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# Applications of Dual Parameter *E*- and *C*-Based Substituent Constants to Inorganic Systems

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The $\Delta E^X - \Delta C^X$ substituent constant analysis is extended to several physicochemical properties of $XCo(DH)_2$ complexes (DH = dimethylgloximate), to the coordination and alkene–metal hydride insertion rates of substituted styrenes into $Cp_2NbH$ and $Cp_2^*NbH$, to the reactions of $X_3SiH$ with $Cr(CO)_5$, and to the reactions of $X_3SiCH = CH_2$ with carbenes. In addition to providing insights about the steric, $\pi$-bonding and normal $\sigma$-bond interactions influencing the physicochemical property, important generalizations result about the mechanism of substituent influences on the fundamental donor–acceptor interactions influencing this chemistry. In addition, the $d^E$ and $d^C$ parameters, the counterparts of $\varrho$ in single scale treatments, permit one to select the best substituent to optimize the property.

## Introduction

The interpretation of reactivity in inorganic and organometallic systems with single scale sets of organic substituent constants has met with limited success.[1,2] The failure of the various sets of single parameter substituent constants in the correlation of properties of organocobaloximes, $XCH_2Co(DH)_2L$, led to the use of a classical dual substituent parameter equation. In order to fit the data, the reported parameters had to be modified.[2] The parameter modification was severely criticized[3] and an alternative analysis was suggested[3] which added a steric term to the inductive and resonance substituent equation

$$\Delta\chi = \varrho_I\sigma_I + \varrho_r\sigma_r + \varrho_s\sigma_s + C \qquad (1)$$

In eq 1, $\sigma_I$, $\sigma_r$, and $\sigma_s$ are Taft-type inductive,[4] resonance,[4] and steric[5] substituent parameters, respectively, $\varrho$ represents the corresponding weighting factors, and $C$ is an intercept parameter. Selecting from the multitude of $\sigma$-scales available[4] and the several steric substituent constant scales,[5] the authors[3] used goodness of fit and *f*-statistics to select scales that fit different sets of experimental data for $CH_2X$ substituted cobaloximes. Correlations of reactivity in systems other than the cobaloximes have not used eq 1[3] or the modified[2] resonance and inductive parameters. The QUALE approach is often used.[6] This is a dual parameter analysis based on electronic and steric contributions. The electronic effect is a one parameter basicity scale based on the $^{13}C$ shift of $Ni(CO)_3PX_3$, the $A_1$ carbonyl stretching vibration of these adducts, or the $pK_B$ values of phosphines. The steric effect usually employs cone angles as steric parameters.

Recently, further exception has been taken to the idea that single parameter substituent scales can mirror the inductive changes induced by a substituent. When physicochemical properties, $\Delta\chi$, are correlated with eq 2, the electrostatic ($E$)-

$$\Delta\chi = E_AE_B + C_AC_B + W \qquad (2)$$

covalent ($C$) dual parameters,[7a–d] of the acids, A, or bases, B, used are both found to change when substituents are changed in a family of donors or acceptors. In eq 2, $W$ accommodates a nonzero intercept.

A set of substituent constants $\Delta E^X$ and $\Delta C^X$ were offered which recognized that changing the substituents, X, in a family of compounds, led to changes in both the $E$ and $C$ values of the compounds in the family. It was suggested[7e,f] that substituent constant analyses should be carried out with eq 3. The

$$\Delta\chi^X = d^E\Delta E^X + d^C\Delta C^X + \Delta\chi^H \qquad (3)$$

$\Delta E^X$ and $\Delta C^X$ parameters are the electrostatic and covalent substituent constants, *i.e.* counterparts of $\sigma$ in the one parameter Hammett and Taft scales, $d^E$ and $d^C$ are the dual parameter counterparts of $\varrho$ and $\Delta\chi^H$ is the value of the physicochemical property for the parent compound. The $\Delta E^X$ and $\Delta C^X$ parameters used[8] in this work are summarized in Table 1.

The $d^E$ and $d^C$ values are related to the sign and magnitude of the electrostatic and covalent sensitivity of the family to substituent change, $s^E$ and $s^C$ respectively, relative to values of

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(8) The parameters used in this article are for the most part those in ref 7. Parameters that differ from those in ref 7 have been improved by the addition of new data. When the $\Delta\chi$ value has been measured for the parent hydrogen compound, it is substituted for $\Delta\chi^X$ in eq 3 along with $\Delta E^H = 0$ and $\Delta C^H = 0$. The parent compound becomes one of the set of simultaneous equations solved for $\Delta\chi^H$, $d^E$ and $d^C$. This procedure prevents the measurement on the parent compound from having undue weight in the data analysis.

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**Table 1.** $\Delta E-\Delta C$ Substituent Constants[a]

| X (*n*) | $\Delta C/\Delta E$ | $3-\Delta E^X$ | $3-\Delta C^X$ | X (*n*) | $\Delta C/\Delta E$ | $3-\Delta E^X$ | $3-\Delta C^X$ |
|---|---|---|---|---|---|---|---|
| $CH(C_2H_5)CH_3$ (0.4) | 4.1 | 0.057 | 0.233 | $CH_2C_6H_5$ (0.6) | –[b] | 0.009 | 0.010 |
| $N(CH_3)_2$ (0.3) | 10.1 | 0.041 | 0.431 | $CH_2CH(CH_3)_2$ (0.5) | 3.6 | 0.039 | 0.141 |
| $CH_3$ (0.2) | 3.8 | 0.034 | 0.128 | $CH_2Si(CH_3)_3$ (0.5) | 4.8 | 0.060 | 0.285 |
| $C_2H_5$ (0.2) | 3.9 | 0.039 | 0.153 | $CF_3$ (0.2) | 4.8 | −0.137 | −0.670 |
| n-$C_3H_7$ (0.4) | 3.9 | 0.043 | 0.172 | Cl (0.2) | 3.8 | −0.120 | −0.461 |
| i-$C_3H_7$ (0.2) | 4.3 | 0.059 | 0.254 | $C_6H_{11}$ (0.4) | 4.4 | 0.058 | 0.278 |
| n-$C_4H_9$ (0.4) | 3.9 | 0.046 | 0.181 | Br (0.2) | 3.9 | −0.118 | −0.456 |
| $CH_2C(CH_3)_3$ (0.5) | 4.3 | 0.048 | 0.204 | I (0.2) | 3.8 | −0.107 | −0.405 |
| $CH_2Cl$ (0.5) | 5.5 | −0.045 | −0.246 | CN (0.2) | 4.6 | −0.192 | −0.874 |
| $CH_2Br$ (0.4) | 5.1 | −0.041 | −0.208 | $NO_2$ (0.3) | 4.5 | −0.213 | −0.968 |
| $CH_2I$ (0.4) | 5.1 | −0.048 | −0.243 | $C_6H_5$ (0.3) | 5.3 | 0.011 | 0.058 |
| $CH_2CF_3$ (0.4) | 4.2 | −0.028 | −0.118 | $CH_2NO_2$ (0.6) | 4.7 | −0.118 | −0.553 |
| $CH_2CN$ (0.4) | 4.7 | −0.076 | −0.357 | $N_3$ (0.8) | 3.7 | −0.171 | −0.759 |
| $CHCl_2$ (0.8) | 4.9 | −0.127 | −0.622 | NCS- (0.6) | 3.5 | −0.125 | −0.442 |
| $C_2H_3$ (0.4) | 2.7 | 0.012 | 0.020 | OCN- (0.5) | 3.5 | −0.099 | −0.345 |

[a] Substituent constants X refer to the inductive or 3-substituent, *n* is 1/weight assigned in data fits, $\Delta C/\Delta E$ is the covalent electrostatic ratio of the parameters. [b] A dash in the $\Delta C/\Delta E$ column implies the ratio is irrelevant because the $\Delta\chi^X$ values will be close to those for hydrogen, $\Delta\chi^H$.

one for pyridine. The *d* values also have contributions from the sign and magnitude of the $E^*$ and $C^*$ values of the physicochemical property studied. These relations are shown with subscripts appropriate for a family of donors reacting with the same acceptor in eqs 4 and 5. For a family of acceptors

$$d_A E = s_B{}^E E_A{}^* \qquad (4)$$

$$d_A C = s_B{}^C C_A{}^* \qquad (5)$$

reacting with a given donor, the A and B subscripts in eqs 4 and 5 are interchanged. Asterisks are used on the parameters for the physicochemical property being analyzed when it is not a solvation-minimized enthalpy.

In most applications of eq 3, the resulting *d* values cannot be separated into the components shown in eqs 4 and 5. However, when the family is held constant in several reactions or in favorable instances where the signs of the components can be estimated, vide infra, further interpretation of the *d* values is possible. The single scale parameter, $\varrho$, also has the same complication with contributions from both family and reactant components.

Two sets of $\Delta E^X$ and $\Delta C^X$ substituent constants are reported. The localized set, labeled $3-\Delta E^X$ and $3-\Delta C^X$, pertains to transmission of the substituent effect through the $\sigma$-bonds and through space.[7e-g] The delocalized set, labeled $4-\Delta E^X$ and $4-\Delta C^X$, pertains to a dominant conjugative mechanism for transmission. Thus, although eqs 1 and 3 both involve dual parameter correlations, they differ completely in the meaning of the parameters. If a data set had appreciable contributions from both conjugative and inductive effects, a linear combination of the 3- and 4-substituent constants would be needed in the $\Delta E-\Delta C$ model.

By virtue of the introduction of a set of dual parameter substituent constants, data that previously required Hammett substituent constants, various sets and dual parameter combinations of Taft substituent constants $\sigma_I$, $\sigma_R$, $\sigma_{R^-}$, etc. as well as the substituent constants $\sigma^+$ could be correlated[7e-g] with the one set of $\Delta E^X$ and $\Delta C^X$ parameters. Comparing the $d^E$ and $d^C$ values for reactions that required these different scales showed that the electrostatic−covalent contributions varied when different one-parameter[7a] substituent constant sets were needed for data fits.

It is to be emphasized that the addition of $\Delta E$ and $\Delta C$ parameters to the electrostatic-covalent model does not correspond to adding more new variables to fit data. The substituent constants are related to ECW and can be used to determine *E* and *C* values for entire families of compounds if those for a few members of the family are known.[7a,b] For example, eqs 6 and 7 can be used to calculate $E_A$ and $C_A$ for

$$E_A{}^X = E_A{}^H + s_A{}^E \Delta E^X \qquad (6)$$

$$C_A{}^X = C_A{}^H + s_A{}^C \Delta C^X \qquad (7)$$

any substituted phenol.[7e,c] The values of $s_A{}^E = -0.83$ and $s_A{}^C = -0.23$ are determined from eqs 6 and 7 using reported $E_A$ and $C_A$ values of a few substituted phenols.[6] The $E_A{}^X$ and $C_A{}^X$ for any new phenol can be determined if the $\Delta E^X$ and $\Delta C^X$ parameters are known. The subscripts in eqs 6 and 7 are changed to B for a family of donors.

The purpose of this article is to test the applicability of the $\Delta E^X$ and $\Delta C^X$ parameters to inorganic and organometallic systems.[8] Increasing the number of successful correlations on different systems enhances the confidence in applying the parameters to the interpretation of new systems. Furthermore, in several of the systems analyzed in this article, the $\Delta E-\Delta C$ interpretations of the factors influencing the reactivity trends are substantially different from the literature conclusions.

## Results and Discussion

**Cobaloximes.** The cobaloximes have been studied extensively[9,10] and the results of this effort summarized.[9] The importance of adenosylcobalamin (adenosyl $B_{12}$, coenzyme $B_{12}$) and methylcobalamin (methyl $B_{12}$) as cofactors for many enzymic processes and vitamin $B_{12}$ (cyanocobalamin) as a metabolic precursor has motivated extensive research on the cobaloximes.[10] The need of inductive, resonance, and steric parameters to correlate[3] the various properties of these complexes suggested that these systems would provide a challenge to the $\Delta E-\Delta C$ model. Though many properties of these complexes have been reported, there are relatively few studies in which the substituent variation encompasses the four groups of substituents described in the Calculation Section. The $\Delta E-\Delta C$ analysis of five data sets that qualify or come close to qualifying are shown in Table 2. In all five instances the average deviations, $\bar{x}$, of the data fits to Equation (2) correspond to the experimental error in the measurement. A good $\bar{x}$ can be misleading if there is only a small variation in the measured property. A quantity called % fit is defined as 100 times $\bar{x}$ divided by the range of calculated values. The large % fit for

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**Table 2.** Physicochemical Studies Involving Variation of X in XCo(DH)2·B Complexes

| | log *K* (XCo·DMSO)[a] | | $\delta^{13}C(CH_3$ of Co-*t*-buPy)[b] | | $\delta^{13}C(Co-P(OMe)_3)$[c] | | XCo-N dist,[d] Å | | XCo−P dist,[e] Å | |
|---|---|---|---|---|---|---|---|---|---|---|
| X | exptl | calcd | exptl | calcd | exptl | calcd | exptl | calcd | exptl | calcd |
| $CH_3$ | 1.73 | 1.73 | 161.84 | 161.67 | 52.24 | 52.22 | 2.068 | 2.080 | 2.418 | 2.417 |
| $C_2H_5$ | 1.71 | 1.72 | 161.59 | 161.61 | 52.16 | 52.15 | 2.084 | 2.084 | 2.415 | 2.418 |
| *n*-$C_3H_7$ | 1.66 | 1.72 | | | 52.20 | 52.20 | | | | |
| *i*-$C_3H_7$ | | | 161.37 | 161.53 | 52.18 | 52.18 | 2.099 | 2.089 | 2.412 | 2.410 |
| $CH_2Cl$ | 1.79 | 1.78 | | | 52.77 | 52.62 | | | | |
| $CH_2Br$ | 1.80 | 1.77 | 162.37 | 162.34 | 52.87 | 52.87 | | | 2.399 | 2.412 |
| $CH_2I$ | 1.82 | 1.77 | | | 52.95 | 52.92 | | | | |
| $CH_2CF_3$ | 1.86 | 1.73 | 162.50 | 162.43 | 53.19 | 53.21 | | | 2.383 | 2.390 |
| $CH_2CN$ | 1.88 | 1.78 | | | 53.40 | 52.35 | | | 2.391 | 2.401 |
| $CH_2C_6H_5$ | 1.75 | 1.74 | 161.73 | 161.85 | 52.46 | 52.34 | | | | |
| $CH_2CH(CH_3)_2$ | 1.69 | 1.73 | | | 52.25 | 51.98 | 2.081 | 2.087 | | |
| $CH_2Si(CH_3)_3$ | 1.51 | 1.68 | 161.67 | 161.69 | 52.54 | 52.56 | 2.091 | 2.082 | | |
| Cl | | | 163.85 | 163.77 | 55.19 | 55.16 | 1.97 | 1.97 | 2.330 | 2.329 |
| Br | | | 163.72 | 163.72 | 55.07 | 55.08 | | | 2.331 | 2.332 |
| $N_3$ | | | 163.68 | 163.78 | 54.64 | 54.61 | 1.973 | 1.967 | | |
| $CH_2NO_2$ | 1.96 | 1.80 | 163.09 | 163.07 | 53.75 | 53.64 | 2.028 | 2.004 | | |
| $CH(C_2H_5)(CH_3)$ | | | | | 52.16 | 52.05 | | | 2.436 | 2.417 |
| $CH_2C(CH_3)_3$ | | | 161.53 | 161.60 | 52.36 | 52.23 | 2.081 | 2.085 | 2.460 | (2.411) |
| $C_6H_{11}$ | | | | | 52.20 | 52.58 | | | | |
| I | | | 163.51 | 163.63 | 54.93 | 54.99 | | | | |
| CN | 1.78 | 1.83 | | | 54.45 | 54.46 | | | | |
| $NO_2$ | 1.85 | 1.84 | 163.81 | 164.02 | 54.57 | 54.68 | | | 2.392 | 2.385 |
| $C_6H_5$ | 1.35 | (1.71) | 162.08 | 162.11 | 52.67 | 52.95 | | | | |
| $C_2H_3$ | 1.74 | 1.74 | 162.06 | 161.81 | 52.41 | 52.28 | 2.073 | 2.073 | | |
| $CHCl_2$ | | | | | 53.41 | 53.27 | | | | |

[a] Log *K* for the displacement of $(CD_3)_2SO$ by $4\text{-}CNC_5H_4N$ from $XCo(DH)_2(CD_3)_2SO$ in $(CD_3)_2SO$. Calculated with $d_B{}^E = 3.25$, $d_B{}^C = -0.84$, and $\chi^H = 1.72$. $\bar{x} = 0.06$. Data from ref 5. [b] $^{13}C$ chemical shift of the $CH_3$ group of $4\text{-}C_4H_9C_5NCo(DH)_2X$. Calculated with $d_B{}^E = -39.57 \pm 0.31$, $d_B{}^C = 6.77 \pm 0.07$, $\chi^H = 162.14$, $\bar{x} = 0.09$ and % fit is 3.4. Though not shown above, the following were included in the fit, substituent/exptl/calcd; SCN/164.36/164.23; NCS/164.03/164.10; OCN/163.97/163.72; $CH_2CO_2CH_3$/162.45/162.42. [c] $^{13}C$ chemical shift of $P(OCH_3)_3$ in $XCo(DH)_2P(OCH_3)_3$ adducts. Calculated with $d_B{}^E = -76.43 \pm 0.3$, $d_B{}^C = 14.98 \pm 0.06$, and $\chi^H = 52.88$. The value of $\bar{x}$ is 0.10. The % fit is 3. Data from ref 9. [d] Cobalt pyridine distance in $XCo(DH)_2C_5H_5N$. $d^E = 1.877 \pm 0.043$, $d^C = -0.306 \pm 0.010$, $\Delta\chi^H = 2.057$, $\bar{x} = 0.008$. The % fit is 6. Data from ref 5. [e] Co−P bond distance of $(C_6H_5)_3P$ adducts of $XCo(DH)_2$ in Å. Calculated with $d_B{}^E = 3.339 \pm 0.35$; $d_B{}^C = -0.723 \pm 0.008$ and $\chi^H = 2.397$. $\bar{x} = 0.006$. The % fit is 9. Data from ref 5.

the log *K* values shows that although the data are fit as well as they can be measured, the $d^E$ and $d^C$ parameters are not well defined.

In addition to the data fits in Table 2, the $^{13}C$ chemical shift of the $\gamma$-carbon of pyridine adducts[9] of $XCo(DH)_2$ also fits eq 2 very well. The fit of 16 substituents from essentially only one of the four recommended groups gave $d^E = -24.76$, $d^C = 3.85$ and $\Delta\chi^H = 137.74$ ($\bar{x} = 0.07$, % fit = 4). The fit of 21 substituents from all four recommended groups for the 4-*tert*-butylpyridine adducts gave (Table 2) an $\bar{x}$ of 0.09 and a % fit of 3.

As with ECW analyses, steric problems and $\pi$-back-bonding will lead to deviations in the data fits. It is interesting to note that even with a small range of measured values, the phenyl substituent is spotted as a deviant system in the rate data for substitution of $(CD_3)_2SO$. The analyses in Table 2 show no regular pattern in the deviations that indicate steric problems for any substituent. This conclusion is in contrast to literature analyses of crystal structure data[5] which are claimed to reflect the importance of steric effects in these systems. The absence of a steric effect is also in contrast to the conclusions[3] on similar systems that were fit to eq 1.

The interpretation of the signs of $d^E$ and $d^C$ provide a unique interpretation of the influence of substituents on the acceptor properties of cobalt. As in the interpretation of $\varrho$ values, the signs and values of d must be considered in the context of the substituent influence on the family ($s^E$, $s^C$) and the demand made by the common reactant ($E^*$, $C^*$) as shown in eqs 3 and 4. Different signs for *s*, the sensitivity of the reaction center to substituent, would indicate that electron releasing substituents (positive $\Delta E$ and $\Delta C$) have opposite influences on the electrostatic bond forming tendencies and the covalent bond forming tendencies of the acceptor cobalt center. Different signs for $E_B{}^*$ and $C_B{}^*$ indicate a different sign for the influence of the electrostatic and covalent properties on the physicochemical property being measured.

Consider the bond distance fit first. Increased covalent and electrostatic bonding of a donor by the cobalt acceptor should increase the bond strength and decrease the bond distance. Though increased covalent and electrostatic bonding lead to positive values of $E_B$ and $C_B$ for a $-\Delta H$ fit, the decrease in distance with increased covalent and electrostatic contributions to acceptor strength would correspond to a negative value for both $E_B{}^*$ and $C_B{}^*$ for the donor. Thus, the sensitivity of the family (X−$Co(DH)_2$) to the inductive influence of these substituents on cobalt must be the cause of the sign reversal in *d*, *i.e.* $s_A{}^E$ and $s_A{}^C$ have different signs. A negative $s_A{}^E$ and a positive $s_A{}^C$ account for the signs of the *d* values for the bond distance fit in Table 2. A negative $s_A{}^C$ indicates that an electron releasing methyl group ($+\Delta E$) leads to a decrease in the tendency of the acceptor cobalt center to undergo electrostatic bonding. A negative $s^E$ coupled with a negative $E_B{}^*$ leads to a positive $d^E$. As a result, a methyl group causes an increase in the Co−P or Co−N distance from reduced electrostatic bonding. A weaker bond is expected for an electrostatic interaction from an electron-releasing substituent because of a smaller partial positive charge on cobalt. By similar arguments, electron-attracting substituents increase the partial positive charge on cobalt, increase $E_A$, and decrease the bond distance.

One might expect that electron-releasing substituents would raise the energy of the metal acceptor orbital and decrease the covalent contribution to the acceptor strength. However, the negative sign of $d^C$ indicates that electron-releasing substituents decrease the distance and increase the cobalt's covalent bond-forming tendencies. With $C_B{}^*$ expected to be negative (strong covalent bonding decreases the distance), $s^C$ is positive, indicating that the metal center becomes more polarizable with methyl substitution and the cobalt's tendency to undergo covalent bonding increases. Changes in the d, s and p orbital character of the orbital employed to form the metal−ligand bond could provide the polarizability mechanism that leads to the observed increase in covalent bonding forming tendencies for the $XCo(DH)_2$ acceptor with electron-releasing substituents. The opposite change in hybridization is induced by electron-withdrawing substituents with negative $\Delta C$ values.

The $^{13}C$ shifts of the coordinated $(CH_3O)_3P$, $C_5H_5N$ or $(CH_3)_3CC_4H_4N$ are consistent with the above bonding trends. As the cobalt becomes a stronger acceptor, the $^{13}C$ shifts become larger in contrast to the distances which became smaller. This corresponds to a positive $E_B$* and $C_B$* for the shift. The above assignment of the signs of $s^E$ and $s^C$ with a positive $E_A$* and $C_A$* lead to the observed signs of $d^E$ and $d^C$ for the $^{13}C$ shifts of adducts with all three donors. The signs of d for the $^{13}C$ shifts are opposite those for the bond distance because of the change in sign of $E_A$* and $C_A$*.

The analysis of the data in Table 2 not only extends the range of systems for which the $\Delta E-\Delta C$ parameters are relevant but illustrates that unique insights result about the influence of substituents on the acidity of the acceptor. The use of $3-\Delta E$ and $3-\Delta C$ substituent constants in the successful correlation of the data discussed above and the poor correlation resulting from the use of $4-\Delta E$ and $4-\Delta C$ parameters indicates that the predominant interaction of the substituent with the cobalt is $\sigma$-bond formation. Previous interpretations[3,9] have invoked resonance and steric effects because the covalency in these systems was not properly represented in the parameters used to analyze the data.

Several studies of cobaloximes have been reported[9−16] in which a limited number of substituents have been employed. Good data fits, where $\bar{x}$ is comparable to experimental error, for such systems only allow one to conclude that no unusual effects (conjugative or steric or solvation) are supported by the measurements. Such effects might be revealed in a properly designed experiment where substituents from all four groups are employed along with substituents whose size varies. Table 3 contains the results from analyses of several limited data sets, involving rate, equilibrium and electrochemical measurements for substituted cobaloximes. In the case of redox potentials, the signs of $d^E$ and $d^C$ are interpreted in terms of the differences in the substituent influence on the metal−ligand bond strengths in the II and III oxidation states. Clearly, the interpretation of this chemistry with any set of parameters must properly assess the changes induced by substituents bound to cobalt on the metal centers tendency to undergo covalent and electrostatic bonding.

**Niobocene Olefin Hydrides.** Equilibrium constants for olefin binding and rates of insertion of olefins into Nb-H bonds have been measured for a series of phenyl substituted styrenes.[17] Table 4 summarizes the results of a $\Delta E-\Delta C$ analysis of this data. Two systems have been studied with enough substituents to provide meaningful data fits. In both instances, the combined fits of data for the 3- and 4-substituents indicate that the substituent effect involves normal inductive and conjugative transfer or withdrawal of electron density to or from the alkene $\pi$-system. There are no steric or unusual conjugative ($\pi$-plus)[3c] interactions that influence the equilibrium or rate data.

**Table 3** Physicochemical Studies Involving Variation of X in $XCo(DH)_2{\cdot}B$ Complexes

| family | $d^E$ | $d^C$ | $\Delta\chi^H$ | no. of subst.[a] (groups) | $\bar{x}$ | % fit | ref |
|---|---|---|---|---|---|---|---|
| log *k* $(XC_6H_4CH_2Co)$[b] | −4.00 | −0.04 | 2.09 | 5(3) | 0.05 | 4 | 12 |
| $E_{1/2}$ $(XC_6H_4CH_2Co)$[c] | −0.011 | −0.121 | 0.80 | 5(3) | 0.006 | 6 | 12 |
| p*K* $(XpyCoH_2O)$[d] | 0.85 | 0.54 | 6.26 | 7(3) | 0.02 | 3 | 13 |
| log *K* $(XpyCo(H_2O))$[e] | 1.19 | −2.235 | −2.48 | 6(3) | 0.06 | 4 | 13 |
| log *k* (XpyCoOH)[f] | 1.12 | −1.11 | 3.41 | 6(3) | 0.05 | 7.9 | 13 |
| p*K*$(XCo(DH)_2Py)$[g] | 78.7 | −13.9 | 12.8 | 5(1) | 0.04 | 1 | 15 |
| p*K*$(XCo(DH)_2H_2O)$[h] | 106 | −19.4 | 11.8 | 7(1) | 0.16 | 6.2 | 15 |
| $\Delta\nu_1$ $(RCo(DH)_2H_2O)$[i] | −18.0 | 2.68 | 22.5 | 7(1) | 0.30 | 50 | 14 |
| $\Delta\nu_2$ $(RCo(DH)_2H_2O)$[j] | −12.9 | 1.9 | 23.9 | 7(1) | 0.27 | 16 | 14 |
| log (*kr* (XCo-B))[k] | 53.6 | −3.4 | −1.7 | 15(2) | 0.55 | 10 | 9 |
| log (*kr* $(XCo(DH)_2$-P))[l] | −44.5 | 19.6 | 2.01 | 5(2) | 0.03 | 5 | 6 |
| $E^{1/2}(XCo(DH)_2H_2O)$[m] | −2.56 | −0.007 | 0.862 | 9(2) | 0.019 | 6 | 11 |

[a] Number of substituents studied and the number of groups involved. [b] The log rate constant for the reaction of $XC_6H_4CH_2Co(DH)_2^+$ with pyridine. [c] $E_{1/2}$ (V) for the (III, IV) redox couple for "$XC_6H_4CH_2Co(DH)_2$". [d] $pK_a$ of the complex $XCo(DH)_2(H_2O)(ClO_4)$ at 25 °C in 2M $NaNO_3$. [e] The log *k* ($M^{-1}$ $s^{-1}$) for the reduction of $XC_5H_4NCo(DH)_2(H_2O)(ClO_4)$ by $Fe^{2+}$ in water at 25 °C, $[ClO_4^-]_T = 2$ M. [f] The log *K* ($M^{-1}$ $s^{-1}$) for the reduction of $XC_5H_4NCo(DH)_2OH$ by $Fe^{2+}$ in water at 25 °C, $[ClO_4^-]_T = 2$ M. [g] The p*K* for proton dissociation from DH in $XCo(DH)_2C_5H_4N$. [h] The log of axial water acid dissociation constant for $RCo(DH)_2H_2O$. Controversy exists about what quantity is being measured.[9] [i] The frequency ($10^3$ $cm^{-1}$) of the high energy electronic transition in $RCo(DH)_2H_2O$ in pH 6.5 aqueous solution. [j] The frequency ($10^3$ $cm^{-1}$) of the low energy electronic transition in $RCo(DH)_2H_2O$ in pH 6.5 aqueous solution. [k] Log pseudo-first-order rate constant for the dissociation of 4-$CNC_5H_4N$ from 4-$CNC_5H_4NCo(DH)_2X$ by $(n\text{-}C_4H_9)_3P$ in $CH_2Cl_2$ at 25 °C. [l] Log ligand exchange rates from NMR for $XCo(DH)_2P(OCH_3)_3$ with $P(OCH_3)_3$ in bromobenzene solvent. The $CH_2Br$ substituent was omitted. It gave a calculated log rate constant of 1.4 compared to the reported value of 0.54. [m] Reduction potentials for $XCo(DH)_2H_2O^+$ in $CH_3CN$ vs SCE.

The equilibrium constants $K_{eq}Cp^*(CH_2{=}CH_2)$ refer to displacement of ethylene by substituted styrenes. Electron-releasing substituents (positive $\Delta E$ and $\Delta C$ values) make log *K* larger with the $d^E$ contribution and smaller with the $d^C$ contribution. Since the reaction involves displacement of ethylene, the equilibrium constants must be interpreted in terms of the relative basicity of the styrenes and ethylene. With comparable contributions from the electrostatic and covalent terms, the products $d^E\Delta E$ and $d^C\Delta C$ should be calculated to see which term dominates. For 4-$N(CH_3)_2$ the $d^E\Delta E$ term is 0.26 and the $d^C\Delta C$ term is −0.49. This suggests that ethylene has a larger free energy of binding from covalent bonding and a smaller one from electrostatic bonding than 4-$N(CH_3)_2C_6H_4$-$CH{=}CH_2$. K for the displacement reaction is facilitated by the electrostatic term and hampered by increasing the covalent bond forming tendency of the $\pi$-system. The net result is poorer binding (a more negative log *K*) by the substituted styrene with more electron releasing substituent, 4-$N(CH_3)_2$, than by styrene.

Electron withdrawing substituents (negative $\Delta E$ and $\Delta C$ values) make log *K* more negative (*K* is smaller) with the $d^E$ contribution and less negative with the $d^C$ contribution. For 3-$CF_3$ the $d^E\Delta E$ term is −0.26 and the $d^E\Delta C$ term +0.37. Considering the displacement reaction, this suggests that ethylene has a larger free energy of binding from electrostatic effects and a smaller one from covalent effects than 3-$CF_3C_6H_4$-$CH{=}CH_2$. Considering, the $\pi$-orbital as a donor, the $N(CH_3)_2$ substituent is expected to increase the $\pi$-electron density and raise the energies of the ethylene $\pi$ orbital. This would increase the electrostatic and covalent interaction with the metal. The $CF_3$ substituent should have the opposite effect. The sign of $d^E$ indicates that the electrostatic interaction is dominated by the electron density in the $\pi$-orbital which increases the olefin

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**Table 4.** Equilibrium and Rate Data for Permethylniobocene and Niobocene Olefin Hydrides

| | log $K_{eq}$ (Cp($H_2C{=}CH_2$)) | | log $K_{eq}$ (Cp($H_2C{=}CHPh$)) | | $\Delta G^*$(Cp*) | | $\Delta G^*$(Cp endo) | | $\Delta G^*$(Cp exo) | |
|---|---|---|---|---|---|---|---|---|---|---|
| | exptl | calcd[a] | exptl | calcd[b] | exptl | calcd[c] | exptl | calcd[d] | exptl | calcd[e] |
| H | −1.33 | −1.27 | 0 | 0.02 | 18.3 | 18.4 | 20.5 | 20.4 | 16.8 | 16.8 |
| 4-$CH_3$ | −1.41 | −1.29 | | | 18.1 | 18.1 | | | | |
| 4-$N(CH_3)_2$ | −1.49 | −1.50 | −1.3 | −1.3 | 17.7 | 17.5 | 20.0 | 20.0 | 17.6 | 17.6 |
| 3-$CH_3$ | −1.20 | −1.28 | | | 18.1 | 18.2 | | | | |
| 3-$N(CH_3)_2$ | −1.19 | −1.44 | | | 18.0 | 18.0 | | | | |
| 3-$CF_3$ | −1.04 | −1.16 | | | 19.4 | 19.1 | | | | |
| 4-$CF_3$ | −1.40 | −1.31 | 1.2 | 1.2 | 19.0 | 19.1 | 21.7 | 21.7 | 16.3 | 16.3 |
| 4-$OCH_3$ | −1.39 | −1.34 | −0.5 | −0.5 | 17.9 | 18.1 | 20.2 | 20.3 | 17.1 | 17.1 |

[a] The log equilibrium constant for displacing ethylene from $Cp_2{}^*Nb(H_2C{=}CH_2)$ by $H_2C{=}CC_6H_4X$ at 25 °C in $C_6D_6$. Calculated with $d^E = 1.89 \pm 0.6$, $d^C = -0.55 \pm 0.1$, and $\Delta\chi^H = -1.27$. $\bar{x} = 0.10$. See ref 2a for 4-X substituent constants. [b] The log equilibrium constant for displacing $H_2C = CHC_6H_5$ from $Cp_2{}^*Nb(H_2C{=}CHC_6H_5)$ by $H_2C{=}CHC_6H_4X$ at 25 °C in $C_6D_6$. Calculated with $d^E = -4.79$, $d^C = -0.74$, and $\Delta\chi^H = -0.016$. $\bar{x} = 0.03$ and the % fit is 1. [c] $\Delta G^{\ddagger}$(50 °C) for olefin insertion into Nb−H for *endo*-$Cp_2{}^*Nb(CH_2{=}CHC_6H_4X)H$. Calculated with $d^E = -2.47 \pm 0.6$, $d^C = -0.60 \pm 0.13$, and $\Delta\chi^H = 18.37$. $\bar{x} = 0.12$ and the % fit is 7. [d] $\Delta G^{\ddagger}$(50 °C) as in footnote *c* for endo-$Cp_2Nb(CH_2 = CH_2C_6H_4X)H$. Calculated with $d^E = -10.6$, $d^C = 1.1$, and $\Delta\chi^H = 20.5$. $\bar{x} = 0.03$. [e] $\Delta G^{\ddagger}$(50 °C) for *exo*-$Cp_2Nb(CH_2{=}CH_2C_6H_4X)H$. Calculated with $d^E = 0.42$, $d^C = 0.82$, and $\Delta\chi^H = 16.8$. $\bar{x} = 0.01$.

**Table 5.** Application of the 3-$\Delta E$ and 3-$\Delta C$ Parameters to Silyl Systems

| | carbenium | | | $SiHR_3$ diss | | | $SiHR_3$ diss | |
|---|---|---|---|---|---|---|---|---|
| $SiR_3$ | exptl | calcd[a] | $SiR_3$ | exp | calcd | $SiR_3$ | exptl | calcd[b] |
| $SiMe_3$ | 2.3 | 2.3 | $SiClMe_2$ | 1.2 | 1.5 | $SiMePh_2$ | 1.3 | 1.0 |
| $SiClMe_2$ | −0.6 | −0.5 | $SiPhMe_2$ | 0.8 | 0.7 | $SiClPh_2$ | 1.9 | 2.3 |
| $SiPhMe_2$ | 1.6 | 1.6 | $SiEt_3$ | 0.4 | 0.3 | $Sibz_3$ | 2.0 | (0.4) |
| $SiEt_3$ | 2.5 | 2.4 | $SiPh_3$ | 2.2 | (1.4) | $SiPhCl_2$ | 3.2 | 3.2 |
| $SiBu_3$ | 2.7 | 2.7 | Si-*i*-$Pr_3$ | 1.4 | (0.5) | $SiCl_3$ | 4.1 | 4.0 |
| $SiBuMe_2$ | 2.3 | 2.4 | $SiMeCy_2$ | 0.5 | 0.8 | $SiPh_2H$ | 1.2 | 1.3 |
| $SiPh_3$ | 0.5 | 0.4 | | | | | | |
| Si-*i*-$Pr_3$ | 2.6 | 2.7 | | | | | | |

[a] Calculated with $d^E = 58.4 \pm 0.5$, $d^C = -10.5 \pm 0.1$, and $\Delta\chi^H = 0.38$. $\bar{x} = 0.07$. % fit = 2. [b] The systems in parentheses were ommitted from the fit. Calculated with $d^E = -39.05 \pm 0.5$, $d^C = 8.11 \pm 0.14$, $\Delta\chi^H = 1.18$, $\bar{x} = 0.20$, and % fit = 4.

sigma basicity for substituents whose $\Delta E$ is positive. The sign of $d^C$ is opposite to that expected for pi-basicity. This sign suggests that the differences in the contribution from the covalent interaction of ethylene and the styrenes are dominated by metal to ligand $\pi$-back-bonding with the substituent influencing the energy of the $\pi^*$-alkene orbitals of the substituted styrenes.

The activation energies for olefin insertion have negative values for both $d^E$ and $d^C$. For the 4-$N(CH_3)_2$ substituent, the $d^E\Delta E$ contribution is −0.35 and the $d^C\Delta C$ contribution −0.53. For the 4-$CF_3$ substituent $d^E\Delta E$ is 0.43 and $d^C\Delta C$ is 0.33. Both covalent and electrostatic contributions are significant with electron-releasing substituents decreasing $\Delta G^*$. This is consistent with a proton transfer mechanism from the metal to the alkene. For a hydride transfer mechanism, forming the metal−carbon bond to one alkene carbon would lead to positive charge developing in the transition state on the adjacent alkene carbon. One could propose that this charge would be stabilized by the inductive properties of electron-releasing substituents. However, in an expected, four center, concerted process reduction of positive charge would be deleterious to hydride transfer; *i.e.* it would be better to stabilize this charge with the hydride. The large $\Delta C$ component found in the $\Delta E$, $\Delta C$ analysis suggests that little charge develops in the transition state as the metal−carbon and carbon−hydrogen bonds form. The hydrogen being transferred in the four−center transition state probably has a slight positive charge, and niobium is the nucleophile in forming the Nb−C bond. The system with the least $\pi$-back-bonding in the ground state (*i.e.* the most negative log *K*) leads to the most nucleophilic niobium for insertion.

The reported[17] equilibrium constants for substitution of styrene by substituted styrenes as well as the free energies of activation for olefin insertion into Nb−H for exo and endo $Cp^2$-Nb $(CH_2{=}CHC_6H_4X)H$ have only been studied with four substituents. Excellent fits result with $\bar{x} \le 0.03$, but the only conclusion that can be drawn is that there is no evidence for any unusual steric effect within each limited series.

**Silicon Systems.** Further diversity in the systems to which $\Delta E$ and $\Delta C$ can be applied is illustrated by the reactivity of silyl compounds.[6,18] These systems were previously analyzed using the QUALE approach.[6,18] Data fits to eq 2, for two different reactions, are shown in Table 5. For the analyses, the $\Delta E$ values for the three substituents on silicon are summed as are the $\Delta C$ values.

The logs of the rate constants for the addition of (*p*-anisylphenyl)carbenium ion to alkenes with pendent silyl groups ($X_3SiCH{=}CH_2$) are fit very well. Substituents from two of the four groups are well represented and there is one substituent, a chlorine, from a third group. The $\Delta\chi^H$ value is the predicted rate for the $SiH_3$ derivative. There is no evidence of any contribution from a steric effect.

The sign reversal of $d^E$ and $d^C$ has to be interpreted in terms of the $s^E E_B{}^*$ and $s^C C_B{}^*$. An increase in the electrostatic and covalent bond forming properties of the $\pi$-system should lower the activation energy and increase the rate. Thus, $E_A{}^*$ and $C_A{}^*$ for the attacking carbenium reactant are expected to be positive. An electrostatic electron-releasing substituent on silicon decreases the acceptor tendency of the silicon to undergo ionic bonding to the attached $CH_2$ group, increasing the negative charge that $CH_2$ can delocalize into the $\pi$ system. This delocalization increases electrostatic, $\pi$ basicity and increases the rate. The expected negative $s^E$ for the inductive effect decreasing the silicon acceptor properties becomes a positive $s^E$ for its influence on $\pi$-basicity.

A covalent electron releasing substituent decreases the covalent acceptor properties of silicon and leads to weaker covalent bonding of silicon to the $CH_2$ group. The weaker covalent bond of silicon to the vinyl group makes the $SiR_3$ group less effective by a covalent interaction at delocalizing the developing positive charge on the alkene from carbenium ion attack. A slower reaction results corresponding to a negative $s^C$.

The data[18] for the logs of the dissociative rate constants of $R_3Si$-H from $Cr(CO)_5(R_3Si{-}H)$ were fit to $\Delta E$ and $\Delta C$ as shown in Table 4. The literature interpretation of this data suggested a significant steric component. The $\Delta E{-}\Delta C$ analysis suggests

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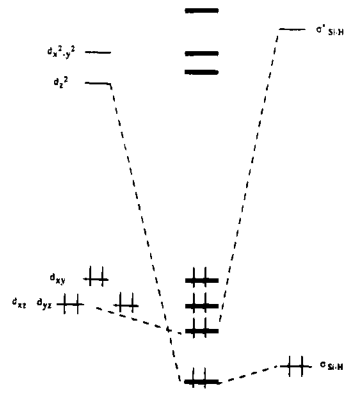

**Figure 1.** Bonding in $Cr(CO)_5R_3Si{-}H$.

that steric effects may be operative in $(C_6H_5)_3SiH$ and $(i\text{-}C_3H_7)_3SiH$, but they do not make a significant contribution in other systems.

The signs of $d^E$ and $d^C$ are opposite and can be understood by considering the bonding of Si−H to $Cr(CO)_5$ as shown in Figure 1. Following the interactions proposed[19] for $HSiCl_3$ bonding to $CpMn(CO)_2$, the six metal electrons are paired up in the $d_{xy}$, $d_{xz}$ and $d_{yz}$ orbitals with the $d_{z^2}$ orbital behaving as the acceptor orbital for the donor Si−H $\sigma$-bond. The $\sigma_{SiH}$ MO, which is largely hydrogen interacts with the $d_{z^2}$ orbital. In addition, $\pi$-back-bonding from the metal to the $\sigma_{SiH}{}^*$ MO (which is largely silicon) also occurs. First consider the influence of substituent change on the $\sigma$-donor properties of the Si−H bond to $Cr(CO)_5$. $E_A{}^*$ and $C_A{}^*$ are both expected to be positive for bond strength because increased electrostatic and covalent properties of a $\sigma$-donor increase the bond strength. This leads to a negative $E_A{}^*$ and $C_A{}^*$ if the rate of dissociation is dominated by bond strength. Substituents with a positive $\Delta E$, increase ionicity and hydric character of the SiH bond; *i.e.*, $s^E$ is positive. This increases the strength of the donor-acceptor interaction by increasing the electrostatic bond forming tendencies for the SiH bond. The positive $s^E$ coupled with a negative $E_A{}^*$ leads to a negative $d^E$ value for dissociation.

A substituent with a positive $\Delta C$ increases the covalency in the SiH bond. This localizes the SiH electron pair and decreases its tendency to undergo three center bonding to chromium. As a result, $s^C$ is negative ($C_B$ is decreased) and coupled to a negative $C_A{}^*$ for dissociation leads to a positive $d^C$ value.

Next consider the metal to Si−H $\pi$-back-bond interaction. The chromium is a donor with a positive $E_B{}^*$ and $C_B{}^*$ for donor−acceptor interaction and negative values for dissociation. A substituent with a positive $\Delta C$ decreases the acceptor properties of silicon, $s^C$ is negative and $d^C$ for dissociation is positive.

In summary, substituents with a positive $\Delta C$ decrease the $\sigma$-donor strength of $\sigma_{SiH}$ and decrease the silicon acceptor strength in the $\pi$-back-bonding interaction. Both covalent effects lead to an increase in the dissociation rate. Substituents with a positive $\Delta E$ increase the $\sigma$-donor strength of $\sigma_{Si-H}$ by increased electrostatic bonding and decrease the dissociation rate. Electron-withdrawing substituents have the opposite effects.

The magnitude of the covalent and electrostatic contributions can be assessed for each system by calculating $d^E\Delta E$ and $d^C\Delta C$. For $Et_3SiH$, the values are −4.6 and +3.7 for the electrostatic and covalent contributions respectively. The electrostatic term dominates causing a net decrease in the rate of dissociation. For $Cl_3SiH$, the electrostatic and covalent contributions are 14.1 and −11.2. The electrostatic term again dominates causing an increase in the rate of dissociation.

A very significant prediction can be made as a result of this analysis. To make the most stable acceptor-$R_3SiH$ adduct *i.e.* the one with the smallest rate of dissociation, strong electron releasing substituents (positive $\Delta E$ and $\Delta C$) should be used with the smallest $\Delta C/\Delta E$ ratio possible. However, most of these ratios are around 3−4, giving rates comparable to $HSiEt_3$. Alternatively, an electron-attracting substituent with a large $\Delta C/\Delta E$ ratio would lead to a more stable adduct than the ethyl derivative. The electron attracting $CH_3S$-substituent has a large $\Delta C/\Delta E$ ratio whose log dissociation rate is predicted to be −0.352. These predictions are made on the basis of a sigma interaction of the substituent with silicon. Since the prediction is based on a $\Delta C/\Delta E$ ratio outside the range of substituents studied, the prediction should be regarded as tentative and illustrative of the power of the model. The optimization of a reaction by proper substituent selection is possible for any system that fits eq 2.

The model developed from the $\Delta E$ and $\Delta C$ analysis of this system can be extended to the chemistry of $R_3SiH$ bonding to other compounds. The substituent trend for $HSiX_3$ bonding to $CpMn(CO)_2$ is opposite that for $Cr(CO)_5$. This result can be accommodated by the $\Delta E{-}\Delta C$ model by increasing the magnitude of $d^C$ relative to $d^E$ so the $d^C\Delta C$ term dominates. This change can be accomplished by increasing the $C^*/E^*$ ratio of the metal complex. This corresponds to weakening the electrostatic sigma bonding contribution, or increasing the covalent $\pi$-back-bond donation by the metal to the $HSiR_3$ ligand.

## Calculation Section

Physicochemical measurements, $\Delta\chi^X$, for a family of X-substituted reactants are fit to eq 3 using the $\Delta E^X$ and $\Delta C^X$ parameters[8] in Table 1. An equation is written for each $\Delta\chi^X$ and the series of simultaneous equations are solved for $d^E$, $d^C$, and $\Delta\chi^H$. When the parent hydrogen has been measured it is entered as an X-substituent with $\Delta E = \Delta C = 0$. In some instances, the data fit is improved considerably by omitting some substituents. The omitted systems are indicated by placing a parentheses around the calculated values in the tables.

The criteria for judging the quality of a fit have been reported.[2a,c] When a $\Delta E{-}\Delta C$ analysis is carried out on a family of compounds, $d^E$ and $d^C$ reflect how changes in covalency and electrostatic properties of the substituent influence the measured property. In order to determine accurate $d^E$ and $d^C$ parameters, substituents that vary in their $\Delta C/\Delta E$ ratios must be used to avoid a shallow minimum in the solution of the simultaneous equations. The ratios for parameters close to zero are irrelevant for the measured property, $\Delta\chi^X$, is dominated by $\Delta\chi^H$. Thus, the magnitude of the parameters is also relevant. One or more substituents from each of the four groups—(I)) $N_3$, $CF_3$, CN, $NO_2$, or $CHCl_2$; (II) $C_2H_3$, H, $CH_2C_6H_5$, or $C_6H_5$; (III) F, Cl, Br, I, OR, OCN, $SCN^-$, or $NCS^-$; (IV) alkyls, $CH_2X$, or $(CH_3)_2N$—should be studied. These will be referred to as the four recommended substituent groups.

Limited systems that result from a study of only a few substituents or of one or two substituent groups are identified as giving rise to tentative parameters. A good fit of limited data enables one to conclude that no evidence for the existence of any unusual effects in the chemistry is revealed by this substituent selection. Tentative parameters should only be used to predict $\Delta\chi^X$ values for new substituents in the groups studied. The $d^E$ and $d^C$ parameters should not be interpreted.

Systems in which the $\bar{x}$ values are larger than the experimental error sometime result even though limited substituents are employed. In this case, one can conclude that the measurements are dominated by factors other than the electronic effects influencing bond strength.

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