations (2-5) and (2-6) 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$^{30}$ when the $\Delta E^X$ and $\Delta C^X$ substituents were used to analyze the phosphine systems of Table 2-2? 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\textsubscript{B}/E\textsubscript{B} ratio in a data fit also apply to fits to Equation (2-7) or to any basicity scale. 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\textsubscript{A} and C\textsubscript{A} values that provide good data fits. Considerable error could result in the E\textsubscript{A} and C\textsubscript{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\textsubscript{B}/E\textsubscript{B} ratios. At worst, if bonding contributions from effects other than \sigma bond formation are accommodated in determining the minimum, the resulting E\textsubscript{A} and C\textsubscript{A} parameters are meaningless.

**Determining the Existence of \pi-Backbonding**

Acceptors in which \pi-backbonding is expected (e.g., spectral shifts of Ni(CO)\textsubscript{3}PX\textsubscript{3}) gave good correlations using the same phosphorus donor parameters as those for acceptors in which only \sigma–bond interactions are involved (e.g., enthalpies of reaction of donors with CF\textsubscript{3}SO\textsubscript{3}H and Al\textsubscript{2}(CH\textsubscript{3})\textsubscript{6}). The data fits for acceptors that can \pi-back-bond are restricted to phosphorus donors while those with acceptors that only \sigma-bond may include phosphines, phosphites, sulfides, amines, pyridines, ethers, etc.

Equations can be derived to show that such a result is possible if the \pi-acceptor properties of the phosphines and phosphites, E\textsubscript{A} and C\textsubscript{A}, decrease proportionately with increasing \sigma-donor strength, E\textsubscript{B} and C\textsubscript{B}. Equations (2-8) and (2-9), where k and k' are proportionality constants, give such a relationship.

\[
E_{\text{A}}^* = E_{\text{A}}^\infty - kE_B
\] (2-8)
The $E_{A}^{\infty}$ and $C_{A}^{\infty}$ terms refer to the $\pi$-acceptor contributions of a phosphorus donor with no $\sigma$-donor strength. When Equation (2-1) or (2-7) is fit to a data set that contains a $\pi$-backbond contribution, the resulting parameters, $E_{A}^{\ast \text{FIT}}$, $C_{A}^{\ast \text{FIT}}$, and $W^{\text{FIT}}$, for the $\pi$-backbonding acceptors are given by Equations (2-10), (2-11), and (2-12). The $E_{B}^{\text{IM}}$ and $C_{B}^{\text{IM}}$ terms represent the electrostatic and covalent backbond-forming tendencies of the metal. The correlation parameters, $E_{A}^{\ast \text{FIT}}$, $C_{A}^{\ast \text{FIT}}$, and $W^{\text{FIT}}$ are difficult to interpret because the separate contributions from $\pi$- and $\sigma$-effects in Equations (2-10) - (2-11) cannot be separated.

\[
E_{A}^{\ast \text{FIT}} = E_{A}^{\ast} - kE_{B}^{\text{IM}} \tag{2-10}
\]

\[
C_{A}^{\ast \text{FIT}} = C_{A}^{\ast} - k'C_{B}^{\text{IM}} \tag{2-11}
\]

\[
W^{\text{FIT}} = W + E_{A}^{\infty}E_{B}^{\text{IM}} + C_{A}^{\infty}C_{B}^{\text{IM}} \tag{2-12}
\]

In these instances, the value of the correlation of the physicochemical property is to detect donor contributions other than $\sigma$ bond strength.

A good data fit to Equation (2-7) will result for acceptors that $\pi$-backbond as long as the same proportionality constants in Equations (2-8) and (2-9) 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 Equation (2-7) will result for acceptors that only $\sigma$-bond, but not for acceptors that also $\pi$-back-bond.
The ECW Interpretation of Phosphine Enthalpies

Several enthalpy changes of reactions and enthalpies of activation have been reported for phosphorus donors. Because 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 Al₂(CH₃)₆ adducts are important data for they include seventeen 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 (-ΔH = -8.5 kcal mol⁻¹) and corresponds to one-half the enthalpy of dissociation of the dimer in solution. Steric effects are evident in the Et₂O and Et₃N adducts. The correlation is illustrated graphically in Figure 2-1a.

The enthalpies of dissociation of phosphorus donors from bis (2,4-dimethylpentadienyl) titanium, Cp₂Ti, are fit very well to Eₐ* = -9.10, Cₐ* = 0.83, W = 13.13 (r² = 0.99, F = 4440) of Equation (2-7). χ is a positive ΔH and as a result, a positive parameter is endothermic. W has the wrong sign for association of THF after the phosphorus ligand is displaced. The W sign arises from changes upon protonation of the metal-phosphorus ligand Eₐₐ Eₐ B and Cₐₐ Cₐ B terms of Equation (2-12) and indicates a π-back-bond 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 (C₂H₅)₃N] reacting with CF₃SO₃H were measured 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 (r²=0.99, F=25000) with an average deviation
Figure 2-1. Calculated and experimental enthalpies of reaction for (a) [Al(CH₃)₃]₂ (■), with Et₂O and Et₃N deviating, and (b) the protonation of CpIr(CO)PR₃ (△), with P(c-hex)₃ deviating.
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\(_3\)H in 1,2 dichloroethane were fit earlier for five reported\(^{50b,53a}\) phosphines. Subsequently, the number of phosphines has increased\(^{53b}\) to eleven. ECW analysis of the larger data set still gives an excellent fit (\(r^2=0.9\)) as illustrated in Figure 2-1b. P(c-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\(_3\)SO\(_3^+\) in the product. The large exothermic W value is not anticipated in view of the CF\(_3\)SO\(_3\)H/phosphine fit. In this case the W corresponds to the \(E_A^{no}E_B^{nM}\) and \(C_A^{no}C_B^{nM}\) terms of Equation (2-12). The enthalpies\(^{53b}\) 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 [\(\eta^1-C_5H_7Ni(CH_3)\)]\(_2\) 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 2-2. Earlier analysis of this system required the removal of PPh\(_2\)Et and P(benzyl)\(_3\) whose improved parameters now fit. Both P(C\(_6\)H\(_5\))\(_3\) and P(OPh)\(_3\) had enthalpies smaller than predicted by ECW and were omitted from the fit. Bulky phosphines like P(i-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
Figure 2-2. Calculated and experimental enthalpies of reaction of \([\text{Ni}(\eta^1\text{-C}_3\text{H}_7\text{CH}_3)]_2\) (■), with PPh₃ and P(OPh)₃ deviating.
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-backbonding, 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-backbond stabilization contribution in this system, i.e., W includes the $E_A^{\kappa}E_B^{\kappa M}$ and $C_A^{\kappa}C_B^{M}$ terms of Equation (2-12).

The average deviation of calculated and experimental enthalpies in all the enthalpy correlations in Table 2-2 is 0.2 kcal mol$^{-1}$ or less. When large % fits (see the footnotes to Table 2-2) 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 category provide excellent correlation statistics but the number of phosphines studied are limited. The results of typical associative reaction correlations are shown in Figure 2-3 and include Co(NO)(CO)$_3$ ($r^2=0.99$, $F=824$), V(CO)$_6$ ($r^2=0.96$, $F=26.8$), and Ru$_6$C(CO)$_{17}$ ($r^2=0.98$, $F=65.5$).

The enthalpies of activation for displacing CO with phosphine in toluene solvent by a mechanism first order in Co($\eta^5$-C$_3$H$_4$CO$_2$Me)(CO)$_2$ and phosphine are reported for twelve phosphines. Large deviations occur for the six phosphines that contain two or
Figure 2-3. Calculated and experimental activation enthalpy for (a) Ru₆C(CO)₁₇ (■) and (b) CoNO(CO)₃ (Δ).
more aromatic substituents. While these ligands have large cone angles, steric effects are not indicated in this system because P(c-hex)₃ is well behaved in the correlation (Figure 2-4) when aromatic phosphines are omitted (r²=0.92, F=44.3). Aromatic solvents are known¹²¹ 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, νCO, for the (η⁵-C₅H₄CO₂Me)Co(CO)L adducts of all the phosphines studied give the excellent correlation shown in Figure 2-4 (r²=0.99, F=280). This is a meaningful result because if π solvent interactions are the cause of the activation enthalpy deviations, they are not expected to have a significant effect on νCO.

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 ΔH¹ value with any donor. This is found in all four systems. Thus, the metal-phosphine interaction involves mainly σ donation. The activation enthalpies for the CO dissociation from Ru(CO)₄PX₃ for seven phosphorus ligands are poorly fit (r²=0.39) with an average deviation of 1.80 kcal mol⁻¹. The fit still was not satisfactory with the bulky P(t-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)₄PX₃ 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(CH₃)₃ enthalpies to ECW,¹²¹ indicate steric repulsion is absent with
Figure 2-4. Activation enthalpies ($\Delta$) and $(2034-v_{\text{CO}})/10$ (■) for Cp(CO$_2$Me)Co(CO)$_2$. The W value is 2034 cm$^{-1}$. 
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 $\theta$ is the donor cone angle, $\theta_{ON}$ the cone angle for the onset of repulsion, and $s$ is the coefficient indicating the severity of the effect. The Kronecker delta, $\delta$, is zero when $\theta < \theta_{ON}$ and 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.91

The three smallest cone angle ligands for Ru(CO)$_4$PX$_3$ are fit to ECW. Adding any other fourth ligand gives an unsatisfactory fit. The plot of the deviations of the excluded donors from the three phosphorus donor fit versus $\theta$ gives an intercept whose magnitude is $s\theta_{ON}$ (dev = $s\theta - s\theta_{ON} = s\theta$ - intercept). A $\theta_{ON}$ value of 128° results from the slope and intercept. This value is substituted into Equation (2-13), 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.

$$\Delta \chi = E_A^*E_B + C_A^*C_B + W + s(\theta - \theta_{ON})\delta$$  \hspace{1cm} (2-13)

The solid line of Figure 2-5 shows the fit of the calculated activation enthalpy from the $E$, $C$, and steric term correlation to the experimental values, and the dashed line and triangles show the fit of only the ECW 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
Figure 2-5. ECW (Δ) and ECW + cone angle fits (■) for the first-order dissociative activation enthalpy of CO from Ru(CO)$_4$PX$_3$. 
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-\((\text{CH}_3\text{Pt}[\text{P(}\text{CH}_3\text{)}_2\text{C}_6\text{H}_5\text{)]_2\text{L})^+(\text{PF}_6)^-\) complexes\(^92\) to ECW were obtained in this and the earlier study. After removal of nitrogen donors and bulky phosphines \((\theta > 160^\circ)\), the \(r^2\) 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, Equation (2-13), does not produce a satisfactory fit even with \(\theta_{\text{ON}}\) equal to zero. Large contributions from steric effects are evident, but other complications exist in this data.

**Interpretation of Spectral Shifts and Redox Potentials**

The \(^{13}\text{C}\) chemical shifts of \(\text{Ni(CO)}_3\text{PX}_3\) relative to \(\text{Ni(CO)}_4\) and the CO stretching frequencies of these adducts are fit very well with \(E_B\) and \(C_B\) \((x = 0.09\) and 1 respectively). Decreasing the formal charge on nickel by a more basic \(\sigma\) bonding phosphine increases Ni-CO \(\pi\)-backbonding which in turn decreases the C-O stretching frequency. On the other hand, \(\pi\)-backbonding 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 \(\pi\)-backbonding to the phosphines. The excellent data fit supports compensating \(\sigma\)- and \(\pi\)-effects in the complexes, Equations (2-10) and (2-11). As expected, \(W\), the shift for a donor with \(E_B=C_B=0\) is larger than any phosphine adduct frequency. However, expected \(\pi\)-backbonding makes interpretation of \(E_A^*,\ C_A^*\) and \(W\) difficult and limits their application to phosphines.
The qualitative interpretation of the trends in $\delta^{13}\text{C}$ of Ni(CO)$_3$PX$_3$ is complicated by changes in the $^{13}\text{C}$ electron population from $\sigma$ and $\pi$ effects as well as the influence of those effects on ground and excited state energies. The more basic phosphine gives rise to a larger $^{13}\text{C}$ shift. The excellent data fit again indicates that compensating $\pi$ and $\sigma$ changes exist, i.e., Equations (2-10) and (2-11) apply. This compensation permits the use of $^{13}\text{C}$ of Ni(CO)$_3$PX$_3$ as a one parameter scale of phosphine $\sigma$-basicity for physicochemical properties with a $C_A^*/E_A^*$ ratio of $\sim 0.1$. The same trends as in Ni(CO)$_3$PX$_3$ are also noted in the fit of the $^{13}\text{C}$ chemical shifts of Cr(CO)$_3$PX$_3$, W(CO)$_3$PX$_3$ and Mo(CO)$_3$PX$_3$ adducts. The $^{13}\text{C}$ shift has been reported for Cr(CO)$_3$py and W(CO)$_3$4-CH$_3$py. In both instances, the pyridine donor had to be omitted from the fit because the $^{13}\text{C}$ calculated from $E_A^*$, $C_A^*$ and W is considerably larger ($\sim 5$ ppm) than measured. This deviation provides strong support for $\pi$-back-bond contributions to the shifts and, as one would expect, indicates that the same $k$ and $k'$ cannot be used in Equations (2-10) and (2-11) for both phosphines and pyridines.

The CO stretching frequencies for Ru(CO)$_4$PX$_3$, $\eta^5$-Cp and $\eta^5$-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.

Fits of the reduction potentials for series of 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 $\pi$-backbonding 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.

**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 log 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, 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. 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 2-2, and the reader is referred to the earlier literature 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 an $s(\theta - \theta_{ON})\delta$ 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 an $s(\theta - \theta_{ON})\delta$ term. Clearly, entropic and enthalpic steric effects would require different parameters. Rather than trying to parameterize 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.

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 2-2 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.

Comparison of ECW and Literature Analyses of Phosphine Reactivity

Typically, phosphorus donor reactivity has been analyzed with a one parameter basicity scale, $\chi$, 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 $\chi$ 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 2-2). If the $\theta$ term paralleled covalency, $\chi/\theta$ would fit phosphorus donor reactivity as well as ECW. A recent “examination” of the ECW parameters with QALE claimed$^{91}$ that $E_B$ and $C_B$ are linear combinations of $\chi$ and $\theta$ with a small contribution from $E_a$, “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\textsuperscript{91} that $E_B$ and $C_B$ are linear combinations of mostly $\chi$ and $\theta$ parameters, will be tested using enthalpies of reaction and activation. Enthalpies best measure bond strengths and avoid a linear free energy assumption.\textsuperscript{12a} For enthalpic systems, ECW uses only two parameters to fit the measurements, so the two QALE parameters $\chi$ and $\theta$ were used in the comparison with the “minor $E_{ar}$” contribution\textsuperscript{91} 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$'$$_2$Ti and [\eta-C$_5$H$_7$Ni(CH$_3$)]$_2$, and enthalpies of activation for associative CO substitution by phosphorus donors in CpCO$_2$MeCo(CO)$_2$ were fit to $\chi$ and $\theta$ to test their “equivalency” to the ECW fits described above. To afford a direct comparison, those donors eliminated from the ECW fit because of steric effects were also omitted in the QALE($\chi,\theta$) fits. The enthalpies of protonation of phosphines by CF$_3$SO$_3$H are fit\textsuperscript{*} with an $r^2$ of 0.98 using QALE($\chi,\theta$). A poor $\chi/\theta$ fit results for [\eta-C$_5$H$_7$Ni(CH$_3$)]$_2$ ($r^2$ is 0.81 with $c_\chi$ = 0.41, $c_\theta$=-0.068 and an intercept of 32.0). The Cp$'$$_2$Ti fit is not much better ($r^2$ is 0.86 with $c_\chi$=-0.52 $c_\theta$=-0.39, and an intercept of 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 an intercept of 42.4). The ($\theta,\chi$) fit of the enthalpies of activation for CO substitution by phosphine in Co(\eta$^5$-C$_3$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 an intercept of 19.2). ECW correlated all these measurements to at least an $r^2$ of 0.9. Clearly, the two parameter sets are not equivalent and the success of ECW

\textsuperscript{*} In Equation 15 of a recent QALE article,\textsuperscript{91} 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 a previously reported set of $E_B$ and $C_B$ for phosphines) should have been $E_A^*$=7.83, $C_A^*$=6.17 and $W$=-6.22 and the $r^2$ is 1.0. The current phosphine parameters give slightly different values.
indicates that the \( \theta \) term is added to \( \chi \) in an inadequate attempt to compensate for changes in the covalency of the acceptor from that of the one parameter \( \chi \) scale.

Our earlier report detailing the inadequacy of one parameter basicity scales\(^{19a}\) predicts that the next step to be taken to improve data fits is to divide the data set into subsets that limit the \( C_{\text{B}}/E_{\text{B}} \) ratios of the donors. As mentioned above, this leads to great correlations with poorly defined parameters.\(^{21,47b} \) When \( \chi/\theta \) give 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 \( \theta \), and treat only \( C_{3v} \) phosphines.\(^{24a,91,93,94,95} \) 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,\(^{27} E_{sr} \), and steric thresholds,\(^{95} \) to make these subsets conform and fit phosphine reactivity trends for many acceptors.\(^{93} \)

ECW is criticized\(^{91} \) with the obvious claim that no two parameters will correlate all phosphine reactivity. It is emphasized\(^{12a} \) that when Equation (2-7) 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 \textit{a priori}. To quote\(^{94} \) “we do not understand the nature of the aryl effect” and “the contributions of \( E_{sr} \) relative to \( \chi \) 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 non-linear 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?”

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 $c_\theta$ steric term usually required in the analyses. The QALE fit of $-\Delta H$ for CF$_3$SO$_3$H to phosphorus donors is excellent, giving fit parameters$^91$ of $\chi = -1.05$, $\theta = -.088$, and $E_{ar} = -1.21$ with an intercept of 51.3. Keeping in mind that $\theta$ is usually ten times larger than $\chi$, a substantial steric effect, $(c_\theta \theta)$, is involved for the enthalpies of protonation by CF$_3$SO$_3$H 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)$_3$PMe$_3$. Front strain steric effects in Brønsted acids are without literature precedent and the QALE conclusion$^91$ that the coefficients from $\chi/\theta$ analyses 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 $\chi$ for increasing basicity, and increasing values of $\theta$ for increasing steric repulsion, the ratio of the coefficients for fitting 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 \([\eta-\text{C}_5\text{H}_5\text{Ni(CH}_3)]_2\) and apparently have an unexplained meaning that is different than the contemporary view. These unaddressed\textsuperscript{24,91} 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 2-1 whose weights are 0.7 or more, an excellent correlation of \(\chi\) to \(E_B\) and \(C_B\) is found \((r^2=0.98, F=606\) and \(r=1.0)\). This is expected because ECW gives an excellent fit to the frequency shifts used to determine the \(\chi\) parameters. The \(C/E\) ratio for the \(\chi\) fit is 0.20 and that for \(\nu \text{Ni(CO)}_3\text{L}\) is 0.23. Any acceptor with a \(C_A/E_A\) ratio of 0.2 will correlate to ECW and to \(\chi\) without need for a linear steric term even for different size acceptors. Next, the \(\theta\) term was fit to \(E_B\) and \(C_B\). When all of the donors used in the \(\chi\) 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 \(\theta\) for these combinations of donors. The omission of all but alkyl-substituted phosphines in the \(\theta\) fit led to the excellent correlation \((r^2=0.93)\) given in Equation (2-14).

\[
\theta_{\text{CALC}} = 399.7\ E_B + 85.1\ C_B - 446.9
\] (2-14)

The \(\theta\) values calculated using Equation (2-14) are plotted vs. literature values in Figure 2-6 with the solid line drawn for the alkyl phosphines. When only alkyl phosphines are studied, \(\chi\) and \(\theta\) will fit data as well as \(E_B\) and \(C_B\) but parameter meaning will differ. The
points in Figure 2-6 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 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 2-6, 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”^{27} 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^{91} of QALE and ECW. Figure 2-6 suggests that when a large number of donors are studied another effect, the phosphite effect proposed in earlier QALE reports,^{73} 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 2-6 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 2-6, an equation similar to Equation (2-14) 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 many possible donor
Figure 2-6. Donor choices for which the cone angle, $\theta$, is linear with $E_B$ and $C_B$. The solid line is a fit of the aliphatic-substituted phosphines to Equation (2-14). Phosphines on the line will fit data to $\chi$ and $\theta$ as well as to $E_B$ and $C_B$. Points marked with $O$ are aliphatic-substituted phosphines, those with $X$ are for phosphines with one aromatic group, those with $\blacksquare$ are for phosphines with two aromatic groups, those with $\Delta$ are phosphines with three aromatic groups, and those with $\blacksquare$ are for phosphites. The dashed lines represent arbitrary donor selections that would also be linear to $E_B$ and $C_B$. 
selections that can have a line drawn through them are illustrated by the dashed lines in Figure 2-6. For these selections, good fits to $\chi$ and $\theta$ 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 $\theta$ deficiency. The line drawn with large dashes will not require a phenyl effect but will need a $\theta_{ON}$ for large cone angles. Figure 2-6 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 $\chi$ and $\theta$ 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 $E_{st}$ contribution." 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 non-linear free energy data sets? Is there meaning in an unprecedented 10 kcal mol$^{-1}$ steric repulsion contribution toward the proton of CF$_3$SO$_3$H when there is none for Ni(CO)$_3$L? 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 coefficients from QALE fits and comparison of these coefficients for different acceptors, more questions will arise about the procedure. Finally, an ECW analysis of $\theta$ indicates that the meaning of the extra terms of QALE are
to compensate for the failed attempt of \( \theta \) to accommodate the widely accepted differences in covalency (softness) that exist in different acceptors.\(^{12a}\)

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 \( E_{\text{tr}} \) parameter, suggests meaningless correlations with only limited value for use in interpolative predictions.
CHAPTER 3

EXTENSION OF THE ELECTROSTATIC-COVALENT MODEL TO 2:1 ADDUCTS

Introduction

Work from this laboratory\(^{12a}\) has shown the utility of the Electrostatic-Covalent Model (ECW), Equation (3-1), for the interpretation of a wide range of physicochemical properties such as enthalpies of interaction, NMR, UV and IR shifts, \(E_{1/2}\) values, rate constants, and activation enthalpies.

\[
\Delta \chi = E_A E_B + C_A C_B + W \tag{3-1}
\]

\(\Delta \chi\) is the magnitude of the physicochemical property (with units of energy), \(E_A\) and \(C_A\) reflect the electrostatic and covalent properties of the acceptor, and \(E_B\) and \(C_B\) parallel the electrostatic and covalent properties of the donor. \(W\) is the value of the physicochemical property when \(E_B=C_B=0\), and as an intercept it contains any contribution to a data set that is independent of the base.

Recent additions (Chapter 2 and reference 30) to the ECW database have significantly increased the relevance of the model to organometallic chemistry by reporting \(E_B\) and \(C_B\) parameters for phosphines and phosphites. The electrostatic and covalent phosphorus donor parameters are determined from data sets that are free of steric effects. When deviations in ECW correlations indicate a steric effect, a procedure is reported (Chapter 2) to confirm these effects quantitatively by adding a cone angle...
term, $s(\theta-\theta_{ON})$, to Equation 3-1. Here $\theta$ is Tolman's cone angle, and $\theta_{ON}$ is the cone angle above which steric effects become operative. ECW analyses indicate that steric effects play a greatly diminished role in understanding phosphine reactivity than suggested by cone angle, $\theta$, and one parameter basicity, $\chi$, models (Chapter 2 and reference 91).

The overestimate of steric contributions to reactivity with $(\chi/\theta)$ is attributed to the failure of any one parameter basicity scale to allow for variation in the covalency (softness) of the different acceptors. In effect, $\theta$ is used as an improper parameter for covalency and in those instances where a successful $(\chi/\theta)$ correlation does result, the acceptor fit parameters are without meaning. In the many instances when $(\chi/\theta)$ correlations fail, new parameters are invented, such as the aryl effect ($E_{ar}$).27

Enthalpies for the reactions of two (or more) donors with a single acceptor or physicochemical properties of adducts with two donors varied usually only allow measurement of the total change for coordinating both donors. Equation 3-1 is not expected to correlate total enthalpies for 2:1 donor-acceptor adduct formation. In the first step of this type of reaction, each base forms a different 1:1 adduct which behaves as an acceptor with different $E_A$ and $C_A$ parameters in the second step to form the 2:1 adduct (vide infra).

A model has been derived96,97 for prediction of the enthalpies of reaction of two bases with metal-metal bonded carboxylates of the general form $M_2(RCO_2)_4$. This equation is extended to the physicochemical properties for 2:1 adducts of acceptors in this article. In order to correlate properties for 2:1 adducts with the ECW model, the two steps are considered separately, as shown in Equations (3-2) and (3-3), where $A$ is the acceptor and $B$ is the same donor for both steps.
A + B → AB \hspace{1cm} (3-2)

AB + B → AB₂ \hspace{1cm} (3-3)

The enthalpy for step one [Equation (3-2)] is given in Equation (3-4), for reactions where \( W=0 \).

\[-\Delta H₁ = EₐEₜ + CₐCₜ \] \hspace{1cm} (3-4)

After one donor molecule has been added, the \( Eₐ \) and \( Cₐ \) parameters will change for the coordination of the second donor molecule. Strong donors are expected to produce a weaker acceptor for the second step than weak donors because of the partial positive charge remaining on the acceptor center. Relationships that express this behavior are given in Equations (3-5) and (3-6), where \( Eₐ^{2nd} \) and \( Cₐ^{2nd} \) are the acceptor parameters for the 1:1 adduct that reacts in the second step and \( k \) and \( k' \) are proportionality constants characteristic of the acceptor that indicate the extent to which base coordination, \( kEₜ \) and \( k'Cₜ \), modifies the acidity for the second step.

\[ Eₐ^{2nd} = Eₐ - kEₜ \] \hspace{1cm} (3-5)

\[ Cₐ^{2nd} = Cₐ - k'Cₜ \] \hspace{1cm} (3-6)

Therefore, the enthalpy of reaction for the addition of the second donor to \( AB \) is given in Equation (3-7) where \( Eₐ^{2nd} \) and \( Cₐ^{2nd} \) have different values for each base.

\[-\Delta H₂ = Eₐ^{2nd}Eₜ + Cₐ^{2nd}Cₜ = (Eₐ - kEₜ)Eₜ + (Cₐ - k'Cₜ)Cₜ \] \hspace{1cm} (3-7)

Combining Equations (3-4) and (3-7) gives the total enthalpy for the two steps in Equation (3-8). Using the reported (Chapter 2) \( Eₜ \) and \( Cₜ \) parameters for the donor molecules, a least squares minimization routine can be used to calculate the best acceptor \( Eₐ \), \( Cₐ \), \( k \), and \( k' \) parameters for the total enthalpy.

\[- \Delta Hₜ = -(\Delta H₁ + \Delta H₂) = 2EₐEₜ - kEₜ^2 + 2CₐCₜ - k'Cₜ^2 \] \hspace{1cm} (3-8)
Because four unknowns need to be determined, a large data set of donors with widely varying $C_B/E_B$ ratios must be studied to obtain a satisfactory solution for the unknowns.

When the 2:1 discussion for $\sigma$ acceptors is extended to acceptors that can undergo $\pi$-back bonding, the $\sigma$-$\pi$ relationships shown in Equations (2-10) and (2-11) are expected to apply for phosphorus donors. Correlations can result for phosphorus donors, but the parameters will contain $\pi$ and $\sigma$-effects that cannot be resolved at present.

The extension of the enthalpy discussion given above to physicochemical properties that arise from coordination of two donors lead to Equation (3-9).

$$\Delta \chi_T = \Delta \chi_1 + \Delta \chi_2 = 2 \ E_A E_B - k E_B^2 + 2 \ C_A C_B - k'C_B^2 + W$$

In this article, successful correlations of 2:1 adduct properties are reported, and the interpretation of the correlations are discussed.

For a given acceptor, the acid in the second step will have an acidity that varies depending on the base attached. As a result there is no average acid parameter that can fit the total enthalpy. All reported literature analyses of 2:1 adducts, tacitly assume that the two steps can be described with an average acceptor parameter when the total physicochemical property is fit to a single acceptor parameter. Before any set of donor parameters can be meaningfully applied to the analysis of 2:1 adducts, it is essential to illustrate mathematically how the equation employed takes into account the changes described above for the 2:1 adducts. The random fitting of 2:1 data to a set of parameters derived for 1:1 adducts may yield a good fit but will lead to meaningless acceptor parameters unless a derivation is provided to accommodate two different acceptors in each step.
Basicities of bidentate donors have not been treated with ECW. Coordination of the first donor atom is treated with Equation (3-1) using constant E_B and C_B values characteristic of the donor reacting as a monodentate. As with 2:1 acceptors, coordination to the first donor atom of the bidentate to an acceptor modifies the donor properties of the second donor atom to a different extent for different acceptors. There is no constant E_B and C_B for the second step if acceptor coordination has an inductive effect that influences basicity. In this article, equations are derived for the analysis of these systems.

Calculations

The nitrogen donor E_B and C_B parameters used in these analyses are listed in Table 3-1. E_B and C_B values for phosphorus donors are listed in Table 2-1. Physicochemical measurements, listed in Table 3-2, were analyzed using the NCSS 5.X (Kaysville, UT) statistical software. Regression analyses were done with the multiple regression module of the software. The measured values for the donors were weighted as in Chapter 2 for phosphorus donors and reference 12a for all other donors. If one uses E_B and C_B as two of the independent variables [as in Equations (3-8) and (3-9)], their coefficients from the regression are 2E_A and 2C_A, respectively, and must be divided by 2 to give the E_A and C_A values. The other two independent variables that are used, E_B^2 and C_B^2, will give coefficients whose values are -k and -k', respectively. Values in Table 3-2 are E_A, C_A, k, and k' and can be substituted directly into Equations (3-8) and (3-9).

To arrive at the reported fits, any system is removed from the data set if it deviates by 2.5 times the average deviation, and the fit is rerun. The fit is repeated until all such systems are removed, with systems previously removed added back if they subsequently
Table 3-1. $E_B$ and $C_B$ parameters for nitrogen donors

<table>
<thead>
<tr>
<th>no.</th>
<th>donor</th>
<th>wt*</th>
<th>$E_B$</th>
<th>$C_B$</th>
<th>$C_B/E_B$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>N(CH₃)₃</td>
<td>1.0</td>
<td>1.21</td>
<td>5.61</td>
<td>4.6</td>
</tr>
<tr>
<td>2</td>
<td>NH(C₂H₅)₂</td>
<td>0.2</td>
<td>1.22</td>
<td>4.54</td>
<td>3.7</td>
</tr>
<tr>
<td>3</td>
<td>N(C₂H₅)₃</td>
<td>1.0</td>
<td>1.32</td>
<td>5.73</td>
<td>4.3</td>
</tr>
<tr>
<td>4</td>
<td>NH₃</td>
<td>1.0</td>
<td>2.31</td>
<td>2.04</td>
<td>0.9</td>
</tr>
<tr>
<td>5</td>
<td>piperidine</td>
<td>0.2</td>
<td>1.44</td>
<td>4.93</td>
<td>3.4</td>
</tr>
<tr>
<td>6</td>
<td>pyridine</td>
<td>1.0</td>
<td>1.78</td>
<td>3.54</td>
<td>2.0</td>
</tr>
<tr>
<td>7</td>
<td>3-CH₃-pyridine</td>
<td>1.0</td>
<td>1.81</td>
<td>3.67</td>
<td>1.9</td>
</tr>
<tr>
<td>8</td>
<td>4-CH₃-pyridine</td>
<td>1.0</td>
<td>1.83</td>
<td>3.73</td>
<td>2.1</td>
</tr>
<tr>
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<td>1.0</td>
<td>1.80</td>
<td>4.21</td>
<td>2.3</td>
</tr>
<tr>
<td>10</td>
<td>NH₂(CH₃)</td>
<td>1.0</td>
<td>2.16</td>
<td>3.12</td>
<td>1.4</td>
</tr>
<tr>
<td>11</td>
<td>quinoline</td>
<td>0.5</td>
<td>2.28</td>
<td>2.89</td>
<td>1.3</td>
</tr>
<tr>
<td>12</td>
<td>NH₂(C₂H₅)</td>
<td>0.7</td>
<td>2.34</td>
<td>3.30</td>
<td>1.4</td>
</tr>
</tbody>
</table>

(a) Weights are those assigned in reference 12a.
deviate by less than 2.5 times the average deviation. Reported donors that are omitted from the final fits are discussed in the text and listed in Table 3-2.

For adduct formation enthalpies involving a series of bases forming 2:1 adducts, Equation (3-8) is solved for the acceptor parameters $E_A$, $C_A$, $k$, and $k'$. Other physicochemical properties, $\Delta \chi$, are fit to Equation (3-9) where constant energy terms or intercepts are represented with a $W$ term. Care must be taken to consider all of the independent energy contributions to a reaction in fitting data to equations and in interpreting fit parameters. The energy components of each reaction or spectral shift are described in the results and discussion section.

Some of the systems discussed in this paper were analyzed using a steric onset term, $s(\theta - \theta_{ON})\delta$. This term, described above, was added to the multiple regression analyses by the following procedure derived earlier (Chapter 2). The larger cone angle systems are removed systematically until a good fit results. A plot of the deviations from this fit versus $\theta$ gives a line whose slope is $s$ and whose intercept at zero deviation is $s\theta_{ON}$.

Results and Discussion

Considerably more information about the influence of electronic, $\pi$-back bonding, and steric effects on physicochemical properties can result when the enthalpies of the individual steps of 2:1 adducts are determined separately. The first step can be fit to Equation (3-1) and the second step used to define $k$ and $k'$. Unfortunately, the chemistry usually does not permit this step resolution, and the total change for both steps is all that can be measured. The results from fits to Equation (3-9) of several reported data sets are given in Table 3-2.
Table 3-2. Acceptor Parameters for 2:1 Adduct Formation

<table>
<thead>
<tr>
<th>system</th>
<th>E_A</th>
<th>C_A</th>
<th>W</th>
<th>k</th>
<th>k'</th>
<th>num.*</th>
</tr>
</thead>
<tbody>
<tr>
<td>$-\Delta H; \text{Ni(DBH)}$</td>
<td>2.2 ± 2.6</td>
<td>2.5 ± 0.6</td>
<td>-4.9 ± 1.9</td>
<td>-0.1 ± 1.5</td>
<td>0.5 ± 0.2</td>
<td>15 (3)</td>
</tr>
<tr>
<td>$-\Delta H; [\text{RhCl(CO)}]_2$</td>
<td>-46.8 ± 15.8</td>
<td>5.0 ± 1.5</td>
<td>45.0 ± 9.0</td>
<td>-59.0 ± 22.4</td>
<td>1.3 ± 0.5</td>
<td>11 (0)</td>
</tr>
<tr>
<td>$\nu\text{CO}; \text{RhCl(CO)}L_2$</td>
<td>-163.2 ± 24.3</td>
<td>-4.1 ± 2.3</td>
<td>2215 ± 14</td>
<td>-116.1 ± 34.4</td>
<td>4.3 ± 0.8</td>
<td>11 (0)</td>
</tr>
<tr>
<td>$-\Delta H; \text{Fe(BDA)(CO)}_3$</td>
<td>34.2 ± 28.5</td>
<td>-8.3 ± 4.6</td>
<td>50.7 ± 22.2</td>
<td>84.8 ± 47.8</td>
<td>-2.3 ± 1.2</td>
<td>16 (3)</td>
</tr>
<tr>
<td>$\nu\text{CO}; \text{Fe(CO)}_3L_2$</td>
<td>-70.9 ± 23.9</td>
<td>-6.4 ± 5.6</td>
<td>2016 ± 25</td>
<td>-43.0 ± 50.0</td>
<td>1.4 ± 1.2</td>
<td>16 (0)</td>
</tr>
<tr>
<td>$-\Delta H; \text{Mo(NBD)(CO)}_4$</td>
<td>-50.0 ± 2.6</td>
<td>3.9 ± 0.3</td>
<td>57.5 ± 2.8</td>
<td>-38.8 ± 2.3</td>
<td>1.4 ± 0.1</td>
<td>11 (1)</td>
</tr>
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<td>$\nu\text{CO}; \text{Mo(CO)}_4L_2$</td>
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<td>-8.2 ± 0.9</td>
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<td>-1.6 ± 0.4</td>
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<td>$-\Delta H; \text{CpRu(COD)Cl}$</td>
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<td>6.4 ± 1.6</td>
<td>75.3 ± 12.8</td>
<td>-94.8 ± 19.8</td>
<td>2.5 ± 0.5</td>
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<tr>
<td>$\nu\text{CO}; \text{Cp}^*\text{Ru(COD)Cl}$</td>
<td>-67.3 ± 22.6</td>
<td>8.1 ± 2.4</td>
<td>62.1 ± 19.7</td>
<td>-91.6 ± 31.0</td>
<td>3.0 ± 0.7</td>
<td>12 (0)</td>
</tr>
<tr>
<td>$^{13}\text{C}; \text{Ni(CO)}_3L'$</td>
<td>8.4 ± 0.4</td>
<td>1.9 ± 0.1</td>
<td>1841 ± 0.5</td>
<td>-</td>
<td>-</td>
<td>38 (0)</td>
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<td>$^{13}\text{C}; \text{Ni(CO)}_2L_2$</td>
<td>-4.9 ± 8.5</td>
<td>2.4 ± 1.0</td>
<td>185.7 ± 4.2</td>
<td>-17.5 ± 13.6</td>
<td>0.3 ± 0.2</td>
<td>9 (0)</td>
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<tr>
<td>$\nu\text{CO}; \text{Ni(CO)}_3L_2$</td>
<td>-54.7 ± 5.2</td>
<td>-12.4 ± 0.7</td>
<td>2145 ± 5</td>
<td>-</td>
<td>-</td>
<td>29 (0)</td>
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<tr>
<td>$\nu\text{CO}; \text{Ni(CO)}_2L_2$</td>
<td>207 ± 72</td>
<td>-26.3 ± 3.4</td>
<td>2042 ± 39</td>
<td>433.8 ± 115.5</td>
<td>5.3 ± 1.3</td>
<td>13 (4)</td>
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<tr>
<td>$\nu\text{CO}; \text{Ir(CO)(Cl)L}_2$</td>
<td>13.5 ± 47.0</td>
<td>-3.1 ± 13.9</td>
<td>1977 ± 29</td>
<td>20.1 ± 60.8</td>
<td>0.2 ± 1.3</td>
<td>15 (2)</td>
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<tr>
<td>$\log k; \text{Ir(CO)(Cl)L}_2$</td>
<td>-11.2 ± 4.9</td>
<td>7.6 ± 2.0</td>
<td>-34.3 ± 4.5</td>
<td>-31.6 ± 13.9</td>
<td>1.6 ± 0.4</td>
<td>13 (2)</td>
</tr>
<tr>
<td>$\log k; \text{Ir(CO)(Cl)L}_2-MeI$</td>
<td>-7.5 ± 2.6</td>
<td>4.8 ± 1.0</td>
<td>-22.4 ± 4.7</td>
<td>-21.5 ± 7.3</td>
<td>1.0 ± 0.2</td>
<td>8 (1)</td>
</tr>
<tr>
<td>$\log k; \text{Ir(CO)(Cl)L}_2$</td>
<td>-26.7 ± 8.9</td>
<td>3.1 ± 2.3</td>
<td>9.3 ± 4.9</td>
<td>-38.3 ± 10.3</td>
<td>1.0 ± 0.2</td>
<td>13 (0)</td>
</tr>
<tr>
<td>$\log k; \text{Ir(CO)(Cl)L}_2-H_2$</td>
<td>68.0 ± 34.9</td>
<td>-4.0 ± 2.0</td>
<td>-47.6 ± 23.3</td>
<td>-83.7 ± 43.6</td>
<td>1.9 ± 0.9</td>
<td>6 (0)</td>
</tr>
<tr>
<td>$\log k; \text{Ir(CO)(Cl)L}_2-O_2$</td>
<td>-43.4 ± 5.2</td>
<td>11.3 ± 1.9</td>
<td>-26.6 ± 7.5</td>
<td>-86.1 ± 13.1</td>
<td>2.6 ± 0.4</td>
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</tr>
<tr>
<td>$\log k; \text{Ir(CO)(Cl)L}_2$</td>
<td>1.5 ± 2.6</td>
<td>2.4 ± 0.9</td>
<td>-12.4 ± 3.8</td>
<td>-2.4 ± 6.6</td>
<td>0.2 ± 0.2</td>
<td>7 (0)</td>
</tr>
<tr>
<td>$\log k; \text{Ir(CO)(Cl)L}_2$</td>
<td>-44.8 ± 3.6</td>
<td>10.0 ± 2.5</td>
<td>-14.2 ± 5.2</td>
<td>-83.8 ± 9.0</td>
<td>2.4 ± 0.3</td>
<td>7 (0)</td>
</tr>
<tr>
<td>$\nu\text{CO}; \text{Mn}_2(\text{CO})_8L_2$</td>
<td>-129.9 ± 28.9</td>
<td>6.9 ± 7.7</td>
<td>2032 ± 35</td>
<td>-185.1 ± 70.8</td>
<td>3.2 ± 1.5</td>
<td>13 (1)</td>
</tr>
<tr>
<td>$\nu; \text{Mn}_2(\text{CO})_8L_2$</td>
<td>-6.5 ± 1.3</td>
<td>0.4 ± 0.4</td>
<td>30.7 ± 1.5</td>
<td>-8.2 ± 3.2</td>
<td>0.1 ± 0.1</td>
<td>12 (1)</td>
</tr>
<tr>
<td>$\nu\text{CO}; \text{Co}_2(\text{CO})_6L_2$</td>
<td>-70.6 ± 79</td>
<td>-38.4 ± 14.2</td>
<td>2272 ± 55</td>
<td>88.5 ± 153.6</td>
<td>-5.5 ± 3.1</td>
<td>10 (1)</td>
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</table>
Table 3-2—continued

<table>
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<th>System</th>
<th>$E_A$</th>
<th>$C_A$</th>
<th>$W$</th>
<th>$k$</th>
<th>$k'$</th>
<th>Num.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$v; \text{Co}_2(\text{CO})_6\text{L}_2$</td>
<td>-2.4 ± 2.9</td>
<td>-1.2 ± 0.7</td>
<td>35.6 ± 2.6</td>
<td>3.0 ± 6.8</td>
<td>-0.2 ± 0.1</td>
<td>8 (1)</td>
</tr>
<tr>
<td>$\log k; \text{Mo(\text{CO})}_2(\text{PR}_3)_2\text{Br}_2$</td>
<td>-184.1 ± 6.6</td>
<td>18.0 ± 0.9</td>
<td>95.0 ± 2.3</td>
<td>-243.5 ± 10.1</td>
<td>6.7 ± 0.3</td>
<td>8 (1)</td>
</tr>
</tbody>
</table>

(a) The total number of donors (N, P, S, As, etc.) studied. In parenthesis is the number of donors excluded to give the reported correlation.
(b) Enthalpy for the addition of 2 ligands to Ni(diacetyl bisbenzoylhydrazone) in benzene. Data from ref. 98 include protonic donors that may hydrogen bond to the solvent. $r^2=0.98$, $F=155.5$. Phosphorus donors were omitted because of π-back bonding.
(c) Enthalpy for the breaking of the dimer and addition of 2 phosphines to each of the monomers with the release of 2 CO in CH$_2$Cl$_2$ at 30°C. Data from ref. 99. $r^2=0.98$, $F=73.4$.
(d) For this system, the $E_A$ reported here is actually 2 $E_A + kE_{CO}$ and $C_A$ is 2 $C_A + k'C_{CO}$. See text for discussion of these values.
(e) CO stretching frequency in RhCl(\text{CO})(\text{PR}_3)_2 in CH$_2$Cl$_2$. Data from ref. 99. $r^2=0.99$, $F=294.7$.
(f) Enthalpy for the displacement of BDA by 2 ligands in THF at 50°C. BDA=benzylidene acetone. Data from ref. 100. $r^2=0.98$, $F=111$. AsPh$_3$ was omitted for incomplete complexation and P(i-C$_3$H$_7$)$_3$ and P(c-hex)$_3$ for steric effects.
(g) CO stretching frequency in Fe(\text{CO})$_2$\text{L}_2 in THF. Data from ref. 100. $r^2=0.98$, $F=130$.
(h) Enthalpy for the displacement of NBD by 2 ligands in THF at 30°C. NBD=norbornadiene. Data from ref. 101. $r^2=0.99$, $F=864.5$. P(OPh)$_3$ was omitted.
(i) CO stretching frequency in Mo(\text{CO})$_3$\text{L}_2 in THF. Data from ref. 101. $r^2=0.98$, $F=92.5$. P(OPh)$_3$ was omitted.
(j) Enthalpy for the displacement of COD by 2 ligands in THF at 30°C. COD=cyclooctadiene. See text for the addition of a steric onset term, $s = -0.83$. Data from refs. 102a,b. $r^2=0.99$, $F=106$.
(k) Enthalpy for the displacement of COD by 2 ligands in THF at 30°C. COD=cyclooctadiene. See text for the addition of a steric onset term, $s = -0.91$. Data from ref. 103. $r^2=0.96$, $F=32$.
(l) $^{13}$C of Ni(\text{CO})$_3$\text{L} in CDCl$_3$ referenced from TMS. Data from refs. 65 and 104. $r^2=0.97$, $F=643.4$. This is a 1:1 system, and no k or k' values are needed to treat the data.
(m) $^{13}$C of Ni(\text{CO})$_3$\text{L}_2 in CDCl$_3$ referenced from TMS. Data from ref. 104. $r^2=0.99$, $F=285.3$. 
(n) CO stretching frequency for Ni(CO)$_3$L in CH$_2$Cl$_2$. Data from ref 105. $r^2=0.95$, $F=248.0$. ECW analysis is from Chapter 2. This is a 1:1 system, and no $k$ or $k'$ values are needed to treat the data.

(o) CO stretching frequency in Ni(CO)$_2$L$_2$ in various solvents. Data from ref. 106. $r^2=0.99$, $F=144.4$. P(OC$_2$H$_5$)$_3$, Pph$_2$(n-C$_4$H$_9$), AsPh$_3$, and PCl$_3$ were omitted.

(p) CO stretching frequency in Ir(CO)L$_2$. Data from ref. 107. $r^2=0.98$, $F=109.9$. P(i-C$_3$H$_7$)$_3$ and P(c-hex)$_3$ were omitted.

(q) log of the reaction rate for the addition of MeI to Ir(CO)ClL$_2$. (1) was done in benzene solvent with $r^2=0.94$, $F=34.0$; and (2) in acetone with $r^2=0.98$, $F=42.0$. Data from ref. 107. P(i-C$_3$H$_7$)$_3$ was omitted from both fits and P(c-hex)$_3$ was also omitted in the benzene fit. It was not studied in the acetone experiment. Additionally, P(Ph-p-CF$_3$)$_3$ was omitted in the acetone fit.

(r) log of the reaction rate for the addition of H$_2$ to Ir(CO)ClL$_2$. (1) was done in toluene solvent with $r^2=0.94$, $F=31.2$; and (2) in DMF. Data from ref. 107. $r^2=0.97$, $F=9.6$.

(s) log of the reaction rate for the addition of O$_2$ to Ir(CO)ClL$_2$. Data from ref. 107. $r^2=0.99$, $F=48.8$.

(t) log of the reaction rate for the loss of O$_2$ from Ir(CO)ClL$_2$(O$_2$). Data from ref. 107. $r^2=0.98$, $F=25.8$.

(u) log of the ratio of forward and reverse rate constants for O$_2$ reaction with Ir(CO)ClL$_2$(O$_2$). Data from ref. 107. $r^2=0.99$, $F=114.5$.

(v) CO stretching frequency of Mn$_2$(CO)$_3$L$_2$ in CH$_2$Cl$_2$ solution. Data from ref. 28. $r^2=0.96$, $x=1.10$ (average deviation), $F=45.1$. PPh$_2$(C$_2$H$_5$)$_3$ was omitted.

(w) Electronic absorption of Mn$_2$(CO)$_3$L$_2$ in CH$_2$Cl$_2$ and hydrocarbon solutions. Data from ref. 28. $r^2=0.99$, $x=0.09$, $F=126.1$. P(i-C$_4$H$_9$)$_3$ was omitted.

(x) CO stretching frequency of Co$_2$(CO)$_3$L$_2$ in CH$_2$Cl$_2$ solution. Data from ref. 28. $r^2=0.91$, $x=1.84$, $F=12.6$. P(n-C$_4$H$_9$)$_3$ was omitted.

(y) Electronic absorption of Co$_2$(CO)$_3$L$_2$ in CH$_2$Cl$_2$ and hydrocarbon solutions. Data from ref. 28. $r^2=0.99$, $x=0.03$, $F=76$. P(n-C$_4$H$_9$)$_3$ was omitted.

(z) Flash photolysis studies of Mo(CO)$_3$(PR$_3$)$_2$Br$_2$. Log of the second order rate constant for recombination of CO to Mo(CO)$_2$(PR$_3$)$_2$Br$_2$ in 1,2 dichloroethane. Data from ref. 78. $r^2=0.99$, $F=575.2$. PPh(C$_2$H$_5$)$_3$ was omitted.
Selected acceptors will be discussed in detail to illustrate the conclusions that can be drawn concerning reactivity. Using the values from Table 3-2, the components of each step toward the total enthalpy or shift can be calculated. The calculation is shown for the two donors studied whose C_b/E_b ratios are the most different. This helps to illustrate how the difference in reactivity of the donors affects the contribution to each step. These values appear in Table 3-3 for each of the systems discussed below.

**Interpretation of Enthalpies of Interaction**

**Ni(DBH)**

The enthalpies for the addition of two donor molecules to diacetyl bisbenzoyl hydrazino nickel (II), Ni(DBH), have been measured\(^9\) in benzene solvent. Correlation of the reported data to Equation (3-9) is poor. Eliminating various combinations of donors can produce good fits but unreasonable signs for the parameters. For example, large negative E_A or C_A values are unreasonable for correlations involving σ bond formation enthalpies. An excellent data fit results \((r^2 = 0.98)\) with reasonable parameters, when phosphines (that are capable of π-back bonding) are omitted and the enthalpy of displacing benzene by itself is entered as zero. Addition of benzene forces a W value that is close in magnitude to the benzene interaction enthalpy. The correlation is illustrated by the plussigns and solid line in Figure 3-1. The donors are numbered in the figure as in Table 3-1. The three phosphines, P(C_2H_5)_3, P(n-C_3H_7)_3, P(n-C_4H_9)_3, were omitted from the correlation and give measured enthalpies that are 4-5 kcal mol\(^{-1}\) larger than predicted because of π-backbond stabilization. Thus, the sum of the π-contributions given by W_FTT-
Table 3-3. Individual components accounting for the total enthalpy or shift for donors with different C_b/E_b ratios

<table>
<thead>
<tr>
<th>Donor</th>
<th>$E_A E_B$</th>
<th>$C_A C_B$</th>
<th>$E_A^{2nd} E_B$</th>
<th>$C_A^{2nd} C_B$</th>
<th>$W$</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta H_{\text{Ni(DBH)}}$</td>
<td></td>
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<td></td>
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<td></td>
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<tr>
<td>N(CH$_3$)$_3$</td>
<td>2.6</td>
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<td>2.8</td>
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<td>-4.9</td>
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<tr>
<td>NH$_3$</td>
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<td>5.1</td>
<td>5.7</td>
<td>3.1</td>
<td>-4.9</td>
<td>14.0</td>
</tr>
<tr>
<td>$\Delta H_{[\text{RhCl(CO)}_2]_2}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P(C$_2$H$_5$)$_3$</td>
<td>-13.1</td>
<td>27.7</td>
<td>-8.5</td>
<td>-12.1</td>
<td>45.0</td>
<td>39.0</td>
</tr>
<tr>
<td>P(Ph-p-CF$_3$)$_3$</td>
<td>-42.6</td>
<td>7.6</td>
<td>6.3</td>
<td>4.6</td>
<td>45.0</td>
<td>20.9</td>
</tr>
<tr>
<td>$\nu_{\text{CO}} \text{RhCl(CO)}_2L_2$</td>
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<td></td>
</tr>
<tr>
<td>P(C$_2$H$_5$)$_3$</td>
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<td>-22.7</td>
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<td>P(Ph-p-CF$_3$)$_3$</td>
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<td>P(Ph-p-CF$_3$)$_3$</td>
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<td>-12.6</td>
<td>-39.1</td>
<td>-7.3</td>
<td>50.7</td>
<td>22.8</td>
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<td>P(Ph-p-CF$_3$)$_3$</td>
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<tr>
<td>P(C$_2$H$_5$)$_3$</td>
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<td>-10.9</td>
<td>-21.2</td>
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<td>PPh$_3$</td>
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<td>11.9</td>
<td>-16.0</td>
<td>-1.1</td>
<td>57.5</td>
<td>17.3</td>
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<td>$\nu_{\text{CO}} \text{Mo(CO)}_4L_2$</td>
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<tr>
<td>P(C$_2$H$_5$)$_3$</td>
<td>-1.7</td>
<td>-45.3</td>
<td>-1.9</td>
<td>3.6</td>
<td>2082</td>
<td>2037</td>
</tr>
<tr>
<td>PPh$_3$</td>
<td>-4.2</td>
<td>-25.0</td>
<td>-5.6</td>
<td>-10.1</td>
<td>2082</td>
<td>2037</td>
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<tr>
<td>$\Delta H_{\text{CpRu(COD)Cl}}$</td>
<td></td>
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<td></td>
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<td></td>
</tr>
<tr>
<td>P(C$_2$H$_5$)$_3$</td>
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<td>35.4</td>
<td>-12.9</td>
<td>-41.4</td>
<td>75.3</td>
<td>35.3</td>
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<tr>
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<td>9.7</td>
<td>12.4</td>
<td>3.9</td>
<td>75.3</td>
<td>23.6</td>
</tr>
<tr>
<td>$\Delta H_{\text{Cp^*Ru(COD)Cl}}$</td>
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<tr>
<td>P(C$_2$H$_5$)$_3$</td>
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<td>44.6</td>
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Figure 3-1. Total measured enthalpy (■) and the calculated 1:1 adduct formation enthalpy (Δ) for Ni(DBH). See text for further discussion.
W and multiplying the $\pi$-parameters by $E_B$ and $C_B$ in Equations (3-4)-(3-6) is 4-5 kcal mol$^{-1}$.

The $E_A$ and $C_A$ values for 1:1 adduct formation of 2.20 and 2.50 result. The lack of donors with a small $C_B/E_B$ ratio leads to a poor definition of the $E_A$ and $k$ values, the former having a t-value of 0.8 and the latter -0.1, but the covalent parameters are well defined. Enthalpies for the first step to form the 1:1 adduct can be calculated with $E_A$ and $C_A$, and the contributions of this step to the total enthalpy are indicated by open triangles in Figure 3-1. These calculated values for the 1:1 enthalpies assume W corresponds to complete dissociation of benzene in the first step. Except for the phosphines, the difference between the calculated 1:1 values and the total enthalpies give the enthalpies for the second step. This result is significant because the enthalpies of the individual steps cannot be measured directly.

As shown in Figure 3-1, the enthalpies for the first step vary widely. The difference between the 1:1 points and the solid line give values for forming the 2:1 adduct from the 1:1 adduct. These enthalpies can be calculated with the $E_A^{2nd}$ and $C_A^{2nd}$ parameters given by Equations (3-5) and (3-6). One notes in Figure 3-1 that donors with the largest $C_B$ values have the smallest -$\Delta H_2$ as expected from Equation 11 and a $k'$ value of 0.49. For the purpose of illustration, the 1:1 adduct with the donor pyridine has $E_A^{2nd}$ and $C_A^{2nd}$ values of 2.4 and 0.8, respectively. A significant decrease in the relative importance of covalency results in the second step as a consequence of coordinating the covalent donor pyridine in the first step. The $k$ value for the $E_A^{2nd}$ parameter is not significant and has a large error. Using Equations (3-4) and (3-7) and assuming all the benzene is dissociated in the first step, the acceptor parameters calculate enthalpies for 1:1
adduct formation with pyridine of -7.9 kcal mol\(^{-1}\) and -7.0 kcal mol\(^{-1}\) for the second step. Incomplete benzene dissociation in step 1 would increase the enthalpy of step 1 and decrease step 2.

The decreased covalent contribution in the 2:1 adducts gives rise to a large \textit{trans} effect in this complex that is covalent in nature. The \textit{trans} effect is expected because both ligands interact with the same set of metal orbitals. Spin state changes also contribute to the acidity differences of the 1:1 and 2:1 acceptors.

\[ \text{[Rh(CO)\(_2\)Cl\(_2\)]} \]

The enthalpies of reaction of \text{[Rh(CO)\(_2\)Cl\(_2\)]} to form 1:1 adducts with a series of donors that are not \(\pi\)-acceptors have been correlated earlier\(^{16b}\) using the ECW model. All enthalpies correlated in ECW are in terms of kcal mol\(^{-1}\) \textit{adduct} so the quantities fit, -\(\Delta H\), are one-half the reported enthalpies of reaction. Using the most recent set of donor parameters,\(^{12a}\) the acceptor parameters for \(\frac{1}{2}\text{[Rh(CO)\(_2\)Cl\(_2\)]}\) of \(E_A = 4.32\), \(C_A = 4.13\), and \(W = -10.39\), where \(W\) is attributed to one-half the enthalpy of dimerization of the acid. The application of Equation 1 to complexes of the phosphines produces \(E_A^{\*\text{FIT}}\), \(C_A^{\*\text{FIT}}\) and \(W^{\text{FIT}}\) parameters that differ from those above because of the \(\pi\)-contributions shown in Equations (2-10) - (2-12). Unfortunately, the enthalpy for only one phosphorus 1:1 donor adduct has been reported.

Reported 2:1 enthalpies involve reaction of \text{[Rh(CO)\(_2\)Cl\(_2\)]} with a donor (B) to cleave the dimer and displace one \text{CO} forming \text{RhB\(_2\)(CO)Cl}. The enthalpies are measured in CH\(_2\)Cl\(_2\) solution where phosphine donors hydrogen bond, and the enthalpy of dissociation of the hydrogen bonding can be incorporated into the resulting fit.
parameters. In the second step of the reaction, a molecule of CO is dissociated by the donor. This enthalpy contribution would lead to Equation (3-10) where $E_{A_{\text{2nd}}} E_{\text{CO}}$ and

$$-\Delta H_T = E_{A}^{\text{FIT}} E_{B} + C_{A}^{\text{FIT}} C_{B} + E_{A_{\text{2nd}}} E_{B} + C_{A_{\text{2nd}}} C_{B} - E_{A_{\text{2nd}}} E_{\text{CO}} - C_{A_{\text{2nd}}} C_{\text{CO}} + W$$  \hspace{1cm} (3-10)

and $E_{A}^{\text{FIT}}$ and $C_{A}^{\text{FIT}}$ indicate the acceptor backbonds to the phosphine. Substituting Equations (3-5) and (3-6) for $E_{A_{\text{2nd}}}$ and $C_{A_{\text{2nd}}}$ leads to:

$$-\Delta H_T = 2E_{A}^{\text{FIT}} E_{B} + 2C_{A}^{\text{FIT}} C_{B} - kE_{B}^{2} - k'C_{B}^{2} - E_{A} E_{\text{CO}} - kE_{B} E_{\text{CO}} - C_{A} C_{\text{CO}} - k'C_{B} C_{\text{CO}} + W$$  \hspace{1cm} (3-11)

By incorporating $E_{A} E_{\text{CO}}$ and $C_{A} C_{\text{CO}}$ into $W$, $k'C_{B} C_{\text{CO}}$ into $C_{A}^{\text{FIT}} C_{B}$, and $kE_{B} E_{\text{CO}}$ into $E_{A}^{\text{FIT}} E_{B}$, Equation (3-12) emerges,

$$-\Delta H_T + \text{Corr} = E_{A}^* E_{B} + C_{A}^* C_{B} - kE_{B}^{2} - k'C_{B}^{2} + W$$  \hspace{1cm} (3-12)

where $E_{A}^* = 2E_{A}^{\text{FIT}} - kE_{\text{CO}}$, $C_{A}^* = 2C_{A}^{\text{FIT}} - k'C_{\text{CO}}$. In the data fit, the enthalpy in units of $C_{A_{\text{2nd}}} C_{\text{CO}}$ give the energy to dissociate CO from the 1:1 adduct, kcal mol$^{-1}$ of adduct is solved for $E_{A}^*$, $C_{A}^*$, $k$, $k'$ and $W$. As shown above, these $E_{A}^*$ and $C_{A}^*$ values are the net of phosphine binding and CO displacement. $E_{A}^*$ and $C_{A}^*$ also contain the $\pi$-component shown in Equations (2-10) and (2-11) (e.g., $E_{A}^* = 2E_{A} - kE_{\text{RM}} - kE_{\text{CO}}$ where $E_{A}$ is 4.32).

The $W$ value also contains the dimer cleavage and CO displacement terms described above and the $\pi$-contributions of Equation 6. The above analysis indicates that an ECW analysis is relevant to this data. Indeed, an excellent data fit to Equation (3-12) results as shown in Table 3-2.

Because half of the reported enthalpy is for reaction with each monomer, the quantity used in the fit for these dimeric systems is half of the reported value from reference 99. While this is a simplification of the system, the use of this value facilitates
the calculation (not the interpretation) of the parameters and adds only a small inaccuracy into the calculated value (less than 2-3 kcal mol\(^{-1}\)).

\( E_B \) and \( C_B \) are not known for CO. Therefore, none of the components of \( E_A^* \), \( C_A^* \), or \( W \) can be determined. However, the exothermicity of the \( W \) term indicates a very substantial amount of \( \pi \)-backbond stabilization. Because step 1 has a \( W \) contribution from \( \pi \)-back bonding, the \( W \) contributions from steps 1 and 2 cannot be resolved, and the enthalpies of the two steps cannot be calculated. The data fit does indicate that there is no evidence for a steric effect in this system, and the parameter magnitudes indicate a significant \( \pi \)-back bond enthalpy component. The parameters for the second step for 2:1 adducts are reduced by \( \sigma \) bonding and are also influenced by \( \pi \)-contributions, for example, \( E_{A*2nd,PTT} = E_{A*PTT} - k_E B - k_2 E_{mM} \) where \( k_2 \) may be positive or negative. Thus, any system that \( \pi \)-backbonds gives fit parameters that at present are impossible to interpret.

The type of derivation and analysis shown above is essential to determine if a complex chemical reaction should fit equations used in correlation analyses and to interpret how the individual energy components are distributed into the fit parameters. In the absence of such derivations, the correlation of a physicochemical property of a complex reaction to 1:1 basicity parameters is a meaningless exercise.

The \( v_{CO} \) stretching frequencies for the product of the 2:1 reaction of \( \text{Rh(CO)(PX}_3)_2\text{Cl} \) are not influenced by CO dissociation and are fit to Equation (3-9).

Both \( E_A \) and \( C_A \) decrease the frequency relative to the \( W \) value for a donor with \( E_B = C_B = 0 \) attached. In agreement with the enthalpy data, no steric interactions are observed with any of the phosphines studied. The IR data were fit to Equation (3-1) in an attempt to gauge the contribution from \( k \) and \( k' \) to the overall fit. If the data fit Equation (3-1) as
well, then either most of the shift would be due to coordination of the first phosphine or the acceptor parameters toward the second donor are not affected to a significant extent by coordination of the first donor. A poorer fit (average deviation of 2.6 cm\(^{-1}\)) was obtained for the fit to Equation (3-1) compared to Equation (3-9) (average deviation of 0.9 cm\(^{-1}\)) indicating that the shift is not dominated by coordination of the first donor.

Table 3-3 indicates that for donors with larger \(C_B/E_B\) ratios, both steps make comparable contributions to the shift. As the \(C_B/E_B\) ratio becomes smaller, the shift is dominated more by the first step. Furthermore, an average set of acceptor parameters do not work because the first step changes the acidity toward coordination of the second donor.

\textbf{Mo(NBD)(CO)\(_4\)}

The enthalpies for the substitution of two phosphorus donors for norbornadiene, NBD, in \textit{Mo(NBD)(CO)\(_4\)} were correlated to Equation (3-9), giving an excellent correlation when \(P(O\text{Ph})_3\) is removed. The remaining phosphorus donors are all fit to within 0.6 kcal mol\(^{-1}\). For a \(\sigma\)-interaction, \(W\) is expected to be endothermic corresponding to dissociation of NBD. The magnitude and exothermicity of the \(W\) value from the phosphorus donor fit suggests that \(\pi\)-back bonding contributes to the acceptor parameters. Pyridine was not used in the correlation and deviates by 19 kcal mol\(^{-1}\) with the calculated enthalpy much smaller than the experimental value. This deviation does not necessarily indicate more extensive \(\pi\)-back bonding in pyridine because pyridine’s \(\sigma\)-interaction is not predicted with the phosphine \(E_A^{\text{FIT}}\) and \(C_A^{\text{FIT}}\) parameters.

As with the enthalpies, the highest energy \(v_{\text{CO}}\) for \textit{cis-Mo(CO)\(_4\)L\(_2\)} gave a good correlation, with an \(r^2\) of 0.98 and an average deviation of 0.9 cm\(^{-1}\) when \(P(O\text{Ph})_3\) was
removed from the fit. In contrast to the enthalpies, where electrostatic and covalent interactions make significant contributions, the frequency shift is dominated by covalency (see Table 3-3) in the interaction. Coordination of the first donor causes a larger shift than coordination of the second. However, the fit to Equation (3-1) is not as good indicating that both steps in the coordination of the donors make significant contributions (especially as the $C_B/E_B$ ratio decreases) to the 2:1 adduct frequency shift.

Fe(BDA)(CO)$_3$

The experimental enthalpies for the displacement of benzylidene acetone, BDA, by phosphorus donors were determined by assuming that the metal complex, as the limiting reagent, was fully complexed when excess phosphine was added. Addition of dienes to trans-Fe(BDA)(CO)$_3$ is shown to proceed through a two-step displacement of BDA.

In the first step, the C=O fragment of the BDA is displaced by one C=C of the diene. In the second step, the C=C of BDA is displaced by the second C=C of the diene. If coordination of phosphorus donors proceeds by a similar mechanism, ECW analysis would treat the first dissociation with a constant W term and the second dissociation by the addition of terms similar to those for CO in Equation (3-12). The W term would not be used for the second step, because the energy needed to displace the C=C bond of BDA is not constant but will differ for each adduct with a different donor attached. If both the C=O and C=C of BDA were displaced when the first phosphine coordinated, this combined enthalpy would be included in a W term that would be added to Equation (3-9). The correlation to Equation (3-9) or (3-12) produces the same set of parameters, so the dissociation pattern cannot be distinguished by the fit. The difference would be in the
magnitude of the coefficients causing ambiguity in their interpretation. Thus, in this and future discussions, it should be realized that a correlation to Equation (3-9) could be a fit to a similar expression like Equation (3-12).

The reported phosphine enthalpies produce a poor correlation to Equation (3-9) even with 5 adjustable parameters. When As(C₆H₅)₃, P(c-hex)₃, and P(i-C₃H₇)₃ were eliminated from the correlation, a good fit results ($r^2 = 0.97$ and an average deviation of 1 kcal mol⁻¹), and the resulting parameters are reported in Table 3-2. Incomplete complexation is the probable cause of the observed 8 kcal mol⁻¹ deviation of As(C₆H₅)₃, and steric effects produce the 11 kcal mol⁻¹ deviation with P(c-hex)₃ and P(i-C₃H₇)₃. The average deviation of the correlation is larger than the reported experimental error, but incomplete complexation for a few systems could lead to a larger error than the precision would indicate.

The resulting Eₐ, Cₐ, k, and k' parameters from the correlation have contributions from both σ and π bonding as well as ligand displacement making their interpretation difficult. One cannot partition the W value over the two steps, so it is not possible to calculate enthalpies for the individual steps.

The CO stretching frequencies for the 2:1 adducts were correlated to Equation (3-9) to confirm a steric effect in the enthalpies. With all of the donors included, an excellent fit resulted with no system deviating by more than 3 cm⁻¹. One possibility to account for a steric effect in the P(c-hex)₃ and P(i-C₃H₇)₃ enthalpies and none in the spectral shifts is domination of the shift differences by coordination of the first phosphine. This suggestion is supported by a fit of the observed shifts to Equation (3-1) providing about as good a fit
to the full data set as the fit to Equation (3-9). Table 3-3 also shows the shift is dominated by the first step, especially for phosphines with small C_B/E_B ratios.

**Cp*Ru(COD)Cl**

The enthalpies for the substitution of cyclooctadiene by phosphorus donors in CpRu(COD)Cl give only a fair fit to Equation 14 \((r^2=0.91, \text{ with an average deviation of } 1.6 \text{ kcal mol}^{-1})\). Steric problems are probably the cause. With the addition of a steric onset term (Chapter 2), \(s(\theta - \theta_{\text{ON}})\delta\), this fit was improved significantly \((r^2=0.99, \text{ with an average deviation of } 0.6 \text{ kcal mol}^{-1})\). The \(s\) value is equal to -0.83 \((\pm 0.13)\). The steric onset angle, \(\theta_{\text{ON}}\), is calculated (see Calculations section) to be 131° for this acceptor. Since the various 1:1 adducts have different size phosphines coordinated, \(s\) is expected to vary for each adduct if the source of strain were intraligand phosphorus donor repulsion. With a varying \(s\) value for each 1:1 adduct, the standard cone angle analysis of steric effects would not apply for the 2:1 adducts. Because the same value works for all adducts, the dominant steric effect must involve the Cp and chlorine ligands. Given the magnitude and sign of \(W\), \(\pi\)-back bonding makes a significant contribution to the enthalpies.

Similar studies were done for Cp*Ru(COD)Cl. Our findings for this complex are very similar to the Cp complex. Again a steric onset is found for phosphines with cone angles larger than 131°. The \(s\) value of -0.91 \((\pm 0.22)\) affects the enthalpies in the same direction as the Cp data. Similar trends are seen in the parameters for the two systems, again indicating the presence of \(\pi\) contributions in the acceptor parameters.
Interpretation of Spectral Shifts

Ni(CO)$_2$L$_2$ and Ni(CO)$_3$L

Spectral shifts for the 2:1 adducts, Ni(CO)$_2$L$_2$, can be fit to Equation (3-9), where $W$ corresponds to the shift of Ni(CO)$_2$ with two donors attached whose $E_B = C_B = 0$ (indicated by $L^o$ below) and also contains a phosphorus ligand $\pi$-back bond component. The $^{13}$C shifts of Ni(CO)$_3$L (where $L$ is a N or As donor) were previously examined (Chapter 2). In those reported analyses, the quantity fit was the difference in the $^{13}$C shift of the 1:1 adduct and Ni(CO)$_4$. In order to afford a comparison to the 2:1 adducts, the $^{13}$C shift relative to TMS$^{104b}$ was fit for the 1:1 Ni(CO)$_3$L adducts, and the parameters are given in Table 3-2. In this case, the $W$ value of 184.1 ppm for Ni(CO)$_3$L$^o$ is significantly upfield from the 191.6 ppm of Ni(CO)$_4$.

When the data$^{104a}$ for $^{13}$C Ni(CO)$_2$L$_2$ is analyzed with the full 2:1 expression of Equation (3-9), the $W$ value calculated for this data set is 185.7 ppm, which represents the $^{13}$C shift of Ni(CO)$_2$L$^o$. The $W$ values obtained for 1:1 and 2:1 adducts are the same within the error of the calculated parameters.

The ECW analysis of $\nu_{CO}$ for Ni(CO)$_3$L complexes$^{104}$ is reported (Chapter 2), and $\nu_{CO}$ for Ni(CO)$_2$L$_2$ is examined in this study. The $W$ values are 2145 and 2187 cm$^{-1}$, respectively compared to the gas phase value of 2143 cm$^{-1}$ for CO. The adsorption of CO on the (100) face of nickel metal is reported.$^{109a}$ Bands at 1850 and 2020 cm$^{-1}$ are observed at all loadings and are assigned to the stretching vibrations of CO in bridge and terminal adsorption sites, respectively.$^{109}$ A band at 2200 cm$^{-1}$ is also observed and is attributed to CO bonded to charged nickel surface atoms. The potential $\pi$-contributions to $W$ do not permit comparison of the these values to the frequencies of adsorbed CO.
Ir(CO)(Cl)L₂

Quantitative studies of the reactivity of Ir(CO)(Cl)L₂ with H₂, CH₃I, and O₂ have been reported.¹⁰⁷ This chemistry was analyzed with the QALE parameters. As reported earlier (Chapter 2), the neglect of softness in the parameters of this approach is tantamount to replacing Hard-Soft or Electrostatic-Covalent with Hard-Steric or Electrostatic-Steric. No account is made for variation in covalency. Furthermore, no account is made for the modification of the acceptor center after the first phosphine coordinates. Thus, even though the data can be fit to the accommodating χ, θ, and Eₘₐ donor parameters, the meaning of the acceptor parameters from the analyses and the significance of the analyses are in doubt. The results of the 2:1 model, ECW analysis provide significant insight into this chemistry.

The log of the equilibrium constant for O₂ binding is given by log (kᵣ/kᵢ), where kᵣ and kᵢ are the rate constants for O₂ pickup and release, respectively. The values are increased from the intercept $W^{PT} (-14.3)$ which corresponds to a donor coordinated with $E_B = C_B = 0$ and a $E^{co}E^{NM} + C^{co}C^{NM}$ contribution. The logs of forward and reverse rate constants are also fit well individually. There is no evidence for a steric effect in any of the measurements characterizing O₂ binding, but only seven donors were studied.

The logs of the rate constant for the oxidative addition of methyl iodide¹⁰⁷ have been measured in benzene and acetone. P(Ph-p-CF₃)₃ was omitted from the acetone study. Because of enthalpic steric effects, P(i-C₃H₇)₃ was omitted from the fits in both solvents, and P(c-hex)₃ was also omitted in the study using benzene. This donor was not studied in acetone.
The log of the rate of H₂ addition to Ir(CO)(Cl)L₂ in toluene gives a good correlation to Equation (3-9) \( (r^2=0.94, \text{ with an average deviation of 0.17}) \). P(c-hex)₃ and P(i-C₃H₇)₃ have been studied with this system, and no evidence of a steric effect is found for any of the large cone angle phosphines.

The \( ν_{CO} \) for Ir(CO)(Cl)L₂ has been fit to Equation (3-9). With P(c-hex)₃ and P(i-C₃H₇)₃ omitted from the fit, a good correlation is found \( (r^2=0.98, \text{ with an average deviation of 1.1 cm}^{-1}) \). The misses for these large cone angle donors are not in the direction that would suggest a steric effect. Their experimental frequencies are lower in energy than those predicted by the acceptor parameters.

The systems described above illustrate the analyses and interpretation of 2:1 adduct physicochemical properties with ECW. This degree of understanding is available for all the systems described in Table 3-2, and the reader is encouraged to investigate those of interest in more detail using the above guidelines.

**Analysis of Bidentate Phosphines**

Reactions of metal acceptors with bidentate phosphines form 2:1 adducts. Coordination of an acceptor in the first step not only changes the metal acceptor properties as discussed above for 2:1 adducts but also changes the donor properties of the remaining phosphine that coordinates in the second step. For bidentate phosphines, \( E_{B1} \) and \( C_{B1} \) are constants that have to be determined for the first step, and Equation (3-9) has to be modified to account for the different \( E_{B2} \) and \( C_{B2} \) values for the donor molecules in the second step. Equation (3-13) represents the generalized form of the 2:1 adduct model, and if the coordinating donors happen to be the same, Equation (3-9) results.
\[ \Delta \chi_T = E_A(E_{B_1} + E_{B_2}) - kE_{B_1}E_{B_2} + C_A(C_{B_1} + C_{B_2}) - k'C_{B_1}C_{B_2} + W \]  

(3-13)

Angelici\textsuperscript{110} has measured the enthalpies of mono- and di-protonation of a series of bidentate phosphines by CF\textsubscript{3}SO\textsubscript{3}H in 1,2-dichloroethane solution. Our earlier analysis of this system (Chapter 2) of the protonation of monodentate donors (using Equation 3-1) yielded the following acceptor parameters: \( E_A^* = 4.51 \), \( C_A^* = 5.70 \), and \( W = 0.84 \). The enthalpies of monoprotonation indicate that the diphosphines are slightly less basic than their monodentate analogues. For example, \( \text{Ph}_2\text{PCH}_2\text{PPh}_2 \) has \( \Delta H_{\text{IP}1} \) of 22.0 kcal mol\(^{-1}\), \( \text{Ph}_2\text{P(CH}_2\text{)PPh}_2 \) a \( \Delta H_{\text{IP}1} \) of 22.8 kcal mol\(^{-1}\) and the monodentate analogue, \( \text{Ph}_2\text{PMe} \), has \( \Delta H_{\text{IP}1} \) of 24.7 kcal mol\(^{-1}\). The lower basicity of the bidentate phosphine is attributed\textsuperscript{110} to the greater electron withdrawing ability of the \(-\text{PPh}_2\) group compared with the \(-\text{H}\).

In order to determine the donor parameters for monodentate coordination of the bidentate phosphines, two or more enthalpies for \textit{monodentate coordination} are needed to solve simultaneous equations for \( E_{B_1} \) and \( C_{B_1} \). Limited data are available on four of the more common bidentate phosphines seen in the literature, \( \text{Ph}_3\text{P(CH}_2\text{)nPPh}_2 \) (where \( n = 1, 2, 3, \) or 4). In addition to the enthalpies of protonation, the \(^{13}\text{C}\) chemical shifts for Ni(CO)\textsubscript{3}L are reported.\textsuperscript{104b} Using these two pieces of data, tentative \( E_{B_1} \) and \( C_{B_1} \) parameters are calculated and given in Table 3-4. In the absence of this information, the assumption is made that the first step in the coordination of the bidentate phosphines will be characterized by the same \( C_B/E_B \) ratio as the monodentate analogue. For example, \( \text{dmpm} \), \( \text{Me}_2\text{P(CH}_2\text{)PMe}_2 \), is assumed to have the \( C_B/E_B \) ratio of 17 reported for the monomer analogue, \( \text{PMe}_3 \) (Table 2-1). Using the \( C_B/E_B \) ratio of the monomer analogue and the enthalpy of mono-protonation by CF\textsubscript{3}SO\textsubscript{3}H, one can calculate an \( E_{B_1} \) and \( C_{B_1} \).
value for the other bidentate phosphines. These values and the abbreviations used for all donors are given in Table 3-4.

Calculation of $E_{B2}$ and $C_{B2}$ for these diphosphines is much more difficult. The enthalpies are reported for the second protonation, so the same assumption could be made using the $C_B/E_B$ ratio of the monomer analogues. However, the donor capabilities of the second phosphine will be affected by coordination to a particular acceptor, thus changing the $E_{B2}$ and $C_{B2}$ values for the diphosphine depending on which acceptor is studied. For the diphosphines with four, five, or six methylene spacer groups, the two enthalpies of protonation are 0.8 kcal mol$^{-1}$ or less apart from each other. For these diphosphines, the acceptor is not making a large influence on second donor site, and, in effect, the two sites are acting electronically independent of each other. Therefore, the $E_{B2}$ and $C_{B2}$ values are assumed to be identical to the $E_{B1}$ and $C_{B1}$ values calculated. Unfortunately, data are not available for reactions of dpppent and dpph with any of the metal complexes studied above. Therefore, no analysis of the parameters for these two diphosphines is possible.

For the other diphosphines, where data are available, several problems preclude the calculation of $E_{B2}$ and $C_{B2}$ parameters. These problems include differing coordination geometries between monomers and bidentate ligands, steric problems, and the creation of torsional strain when both ends of the bidentate ligands are coordinated, *vide infra*. If systems were available where these problems are minimized, $E_{B2}$ and $C_{B2}$ could be calculated using Equations (3-14) and (3-15), where $m$ and $m'$ are proportionality constants related to the effect of the acceptor on the second coordinating donor.

$$E_{B2} = E_{B1} - mE_A$$  \hspace{1cm} (3-14)

$$C_{B2} = C_{B1} - m'C_A$$  \hspace{1cm} (3-15)
Table 3-4. Tentative $E_{B1}$ and $C_{B1}$ parameters for Diphosphines

<table>
<thead>
<tr>
<th>diphosphine $^a$</th>
<th>$E_{B1}$</th>
<th>$C_{B1}$</th>
<th>analogue $^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ph$_2$P(CH$_2$)PPh$_2$ (dppm)</td>
<td>0.56</td>
<td>3.27</td>
<td>Ph$_2$PMe</td>
</tr>
<tr>
<td>Ph$_2$P(CH$_2$)$_2$PPh$_2$ (dppe)</td>
<td>0.65</td>
<td>3.34</td>
<td>Ph$_2$PMe</td>
</tr>
<tr>
<td>Ph$_2$P(CH$_2$)$_3$PPh$_2$ (dppp)</td>
<td>0.60</td>
<td>3.48</td>
<td>Ph$_2$PMe</td>
</tr>
<tr>
<td>Ph$_2$P(CH$_2$)$_4$PPh$_2$ (dppb)</td>
<td>0.59</td>
<td>3.70</td>
<td>Ph$_2$PMe</td>
</tr>
<tr>
<td>Ph$_2$P(CH$_2$)$_5$PPh$_2$ (dpppent)</td>
<td>0.57 $^c$</td>
<td>3.75 $^c$</td>
<td>Ph$_2$PMe</td>
</tr>
<tr>
<td>Ph$_2$P(CH$_2$)$_6$PPh$_2$ (dpph)</td>
<td>0.58 $^c$</td>
<td>3.82 $^c$</td>
<td>Ph$_2$PMe</td>
</tr>
<tr>
<td>Me$_2$P(CH$_2$)PMe$_2$ (dmpm)</td>
<td>0.30 $^c$</td>
<td>5.06 $^c$</td>
<td>PMe$_3$</td>
</tr>
<tr>
<td>Et$_2$P(CH$_2$)$_2$PEt$_2$ (depe)</td>
<td>0.26 $^c$</td>
<td>5.14 $^c$</td>
<td>PEt$_3$</td>
</tr>
</tbody>
</table>

(a) Unless otherwise indicated, these parameters are calculated using the first enthalpy of protonation by CF$_3$SO$_3$H in 1,2-dichloroethane ($-\Delta H_{\text{IP1}}$) from reference 110 and the $^{13}$C chemical shift for Ni(CO)$_3$L from reference 104b.

(b) $C_{B}/E_{B}$ ratios for the monomers are: Ph$_2$PMe: 6.6; PMe$_3$: 17; PEt$_3$: 20.

(c) Calculated using $-\Delta H_{\text{IP1}}$ and the $C_{B}/E_{B}$ ratio of the monomer analogue.
For a given system, one would have to solve $E_A$, $C_A$, $k$, $k'$, and $W$ values from 2:1 monomer studies and then apply those values to Equation (3-9) or (3-13) with the data for bidentate phosphines by substituting in Equations (3-14) and (3-15). With several such systems, the best $m$ and $m'$ values could be calculated for each diphosphine. The current systems are not able to be used in this manner for several reasons.

For the reaction of Fe(BDA)(CO)$_3$ with monodentate phosphines, it is observed that the two phosphines coordinate $trans$ to each other. This geometry is not possible for a bidentate phosphine, and it is observed$^{100b}$ that the two ends must bind in $cis$ positions. The acceptor parameters that we are trying to use to model the bidentate phosphines are those calculated using data from the monomer phosphines binding $trans$ to each other, so they will not be applicable to another geometric arrangement. This same situation is not found for the reaction of Mo(NBD)(CO)$_4$, where both the monomer and bidentate phosphines are reported$^{101}$ to bind in $cis$ positions.

Perhaps the most important reason why the bidentate phosphines are not able to be modeled with the same acceptor parameters used for monomers is the problem of torsional ring strain. When the bidentate phosphines discussed here coordinate at both ends, a metallacycle of between four and seven members is formed. The ring strain of organic rings has been studied extensively,$^{111}$ and six-membered rings are found to be most stable. It is likely then that complexes with dppm and dppe will exhibit ring strain as they are forming four- and five-membered rings. These torsional ring strain energies have been discussed for Mo(P-P)(CO)$_4$,$^{101}$ Fe(P-P)(CO)$_3$,$^{100b}$ Cp*Ru(P-P)Cl,$^{102c}$ and CpRu(P-P)Cl.$^{102d}$ The ruthenium complexes show 13.2 and 10.0 kcal mol$^{-1}$ of ring strain energy in the four-membered ring, respectively. For the molybdenum and iron complexes, stabilities
for the four-membered rings are reported relative to larger rings, and they are over 10 kcal mol\(^{-1}\) less stable in both cases. The five-membered rings do not show as much strain energy and are nearly as stable as the six-membered rings.

The difficulties that are addressed in this section do not allow for the calculation of donor parameters for the second site that will predict the total enthalpies of reaction. In addition to those listed above, we report here the steric problems with the ruthenium complexes, which may be operative when trying to coordinate the second end of a large bidentate phosphine. Tolman\(^{23}\) reports cone angles for bidentate phosphines as 121°, 125°, and 127° for dppm, dppe, and dppp, respectively. This number is referred to as the value “for half of the chelate assuming P-M-P angles in M[R\(_2\)P(CH\(_2\))\(_n\)PR\(_2\)] of 74°, 85°, and 90° for \(n=1, 2,\) or 3, respectively.”\(^{23}\) The value for the entire chelate will certainly exceed the 131° steric threshold that we report for the ruthenium complexes. Because of the many problems that have been discussed here, it is not feasible to try to report parameters that will take all of these factors into consideration. The \(E_{B1}\) and \(C_{B1}\) parameters that appear in Table 3-4 are the most reliable. These parameters, however, are not especially useful without parameters for the second donor site. More data will need to be collected in which problems of geometry and steric strain are absent. The problem of torsional strain will always be present with the shorter diphosphines. More data will also allow calculation of refined \(E_{B1}\) and \(C_{B1}\) parameters and may allow for further study of the second donor site.
Conclusions

An extension of the Electrostatic-Covalent Model for donor-acceptor chemistry has been presented to include acceptors which coordinate two donors. Reactions involving the addition of two monomer phosphines are fit very well to this extension. Coordination of the first donor is shown to change the acceptor for the second donor. These reactions are complex with both σ and π bonding operative, and their relative importances cannot be separated [Equations (2-10) - (2-11)]. An explanation is given that shows how both σ and π effects can be incorporated into the ECW parameters, while still maintaining acceptable correlations and providing meaningful parameters (Table 3-2).

The analysis and calculation of the interaction of a two-step adduct formation between two identical donors and an acceptor requires the separation of the interactions of the individual donors. The second-step enthalpy is not merely the interaction of the second donor with the first-step phosphine adduct, but it includes any change in the interaction of the first-step donor with the acceptor. Once the system is formed with two identical donors interacting with the acceptor, the total interaction of each donor is indistinguishable. Each system must be analyzed for the complexity of the interactions included in the calculated parameters. Several representative systems are discussed in detail in order to illustrate this type of analysis. This analysis renders a unique view of reactivity by allowing the separation of total enthalpies or shifts into contributions from individual steps, including their electrostatic and covalent components (Table 3-3).

Analysis of bidentate phosphine reactivity has also been carried out. Parameters derived for monomer phosphine coordination cannot be used with the bidentate phosphines. Geometric and steric considerations are observed which cause the bidentate
reactivity to be different than that of two monomers. Torsional ring strain has been reported earlier for the smaller bidentate phosphines, and this strain hampers our correlation of their reactivity to the extended model. More data are needed to aid the understanding of this class of phosphines.
CHAPTER 4
DONOR-ACCEPTOR AND POLARITY PARAMETERS
FOR HYDROGEN BONDING SOLVENTS

Introduction

There are numerous reports and excellent reviews\textsuperscript{34b,38a,42d,112} on the use of the
solvatochromism of various probes to estimate solvent polarity. The more common
probes, which include $E_r(30)$,\textsuperscript{34b,38a} $Z$ value,\textsuperscript{39} $\pi^*$,\textsuperscript{42} and SPP\textsuperscript{N,113} cover a wide range of
solvent polarity. Work in this laboratory\textsuperscript{45c} has consolidated these and other
solvatochromic data into the Unified Solvation Model (USM), revealing a combination of
specific and non-specific interactions in most of the reported scales. By eliminating
specific interactions in the USM, a composite scale, $S'$, of solvent polarity for non-specific
interactions results that encompasses most of the data for non-specific interactions from all
of the more common scales. The influence of nonspecific solvation on physicochemical
properties of solutes is estimated with USM using Equation (4-1), where $S'$ is the solvent
polarity parameter, $\Delta \chi$ (with units of energy) is the solvent dependent value of the
physicochemical property, $P$ is the measure of the susceptibility of the solute to solvation,
and $W$ is the value of $\Delta \chi$ when $S'$ is zero.

$$\Delta \chi = S'P + W$$ \hspace{1cm} (4-1)

Because extrapolation of solvent polarity to $S'=0$ may not remove the dispersion
component, the $W$ value is not necessarily the gas phase value. Values for $S'$ have been
established for over 50 donor solvents involved in non-specific interactions with more than
30 solute probes. Use of \(S'\) in correlations enables one to attribute deviations in data fits to specific interactions as opposed to looking for a good correlation by finding one of the several scales that will average in specific effects.

Alcohols and other protic solvents are widely used, but invariably cause problems in correlations to solvation parameters. These solvents were only briefly treated in the USM. An increased understanding of the specific and non-specific components of the reactivity of this important class of solvents is desired. Alcohol solvents are complicated by their amphoteric nature. In order to establish acceptor parameters, systems must be selected in which the probe is clearly an electron pair donor and the solvent alcohol the acceptor. An independent data fit to determine the alcohol donor parameters must use systems in which the probe is clearly an acceptor and the solvent alcohol a donor.

Various attempts have been made to account for the specific acceptor interaction of protic solvents using one parameter scales. Abraham's \(\alpha_2^H\) scale of hydrogen bond acidity is based on equilibrium constants measured in \(\text{CCl}_4\). Taft and Kamlet added an \(\alpha\) term for acceptor solvents capable of hydrogen bonding and a \(\beta\) term for donor solvents. Catalán's \(\text{SPP}^N\) scale has been extended in recent work to include hydrogen bonding solvents.

The pitfalls associated with the use of one parameter scales to describe donor-acceptor interactions and the demonstrated utility of USM to separate specific and non-specific interactions led to a reexamination of protic solvents by treating the non-specific donor-acceptor interaction with the USM model, and the specific interaction with the added terms in Equation (4-2).

\[
\Delta\chi = E_A^*E_B^* + C_A^*C_B^* + S'P + W
\] (4-2)
In Equation (4-2), $\Delta \chi$ is the physicochemical property, $E_A'$ and $C_A'$ are the electrostatic and covalent acceptor parameters of the aggregated alcohol solvent molecules, and $E_B^*$ and $C_B^*$ are the corresponding parameters for the response of the donor probe to electrostatic and covalent interactions. The $W$ parameter is the value of $\Delta \chi$ when $E_B^* = C_B^* = 0$. The prime symbols are used to indicate that the parameters refer to systems where the neat solvent is the acceptor. In the case of alcohol solvents, the $E$ and $C$ parameters for the solution aggregates would differ from those of the monomer.

With the alcohol functioning as a donor solvent toward an acceptor probe, Equation (4-2) takes the form shown in (4-3), where $E_B'$ and $C_B'$ are the donor parameters.

$$\Delta \chi = E_A'^*E_B' + C_A'^*C_B' + S'P + W \quad (4-3)$$

$E_A'^*$ and $C_A'^*$ are the acceptor probe response parameters. Analyses with Equations (4-2) and (4-3) provide increased understanding of the solvation process by providing the specific and non-specific components. It is significant that many of the basic solvent $E_B$ and $C_B$ parameters, as well as the acidic solvent $E_A$ and $C_A$ parameters, are obtained independently\textsuperscript{12a} and are not simply two more adjustable parameters to fit solvent shifts.

**Experimental and Calculations**

**Data Fits**

For each donor solute (probe) studied in donor solvents whose $S'$ values are known, the physicochemical data, $\Delta \chi$, are substituted into Equation (4-1) leading to several simultaneous equations for each solute. Using a least squares minimization routine, a $P$ and $W$ value are calculated for each solute. The above systems involve only
non-specific interactions. For donor solutes studied in alcohol as well as donor solvents, the combined data are fit to Equation (4-2). $E_A$ and $C_A$ are set at zero for the donor solvents and, if known, the reported values are entered and fixed for the protic solvents. Reported $P$ and $W$ probe parameters from non-specifically interacting donor solvents are entered and fixed in the data fit of these probes in protic solvents. The program solves for the unknown parameters giving best fit $E_A'$, $C_A'$, and $S'$ values for hydrogen bonding solvents and the best fit $E_B^*$, $C_B^*$, $P$, and $W$ for new probes.

The values reported earlier for 7-amino-4-methylcoumarin (coum) and 7-N-dimethylamino-4-methylcoumarin (dmcoum) were calculated incorrectly. The revised $P$ and $W$ values used in this fit are -1.39 and 27.86 and -1.33 and 26.76, respectively.

An experimental procedure was reported earlier for the separation of specific and non-specific contributions to the observed shift of betaine. Results were obtained for non-specific solvation of this probe in the solvents methanol, ethanol, butan-1-ol, 2-methylpropan-2-ol, octan-1-ol, and dichloromethane. The non-specific solvation shifts of betaine in these solvents were entered in the data fit with $E_B^*$ and $C_B^*$ fixed at 0 because no specific interactions are involved.

In addition to spectral shifts, the enthalpies of interaction of alcohols with donors in non-solvating solvents were included in the fit. These results have no non-specific contributions so $P$ is set at zero. In combining this and pure solvent data, the assumption is made that the alcohol aggregates that exist in the non-solvating solvents and in the neat alcohol have similar $E_A'$ and $C_A'$ values. The spectral probes and enthalpies of interaction for hydrogen bonding solvents lead to a total of 453 simultaneous equations, which were solved for 16 $S'$ values, as well as $E_A'$ and $C_A'$ for 15 hydrogen bonding solvents ($E_A$ and
C\textsubscript{A} values for 2,2,2 trifluoroethanol, CH\textsubscript{2}Cl\textsubscript{2}, and CHCl\textsubscript{3} were fixed at previously reported values\textsuperscript{12a}). E\textsubscript{B}* and C\textsubscript{B}* values were determined for 43 donor probes.

The systems in which the alcohols are acting as donors were treated in a separate fit. Systems were first chosen where non-specific interactions were minimized through the use of poorly solvating solvents such as cyclohexane or CCl\textsubscript{4}. Several probes, whose E\textsubscript{A*}, C\textsubscript{A*}, and W values were reported earlier,\textsuperscript{12a} were fixed. For new acceptor probes, bases whose E\textsubscript{B} and C\textsubscript{B} values are known were fixed and combined with the basic alcohol data. The data was fit to Equation (4-2) to determine the new probe E\textsubscript{A*}, C\textsubscript{A*}, and W parameters, and the best fit E\textsubscript{B} and C\textsubscript{B} values for the alcohols.

Several solvents have only limited data available, leading to tentative parameters that are assigned low weights in Table 4-1. These weights should be used in subsequent analyses, and if large deviations occur, the solvent parameters should be redetermined by refitting all available data. The procedure for adding or revising probes or solvents is reported.\textsuperscript{12a,45c}

The probe E\textsubscript{B}* and C\textsubscript{B}* parameters, listed in Table 4-2, have been determined using acceptors whose C\textsubscript{A}/E\textsubscript{A} ratio is limited to the range of 0.1 to 1. Applications should be limited to acceptors whose ratio falls in this range, and the parameters should be redetermined as new systems outside this range become available.

\textsuperscript{13}C NMR Solvatochromism Experiment

Approximately 0.1 M solutions of 4-nitrobenzoic acid (NBA) were prepared in the following solvents: methanol; ethanol; propan-1-ol; propan-2-ol; butan-1-ol; 2-methylpropan-2-ol; acetonitrile; N,N-dimethylacetamide; N,N-dimethylformamide;
<table>
<thead>
<tr>
<th>solvent (C_A/E_A)</th>
<th>wt^a</th>
<th>E_A</th>
<th>C_A</th>
<th>S'</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2O^b (0.58)</td>
<td>0.5</td>
<td>1.35</td>
<td>0.78</td>
<td>3.86</td>
</tr>
<tr>
<td>CH3OH (0.58)</td>
<td>1</td>
<td>1.27</td>
<td>0.74</td>
<td>2.87</td>
</tr>
<tr>
<td>C2H5OH (0.58)</td>
<td>1</td>
<td>1.15</td>
<td>0.67</td>
<td>2.79</td>
</tr>
<tr>
<td>n-C3H7OH (0.58)</td>
<td>0.6</td>
<td>1.17</td>
<td>0.68</td>
<td>2.68</td>
</tr>
<tr>
<td>i-C3H7OH (0.58)</td>
<td>1</td>
<td>1.19</td>
<td>0.69</td>
<td>2.40</td>
</tr>
<tr>
<td>n-C4H9OH (0.70)</td>
<td>1</td>
<td>1.05</td>
<td>0.74</td>
<td>2.75</td>
</tr>
<tr>
<td>t-C4H9OH (0.58)</td>
<td>1</td>
<td>1.14</td>
<td>0.66</td>
<td>2.46</td>
</tr>
<tr>
<td>n-C5H11OH^c (0.54)</td>
<td>0.2</td>
<td>1.27</td>
<td>0.68</td>
<td>2.35</td>
</tr>
<tr>
<td>n-C6H13OH (0.61)</td>
<td>0.2</td>
<td>1.14</td>
<td>0.70</td>
<td>2.51</td>
</tr>
<tr>
<td>C6H11OH (0.41)</td>
<td>0.6</td>
<td>1.23</td>
<td>0.50</td>
<td>2.22</td>
</tr>
<tr>
<td>n-C8H17OH^d (1.0)</td>
<td>0.4</td>
<td>0.89</td>
<td>0.87</td>
<td>2.62</td>
</tr>
<tr>
<td>CF3CH2OH (0.51)</td>
<td>0.8</td>
<td>2.07</td>
<td>1.06</td>
<td>3.05</td>
</tr>
<tr>
<td>HC(O)NH2^d (0.16)</td>
<td>0.6</td>
<td>2.00</td>
<td>0.32</td>
<td>2.22</td>
</tr>
<tr>
<td>HCONH(CH3)^d (0.12)</td>
<td>0.2</td>
<td>1.25</td>
<td>0.15</td>
<td>2.56</td>
</tr>
<tr>
<td>CH2Cl2^d (0.13)</td>
<td>1</td>
<td>0.86</td>
<td>0.11</td>
<td>2.03</td>
</tr>
<tr>
<td>CHCl3^d (0.28)</td>
<td>1</td>
<td>1.56</td>
<td>0.44</td>
<td>1.63</td>
</tr>
<tr>
<td>CH3COOH (0.27)</td>
<td>0.2</td>
<td>3.39</td>
<td>0.91</td>
<td>1.28</td>
</tr>
<tr>
<td>C6H5CH2OH (0.46)</td>
<td>0.2</td>
<td>1.19</td>
<td>0.55</td>
<td>2.62</td>
</tr>
</tbody>
</table>

(a) Weight. Probes with measured enthalpies and 12 defined spectral probes are assigned a weight of 1. If no enthalpies are reported, 0.2 is subtracted. If there are only 10 different types of spectral probes, 0.1 is subtracted; if only 8 probes, 0.2 is subtracted; if only 6 probes, 0.4 is subtracted; and if only 4 probes, 0.6 is subtracted.

(b) Hydrophobic probes give poor results in water, as do several other probes that are well-behaved in the alcohols studied, e.g., C3H5NO (PYNO).

(c) The S’ value is poorly defined because of limited data.

(d) Lower weights may have to be used with weakly basic probes because of incomplete complexation in these solvents.
dimethyl sulfoxide; chloroform; dichloromethane; and ethyl ether. All solvents were purified according to published methods, and the $^{13}$C spectra were obtained using a Varian VXR 300. An external lock and reference of deuterated acetone and TMS in a sealed capillary tube were used during each run. The chemical shifts (relative to TMS) of all carbons in the NBA-solvent adduct were recorded.

Results and Discussion

**Acceptor Solvent and Donor Probe Parameters**

The resulting $E_A'$, $C_A'$, and $S'$ values for the protic solvents included in this data fit are listed in Table 4-1. The non-specific interactions in methanol and ethanol are characterized by $S'$ values comparable to DMF. The polarity decreases with alkyl chain length, while chain branching leads to a larger decrease. The solvent values of $E_A'$ and $C_A'$ in combination with the probe $E_B^*$ and $C_B^*$ give the specific donor-acceptor component of the property examined. The exceptional solvent properties of alcohols for basic solutes is due to contributions from both specific and non-specific interactions. The parameters permit determination of the relative importance of these two effects for different solutes.

Table 4-2 lists the probe name and abbreviation as well as the intercept (W), susceptibility (P), and the electrostatic and covalent donor parameters ($E_B^*$ and $C_B^*$). The P and W parameters include those previously reported and the new probes labeled as Fe2, Fe3, MoTp3, MoTp6, TEMPO, and Nile Red. The sign of the P value gives the direction of the solvent influence.
Table 4-2. Probe Parameters

<table>
<thead>
<tr>
<th>Probe (Symbol)</th>
<th>( E_b^* )</th>
<th>( C_b^* )</th>
<th>( P )</th>
<th>( W )</th>
<th>wgt*</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \nu ); N,N-Diethyl-4-nitroaniline (NNE4NO2AN) ( ^b )</td>
<td>-1.43</td>
<td>3.23</td>
<td>-1.69</td>
<td>29.31</td>
<td>0.9</td>
</tr>
<tr>
<td>( \nu ); N,N-Dimethyl-2-nitroaniline (NNM2NO2AN) ( ^c )</td>
<td>-0.69</td>
<td>2.01</td>
<td>-0.99</td>
<td>26.19</td>
<td>1</td>
</tr>
<tr>
<td>( \nu ); 4-nitroanisole (4 NO2ANISOL) ( ^d )</td>
<td>-0.92</td>
<td>2.72</td>
<td>-1.29</td>
<td>35.51</td>
<td>0.9</td>
</tr>
<tr>
<td>( \nu ); N,N-Dimethyl-2-nitrotoluidine (NNM2NO2TOL) ( ^e )</td>
<td>-0.32</td>
<td>1.37</td>
<td>-0.95</td>
<td>25.60</td>
<td>1</td>
</tr>
<tr>
<td>( \nu ); 4-(2,4,6-triphenyl-1-pyridino)-2,6-diphenylphenoxide (Betaine) ( ^f )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \nu ); 2-(dimethyl-amino)-7-nitrofluorene (DMANF) ( ^g )</td>
<td>-1.10</td>
<td></td>
<td></td>
<td>26.20</td>
<td>1</td>
</tr>
<tr>
<td>( \nu ); 2-fluoro-7-nitrofluorene (FNF) ( ^g )</td>
<td></td>
<td></td>
<td>-0.65</td>
<td>31.60</td>
<td>1</td>
</tr>
<tr>
<td>( \Delta \nu ); FNF-DMANF ( ^h )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \Delta \nu ); Di-tert-butyl nitroxide (ANTBUNO) ( ^i )</td>
<td>0.33</td>
<td>0.00</td>
<td>0.24</td>
<td>13.967</td>
<td>1</td>
</tr>
<tr>
<td>( \Delta \nu ); 4-Amino-2,2,6,6-tetramethylpiperidine-1-oxyl (ANPIPNO) ( ^i )</td>
<td>0.21</td>
<td>0.16</td>
<td>0.229</td>
<td>14.072</td>
<td>1</td>
</tr>
<tr>
<td>( \nu ); N,N-(Dimethyl)thiobenzamide S-oxide [C(_6)H(_5)CSO(NMe(_2))] ( ^j )</td>
<td>1.21</td>
<td>2.85</td>
<td>1.27</td>
<td>78.28</td>
<td>1</td>
</tr>
<tr>
<td>( \nu ); Pyridine-N-oxide (NUPYNO) ( ^k )</td>
<td></td>
<td></td>
<td></td>
<td>35.00</td>
<td>0.8</td>
</tr>
<tr>
<td>( \delta ) ( ^{13} )P; Triethylphosphine oxide (ET(_3)PO) ( ^l )</td>
<td>5.87</td>
<td>3.75</td>
<td>5.09</td>
<td>-8.91</td>
<td>0.9</td>
</tr>
<tr>
<td>( \delta ) ( ^{13} )C; N,N-Diethylbenzamide (C13DEBZAM) ( ^m )</td>
<td>1.49</td>
<td>1.43</td>
<td>0.92</td>
<td>29.79</td>
<td>0.8</td>
</tr>
<tr>
<td>( \nu ); a-[4-(N,N-Dimethylamino)phenyl]aminoacetooacetanilide ( ^n )</td>
<td>-3.02</td>
<td>4.38</td>
<td>-2.41</td>
<td>73.91</td>
<td>1</td>
</tr>
<tr>
<td>( \delta ) ( ^{13} )C; Pyridine-N-oxide (C13PYNO) ( ^o )</td>
<td>0.69</td>
<td>5.28</td>
<td>1.92</td>
<td>-19.80</td>
<td>1</td>
</tr>
<tr>
<td>( \delta ) ( ^{13} )C; Pyridine (C13PY) ( ^p )</td>
<td>-0.28</td>
<td>3.69</td>
<td>0.89</td>
<td>-16.53</td>
<td>1</td>
</tr>
<tr>
<td>( \nu ); 7-amino-4-methylcoumarin (coum) ( ^q )</td>
<td>-0.13</td>
<td>-1.12</td>
<td>-1.39</td>
<td>27.86</td>
<td>0.7</td>
</tr>
<tr>
<td>( \nu ); 7-N-dimethylamino-4-methylcoumarin (dmcoum) ( ^q )</td>
<td>-0.41</td>
<td>-0.48</td>
<td>-1.33</td>
<td>26.76</td>
<td>1</td>
</tr>
<tr>
<td>Brownstein's S' Parameter [s' (bst)] ( ^r )</td>
<td>0.10</td>
<td>0.03</td>
<td>0.09</td>
<td>-0.392</td>
<td></td>
</tr>
<tr>
<td>( \nu ); 4,4'-Bis(dimethylamino)benzophenone (Michler's ketone) ( ^s )</td>
<td>-1.15</td>
<td>0.60</td>
<td>-1.18</td>
<td>31.38</td>
<td>0.8</td>
</tr>
<tr>
<td>( \nu ); cis-Dicyanobis(1,10-phenanthroline) iron(II) (FePhen) ( ^s )</td>
<td>1.38</td>
<td>-0.08</td>
<td>1.38</td>
<td>12.49</td>
<td>1</td>
</tr>
<tr>
<td>( In ) ( \tau )</td>
<td>-1.02</td>
<td>-0.33</td>
<td>-1.37</td>
<td>11.74</td>
<td>0.7</td>
</tr>
</tbody>
</table>
Table 4-2—continued

<table>
<thead>
<tr>
<th>Probe (Symbol)</th>
<th>$E_B^*$</th>
<th>$C_B^*$</th>
<th>P</th>
<th>W</th>
<th>wgt*</th>
</tr>
</thead>
<tbody>
<tr>
<td>In TauNR $^1$</td>
<td>-1.11</td>
<td>-0.55</td>
<td>-1.28</td>
<td>11.86</td>
<td>0.7</td>
</tr>
<tr>
<td>$\nu$; cis-Dicyanobis(1,10-phenanthroline) ruthenium (II) (RuPhen) $^u$</td>
<td>1.33</td>
<td>0.30</td>
<td>1.11</td>
<td>16.99</td>
<td>0.9</td>
</tr>
<tr>
<td>$\nu$; bis-(bipyridyl) dichloro platinum (PtBPY2Cl2) $^v$</td>
<td>1.37</td>
<td>-1.46</td>
<td>1.86</td>
<td>20.58</td>
<td>1</td>
</tr>
<tr>
<td>$\nu$; tetracarbonyl bipyridine tungsten (WCO4BPY) $^w$</td>
<td>0.95</td>
<td>-3.24</td>
<td>2.37</td>
<td>15.34</td>
<td>0.8</td>
</tr>
<tr>
<td>$\nu$; tetracarbonyl bipyridine molybdenum (MoCO4BPY) $^w$</td>
<td>0.76</td>
<td>-2.77</td>
<td>2.15</td>
<td>16.51</td>
<td>0.8</td>
</tr>
<tr>
<td>$\nu$; tetracarbonyl bipyridine chromium (CrCO4BPY) $^w$</td>
<td>1.09</td>
<td>-3.86</td>
<td>2.36</td>
<td>14.68</td>
<td>1</td>
</tr>
<tr>
<td>$\nu$; tetracarbonyl phenanthroline tungsten (WCO4phen) $^w$</td>
<td>1.45</td>
<td>-4.28</td>
<td>2.24</td>
<td>15.70</td>
<td>0.9</td>
</tr>
<tr>
<td>$\nu$; Fe(LL II)$_2$(CN)$_2$ LL II=Schiff Base ligand 2 (Fe2) $^x$</td>
<td>0.75</td>
<td>0.12</td>
<td>0.56</td>
<td>13.40</td>
<td>1</td>
</tr>
<tr>
<td>$\nu$; bis-(2,2'-bipyridyl)biscyano iron(II) (Fe3) $^y$</td>
<td>1.90</td>
<td>-1.90</td>
<td>1.57</td>
<td>12.32</td>
<td>0.8</td>
</tr>
<tr>
<td>$\nu$; [{(Mo(NO)Tp*Cl}0(L-L)] (L-L)=4-NC$_3$H$_4$(CH=CH)$_4$C$_5$H$_4$N-4' (MoTp3) $^z$</td>
<td>0.89</td>
<td>-1.17</td>
<td>1.13</td>
<td>15.15</td>
<td>0.9</td>
</tr>
<tr>
<td>$\nu$; [{(Mo(NO)Tp*Cl}0(L-L)] (L-L)=4-NC$_3$H$_4$(CH=CH)$_4$C$_5$H$_4$N-4' (MoTp6) $^z$</td>
<td>0.50</td>
<td>-0.53</td>
<td>0.88</td>
<td>15.93</td>
<td>0.5</td>
</tr>
<tr>
<td>$\nu$; Nile Red $^{**}$</td>
<td>-0.85</td>
<td>0.82</td>
<td>-1.11</td>
<td>21.66</td>
<td>1</td>
</tr>
<tr>
<td>$\nu$; 2,2,6,6-tetramethylpiperidine-N-Oxyl radical (TEMPO) $^{bb}$</td>
<td>0.50</td>
<td>0.21</td>
<td>0.31</td>
<td>20.67</td>
<td>1</td>
</tr>
</tbody>
</table>

(a) The weight assigned here is equal to $1/[5*(0.3 * x)^{1/2}]$. This is consistent with the scheme used in previous papers, where ‘n’ was used as a weighting factor, and a smaller ‘n’ value gave more weight. We have changed this so that a larger ‘wgt’ means more weight is given.

(b) Electronic transition energy in $10^3$ cm$^{-1}$. Data from ref. 118a. x=0.15 % fit=6.

(c) Electronic transition energy in $10^3$ cm$^{-1}$. Data from ref 118b. x=0.05 % fit=4.

(d) Electronic transition energy in $10^3$ cm$^{-1}$. Data from ref 118a. x=0.15 % fit=11.

(e) Electronic transition energy in $10^3$ cm$^{-1}$. Data from ref. 118b. x=0.07 % fit=5.

(f) Transition energy in kcal mol$^{-1}$. No $E_B$ and $C_B$ values are given because this probe is not recommended for use with specific effects. Data from ref. 34b and 38a. x=0.42 % fit=4.
Transition energy in cm$^{-1}$. No $E_B$ and $C_B$ values are given because these probes are not recommended for use with specific effects. Data from refs. 113 and 116. DMANF: $x=0.16$ % fit=12. FNF: $x=0.16$ % fit=13.

Difference in the transition energies of FNF and DMANF in cm$^{-1}$. No $E_B$ and $C_B$ are given because this probe is not recommended for use with specific effects.

The nitrogen hyperfine coupling constant in cm$^{-1} \times 10^4$. Data from ref. 119 where $A_N$ is reported as the line separation in gauss, which is actually $A_N/g\beta$. Since $g$ is not given, it is assumed to be 2.0047 and $\beta=4.6658 \times 10^5$ cm$^{-1}$/G. Multiplying the line separation by $9.3591 \times 10^3$ gives $A_N$ in units of cm$^{-1} \times 10^4$. The fit is run by multiplying the numbers by $10^4$. ANTUNBUNO: $x=0.04$ % fit=9. ANPIPNO: $x=0.04$ % fit=10.

Transition energy in kcal mol$^{-1}$. Data from ref. 120. $x=0.21$ % fit=4.

Transition energy in 10$^3$ cm$^{-1}$. Data from ref. 121. $x=0.07$ % fit=3.

$3^1P$ chemical shift in ppm. Data from ref. 122. $x=0.08$ % fit=1.

Difference in $^{13}C$ chemical shift (in ppm) of C=O and C(1) of the phenyl ring. Data from personal communication with Y. Marcus. $x=0.03$, % fit=2.

Transition energy in kcal mol$^{-1}$. Data from ref. 124. $x=0.09$, % fit=3.

Difference in $^{13}C$ chemical shift (in ppm) between $\gamma$ and $\alpha$ carbons. Data from ref. 125. $x=0.59$, % fit=8.

$^{13}C$ chemical shift in ppm. Data from ref. 126. $x=0.08$, % fit=2.

Transition energy in kcal mol$^{-1}$. Data from ref. 127. coum: $x=0.23$ % fit=12. dmcoum: $x=0.08$ % fit=4.

Dimensionless reactivity scale. Data from ref. 128. $x=0.03$, % fit=10.

Transition energy in 10$^3$ cm$^{-1}$. Data from ref. 129. MichKet: $x=0.10$, % fit=4. FePhen: $x=0.10$ % fit=4.

Excited state lifetime of Rose Bengal. Data from ref. 130. LnTau: $x=0.06$ % fit=3. LnTauNR: $x=0.07$, % fit=3.

Transition energy in 10$^3$ cm$^{-1}$. Data from ref. 131. $x=0.16$, % fit=5.

Transition energy in 10$^3$ cm$^{-1}$. Data from ref. 132. $x=0.34$, % fit=9.

Transition energy in kcal mol$^{-1}$. Data from ref. 133. WCO4BPY: $x=0.09$, % fit=8. MoCO4BPY: $x=0.17$ % fit=14. CrCO4BPY: $x=0.13$, % fit=10. WCO4PHEN: $x=0.19$, % fit=16.

Transition energy in kcal mol$^{-1}$. Data from ref. 134a. $x=0.11$, % fit=7.

Transition energy in 10$^3$ cm$^{-1}$. Data from ref. 135. $x=0.16$, % fit=10.

Transition energy in nm. Data from ref. 136. MoTp3: $x=0.14$, % fit=8. MoTp6: $x=0.23$, % fit=13.

Transition energy in 10$^3$ cm$^{-1}$. Data from ref. 137. $x=0.12$, % fit=7.

Transition energy in 10$^3$ cm$^{-1}$. Data from ref. 138. $x=0.05$, % fit=4.
Weak donor spectral probes dissolved in weak acceptor solvents sometimes deviate from the fit in a direction that suggests incomplete complexation. With a positive P value, incomplete complexation of a solute leads to an experimental value that is smaller than the calculated value. For probes with negative P values, the experimental value is larger than the calculated value. Weak donor probes in the solvents CH₂Cl₂, CHCl₃, and NMF, have been omitted from the data fit. When one considers the complexity from the existence of multiple donor sites in many probes, the fact that so many systems are well behaved is more surprising than finding that some miss. Many of the exceptions found in this data fit are also encountered in the solvent polarity literature and have been referred to as “spectral anomalies” or “spurious effects.”

The footnotes to Table 4-2 indicate the average deviation and percent fit for each solute studied. The percent fit is the average deviation divided by the range of the values of the physicochemical property in that system times one hundred. The use of these quantities has been discussed earlier.⁴⁷c,¹⁴⁰

Various Probes and Scales

In this section we shall examine in detail probes that form the basis for the more common scales of solvent polarity and hydrogen bond acidity. Analyses of these probes with Equation (4-2) indicate the extent to which contributions from specific and non-specific interactions are included causing the different scales to provide different measures of “solvent polarity.” The resolution into specific and non-specific solvation provides a reinterpretation of the measurements and in most instances incorporates the data into the USM. The diversity of scales and the good fit of all this data to USM emphasizes the
deficiencies in other models that combine specific and non-specific solvation into a single polarity parameter.

(C$_2$H$_5$)$_3$PO and the Acceptor Number Scale

The $^{31}$P shift of (C$_2$H$_5$)$_3$PO is the basis for the acceptor number (AN)$^{122}$ scale, which is proposed to be a measure of solvent acidity$^{123}$. The relationship between AN and the $^{31}$P shift is given in Equation (4-4), where $\delta_S$ is the $^{31}$P shift in a given solvent,

$$AN = 2.348 \times (\delta_S - \delta_H)$$  \hspace{1cm} (4-4)

and $\delta_H$ is the $^{31}$P shift in hexane (-1.68 ppm).

The $^{31}$P chemical shift of (C$_2$H$_5$)$_3$PO was treated in the master fit instead of AN and shows an excellent correlation to $E_A$, $C_A$, and $S'$. Both 2-methylpropan-2-ol and CHCl$_3$ were omitted from the fits. A steric interaction, involving the ethyl groups of the Et$_3$PO and the tert-butyl group of the alcohol, may force a linear P-O--H-O geometry. This leads to a weaker interaction than bonding in an angular manner to an sp$^2$ oxygen lone pair of the phosphine oxide for which $E_B^*$ and $C_B^*$ apply. A larger shift is calculated than is observed. A similar steric problem is anticipated and found for chloroform. Propan-2-ol and CH$_2$Cl$_2$ are less bulky and well behaved. The resulting $E_B^*$ and $C_B^*$ parameters for the (C$_2$H$_5$)$_3$PO chemical shift (Table 4-2) show an increased shift from both electrostatic and covalent bond interactions. Mayer reports$^{122}$ that the 2-methylpropan-2-ol shift is smaller than expected and attributes the deviation to chain branching. CHCl$_3$ has a larger $^{31}$P chemical shift than would be expected$^{122}$ in many acceptor correlations.

The $^{31}$P chemical shifts of (C$_2$H$_5$)$_3$PO in various donor solvents, in which a specific interaction is not expected ($E_A = C_A = 0$), show significant solvent dependent changes from
non-specific solvation. Thus, attributing the shift in acceptor solvents to specific interactions, as suggested in the AN literature, leads to an overestimate of the acceptor properties of the solvent and in several instances, an assignment of acceptor properties to solvents that are not acceptors.

In a recent article, Riddle and Fowkes analyzed the AN scale and concluded that it contains both specific and non-specific solvation contributions. The non-specific contribution to the $^{31}$P shift (and thus the AN) was calculated using surface and interfacial tensions. Their estimates are much different than ours. With ethanol, the USM estimation of the non-specific contribution to the $^{31}$P chemical shift is 5.29 ppm, compared to -0.83 ppm from surface and interfacial tensions. Even the sign of the latter is contrary to expectation indicating USM provides a more reasonable estimate of specific and non-specific solvation.

**NUPYNO/C13PYNO**

As reported earlier, the energies of the electronic transition, NUPYNO, and $^{13}$C shift of pyridine-N-oxide correlate well to Equation (4-1) with basic solvents. When hydrogen bonding solvents are treated with Equation (4-2), fixing P and W at their values from the basic solvent fit, a good correlation results giving $r^2=0.99$, with $x=0.07$ for NUPYNO. Limited $^{13}$C data for alcohols lead to the tentative values in Table 4-2. Water is omitted as the only system that deviates and does so in both measurements. The $^{13}$C value employed is the chemical shift of the $\gamma$ carbon minus the chemical shift of the $\alpha$ carbon. Contrary to literature assumption, the resulting solute P and basicity parameters given in Table 4-2 indicate that the shift difference contains both specific and
non-specific interactions. The shift difference does provide an excellent probe of solvation employing Equation (4-2).

**FEPHEN/RUPHEN**

The electronic spectral shifts of bis-(1,10-phenanthroline) dicyano metal complexes [iron (II) and ruthenium (II), FEPHEN and RUPHEN, respectively] in basic solvents were previously treated by USM.\(^{45c,139}\) In protic solvents, FEPHEN is well behaved, with 2-methylpropan-2-ol deviating in the direction of a steric effect. This explanation is negated by CHCl\(_3\), which is well behaved with appreciable contributions to the shift in the electronic spectra from specific and non-specific interactions. In the RUPHEN system, chloroform and water deviate. Water was not studied with FEPHEN. More solvents need to be studied to detect patterns in these deviations. The deviant solvents are not included in the master fit. The parameters for both probes are given in Table 4-2.

**DMANF and FNF and the SPP\(^N\) scale**

A fit of the DMANF shifts\(^{113,116}\) to S' in basic solvents is reported\(^{139}\). Significant deviations were found in the n-alkane solvents, and these are attributed to probe aggregation. Deviations in aromatic solvents are attributed to specific \(\pi\)-complexation. Alkane and aromatic solvents were omitted in these and the earlier correlations.\(^{139}\) With the inclusion of nitromethane (omitted earlier\(^{139}\)), the \(r^2\) is found to be 0.91 (with an average deviation of 0.20). This gives a new \(P\) value of -1.10 and a new \(W\) value of 26.20. A similar fit adding CH\(_3\)NO\(_2\) to FNF gave an \(r^2\) of 0.86 (with an average deviation of 0.15), and \(P= -0.65\) and \(W=31.60\), with parameters similar to those reported earlier.\(^{139}\) CH\(_3\)CN was omitted from both fits.
Catalán et al. claim\textsuperscript{113,116} that the difference in the shifts of DMANF and FNF ($\Delta \nu$) in a given solvent subtract out spurious solvation effects and specific interactions with these solutes providing a measure of non-specific solvation. The SPP\textsuperscript{N} scale is based on this premise. In order to evaluate this suggestion, $\Delta \nu$ was fit to Equation (4-1), giving $r^2=0.90$ and an average deviation of 0.08 (with acetonitrile and dioxane removed in all cases). Removal of all $\pi$ and alkane solvents from the fit improves the $r^2$ to 0.92 ($x=0.05$). Adding only the $\pi$-solvents back into the fit gives $r^2$ value to 0.89 ($x=0.07$). Putting only the alkane solvents back into the fit gives $r^2=0.93$ ($x=0.06$). The improved average deviation with $\pi$-solvents excluded shows that the difference in the DMANF and FNF transition energies cancels the aggregation problems in alkane solvents but only partially corrects for the $\pi$-complexation in aromatic solvents. The differences in the shift of the extensive set of solvents studied by Catalán et al.\textsuperscript{113,116} provide an excellent probe of non-specific solvation for basic, non-aromatic solvents.

Next the evaluation of the cancellation of specific hydrogen bonding with the shift difference was evaluated. When the alcohols are added to the difference fit reported above, the $r^2$ decreases to an unacceptable value of 0.77. Specific interactions are different in the two probes and are not canceled with the transition energy difference. The transition energy difference in DMANF and FNF in hydrogen bonding solvents were fit to Equation (4-2) to determine $E_b^*$ and $C_b^*$ parameters for the specific interaction. Even with the omission of acetic acid and $\text{CH}_2\text{Cl}_2$, a poor $r^2$ of 0.67 resulted. Similar fits of the transition energies of DMANF and FNF individually gave $r^2$ values of 0.82 and 0.75, respectively. These poor fits of the individual probes and their differences indicate that
these measurements cannot be used to evaluate solvation effects when specific hydrogen bonding interactions exist.

Taft/Kamlet Systems

Taft and Kamlet have studied a series of nitro-substituted anilines, anisoles, and toluidines as probes for their polarity, \( \pi^* \), acidity, \( \alpha \), and basicity, \( \beta \), scales. Two of the more extensively studied compounds, labeled NNE4NO2AN and 4NO2ANISOL, were included in the master fit. Weakly acidic \( \text{CH}_2\text{Cl}_2 \) misses in both systems, in a direction that suggests incomplete complexation. As suggested earlier for weak acceptor probes in weak donor solvents, incomplete complexation leads to free and complexed species in solution, giving an average of band positions that lead to an experimental shift that is smaller than calculated with the fit parameters. With the even weaker donor probe 4NO2ANISOL, \( \text{CHCl}_3 \) and formamide both miss in the same direction as \( \text{CH}_2\text{Cl}_2 \). The 4NO2ANISOL probe is poorly behaved in water, possibly due to probe aggregation.

With NNM2NO2AN and NNM2NO2TOL, the nitro group is positioned ortho to the substituted aniline group. These probes are well behaved in the USM analysis for alcohols, with only \( \text{CH}_2\text{Cl}_2 \) missing because of incomplete complexation. All of the above probes are included in the master fit with the deviant solvents omitted. The resulting \( E_B^* \) and \( C_B^* \) parameters are given in Table 4-2.

In the design of the \( \pi^* \), \( \alpha \), and \( \beta \) scales, more than one probe is used as a measure of solvent properties to average the solvatochromic effect of the solvent and to remove "spectral anomalies" that may exist in one probe, but not in another. The \( \pi^* \) scale, referenced to cyclohexane as zero, is reported to treat non-specific interactions. The
probes are assigned s values, which are the counterparts of P in the USM, with sπ* corresponding to PS'. The π* scale was extended to protic solvents with the addition of an α term to include specific acceptor interactions. Using the most recent π*-α parameters, the alcohols were analyzed with USM to determine the correlation of π* to S' and α to EA and CA for the alcohols in this report. Equations (4-5) and (4-6) result. As shown by r², a large deviation is found for the limited range of π* and S' for alcohols.

\[
\pi^* = 0.08 (\pm 0.11) S' + 0.43 (\pm 0.30) \quad (r^2=0.04, n=11, x=0.18, F=0.46) \quad (4-5)
\]

\[
\alpha = 0.03 (\pm 0.14) E_A + 1.14 (\pm 0.28) C_A \quad (r^2=0.94, n=11, x=0.21, F=68.28) \quad (4-6)
\]

R² is excellent for the correlation of α to EA and CA.

It is noted that for all the red-shifted (negative P), nitro-substituted aromatics (Kamlet/Taft, Catalán probes), the electrostatic contribution from the specific interaction to the shift is in the same direction as the non-specific interaction, but the covalent contribution is in the opposite direction indicating a stronger covalent contribution in the ground state than excited state.

**Betaine and the E₇(30) Scale**

Solvent shifts in the electronic spectra of the basic probe pyridinium-N-phenoxide [Betaine, E₇(30)] have been measured in many solvents. For non-specific solvation in donor solvents, E₇(30) values correlate extremely well to S'. If there were no specific contributions to the betaine shift in alcohols, E₇(30) would correlate to S'. The poor correlation of E₇(30) for all hydrogen bonding solvents to S' (r²=0.73, with an average deviation of 3.10) shows E₇(30) is not a non-specific solvent polarity probe for alcohols. Furthermore, no single parameter can be expected to provide the varying
contributions from specific and non-specific interactions that exist in other systems to which the parameter may be applied.

Holding the $P$ and $W$ for betaine fixed at the values from the donor solvent fit, the shifts in alcohols (weighted as in Table 4-1) are fit to $E_A$, $C_A$, and $S'$ giving poor results ($r^2=0.77$, with an average deviation of 3.94). Chloroform, $\text{CH}_2\text{Cl}_2$, and 2-methylpropan-2-ol have experimental $E_T(30)$ values considerably smaller than the calculated values. The reported shift for betaine in methanol is much larger than in other alcohols and is much larger than calculated with USM. Water also causes problems with this solute not only in USM but also in the $E_T(30)$ correlations giving a value smaller than expected. Hydrolysis, aggregation, and low solubility in water ($2 \times 10^{-6} \text{ mol L}^{-1}$) are reported problems.

When $\text{CH}_2\text{Cl}_2$, $\text{CHCl}_3$, 2-methylpropan-2-ol, water, and methanol were omitted from the data fit to solve for $E_B^*$ and $C_B^*$ for betaine (fixing the $P$ and $W$ values to that of the donor solvent fit), a poor correlation still resulted ($r^2=0.86$, with an average deviation of 3.14). The poor correlations can be rationalized. Limited access to the betaine oxygen donor center could lead to steric problems of varying degrees with all alcohols except $\text{CH}_3\text{OH}$ which forms strong hydrogen bonds utilizing the sp$^2$ oxygen lone pairs. Linear chain alcohols form weaker, linear N-O--H-OR hydrogen bonds because of steric effects, and branched-chain alcohols interact weakest by accessing only the largely oxygen π molecular orbital. Each donor type requires a different $E_B^*$ and $C_B^*$ value and in some systems, mixtures of adducts could exist. The net result is that though betaine is an excellent probe for non-protic solvents it is a poor probe for acceptor solvents.
Z-value/Z’

Kosower has outlined some of the problems involved in the determination of Z-values. The scale is based on the transition energy for the longest-wavelength band observed in 1-ethyl-4-carbomethoxypyridinium iodide (pyridinium iodide 214). A negative solvatochromism is reported for this probe (consistent with the reported positive P value of 13.23). In the more polar solvents, this transition is shifted into the region of the stronger \( \pi \rightarrow \pi^* \) transition of the pyridinium ion, and Z-values are obtained by extrapolating transitions in solvent mixtures. Because pyridinium iodide 214 is not soluble in nonpolar solvents, it is necessary to use an alternate probe (1-ethyl-4-carbomethoxypyridinium iodide 360). The measurements in non-polar solvents are extrapolated to zero ionic strength because ion-pair aggregation leads to a shift that is too large.

Because of these complications, Z-values were not included in the master fit of the solvation data. The solvent \( E_A, C_A \) and \( S' \) parameters and weights in Table 4-1 were correlated to the Z-value for alcohol solvents using \( P \) and \( W \) values from Table 4-2.

\[
Z - PS' - W = 6.66 \pm 1.46 E_A + 5.46 \pm 2.55 C_A \quad (r^2=0.99, n=7, x=1.22) \quad (4-7)
\]

The average deviation of 1.22 kcal mol\(^{-1}\), which translates to a 426 cm\(^{-1}\) miss, gives an excellent \( r^2 \) because of the large shifts observed for this probe.

Griffiths and Pugh suggested change of water’s Z-value from 94.6 to 91.8 would lead to a larger deviation for water in our fit. Medda and coworkers chose a derivative of 214 for their \( Z' \) scale. \( Z' \), gives a comparable correlation [Equation (4-8)] to \( E_A, C_A \) and \( S' \) as Z does.

\[
Z' - PS' - W = 9.56 \pm 1.31 E_A + 5.93 \pm 2.31 C_A \quad (r^2=0.99, n=8, x=1.23) \quad (4-8)
\]
NMP

The enthalpies for hydrogen bonding to N-methylpyrrolidinone (NMP)\(^{143}\)\( (E_B=2.12, C_B=1.65)\)\(^{12\alpha}\) were included in our data fit fixing \(E_B\) and \(C_B\) at the reported values. Because the measurements were done in 1,2-dichloroethane (DCE), a constant enthalpy contribution, \(W\), from solvation of the NMP could exist so Equation (4-2) was used with \(PS'\) set at zero to fit enthalpies of hydrogen bonding to several substituted phenols whose \(E_A\) and \(C_A\) values are known. The constant \(W\) value (calculated to be 1.54 kcal mol\(^{-1}\)) was subtracted from the reported enthalpies for all the alcohols and CHCl\(_3\) and these systems were included in the master fit with \(S'\) set at zero to determine \(E_{A'}\) and \(C_{A'}\) for the aliphatic alcohols. An excellent fit results \((r^2=0.96, x=0.14)\).

Abraham's \(\alpha_2^H\) scale

Abraham et al. have developed a scale\(^{143}\) of hydrogen bond acidity to treat specific interactions using equilibrium constants, \(K^i\), for complexation of a series of acids with a series of bases in dilute solutions in CCl\(_4\). The \(\alpha_2^H\) scale arises from a fit of hydrogen bonding equilibrium constants to the following equation:

\[
\log K^i = L_B \log K_A^{Hi} + D_B
\]

(4-9)

where \(L_B\) and \(D_B\) are empirical base parameters and \(\log K_A^{Hi}\) is an acid parameter. The acid parameter is converted into a hydrogen bond acidity parameter, \(\alpha_2^H\), using the following relationship:

\[
\alpha_2^H = (\log K_A^{Hi} + 1.1)/4.636
\]

(4-10)
Some of the acids show family-dependent behavior toward a series of bases as do some families of bases toward acids. These family dependent combinations were eliminated from the systems used to determine \( \alpha_2^H \).

As claimed, the \( \alpha_2^H \) scale measures the specific interaction as shown by an excellent correlation to ECW. Using the \( E_A^* \), \( C_A^* \), and weights given in Table 4-1 eight aliphatic alcohols, pyrrole, and 17 substituted phenols were correlated to \( E_A \) and \( C_A \). The correlation is given in Equation (4-11). Acetic acid, \( CHCl_3 \), and \( CH_2Cl_2 \) deviate and were omitted. The \( \alpha_2^H \) scale is an acidity scale that can be used as a reference scale to correlate data for alcohols and phenols subject to the limitations discussed for one parameter scales.\(^{19a}\)

**Addition of New Solvents to the USM**

The addition of new solvents to the USM will be illustrated using data for benzyl alcohol and acetic acid. These acceptor solvents were not included in the master fit because of potential complications from \( \pi \)-solute-\( \pi \)-solvent charge transfer interactions in the former and acid dimerization in the latter. These interactions would distort the master fit introducing error in the parameters. Benzyl alcohol was subsequently analyzed using Equation (4-2). The \( \Delta\chi \) for the probes studied in this solvent, and their \( E_B^* \), \( C_B^* \), \( P \), and \( W \) values reported in Table 4-2 are used to generate a series of equations that are solved for \( E_A, C_A \), and \( S' \) for benzyl alcohol. Table 4-3 reports the results after several probes that gave large deviations (2.5 times the average deviation) were removed from the fit. The deviant systems include NNE4NO2AN, NNM2NO2AN, 4NO2ANISOL,
NNM2NO2TOL, DMANF, FNF, C13DEBZAM, and Michler's ketone. The omitted probes show a pattern of \( \pi-\pi^* \) interactions dominating hydrogen bonding because of the weak probe basicity. Benzyl alcohol is reported\textsuperscript{144} to give poor fits to \( \pi^* \) and \( \alpha \) in many analyses. The fit of the remaining systems to Equation (4-2) gives \( E_A=1.19, \quad C_A=0.55, \quad \text{and} \quad S'=2.62 \), with an \( r^2=0.99 \) and \( x=0.10 \). Inclusion of some probes where \( \pi \) complexation is possible suggests that the donor sites in these probes are strong enough that the hydrogen bonding interaction dominates the potential \( \pi \) complexation. The parameters for benzyl alcohol should be used with caution toward weakly basic \( \pi \) solutes.

Acetic acid forms cyclic dimers in solution and the gas phase, which are broken when the carboxyl proton undergoes a specific interaction with a donor to form an adduct. Dimerization is offered\textsuperscript{115b} as the reason when acetic acid does not fit in solvatochromic comparisons. Weak donor probes would be incompletely complexed in acetic acid and the observed shift would be less than calculated. Table 4-3 shows the fit of acetic acid with the probes that are well behaved in this study. The solution of this data set gives \( E_A=3.39, \quad C_A=0.91, \quad \text{and} \quad S'=1.28 \) (\( r^2=0.99, \quad x=0.10 \)). The probes Z-VALUE, C6H5CSO(NMe2), and MoTp3 were omitted from this fit.

**Data Fit for Alcohols as Donors**

Toward strong acid solutes, alcohols behave as donors whose specific interaction is characterized by \( E_B \) and \( C_B \). In these systems, care has to be taken to be certain that the alcohol is not the acceptor. The donor parameters for alcohols (Table 4-4) were determined from a separate master fit of the data for the acidic probes listed in Table 4-5. All of the systems listed in Table 4-5 were fit very well to Equation (4-2), with a few
Table 4-3. Data Fits for Benzyl Alcohol and Acetic Acid Solvents

<table>
<thead>
<tr>
<th>Probe</th>
<th>Benzyl Alcohol</th>
<th>Acetic Acid</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>((\chi - W)_{exp})</td>
<td>((\chi - W)_{cal}^a)</td>
</tr>
<tr>
<td>NNE4NO2AN</td>
<td>-3.06</td>
<td>(-4.35)</td>
</tr>
<tr>
<td>NNM2NO2AN</td>
<td>-3.76</td>
<td>(-2.98)</td>
</tr>
<tr>
<td>4NO2ANISOL</td>
<td>-2.92</td>
<td>(-2.30)</td>
</tr>
<tr>
<td>NNM2NO2TOL</td>
<td>-2.92</td>
<td>(-2.12)</td>
</tr>
<tr>
<td>DMANF</td>
<td>-3.80</td>
<td>(-3.15)</td>
</tr>
<tr>
<td>FNF</td>
<td>-2.49</td>
<td>(-1.80)</td>
</tr>
<tr>
<td>Betaine</td>
<td>31.17</td>
<td>31.25</td>
</tr>
<tr>
<td>Z-value</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ANTBUNO</td>
<td>1.26</td>
<td>1.03</td>
</tr>
<tr>
<td>ANPIPNO</td>
<td>1.17</td>
<td>0.94</td>
</tr>
<tr>
<td>NUPYNO</td>
<td>4.60</td>
<td>4.44</td>
</tr>
<tr>
<td>ET3PO</td>
<td>29.76</td>
<td>29.77</td>
</tr>
<tr>
<td>S (bst)</td>
<td>0.40</td>
<td>0.49</td>
</tr>
<tr>
<td>C13DEBZam</td>
<td>5.77</td>
<td>(4.97)</td>
</tr>
<tr>
<td>Michket</td>
<td>-4.90</td>
<td>(-4.12)</td>
</tr>
<tr>
<td>PhCSO(NMe2)</td>
<td>6.40</td>
<td>6.35</td>
</tr>
<tr>
<td>FEPHEN</td>
<td>5.37</td>
<td>5.22</td>
</tr>
<tr>
<td>WCO4BPY</td>
<td>5.48</td>
<td>5.56</td>
</tr>
<tr>
<td>MoCO4BPY</td>
<td>5.03</td>
<td>5.01</td>
</tr>
<tr>
<td>Fe2</td>
<td>2.40</td>
<td>2.43</td>
</tr>
<tr>
<td>Fe3</td>
<td>5.86</td>
<td>5.82</td>
</tr>
<tr>
<td>CrCO4BPY</td>
<td>5.31</td>
<td>5.35</td>
</tr>
<tr>
<td>WCO4PHEN</td>
<td>5.43</td>
<td>5.24</td>
</tr>
<tr>
<td>MoTp3</td>
<td></td>
<td>2.74</td>
</tr>
</tbody>
</table>

(a) Calculated with 1.19 \((\pm 0.07) E_B^* + 0.55 (\pm 0.02) C_B^* + 2.62 (\pm 0.07) P + W\), using W values from Table 2, \(r^2=0.9998\), \(x=0.10\). Systems with values in parenthesis were not included in the overall fit.

(b) Calculated with 3.39 \((\pm 0.20) E_B^* + 0.91 (\pm 0.05) C_B^* + 1.28 (\pm 0.20) P + W\), using W values from Table 2, \(r^2=0.9999\), \(x=0.10\). Systems with values in parenthesis were not included in the overall fit.
Table 4-4. Alcohol $E_B$ and $C_B$ parameters

<table>
<thead>
<tr>
<th>solvent ($C_B/E_B$)</th>
<th>wt$^*$</th>
<th>$E_B$</th>
<th>$C_B$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$O (0.82)</td>
<td>0.3</td>
<td>1.36</td>
<td>1.12</td>
</tr>
<tr>
<td>CH$_3$OH (0.49)</td>
<td>1.0</td>
<td>1.90</td>
<td>0.93</td>
</tr>
<tr>
<td>C$_2$H$_5$OH (0.48)</td>
<td>1.0</td>
<td>1.96</td>
<td>0.95</td>
</tr>
<tr>
<td>n-C$_3$H$_7$OH (0.49)</td>
<td>1.0</td>
<td>1.98</td>
<td>0.97</td>
</tr>
<tr>
<td>i-C$_3$H$_7$OH (0.49)</td>
<td>1.0</td>
<td>2.00</td>
<td>0.98</td>
</tr>
<tr>
<td>n-C$_4$H$_9$OH (0.49)</td>
<td>1.0</td>
<td>1.98</td>
<td>0.97</td>
</tr>
<tr>
<td>i-C$_4$H$_9$OH (0.49)</td>
<td>0.5</td>
<td>1.98</td>
<td>0.97</td>
</tr>
<tr>
<td>t-C$_4$H$_9$OH (0.49)</td>
<td>1.0</td>
<td>2.05</td>
<td>1.00</td>
</tr>
<tr>
<td>CH$_2$=CHOH (0.90)</td>
<td>0.5</td>
<td>1.60</td>
<td>1.44</td>
</tr>
<tr>
<td>C$<em>6$H$</em>{11}$OH (0.86)</td>
<td>0.5</td>
<td>1.73</td>
<td>1.49</td>
</tr>
<tr>
<td>n-C$<em>8$H$</em>{17}$OH (0.49)</td>
<td>0.7</td>
<td>2.00</td>
<td>0.97</td>
</tr>
<tr>
<td>CF$_3$CH$_2$OH (4.0)</td>
<td>0.2</td>
<td>0.50</td>
<td>2.06</td>
</tr>
</tbody>
</table>
Table 4-5. Parameters for Systems in Alcohol basicity

<table>
<thead>
<tr>
<th>Shift or Reaction</th>
<th>$E_A^*$</th>
<th>$C_A^*$</th>
<th>$W$</th>
<th>wt*</th>
</tr>
</thead>
<tbody>
<tr>
<td>log $K_c$ 4-nitroaniline</td>
<td>1.78</td>
<td>1.08</td>
<td>-5.04</td>
<td>0.8</td>
</tr>
<tr>
<td>log $K_1$ 3,4-dinitrophenol</td>
<td>4.80</td>
<td>0.86</td>
<td>-6.77</td>
<td>0.7</td>
</tr>
<tr>
<td>$\Delta v$ (OH) (CF$_3$)$_3$COH</td>
<td>227</td>
<td>152</td>
<td>-167</td>
<td>0.5</td>
</tr>
<tr>
<td>$\Delta v$ (OH) 4-fluorophenol</td>
<td>163</td>
<td>101</td>
<td>-171</td>
<td>0.3</td>
</tr>
<tr>
<td>$\Delta v$ (OH) phenol</td>
<td>167</td>
<td>109</td>
<td>-205</td>
<td>0.3</td>
</tr>
<tr>
<td>log $K$ 3,5 dichlorophenol</td>
<td>68</td>
<td>-136</td>
<td>-1.0</td>
<td>1</td>
</tr>
<tr>
<td>log $K$ 3 nitrophenol iso-octane</td>
<td>183</td>
<td>-376</td>
<td>1.43</td>
<td>1</td>
</tr>
<tr>
<td>log $K$ 3 nitrophenol C$<em>6$H$</em>{12}$</td>
<td>114</td>
<td>-232</td>
<td>-0.51</td>
<td>1</td>
</tr>
<tr>
<td>log $K$ 4 fluorophenol</td>
<td>1.09</td>
<td>0.40</td>
<td>-1.29</td>
<td>0.6</td>
</tr>
<tr>
<td>log $K$ phenol</td>
<td>-120</td>
<td>257</td>
<td>-9.07</td>
<td>1</td>
</tr>
<tr>
<td>p$K_{HB}$</td>
<td>1.68</td>
<td>1.12</td>
<td>-3.42</td>
<td>1</td>
</tr>
<tr>
<td>p$K_{BH^+}$</td>
<td>71</td>
<td>-143</td>
<td>-4.6</td>
<td>1</td>
</tr>
<tr>
<td>log $k$ ROH$_2^+$</td>
<td>-11.3</td>
<td>-7.1</td>
<td>31.2</td>
<td>1</td>
</tr>
<tr>
<td>$\Delta^{13}$C CF$_3$COOH</td>
<td>-1514</td>
<td>3103</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>$\Delta^{13}$C CF$_2$COOH</td>
<td>-1903</td>
<td>3900</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>log $K_b$</td>
<td>0.90</td>
<td>-0.98</td>
<td>-0.27</td>
<td>1</td>
</tr>
<tr>
<td>$-\Delta H$ phenol</td>
<td>2.27</td>
<td>1.07</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>$-\Delta H$ n-C$_3$H$_7$OH</td>
<td>1.17</td>
<td>0.68</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>$-\Delta H I_2^+$</td>
<td>0.50</td>
<td>2.00</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>$^{13}$C nitrobenzoic acid</td>
<td>-0.69</td>
<td>0.31</td>
<td>164.5</td>
<td>0.7</td>
</tr>
</tbody>
</table>

(a) The weight assigned here is equal to $1/[5^*(0.3 * x)^{1/2}]$. This is consistent with the scheme used in earlier papers, where 'n' was used as a weighting factor, and smaller 'n' value gave more weight. We have changed this so that a larger "wgt" means more weight is given.

(b) log K for the reaction between p-nitroaniline and the alcohol in aqueous solution. Data from ref. 146, x=0.20, % fit=20.

(c) log K for the reaction between 3,4 dinitrophenol and the alcohol in highly dilute C$_6$H$_{12}$ solution. Data from ref. 147, x=0.28, % fit=8.

(d) Change in the O-H stretching frequency of (CF$_3$)$_3$COH upon adduct formation in FC75. Data from refs. 148 and 149.

(e) Change in the O-H stretching frequency of 4-fluorophenol upon adduct formation in CCl$_4$. Data from ref. 148, x=2.16, % fit=2.

(f) Change in the O-H stretching frequency of phenol upon adduct formation in CCl$_4$. Data from ref. 148, x=1.60, % fit=5.

(g) log K for the reaction between 3,5-dichlorophenol and the alcohol in C$_6$H$_{12}$. Data from ref. 148, x=0.02, % fit=4.

(h) log K for the reaction between 3-nitrophenol and the alcohol in iso-octane. Data from ref. 148, x=0.02, % fit=4.

(i) log K for the reaction between 3-nitrophenol and the alcohol in C$_6$H$_{12}$. Data from
ref. 148, x=0.02, % fit=4.

(j) log K for the reaction of 4-fluorophenol with the alcohol in CCl₄. Data from ref. 148, x=0.32, % fit=11.

(k) log K for the reaction between phenol and the alcohol. Data from ref. 150, x=0.08, % fit=14.

(l) pK based on the OH shift of (CF₃)₂COH and the log K value for 4-fluorophenol. Data from ref. 148, x=0.03, % fit=1.

(m) pK based on the ¹³C shift of two carbons in the alcohol. Data from ref. 151, x=0, % fit=0.

(n) log of the rate constant for protonation of the alcohol by HBr at 163 K. Data from ref. 152, x=0.14, % fit=6.

(o) Change in ¹³C chemical shift of the primary carbon upon addition of a 1M solution of CF₃COOH. Data from ref. 153, x=0.16, % fit=4.

(p) Difference in the shift of C-1 and C-2 in the alcohols upon addition of CF₃COOH. Data from ref. 153, x=0.03, % fit=1.

(q) log K₆ for 5% v/v solutions in dilute HCl at ionic strength=1.0 and 25°C. Data from ref. 154, x=0.17, % fit=17.

(r) Enthalpy (in kcal mol⁻¹) of dimerization in CCl₄. Data from ref. 155.

(s) Enthalpy (in kcal mol⁻¹) of interaction with I₂ in CCl₄ or n-heptane. Data from ref. 145.

(t) ¹³C chemical shift of the carboxylate carbon of 4-nitrobenzoic acid in neat solvents. The P value calculated for this system is 1.08. Data from this work, x=0.25, % fit=16.
exceptions. The enthalpies of donor alcohol interaction with iodine were fit poorly. The enthalpies reported\textsuperscript{144} for methanol, ethanol, and 2-methylpropan-2-ol are small compared to ethers.\textsuperscript{12a} These data were assigned low weights in the master fit giving 1 kcal mol\textsuperscript{-1} deviations but predicted enthalpies in the range expected.

The fit of $\Delta v(\text{OH})$ for (CF$_3$)$_3$COH, was poor for to donor solvents with known $E_B$ and $C_B$ values. No logical pattern could be found in the misses so the systems were not used to determine alcohol basicity.

The log $K$ for 4-fluorophenol, which includes a wide range of donors, was fit with an average deviation of 0.32. These are the largest misses that are seen with any of the log $K$ systems studied.

**NMR Solvatochromism Experiment**

Limited data are available for systems in which the alcohol is clearly the donor, so a series of measurements were carried out using the $^{13}$C of the carboxylate carbon of 4-nitrobenzoic acid as a basic solvent probe. The experimental values in several donor solvents are given in Table 4-6. The NMR data in non-protic basic solvents were fit to the USM with the results given in Equation (4-12).

$$^{13}\text{C} = 0.10 \pm 0.11 \times E_B + 0.65 \pm 0.05 \times C_B + 1.26 \pm 0.24 \times S' + 161.7 \pm 0.7 \quad (4\text{-}12)$$

An excellent fit with $r^2=0.95$ and an average deviation of 0.1 ppm resulted. NMP was removed from this fit because the $E_B$ and $C_B$ values are tentative. Both specific and non-specific interactions contribute to the observed shift. The calculated coefficients and error in $E_B$ suggest that the shifts are dominated by covalency. Next, the alcohols were added to the fit using the procedure described in the calculations section. A poor fit results, with
Table 4-6. Spectroscopic Data for 4-nitrobenzoic acid in various solvents

<table>
<thead>
<tr>
<th>solvent</th>
<th>$^{13}\text{C}_{\exp}^{\text{a}}$</th>
<th>$^{13}\text{C}_{\text{cal}}^{\text{b}}$</th>
<th>$S^{\text{c}}$</th>
<th>$E_B$</th>
<th>$C_B$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$OH</td>
<td>167.6 (166.1)</td>
<td></td>
<td>2.86</td>
<td>d</td>
<td>d</td>
</tr>
<tr>
<td>C$_2$H$_5$OH</td>
<td>167.0 (166.0)</td>
<td></td>
<td>2.79</td>
<td>d</td>
<td>d</td>
</tr>
<tr>
<td>n-C$_3$H$_7$OH</td>
<td>166.3 (165.9)</td>
<td></td>
<td>2.67</td>
<td>d</td>
<td>d</td>
</tr>
<tr>
<td>i-C$_3$H$_7$OH</td>
<td>166.2 (165.7)</td>
<td></td>
<td>2.52</td>
<td>d</td>
<td>d</td>
</tr>
<tr>
<td>n-C$_4$H$_9$OH</td>
<td>166.3 (166.0)</td>
<td></td>
<td>2.75</td>
<td>d</td>
<td>d</td>
</tr>
<tr>
<td>t-C$_4$H$_9$OH</td>
<td>166.3 (165.6)</td>
<td></td>
<td>2.46</td>
<td>d</td>
<td>d</td>
</tr>
<tr>
<td>DMA</td>
<td>166.0 166.2</td>
<td></td>
<td>2.70</td>
<td>2.35</td>
<td>1.31</td>
</tr>
<tr>
<td>DMF</td>
<td>166.4 166.3</td>
<td></td>
<td>2.80</td>
<td>2.19</td>
<td>1.31</td>
</tr>
<tr>
<td>acetone</td>
<td>166.0 165.9</td>
<td></td>
<td>2.58</td>
<td>1.74</td>
<td>1.26</td>
</tr>
<tr>
<td>CH$_3$CN</td>
<td>166.0 166.1</td>
<td></td>
<td>3.00</td>
<td>1.64</td>
<td>0.71</td>
</tr>
<tr>
<td>NMP</td>
<td>165.8 (166.3)</td>
<td></td>
<td>2.62</td>
<td>2.62</td>
<td>1.65</td>
</tr>
<tr>
<td>DMSO</td>
<td>166.7 166.6</td>
<td></td>
<td>3.00</td>
<td>2.40</td>
<td>1.47</td>
</tr>
<tr>
<td>pyridine</td>
<td>167.2 167.2</td>
<td></td>
<td>2.44</td>
<td>1.78</td>
<td>3.54</td>
</tr>
</tbody>
</table>

(a) $^{13}\text{C}$ chemical shift relative to TMS in pure solvent of the carboxylate carbon at 25° C.
(b) Calculated using Equation (4-12). Values in parenthesis were not included in the overall fit.
(c) $S'$ values from this work and from ref. 12a.
(d) Donor parameters found in Table 4-4.
\[ r^2 = 0.14. \] The \(^{13}\)C chemical shift of NBA is an excellent measure of specific and non-specific solvation properties for non-protic basic solvents but not for protic solvents. The problem could arise from amphoteric alcohols acting as bases to hydrogen bond the carboxy proton and also as acceptors to hydrogen bond to the carboxylate conjugate base.

**E\(_A\) and C\(_A\) Parameters for Substituted Phenols**

It has been shown\(^{30,48,156}\) that the substituent constants \(\Delta E^X\) and \(\Delta C^X\) can be used to calculate \(E_A\) and \(C_A\) values for families of acceptors. The equations are given in (4-14) and (4-15), where \(E_A^H\) and \(C_A^H\) are the \(E\) and \(C\) values for the parent hydrogen compound.

\[
E_A^X = s_A^E \Delta E^X + E_A^H \quad (4-14)
\]
\[
C_A^X = s_A^C \Delta C^X + C_A^H \quad (4-15)
\]

Using Equations (4-14) and (4-15), one can calculate the \(E_A^X\) and \(C_A^X\) parameters for any of the seventy-seven 3- or 4-substituted phenols whose substituent constants, \(\Delta E^X\) and \(\Delta C^X\), are known. The proportionality constants \(s_A^E\) and \(s_A^C\) measure the sensitivity of the \(E\) and \(C\) values to substituent change relative to \(s_B^E=1\) and \(s_B^C=1\) for the pyridine family. Using the latest \(\Delta E^X\) and \(\Delta C^X\) values that have been reported\(^{30}\) and those phenols whose \(E_A\) and \(C_A\) values have been determined from enthalpy studies, \(s_A^E\) and \(s_A^C\) have been redetermined for the phenol family to be -0.817 (±0.014) and -0.225 (±0.003), respectively. Calculating the \(E_A^X\) and \(C_A^X\) for reported \(\Delta E^X\) and \(\Delta C^X\) substituent constants with Equations (4-14) and (4-15), one can estimate enthalpies of reaction for seventy-seven 3- and 4-substituted phenols with the more than eighty bases in the ECW correlation.
Conclusions

This work reports parameters for alcohols and other hydrogen bonding solvents that enable determination of the specific and non-specific components of solvent influences. The reported solvent polarity parameters for protic solvents afford a quantitative assessment of the solvent influence on chemical reactions, providing information about the basicity and polarity of transition states. A wide variety of systems, including enthalpies of interaction and spectral shifts, have been correlated providing new insights about the relative importance of specific and non-specific solvent influences. The protic solvent parameters are used to analyze several common solvent polarity scales and the limitations of these scales are determined.

Procedures are given for analyzing new probes and adding new solvents to the model. Several probes, such as \((\text{C}_2\text{H}_5)_3\text{PO}\), Michler’s Ketone, the \(^{13}\text{C}\) and \(v(\text{NO})\) for pyridine-N-oxide, Z-values, and FEPHEN have shown great utility in the characterization of both specific and non-specific components of hydrogen bonding solvents. The enthalpies of hydrogen bonding to NMP, and the \(\alpha_2^H\) parameters are useful measures of the specific interaction. These probes are recommended for use in the determination of donor-acceptor and polarity parameters for new solvents.
CHAPTER 5
MESITYL OXIDE AS A PROBE OF SOLVENT POLARITY AND ACIDITY

Introduction

Numerous reports\textsuperscript{34b,38a,42c,112a,113,116} have been given on the use of solvatochromism of various probes to estimate solvent polarity. Work in this laboratory\textsuperscript{12a,17,45b,45c,139} has consolidated many of the common scales of solvent polarity into the Unified Solvation Model (USM), revealing a combination of specific and non-specific interactions in most of the reported scales. By eliminating systems involving specific (\textit{i.e.}, donor-acceptor) interactions, a composite scale, \( S' \), of solvent polarity for non-specific interactions results that encompasses most of the data from all of the more common scales. The influence of non-specific solvation on physicochemical properties of solutes is estimated in USM using Equation (5-1), where \( S' \) is the solvent polarity parameter, \( \Delta \chi \) (with units of energy) is the solvent dependent value of the physicochemical property, \( P \) is the measure of the susceptibility of the solute to solvation, and \( W \) is the value of \( \Delta \chi \) when \( S' \) is zero.

\[ \Delta \chi = S'P + W \] (5-1)

Values for \( S' \) have been established for over 50 donor solvents\textsuperscript{12a,17,45c} involved in non-specific interactions with more then 40 solute probes. \( S' \) values have also been determined (Chapter 4) for 18 hydrogen bonding solvents using the same probe molecules. For solvents capable of hydrogen bonding, specific interactions also contribute to solvation. The USM approach allows for the separation of specific and non-specific
interactions according to Equation (5-2), where $E_A$ and $C_A$ are the electrostatic and covalent contributions of the acceptor to the physicochemical property, and $E_B$ and $C_B$ are the donor counterparts.

$$
\Delta \chi = E_A E_B^* + C_A C_B^* + S'P + W \quad (5-2)
$$

These parameters have been determined\textsuperscript{12a,17} for a wide range of donors and acceptors and are used to calculate the specific contributions to the physicochemical properties.

The acidity of solid acids, pure solvents, and solutions has been measured with many probe molecules. Acetone (and several other ketones),\textsuperscript{157,158} mesityl oxide,\textsuperscript{158} and various phosphine oxides\textsuperscript{159} have been used extensively. The $^{13}$C shift of the $\beta$ carbon in mesityl oxide has been shown\textsuperscript{158} to be especially sensitive to solvent and solid acidity. Farcasiu and coworkers have studied\textsuperscript{158c,d} the acidity of BF$_3$/H$_2$O solutions and a wide range of H$_2$SO$_4$ solutions. They have observed that the carbonyl carbon is also sensitive to solvent and solid acidity, but to a lesser extent. This sensitivity is due to the partial positive charge that can be found on the $\beta$ and carbonyl carbons of the protonated form of mesityl oxide (Figure 5-1).

\[
\text{Figure 5-1. Protonation of mesityl oxide gives two possible resonance forms.}
\]

Because of the limited studies using mesityl oxide as a probe for solvent polarity and acidity, we have measured its chemical shifts in many donor and hydrogen bonding solvents. These measurements have been analyzed using USM. Use of the USM allows
for the separation of the specific and non-specific contributions to the chemical shift. The S' values for several solvents not studied previously have been determined using probes molecules from earlier work (Chapter 4).

**Experimental**

Approximately 0.5 M solutions of mesityl oxide (Registry #141-79-7) in various donor and acceptor solvents were prepared. For non-polar solvents, such as n-alkanes, at least three solutions were made with a wide range of concentrations. These solvents may not solvate probe molecules well and, in these solutions, probe-probe interactions may dominate rather than solvent-probe interactions. All solvents were purified according to published methods.117

$^{13}$C NMR analyses were done using a Varian VXR-300 acquiring proton decoupled spectra. An external lock of deuterated acetone and an external reference of TMS were used in a sealed capillary. Spectra were acquired at room temperature with around 500 transients typically collected for each sample. Tables 5-1 and 5-2 show the uncorrected chemical shifts for the carbonyl and β carbons of mesityl oxide.

**Calculations**

**Volume Susceptibility**

Because the TMS reference was contained in an external capillary, the possibility exists that differences in the bulk susceptibility of the TMS solution and the mesityl oxide solution may contribute to the observed chemical shifts. A correction was applied according to published methods.160 Equation (5-3) gives the formula used for correcting the chemical shifts, where $\delta_{\text{obs}}$ is the observed chemical shift, $\delta_{\text{corr}}$ is the corrected value,
Table 5-1. Uncorrected $^{13}$C Chemical Shifts of Mesityl Oxide in Donor and Non-Polar Solvents

<table>
<thead>
<tr>
<th>solvent</th>
<th>$^{13}$C β</th>
<th>$^{13}$C carb</th>
<th>$S'$ a</th>
</tr>
</thead>
<tbody>
<tr>
<td>methylcyclohexane b</td>
<td>152.65</td>
<td>194.55</td>
<td>c</td>
</tr>
<tr>
<td>cyclohexane</td>
<td>152.70</td>
<td>194.56</td>
<td>1.11</td>
</tr>
<tr>
<td>n-pentane b</td>
<td>152.72</td>
<td>194.63</td>
<td>0.57 d</td>
</tr>
<tr>
<td>n-hexane b</td>
<td>152.74</td>
<td>194.65</td>
<td>0.68 d</td>
</tr>
<tr>
<td>N(C₂H₅)₃</td>
<td>152.79</td>
<td>194.91</td>
<td>1.43</td>
</tr>
<tr>
<td>o-xylene</td>
<td>152.82</td>
<td>195.51</td>
<td>e</td>
</tr>
<tr>
<td>p-xylene</td>
<td>152.86</td>
<td>195.52</td>
<td>e</td>
</tr>
<tr>
<td>m-xylene</td>
<td>152.89</td>
<td>195.54</td>
<td>e</td>
</tr>
<tr>
<td>toluene</td>
<td>152.99</td>
<td>195.81</td>
<td>1.66</td>
</tr>
<tr>
<td>CCl₄</td>
<td>153.21</td>
<td>195.36</td>
<td>1.49</td>
</tr>
<tr>
<td>ethyl ether</td>
<td>153.22</td>
<td>195.67</td>
<td>1.73</td>
</tr>
<tr>
<td>benzene</td>
<td>153.24</td>
<td>196.30</td>
<td>1.73</td>
</tr>
<tr>
<td>THF</td>
<td>153.35</td>
<td>196.30</td>
<td>2.08</td>
</tr>
<tr>
<td>o-dichlorobenzene</td>
<td>153.37</td>
<td>196.18</td>
<td>2.10</td>
</tr>
<tr>
<td>fluorobenzene</td>
<td>153.46</td>
<td>196.57</td>
<td>e</td>
</tr>
<tr>
<td>hexafluorobenzene</td>
<td>153.59</td>
<td>195.66</td>
<td>e</td>
</tr>
<tr>
<td>ethyl acetate</td>
<td>153.75</td>
<td>196.81</td>
<td>2.15</td>
</tr>
<tr>
<td>pyridine</td>
<td>153.87</td>
<td>197.41</td>
<td>2.44</td>
</tr>
<tr>
<td>1,2 dichloroethane</td>
<td>154.03</td>
<td>197.45</td>
<td>e</td>
</tr>
<tr>
<td>NMP</td>
<td>154.10</td>
<td>197.62</td>
<td>2.62</td>
</tr>
<tr>
<td>DMA</td>
<td>154.13</td>
<td>197.69</td>
<td>2.70</td>
</tr>
<tr>
<td>nitrobenzene</td>
<td>154.22</td>
<td>197.39</td>
<td>2.61</td>
</tr>
<tr>
<td>2-butalanone</td>
<td>154.32</td>
<td>197.64</td>
<td>2.50</td>
</tr>
<tr>
<td>acetone</td>
<td>154.47</td>
<td>197.92</td>
<td>2.58</td>
</tr>
<tr>
<td>mesityl oxide (neat)</td>
<td>154.6 f</td>
<td>198.2 f</td>
<td>2.81 g</td>
</tr>
<tr>
<td>DMF</td>
<td>154.63</td>
<td>198.34</td>
<td>2.80</td>
</tr>
<tr>
<td>acetonitrile</td>
<td>154.93</td>
<td>198.83</td>
<td>3.00</td>
</tr>
<tr>
<td>1,1,2,2 tetrachloroethane</td>
<td>154.95</td>
<td>198.48</td>
<td>e</td>
</tr>
</tbody>
</table>

(a) S' values are from references 12a and 45c.
(b) Multiple runs were done with these solvents to gauge the probe concentration dependence. No significant differences were seen in the chemical shifts with different probe concentrations.
(c) No S' value has been previously determined for this solvent.
(d) Estimated in reference 46.
(e) Tentative S' parameter for this solvent is determined in this chapter.
(f) Chemical shift values from reference 161.
(g) Tentative S' parameter based on the chemical shifts reported here and using the P and W values from Equations (5-7) and (5-8).
Table 5-2. Uncorrected $^{13}$C Chemical Shifts of Mesityl Oxide in Acceptor Solvents

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$^{13}$C carb</th>
<th>$^{13}$C $\beta$</th>
<th>$E_A^*$</th>
<th>$C_A^*$</th>
<th>$S'*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_2$Cl$_2$</td>
<td>197.99</td>
<td>154.39</td>
<td>0.86</td>
<td>0.11</td>
<td>2.03</td>
</tr>
<tr>
<td>CDCl$_3$</td>
<td>198.52</td>
<td>154.91</td>
<td>1.56</td>
<td>0.44</td>
<td>1.63</td>
</tr>
<tr>
<td>n-C$<em>8$H$</em>{17}$OH</td>
<td>198.00</td>
<td>155.11</td>
<td>0.89</td>
<td>0.87</td>
<td>2.62</td>
</tr>
<tr>
<td>t-C$_4$H$_9$OH</td>
<td>198.38</td>
<td>155.28</td>
<td>1.14</td>
<td>0.66</td>
<td>2.46</td>
</tr>
<tr>
<td>n-C$_4$H$_9$OH</td>
<td>198.66</td>
<td>155.55</td>
<td>1.05</td>
<td>0.74</td>
<td>2.75</td>
</tr>
<tr>
<td>i-C$_3$H$_7$OH</td>
<td>198.91</td>
<td>155.63</td>
<td>1.19</td>
<td>0.69</td>
<td>2.40</td>
</tr>
<tr>
<td>C$_2$H$_5$OH</td>
<td>199.28</td>
<td>155.87</td>
<td>1.15</td>
<td>0.67</td>
<td>2.79</td>
</tr>
<tr>
<td>CH$_3$OH</td>
<td>200.38</td>
<td>156.58</td>
<td>1.27</td>
<td>0.74</td>
<td>2.87</td>
</tr>
<tr>
<td>CH$_3$COOH</td>
<td>201.56</td>
<td>157.97</td>
<td>3.39</td>
<td>0.91</td>
<td>1.28</td>
</tr>
<tr>
<td>CF$_3$COOH</td>
<td>207.81</td>
<td>169.83</td>
<td>b</td>
<td>b</td>
<td>b</td>
</tr>
</tbody>
</table>

(a) $E_A$, $C_A$, and $S'$ values for the alcohols are from Chapter 4. $E_A$ and $C_A$ for CH$_2$Cl$_2$ and CDCl$_3$ are from ref. 12a.

(b) No parameters have been calculated for this solvent. CF$_3$COOH is listed here simply to show the large range of shifts possible.
$(\chi_v)_\text{ref}$ is the volume susceptibility of the external standard (TMS in this case), and $\chi_v$ is the volume susceptibility of the studied sample.

$$\delta_{\text{corr}} = \delta_{\text{obs}} + \{(2/3)\pi [(\chi_v)_\text{ref} - (\chi_v)]\} \times 10^6 \quad (5-3)$$

If this sample is a solution (as is the case in this work), $\chi_v$ will have contributions from both the solute and the solvent. Equation (5-4) shows the individual components related by their volume fractions ($\Phi_1$ and $\Phi_2$) in the solution, and $\chi_{v1}$ and $\chi_{v2}$ for the pure solute and solvent, respectively. The $\chi_v$ values for mesityl oxide and TMS are $-0.534 \times 10^6$ and $-0.5299 \times 10^6$, respectively. All mesityl oxide solutions studied here were between 90 and 95 volume % solvent, based on the mass of solute added and assuming ideal mixing.

Volume susceptibility, $\chi_v$, for each pure solvent and for the mesityl oxide solutions in that solvent are given in Table 5-3. The corrections calculated from Equation (5-3), $\chi_v\text{ corr.}$, are small and are also shown in Table 5-3 along with the corrected chemical shifts.

**Fits of Experimental Data**

Fits of the mesityl oxide data were done to Equations (5-1) and (5-2) using NCSS (Kaysville, UT) with its multiple regression module. $S'$ values for several solvents were calculated using a master fit program written onsite. The program allows for the solution of Equation (5-1) using data found in the literature. Probes were used whose $P$ and $W$ values were determined earlier (Chapter 4). These values were fixed, and the $S'$ values for solvents were allowed to float. A series of simultaneous equations is solved for the best $S'$ values for the solvents studied.
Table 5-3. Corrected $^{13}$C chemical shifts for all solvents studied

<table>
<thead>
<tr>
<th>Solvent</th>
<th>solv. $\chi_V$</th>
<th>soln. $\chi_V$</th>
<th>$\chi_V$ corr.</th>
<th>corr. $^{13}$C carb.</th>
<th>corr. $^{13}$C $\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>iso-octane</td>
<td>-0.5958</td>
<td>-0.592</td>
<td>0.13</td>
<td>194.44</td>
<td>152.62</td>
</tr>
<tr>
<td>n-pentane</td>
<td>-0.5472</td>
<td>-0.546</td>
<td>0.03</td>
<td>194.66</td>
<td>152.75</td>
</tr>
<tr>
<td>n-hexane</td>
<td>-0.565</td>
<td>-0.563</td>
<td>0.07</td>
<td>194.72</td>
<td>152.81</td>
</tr>
<tr>
<td>methylcyclohexane</td>
<td>-0.6181</td>
<td>-0.610</td>
<td>0.17</td>
<td>194.72</td>
<td>152.82</td>
</tr>
<tr>
<td>cyclohexane</td>
<td>-0.627</td>
<td>-0.620</td>
<td>0.19</td>
<td>194.75</td>
<td>152.89</td>
</tr>
<tr>
<td>N(C$_2$H$_5$)$_3$</td>
<td>-0.586</td>
<td>-0.583</td>
<td>0.11</td>
<td>195.02</td>
<td>152.90</td>
</tr>
<tr>
<td>carbon tetrachloride</td>
<td>-0.691</td>
<td>-0.679</td>
<td>0.31</td>
<td>195.67</td>
<td>153.52</td>
</tr>
<tr>
<td>p-xylene</td>
<td>-0.6226</td>
<td>-0.617</td>
<td>0.18</td>
<td>195.70</td>
<td>153.04</td>
</tr>
<tr>
<td>m-xylene</td>
<td>-0.6235</td>
<td>-0.618</td>
<td>0.18</td>
<td>195.72</td>
<td>153.07</td>
</tr>
<tr>
<td>o-xylene</td>
<td>-0.644</td>
<td>-0.637</td>
<td>0.22</td>
<td>195.73</td>
<td>153.04</td>
</tr>
<tr>
<td>hexafluorobenzene</td>
<td>-0.627</td>
<td>-0.622</td>
<td>0.19</td>
<td>195.85</td>
<td>153.78</td>
</tr>
<tr>
<td>toluene</td>
<td>-0.6179</td>
<td>-0.612</td>
<td>0.17</td>
<td>195.98</td>
<td>153.16</td>
</tr>
<tr>
<td>ethyl ether</td>
<td>-0.534</td>
<td>-0.534</td>
<td>0.01</td>
<td>195.68</td>
<td>153.23</td>
</tr>
<tr>
<td>benzene</td>
<td>-0.611</td>
<td>-0.606</td>
<td>0.16</td>
<td>196.46</td>
<td>153.40</td>
</tr>
<tr>
<td>tetrahydrofuran</td>
<td>-0.6417</td>
<td>-0.635</td>
<td>0.22</td>
<td>196.52</td>
<td>153.57</td>
</tr>
<tr>
<td>o-dichlorobenzene</td>
<td>-0.748</td>
<td>-0.731</td>
<td>0.42</td>
<td>196.60</td>
<td>153.79</td>
</tr>
<tr>
<td>fluorobenzene</td>
<td>-0.623</td>
<td>-0.618</td>
<td>0.18</td>
<td>196.75</td>
<td>153.64</td>
</tr>
<tr>
<td>ethyl acetate</td>
<td>-0.554</td>
<td>-0.553</td>
<td>0.05</td>
<td>196.86</td>
<td>153.80</td>
</tr>
<tr>
<td>pyridine</td>
<td>-0.611</td>
<td>-0.606</td>
<td>0.16</td>
<td>197.57</td>
<td>154.03</td>
</tr>
<tr>
<td>nitrobenzene</td>
<td>-0.604</td>
<td>-0.599</td>
<td>0.15</td>
<td>197.54</td>
<td>154.37</td>
</tr>
<tr>
<td>2-butanone</td>
<td>-0.509</td>
<td>-0.511</td>
<td>-0.04</td>
<td>197.60</td>
<td>154.28</td>
</tr>
<tr>
<td>acetone</td>
<td>-0.46</td>
<td>-0.47</td>
<td>-0.13</td>
<td>197.79</td>
<td>154.34</td>
</tr>
<tr>
<td>N,N-dimethylacetamide</td>
<td>-0.603</td>
<td>-0.599</td>
<td>0.14</td>
<td>197.83</td>
<td>154.27</td>
</tr>
<tr>
<td>N-methylpyrrolidinone</td>
<td>-0.67</td>
<td>-0.66</td>
<td>0.27</td>
<td>197.89</td>
<td>154.37</td>
</tr>
<tr>
<td>1,2 dichloroethane</td>
<td>-0.7567</td>
<td>-0.742</td>
<td>0.44</td>
<td>197.89</td>
<td>154.47</td>
</tr>
<tr>
<td>N,N-dimethylformamide</td>
<td>-0.613</td>
<td>-0.609</td>
<td>0.17</td>
<td>198.51</td>
<td>154.80</td>
</tr>
<tr>
<td>acetonitrile</td>
<td>-0.534</td>
<td>-0.534</td>
<td>0.01</td>
<td>198.84</td>
<td>154.94</td>
</tr>
<tr>
<td>1,1,2,2 tetrachloroethane</td>
<td>-0.856</td>
<td>-0.837</td>
<td>0.64</td>
<td>199.14</td>
<td>155.59</td>
</tr>
<tr>
<td>dichloromethane</td>
<td>-0.733</td>
<td>-0.721</td>
<td>0.40</td>
<td>198.39</td>
<td>154.79</td>
</tr>
<tr>
<td>octan-1-ol</td>
<td>-0.64</td>
<td>-0.63</td>
<td>0.22</td>
<td>198.22</td>
<td>155.33</td>
</tr>
<tr>
<td>chloroform</td>
<td>-0.74</td>
<td>-0.73</td>
<td>0.41</td>
<td>198.93</td>
<td>155.32</td>
</tr>
<tr>
<td>2-methyl-propan-2-ol</td>
<td>-0.611</td>
<td>-0.606</td>
<td>0.16</td>
<td>198.54</td>
<td>155.44</td>
</tr>
<tr>
<td>butan-1-ol</td>
<td>-0.617</td>
<td>-0.611</td>
<td>0.17</td>
<td>198.83</td>
<td>155.72</td>
</tr>
<tr>
<td>propan-2-ol</td>
<td>-0.5985</td>
<td>-0.594</td>
<td>0.13</td>
<td>199.04</td>
<td>155.76</td>
</tr>
<tr>
<td>ethanol</td>
<td>-0.575</td>
<td>-0.572</td>
<td>0.09</td>
<td>199.37</td>
<td>155.96</td>
</tr>
<tr>
<td>methanol</td>
<td>-0.53</td>
<td>-0.53</td>
<td>0.00</td>
<td>200.38</td>
<td>156.58</td>
</tr>
<tr>
<td>acetic acid</td>
<td>-0.551</td>
<td>-0.550</td>
<td>0.04</td>
<td>201.60</td>
<td>158.01</td>
</tr>
</tbody>
</table>

(a) Volume susceptibility of the pure solvent divided by $10^6$. Unless otherwise noted, these values are from reference 162. Sometimes the reference gives mass
susceptibility, which can be converted to volume susceptibility with $\chi_v = (\chi_m/M)\rho$, where $M$ is the molar mass of the solvent, $\rho$ is the solvent density, and $\chi_m$ is the mass susceptibility.

(b) Volume susceptibility (divided by $10^6$) of the solution of mesityl oxide in the solvent listed. Calculated according to Equation (5-4), assuming ideal mixing.

(c) Correction applied the chemical shift values given in Table 5-1. This correction is calculated using Equation (5-3).

(d) Estimated using Pascal’s constants from reference 162a.
Results and Discussion

Mesityl Oxide in Various Solvents

Table 5-1 shows the uncorrected carbonyl and β carbon chemical shifts of mesityl oxide in donor solvents. Also listed are the S' values for these solvents. A correlation to Equation (5-1) for only donor solvents will give the non-specific contribution to the mesityl oxide chemical shift and the P and W parameters for mesityl oxide as a probe. For the β carbon, the correlation is given in Equation (5-5) [in the form of Equation (5-1)].

\[
\delta \beta \ ^{13}C = 1.16 (\pm 0.09) \ S' + 151.22 (\pm 0.19) \ (n=17, \ x=0.16, \ r^2=0.92)
\]  

(5-5)

For the carbonyl carbon, Equation (5-6) gives the non-specific correlation.

\[
\delta \text{carb}\ ^{13}C = 2.18 (\pm 0.11) \ S' + 192.03 (\pm 0.25) \ (n=17, \ x=0.21, \ r^2=0.96)
\]  

(5-6)

For solvents with S' values less than 1.11, multiple runs were performed using varying probe concentrations. No differences were observed in the position of the chemical shifts of solutions with solute concentrations between 0.4 and 1.0 M. This is a smaller range than has been used in other studies. Therefore, probe-probe interactions do not dominate over solvent-probe interactions (at these concentrations), as might be expected with poorly solvating solvents.

Table 5-2 shows the uncorrected carbonyl and β carbon chemical shifts for mesityl oxide in acceptor solvents. The E_A, C_A, and S' values for these solvents, determined earlier (Chapter 4) are also listed there. Correlations of these chemical shifts were done with the Unified Solvation Model, Equation (5-2). For the β carbon, the donor parameters, E_B* and C_B*, are calculated [using P = 1.16 and W = 151.22, from Equation]
(5-5)] to be 1.55 (± 0.17) and -0.44 (± 0.38), respectively. The correlation is very good with $r^2=0.98$ and an average deviation of 0.26 ppm.

The correlation of the carbonyl chemical shift is also very good ($r^2=0.98$, $x=0.3$).

Using the previously determined [from Equation (5-6)] $P = 2.18$ and $W = 192.03$, the donor parameters, $E_B*$ and $C_B*$, are $2.57 (± 0.18)$ and $-2.39 (± 0.39)$, respectively. The importance and usefulness of these parameters is discussed below.

**Correlations of Corrected Chemical Shifts**

Using the procedure outlined in the Calculations section, the $\beta$ and carbonyl chemical shifts were corrected for differences in volume susceptibility between the capillary tube that contained the TMS and the sample in the NMR tube. The magnitude of the correction and the corrected chemical shift values appear in Table 5-3. Overall the correlations of the corrected values are improved over those seen with the uncorrected values. For the $\beta$ carbon, the non-specific correlation is given in Equation (5-7), in the form of Equation (5-1).

$$\delta \beta ^{13}C = 1.09 (± 0.08) S' + 151.50 (± 0.17) \quad (n=17, \ x=0.12, \ r^2=0.93) \quad (5-7)$$

For the carbonyl carbon, Equation (5-8) gives the non-specific correlation. Using the $P$ and $W$ values given in Equations (5-7) and (5-8), one can calculate the specific contribution to the chemical shift with Equation (5-2). $E_B*$ and $C_B*$ values have been calculated for the $\beta$ and carbonyl carbon chemical shifts in hydrogen bonding solvents.

For the $\beta$ carbon, these are $1.57 (± 0.10)$ and $-0.45 (± 0.23)$, respectively. For the carbonyl carbon, $E_B*$ and $C_B*$ are $2.59 (± 0.14)$ and $-2.40 (± 0.32)$, respectively.
Importance of Mesityl Oxide $E_B^*$ and $C_B^*$ Parameters

Calculation of $E_B^*$ and $C_B^*$ parameters for both the carbonyl and $\beta$ carbons is extremely significant because now they can be used in the determination of $E_A$ and $C_A$ values for new solvents or for solid acids. For example, Haw et al.\textsuperscript{158a} have adsorbed mesityl oxide onto several zeolites. If at least four or five other probe molecules (such as those in Table 5-4, whose $E_B^*$ and $C_B^*$ were reported in Chapter 4) were also adsorbed onto these zeolites, one could calculate [using Equation (5-2)] the best $E_A$, $C_A$, and $S'$ for these solids. In the case of a solid, the $S'$ would not refer to a non-specific solvent parameter, but would be related to the surface polarity. This type of experiment has been discussed in the literature.\textsuperscript{163} Others have used varying methods to determine and alter the polarity of solid surfaces.\textsuperscript{164}

Comparison of USM with other Mesityl Oxide Work

This work has presented correlations of the $\beta$ and carbonyl chemical shifts to the Unified Solvation Model. Others\textsuperscript{158c,d} have used the difference in the $\beta$ and $\alpha$ carbon chemical shifts ($\Delta \delta$) as a measure of solvent acidity. In highly acidic solvents, such as 50% $H_2SO_4$ and greater (which are more acidic than any studied here), the $\beta$ carbon (and thus $\Delta \delta$) is shown\textsuperscript{158c} to be sensitive to probe concentration. For solutions such as these, the authors\textsuperscript{158c} use several concentrations and extrapolate to infinite dilution to obtain $\Delta \delta^0$ for the solution. This extrapolation is used to try to determine an absolute acidity of the solvent with no probe molecule in solution. The intent of that work is to have a measure of the acidity of solutions that can be correlated with a known scale of acidity such as Hammett's $-H_0$. While $\Delta \delta$ is a good relative measure for strongly acidic
Table 5-4. P and W parameters for donor probes used in this study

<table>
<thead>
<tr>
<th>probe</th>
<th>P*</th>
<th>W*</th>
</tr>
</thead>
<tbody>
<tr>
<td>v; DMANF</td>
<td>-1.29</td>
<td>26.54</td>
</tr>
<tr>
<td>v; FNF</td>
<td>-0.74</td>
<td>31.80</td>
</tr>
<tr>
<td>v; E_{r}(30)</td>
<td>8.61</td>
<td>19.63</td>
</tr>
<tr>
<td>v; Michler’s Ketone</td>
<td>-1.18</td>
<td>31.38</td>
</tr>
<tr>
<td>v; 4-nitroanisole</td>
<td>-1.29</td>
<td>35.51</td>
</tr>
<tr>
<td>v; N,N-diethyl-4-nitroaniline</td>
<td>-1.69</td>
<td>29.31</td>
</tr>
<tr>
<td>v; 7-amino-4-methylcoumarin</td>
<td>-1.39</td>
<td>27.86</td>
</tr>
<tr>
<td>v; N,N-dimethylamino-4-methylcoumarin</td>
<td>-1.33</td>
<td>26.76</td>
</tr>
<tr>
<td>An; di-tert-butyl aminoxyl</td>
<td>0.24</td>
<td>13.96</td>
</tr>
<tr>
<td>An; 4-amino-2,2,6,6-tetramethylpiperidin-1-oxyl</td>
<td>0.229</td>
<td>14.07</td>
</tr>
<tr>
<td>v; tetracarbonylbipyridine chromium</td>
<td>2.36</td>
<td>14.68</td>
</tr>
<tr>
<td>v; tetracarbonylbipyridine molybdenum</td>
<td>2.15</td>
<td>16.51</td>
</tr>
<tr>
<td>v; tetracarbonylbipyridine tungsten</td>
<td>2.37</td>
<td>15.34</td>
</tr>
<tr>
<td>v; tetracarbonylphenanthroline tungsten</td>
<td>2.24</td>
<td>15.70</td>
</tr>
<tr>
<td>v; cis-dicyanobis(1,10-phenanthroline) iron (II)</td>
<td>1.38</td>
<td>12.49</td>
</tr>
<tr>
<td>v; DMANBIT</td>
<td>-1.74</td>
<td>23.11</td>
</tr>
<tr>
<td>v; 2,2,6,6-tetramethylpiperidine-N-oxyl radical</td>
<td>0.31</td>
<td>20.67</td>
</tr>
<tr>
<td>v; Nile Red</td>
<td>-1.11</td>
<td>21.66</td>
</tr>
<tr>
<td>v; Phenol Blue</td>
<td>-0.73</td>
<td>18.85</td>
</tr>
<tr>
<td>v; 9,9’-bianthryl</td>
<td>-0.08</td>
<td>25.76</td>
</tr>
<tr>
<td>v; N-(9-anthryl)carbazole</td>
<td>-0.13</td>
<td>26.09</td>
</tr>
<tr>
<td>v; N,N’-bicarbazyl</td>
<td>0.01</td>
<td>30.46</td>
</tr>
<tr>
<td>v; 1-methyl-5-nitroindole</td>
<td>-1.76</td>
<td>29.10</td>
</tr>
<tr>
<td>v; α-perfluoroalkyl-β,β-dicyanovinyl dye #4</td>
<td>-0.80</td>
<td>20.43</td>
</tr>
</tbody>
</table>

(a) P and W values were calculated in references 45c,139, and Chapter 4, unless otherwise noted.
(b) Electronic transition in 10^3 cm^{-1}. Data from ref. 165. average deviation = 0.11. CH_3NO_2 was omitted from this correlation.
(c) Aromatic solvents were removed from the correlation.
(d) Electronic transition in 10^3 cm^{-1}. Data from ref. 166. average deviation = 0.06.
(e) Electronic transition in 10^3 cm^{-1}. Data from ref. 166. average deviation = 0.07.
(f) Electronic transition in 10^3 cm^{-1}. Data from ref. 166. average deviation = 0.07.
(g) Electronic transition in 10^3 cm^{-1}. Data from ref. 167. average deviation = 0.19.
(h) Electronic transition in 10^3 cm^{-1}. Data from ref. 168. average deviation = 0.09.
solutions, its applicability to solvents other than acids is limited. For the nonpolar and donor solvents in Table 5-1, the $\Delta\delta$ values are nonzero, indicating acidity as $\Delta\delta$ is defined. Farcasiu$^{158c}$ dealt mostly with very strongly acidic solutions, and those used in the present work would be termed "non-acidic" in comparison, thus not necessitating the use of several concentrations of probe molecule. $\Delta\delta$ is also proposed to subtract out the "medium effects" caused by the use of an external standard of CDCl$_3$, which have been corrected in the present work. Results presented here show that both the $\beta$ and carbonyl carbons are sensitive to acidity and polarity, so these chemical shifts are proposed for use rather than the use of a difference in two chemical shifts.

The separation of the chemical shifts into specific and non-specific contributions can be done through the use of the USM correlations given above. As an example, using Tables 5-1 and 5-2, one can see that ethanol and DMF have $S'$ values that are about the same (2.80 and 2.79, respectively). Therefore, their contributions to non-specific solvation will be the same. It can be seen that the chemical shifts in ethanol are more downfield, indicating the acidity (specific interactions) of ethanol causes the additional shift. Specific interactions are not present in DMF, as it is a donor like mesityl oxide.

In this study, mesityl oxide is being used as a donor probe. Its use as a solvent is also possible. Table 5-1 shows that neat mesityl oxide has chemical shifts similar to those of solvents with the largest $S'$ values. Presently, only two measurements are available for estimating the $S'$ value of mesityl oxide. These are the two chemical shifts reported in Table 5-1. None of the probe molecules studied here or earlier (Chapter 4) have used mesityl oxide as a solvent, so only a tentative $S'$ value can be calculated. This value is 2.81, which is among the solvents with large $S'$ values. It is, however, significantly larger
than acetone, a ketone with similarities in structure. Measurements of a few other probes molecules in mesityl oxide would provide the data needed to better define this $S'$ value.

**Addition of Other Solvents and Probes to USM**

Solvatochromism data are available for several solvents not previously studied with USM. Using probes and their $P$ and $W$ values (Table 5-4) from recent work, $^{139}$ one can calculate tentative $S'$ parameters for these solvents using Equation (5-1). In addition to earlier probes, several new probes have also been added. These include Phenol Blue, $^{165}$ 9,9'-Bianthryl, $^{166}$ N-(9-Anthryl)carbazole, $^{166}$ N,N'-Bicarbazyl, $^{166}$ and 1-methyl-5-nitroindoline. $^{167}$ These tentative $S'$ parameters appear in Table 5-5.

In the examination of Tables 5-1 and 5-5, one would expect that the tentative $S'$ parameter calculated for a new solvent would place that solvent in roughly the correct position based on the mesityl oxide chemical shifts. For most of the solvents studied with mesityl oxide whose $S'$ values were not previously known, this is the case. Two notable exceptions are 1,2-dichloroethane and 1,1,2,2-tetrachloroethane. Their tentative parameters, which are based on many probe molecules, do not correspond well to the chemical shifts that were measured and are given in Table 5-1. The use of halogenated solvents with covalent solutes has been discussed earlier $^{12a,45b}$ and should be avoided. We presume the tentative parameters to be applicable to a wider range of probe molecules, but they appear to miss with the mesityl oxide in particular.

Another probe, $\alpha$-perfluoroalkyl-\(\beta,\beta\)-dicyanovinyl dye #4, is one of a series of fifteen fluorinated probes that have been synthesized. $^{168}$ The solvatochromism of dye #4 has been studied in a wide range of non-polar, donor, and acceptor solvents. A $P$ value of
-0.80 and a W of 20.43 have been calculated for this probe. The other probes have only been studied in perfluorohexane, acetone, and DMSO. Tentative P and W values could be obtained for this series of probes.

Conclusions

NMR chemical shifts have been measured for the carbonyl and β carbons of mesityl oxide in nonpolar, donor, and acceptor solvents. These chemical shifts are extremely sensitive to the acid-base and polarity properties of the solvent. The chemical shifts have been correlated successfully to the Unified Solvation Model. This allows for the separation of the specific and non-specific contributions to the chemical shifts. These correlations also allow for the calculation of E_B^* and C_B^* parameters for the carbonyl and β carbons of mesityl oxide, which can in turn be used in the determination of the acidity parameters, E_A and C_A, for other solvents or strong solid acid catalysts.
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BIOGRAPHICAL SKETCH


Steven attended Albright College in Reading, Pennsylvania, as a chemistry major. He did undergraduate research with Dr. William Birdsall studying the synthesis of novel Schiff base complexes of copper and nickel with 2-acetylpyrrole and pyrrole-2-carboxaldehyde. He graduated with a B.S. in 1993 and entered the doctoral program at the University of Florida. His graduate research was done under the direction of Dr. Russell S. Drago in the area of donor-acceptor chemistry of phosphines, hydrogen bonding solvents, and strong solid acid catalysts. Steven will teach at The First Academy in Orlando following graduation.
I certify that I have read this study and that in my opinion it conforms to the acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

David E. Richardson, Chairman
Professor of Chemistry

I certify that I have read this study and that in my opinion it conforms to the acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

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I certify that I have read this study and that in my opinion it conforms to the acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Michael J. Scott
Assistant Professor of Chemistry

I certify that I have read this study and that in my opinion it conforms to the acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

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I certify that I have read this study and that in my opinion it conforms to the acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

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Professor of Foundations of Education
This dissertation was submitted to the Graduate Faculty of the Department of Chemistry in the College of Liberal Arts and Sciences and to the Graduate School and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

December 1998

Dean, Graduate School