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Article

Comments on the Electrostatic Minimum Potential (V_{min}) as a Measure of the Electron-Donating Power of PZ_3

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In a recent publication, Suresh and Koga suggested that the molecular electrostatic potential minimum (V_{min}) could be used as a quantitative measure of the "σ donating power" of substituted phosphorus(III) ligands. In support of this assertion, they showed linear correlations between a number of physicochemical properties and V_{min}. Our examination of the analyses of the sets of experimental data used to support this assertion shows unequivocally that the variations in the properties cannot be described by a single parameter. Therefore, the utility of V_{min} as a measure of the "σ donating power" of substituted phosphorus(III) ligands remains unsubstantiated.

Introduction

Recently, Suresh and Koga[1] suggested that the molecular electrostatic potential minimum (V_{min}) alone could be used as a quantitative measure of the "σ donating power" of substituted phosphine ligands. If this were true, then V_{min} would be a direct measure of the electron-donating power of phosphines as opposed to indirect measures such as terminal carbonyl-stretching frequencies (ν_{CO}) or pK$_a$ values of HPR_3^+. In support of this assertion, the authors found, in all but one case, linear correlations between a number of calculated properties of phosphine complexes (e.g., ΔE_{rx}) as well as experimental data (pK$_a$, ν_{CO}, $\Delta H°$, $E°$) and V_{min}. The exception was the correlation of V_{min} with the calculated ΔE_{rx} values for the reaction between MnH_3NH_3 and PZ_3. It is implied that the lack of correlation in this latter system can be attributed to π-back-bonding. It follows from the authors' arguments that the linear relationships that they observe between a property and V_{min} indicate the lack of involvement of other stereoelectronic effects. A closer examination of the authors' analyses reveals that the relationships between V_{min} and the physicochemical properties considered are not as simple as suggested.

Discussion

In the following discussion we will show (A) that the PR_3 (R = alkyl) and $P(p\text{-}XC_6H_4)_3$ families must be treated separately when doing a one-parameter correlation analysis and (B) that a linear correlation between a property and a parameter does necessarily convey fundamental information with a restricted set of data and in the absence of a model of ligand effects.

There are a number of pieces of evidence that militate against V_{min} as the single descriptor of the properties considered by Suresh and Koga. First, an important part of their argument revolves around the putative linear relationships observed between both V_{min} and $E°$ (229 K) and $\Delta H°$ for reaction 1.[2,3] We have recreated these plots in Figure 1A,B. In addition, we have included the point for $P(OCH_2CH_2Cl)_3$,[4] which was not included in the plots in the Suresh and Koga paper.

$$\eta\text{-Cp(CO)(L)Fe(COMe)}^+ + e = \eta\text{-Cp(CO)(L)Fe(COMe)}^0 \quad (1)$$

It appears that there is a linear relationship between $E°$ (229 K) and V_{min} when the point (on the far right) for $P(OCH_2CH_2Cl)_3$ is ignored (Figure 1A). The same can be said for the plot of $\Delta H°$ versus V_{min} (Figure 1C). If the plots of $E°$ (229 K) and $\Delta H°$ versus V_{min} were truly linear, then the plot of $\Delta S°$ versus V_{min} must also be linear. Inspection of Figure 1E shows that this is not the case unless the two points on

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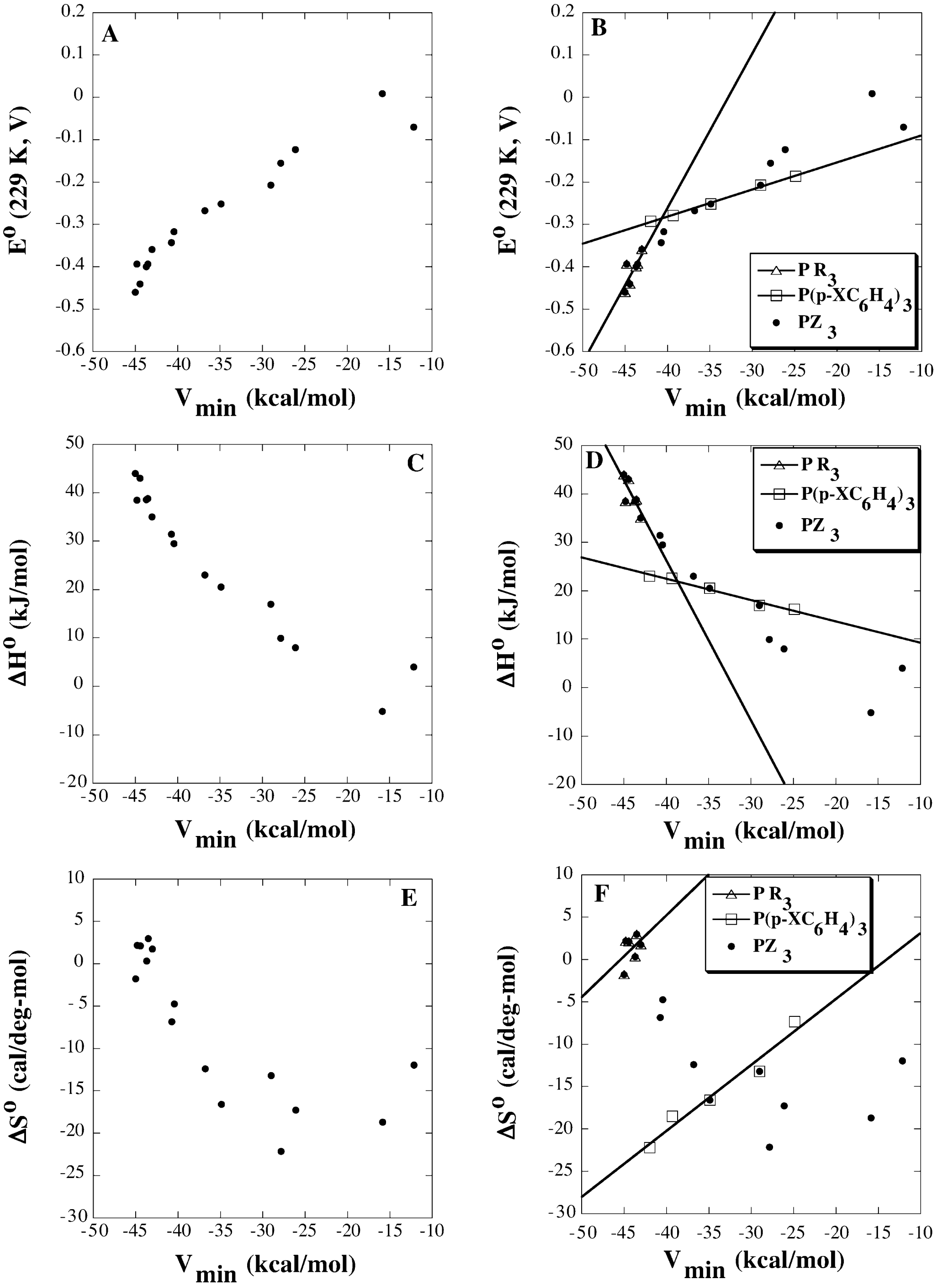

Figure 1. Plots of $E°$, $\Delta H°$, and $\Delta S°$ for reaction 1 versus V_{min}. Plots B, D, and F include data for $P(p\text{-}XC_6H_4)_3$ (X = MeO, Me, Cl) whose V_{min} values were calculated via the QALE model (see text). The lines in B, D, and F are drawn through the points for the families PR_3 and $P(p\text{-}XC_6H_4)_3$.

the right side of Figure 1E are ignored. The scatter in $\Delta S°$ cannot be attributed to noise since $\Delta S°$ along with $E°$ and $\Delta H°$ give excellent multiparameter fits with the QALE model[3] (quantitative analysis of ligand effects).[2]

The second piece of evidence that indicates that more than one parameter is involved comes from a property versus property plot ($E°$ versus $\Delta H°$, Figure 2) for reaction 1.[5] The importance of a property versus property plot is that its interpretation is independent of any model. If both these properties depend linearly on a single-parameter only, then a single line must result. It is easily seen that the data fall along three lines, each corresponding to a different family of ligands, PR_3, $P(p\text{-}XC_6H_4)_3$, and $P(O\text{-}p\text{-}XC_6H_4)_3$ (vide infra). This means that at least two parameters are needed to describe the variations in $E°$ and $\Delta H°$.

The third piece of evidence that $E°$ and $\Delta H°$ (reaction 1) cannot be linearly related to a single parameter comes from a consideration of the fan-shaped plots[2] that result when $E°/T$ is plotted versus $1/T$ as shown in Figure 3. It is clear that PR_3 and $P(p\text{-}XC_6H_4)_3$ form families that exhibit isoequilibrium temperatures that are statistically distinguishable. Even the data for $P(O\text{-}p\text{-}XC_6H_4)_3$ appear to show a region of

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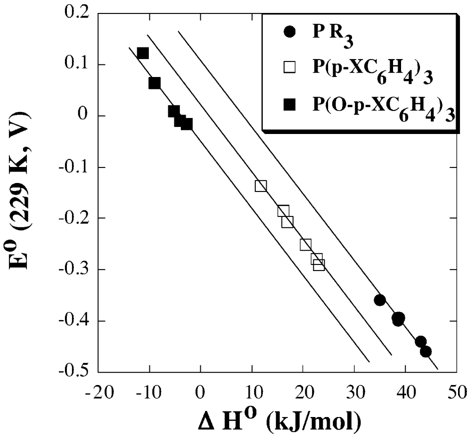

Figure 2. Plot of $E°$ versus $\Delta H°$ for reaction 1.

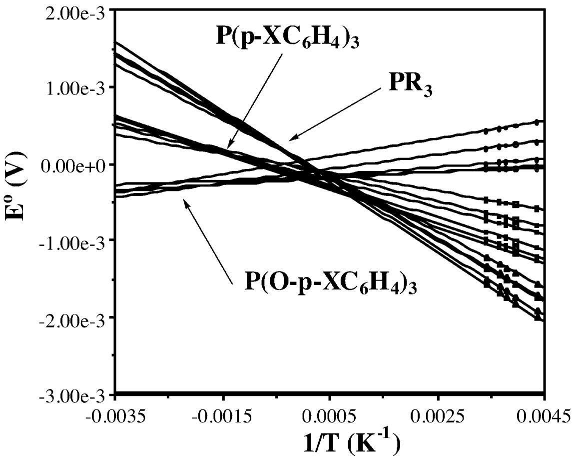

Figure 3. Plots of $E°/T$ for reaction 1 versus 1/*T*.

intersection that is certainly different from those for PR_3 and $P(p\text{-}XC_6H_4)_3$. These observations demand that these families of PZ_3 must be responding to effectively single variables (linear combination of parameters) and these variables must be different for each family. Again, it is important to note that this conclusion is independent of any model.

Clearly, based on these three pieces of evidence, V_{min} alone cannot describe the variations in $E°$ and $\Delta H°$.

An Apparent Linear Correlation Might Not Be Correct

It is a commonly held notion that a linear correlation between two properties conveys fundamental information about the relationship between the two properties. For example, the plots displayed in Figure 1A,B suggest that V_{min} is playing an important role in determining $E°$ and $\Delta H°$. This might be true but we will show that a simple linear correlation between two properties does not necessarily provide any fundamental information in the absence of a model and in fact can lead to the wrong conclusion. For a definitive answer, the behavior of the individual families must be examined. We will illustrate this concept below. We start with a system where a linear correlation is approximately correct and then progress to a system where a linear correlation leads to an incorrect conclusion.

It is important to note that the isoequilibrium behavior of PR_3 and $P(p\text{-}XC_6H_4)_3$ in reaction 1 demands that data for these two families of ligands be treated separately. If the property is responding to a single parameter, then the data for the families must form a single line when plotted versus this parameter. If the data do not form a single line, then more than one parameter is involved. Also, it is important to note the well-accepted fact that within the family of $P(p\text{-}XC_6H_4)_3$ only their σ donor ability changes as the substituent X changes.[6−8]

Now, consider a plot of $E°$ (reaction 1) for PR_3 and $P(p\text{-}XC_6H_4)_3$ versus the QALE [5,6,9] σ donor parameter χ_d. These points give a linear plot with a high correlation coefficient ($r^2 = 0.995$) and excellent standard errors. (Figure 4A). *However, the high degree of correlation alone is not sufficient to say that there is a real linear relationship between* $E°$ *and only* χ_d. We know from the three pieces of evidence presented above that the PR_3 and $P(p\text{-}XC_6H_4)_3$ families must respond to at least two different parameters. Therefore, the plot in Figure 4A, which shows a single line through the points, cannot be correct and is actually misleading because it implies that PR_3 and $P(p\text{-}XC_6H_4)_3$ constitute a single family.[2] Figure 4B shows the correct graphical analysis.

However, because the line drawn through all the points in Figure 4A essentially parallels the line drawn through the points for $P(p\text{-}XC_6H_4)_3$ in Figure 4B, we can safely state that for this set of ligands $E°$ depends mainly on χ_d.

In Figure 1B, we replot the $E°$ values of reaction 1 versus V_{min}. For illustrative purposes and clarity, we extended the range of the $P(p\text{-}XC_6H_4)_3$ data by calculating V_{min} values for X = MeO, Me, and Cl via the QALE model.[10] The inclusion of these points does not alter the slope of the line drawn through the two points for $P(p\text{-}XC_6H_4)_3$ (X = H, F) for which Suresh and Koga presented V_{min} values. In Figure 1D, we make the same presentation for $\Delta H°$. In both cases, we observe that the points for PR_3 and $P(p\text{-}XC_6H_4)_3$ form lines with very different slopes. Once again, we see that V_{min} cannot be the single parameter describing variations in these properties.

In another of their analyses, Suresh and Koga plot ν_{CO} for $Ni(CO)_3(PZ_3)$ versus V_{min} (Figure 5A) and observed what appears to be a reasonably good linear relationship. However, when the appropriate lines are drawn through the points for

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(10) It is interesting and probably noteworthy that V_{min} is well-described by the QALE model.[5,11] $V_{min} = -(101 \pm 5) + (2.7 \pm 0.1)\chi_d + (0.30 \pm 0.03)\theta - (5.1\pm0.6)E_{ar}$. $n = 24$, $s = 1.474$, and r2 = 0.971. A reviewer noted that he had recently calculated some new V_{min} (kcal/mol) values for $PH(CH_2CH_2CN)_2$, $PH(octyl)_2$, $PEtMe_2$, and PEt_2Me (−17.0, −39.4, −42.9, and −43.1). Using the QALE equation, we obtain −19.3, −40.1, −42.5, and −43.1, respectively. This attests to the utility of the QALE equation. Using this equation, we calculated V_{min} values for $P(p\text{-}MeOC_6H_4)_3$, $P(p\text{-}MeC_6H_4)_3$, and $P(p\text{-}ClC_6H_4)_3$ (−42.0, −39.3, and −24.9). Almost identical values of V_{min} can be calculated from the linear relationship between V_{min} and χ_d for PPh_3, $PPh_2(p\text{-}FC_6H_4)$, and $P(p\text{-}FC_6H_4)_3$.

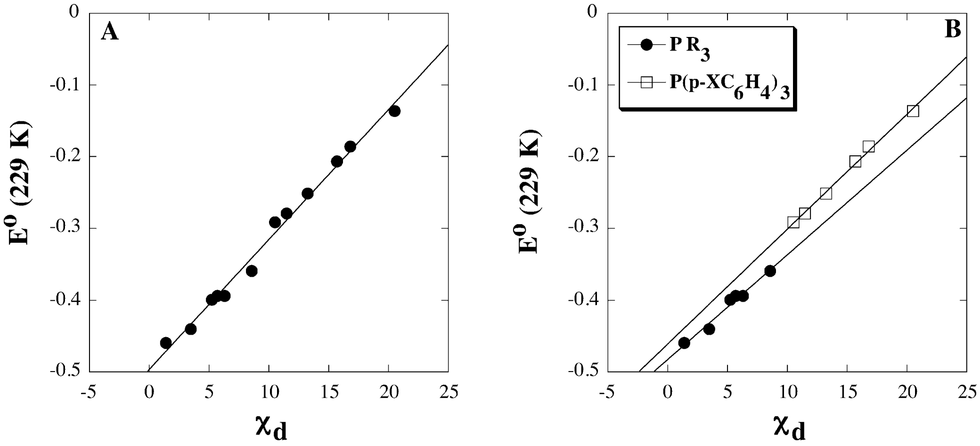

Figure 4. Plots of $E°$ (reaction 1) versus the QALE electronic parameter χ_d. Plot A displays the best fit line for **all** PR_3 and $P(p\text{-}XC_6H_4)_3$ data. Plot B shows the best fit line for each family.

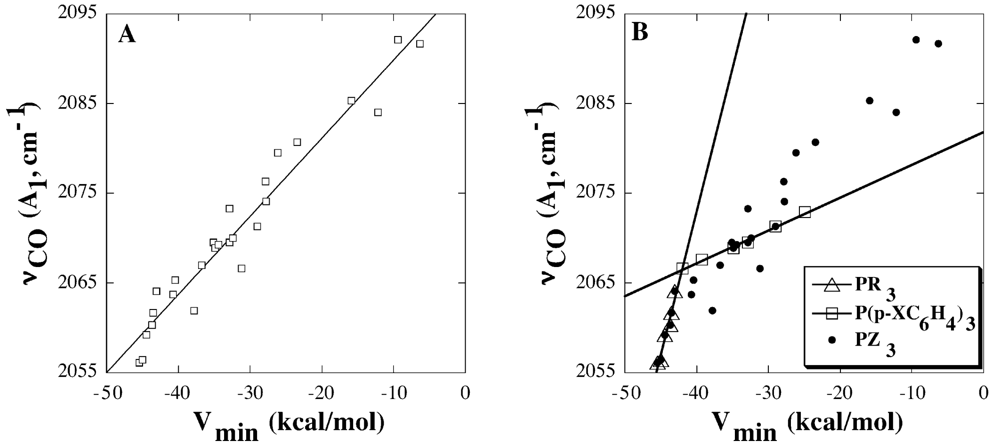

Figure 5. Plots of ν_{CO} (A_1, $Ni(CO)_3(PZ_3)$) versus V_{min}. The points for $P(p\text{-}XC_6H_4)_3$ (X = MeO, Me, Cl) were added to the plot displayed in 5B. The best fit lines are drawn through the data for $P(p\text{-}XC_6H_4)_3$ (X = MeO, Me, H, F, Cl) (open squares) and for PR_3 (open triangles). The V_{min} values for the MeO, Me, and Cl derivatives were calculated via the QALE model.[10]

PR_3 and $P(p\text{-}XC_6H_4)_3$, it is obvious that they have very different slopes; therefore, a single linear relationship for PR_3 and $P(p\text{-}XC_6H_4)_3$ is not appropriate for these two families and, therefore, it is inappropriate for the total set of PZ_3. The observation that the line in Figure 5A and the line through the points for $P(p\text{-}XC_6H_4)_3$ in Figure 5B both have a positive slope suggests that V_{min} might be playing a role in determining the variation in ν_{CO}.

Suresh and Koga assert that the validity of V_{min} as a measure of the σ electron donor power of the phosphines is established by the observation of a linear correlation between V_{min} and the pK_a values of HPR_3^+, one of the most commonly used measures of σ electron donor ability. In support of this assertion, they presented the plot (filled circles) shown in Figure 6. If there were truly a linear relationship between V_{min} and pK_a, then the points for $P(p\text{-}XC_6H_4)_3$ should also fall along this line. Suresh and Koga used only the point for PPh_3 in their analysis. The pK_a data for other $P(p\text{-}XC_6H_4)_3$ were reported by Allman and Goel.[12] Suresh and Koga reported V_{min} for $P(p\text{-}FC_6H_4)_3$ and we have augmented the set of V_{min} values with values for $P(p\text{-}XC_6H_4)_3$ (X = Me, MeO, Cl) (vide supra). When these points are added to Figure 6 and the best fit line is drawn through them (open squares), it can be seen that the slope of this line is significantly different from the slope of the line drawn by Suresh and Koga. This leads to the inescapable conclusion that if the pK_a values are regarded as a measure of σ donor ability of PZ_3, then V_{min} is not a measure of the σ donor ability of PZ_3.

Suresh and Koga could have also reached this conclusion if they had included the points for the phosphines $P(p\text{-}FC_6H_4)_3)$,[12] $P(t\text{-}Bu)_3$,[12] $PPhEt_2$,[13] and PPh_2Me[14] and the phosphites $P(OMe)_3$,[14] $P(OEt)_3$,[15] and $P(OPh)_3$[15] for which the pK_a values are available. When these points are included in Figure 6A (open circles), we see that there is a great degradation of the linear correlation.

Thus, it can be seen that the putative linear correlations (Figures 1A, 1C, 5A, and 6A) between a variety of properties and V_{min} are fortuitous.

Finally, although Suresh and Koga did not examine $\Delta S°$ for reaction 1, its analysis provides a dramatic example of how a simple correlation analysis can lead one astray. In

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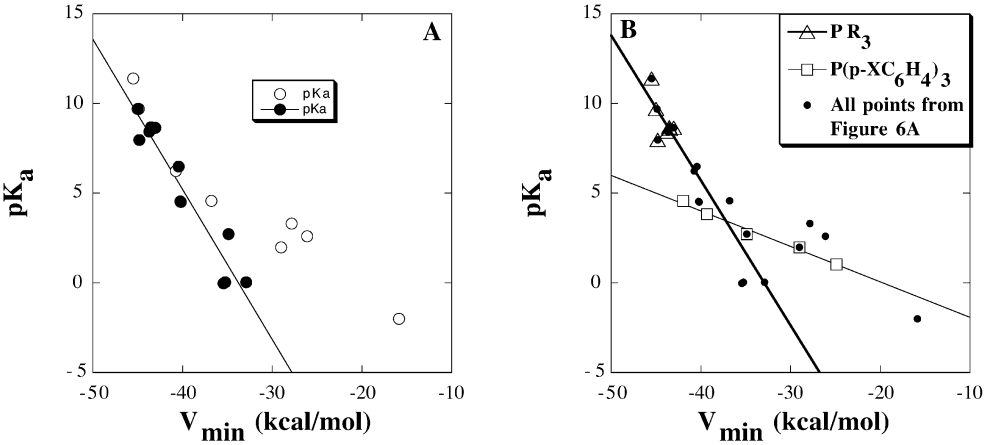

Figure 6. Plots of pK$_a$ values of HPZ$_3^+$ versus V_{min}. (A) The best fit line is drawn through the data considered by Suresh and Koga (filled circles). The data not included by Suresh and Koga are shown as open circles. (B) The points for P(p-XC$_6$H$_4$)$_3$ (X = MeO, Me, Cl) were added to the plot displayed in 6A. The best fit lines are drawn through the data for P(p-XC$_6$H$_4$)$_3$ (X = MeO, Me, H, F, Cl) (open squares) and for PR$_3$ (open triangles). The V_{min} values for the MeO, Me, and Cl derivatives were calculated via the QALE model.[10]

Figure 1E we show a plot of $\Delta S°$ versus V_{min}. If we ignore the two points on the far right side of the plot, there appears to be a reasonable linear relationship between $\Delta S°$ and V_{min} that indicates that $\Delta S°$ *becomes more positive as* V_{min} *becomes more negative (solid line in Figure 1F)*. Let us examine how the P(p-XC$_6$H$_4$)$_3$ behave because this behavior tells us how $\Delta S°$ is really responding to the electron-donor ability of PZ$_3$. These points have been added to Figure 1F and the best fit line drawn through them (open squares). This line is virtually orthogonal to the line drawn through all the points and indicates that for the family of P(p-XC$_6$H$_4$)$_3$ $\Delta S°$ *becomes more negative as* V_{min} *becomes more negative (lower line in Figure 1F)*. Thus, the simple correlation and the analysis of the P(p-XC$_6$H$_4$)$_3$ data give diametrically opposed results. *The lesson is that simple linear correlations might not be meaningful in the absence of a model of ligand effects and when dealing with a limited set of data.*

In conclusion, our examination of the analyses of the sets of experimental data considered by Suresh and Koga shows that, in general, one cannot associate the inherent "σ donating power" with the V_{min} of the unperturbed gas-phase phosphine ligand. Therefore, the utility of V_{min} as a measure of the "σ donating power" of substituted phosphorus(III) ligands remains unsubstantiated.

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