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A Molecular Mechanics Model of Ligand Effects. 3. A New Measure of Ligand Steric Effects

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Molecular mechanics methods have been employed to compute energy-minimized structures for a large number of $Cr(CO)_5L$ complexes, where L is CO, trialkyl- or triarylphosphine, mixed trialkyl/arylphosphine, phosphite, alkyl/aryl/alkoxyphosphine, or one of 8 analogous arsenic ligands. The energy-minimized structures are employed to compute a new measure of ligand steric effect, the ligand repulsive energy, E_R, obtained by computing the van der Waals repulsive force acting between the ligand and $Cr(CO)_5$ fragments along the Cr–P axis, at the equilibrium Cr–P distance, r_e. The repulsive force is multiplied by r_e to obtain E_R: $E_R = [\partial E_{vdW}(\text{repulsive})/\partial r(\text{Cr–P})]r_e$. Values of E_R correlate very well with Tolman's cone angle values, θ, for all phosphines. Phosphites and arsenic ligands depart from the same correlation, but the overall correlation for 69 ligands is fair ($r_{corr} = 0.857$). The comparative effectiveness of E_R and θ in linear free energy correlations of kinetics and equilibrium data is analyzed for a large body of literature results. E_R and θ are comparably effective in terms of a superficial analysis based on correlation coefficients alone. The limitations and advantages of E_R as a measure of ligand steric effect are described.

The previous two papers in this series have been concerned with the molecular mechanics energies of phosphite[1] and phosphine[2] ligands and their complexes with a prototypical metal carbonyl binding site, $Cr(CO)_5$. The intent of these studies has been to discern the contributions to the energy change on complex formation that arise in the molecular mechanics model and to learn how these contributions change as a function of the ligand steric requirement.[3]

The results indicate that phosphite and phosphine ligands respond differently to the steric forces that operate in complex formation. The major difference between them is that phosphites are somewhat more flexible. Bending modes, involving either P–O–C bonds or oxygen lone-pair orbitals, absorb most of the variation in steric strain occasioned by increased branching in the ligands. In phosphines, the increased potential energy is absorbed largely in bond-stretching modes.

In this contribution, the molecular mechanics calculations have been extended to a large and varied series of phosphorus ligands, and to several arsenic ligands. The computational results for 69 $Cr(CO)_5$–ligand complexes are employed to investigate how the molecular mechanics method can be employed to assess the relative steric effects of ligands. The analysis begins with a brief discussion of previously developed concepts and theoretical work relating to steric effects in linear free energy relationships (LFER). Secondly, the total change in molecular mechanics energy in the process described in eq 1 is evaluated as a measure of ligand steric effect.

$$Cr(CO)_5 + PR_3 \rightarrow Cr(CO)_5PR_3 \qquad (1)$$

A new measure of ligand steric effect based on molecular mechanics calculations, the *ligand repulsive energy*, E_R, is presented and compared with other measures such as the cone angle.[4] The new parameter is evaluated in terms of its success in correlating kinetics, equilibrium, and other data involving series of phosphorus ligands.

Historical Development

Steric effects were first recognized as important in reactivity and equilibrium studies by organic chemists.[5] Ingold's early work on nucleophilic substitution is of particular importance.[6] In addition to amassing kinetics data to demonstrate the steric effects of nucleophiles in S_N2 reactions, the Ingold school also employed force field models to compute steric energies. Also of relevance to the present studies is Brown's classic work on strain energies in formation of Lewis acid–base adducts.[7] These early investigations pointed the way toward a conceptual basis for understanding how steric effects arise.

The most successful attempts to account quantitatively, albeit empirically, for steric effects on chemical reactivity were those of Taft,[8] who developed the so-called E_s parameters. Taft built upon Hammett's linear free energy formulation, expressed in the Hammett equation,[9] $\log (k_i/k_0) = \sigma_i\rho$, where k_0 represents the rate constant for the reference substituent (H), ρ is a measure of the susceptibility of the reaction to changes in electron density in the transition state, and σ_i is a measure of the effect of a substituent replacing hydrogen (for which $\sigma = 1$) and giving rise to the rate constant k_i. The more general relationship, eq 2, takes

$$\log (k_i/k_0) = E_{si}s + \sigma_i^*\rho^* \qquad (2)$$

into account steric and electronic effects. The substituent is now characterized by two constants, the steric term E_{si} and the electronic term σ_i^*. The particular reaction is characterized by measures of sensitivity to steric and electronic effects, s and ρ^*, respectively.

The development of LFER's in inorganic chemistry took a rather different path. There was a strong emphasis on kinetic parameters for particular reactions, for example, reactivity parameters for nucleophiles reacting with CH_3I or *trans*-$[Pt(py)_2Cl_2]$.[10] In a similar vein, the Edwards equation[11] relates nucleophilic behavior in equilibria or rate processes to proton basicity and redox behavior. In these approaches, no account is taken of a steric contribution to the reactivity, even though the reactions are in many cases associative in nature. In such circumstances, steric effects alter the relative values of the derived

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parameters.[12] Nucleophilicity parameters obtained in such studies do not successfully predict relative rates in other than closely related reactions.

In organometallic chemistry, there has been a general recognition that both steric and electronic factors are important in determining the relative reactivity effects of ligands such as phosphines and phosphites. Ligand basicities have been measured in terms of free energies and enthalpies of adduct formation with group 13 Lewis acids such as BH_3, BF_3, or $GaMe_3$,[13] gas-phase proton affinities,[14] pK_a or half-neutralization potentials in polar aprotic media,[15] or enthalpies of protonation in nonaqueous solvent.[16] These methods are not readily applied consistently to a large and varied set of phosphorus and related ligands.

The frequency of the IR-active totally symmetric stretch of the three CO groups in $LNi(CO)_3$ complexes has been widely employed as an effective measure of the net relative electron density at Ni, and thus as a measure of the donor capacity of the ligand L.[4,17] An alternative measure is the ^{13}C chemical shift of the same three CO groups, for which an extensive body of data is available.[18]

The most frequently employed measure of the steric properties of phosphorus and related ligands has been the cone angle, θ, defined by Tolman.[4] The cone angle is the apex angle of a cylindrical cone, centered along the 3-fold axis, 2.28 Å from the center of the P atom, which just touches the outermost atoms of a CPK molecular model of the ligand. The surfaces of these atoms are determined by their van der Waals radii.

A relationship analogous to eq 2 was first employed in organometallic chemistry by Schenkluhn and co-workers.[19,20] Subsequently, an expression of the form of eq 3 has been widely

$$\ln k^J_i = a_J E_i + b_J S_i + c_J \qquad (3)$$

employed.[21-27] The rate constant k^J_i represents the value for the ith ligand in reaction set J. E_i and S_i represent the electronic and steric parameters of the ith ligand; a_J and b_J represent the sensitivities of ln k to variations in the electronic and steric parameters, respectively, of the ligand. The constant c_J is the value of ln k^J_i for the hypothetical reference reactant with zero values for E_i and S_i. Most usually, the electronic parameter is associated with the parameter χ_i based on the A_1 symmetry IR stretching frequency in $LNi(CO)_3$[4,17] or δ_i, the ^{13}C chemical shift of the CO groups in the same compounds relative to $Ni(CO)_4$;[18] the steric parameter is associated with θ.[4]

The Number and Nature of Ligand Steric and Electronic Parameters

The application of expressions such as eqs 2 and 3 implies that electronic and steric effects are separable. While separability may seem obvious enough conceptually, the difficulty arises in ensuring that the particular measures chosen actually measure purely electronic or purely steric effects.

By analogy with the classification employed for substituent effects in organic chemistry,[28] the electronic effects of ligands may be considered to possess four components: (a) field effects, which reflect the electric fields arising from charges or dipolar charge distribution in the ligand that affect the reaction site; (b) electronegativity effects, which measure the net electron donation or withdrawal of charge from the reaction site by the ligand, relative to a reference ligand; (c) polarizability effects, which measure perturbations in the charge distribution within the ligand resulting from electric fields, and which in turn perturb the electronic environment at the reaction site (the London dispersion interaction operating between the ligand and the remainder of the molecule also affects electronic energy levels and charge distribution); (d) resonance, or long-distance π-electron-transfer effects. This last effect, which in organic systems might be strongly operative in a given reaction for aryl substituents such as p-$N(CH_3)_2$, has no precise analogue in organometallic chemistry, although attempts to separate σ- and π-bonding effects[29] are motivated by similar considerations.

Just as there has been an elaboration of the substituent parameters in organic chemistry based on distinctions between electron-demanding and electron-releasing transition states and the operation of resonance effects,[30] there have been attempts to dissect the electronic parameter in eq 3 to account for π backbonding or π donation by phosphorus ligands.[29] Further, it has been argued that in a given reaction system there may exist a threshold of ligand steric requirement below which a ligand exerts no steric effect.[23a,26,31,32]

The approach adopted here is to employ the minimum number of parameters necessary to define the dependence of reaction rate on ligand characteristics. Most often, the primary goal in employing a LFER such as eq 3 is to gain insights into the nature of the transition state in relation to the ground state. The sign of the coefficient a_J indicates whether the transition state is electron-demanding or electron-releasing relative to the ground state. The sign of b_J indicates whether an increasing steric requirement of the ligand impedes or accelerates the reaction. The *magnitudes* of a_J and b_J provide information on the degrees to which the electronic and steric effects operate, as compared with related reactions.

Marked departures from an otherwise reasonably good correlation by a particular ligand or group of ligands may provide additional insights into the nature of the reaction. However, the number and variety of data reported in any given reactivity series often do not justify analysis of the data in terms of more than the three disposable parameters of eq 3. Further, the accuracy with which the primary electronic and steric parameters can be specified may not be high enough to justify the addition of still more parameters. This is not to suggest that the interpretations of kinetics or equilibrium data in terms of special considerations are invalid, when the number and quality of data support them. However, such approaches, while interesting and useful, are less

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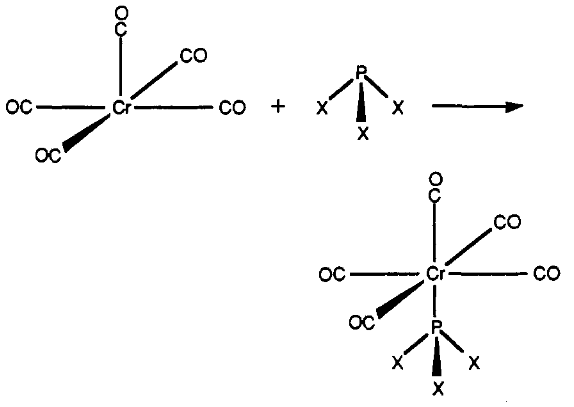
general than applications of eq 3 to data for a limited number of well-chosen ligands.

Steric Effects in Molecular Mechanics

In molecular mechanics, steric effects are exerted through the van der Waals interactions between all atoms separated by at least two other atoms in the connectivity diagram for the molecule. The van der Waals attractive and repulsive terms give rise to the forces that distort the molecule from the equilibrium values of bond distance and angle. The molecular mechanics energy is the net of all the potential energy terms relative to the idealized system, with all bonds and angles at their strain-free equilibrium values, which is taken to be at zero energy. The goal is to extract from the components of the molecular mechanics energy a quantity that represents the steric effect of a substituent or ligand.

Consider the reaction of a ligand L with a prototypical organometallic reaction center, which we will choose to be $Cr(CO)_5$:



(4)

The molecular mechanics energy change in this process is obtained as described in the previous papers in this series,[1,2] by computing the energy-minimized structures for $Cr(CO)_5$, the ligand L, and the complex $Cr(CO)_5L$. Then

$$\Delta E = E_{\mathrm{CrP}} - E_{\mathrm{P}} - E_{\mathrm{Cr}} \qquad (5)$$

In the process we obtain the energy difference for each component of the total energy change: bond stretch, bond bend, bond torsion, and van der Waals. At first sight it might seem that the total energy change, ΔE_T, would be an appropriate measure of the ligand steric requirement. The difficulty, however, is that the van der Waals term contains both attractive and repulsive terms. To achieve a clean separation of steric and electronic properties, the steric term should be a measure solely of repulsive interactions. The attractive component of the van der Waals term arises from the London dispersion energies between nonbonded atoms.[33,34] In complexes of L with a metal center, the dispersion energies between the atoms of L and the metal-containing fragment affect the electronic energy levels,[35] and thus affect the values of observables such as the CO stretching frequencies or ^{13}CO chemical shifts, employed as measures of the electronic influence of L. For example, the totally symmetric CO stretching mode in matrix-isolated $Cr(CO)_5Xe$ occurs at 2088.6 cm^{-1}, as compared with the corresponding value of 2092.4 cm^{-1} in $Cr(CO)_5Ar$.[36] Although there may be small differences in the geometries of the two complexes, occasioned by the different sizes of Ar and Xe, the frequency shift is primarily a reflection of an apparent change in CO stretching force constant, which in turn can be ascribed to a difference in dispersion energy interactions of the rare gas atoms with $Cr(CO)_5$.

The steric and electronic components of the energy change are thus intermingled in molecular mechanics, and the total energy change is not a valid measure of the ligand steric effect. Figure 1 shows the correlation of ΔE_T for complex formation, eq 5, with the Tolman cone angle, for a large number of phosphorus and several arsenic ligands or widely varying character (vide infra). Clearly, the correlation is very poor.

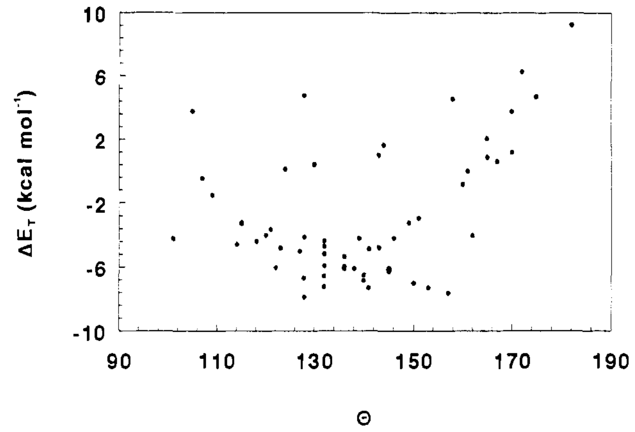


Figure 1. Total molecular mechanics energy change, ΔE_T, upon formation of $Cr(CO)_5L$ complexes vs cone angle values for L.

The Ligand Repulsive Energy, E_R

An effective computational measure of ligand steric requirement must take into account that steric forces are short-range and repulsive. Secondly, it must permit evaluation of the steric effect of each ligand in an appropriate conformation; that is, one that is more or less typical of the ligand bound to a metal center.

The molecular mechanics calculation of the energy-minimized structure for binding of L to $Cr(CO)_5$ provides a model for the conformation of the bound ligand. While the energy change computed for reaction 4 is not in itself an appropriate measure of the steric requirement of L, the calculation contains elements from which an appropriate measure can be extracted.

The approach taken in this contribution is to regard $Cr(CO)_5L$ as a prototypical metal–ligand complex and look to the computed structure for elements that will serve as a measure of pure steric effect, as opposed to examining the ligand alone. Given the predominantly nonbonded repulsive nature of the steric term, the focus should be, not on the total van der Waals interaction between ligand and metal, but only on the repulsive part of that interaction, for the lowest energy structure for the complex. The force acting between the ligand and the metal center, arising solely from the van der Waals repulsive forces between the two groups of atoms and acting along the Cr–P bond axis, is intuitively appealing as a measure of the steric interaction.

Using the facilities available in BIOGRAF, it is possible to change the form of the assumed potential function representing the van der Waals term in the total potential. Our procedure is as follows:

(1) Obtain the energy-minimized structure for $Cr(CO)_5L$ using MMP2, as described.[1,2]

(2) Next, replace the exponential-6 form of the van der Waals potential employed in the energy minimization by a purely repulsive form (eq 6). Here D_0 represents the potential well depth

$$E_{\mathrm{vdW}} = \sum D_0 \exp[\gamma[(r_0 - r)/r_0]] \qquad (6)$$

in the full exponential-6 expression, γ is typically 12.5, r is the interaction distance, and r_0 is the sum of the two scaled van der Waals radii for the interacting atoms. (In this process, change the van der Waals diameter for C(sp^2) from 3.88 to 4.08 Å, an empirical modification.[37]) In keeping with the standard procedure,

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[37] The empirical correction to r_0 for C(sp^2) was implemented because it became evident that the calculations were leading to E_R values for arylphosphines that were systematically too small (see Methods section). It should be pointed out that the empirical correction to r_0 for C(sp^2) was not set to provide a good fit with θ values; rather, it was chosen to improve the correlations with kinetics data.

the sum is over all atoms separated by two or more bonds in the bonding diagram for the molecule.

(3) With all bond distances, angles, and torsions within the molecule except the Cr–P bond distance fixed at the values for the energy-minimized structure, compute the van der Waals repulsive energy as a function of the Cr–P bond distance, in the vicinity of r_e, the value found for the energy-minimized structure. Since all internal coordinates are frozen, the only van der Waals energy terms that vary are the purely repulsive ones between ligand atoms and those in $Cr(CO)_5$. The ligand–$Cr(CO)_5$ repulsive force is the gradient of the computed van der Waals repulsive energy with respect to the Cr–P distance at the equilibrium Cr–P distance, r_e. In practice, the computed energy varies nearly linearly with respect to the Cr–P distance over about 0.08 Å on each side of the r_e. The computed gradient is then multiplied by r_e to yield the *ligand repulsive energy*, E_R (eq 7). Because of the steep

$$E_R = r_e[\partial E_{vdW}(\text{repulsive})/\partial r(\text{Cr–P})] \tag{7}$$

distance dependence of the repulsive function in eq 6, only atom pairs separated by very short distances contribute to the energy. Of those, only the atom pairs whose interatomic distances change significantly with variation in Cr–P distance make major contributions to the repulsive energy gradient. Thus, E_R has the character of an integration over the important repulsive interactions between ligand and $Cr(CO)_5$, at the interface between the two entities. Because the repulsive energy is calculated only for atoms separated by at least two bonds, the P–Cr and P–carbonyl carbon repulsive interactions and the repulsive interaction between Cr and the other three atoms bound to the phosphorus are not included in the summation for phosphorus ligands. Analogous terms would also be absent in calculations for other ligand types. Inclusion of these terms in a measure of the steric properties of the ligand would be inappropriate for the same reasons that it is inappropriate to include them in the usual calculation of the total molecular mechanics energy; the interactions between bound atoms or atoms separated by one other atom are expressed in the stretching and bending force constants, respectively. In any event, the significant *variations* among ligands would not arise in these terms; rather, they arise in the interactions involving atoms further removed from phosphorus.

Scaling of the repulsive force by multiplying by r_e is based in part on the following considerations: Imagine two ligands that possess quite different steric requirements, or different assumed strain-free Cr–L distances, such that the r_e values differ significantly, yet which give rise to the same value of ∂E_{vdW}(repulsive)/r(Cr–P). The ligand which gives rise to this gradient at the larger distance is presumably larger, particularly if the two ligands have the same value for the strain-free equilibrium metal–ligand distance. Scaling by r_e expresses this inequality.

The quantity E_R can be interpreted as the energy required to move the ligand a distance r_e against a *constant* force equal to the repulsive force it experiences at the equilibrium distance, r_e. Alternatively, it may be thought of as the repulsive force experienced by the ligand in the energy-minimized structure, scaled by its equilibrium distance from the metal center.

Results and Discussion

Table I lists values of the Tolman cone angle, Bodner's electronic parameter values based on ^{13}CO chemical shifts (δ), total energy change ΔE_T upon binding to $Cr(CO)_5$, and E_R values in the $Cr(CO)_5L$ complex, for an extensive series of ligands. The ligands listed include 8 phosphites and 19 trialkylphosphines for which molecular mechanics calculations have been reported,[1,2] CO, triphenylphosphine, and several meta- or para-substituted derivatives, diphenylalkyl, phenyldialkyl, and mixed alkyl/phenyl/alkoxy ligands, and 8 arsenic ligands, for a total of 69. The θ values listed are Tolman's values,[4] or were obtained for unsymmetrical ligands by using an arithmetic average of the half-angles for each group. A similar averaging rule was employed to estimate the δ values for ligands for which experimental values were not reported.

Table I. Steric and Electronic Parameters of Phosphorus and Arsenic Ligands

ligand	δ[a]	θ[b]	E_R[c]	ΔE_T[c]
CO	0	95	7	
PMe$_3$	5.05	118	39	−4.39
PEt$_3$	5.54	132	61	−4.71
P(*n*-Bu)$_3$	5.69	132	64	−5.93
P(*i*-Bu)$_3$	5.40	143	83	1.00
P(*i*-Pr)$_3$	6.20	160	109	−0.83
PCy$_3$[d]	6.32	170	116	1.19
P(*t*-Bu)$_3$	6.37	182	154	9.24
PMe$_2$Et	5.21	123	48	−4.82
PMe$_2$(*i*-Pr)	5.43	132	57	−4.37
PMe$_2$(*t*-Bu)	5.48	139	66	−4.21
PEt$_2$Me	5.36	127	57	−5.02
PEt$_2$(*i*-Pr)	5.77	141	75	−4.87
PEt$_2$(*t*-Bu)	5.82	149	90	−3.24
P(*i*-Pr)$_2$Me	5.82	146	78	−4.20
P(*i*-Pr)$_2$Et	5.99	151	91	−2.96
P(*i*-Pr)$_2$(*t*-Bu)	6.26	167	123	0.60
P(*t*-Bu)$_2$Me	5.92	161	113	0.00
P(*t*-Bu)$_2$Et	6.09	165	125	0.87
P(*t*-Bu)$_2$(*i*-Pr)	6.31	175	127	4.67
PCy$_2$H	5.35	143	66	−4.80
PCyH$_2$	4.07	115	32	−3.22
PPh$_3$	4.30	145	75	−6.08
P(*p*-ClPh)$_3$	3.54	145	74	
P(*m*-CH$_3$Ph)$_3$	4.48	145	79	−6.16
P(*m*-ClPh)$_3$	3.40	145	78	
P(*p*-MePh)$_3$	4.50	145	74	
P(*p*-OCH$_3$Ph)$_3$	4.43	145	76	−6.28
P(*p*-FPh)$_3$	3.77	145	74	−6.21
P(*m*-*t*-BuPh)$_3$	4.60	145	83	
P(*o*-CH$_3$Ph)$_3$	3.67	194	113	
PPh$_2$H	3.93	128	38	−4.14
PPh$_2$Me	4.53	136	57	−6.10
PPh$_2$Et	4.78	140	66	−6.52
PPh$_2$Bu	4.74	140	66	−6.85
PPh$_2$(*i*-Bu)	4.76	144	71	
PPh$_2$(*i*-Pr)	4.78	150	75	−7.02
PPh$_2$Cy	5.07	153	77	−7.31
PPh$_2$Bz[e]	4.20	152	74	
PPh$_2$(*t*-Bu)	4.80	157	97	−7.64
PPh$_2$Cl	2.49	138	48	−6.10
PPhMe$_2$	4.76	122	44	−6.04
PPhEt$_2$	5.36	136	57	−5.35
PPhBu$_2$	5.29	136	77	−5.98
PPhCy$_2$	5.80	162	105	−4.02
PPh(*t*-Bu)$_2$	5.35	170	124	3.74
PBz$_3$[e]	3.98	165	82	2.04
P(OCH$_2$)$_3$CCH$_3$	2.60	101	25	−4.22
P(OMe)$_3$	3.18	107	52	−0.44
P(OEt)$_3$	3.61	109	59	−1.51
P(O-*n*-Bu)$_3$	3.95	110	64	
P(O-*i*-Pr)$_3$	3.90	130	74	0.43
P(O-*i*-Pr)$_2$(O-*t*-Bu)	3.90	144	78	1.64
P(O-*i*-Pr)(O-*t*-Bu)$_2$	3.90	158	90	4.53
P(O-*t*-Bu)$_3$	3.90	172	99	6.24
P(OPh)$_3$	1.69	128	65	4.75
PPh$_2$(OMe)	3.96	132	62	−5.19
PPh$_2$(OEt)	4.27	132	62	−7.24
PMe$_2$(OPh)	3.90	121	57	−3.66
PPh(OMe)$_2$	3.48	120	69	−4.02
PEt(OMe)$_2$	4.36	115	69	−3.29
AsMe$_3$	4.46	114	27	−4.58
AsEt$_3$	5.33	128	40	−6.70
As(*n*-Bu)$_3$	5.26	128	44	−7.88
AsPh$_3$	4.16	141	44	−7.31
AsPhMe$_2$	4.80	123	30	
AsPhEt$_2$	4.89	132	36	−6.57
As(OEt)$_3$	3.22	105	40	3.78
As(OPh)$_3$	1.55	124	42	0.13

[a] ^{13}C chemical shift in $LNi(CO)_3$ complexes, downfield in ppm,[18] from $Ni(CO)_4$. [b] Tolman cone angle, degrees.[4] [c] kcal mol^{-1}. [d] Cy = cyclohexyl, C_6H_{11}. [e] Bz = benzyl, CH_2Ph.

Figure 1 shows a plot of ΔE_T vs θ. Clearly, these two quantities are not well-correlated, for reasons discussed above. On the other

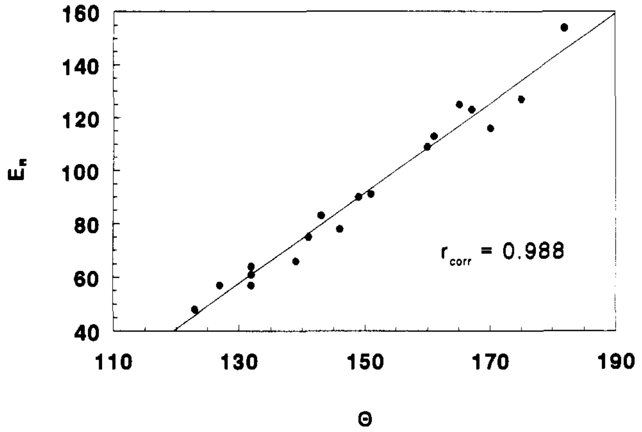

Figure 2. Ligand repulsive energy, E_R, vs cone angle, θ, for trialkylphosphines.

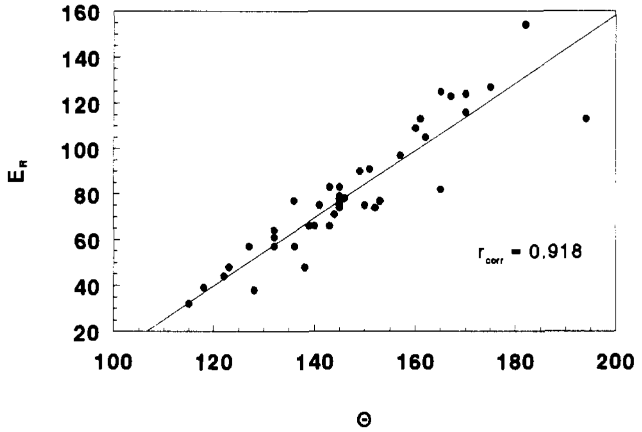

Figure 3. Ligand repulsive energy, E_R, vs cone angle, θ, for all alkyl-, aryl-, or mixed alkyl/arylphosphines.

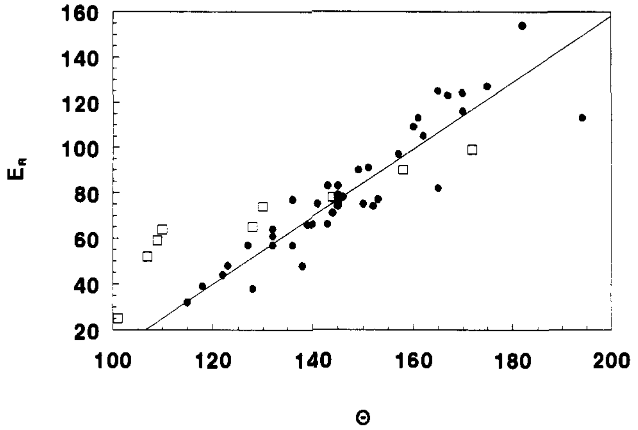

Figure 4. Ligand repulsive energy, E_R, vs cone angle, θ, for alkyl- and arylphosphines (●) and for trialkyl phosphites (□).

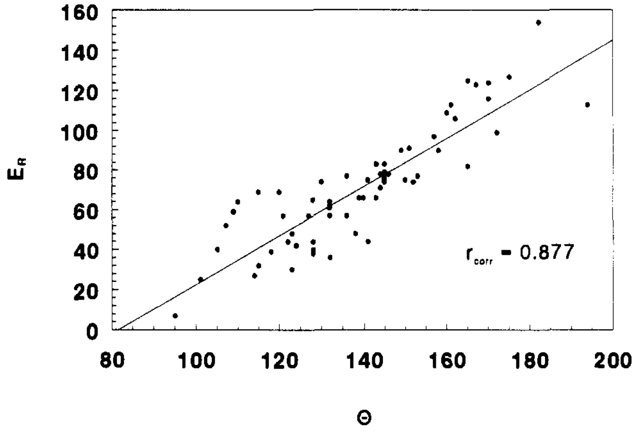

Figure 5. Ligand repulsive energy, E_R, vs cone angle, θ, for all ligands (Table I).

hand, E_R values correlate rather well with cone angle. The plot of E_R vs θ for the trialkylphosphines is shown in Figure 2. The correlation coefficient is remarkably high, 0.985; there are no substantial departures. The close correlation between E_R and θ is remarkable in part because the conformations of several of the ligands in this series are different in the two computations. For example, $P(n\text{-}Bu)_3$ is assumed in calculating θ to be in a conformation that minimizes the measured cone angle. By contrast, in the computation of E_R for this ligand, the conformation that prevails in the energy-minimized structure was employed. As shown in Figure 3 of ref 2, this conformation is greatly different from that used in calculating θ. Even the $P(i\text{-}Bu)_3$ ligand, which gives rise to an anomalous ΔE_T value,[2] is well-behaved in the correlation, as is PCy_3, for which the appropriate value of cone angle is not clear[38a,b] (we have employed Tolman's estimate).

The E_R values obtained for $P(t\text{-}Bu)_3$ and $P(t\text{-}Bu)_2(i\text{-}Pr)$ deserve comment, because the molecular mechanics calculations for the $Cr(CO)_5$ complexes of these two ligands led to exceptionally long equilibrium Cr–P distances, in excess of 2.73 Å.[2] These large values indicate that it is not possible to form a normal Cr–P bond of force constant in the range of 1.9 mdyn $Å^{-1}$, because of excessive steric strain between ligand and metal center. The computed values of Cr–P distance in these two cases are in part an artifact of the formulation of the bond stretching potential at large departures from the equilibrium bond distance.[1,2] Nevertheless, while the Cr–P distances are not quantitatively on the same basis as the values for the other ligands, the larger values appropriately reflect the larger steric requirement of the ligand. The E_R values computed for these ligands using the energy-minimized structures seem reasonable in comparison with those for the other trialkylphosphines; the $P(t\text{-}Bu)_3$ value is above the regression line of Figure 2, while that for $P(t\text{-}Bu)_2(i\text{-}Pr)$ is slightly below it.

When PPh_3 and its meta- and para-substituted derivatives and all ligands containing phenyl groups and alkyl groups are added to the trialkylphosphines, a total of 46 ligands, the correlation remains remarkably good except for a few ligands, notably $P(Bz)_3$, $P(t\text{-}Bu)_3$, and $P(o\text{-}CH_3Ph)_3$ (Figure 3). Even with these three points the correlation coefficient is 0.918. This correlation is important because it shows that the phenyl group, with the small empirical modification of the van der Waals radius for sp^2 carbon, fits well with the alkyl groups. It should be noted that some of the departures from linearity arise because the cone angles for nonsymmetrical ligands are assumed to be weighted-average values, whereas the E_R values are calculated for each ligand. For PR_2R' ligands, the computed E_R values are often lower than would be predicted from a weighted average of the values for PR_3 and PR'_3 ligands, because the ligand can accommodate in binding to the metal by tilting with respect to the Cr–P bond.[2]

Figure 4 shows the data for $P(OR)_3$ compounds, superimposed on the correlation for the alkyl- and arylphosphine ligands. Here, substantial differences between E_R and θ as measures of steric requirement are seen. The phosphites of lower θ have comparatively high E_R values, because the lone pairs are more prominently weighted in the molecular mechanics calculation than in the CPK models of these ligands.[38c] On the other hand, for phosphites of larger θ, the E_R values are lower, because in the molecular mechanics model the phosphites are comparatively flexible ligands, more capable than the trialkylphosphines of distortions that relieve strong repulsive forces.[2]

Figure 5 shows the plot of E_R vs θ for the entire set of ligands, including 8 arsenic ligands. The overall correlation is fair; the correlation coefficient is 0.857. It is remarkable that the E_R values, derived from an entirely computational model of the metal–ligand

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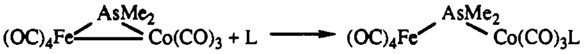
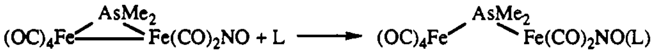
Table II. Correlation Coefficients r from Application of Eq 3 to Associative Substitution Reactions

reaction	ref	n^a	$r(E_R)$	$r(\theta)$
$CpRh(CO)_2 + L \longrightarrow CpRh(CO)L + CO$	40	7	0.975	0.786
$Cp^*Co(CO)_2 + L \longrightarrow Cp^*Co(CO)L + CO$	41	8	0.957	0.842
$CpZr(CO)_2 + L \longrightarrow CpZr(CO)L + CO$	42	6	0.908	0.737
$CoNO(CO)_3 + L \longrightarrow CoNO(CO)_2L + CO$	15d	13	0.730	0.766
$(\eta^5\text{-}C_9H_7)Mn(CO)_3 + L \longrightarrow (\eta^5\text{-}C_9H_7)Mn(CO)_2L + CO$	43	7	0.843	0.871
$V(CO)_6 + L \longrightarrow V(CO)_5L + CO$	44	8	0.653	0.875
$Fe(NO)_2(CO)_2 + L \longrightarrow Fe(NO)_2(CO)L + CO$	45	9	0.953	0.978
$CpMn(CO)_2NCMe^+ + L \longrightarrow CpMn(CO)_2L^+ + MeCN$	22	6	0.998	0.998
$MeCpMn(CO)_2N^+ + L \longrightarrow MeCpMn(CO)_2L^+ + N$	21	10	0.869	0.952
$Co_2(\mu\text{-}C_2Ph_2)(CO)_6 + L \longrightarrow Co_2(\mu\text{-}C_2Ph_2)(CO)_5L + CO$	46	7	0.843	0.899
 $(OC)_4Fe(\mu\text{-}AsMe_2)Co(CO)_3 + L \longrightarrow (OC)_4Fe(\mu\text{-}AsMe_2)Co(CO)_3L$	47	8	0.990	0.970
$Fe_2(CO)_6(SR)_2 + L \longrightarrow Fe_2(CO)_5L(SR)_2 + CO$	48	7	0.977	0.846
 $(OC)_4Fe(\mu\text{-}AsMe_2)Fe(CO)_2NO + L \longrightarrow (OC)_4Fe(\mu\text{-}AsMe_2)Fe(CO)_2NO(L)$	49	9	0.800	0.949
$Ir_4(CO)_{12} + L \longrightarrow Ir_4(CO)_{11}L + CO$	50	6	0.851	0.978
$Re_7C(CO)_{21}Rh(CO)_2{}^{2+} + L \longrightarrow Re_7C(CO)_{21}Rh(CO)L^{2+} + CO$	51	13	0.979	0.861
$(\eta^5\text{-}C_6H_7)Fe(CO)_3{}^+ + L \longrightarrow (\eta^4\text{-}C_6H_7L)Fe(CO)_3{}^+$	52	7	0.801	0.565
$(\eta^5\text{-}CH_3C_5H_4)Mn(CO)(L)(H)(SiHPh_2) + PBu_3 \longrightarrow H_2SiPh_2 + (\eta^5\text{-}CH_3C_5H_4)Mn(CO)(L)PBu_3$	53	6	0.980	0.973
$[Ru(OH_2)(bpy)_2L]^{2+} + MeCN \longrightarrow [Ru(NCMe)(bpy)_2L]^{2+} + H_2O$	54	11	0.844	0.859
$Mo(CO)_2(CH_2Cl_2)L_2Br_2 + CO \longrightarrow Mo(CO)_3L_2Br_2 + CH_2Cl_2$	25	8	0.935	0.830
$Rh_4(CO)_9[P(OCH_2)_3CEt]_3 + L \longrightarrow Ru_4(CO)_8[P(OCH_2)_3CEt]_3L + CO$	55	8	0.788	0.916

[a] This differs from the number in the experimental set if either the steric or the electronic parameter is missing for a ligand, and cannot be reasonably estimated, or if there are substantial reasons to exclude a datum, such as reported experimental difficulties or very marked departure from the regression line in correlations with both θ and E_R.

interaction and based on the repulsive force acting between ligand and metal complex, should correlate as well as they do with the cone angles, derived from measurements of the geometrical properties of space-filling models of the ligands alone. The ligand "surface" in the space-filling mechanical models is representative of the points in space at which a repulsive interaction with other nonbonded atoms becomes important. The cone angle is a rough measure of the extent of this repulsive surface from the vantage point of a metal center. The computed quantity, E_R, is a more direct computational assessment of the repulsive interaction of the ligand with a representative organometal complex.

The significant departures within the generally good overall correlation arise from a variety of effects. The arsenic ligands provide an additional example of a systematic difference between E_R and θ values; the E_R values are lower than Tolman's θ values would predict. The θ values for these ligands are systematically lower than for the corresponding phosphines because the metal–As distance is longer.[4] In the molecular mechanics model, the low E_R values similarly arise because the distances between atoms of the ligand and those of the $Cr(CO)_5$ are generally longer as a result of the longer Cr–As bond. Because the repulsive forces have such a steep dependence on distance, however, the systematic lowering in E_R value as compared with the case of the corresponding phosphorus ligands is quite large.

Steric Thresholds

It is noteworthy that the correlation between E_R and θ (Figure 5) has a nonzero intercept; E_R approaches zero at $\theta \approx 82°$. This value may be termed the *absolute steric threshold.* It is of purely steric origin, in that it corresponds to the onset of a significant repulsive ligand–metal center interaction. The value of this threshold is much smaller than any value postulated to account for departures from expected linear free energy relationships involving phosphorus ligands.[23a,26,31,32] The value of the absolute steric threshold should be dependent on the characteristics of the metal center. Presumably, for a more crowded center, the value should be lower.

The absolute steric threshold should be distinguished from an apparent steric threshold, which is reflected in the variation in total energy change, ΔE_T, for the $Cr(CO)_5$–ligand interaction as a function of ligand size. The apparent steric threshold is seen, for example, in the variations in ΔE_T vs θ for the trialkylphosphine complexes of $Cr(CO)_5$ (Figure 4 of ref 2). In this case, ΔE_T is virtually independent of θ up to a ligand cone angle of about 145° and then increases monotonically with θ. The variation in ΔE_T with ligand size results from a counterbalancing of repulsive energies by a corresponding dispersion energy term, up to a certain range of ligand size. Beyond this point, as the ligand grows larger, the repulsive energies, and the corresponding reflections of these in bond stretching, bending, and torsional modes, increasingly dominate.

The absolute steric threshold is roughly the computational equivalent of the steric thresholds claimed from analyses of kinetics data. Clearly, the cone angle value at which it occurs will depend on the metal center and the choices of parameters employed in a linear free energy analysis. In addition, however, the effect may also depend on the type of ligand. Phosphites may not exhibit the effect as readily as phosphines, because of their generally

Table III. Correlation Coefficients *r* from Application of Eq 3 to Various Reactions, Product Distributions and Properties

	ref	n^a	$r(E_R)$	$r(\theta)$
Reaction				
$2Co(dh)_2L + PhCH_2Br \longrightarrow BrCo(dh)_2L + PhCH_2Co(dh)_2L$	56	10	0.983	0.912
$Re(CO)_4L\cdot + BuSSR \longrightarrow Re(CO)_4(L)SBu + SBu\cdot$	27	8	0.958	0.943
$Re(CO)_4L\cdot + CH_2Br_2 \longrightarrow Re(CO)_4(L)Br + CH_2Br\cdot$	24	8	0.924	0.924
$Re(CO)_4L\cdot + CCl_4 \longrightarrow Re(CO)_4(L)Cl + CCl_3\cdot$	24	8	0.839	0.765
$2Mn(CO)_4L\cdot \longrightarrow Mn_2(CO)_8L_2$	57	6	0.946	0.983
$(\mu\text{-}H)Ru_3(\mu\text{-}CNMe_2)(CO)_9L \longrightarrow$ isomerism	58	9	0.843	0.477
$CpMo(CO)_2LCOMe \longrightarrow CpMo(CO)_2LMe + CO$	59	9	0.855	0.948
$(diars)Fe(CO)_2LMe^+ + P(OMe)_3 \longrightarrow (diars)Fe(CO)COMe(L)P(OMe)_3$	60	7	0.863	0.969
$Ru(CO)_4L + L' \longrightarrow Ru(CO)_3LL' + CO$ (Dissociative)	61	16	0.912	0.814
$Ru(CO)_3(L)(SiCl_3)_2 + L' \longrightarrow Ru(CO)_2(L')(L)(SiCl_3)_2 + CO$ (Dissociative)	62	17	0.802	0.962
trans-$W(CO)_4(PPhMe_2)L \rightleftharpoons$ *cis*-$W(CO)_4(PPhMe_2)L$ (K_{eq})	63	11	0.907	0.925
Properties				
^{199}Hg Chemical Shift in $[(\eta^5\text{-}C_5H_5)(CO)_2(L)Mo]_2Hg$	64	9	0.856	0.894
Ln(% 2-*trans* product) in $(\eta^3\text{-}C_5H_9)Ni(CH_3)(L) + CO$ reaction	19b	15	0.852	0.839
ΔH for reaction $[(\eta^3\text{-}C_5H_9)Ni(\mu\text{-}CH_3)]_2 + 2L \longrightarrow 2(\eta^3\text{-}C_5H_9)Ni(CH_3)(L)$	19a[b]	14	0.858	0.905
Symmetric Deformation Coordinate in PR_3 complexes of any element	65	12	0.950	0.929

[a] This differs from the number in the experimental set if either the steric or the electronic parameter is missing for a ligand, and cannot be reasonably estimated, or if there are substantial reasons to exclude a datum, such as reported experimental difficulties or very marked departure from the regression line in correlations with both θ and E_R. [b] Omit PPh_3 datum.

greater flexibility in accommodating to variations in repulsive energies.

Correlations of Kinetics and Equilibrium Data

Free energy relationships such as eq 3 represent an important application of ligand steric and electronic parameters. Accordingly, a body of published kinetics, equilibrium, and properties data has been subjected to multivariate analysis. The steric effect of the ligand is represented by either θ or E_R; the electronic parameter is represented by δ.[39] (Correlations with ΔE_T as a measure of ligand steric effect yielded generally very poor results, as might be expected from the correlation with cone angle shown in Figure 1.)

Tables II and III list the chemical systems for which the analysis was carried out. For each correlation are listed the number of ligands in the correlation and the correlation coefficients. The only criterion applied in choosing the data sets was that there be at least 6 ligands in the set. The substitution reactions are mainly associative in character, although in some cases the reaction might be characterized as associative interchange (I_a). In the reactions of Table II, L is an entering ligand in all but the last three cases. The reactions listed in Table III include several atom-transfer processes and examples of decarbonylation, insertion, isomerization, and CO dissociation.

Perusal of the tables shows that in some cases E_R affords the better correlation, while θ is better in others. Any of several factors may operate in a given reaction series to cause substantial departures from the predicted linear relationship. Individual ligands exert different effective steric demands from one reaction to the next, as a result of the steric and electronic characteristics of the transition state. When bound to a metal center undergoing reaction (that is, when acting as a spectator ligand), a given ligand might be expected to exert a comparatively different influence

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(39) The Bodner chemical shift parameter correlates very well with the χ parameter. A linear correlation of the values for 38 ligands, using values for χ reported by Bartik et al.[17] and a few interpolated values, yielded a correlation coefficient of 0.95; the few ligands that depart significantly from the linear correlation are comparatively uncommon ones.

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than when it is an attacking reagent in an associative displacement process. Beyond this, the kinetics data are often attended by substantial experimental uncertainties. Finally, δ is not an entirely satisfactory measure of ligand electronic character.

For these reasons, the superficial level of analysis represented by the comparative correlation coefficients does not provide a rigorous basis for evaluating the relative effectiveness of θ and E_R as measures of ligand steric requirement. It is clear, however, that E_R is at least as effective as θ in linear free energy correlations. More detailed study of the regression analyses for the data sets of Tables II and III, as well as of additional kinetics, equilibrium, and properties data, may reveal systematic trends that yield additional insights.

Limitations and Advantages of E_R Values

(A) The E_R values have several limitations:

(1) As calculated, they apply to interaction of the ligands with a single metal center, $Cr(CO)_5$. With a different metal center, of a more asymmetric character, the relative ordering of the ligands might be altered. Answering this question will require additional computational work, employing a significantly different metal center, such as $(\eta^5\text{-}C_5H_5)RhCO$. However, it is our expectation that the variations will be minor.

(2) The results may be influenced by some of the many choices of force field parameters that must be specified to carry out the molecular mechanics calculations. We doubt that this will prove to be a source of difficulty. In the course of the work, several parameters were varied to determine the effects on final structure, with little or no variation in the final results. For example, the most appropriate van der Waals distance parameter for Cr is not known. The quantity was varied by as much as 30%, with little effect on relative ΔE_T or E_R values. Further, it should be noted that the energy-minimized structure is the starting point for the calculation of the repulsive force between ligand and metal complex. The calculated values for E_R are relatively insensitive to variations in the force field that produce only minor alterations in the final structure.

(3) The computed results apply to gas-phase conditions; conceivably, solvent effects could play a role. However, the E_R calculation for a given energy-minimized structure should be virtually independent of solvent. Thus, the solvent can influence the relative E_R values only by altering the energy-minimized structure. For example, the relative energies of various ligand conformations in the ligand–metal complex could differ in a polar solvent from those in a nonpolar solvent. The solvent would not be expected to exert a major effect on the relative energies of ligand conformations, with the possible exception of the phosphites.

(4) The computed values of E_R might be quite different for structures that have different ligand conformations but which are close in energy. In these circumstances the determination of which structure to choose for the calculation of E_R is critical. Slight variations in the force field parameters could change the relative ordering of energies of structures that could give rise to significantly different values of E_R. This situation did not arise in the present work. Most commonly, a single structure having a lowest energy conformation can be identified or a choice can be made between energetically equivalent structures on the basis of bond distance or angle values.

(B) The computed quantity, E_R, offers several advantages over the cone angle as a measure of ligand steric requirement:

(1) In contrast to the cone angle, E_R values are computed for each ligand in a conformation appropriate to its binding to a metal center, on the basis of the molecular mechanics energy minimization. This conformation often differs substantially from the folded-back conformation chosen in calculating θ values and may also differ significantly from that for the free ligand. Secondly, for phosphites and related ligands, the oxygen lone pairs are explicitly accounted for. This is not true for the CPK models on which θ values are based.

(2) E_R values can be computed with equal ease for ligands that are symmetrical, e.g., PMe_3, or unsymmetrical, e.g., $P(t\text{-}Bu)_2Me$. By contrast, the cone angles for such ligands are defined in terms of an arithmetic averaging procedure or by a more elaborate averaging of the half-cone angle over the entire ligand.[38b,66]

(3) The E_R concept is, in principle, capable of extension to ligands of nearly any kind, including nitrogen, oxygen, or sulfur donor ligands or even organic ligands such as alkyl groups, alkenes, or alkynes. To carry out such computations, it will be necessary to establish appropriate force field parameters, so that the correct minimum-energy structure is obtained. However, because E_R is based on the van der Waals repulsive force acting between the ligand and metal center, it is likely to be comparatively insensitive to the details of the force field; it is only necessary that a configuration reasonably close to the minimum-energy configuration be found.

(4) Values of E_R could also be computed for interactions of ligands with a metal center other than $Cr(CO)_5$. It is anticipated that the $Cr(CO)_5$-based values will prove to be generally representative of a broad range of reaction situations. However, the method could be tailored to deal with a specific reaction center.

Summary and Conclusions

A new measure of ligand steric requirement, the ligand repulsive energy, E_R, has been defined and computed for a set of 69 ligands of widely varying steric and electronic requirements. The new parameter is entirely computational in character and follows from application of the MMP2 molecular mechanics algorithms to interaction of ligands with a prototypical metal center, $Cr(CO)_5$. The procedure for computing E_R is based straightforwardly on extensions of molecular mechanics calculations. The level of correlation of the derived E_R values with the traditional Tolman cone angles is remarkably good, particularly for trialkylphosphines and mixed alkyl/phenylphosphines. However, distinct differences between E_R and θ values are seen, so that correlations with experimental kinetics and equilibrium data in many cases afford disparate correlation coefficients.

The fact that an alternative set of parameters representing ligand steric requirements can yield empirical correlations different from but as good overall as those obtained using θ suggests further that one should proceed with considerable caution in ascribing departures from linear free energy relationships such as eq 3 to special factors such as steric thresholds or ligand π-acid or -base character. The effective *accuracy* with which a steric parameter can be specified is far lower than the precision with which it can be measured by Tolman's procedure or computed by the procedure outlined here. Each ligand has not one, but a range, of steric requirements, depending on the nature of the reaction, solvent, and so on. For ligands that are rather stiff and have a single lowest energy conformation that is significantly lower in energy than others, the range of steric parameters is small. For other ligands it may be quite large.

The use of a simple expression such as eq 3 has the virtue that it assumes the minimum amount of information about the reaction and yields the most important information a LFER is likely to provide, the signs and magnitudes of the coefficients.

Methods

All molecular mechanics calculations were carried out using BIOGRAF, a comprehensive package of molecular modeling tools developed by Molecular Simulations, Inc., Sunnyvale CA. The force field model employed is MMP2; modifications and additions to the parameter set used have been described[1,2] or are listed in Table IV. In Table IV, where the symbol P or As appears without further label, the value for the parameter involved applies to only the free or coordinated ligand, or is the same for free and coordinated ligand. Where a difference in the parameter between free and coordinated ligands has been assumed, the free and coordinated ligands are designated by the suffixes _3 and _4, respectively.

The parameter values involving arsenic were estimated by analogy with those assumed for P. The van der Waals diameter for As is assumed to be 4.70 Å, and the van der Waals bonding energy (that is, the energy

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(66) (a) Alyea, E. C.; Dias, S. A.; Ferguson, G.; Restivo, R. J. *Inorg. Chem.* **1977**, *16*, 2329. (b) Alyea, E. C.; Dias, S. A.; Ferguson, G.; Parvez, M. *Inorg. Chim. Acta* **1979**, *37*, 45.

Table IV. Force Field Parameters

Bond Distances and Force Constants

bond	bond dist, Å	force const, mdyn/Å	bond	bond dist, Å	force const, mdyn/Å
P-H	1.44	2.95	As-C(sp^3)	1.98	2.60
P-Cl	2.05	1.90	As-C(sp^2)	1.95	2.60
C(sp^2)-Cl	1.75	3.47	As-Cr	2.47	1.46
C(sp^2)-F	1.38	5.38	As-O	1.82	2.64

Bond Angles and Bending Force Constants

bond angle type	bond angle, deg	k_b, mdyn Å/rad^2
P-C(sp^3)-C(sp^2)	109	0.45[a]
As-C(sp^3)-C(sp^2)	109	0.45[a]
C(sp^2)-P-Cl	98	0.49
C(sp^2)-P-H	98	0.49
C(sp^2)-P-C(sp^2)	98	0.48
C(sp^2)-P-C(sp^3)	98	0.48
C(sp^3)-As_4-C(sp^3)	100	0.45
C(sp^3)-As_4-C(sp^2)	99	0.45
C(sp^2)-As_4-C(sp^2)	98	0.45
C(sp^3)-As_3-C(sp^3)	95	0.45
C(sp^3)-As_3-C(sp^2)	92	0.45
C(sp^2)-As_3-C(sp^2)	92	0.45
O-As-C(sp^2)	98	0.42
O-As_4-O	100	0.42
O-As_3-O	98	0.42
H-P-H	95	0.48
Cl-C(sp^2)-C(sp^2)	120	0.62[a]
F-C(sp^2)-C(sp^2)	120	0.66[a]
Cr-P-C(sp^2)	112	0.21
Cr-P-H	112	0.21
Cr-As-C(sp^3)	112	0.17
Cr-As-C(sp^2)	114	0.17
Cr-As-O	116	0.28
As-O-C(sp^3)	116	0.69
As-O-C(sp^2)	116	0.69

[a] Stretch-bend interaction force constant = 0.12 mdyn/rad.

minimum characteristic of a nonbonding As-As interaction) is assumed to be 0.275 kcal mol^{-1}.

Torsional barriers involving Cr were assumed as before[1,2] to be zero. The torsional energies associated with As were assumed to be the same as for P. It should be noted that while the parameters associated with As are little more than reasonable guesses, the effects of changes in the assumed values on the final computed energies and energy-minimized structures are small.

In calculations involving arylphosphines, the question arises as to the appropriate Cr-P distance. From the crystal structure data for $Cr(CO)_5PPh_3$,[67] the Cr-P distance is estimated to be 2.40 Å. Use of 2.350 Å as the assumed strain-free Cr-P distance in the molecular mechanics calculation yields a computed equilibrium Cr-P distance of 2.372 Å. Increasing the assumed strain-free Cr-P distance to 2.380 Å results in a computed equilibrium distance of 2.401 Å in the energy-minimized structure, in agreement with the observed structure. The total molecular mechanics energy of the structure corresponding to the larger assumed Cr-P distance is only about 0.19 kcal mol^{-1} lower. Because we have carried out calculations for a large number of ligands involving both alkyl and aryl groups, in the interests of simplicity the strain-free Cr-P distance has been assumed to equal 2.350 Å in all cases.

In calculations of mixed alkyl/alkoxy or aryl/alkoxy ligands, the strain-free Cr-P distance was assumed to be 2.335 Å in $PR_2(OR)$ compounds and 2.315 Å in $PR(OR)_2$ compounds, values intermediate between the 2.298 Å assumed for phosphites and the 2.350 Å assumed for trialkyl- or triarylphosphines. The effects of making such minor interpolative adjustments on either energies or energy-minimized structures are insignificant.

The energy-minimization computations for a series of 8 phosphites[1] and 19 trialkylphosphines[2] and their $Cr(CO)_5$ complexes have been described. The same procedures were employed in obtaining energy-minimized structures for all of the other $Cr(CO)_5$ complexes listed in Table I and for most of the corresponding ligands.

The procedure for calculating E_R begins with the energy-minimized structure. The van der Waals term in the energy expression is changed from the exponential-6 form employed in the energy minimization to the purely repulsive form give in eq 6. The total energy of the $Cr(CO)_5$–ligand complex is then recalculated, keeping all atomic coordinates frozen, and the van der Waals energy noted. The calculation is repeated at a series of Cr-P distances around the equilibrium Cr-P distance, by moving the ligand along the Cr-P bond axis, keeping all internal coordinates constant within the ligand and within $Cr(CO)_5$. From a graph of van der Waals energy vs the Cr-P distance, the slope at r_e yields $\partial E_{vdW}(\text{repulsive})/\partial r(\text{Cr–P})$. This value is multiplied by r_e to yield E_R.

In computing E_R, it became evident that the values for PPh_3 and other phenyl-containing ligands were too small relative to the values for the trialkylphosphines. To correct for this, a single empirical correction has been applied, by increasing the nonbonded van der Waals diameter for C(sp^2) from 3.88 to 4.08 Å. It is not surprising that an empirical adjustment of this kind should be necessary. The van der Waals distance parameter for C(sp^2) was chosen empirically in parametrizing MMP2, to fit criteria such as conformational equilibria and rotational barriers. A different value for the van der Waals term for C(sp^2) is needed to reflect the repulsive interactions between the π electrons of the phenyl rings and the metal carbonyl fragments in computing E_R. It should be emphasized that the larger van der Waals radius is applied only to C(sp^2), and *only for the purposes of calculating E_R, after an energy-minimized structure is obtained using the standard MMP2 parameters.*

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