

Quantifying the Electron-Donating Strength of Phosphine Ligands

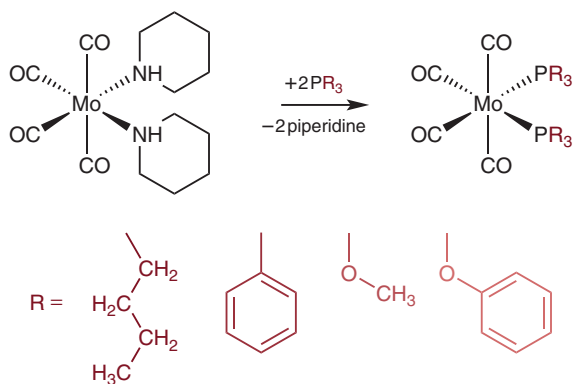
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The electron-donating ability of a ligand is one of the most important properties that students encounter in their study of inorganic chemistry. Properties of metal complexes ranging from color to oxidation potential are greatly affected by the donor and acceptor strength of the supporting ligands (1, 2). From metalloproteins in nature to synthetic organometallic catalysts, varying ligand-donor strength is one of the most direct ways of “tuning” the reactivity of a metal center (1–3). It is therefore essential for student success that they can judge the electron-donor strengths of different ligands and predict their impact on the properties of a metal center.

Despite the central role played by ligand-donor ability in coordination chemistry, students are often provided with few tools for estimating this property for a given ligand. Common descriptions of ligands using Lewis structures and molecular orbital theory explain how they bind to metals (e.g., as σ -donors or π -acceptors), but they do not provide much insight into quantifying the strength of these interactions. This is especially true for ligands whose “net” donor ability results from a mixture of both electron-donor and -acceptor interactions (1, 2). Consequently, students often learn only the relative donor strength of different ligands in a qualitative way that is not easily applied to solving real-world chemical problems.

One method that can make abstract physicochemical properties easier to understand and use is to assign quantitative values to these properties. The Hammett σ -parameters in organic chemistry are excellent examples of quantifying the electronic effect of chemical substituents in a concrete fashion (4). A number of similar electronic parameters have been devised for quantifying the electron-donor ability of ligands as well (5–9). Importantly, many of these parameters show excellent mathematical correlations with the properties of metal complexes, including the CO stretch of metal–carbonyls (5–9). We have



Scheme 1. General synthetic scheme for $\text{cis-Mo(CO)}_4(\text{PR}_3)_2$ complexes used in this laboratory.

incorporated discussions of these quantitative parameters into our undergraduate inorganic chemistry classes and have found them useful for helping students understand ligand-donor ability in a more concrete way.

Presented herein is a laboratory experiment we currently use in our undergraduate inorganic chemistry course in which students examine the property of ligand-donor strength and its impact on a transition-metal center. Students synthesize a series of four $\text{cis-Mo(CO)}_4(\text{PR}_3)_2$ complexes with ligands having a wide range of electron-donating strengths: $\text{PR}_3 = \text{P}(n\text{-butyl})_3$, PPh_3 , P(OMe)_3 , and P(OPh)_3 ; see Scheme 1.¹ These complexes are characterized by FT-IR spectroscopy, with an A_1 carbonyl stretch (νCO_{Mo}) used as a handle for measuring the electron density of the molybdenum center. Using these data, students qualitatively rank the electron-donor strength of this series of PR_3 ligands. Moreover, students use the Tolman electronic parameter (TEP), the quantitative analysis of ligand effects (QALE) model, and the molecular electrostatic potential (MESP) as quantitative measures of phosphine donor strength. By developing linear correlations between these parameters and their experimental νCO_{Mo} data, students can estimate the νCO_{Mo} values for additional $\text{cis-Mo(CO)}_4(\text{PR}_3)_2$ complexes not synthesized in this laboratory. This combined qualitative and quantitative investigation provides students with valuable insight into ligand-donor ability and its application in tuning the properties of a metal complex.

Qualitative Descriptions of Phosphine Bonding

Tertiary phosphines are ideally suited for exploring ligand electronic effects. Their ability to act as both σ -donors and π -acceptors helps to familiarize students with the general types of ligand properties encountered in coordination chemistry (1, 2). Moreover, by changing the electron-withdrawing or -donating nature of the R groups, their net donor strength can be varied over a wide range in a systematic fashion (1, 2). This variability within an analogous series of ligands allows students to clearly elucidate substituent effects while avoiding complicating factors, such as comparing the donor strength of phosphines and thioethers (10).

Both the donor–acceptor properties of phosphines and the varying magnitude of these interactions can be qualitatively explained to students using a combination of Lewis structures or molecular orbital (MO) theory (1, 2). For instance, the enhanced π -acidity of P(OMe)_3 relative to $\text{P}(n\text{-butyl})_3$ is ascribed to a lowering in energy of the $\text{P-R} \sigma^*$ -orbital with more electronegative R groups, allowing for more efficient metal– PR_3 backbonding (2). This type of explanation is effective in allowing students to qualitatively rank the donor ability of different phosphines. Unfortunately, neither Lewis structures nor MO theory are easily applied to quantifying the magnitude of these differences. Such differences in donor ability are more effectively quantified using methods described below.

Quantifying Phosphine Donor Ability

Tolman Electronic Parameter

The most widely used parameter for quantifying the donor ability of a phosphine ligand is the Tolman electronic parameter (5, 6). The TEP for a particular PR_3 ligand is an empirical quantity obtained by measuring the IR spectrum of its $\text{Ni}(\text{CO})_3(\text{PR}_3)$ complex, νCO_{Ni} . Because the νCO value for a metal–carbonyl is a good indicator of the electron density on the metal center, the TEP can be used as a simple measure of the combined σ -donor– π -acceptor strength of a phosphine (5, 6).

The TEP has been shown to correlate linearly with the νCO values for many metal– PR_3 complexes (5–7), demonstrating its usefulness as a general indicator of phosphine donor ability:

$$\nu\text{CO}_{\text{metal}} = a \nu\text{CO}_{\text{Ni}} + b \quad (1)$$

Once two different metal–CO complexes with different PR_3 ligands are characterized, the linear coefficients a and b in eq 1 can be determined. This correlation can then be used to estimate the νCO value and, consequently, to predict the impact of any given PR_3 ligand on the electronic properties of a metal complex even before the complex is synthesized.

Quantitative Analysis of Ligand Effects

Whereas the TEP describes the overall donor ability of a tertiary phosphine with a single parameter, the quantitative analysis of ligand effects model uses four different parameters to more accurately elucidate the σ -donating (χ_d), π -accepting (π_p), aryl (E_A), and steric (θ) effects of ligand substituents (5, 8). The values of these parameters have been determined for common phosphines through the statistical analysis of hundreds of sets of experimental data and are available in the literature (5, 8). Like the TEP values, QALE values have been shown to correlate linearly with the νCO value for a variety of metal–carbonyls, as follows:

$$\nu\text{CO}_{\text{metal}} = a\chi_d + b\theta + cE_A + d\pi_p + e \quad (2)$$

While the QALE provides a more complete picture of a phosphine's donor–acceptor ability than the TEP, determining χ_d , π_p , E_A , and θ for each ligand is more difficult, requiring the characterization of a large number of metal complexes. Moreover, because there are five coefficients in eq 2, $\nu\text{CO}_{\text{metal}}$ must be measured using at least five different PR_3 ligands to determine a , b , c , d , and e . For these reasons, the QALE is most useful for well-studied ligands for which there exists significant experimental data and is not useful for new or relatively unexplored ligands (5).

Molecular Electrostatic Potential

Other researchers have developed purely theoretical methods for quantifying phosphine donor strength, allowing this property to be estimated even for ligands that have yet to be synthesized. One readily calculated property that is related to ligand basicity is the molecular electrostatic potential (MESP) (5, 9). The MESP map of a molecule describes the charge distribution within that molecule, with negative values indicating areas of increased electron density (5, 9). For phosphines, the electrostatic potential is therefore negative in the lone pair region, with the absolute minimum value (V_{min}) having been shown to be a good indicator of net donor ability (5, 9).

The calculated value of V_{min} reflects the impact of the substituents on the phosphorus atom and has been shown to correlate with ligand basicity (5, 9). For example, electron-donating *n*-butyl groups yield a more negative value of V_{min} (–43.17 kcal/mol) than more electronegative methoxy groups (–34.58 kcal/mol) (9b). V_{min} has also been shown to correlate with the $\nu\text{CO}_{\text{metal}}$ of metal–phosphine complexes in a linear fashion:

$$\nu\text{CO}_{\text{metal}} = aV_{\text{min}} + b \quad (3)$$

Thus, V_{min} can be used like the TEP to predict the impact of a phosphine on the properties of a metal center, with the important advantage that it can be estimated without the synthesis of a metal complex or even the ligand itself (5, 9).

Experimental Summary and Discussion

Synthesis of *cis*- $\text{Mo}(\text{CO})_4(\text{PR}_3)_2$ Complexes

The series of four *cis*- $\text{Mo}(\text{CO})_4(\text{PR}_3)_2$ complexes examined in this laboratory can be synthesized by students in one 3–4 hour laboratory period from *cis*- $\text{Mo}(\text{CO})_4(\text{piperidine})_2$ using modifications of procedures reported in this *Journal* (11) and others (12) (see the accompanying online material for full synthetic details). We have carefully chosen the ligands $\text{P}(n\text{-butyl})_3$, PPh_3 , $\text{P}(\text{OMe})_3$, and $\text{P}(\text{OPh})_3$ to span the range of electron-donating and -accepting properties commonly available for PR_3 ligands, thereby providing the students with the maximum observable shift in νCO_{Mo} .

The *cis*- $\text{Mo}(\text{CO})_4(\text{PR}_3)_2$ complexes can be isolated from the reaction mixtures as previously reported in the literature, allowing students to obtain FT-IR spectra of the purified compounds (11, 12). Alternatively, we have found that measuring the spectrum of a drop of the crude reaction solutions between two salt plates or directly on the window of an ATR-equipped instrument yields similar results while eliminating the time-consuming isolation procedures. The spectrum of each complex contains four carbonyl bands in the ca. 1850–2050 cm^{-1} region, consistent with their C_{2v} symmetry (11, 12). However, we use only the A_1 stretch around ca. 2000–2050 cm^{-1} for comparing the different complexes owing to the often overlapping and unresolved nature of the lower-energy bands.

A representative IR spectrum of student data is shown in Figure 1. From this plot, students can observe how more

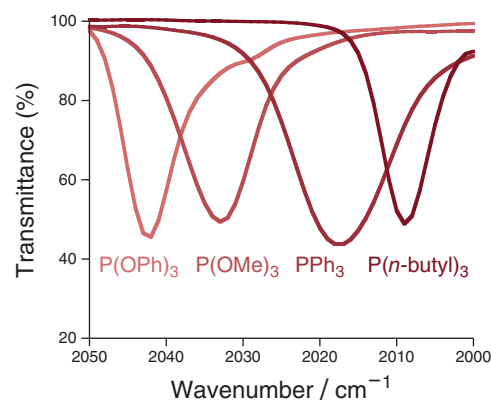


Figure 1. Representative plot of student FT-IR data for the A_1 stretch of four *cis*- $\text{Mo}(\text{CO})_4(\text{PR}_3)_2$ complexes measured in crude reaction solutions by ATR (normalized for comparison).

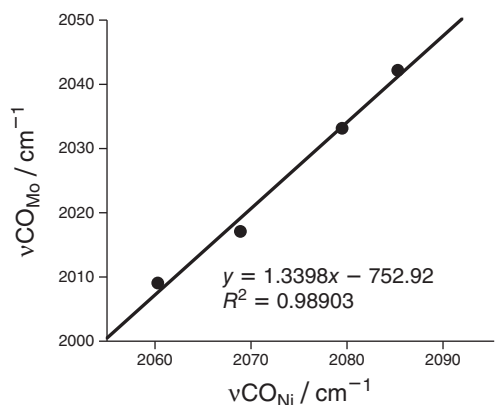


Figure 2. Plot of νCO_{Mo} versus the Tolman parameter, νCO_{Ni} .

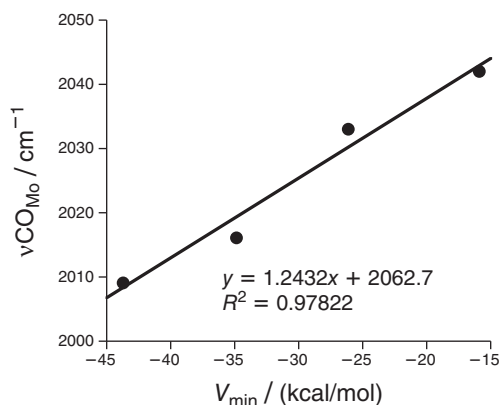


Figure 3. Plot of νCO_{Mo} versus the minimum electrostatic potential, V_{min} .

electron-withdrawing substituents result in decreased metal–CO backbonding and a progressively stronger C≡O bond, consistent with qualitative predictions based on inductive effects (1, 2). Indeed, the CO stretch with the most acidic ligand, P(OPh)₃ ($\nu\text{CO}_{\text{Mo}} = 2042 \text{ cm}^{-1}$), shifts by 33 cm^{-1} when the strongly donating P(*n*-butyl)₃ is used ($\nu\text{CO}_{\text{Mo}} = 2009 \text{ cm}^{-1}$). These results provide students with a clear demonstration of how the properties of a metal center can be tuned through systematic and incremental changes in an analogous series of ligands.

Quantitative Analysis of Vibrational Data

For quantitative insight into phosphine donor ability, students use νCO_{Ni} , V_{min} , and the QALE parameters to derive linear correlations between phosphine donor strength and their νCO_{Mo} data. These parameters for each ligand can be found in Table 1 of the online material. The correlation using the Tolman parameter is determined by plotting the four experimental νCO_{Mo} values from Figure 1 (y axis) versus the respective νCO_{Ni} values (x axis) as shown in Figure 2. Analysis of the data reveals an excellent linear relationship between νCO_{Mo} and νCO_{Ni} ($R^2 = 0.98903$):

$$\nu\text{CO}_{\text{Mo}} = 1.3398 \nu\text{CO}_{\text{Ni}} - 752.92 \text{ cm}^{-1} \quad (4)$$

The parameters from this equation can be compared with the values of slope (1.686) and intercept (-1468.8 cm^{-1}) obtained by Crabtree in his investigation of *cis*-Mo(CO)₄(PR₃)₂ complexes using mono- and bidentate phosphine ligands (7). An analogous treatment of the data using V_{min} as the measure of phosphine donor ability is also performed. Plotting νCO_{Mo} versus V_{min} (Figure 3) followed by regression analysis also results in an excellent linear correlation ($R^2 = 0.97822$):

$$\nu\text{CO}_{\text{Mo}} = 1.2432 V_{\text{min}} + 2062.7 \text{ cm}^{-1} \quad (5)$$

To perform a similar analysis using the QALE parameters and νCO_{Mo} , students must determine the five linear coefficients a , b , c , d , and e for eq 2. With only four experimental νCO_{Mo} values, this is not possible. An additional νCO_{Mo} value for PR₃ = PPh₂Me is provided to facilitate this calculation. Using all five νCO_{Mo} values and the ligand parameters χ_{d} , π_{p} , E_{A} , and

θ , students can perform a multivariable linear regression analysis to obtain eq 6 (see the online material for details):

$$\nu\text{CO}_{\text{Mo}} = (4.837 \chi_{\text{d}} - 0.09062 \theta - 11.067 E_{\text{A}} - 10.268 \pi_{\text{p}} + 1995.9) \text{ cm}^{-1} \quad (6)$$

Application of Linear Correlations

As a final test, students use their three linear correlations to predict νCO_{Mo} for PR₃ = PPhMe₂, P(NMe₂)₃, and PH₃ (the appropriate ligand parameters are found in the online material). Students typically arrive at several important conclusions: (a) all three methods predict an accurate and similar νCO_{Mo} value for PPhMe₂, (b) the TEP and V_{min} give reasonable values for P(NMe₂)₃ (QALE parameters are not available for this ligand), and (c) V_{min} is particularly useful in the cases like PH₃ where there is no available TEP or QALE data. Overall, these quantitative approaches, combined with a traditional qualitative comparison of ligand-donor properties, provide students with important insight into phosphine donor strength that can be applied to solving practical chemical problems.

Hazards

Molybdenum hexacarbonyl and its derivatives are toxic solids. Piperidine, heptane, and tetrahydrofuran are toxic, flammable liquids. Dichloromethane is a toxic and potentially carcinogenic liquid. Triphenylphosphine is an irritant and a potential neurotoxin. Triphenylphosphite and trimethylphosphite are toxic, flammable liquids. Tributylphosphine is a toxic liquid that is potentially flammable in air, and it should be dispensed using syringes. All manipulations described herein should therefore be performed in a fume hood while wearing gloves, goggles, and using proper safety precautions to avoid contact with reagents or products.

Acknowledgment

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Note

1. The term phosphine is generally used to refer to phosphorus(III) ligands having alkyl or aryl substituents, whereas phosphite is used for phosphorus(III) ligands having alkoxy substituents. For simplicity, we have used the term phosphine to describe all PR_3 ligands and "R" to represent any substituent on the phosphorus atom.

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