

# Quantitative Separation of $\sigma$ - and $\pi$ -Components of Transition Metal-Phosphorus Bonding and the Application of Ligand Effects in Organometallic Chemistry

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The  $\sigma$ - and  $\pi$ -components of transition metal-phosphorus bonding and the effects of phosphorus(III) ligands on the kinetics and mechanisms of various organometallic reactions have been studied. On the basis of the correlation of the  $E_{1\sigma'}$  values of  $\eta$ -MeCp(CO)<sub>2</sub>MnL with the  $pK_a$  values of  $R_3PH^+$ , the ligands have been divided into three classes: class I ( $\sigma$ -donor/ $\pi$ -donor)  $R_3P$  (R = Et, Bu, Cy); class II ( $\sigma$ -donor)  $Me_2P$ ,  $R_{3-x}Ph_xP$  ( $x = 1, 2$ ; R = Et, Me), ( $p$ -XPh)<sub>3</sub>P (X = H, Me, OMe); class III ( $\sigma$ -donor/ $\pi$ -acceptor) ( $p$ -ClPh)<sub>3</sub>P, (RO)<sub>3</sub>P (R = Ph, Me, Et, *i*-Pr), Ph<sub>2</sub>(MeO)P. The  $\pi$ -acceptor abilities of the class III ligands are small in comparison to those of the strong  $\pi$ -acids, carbon monoxide, and *tert*-butyl isocyanide. The steric and electronic ligand properties are related to the reaction parameters by the equation:  $\log k$  (or  $\log K$ ) =  $f_1(\theta) + f_2(pK_a) + f_3(E_{\sigma a}) + f_4(E_{\pi b})$ . The contributions of the last two terms, which denote the  $\pi$ -effects, are negligible for most reactions. The  $\sigma$ -electronic and steric ligand effects have been separated quantitatively by a graphical method. The resulting steric and electronic profiles provide new and important insights into the rate-determining and pre-rate-determining steps of fundamental organometallic reactions. The concepts of the steric threshold, steric sensitivity, and intrinsic reactivity are introduced. This analysis has been applied to ligand dissociation reactions, entering ligand dependent substitution reactions, oxidative-addition reactions, and nucleophilic addition to unsaturated hydrocarbon ligands as found in the literature. In many cases these analyses support and quantify the interpretations of the original authors. One important exception is the addition of O<sub>2</sub> to Vaska's compound, which is shown to involve a pre-equilibrium dissociation of an ancillary phosphorus ligand.

## Introduction

Ligand effects are the changes that occur in the kinetics and thermodynamics of reactions when the electronic and steric properties of ligands or incipient ligands are altered. These effects have been used for nearly two decades to probe the mechanisms of organometallic reactions.<sup>1</sup> The insights gained from such studies are important in our understanding and design of stoichiometric and catalytic processes.<sup>2</sup>

Because of the central role played by phosphorus (III) compounds in these studies, in organometallic chemistry, and in catalysis in general, there has been considerable interest in the steric and electronic factors that influence metal-phosphorus bonding.<sup>3,4</sup> The most commonly used measure of the steric requirements are the cone angles ( $\theta$ )<sup>5</sup> of the free ligands. Although several methods of measuring cone angles have been proposed,<sup>6,7</sup> the cone angle as defined by Tolman<sup>8</sup> has been routinely invoked to explain qualitatively, in part, the reactivity patterns of certain organometallic complexes and the nucleophilicities of phosphorus bases (*vide infra*). The electronic properties of the phosphorus ligands are commonly divided into  $\sigma$ -donicity and  $\pi$ -acidity.<sup>3</sup> Tolman's  $\chi_i$  values for Ni(CO)<sub>3</sub>L are a measure of the net electron donor abilities of the ligands and include both  $\sigma$ - and  $\pi$ -effects (*vide infra*).<sup>9</sup> The

Brønsted basicities of the phosphorus(III) compounds ( $pK_a$  values of  $R_3PH^+$ <sup>10,11</sup>) have been used as a measure of the  $\sigma$ -donicities of the ligands. The good linear free energy relationships (LFER), occasionally observed between these  $pK_a$  values and the  $\log k$  of a number of organometallic reactions, support the validity of this approach (*vide infra*).<sup>12-14</sup> (It has been observed that the  $pK_a$  values of the conjugate acids of amines often correlate with the reactivities of organometallic complexes containing these amines.<sup>15</sup>)

A quantitative evaluation of the  $\pi$ -acidity of a ligand has proved to be elusive. Graham<sup>16</sup> and then Treichel<sup>17</sup> attempted to separate the  $\sigma$ - and  $\pi$ -bonding properties of the phosphorus(III) ligands by analyses of the force constants of the carbonyl stretching frequencies of a series of molybdenum and tungsten complexes (LM(CO)<sub>5</sub>). These analyses, however, led to some rather bizarre observations; *i.e.*, Bu<sub>3</sub>P is a better  $\pi$ -acid ligand than Ph<sub>3</sub>P. These scales of  $\pi$ -acidity have not been widely used. Bodner<sup>7</sup> has estimated the donor/acceptor ratios of phosphorus ligands from analyses of the <sup>13</sup>C NMR chemical shifts of the carbonyl carbons in (CO)<sub>3</sub>NiL. The qualitative nature of these evaluations does not make them useful in correlations with kinetic or thermodynamic data. Thus, up until now  $\sigma$ - and  $\pi$ -effects have not been separated effectively.

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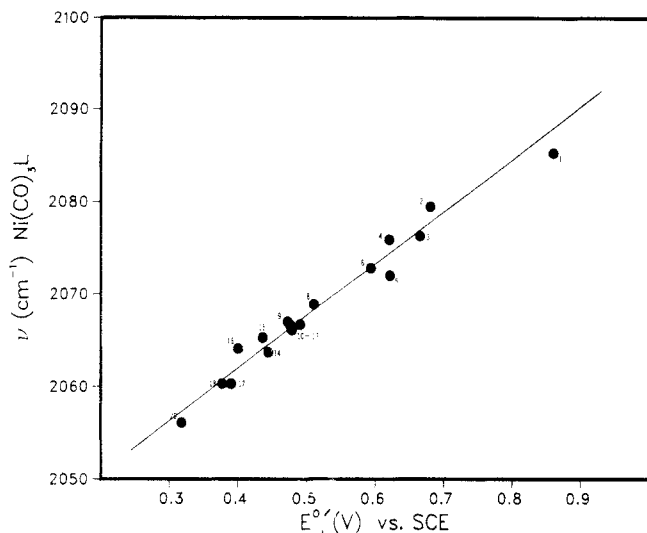
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**Figure 1.** The correlation of the  $A_1$  carbonyl stretching frequencies of  $Ni(CO)_3L$  vs.  $E_L^{\circ'}$  of  $\eta\text{-MeCpMn(CO)}_2L$ . Data are taken from Table I.

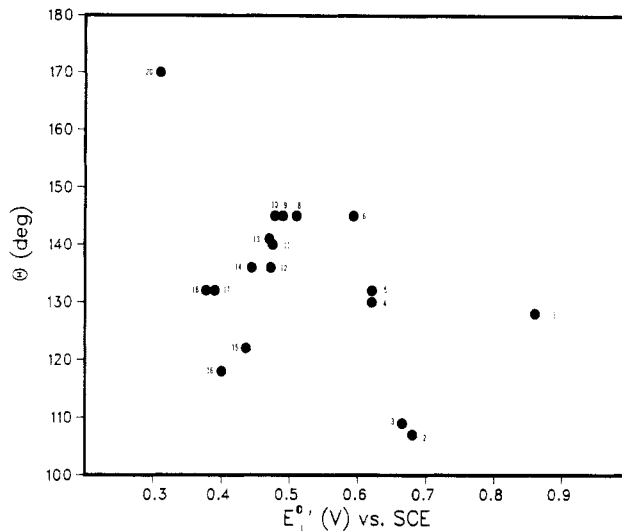
Despite the problems concerning the separation of  $\sigma$ - and  $\pi$ -effects, numerous papers have reported correlations of rate data with steric (cone angles) and electronic ( $pK_a$  and  $\chi_i$  values) parameters. In fact, mathematical relationships between reaction parameters and electronic and steric properties of the phosphorus ligands have been obtained via multilinear<sup>18</sup> or linear<sup>19</sup> regression analyses for the reactions of methyl ( $\eta^3$ -allyl)nickel phosphine complexes ( $\chi_i$  values and  $\theta$ )<sup>18</sup> and the associative ligand substitution reactions of certain manganese radical cations ( $pK_a$  values and  $\theta$ ).<sup>19</sup> (We believe that there are serious problems with these analyses (vide infra).) Generally, however, the correlations between kinetic or thermodynamic and steric or electronic parameters are rather poor with the exception of the few  $pK_a$  correlations noted above. We believe that the poor correlations of steric and electronic parameters with the reaction parameters  $\log k$  and  $\log K$  are associated with the failure to separate the steric and electronic components of phosphorus-metal bonding and to separate the electronic contribution into its  $\sigma$ - and  $\pi$ -components. Clearly, this constitutes an important problem with ramifications in all domains of organometallic chemistry.

Our research group became interested in ligand effects when we required a technique that would allow us to probe the origins of the rate enhancements of certain organometallic reactions that occur when transition-metal organometallic complexes undergo one electron redox processes.<sup>20</sup> A survey of the literature showed that ligand effects had been used, for the most part, only in a qualitative manner. Consequently, we embarked on a program to quantify the use of ligand effects in studies of organometallic reaction mechanisms. We now present a description of our findings based on research from our laboratories and kinetic and thermodynamic data as found in the literature.

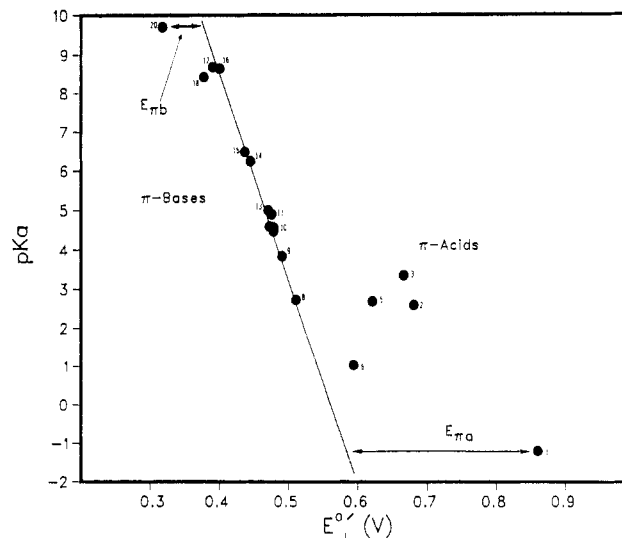
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**Figure 2.** The correlation of the cone angles ( $\theta$ ) of the phosphorus(III) bases vs.  $E_L^{\circ'}$  of  $\eta\text{-MeCpMn(CO)}_2L$ . Data are taken from Table I.



**Figure 3.** The correlation of the  $pK_a$  values of  $R_3PH^+$  vs.  $E_L^{\circ'}$  of  $\eta\text{-MeCpMn(CO)}_2L$ . The line is drawn through the class II ligands. Data are taken from Table I.

### Separation of $\sigma$ - and $\pi$ -Electronic Effects in Metal-Ligand Bonding

Central to the quantitative use of ligand effects are the separation of  $\sigma$ - and  $\pi$ -electronic effects and an evaluation of the relative importance of each. Presented in this section is the rather simple method that we have used to evaluate quantitatively the relative  $\sigma$ -donicities,  $\pi$ -acidities, and  $\pi$ -basicities of phosphorus(III) ligands. Various steric and electronic ligand properties are displayed in Table I. Analyses (in terms of steric and electronic factors) of the kinetic and thermodynamic data of several different reactions, which have been reported by others in the literature, are then presented.

The assessment of the  $\pi$ -acidities and  $\pi$ - and  $\sigma$ -basicities of the phosphorus ligands is based on analyses of the correlations of the  $E_L^{\circ'}$  values of the complexes  $\eta\text{-MeCp(CO)}_2MnL$ <sup>19,21</sup> with the  $pK_a$  values<sup>10,11</sup> of the protonated phosphorus(III) compounds and the symmetric carbonyl stretching frequencies of  $Ni(CO)_3L$  as reported by Tol-

(21) A number of the  $E_L^{\circ'}$  values for  $\eta\text{-MeCp(CO)}_2MnL$  have been reported previously. Reference 19 and; Hershberger, J. W.; Klinger, R. J.; Kochi, J. K. *J. Am. Chem. Soc.* 1983, 105, 61-73.

Table I. Electrochemical, Infrared ( $\text{cm}^{-1}$ ),  $\text{p}K_a$ , and Cone Angle Data (deg) for  $\eta\text{-MeCp}(\text{CO})_2\text{MnL}$ 

|    | L                                 | $E_L^{\circ a}$     | $E_\sigma^b$ | $E_{\pi b}^b$ | $E_{\pi a}^b$ | $\text{p}K_a^c$     | (CO) <sup>d</sup> | $\theta^d$ |
|----|-----------------------------------|---------------------|--------------|---------------|---------------|---------------------|-------------------|------------|
| 1  | (PhO) <sub>3</sub> P              | 0.86                |              |               | 0.261         | -1.20               | 2085.3            | 128        |
| 2  | (MeO) <sub>3</sub> P              | 0.680               | 0.515        |               | 0.165         | 2.60                | 2079.5            | 107        |
| 3  | (EtO) <sub>3</sub> P              | 0.665               | 0.50         |               | 0.165         | 3.35                | 2076.3            | 109        |
| 4  | ( <i>i</i> -PrO) <sub>3</sub> P   | 0.62                |              |               |               | (4.0)               | 2075.9            | 130        |
| 5  | Ph <sub>2</sub> (MeO)P            | 0.62 <sup>e</sup>   | 0.51         |               | 0.11          | (2.69) <sup>f</sup> | 2072.0            | 132        |
| 6  | ( <i>p</i> -ClPh) <sub>3</sub> P  | 0.593               | 0.545        |               | 0.048         | 1.03                | 2072.8            | 145        |
| 7  | ( <i>p</i> -FPh) <sub>3</sub> P   |                     |              |               |               | 1.97                |                   | 145        |
| 8  | Ph <sub>3</sub> P                 | 0.51                |              |               |               | 2.73                | 2068.9            | 145        |
| 9  | ( <i>p</i> -MePh) <sub>3</sub> P  | 0.49                |              |               |               | 3.84                | 2066.7            | 145        |
| 10 | ( <i>p</i> -MeOPh) <sub>3</sub> P | 0.478               |              |               |               | 4.57                | 2066.1            | 145        |
| 11 | EtPh <sub>2</sub> P               | 0.475               |              |               |               | (4.90) <sup>e</sup> | 2066.7            | 140        |
| 12 | MePh <sub>2</sub> P               | 0.472               |              |               |               | 4.59                | 2067.0            | 136        |
| 13 | BuPh <sub>2</sub> P               | 0.47 <sup>e,g</sup> |              |               |               | (5.0) <sup>e</sup>  |                   | 141        |
| 14 | Et <sub>2</sub> PhP               | 0.444               |              |               |               | 6.25                | 2063.7            | 136        |
| 15 | Me <sub>2</sub> PhP               | 0.436               |              |               |               | 6.49                | 2065.3            | 122        |
| 16 | Me <sub>3</sub> P                 | 0.40                |              |               |               | 8.65                | 2064.1            | 118        |
| 17 | Et <sub>3</sub> P                 | 0.393               | 0.397        | 0.004         |               | 8.69                | 2060.3            | 132        |
| 18 | Bu <sub>3</sub> P                 | 0.377               | 0.404        | 0.027         |               | 8.43                | 2060.3            | 132        |
| 19 | ( <i>i</i> -Bu) <sub>3</sub> P    |                     |              |               |               | 7.97                | 2059.7            | 143        |
| 20 | Cy <sub>3</sub> P                 | 0.310               | 0.38         | 0.070         |               | 9.70                | 2056.1            | 170        |

<sup>a</sup>Cyclic voltammetry, volts, 0.2 M LiClO<sub>4</sub>, AN, -45 °C, SCE, 200 mV s<sup>-1</sup>. <sup>b</sup>See text for definitions. <sup>c</sup>References 10, 11, and 36 except where noted. <sup>d</sup>Reference 5. <sup>e</sup>Reference 21. <sup>f</sup>Estimated based on the  $\text{p}K_a$  values of (MeO)<sub>3</sub>P and Ph<sub>3</sub>P. <sup>g</sup> $E^\circ$  value is estimated for acetonitrile based on data obtained on a methylene chloride solution.

man.<sup>9</sup> The good linear correlation of the  $E_L^{\circ}$  values (Figure 1) with the infrared data for the nickel complexes is consistent with the  $E_L^{\circ}$  values being a function of the electronic character of the ligand and not of steric factors.<sup>9,22</sup> Supporting this contention is the lack of correlation between the cone angles and  $E_L^{\circ}$  values which is shown in Figure 2. The  $E_L^{\circ}$  values were then correlated with the  $\text{p}K_a$  values of the conjugate acids of the phosphorus bases (Figure 3). The plot of the  $E_L^{\circ}$  values from 0.40 V (PMe<sub>3</sub>) to 0.51 V (Ph<sub>3</sub>P) is remarkably linear with a correlation coefficient of -0.996 for the eight points. Without a doubt the ease of oxidation of the metal depends only on the  $\sigma$ -donicity of this group of bases, which we have designated as *class II* ( $\sigma$ -donor) ligands. This class of ligands includes several para-substituted triarylphosphines (but not (*p*-ClPh)<sub>3</sub>P) and a number of mixed alkyl- and arylphosphines with cone angles that range from 118° (Me<sub>3</sub>P) to 145° (triarylphosphines). (Correlation of the  $\chi_i$  values with the  $\text{p}K_a$  values gives a plot similar to that displayed in Figure 3 except that there is greater scatter of the points for the class II ligands.)

It is noteworthy that none of these class II bases is indicated to participate in significant  $\pi$ -bonding to the metal. The absence of back-bonding is not surprising in light of recent theoretical studies which show that  $d_\pi$ - $d_\pi$  bonding is not important between fluorophosphines and transition metals because the phosphorus d orbitals are too high in energy.<sup>23-25</sup> The back-bonding is attributed to an interaction between the metal d orbitals and the  $\sigma^*$  orbitals of the phosphine.<sup>23</sup> The d orbitals of the alkyl- and arylphosphines are even less accessible energetically, and the  $\sigma^*$  orbitals are of higher energy because of the lower polarity of the P-C bond; hence, back-bonding is less important.

Above 0.51 V (Figure 3) all the points lie to the higher potential side of the lines determined by the class II ligands. Each of these complexes is more difficult to oxidize than is predicted by its  $\text{p}K_a$  value, thereby demonstrating that each of these ligands is a poorer electron donor overall

than anticipated on the basis of its  $\text{p}K_a$  value. This diminished electron donicity is attributed to the onset of  $\pi$ -acidity of the ligands. As a consequence, their  $\sigma$ -electron donor ability is partially offset by the removal of electron density through back-bonding into the  $\pi^*$  orbitals of the ligand. This leads to stabilization of the manganese(I) state relative to the manganese(II) state, where back-bonding should be greatly diminished and a larger than expected  $E_L^{\circ}$  value is observed. The difference ( $E_{\pi a}$ ) between the observed  $E_L^{\circ}$  value and  $E_\sigma$  (the  $E_L^{\circ}$  predicted by the  $\text{p}K_a$  value of the ligand) for these *Class III* ( $\sigma$ -donor/ $\pi$ -acceptor) ligands is probably a good quantitative measure of their relative  $\pi$ -acidities. Thus, it can be seen that the order of  $\pi$ -acidity is (PhO)<sub>3</sub>P > (RO)<sub>3</sub>P > (*p*-ClPh)<sub>3</sub>P as expected.

Below 0.40 V, the points deviate to the lower potential side of the line in Figure 3. Each complex is more easily oxidized than is predicted by its  $\text{p}K_a$  value. We assign this enhanced electron richness of the complexes containing the *class I* ( $\sigma$ -donor/ $\pi$ -donor) ligands to the  $\pi$ -basicities ( $E_{\pi b}$ , which is the difference between  $E_\sigma$  and  $E_L^{\circ}$ ) of the ligands. Et<sub>3</sub>P is seen to have, possibly, a slight  $\pi$ -basicity whereas Bu<sub>3</sub>P clearly exhibits  $\pi$ -basicity. Cy<sub>3</sub>P (tricyclohexylphosphine), which is one of the most commonly encountered of the bulky phosphine ligands, is the most  $\pi$ -basic ligand that we have studied. The  $\pi$ -interaction between the class I ligands and the metal may occur via filled metal d orbitals and the highest filled P-R bonding molecular orbitals ( $\sigma_e^{25}$ ) which are relatively high in energy.<sup>26</sup> These orbital interactions are probably repulsive in nature.

There appears to be a correlation between the  $\pi$ -basicities and cone angles of the alkyl phosphines; hence, we were concerned that the  $\pi$ -basicities of these class I ligands were, in actuality, a manifestation of their steric demands. There are several observations that argue against this possibility. Bohling and co-workers<sup>27</sup> note that the  $E_L^{\circ}$  values for a series for hexakis(aryl isocyanide)chromium complexes correlate well with  $\sigma_p$ - and  $\sigma_o$ -substituent constants. This correlation holds even for the rather bulky,

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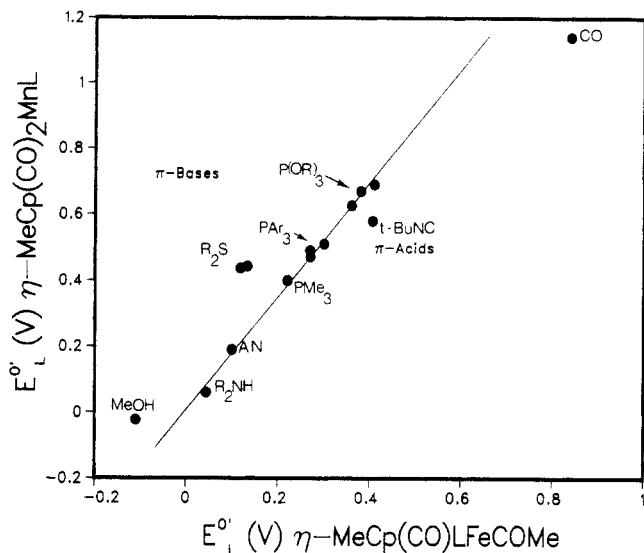
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**Figure 4.** The correlations of  $E_L^0$  values of  $\eta\text{-MeCpMn(CO)}_2\text{L}$  vs. the  $E_L^0$  values for  $\eta\text{-MeCp(CO)LFe(COMe)}$ . Cyclic voltammetry data were obtained under the conditions described in Table I. The line is drawn through the class II ligands.

hexakis(2,6-diisopropylphenyl isocyanide)chromium for the 0/+1 oxidation. This demonstrates that for these chromium isocyanide complexes in low oxidation states, steric effects are not playing a major role in determining the  $E_L^0$  values. Steric factors, however, do play an increasingly important role in determining the  $E_L^0$  values for oxidations of these chromium complexes in the higher oxidation states (+1/+2, +2/+3); the more sterically encumbered complexes become progressively more difficult to oxidize in higher oxidation states than are predicted by their  $\sigma_p$  or  $\sigma_o$  values. We find the opposite for the class I ligands in that their manganese complexes are more easily oxidized than predicted. Lastly, if the  $\pi$ -basicity were only steric in origin, it would be difficult to account for the fact that  $\text{Bu}_3\text{P}$  with a cone angle of  $132^\circ$  is a  $\pi$ -base whereas  $\text{Et}_3\text{P}$ , with the same cone angle, is not or at the least is not a very strong  $\pi$ -base.

Although the class I and class III ligands show  $\pi$ -effects, the importance of these effects relative to that of carbon monoxide or other strong  $\pi$ -acids or -bases is not apparent. In addition, it seems likely that the boundaries of the three classes of phosphorus ligands will be dependent on the  $\pi$ -basicity of the metal to which they are coordinated. The more  $\pi$ -basic metals will accentuate the metal-ligand  $\pi$ -interactions. This difference in  $\pi$ -interactions has allowed the measurement of the relative importance of the  $\pi$ -effects of a variety of ligands via a correlation of the  $E_L^0$  values for complexes containing metals of differing  $\pi$ -basicities.<sup>28</sup> Figure 4 shows such a correlation for the complexes  $\eta\text{-MeCp(CO)}_2\text{MnL}$  and  $\eta\text{-MeCp(CO)LFe(COMe)}$ , which contains the more electron-rich iron center (based on terminal carbonyl stretching frequencies<sup>19,20</sup>). There is a linear relationship between the  $E_L^0$  values of the two classes of complexes when L are  $\sigma$ -donor ligands (class II phosphines, amines, nitriles). The data points deviate from the line for complexes containing the ligands that exhibit  $\pi$ -effects. Since iron is a better  $\pi$ -base than manganese in these complexes, it is expected and observed that when L is a  $\pi$ -acid, the iron complex is disproportionately more difficult to oxidize than the analogous manganese complex.

An iron complex containing a  $\pi$ -base ligand is more easily oxidized. Hence, the  $\pi$ -base ligands lie to the left of the line in Figure 4, while the  $\pi$ -acid ligands lie to the right of the line. The results are in agreement with our chemical experience. Both methanol and dimethyl sulfide are bases.<sup>29</sup> Nitriles, amines, and class II phosphines are only  $\sigma$ -donors. Carbon monoxide is a strong  $\pi$ -acid<sup>3</sup> and lies well to the right of the line. *tert*-Butyl isocyanide is seen to be a  $\pi$ -acid, but its  $\pi$ -acidity is only 50% that of carbon monoxide.<sup>30</sup> Interestingly, the simple alkyl phosphites lie very near or on the line, indicating that their  $\pi$ -bonding ability is small compared to other  $\pi$ -base or  $\pi$ -acid ligands. Although there is structural evidence for  $\pi$  interactions in the complexes  $\text{Cr(CO)}_5\text{L}$ ,<sup>31</sup> our perusal of the literature has failed to uncover any kinetic or thermodynamic evidence for important  $\pi$ -interactions between phosphites or phosphines and transition metals. (This is not to say that such interactions are not important for fluorophosphines or other very strong  $\pi$ -acid phosphorus ligands. At present, we have no information concerning the  $\pi$ -acidities of these ligands.)

The interpretation of the data displayed in Figure 4 requires caution when the relative  $\sigma$ - or  $\pi$ -basicities of different classes of ligands are compared. These properties depend on the hardness or softness of the respective coordinating atoms of the ligands. A striking example is found in the relative ease of oxidation of amine and phosphine complexes. On the basis of terminal carbonyl stretching frequencies of the complexes  $\eta\text{-Cp(CO)-FeCOCH}_2\text{CHMeNH}_2\text{Bz}$  ( $1920\text{ cm}^{-1}$ )<sup>32</sup> and  $\eta\text{-Cp(CO)-(PPh}_3\text{)FeCOMe}$  ( $1910\text{ cm}^{-1}$ ),<sup>20</sup> the phosphine complex should be more easily oxidized. However, quite the opposite is observed—the  $E_L^0$  value for the amine complex is 0.05 V whereas that for the phosphine complex is 0.28 V. This seemingly anomaly is better understood when it is realized that the  $E_L^0$  values are a measure of the energy differences between the iron(II) and iron(III) states of the two complexes and not just the electron richness of the iron(II) complexes. Although the iron(II) amine complex is less electron rich than the phosphine complex, it is closer in energy to the iron(III) amine complex than the iron(II) phosphine complex is to the energy of the iron(III) phosphine complex. Undoubtedly, the smaller energy gap for the amine complexes is attributable to the fact that the amine is a hard base<sup>33</sup> and better able to stabilize the higher oxidation state than the phosphine. A similar problem is encountered when the  $\pi$ -basicities of the dialkyl sulfides and methanol are compared. Both the destabilization of the iron(II) state, which should be greater for the softer sulfur  $\pi$ -bases, and the stabilization of the iron(III) state, which should be greater for the methanol (hard  $\pi$ -base) complex, will lead to unusually low  $E_L^0$  values. This ambiguity is not encountered with the  $\pi$ -acid ligands since the  $\pi$ -acid effect will be diminished in the higher oxidation states regardless of the ligand. Thus, we feel comfortable in comparing the  $\pi$ -acidities of isocyanide and carbon monoxide (*vide supra*), both of which coordinate through carbon. The failure to observe  $\pi$ -acid effects for the phosphites and related ligands in Figure 4 cannot be attributed to comparable  $\pi$ -acid effects in both the higher and lower oxidation states of the metal, since

(29) Basolo, F.; Pearson, R. G. *Mechanism of Inorganic Reactions. A Study of Metal Complexes in Solution*, 2nd ed.; Wiley: New York, 1967.

(30) Organic isocyanides have been predicted to be strong  $\pi$ -acids. Sarapu, A. C.; Fenske, R. F. *Inorg. Chem.* 1975, 14, 247.

(31) Cotton, F. A.; Darensbourg, D. J.; Isley, W. A. *Inorg. Chem.* 1981, 20, 578.

(32) Javaheri, S.; Giering, W. P. *Organometallics* 1984, 3, 1927-8.

(33) Pearson, R. G. *J. Chem. Educ.* 1968, 45, 581-87, 643-648.

(28) Several groups have correlated the  $E_L^0$  values of related classes of organometallic complexes. (a) Hershberger, J. W.; Kochi, J. K. *Polyhedron* 1983, 2, 929-34. (b) Chatt, J.; Kan, C. T.; Leigh, J.; Pickett, C. J.; Stanley, D. R. *J. Chem. Soc., Dalton Trans.* 1980, 2032.

the  $\pi$ -effects are clearly evident in Figure 3. Thus, it seems reasonable that the  $\pi$ -acidities of the class III ligands, which we have studied, are insignificant when compared to those of the isocyanide and carbon monoxide.

In summary, we have classified the phosphorus(III) ligands according to their  $\sigma$ - and  $\pi$ -basicities and  $\pi$ -acidities. Although the class I and class III ligands show  $\pi$ -effects, it must be recognized that these effects are small in comparison to those of other strong  $\pi$ -acids or -bases.

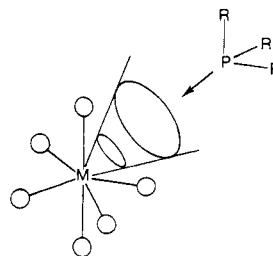
### Ligand Effects in the Analysis of Kinetic and Thermodynamic Data for Organometallic Reactions

A consideration of the data displayed in Table I shows that it is possible to separate and evaluate the contributions of the various steric and electronic factors effecting a given reaction. These analyses take advantage of the fact that many para-substituted triarylphosphines are only  $\sigma$ -donors and not  $\pi$ -acids or  $\pi$ -bases and that the steric demands of these substances can be assumed to be invariant. It is assumed that the  $\log k$  or  $\log K$  is a function of the steric size (Tolman's cone angle,  $\theta$ ), the  $\sigma$ -donicity ( $pK_a$  value of the protonated base), the  $\pi$ -acidity ( $E_{\pi a}$ ) and the  $\pi$ -basicity ( $E_{\pi b}$ ) of the ligand. Furthermore, it has been assumed that the  $\sigma$ - and  $\pi$ -effects are not coupled.

$$\log k(\text{or } \log K) = f_1(\theta) + f_2(pK_a) + f_3(E_{\pi a}) + f_4(E_{\pi b}) \quad (1)$$

As will be described later, the relationship between  $\log k$  or  $\log K$  and  $pK_a$  (for the triaryl phosphines) is linear whereas the relationship between cone angle and  $\log k$  or  $\log K$  need not be linear. Insufficient data exists to fully characterize nature of the relationship between the  $\pi$ -effects and  $\log k$  or  $\log K$  as such effects do not appear to be very important for most reactions described in the literature. The four contributions can be separated graphically. The linear relationship between  $\log k$  or  $\log K$  and  $pK_a$  is termed the electronic profile and is readily established by using data for class II ligands with constant (most commonly the para-substituted triarylphosphines) or insignificant steric requirements (vide infra). The electronic profile may also be constructed from the data for any of the phosphorus(III) ligands that meet the aforementioned steric requirements if  $\pi$ -effects are not important. The value of  $\log k$  or  $\log K$  predicted for other ligands by this linear relationship is called  $\log k_c$  or  $\log K_c$ . If steric effects are not important, all class II ligands will fall on the line established by the arylphosphines (vide infra). If steric effects are important, then the class II ligands that differ in size from the arylphosphines will deviate from this line. The magnitude of this deviation ( $\log k_{\text{obsd}} - \log k_c$ ) is related to  $f_1(\theta)$ . Thus, the plot of ( $\log k_{\text{obsd}} - \log k_c$ ) vs. cone angle for the class II ligands generates the steric profile of the reaction and exposes the relationship between  $\log k_{\text{obsd}}$  and cone angle. The deviation of the data points of the class I and class III ligands from the steric profile is then attributed to  $\pi$ -effects and will be related to  $E_{\pi a}$  or  $E_{\pi b}$  of the ligands. Every reaction type will exhibit characteristic electronic and steric profiles.

Analyses of the electronic and steric profiles of a reaction provide considerable information concerning the nature of the rate-determining and pre-rate-determining steps. The slope of the electronic profile will indicate the importance of covalent bonding in the transition state for nucleophile dependent substitution reactions.<sup>12</sup> When the phosphorous ligands are ancillary, the slope will afford information concerning electron density on the metal in the transition state, the involvement of pre-rate-determining steps (i.e., dissociation), and ground-state vs. transition-state stabilization. The steric profile will show



**Figure 5.** Illustration of the conical channel leading to the metal in the transition state of an associative ligand substitution reaction.  $PR_3$  designates the incoming phosphorus nucleophile. The conical cross sections represent the positions occupied by the nucleophile in transition states with long and short metal phosphorus distances.

the steric threshold ( $\theta_{st}$ )—the value of the cone angle of the ligands above which steric effects become evident. In the simplest terms, the steric threshold is envisaged as a measure of the area of the cross section of a conical channel with the metal at the apex, which the phosphorus ligands must pass through or occupy in the transition state (Figure 5). The steric threshold will be a function of the amount of covalent bonding between the incipient phosphorus ligand in the transition state, the size of other ancillary ligands, the metal, and the coordination number of the metal. The slope of the steric profile after the steric threshold is defined as the steric sensitivity and is a measure of the ability of the complex to accommodate larger ligands. Complexes that are flexible in their steric demands will exhibit small slopes, whereas those that are rigid will exhibit large slopes.

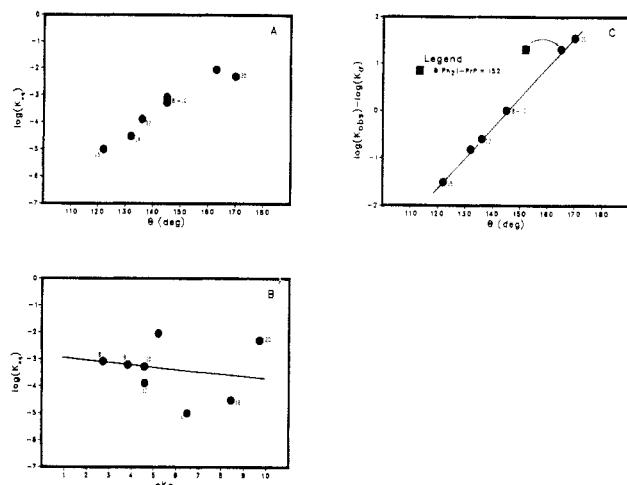
In order to test this procedure, we perused the literature for kinetic and/or thermodynamic studies which utilized the requisite combination of phosphorus bases. Unfortunately, only a few of the scores of papers that we examined report the required data. Most of the reported studies used one or two phosphines from each of the three classes. Our analyses of the suitable sets of data are exciting, satisfying, and in several cases rather perplexing. These analyses are presented in the following section.

### Separation of Steric and Electronic Ligand Effects for Several Reactions As Reported in the Literature

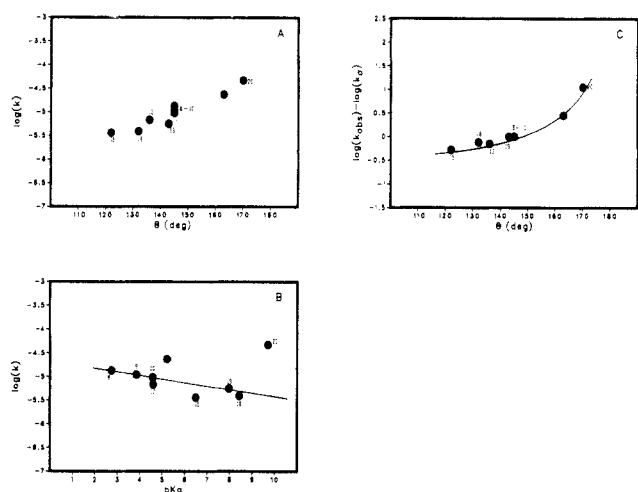
The discussion begins with an evaluation of the dissociative reactions that involve the phosphorus(III) bases in a direct or ancillary role. This is followed by our analyses of ligand-dependent substitution reactions involving phosphorus nucleophiles. Attention is then turned to the oxidative-addition reactions of cobalt and iridium complexes in which the phosphorus ligands were thought to play only an ancillary role. The addition of phosphorus bases to coordinated hydrocarbons is then considered. Finally, there is an evaluation of the work of Schenkluhn's group,<sup>18</sup> which has attempted the most ambitious separation of electronic and steric ligand effects in the chemistry of allylnickel complexes. In many instances, our analyses support and quantify the conclusions of the original authors. In other cases, our analyses shed new and important light on well-known reactions.

### Dissociative Reactions

The labilization of a carbon monoxide ligand by the incorporation of a phosphorus(III) ligand is a well-documented phenomenon<sup>34</sup> that has taken on special importance in the study of metal carbonyl clusters.<sup>35</sup> Perhaps

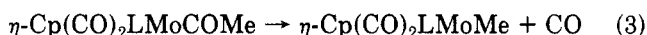
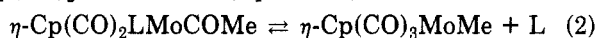


**Figure 6.** Analysis of  $\log(K_{\text{obs}})$  for reaction 2. The numbers in the diagram refer to the ligands listed in Table I. The unlabeled datum point in this set of figures refers to *i*-PrPh<sub>2</sub>P: (a)  $\log(K_{\text{obs}})$  vs.  $\theta$ ; (b) electronic profile (the line is drawn through the data points for (*p*-XPh)<sub>3</sub>P (X = Cl, H, Me, MeO)); (c) steric profile. Data are taken from ref 36.



**Figure 7.** Analysis of  $\log(k)$  for the decarbonylation of the  $\eta$ -Cp(CO)<sub>2</sub>LMO(COMe) (eq 3): (a)  $\log(k)$  vs.  $\theta$ ; (b) electronic profile (the line is drawn through the data points for (*p*-XPh)<sub>3</sub>P, (X = H, Me, MeO)); (c) steric profile. Data are taken from ref 36.

the best set of usable data was reported by Barnett and Pollmann for the reactions of the well-studied complex  $\eta$ -Cp(CO)<sub>2</sub>LMOCOMe<sup>36</sup> (eq 2 and 3). The rate constants



for reaction 3, which proceeds by rate-determining loss of an ancillary carbon monoxide, and the equilibrium constants for reaction 2 were observed to be particularly sensitive to the steric requirements of the phosphine ligands (Figures 6 and 7). The electronic profile for the equilibria was established by plotting  $\log K$  vs.  $pK_a$  for the class II ligands and then fitting the best line to the data for para-substituted triarylphosphines (Figure 6b). The deviation ( $\log K_{\text{obsd}} - \log K_e$ ) of the other class II phosphines from this line was then plotted against cone angle to establish the steric profile of the equilibria. The good linear relationship between ( $\log K_{\text{obsd}} - \log K_e$ ) and cone

angle is displayed in Figure 6c. Only the point for Ph<sub>2</sub>(*i*-Pr)P lies substantially off the line, thereby suggesting that the literature value<sup>5</sup> for the cone angle (152°) of this ligand may underestimate its size. A value of 164° places the point on the line in Figure 6c and is in accord with the kinetic analysis that follows. Although it is dangerous to make the generalization that all dissociative reactions will exhibit linear steric profiles, we will encounter similar steric profiles for certain oxidative-addition reactions of iridium complexes (vide infra), thereby suggesting the involvement of reversible dissociations of ancillary phosphine ligands.

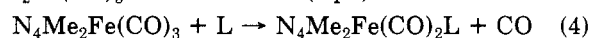
The kinetics of reaction 3 show a large sensitivity to the steric but not the electronic properties of the ancillary ligands. The electronic and steric profiles for the reaction are shown in Figure 7. The electronic profile (Figure 7b) shows a small dependence on the  $\sigma$ -donicities of the ligands—a change of 9  $pK_a$  units effects less than an order of magnitude change in the rate of reaction. The steric profile (Figure 7c) is a smooth curve whose gradient rapidly increases at higher cone angles. Since Cy<sub>3</sub>P falls on what appears to be the extension of the curve established by the data for class II ligands, it appears that  $\pi$ -base effects for Cy<sub>3</sub>P are not important in this reaction. This analysis supports Barnett's contention that the rate of reaction is dominated by steric factors—an increase in cone angle of 48° effects an almost two-decade change in the rate constant. The nature of the dependence of  $\log k$  on the cone angle demonstrates that this relationship need not be linear.

It must be noted that increasing basicity of the phosphorus ligand effects a decrease in the rate of reaction 3. This is consistent with a preferential stabilization of the ground state relative to the transition state. Unfortunately, we are unable to determine, with the data in hand, the generality of this electronic dependence. It is, however, noteworthy that labilization of carbon monoxide in Ir<sub>4</sub>(CO)<sub>11</sub>L appears to show the opposite trend—the rate of loss of carbon monoxide is accelerated by increasing the basicity of the phosphorus ligand.<sup>35</sup>

### Nucleophile-Dependent Substitution Reactions

Nucleophile-dependent substitution reactions of organometallic complexes are of growing concern with the recognition that odd-electron complexes are particularly prone to this reaction<sup>19,21,37</sup> and that these complexes may play important roles in catalysis.<sup>38</sup> Our analyses of the literature data for these reactions are complicated by the lack of data for the triarylphosphines or other series of isosteric bases. For these cases we have assumed that there are no steric effects for small incoming nucleophiles such as (MeO)<sub>3</sub>P and Me<sub>3</sub>P. The data points for these small phosphorus nucleophiles were used to establish the electronic profiles for these reactions. The results of our analyses (Table II) include  $\theta_{\text{st}}$  (steric threshold),  $d(\log k_{\text{obsd}} - \log k_e)/d\theta$  (steric sensitivity),  $d(\log k_e)/d(pK_a)$  of the electronic profiles, and the intrinsic reactivities (defined as  $\log k$  at  $pK_a = 2.60$ ). Each of these parameters is discussed below.

Probably the most striking feature of the ligand dependent substitution reaction is the very dramatic steric threshold ( $\theta_{\text{st}}$ ). The displacement of carbon monoxide from N<sub>4</sub>Me<sub>2</sub>Fe(CO)<sub>3</sub> is illustrative (eq 4). There are no ob-



(37) Shi, Q.-Z.; Richmond, T. G.; Troglor, W. C.; Basolo, F. *J. Am. Chem. Soc.* **1984**, *106*, 71–76.

(38) (a) Wegman, R. W.; Brown, T. L. *J. Am. Chem. Soc.* **1980**, *102*, 2494. (b) Krusic, P. J.; San Filippo, J.; Hutchinson, B.; Daniels, L. M. *J. Am. Chem. Soc.* **1981**, *103*, 2129.

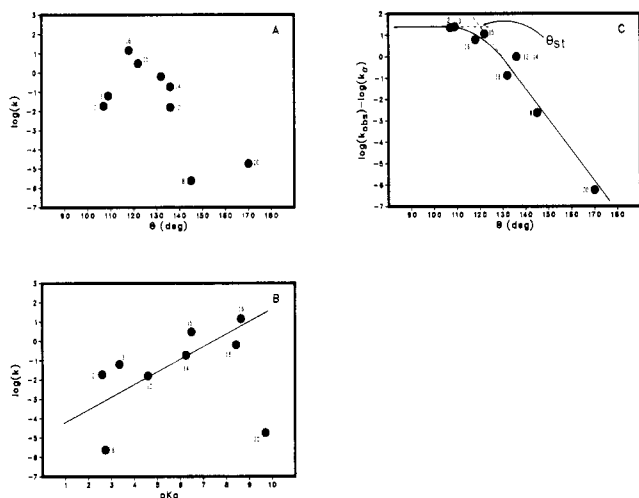
(35) Sonnenberger, D. C.; Atwood, J. D. *J. Am. Chem. Soc.* **1982**, *104*, 2113–16.

(36) Barnett, K. W.; Pollman, T. G. *J. Organomet. Chem.* **1974**, *69*, 413–21.

**Table II. Compilation of Kinetic Parameters for the Ligand Dependent Substitution Reactions Involving Phosphorus(III) Nucleophiles**

| complex                    | leaving group        | $\theta_{st}$ | $d \log k_{\sigma}/dpK_a$ | $d(\log k_{obsd} - \log k_{\sigma})/d\theta$ | intrinsic reactivity |
|----------------------------|----------------------|---------------|---------------------------|--|----------------------|
| $C_5Me_5Rh(CO)_2^a$        | CO                   | 122           | 0.16                      | -0.098                                       | -3.50                |
| $C_5H_5Rh(CO)_2^b$         | CO                   | 142           | 0.15                      | -0.066                                       | -3.50                |
| $C_5Me_5Co(CO)_2^c$        | CO                   | 122           | 0.22                      | -0.10  | -4.05                |
| $N_4Me_2Fe(CO)_3^d$        | CO                   | 129           | 0.54                      | -0.18  | -1.73                |
| $V(CO)_6^e$                | CO                   | 135-142       | 0.38                      | -0.29  | -0.16                |
| $Mo(CO)_6^f$               | CO                   | 135-142       | 0.12                      |  | -1.34                |
| $W(CO)_6^g$                | CO                   | 135-142       | 0.11                      |  | -3.78                |
| $MeCp(CO)_2Mn-4-NO_2Py^+h$ | 4-NO <sub>2</sub> Py | 145-160       | 0.52                      |  | +1.14                |
| $MeCp(CO)_2MnAN^+i$        | AN                   | >145          | 0.71                      |  | +3.97                |
| $C_6H_7Mn(CO)_3^j$         | CO                   | 118           | 0.20                      | -0.054                                       | -4.49                |
| $Fe(NO)_2(CO)_2^k$         | CO                   | 150           | 0.41                      | -0.075                                       | -3.43                |
| $Co(NO)(CO)_3^l$           | CO                   | >145          | 0.36                      |  | -2.98                |

<sup>a</sup> 60 °C, ref 41. <sup>b</sup> 40 °C, ref 11. <sup>c</sup> 70 °C, ref 41. <sup>d</sup> 70 °C, ref 38. <sup>e</sup> 25 °C, ref 36. <sup>f</sup> 130.7 °C, ref 42. <sup>g</sup> 165.7 °C, ref 42. <sup>h</sup> 22 °C, ref 19. <sup>i</sup> 25 °C, ref 21. <sup>j</sup> 60 °C, ref 39. <sup>k</sup> 25 °C, ref 14. <sup>l</sup> 25 °C, ref 13.

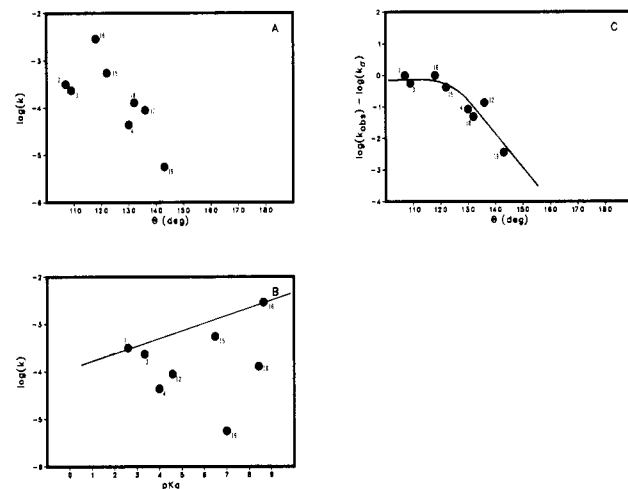


**Figure 8.** Analysis of the ligand dependent substitution reactions of  $(N_4Me_2)Fe(CO)_3$  (eq 4). (a)  $\log(k_2)$  vs.  $\theta$ ; (b) electronic profile (the line is drawn through the data points for  $MePh_2P$  and  $Et_2PhP$ ); (c) steric profile. The dotted lines are the extrapolations of the two parts of the curve that are used to calculate the steric threshold  $\theta_{st}$ . Data are taken from ref 39.

vious correlations between the rate data and either the  $pK_a$  values or the cone angles of the phosphines (Figure 8). The electronic profile (Figure 8b) was constructed by utilizing the data for the class II ligands  $Et_2PhP$  and  $MePh_2P$ , both of which have cone angles of  $136^\circ$ . The steric profile (Figure 8c) shows a sharp break between  $122^\circ$  and  $135^\circ$ . A value for  $\theta_{st}$  ( $128^\circ$ ) is obtained when the portion of the steric profile after the break in the curve is extrapolated back to  $(\log k_{obsd} - \log k_{\sigma}) = \text{constant}$ .

For several of the reactions we were unable to determine a specific value for  $\theta_{st}$  because only one point or no points were measured for ligands with cone angles greater than  $\theta_{st}$ . When only one data point is reported above the steric threshold, a range for  $\theta_{st}$  is given since the actual value will depend on the slope of the steric profile above  $\theta_{st}$  which cannot be determined accurately. When no data are available above  $\theta_{st}$ , it is noted that  $\theta_{st}$  is greater than the cone angle of the largest reported ligand. The steric thresholds range from  $118^\circ$  for the indenyl manganese complex  $\eta^5-C_9H_7Mn(CO)_3$ <sup>40</sup> to greater than  $145^\circ$  for a number of complexes.

The full chemical significance of the steric threshold cannot be appreciated until  $\theta_{st}$  is considered in conjunction



**Figure 9.** Analysis of the ligand substitution reactions of  $\eta-Me_5C_5Rh(CO)_2$  (eq 5): (a)  $\log(k)$  vs.  $\theta$ ; (b) electronic profile (the line is drawn through the data points for  $Me_3P$  and  $(MeO)_3P$ ); (c) steric profile. Data are taken from ref 41.

with  $d \log k_{\sigma}/d(pK_a)$ , the slope of the electronic profile. The steric threshold is envisioned as a measure of the area of a cross section of a conical channel leading to the metal (Figure 5). The cross section tells us nothing about the size of the channel when considered by itself. The size of the conical channel can be determined if the normal distance from the cross section to the apex of the channel (M-L bond length in the transition state) as well as the area of the cross section is known. The slope of the electronic profile,  $d \log k_{\sigma}/d(pK_a)$ , is thought to be proportional to the degree of bond making between the metal and the incipient ligand in the transition state.<sup>12</sup> The slope is then inversely proportional to the M-L bond distance in the transition state. Thus,  $d \log k_{\sigma}/d(pK_a)$  and  $\theta_{st}$  define the size of the conical channel, and both of these parameters must be considered when comparing the geometries of transition states of related reactions. A large value of  $d \log k_{\sigma}/d(pK_a)$  and a small value of  $\theta_{st}$  indicate a congested transition state with extensive metal-ligand bonding. In contrast, a small value of  $d \log k_{\sigma}/d(pK_a)$  and a large value of  $\theta_{st}$  are diagnostic of an open transition state with little metal-ligand bonding.

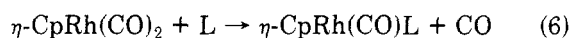
It is interesting to compare the ligand effects for the displacement of carbon monoxide from  $\eta-Me_5C_5Rh(CO)_2$ <sup>41</sup> and  $\eta-C_5H_5Rh(CO)_2$ <sup>11</sup> (eq 5 and 6 and Figure 9). The former complex was thought to be less reactive because of steric effects and ground-state stabilization.<sup>41</sup> As ex-

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(40) Ji, L.-M.; Rerek, M. E.; Basolo, F. *Organometallics* 1984, 3, 740-45.

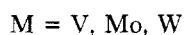
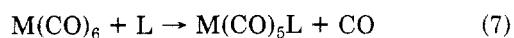
(41) Rerek, M. E.; Basolo, F. *Organometallics* 1983, 2, 372-76.

pected, the steric threshold for the  $\text{Me}_5\text{C}_5$  complex is smaller ( $122^\circ$ ) than that for the  $\text{C}_5\text{H}_5$  complex ( $142^\circ$ ). Surprisingly, the slopes of the electronic profiles,  $d \log k_\sigma/d(\text{p}K_a)$ , are virtually the same for the two sets of reactions, thereby indicating that the degrees of bond making in the transition states are nearly identical. The reactivities of the two complexes may be compared directly for ligands with cone angles less than the steric threshold for  $\eta\text{-Me}_5\text{C}_5(\text{CO})_2\text{Rh}$ . For example, the rate constant ( $\log k = -4.21$ ) for the substitution reaction of  $\eta\text{-Me}_5\text{C}_5(\text{CO})_2\text{Rh}$  involving  $(\text{EtO})_3\text{P}$  was measured at  $40^\circ\text{C}$  and the analogous rate constant ( $\log k = -3.45$ ) at this temperature for  $\eta\text{-Cp}(\text{CO})_2\text{Rh}$  was readily calculated from its electronic and steric profiles. Hence, the reactivities of the two complexes in the absence of steric effects are very similar. Although there appears to be a slight ground-state stabilization for  $\eta\text{-Me}_5\text{C}_5(\text{CO})_2\text{Rh}$ , it is clear that the transition states of the two reactions are similar. The major difference is that the conical channel for approach to the rhodium in  $\eta\text{-Me}_5\text{C}_5\text{Rh}(\text{CO})_2$  is more congested than that in  $\eta\text{-C}_5\text{H}_5\text{Rh}(\text{CO})_2$  (eq 5 and 6).



Predicated on our analysis of the aforementioned rhodium complexes and in order to compare the reactivities of different complexes, we introduce the term intrinsic reactivity. Intrinsic reactivity is  $\log k$  for a nucleophilic substitution reaction under conditions where steric effects are not important. Intrinsic reactivities may be used to compare the reactivities of sets of complexes when all other chemical and physical conditions are equivalent. Since the smallest steric threshold that we have determined is  $118^\circ$ , we have defined the intrinsic reactivity as  $\log k$  at the  $\text{p}K_a$  value of 2.60 for the commonly encountered  $(\text{MeO})_3\text{P}$  ( $\theta = 107^\circ$ ), although data for any ligand with a cone angle less than  $110^\circ$  should be suitable. For some reactions, data have been reported for  $(\text{MeO})_3\text{P}$ , whereas for other reactions these data have been calculated from the electronic and steric profiles. The intrinsic reactivities of several ligand-dependent substitution reactions are entered in Table II. The intrinsic reactivities are related to the amount of bond breaking and bond making in the transition state. For example, a reaction with a small value of  $d \log k_\sigma/d\text{p}K_a$  and a low value for the intrinsic reactivity would indicate a transition state with relatively little bond making and a great deal of bond breaking. For the reactions carried out at  $25^\circ\text{C}$ , the intrinsic reactivities vary from  $-3.43$  to  $3.97$  which corresponds to more than a seven-decade change in the rate constants.

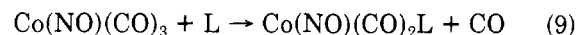
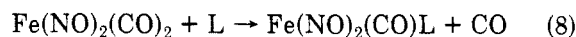
The three hexacarbonyls  $\text{V}(\text{CO})_6$ ,<sup>37</sup>  $\text{Mo}(\text{CO})_6$ ,<sup>42</sup> and  $\text{W}(\text{CO})_6$ <sup>42</sup> all exhibit similar steric thresholds for the substitution of a carbon monoxide by the phosphorus bases (equation 7). The transition state for the  $\text{V}(\text{CO})_6$  has more



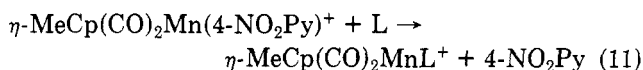
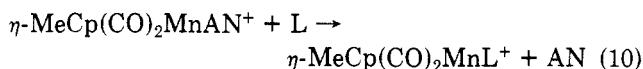
M-L bonding (based on the value of  $d \log k_\sigma/d\text{p}K_a$ ) and, therefore, is less congested than those of the other two complexes. Both  $\text{W}(\text{CO})_6$  and  $\text{Mo}(\text{CO})_6$  exhibit relatively little covalent bonding, which suggests that the substitution reactions might be described as proceeding via  $\text{I}_d$  mechanisms.<sup>43</sup> The greater degree of bond making for

$\text{V}(\text{CO})_6$  may be associated with an attractive interaction between the HOMO orbital of the nucleophile and the partially filled d orbital of the vanadium. The analogous interactions for the group 6 metals involve filled orbitals and would be repulsive in nature.

The substitution reactions of the nitrosyl complexes described in eq 8<sup>14</sup> and 9<sup>13</sup> exhibit considerable bond making in the transition states. The relatively low intrinsic reactivities suggest that there is also considerable bond breaking. The steric thresholds are large, consistent with nucleophilic attack on metals of low coordination number.



The substitution reactions of the formally octahedral manganese complexes shown in eq 10<sup>21</sup> and 11<sup>19</sup> are rather unusual in that they exhibit the largest values of  $d \log k_\sigma/d(\text{p}K_a)$  and yet exhibit large steric thresholds.<sup>44</sup>



Taken at face value these observations indicate a very open transition state with a high degree of bond making. This interpretation requires the involvement of a coordinatively unsaturated complex which would also be highly electron deficient. Such a complex is expected to show little selectivity toward incoming nucleophiles, which is contrary to actual observations. Alternatively, the high values of  $d \log k_\sigma/d(\text{p}K_a)$  may reflect an electrostatic attraction of the cationic complexes for the electron-rich phosphorus bases. In this case, covalent bonding between the metal and the incoming nucleophiles may not be very important. The large steric thresholds are then consonant with transition states with long M-L distances.

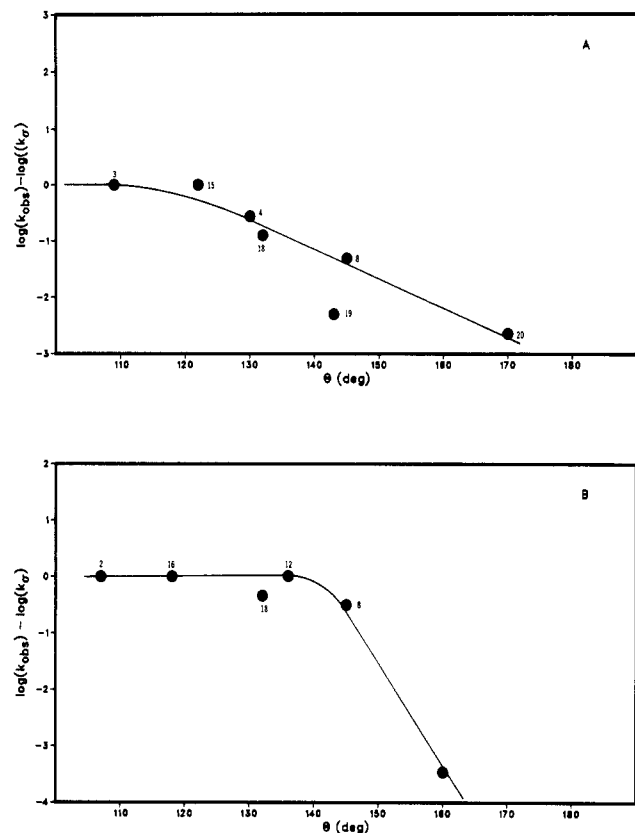
Steric sensitivity, which is defined as the slope of the steric profile ( $d(\log k_{\text{obsd}} - \log k_\sigma)/d\theta$ ) after the steric threshold, provides information about the ability of the complexes to sterically accommodate the incoming ligand. For example, a complex that is relatively rigid in the transition state will show a very dramatic decrease in reactivity after the steric threshold. In contrast, a complex that can accommodate larger ligands by compression of ancillary ligands, changes in bonding modes of ancillary ligands, or coordination sphere expansion will show a reduced sensitivity to steric effects which will be reflected in a smaller steric sensitivity. The complexes exhibiting the smallest steric sensitivities are the cyclopentadienyl complexes<sup>11,41</sup> and in particular the indenyl complex  $\eta^5\text{-C}_9\text{H}_7\text{Mn}(\text{CO})_3$ ,<sup>40</sup> whereas those with largest slopes are  $\text{V}(\text{CO})_6$ <sup>37</sup> and  $\text{N}_4\text{Me}_2\text{Fe}(\text{CO})_3$ .<sup>39</sup> The steric profiles of the  $\text{V}(\text{CO})_6$  and  $\eta^5\text{-C}_9\text{H}_7\text{Mn}(\text{CO})_3$  reactions are displayed in Figure 10. The lower sensitivities of the cyclopentadienyl complexes may be attributed to ring slipping<sup>11,41</sup> which opens a coordination site for the incoming ligand in the transition state. Ring slippage would be most important

(44) Kochi and co-workers<sup>19,21</sup> have reported the results of their very elegant electrochemical studies of the associative ligand substitution reactions of the odd-electron radical cations  $\eta\text{-MeCp}(\text{CO})_2\text{MnAn}^+$  and  $\eta\text{-MeCp}(\text{CO})_2\text{Mn}(4\text{-NO}_2\text{Py})^+$ . A multiparameter linear equation was devised to related  $\log(k)$  (second-order rate constants for the displacement of the nitrogen ligands) to the  $\text{p}K_a$  values and cone angles of the phosphorus bases. Their data, however, included many estimated  $\text{p}K_a$  values. When these estimated  $\text{p}K_a$  values are replaced by experimentally determined  $\text{p}K_a$  values,<sup>10,11</sup> then the plots of  $\log(k)$  vs.  $\text{p}K_a$  show a remarkably good linear relationship. Only for the bulky *i*-Pr $\text{H}_2\text{P}$  is there a small though detectible steric contribution.

(42) Graham, J. R.; Angelici, R. J. *Inorg. Chem.* 1967, 6, 2082-85.

(43) Langford, C. H.; Gray, H. B. "Ligand Substitution Processes"; W. A. Benjamin: New York, 1965.





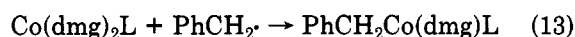
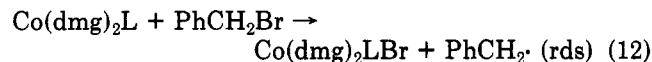
**Figure 10.** Steric profiles for the ligand dependent substitution reactions of (a)  $(\eta^5\text{-C}_9\text{H}_7)\text{Mn}(\text{CO})_3$  and (b)  $\text{V}(\text{CO})_6$ . The unlabeled point refers to  $(i\text{-Pr})_3\text{P}$ . These profiles show the extremes in steric sensitivities that we have observed. Data are taken from ref 40 and 37, respectively.

for the idenyl complex which shows the lowest steric sensitivity although it has the smallest steric threshold.

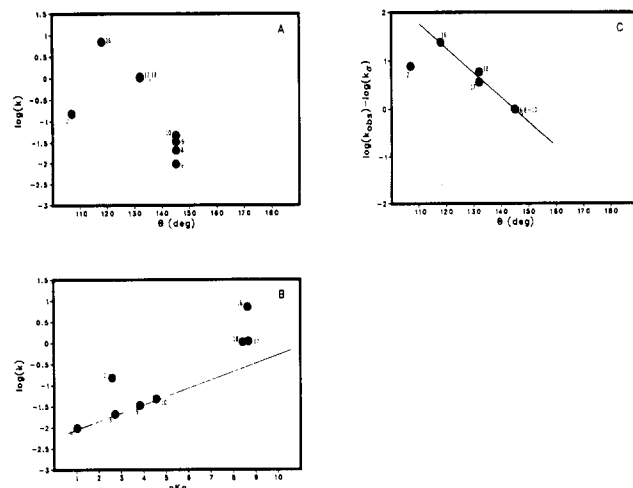
### Oxidative Addition Reactions

The application of our analysis to several sets of data for the kinetics of oxidative-addition reactions lends support to the current views concerning the factors that influence the reactivity of  $\text{Co}(\text{dmg})_2\text{L}$  and provides new and important insights into the chemistry of Vaska's compound.

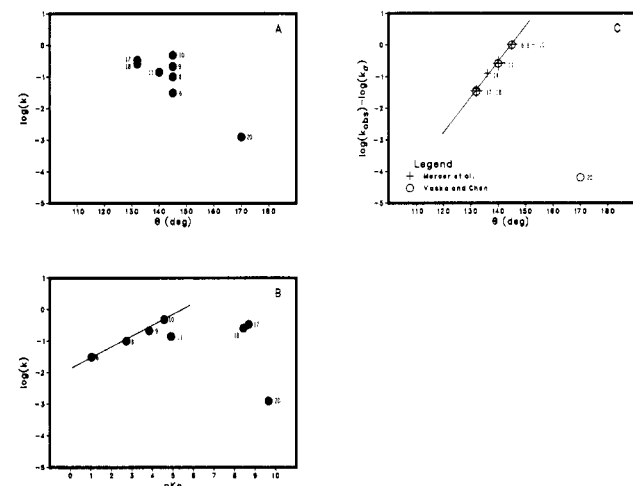
Halpern and Phelan<sup>45</sup> observed that the oxidative addition of benzyl bromide to  $\text{Co}(\text{dmg})_2\text{L}$  is strongly inhibited by increasing size and mildly accelerated by increasing basicity of the axial phosphorus ligand (eq 12 and 13). There is a good linear correlation between  $\log k$  (second-order rate constants) and substituent constants for the para-substituted arylphosphine complexes.<sup>45</sup> Our analysis



(Figure 11) shows that both electronic and steric effects of the axial ligands play important roles in determining the reactivities of the complexes. Thus, a change of 9  $\text{pK}_a$  units in the basicity of the ligand effects about a 100-fold increase in rate whereas an increase of  $38^\circ$  in the cone angles of this set of ligands has an equal but opposite effect on the rate. These ligand effects are consonant with the properties expected of an oxidative-addition reaction—the rate of reaction is increased by increasing electron donicity but decreased by increasing size of L.



**Figure 11.** Analysis of the oxidative-addition reaction of  $\text{C}_6\text{H}_5\text{CH}_2\text{Br}$  to  $\text{Co}(\text{dmg})_2\text{L}$  (eq 12 and 13): (a)  $\log(k_2)$  vs.  $\theta$ ; (b) electronic profile (line is drawn through the data points for  $(p\text{-XPh})_3\text{P}$  ( $\text{X} = \text{Cl}, \text{H}, \text{Me}, \text{MeO}$ )); (c) steric profile. Data are taken from ref 45.



**Figure 12.** Analysis of the oxidative addition of  $\text{O}_2$  to  $\text{IrCl}(\text{CO})\text{L}_2$  (eq 14–16): (a)  $\log(k_2)$  vs.  $\theta$ ; (b) electronic profile (the line is drawn through the data points for  $(p\text{-XPh})_3\text{P}$  ( $\text{X} = \text{Cl}, \text{H}, \text{Me}, \text{MeO}$ )); (c) steric profile. Point off the line corresponds to  $\text{C}_6\text{H}_5\text{P}$ . Data are taken from ref 46a and 46b.

The numerous texts and monographs that use the chemistry of Vaska's compound,  $\text{Ir}(\text{CO})\text{ClL}_2$ , to illustrate fundamental organometallic reactions attest to the important role that these iridium compounds have played in the development of organometallic chemistry.<sup>3</sup> The oxidative-addition reactions involving small molecules such as  $\text{O}_2$ ,<sup>46</sup>  $\text{H}_2$ ,<sup>46c</sup> and  $\text{MeI}$ <sup>47</sup> follow second-order kinetics, thereby suggesting that these reactions involve direct addition of the oxidant to the parent complex. The observations of complex kinetics for the oxidative addition of aryl iodides,<sup>48</sup> and the rapid interchange of free and coordinated phosphines,<sup>49</sup> point to a more complicated

(46) (a) Vaska, L.; Chen, L. S. *J. Chem. Soc., Chem. Commun.* 1971, 1080. (b) Mercer, E.; Petersen, W.; Jordan, F. *J. Inorg. Nucl. Chem.* 1972, 34, 3290. (c) Ugo, R.; Pasini, A.; Fusi, A.; Cimini, S. *J. Am. Chem. Soc.* 1972, 94, 7364–70.

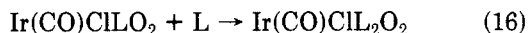
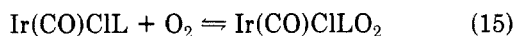
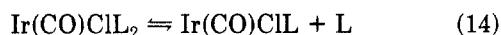
(47) (a) Labinger, J. A.; Osborn, J. A.; Coville, N. J. *Inorg. Chem.* 1980, 19, 3236–43. (b) Thompson, W. H.; Sears, C. T., Jr. *Inorg. Chem.* 1977, 16, 769–774. (c) Chock, P. B.; Halpern, J. *J. Am. Chem. Soc.* 1966, 88, 3511–14. (d) Pearson, R. G.; Muir, W. R. *J. Am. Chem. Soc.* 1970, 92, 5519.

(48) Mureinik, R. J.; Weitzberg, M.; Blum, J. *Inorg. Chem.* 1979, 18, 915.

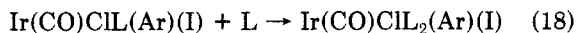
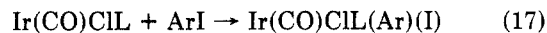
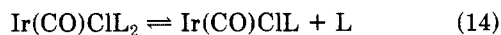
(49) (a) Garrou, P. E. *Adv. Organomet. Chem.* 1984, 23, 95–129. (b) Garrou, P. E.; Hartwell, G. E. *Inorg. Chem.* 1976, 15, 646–50.

chemistry for these complexes. Consider, for example, the addition of O<sub>2</sub> to Vaska's compound. Vaska and Chen<sup>46a</sup> observed that the rate of the second-order addition of O<sub>2</sub> to Ir(CO)ClL<sub>2</sub> increased as the basicities of L increased. Our analysis (Figure 12), which uses data from the Vaska paper and a paper by Mercer et al.,<sup>46b</sup> shows that this is the case. There is, however, a rather unexpected steric dependence. The rate of reaction increases as the size of the ligand increases; however, the complex containing Cy<sub>3</sub>P, the most sterically encumbered ligand, is the least reactive. The shape of the steric profile appears to be a composite of the steric profiles of pre-rate-determining and rate-determining steps. One step must exhibit steric acceleration. Another must exhibit steric inhibition with a rather dramatic steric threshold. The mechanism shown in eq 14–16 accounts for the second-order kinetics of the reaction (provided the equilibria described in reactions 14 and 15 are rapidly established in comparison to the rate of reaction 16) and the ligand steric effects. The first step in the reaction is the reversible dissociation of a phosphorus ligand. The rapid exchange of the ancillary phosphorus ligands observed for Vaska's compounds demonstrates the lability of these ligands.<sup>49</sup> The steric profile for reaction 14 is expected to be linear (predicted from our analysis of Barnett's data for η-C<sub>5</sub>H<sub>5</sub>-(CO)<sub>2</sub>LMoCOMe (vide supra)). This accounts for the steric acceleration of the reaction for ligands with small cone angles. The reversible addition of the small dioxygen molecule to the coordinatively unsaturated (or solvated) Ir(CO)ClL (reaction 15) is expected to be relatively insensitive to steric effects and show a very large steric threshold. The last and rate-determining step (reaction 16), which involves nucleophilic readdition of the phosphorus ligand to Ir(CO)ClO<sub>2</sub>, should exhibit a steric profile with a steric threshold similar to that observed for entering ligand dependent substitution reactions. Steric inhibition of this last step would account for the low reactivity of the Cy<sub>3</sub>P complex.

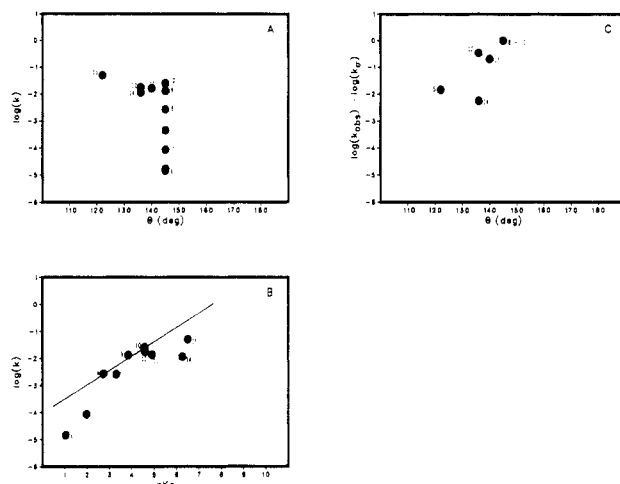
The electronic profile (Figure 12b) for the addition of oxygen to Ir(CO)ClL<sub>2</sub> shows that the rate of reaction is accelerated by increasing basicity of L. Reaction 14 is decelerated<sup>48</sup> whereas reaction 15 (oxidative addition) may be accelerated by increasing basicity. The effect of basicity on the last step is in doubt. Increasing σ-donicity of the ancillary ligand in Ir(CO)ClO<sub>2</sub> should retard the addition of another phosphorus base. On the other hand, increasing basicity of the nucleophile will accelerate the reaction.



This reaction scheme is a variation of the mechanism proposed by Mureinik et al.<sup>48</sup> for the oxidative addition of ArI to Ir(CO)ClL<sub>2</sub> (eq 14, 17, and 18). The rate-de-



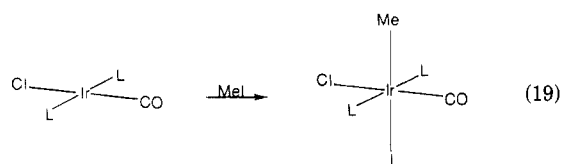
termining step in this mechanism is the oxidative addition of the ArI to the coordinatively unsaturated intermediate Ir(CO)ClL rather than the readdition of the L group as we propose for the addition of dioxygen. Undoubtedly, this can be attributed to the low reactivity of aryl iodides toward oxidative addition. Mureinik felt that the mechanism for the addition of the aryl iodides was unusual for the iridium complexes and that it was the result of the high temperatures required for the reaction to proceed at a



**Figure 13.** Analysis of the oxidative addition of CH<sub>3</sub>I to IrCl(CO)L<sub>2</sub> (eq 19): (a) log(*k*<sub>2</sub>) vs. θ; (b) electronic profile (solid line is drawn through the data points for (*p*-XPh)<sub>3</sub>P (X = H, Me, MeO); dotted line is drawn through the data points for (*p*-XPh)<sub>2</sub>P (X = Cl, F, H, Me, MeO)); (c) steric profile. Data are taken from ref 47b.

reasonable rate. Predicated on our results, we believe that Mureinik's mechanism may be quite common in the chemistry of Vaska's complex.

The oxidative addition of methyl iodide to Vaska's compound (eq 19), which has been studied by a number



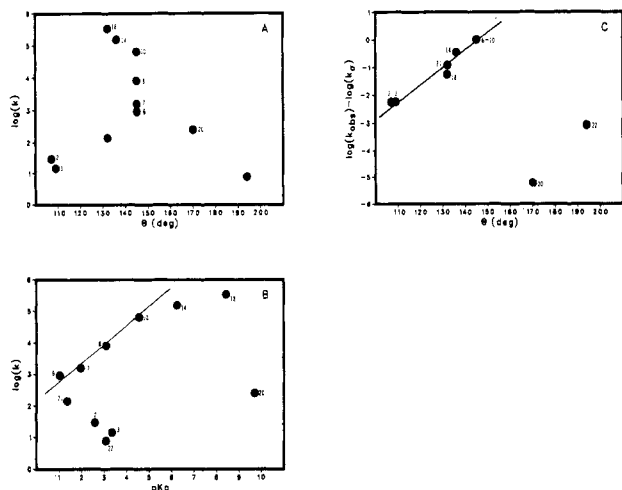
of groups,<sup>47</sup> follows a nonradical pathway<sup>47a</sup> obeying second-order kinetics.<sup>47b,c</sup> The methyl and iodo groups as well as the ancillary phosphines are trans in the final hexacoordinate product. The product fails to incorporate <sup>131</sup>I when the addition is performed in a solution containing <sup>131</sup>I.<sup>47d</sup> Thompson and Sears,<sup>47b</sup> who studied the ligand effects of phosphines on the rate of the reaction, observed that log *k* for the second-order rate constants correlated with the Kabachnic<sup>50</sup> substituent constants but not with the Hammett σ values. The reactivities of the mixed methyl- and ethylphenylphosphines do not correlate with either their basicities or cone angles.

Our analysis (Figure 13) of the ligand effects indicates that the mechanism of this reaction is complex and may involve competing reaction pathways. There is not a good linear relationship between the p*K*<sub>a</sub> values for the triarylphosphines and log *k* (Figure 13b). The slope (0.96) of a best fit line forced through the five points for the complexes containing the triarylphosphines is the largest encountered for any reaction that we have analyzed. The slope is greater than that observed for the addition of benzyl bromide to Co(dmg)<sub>2</sub>L (0.19)<sup>45</sup> or for the reaction between L and EtI (0.29).<sup>51</sup> The slope is much greater than that observed for other reactions of Ir(CO)ClL<sub>2</sub> (O<sub>2</sub>, 0.33;<sup>46a</sup> H<sub>2</sub>, 0.14<sup>46c</sup>). On the other hand, a good linear relationship is obtained when only the class II triarylphosphines are used to determine the electronic profile.

(50) Nastyukova, T. A.; Kabachnic, M. I. *Russ. Chem. Rev. (Engl. Transl.)* 1969, 38, 795–811.

(51) Henderson, W. A., Jr.; Buckler, S. A. *J. Am. Chem. Soc.* 1960, 82, 5794–5800.

(52) Atton, J. G.; Kane-Maguire, L. A. P. *J. Chem. Soc., Dalton Trans.* 1982, 1491–98.

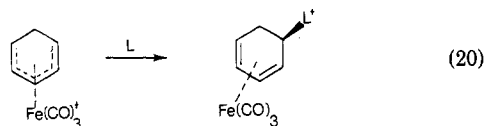


**Figure 14.** Analysis of the nucleophilic addition of phosphorus(III) bases to the hexadienyl ligand of  $(\eta^5\text{-C}_6\text{H}_7)\text{Fe}(\text{CO})_3^+$ . Points labeled 21 and 22 refer to  $(\text{NCCH}_2\text{CH}_2)_3\text{P}$  and  $(o\text{-MePh})_3\text{P}$ , respectively: (a)  $\log(k)$  vs.  $\theta$ ; (b) electronic profile (line is drawn through the data points for  $(p\text{-XPh})_3\text{P}$  ( $\text{X} = \text{Cl}, \text{H}, \text{Me}, \text{MeO}$ )); (c) steric profile. Data are taken from ref 52.

This analysis gives a slope (0.53) that corresponds more closely with the slopes observed for the addition of dihydrogen or dioxygen to Vaska's compound. The deviation of the class III ligands,  $(p\text{-FPh})_3\text{P}$  and  $(p\text{-ClPh})_3\text{P}$ , from the electronic profile parallels their  $\pi$ -acidities, suggesting that some step in the mechanism may be particularly sensitive to the  $\pi$ -effects of the ligands. A simple steric profile could not be obtained (Figure 13c), thereby suggesting that competing reactions may be involved in the mechanism of the reaction.

### Nucleophilic Addition to Coordinated Ligands

Atton and Kane-Maguire<sup>50</sup> studied the nucleophilicities of phosphorus bases for addition to the hexadienyl ligand of  $\eta^5\text{-C}_6\text{H}_7\text{Fe}(\text{CO})_3^+$ . A good LFER was found between the  $pK_a$  values of the triarylphosphines and  $\log k$  (second-order rate constants) for what was believed to be a one-step nucleophilic addition reaction (eq 20). In addition, it was



noted that the deviations of other data points from this line are probably a quantitative measure of the steric requirements of the phosphines in the addition reactions. The quantification of the steric requirements of the reaction was, however, taken no further. Our analysis of the data (Figure 14) is in agreement with that of the authors and shows that the rate increases with basicity. Surprisingly, the steric profile (Figure 14c) shows that the rate of reaction increases as the size of the incoming nucleophile increases, except for the very bulky  $\text{Cy}_3\text{P}$  and  $(o\text{-MePh})_3\text{P}$ . (The point for  $(\text{PhO})_3\text{P}$  inexplicably does not correlate well

and has been left out of the analysis.) The steric profile clearly shows that the unusually low reactivity  $(\text{MeO})_3\text{P}$  is due to its small size and not to an electronic effect. The results of our analysis are inconsistent with simple nucleophilic addition of the phosphorus base to the substrate.

### Ligand Effects in the Chemistry of $(\eta\text{-Allyl})\text{nickel}$ Complexes

Schenkluhn and co-workers<sup>18</sup> attempted to separate quantitatively the contributions of steric and electronic factors in determining product distributions for a number of reactions of  $(\eta^3\text{-allyl})\text{nickel}$  complexes.<sup>18</sup> The procedure involved the correlations of thermodynamic and product distribution data with cone angles and Tolman  $\chi_i$  values. The studies generally included complexes containing a rich variety of phosphorus ligands that spanned a wide range of cone angles and  $\chi_i$  values. Multilinear regression analyses revealed the relationships between the reaction properties and the ligand properties. While we do not question this analytical procedure, which, in fact, resembles our own, we do not believe that  $\chi_i$  values are the appropriate electronic parameters to be used in the analyses. The  $\chi_i$  values include significant contributions from both  $\sigma$ - and  $\pi$ -effects. If the relative contributions to the reaction parameters are not the same as the contributions to the  $\chi_i$  values, then this approach may lead to erroneous interpretations. It is noteworthy that Schenkluhn observed that data for many class II phosphines did not correlate well.<sup>18a</sup> This lack of correlation for the class II ligands constitutes a fundamental problem with this approach that masks the true relationship between the reaction parameters and ligand properties. A good example of this problem is illustrated by a consideration of our data shown in Figure 3. If the class II phosphines are excluded from consideration, then a reasonably good (although erroneous) linear correlation appears to exist between the  $E_L^\circ$  values and the  $pK_a$  values of the class I and class III ligands, with the class II ligands lying significantly off the line. The incorrect conclusion is then reached that the  $E_L^\circ$  values for all ligands correlate linearly with the  $pK_a$  values for the phosphorus bases. We are unable to reanalyze the Schenkluhn work because of the lack of appropriate kinetic data.

### Conclusions

It has been demonstrated in this paper that ligand effects provide a powerful, general, and simple method of probing organometallic reaction mechanisms. These ligand effects give insight into the nature of the rate-determining steps of important organometallic reactions, as well as insight into pre-rate-determining steps that may be invisible to standard kinetic analyses. The reactivities of the phosphorus(III) ligands considered in this paper are mainly dominated by steric effects and  $\sigma$ -donicities. Even though these phosphorus ligands may function as  $\pi$ -acids or  $\pi$ -bases, these  $\pi$ -effects have relatively little impact on the reactivities of the phosphorus bases or their metal complexes.