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Quantifying the Electronic Effect of Substituted Phosphine Ligands via Molecular Electrostatic Potential

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Values of the molecular electrostatic potential minimum (V_{min}) corresponding to the lone pair region of several substituted phosphine ligands (PR_3) have been determined at the DFT level. The V_{min} value is proposed as a quantitative measure of the electronic effect of the PR_3 ligands. Good linear correlation between V_{min} and Tolman electronic parameter of PR_3 has been obtained. V_{min} is also proportional to the pK_a values of the conjugate acids of PR_3, viz., $[PR_3H]^+$. Further, the ΔE values of the reaction $Ni(CO)_3 + PR_3 \rightarrow Ni(CO)_3PR_3$ and $ScH_3 + PR_3 \rightarrow ScH_3PR_3$ are also linearly proportional to the V_{min} values. However, if there is a strong metal to phosphorus π-back-bonding, the ΔE and V_{min} do not fit to a line. It is also found that the standard reduction potential as well as the enthalpy change corresponding to the electrochemical couple η-Cp(CO)(PR_3)(COMe)Fe^+/η-Cp(CO)(PR_3)(COMe)-Fe^0 is linearly proportional to the V_{min} values of PR_3. These correlations suggest that V_{min} is a quantitative measure of the σ-donating ability of the phosphine. It is hoped that, in phosphine–metal coordination chemistry, the V_{min} based electronic parameter could be more advantageous than ν-CO and pK_a based electronic parameters as it solely represents the inherent electronic property of the ligand.

Introduction

Substituted phosphine ligands are one of the most important classes of ligands in the field of organometallic chemistry. For instance, around 4000 complexes containing the ligand triphenylphosphine have been structurally determined using X-ray crystallographic techniques.[1] These ligands are very popular because, by the choice of appropriate substituents, they can be finely tuned for the electronic and steric demands of a desired organometallic complex.[2] Further, this feature enables them to find many applications in the field of homogeneous organometallic catalysis.[3,4] Usually, the substituent effect on P is described using a linear free energy relationship involving the pK_a values of the conjugate acids of phosphines and Taft's σ^* values of the substituent.[5] The electronic effects of substituted phosphine ligands[6,7] have been estimated from the carbonyl stretching frequencies of $Ni(CO)_3L$ or $Cr(CO)_5L$ type complexes. Generally, an electron-donating L decreases the CO stretching frequency.[6] This is because of the fact that the electron rich metal center participates in a more effective back-bonding to the pπ^* orbital of the CO ligand resulting in a weakening of the C−O bond. Note that, in this way, we get the electronic property of L by examining the property of its metal complex, which in a sense is an indirect approach. Is there a property of L

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that can directly tell us the electron-donating character of it?

The molecular electrostatic potential (MESP) is an important and widely used quantity for understanding molecular reactivity, intermolecular interactions, molecular recognition, electrophilic reactions, substituent effects and a variety of chemical phenomena.[8−12] Politzer and co-workers have been prolific in applying MESP as a tool to a large variety of such chemically interesting problems;[13−16] e.g., they have studied a correlation between the MESP minimum and Taft substituent constants σ_I and σ_R for substituted amines.[13] Further, they have demonstrated that, in the case of para-substituted anilines, the MESP minimum associated with the amine lone pairs is a highly sensitive indicator of the electron-donating and electron-attracting tendencies of the para substituents.[14] Moreover, the MESP minima of a series of azines, aliphatic amines, substituted pyridines, and aniline derivatives have been found to show linear correlations with the experimental pK_a values of their conjugate acids to a limited extent.[15−17] In a recent work, Suresh and Gadre[18] obtained quantitative values for the electron-donating and -withdrawing power of a substituent in a benzene ring from MESP topography corresponding to the π region of the aryl ring. The MESP-derived electronic descriptor correlated very well with the classic Hammett σ constants.[19] It is expected that the subtle electronic effects occurring at the lone pair region of a substituted phosphine ligand as a result of the electron-donating and -withdrawing effect of the substituents can be obtained from the MESP topography of it.

The aim of the present work is therefore to characterize the lone pair region of various substituted phosphine ligands using the MESP. Because the lone pair is used in the coordinate bond formation with the metal, it is possible that its characterization using MESP could give us a direct approach to quantify the electron-donating power of the phosphine ligand.

Method

The MESP generated by a molecule can be calculated rigorously from its electron density, $\rho(\mathbf{r})$, distribution by employing the equation

$$V(\mathbf{r}) = \sum_{A}^{N} \frac{Z_A}{|\mathbf{r} - \mathbf{R}_A|} - \int \frac{\rho(\mathbf{r}')d^3\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|} \qquad (1)$$

where Z_A is the charge on nucleus A, located at $\mathbf{R}_A$. It is also interpreted as a quantity directly related to the interactive behavior of a molecule with a unit test positive charge.

Lone pair regions of a molecule are regions of enhanced electron density. Therefore, they normally show high negative MESP due to the larger value of the electronic term in eq 1 as compared to the nuclear term. The global minimum or the most negative valued point (designated here as V_{min}) in this region can be obtained from the MESP topography calculation. In other words, at V_{min}, the $\nabla V(\mathbf{r}) = 0$ and the Hessian matrix of $V(\mathbf{r})$ will have three positive eigenvalues.[12]

Optimized geometries of 33 PR_3 ligands (P(t-Bu)$_3$, P(i-Bu)$_3$, P(i-Pr)$_3$, PCy_3, P(n-Bu)$_3$, P(n-Pr)$_3$, PEt_3, PMe_3, PEt_2Ph, PCy_2H, PMe_2Ph, P(n-Bu)$_2$H, P(NMe$_2$)$_3$, $PMePh_2$, P(i-Bu)H$_2$, P(n-Bu)H$_2$, P(CHCH$_2$)$_3$, PPh_3, P(CHCH$_2$)Ph$_2$, P(p-C$_6$H$_4$F)Ph$_2$, $PHPh_2$, P(m-C$_6$H$_4$F)Ph$_2$, P(o-Tol)$_3$, P(p-C$_6$H$_4$F)$_3$, PH_3, P(OEt)$_3$, P(m-C$_6$H$_4$F)$_3$, P(OMe)$_3$, $PClPh_2$, P(OPh)$_3$, P(OCH$_2$CH$_2$Cl)$_3$, PCl_2Ph, P(OCH$_2$CCl$_3$)$_3$) have been obtained at B3LYP/6−31G(d,p) level[20] density functional theory

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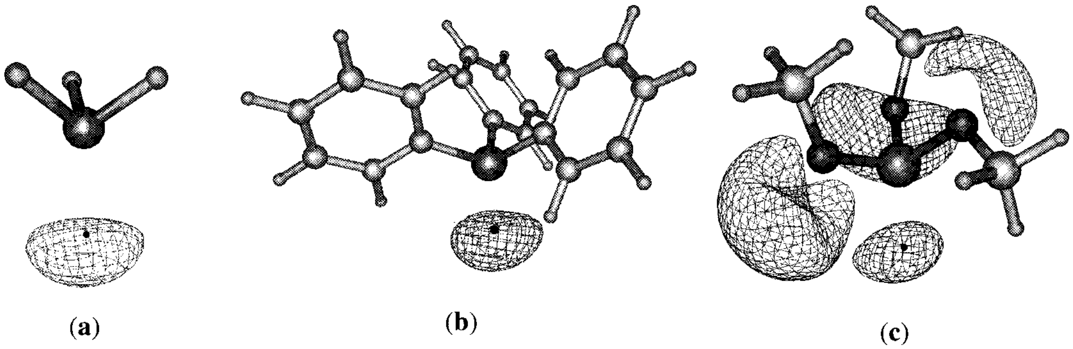

Figure 1. MESP isosurface (−18.8 kcal/mol) near the P lone pair of (a) PH_3, (b) PPh_3, and (c) $P(OMe)_3$. The dark dot in the surface is the V_{min}.

calculations using the Gaussian 98 set of programs.[21] Note that in the PR_3 notation, R is used in general as any substituent. Further, all the PR_3 geometries were confirmed as minima by a frequency calculation. The calculation of MESP and the V_{min} corresponding to the lone pair of the PR_3 ligand has also been done using the Gaussian 98 set of programs. Moreover, complex formation of 11 different phosphine ligands with $Ni(CO)_3$ is studied and the reaction energies have been determined at the B3LYP/6−31G(d,p) level.

Results and Discussion

In Figure 1, visual representations of the lone pair region of PH_3, PPh_3, and $P(OMe)_3$ can be seen in terms of the MESP isosurface with value −18.8 kcal/mol. Similar lone pair MESP isosurfaces can be drawn for all the ligands. A three-dimensional search for the minimum value of the MESP (V_{min}) surrounding the lone pair region of all the PR_3 ligands is done by MESP topography calculation. All the ligands yielded V_{min}. The value of V_{min} and the distance of it from P (designated as d_{CP}) are analyzed (cf. Table 1). As expected, the V_{min} value and d_{CP} show different magnitudes depending on the electronic nature of the substituent. The most negative value of V_{min} (−45.48 kcal/mol) is found for P(*t*-Bu)$_3$ at the shortest d_{CP} distance of 1.723 Å. On the other hand, the least negative value of V_{min} (−6.30 kcal/mol) is found for $P(OCH_2CCl_3)_3$ at the longest d_{CP} distance of 2.022 Å. In general, when the d_{CP} distance decreases, the V_{min} value becomes more negative.

Table 1. Substituted Phosphine Ligands and Their Various Properties[a]

ligand	V_{min} (kcal/mol)	d_{CP} (Å)	ν-CO (cm^{-1})	pK_a	ΔE (kcal/mol)	$\Delta H°$ (kcal/mol)	$E°$ (V)
P(*t*-Bu)$_3$	−45.48	1.723	2056.1				
PCy_3	−44.99	1.741	2056.4	9.7		10.5	−0.4597
P(*i*-Bu)$_3$	−44.80	1.745		7.97		9.2	−0.3939
P(*i*-Pr)$_3$	−44.47	1.745	2059.2		−31.55	10.3	−0.4406
P(*n*-Bu)$_3$	−43.71	1.750	2060.3	8.43		9.23	−0.3994
PEt_3	−43.51	1.749	2061.7	8.69	−31.59	9.25	−0.3941
P(*n*-Pr)$_3$	−43.47	1.750		8.64			
PMe_3	−43.02	1.750	2064.1	8.65	−30.53	8.37	−0.3593
PEt_2Ph	−40.76	1.753	2063.7		−30.46	7.53	−0.3426
PMe_2Ph	−40.41	1.754	2065.3	6.5	−29.91	7.05	−0.317
PCy_2H	−40.24	1.772		4.55			
P(*n*-Bu)$_2$H	−40.16	1.770		4.51			
$P(NMe_2)_3$	−37.79	1.740	2061.9		−30.18		
$PMePh_2$	−36.76	1.778	2067		−29.46	5.5	−0.2674
P(*i*-Bu)H$_2$	−35.46	1.802		−0.02			
P(*n*-Bu)H$_2$	−35.24	1.802		−0.03			
$P(CHCH_2)_3$	−35.09	1.779	2069.5				
PPh_3	−34.85	1.816	2068.9	2.73		4.9	−0.2515
$P(CHCH_2)Ph_2$	−34.44	1.789	2069.3				
P(*p*-C$_6$H$_4$F)Ph$_2$	−32.88	1.786	2069.5				
$PHPh_2$	−32.88	1.801	2073.3	0.03			
P(*m*-C$_6$H$_4$F)Ph$_2$	−32.41	1.792	2070				
P(*o*-Tol)$_3$	−31.16	1.761	2066.6				
P(*p*-C$_6$H$_4$F)$_3$	−29.03	1.789	2071.3			4.04	−0.2068
PH_3	−28.22	1.850					
$P(OEt)_3$	−27.85	1.828	2076.3		−28.78	2.37	−0.1551
P(*m*-C$_6$H$_4$F)$_3$	−27.77	1.806	2074.1				
$P(OMe)_3$	−26.12	1.840	2079.5		−28.72	1.91	−0.1235
$PClPh_2$	−23.43	1.865	2080.7				
$P(OPh)_3$	−15.88	1.916	2085.3				0.0094
$P(OCH_2CH_2Cl)_3$	−12.18	1.899	2084		−26.63	−1.24	
PCl_2Ph	−9.38	2.014	2092.1				
$P(OCH_2CCl_3)_3$	−6.30	2.022	2091.7		−25.67		

[a] See text for details.

Here we note that the simplest phosphine ligand PH_3 is generally described as an unsubstituted phosphine. Its V_{min} value is −28.22 kcal/mol. As compared to this value, in the case of a phosphine ligand with an electron-donating substituent, a more negative V_{min} is expected due to an enhancement in the electron density around the phosphorus lone pair region. Similarly, an electron-withdrawing group is expected to decrease the negative character of the V_{min}. In this respect, among the 33 ligands studied here, the tris(*tert*-butyl)phosphine ligand having the largest negative value of V_{min} is considered as the most electron donating ligand. The ligands that have showed more negative character to V_{min} than that of PH_3, viz., P(*t*-Bu)$_3$, PCy_3, P(*i*-Bu)$_3$, P(*i*-Pr)$_3$, P(*n*-Bu)$_3$, PEt_3, P(*n*-Pr)$_3$, PMe_3, PEt_2Ph, PMe_2Ph, PCy_2H, P(*n*-Bu$_2$)H, $P(NMe_2)_3$, $PMePh_2$, P(*i*-Bu)H$_2$, P(*n*-Bu)H$_2$, $P(CHCH_2)_3$, PPh_3, $P(CHCH_2)Ph_2$, P(*p*-C$_6$H$_4$F)Ph$_2$, $PHPh_2$, P(*m*-C$_6$H$_4$F)Ph$_2$, P(*o*-Tol)$_3$, and P(*p*-C$_6$H$_4$F)$_3$, are therefore more electron donating than PH_3 (they are listed in the decreasing order of electron donation). On the other hand, the V_{min} values of ligands $P(OEt)_3$, P(*m*-C$_6$H$_4$F)$_3$, $P(OMe)_3$, $PClPh_2$, $P(OPh)_3$, $P(OCH_2CH_2Cl)_3$, PCl_2Ph, and $P(OCH_2CCl_3)_3$ are found to be less negative than the V_{min} value of PH_3. They are therefore considered as less electron donating than PH_3.

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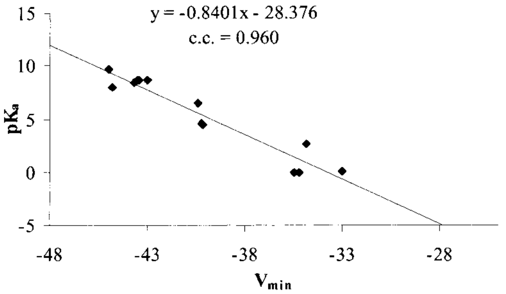
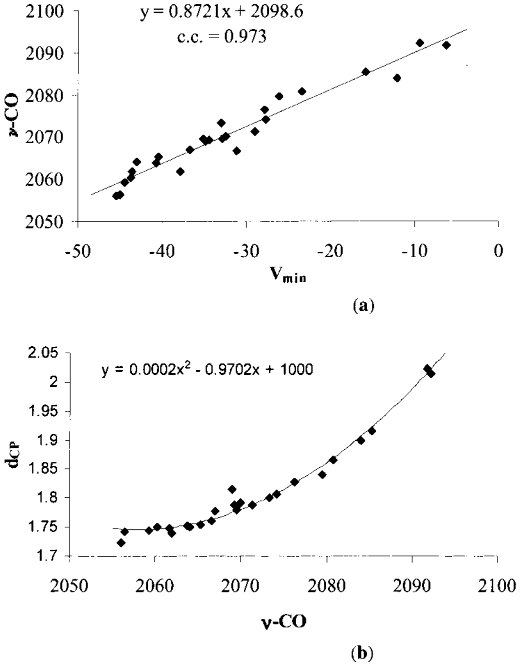


Figure 2. Correlation between $V_{\min}$ and pK_a values of the conjugated acids of phosphine ligands ($[PR_3H]^+$). $V_{\min}$ is in kcal/mol.



(**a**)

(**b**)

Figure 3. Correlations between the Tolman electronic parameter (ν-CO) and (a) $V_{\min}$ and (b) d_{CP}. See Table 1 for details.

Usually, the experimentally obtained pK_a values of the conjugate acids of phosphates ($[PR_3H]^+$) are used as an index of this electron-donating property of the ligand.[5,6a] The validity of using $V_{\min}$ as a measure of the electron-donating power of the phosphine ligands can be tested by correlating it with pK_a values. A linear correlation between the two quantities exists (cf. Figure 2), which suggests the usefulness of $V_{\min}$ as a measure of the subtle electronic changes occurring at the lone pair region of the phosphine ligand. A further test to confirm this statement can be obtained by correlating the $V_{\min}$ values to the most widely used experimental index that quantifies the electronic effect of phosphine ligands, viz., the Tolman electronic parameter[6a] designated here as ν-CO (the ν-CO values correspond to the asymmetrical stretching[6a] frequency of carbonyl groups in $Ni(CO)_3L$ in CD_2Cl_2). In Figure 3, the $V_{\min}$ values are plotted against the experimental values of ν-CO and both quantities are found to be linearly correlated (correlation coefficient, c.c. = 0.973), obeying the following equation:

$$\nu\text{-CO} = 0.8798(V_{\min}) + 2098.8 \qquad (2)$$

There is also an interesting and nearly parabolic correlation between the distance of the MESP critical point from phosphorus (d_{CP}) and the ν-CO stretching values (cf. Figure 3b).

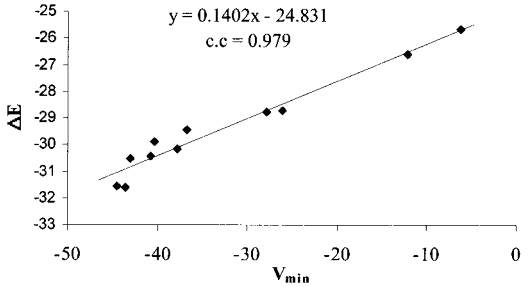


Figure 4. Correlations between $V_{\min}$ and the energy (ΔE) of the reaction $PR_3 + Ni(CO)_3 \rightarrow Ni(CO)_3PR_3$. $V_{\min}$ and ΔE are in kcal/mol.

We have also optimized the geometries of a representative set of 11 $Ni(CO)_3PR_3$ complexes (PR_3 = P(i-Pr)$_3$, PEt_3, PMe_3, PEt_2Ph, PMe_2Ph, $P(NMe_2)_3$, $PMePh_2$, $P(OEt)_3$, $P(OMe)_3$, $P(OCH_2CH_2Cl)_3$, and $P(OCH_2CCl_3)_3$) and computed the energy released (ΔE) in the complex formation reaction, viz.,

$$PR_3 + Ni(CO)_3 \rightarrow Ni(CO)_3PR_3 \qquad (3)$$

at the B3LYP/6−31G(d,p) level, and it is depicted in Table 1. Since the driving force for the reaction is the donation of the lone pair electrons from phosphorus to nickel, the ΔE value would mainly correspond to the electron-donating strength of PR_3. It is also noted that ΔE can be affected to some extent by the nickel to phosphorus π-back-bonding. However, in the complex $Ni(CO)_3PR_3$, such a π-back-bonding is expected to be small due to the strong π-acceptor character of the carbonyl ligands, which would lead to the acceptance of d-orbital electrons from nickel to the antibonding π^* orbitals of the CO group. Therefore one would expect a linear correlation between the lone pair strength of PR_3 in terms of its $V_{\min}$ value and the ΔE value. There is indeed such a correlation, and it is shown in Figure 4. Note that, in this case, the linear correlation suggests the use of $V_{\min}$ for the interpretation of the σ-donating ability of the phosphine ligand. A further illustration of this feature of $V_{\min}$ can be tested by considering a d^0 complex where the π-back-bonding cannot exist. The formation of ScH_3PR_3 as shown in eq 4 is used for this purpose (only five phosphine ligands, viz., P(i-Pr)$_3$, PMe_3, PMe_2Ph, $P(OMe)_3$, and PCl_2Ph, are chosen as test cases).[22]

$$ScH_3 + PR_3 \rightarrow ScH_3PR_3 \qquad (4)$$

It is found that the $V_{\min}$ and the ΔE of the reaction in kcal/mol for PR_3 = P(i-Pr)$_3$, PMe_3, PMe_2Ph, $P(OMe)_3$, and PCl_2Ph in the order ($V_{\min}$, ΔE) are (−44.47, 22.63), (−43.02, 22.58), (−40.41, 19.66), (−26.12, 14.55), and (−9.38, 3.79), respectively. These points when plotted on a graph showed an excellent linear correlation (c.c. = 0.993).

If the metal and phosphorus have a strong π-back-bonding, $V_{\min}$ may not be used as a good indicator of the energy

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[22] For this B3LYP computation, the LanL2DZ basis set is used for the metal. For all other atoms the 6−31G(d,p) basis is used.

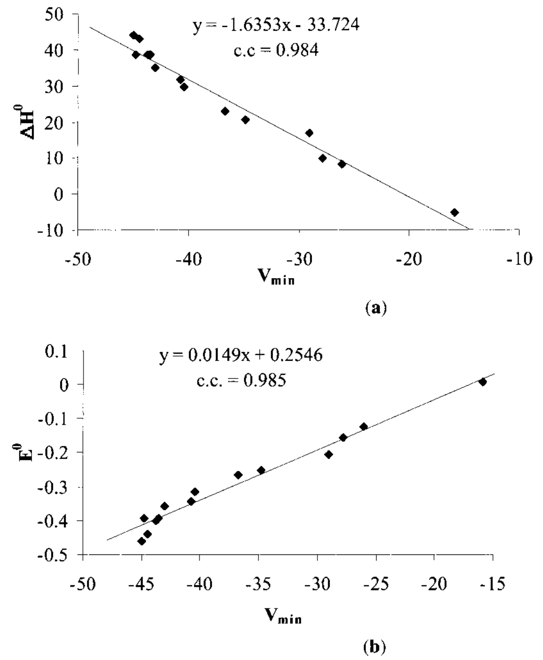

Figure 5. Correlations between V_{min} and the $\Delta H°$ and $E°$ values of the electrochemical reaction η-Cp(CO)(PR$_3$)(COMe)Fe$^+$ + e$^-$ → η-Cp(CO)-(PR$_3$)(COMe)Fe^0. See Table 1 for details.

released during the coordination of a phosphine ligand to a metallic moiety. To explore this possibility, we have constructed a model reaction involving MnH_3NH_3 and PR_3 as shown in eq 5 (PR_3 = P(i-Pr)$_3$, PMe_3, PMe_2Ph, P(OMe)$_3$, and PCl_2Ph). The complex $MnH_3NH_3PR_3$ has a trigonal

$$MnH_3NH_3 + PR_3 \rightarrow MnH_3NH_3PR_3 \qquad (5)$$

bipyramidal geometry wherein the NH_3 and PH_3 ligands occupy the axial positions. A strong metal to phosphorus π-back-bonding is expected in this complex due to mainly two factors, viz., (i) Mn in its +3 oxidation state has two lone pair d orbitals, and (ii) the H and NH_3 are not strong π-acceptor ligands. In this case, the ΔE of the reaction (23.72, 23.03, 25.11, 30.85, and 22.74 kcal/mol for PR_3 = P(i-Pr)$_3$, PMe_3, PMe_2Ph, P(OMe)$_3$, and PCl_2Ph, respectively) was not proportional to the V_{min} values.

In a recent work, Fernandez et al.[23] have investigated the electrochemical reaction

$$\mathrm{Cp(CO)(PR_3)(COMe)Fe^+ + e^- \rightarrow \eta\text{-}Cp(CO)(PR_3)(COMe)Fe^0} \qquad (6)$$

for a systematic and quantitative study of ligand effects. They have reported the enthalpy change ($\Delta H°$), the entropy change ($\Delta S°$), and the standard reduction potentials ($E°$) of this reaction for a large number of substituted phosphine ligands. We find that the both $\Delta H°$ and $E°$ values are linearly proportional to the V_{min} values (cf. Figure 5).

All these correlations (Figures 2−5) thus suggest that the inherent electron-donating strength of phosphine ligands can be derived from the V_{min} of the unperturbed phosphine ligand (free gas phase ligand). The important advantage is that we no longer require the phosphine−metal complex or the protonated form of phosphine ligand for finding out the electron-donating power of that ligand.

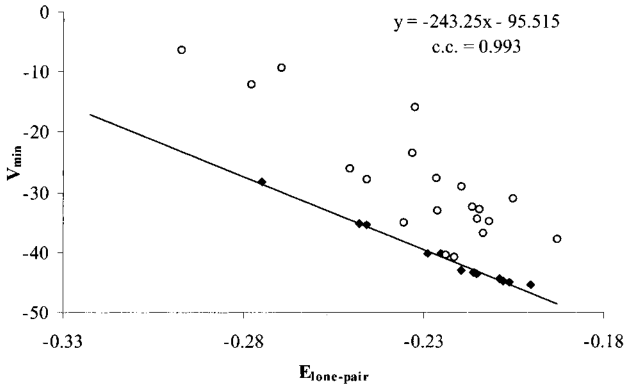

Figure 6. Correlation between the energy of the phosphorus lone pair orbital ($E_{lone-pair}$) and V_{min}. The correlation line represents only those PR_3 ligands where R = H or alkyl substituent. See Table 1 for details.

One may also consider the phosphorus lone pair orbital energy values ($E_{lone-pair}$) of the ligands as a criterion of ligand strength.[7a] The advantage of using this quantity for such a purpose can be tested by comparing it with the already discussed V_{min}, ν-CO, pK_a, ΔE, $\Delta H°$, and $E°$ values. It is found that phosphorus lone pair electrons of all the PR_3 ligands occupy the highest occupied molecular orbital (HOMO). The orbital energies ($E_{lone-pair}$) of these HOMOs are depicted in Table 1. In Figure 6, the $E_{lone-pair}$ is plotted against the V_{min} values. In this figure, the correlation line is drawn for PR_3 ligands with H or alkyl groups as substituents. A very good agreement between the two quantities can be seen for this set of ligands (c.c. = 0.993). Most of the ($E_{lone-pair}$, V_{min}) points corresponding to other ligands are far off from this line, but generally an increase in the V_{min} value corresponds to a decrease in the $E_{lone-pair}$ value. It is therefore obvious that, unlike V_{min} values, $E_{lone-pair}$ may not show good linear correlations with ν-CO, pK_a, ΔE, $\Delta H°$, and $E°$ values (the c.c. values for the linear correlations of ($E_{lone-pair}$, ν-CO), ($E_{lone-pair}$, pK_a), ($E_{lone-pair}$, ΔE), ($E_{lone-pair}$, $\Delta H°$), and ($E_{lone-pair}$, $E°$) are 0.860, 0.775, 0.848, 0.753, and 0.752, respectively). This analysis suggests that V_{min} is superior to $E_{lone-pair}$ for classifying the lone pair strength of substituted phosphine ligands.

Conclusion

The electron-donating power of a substituted phosphine ligand depends on the electron rich character of its lone pair. A simple and direct way to obtain this lone pair strength is to find the MESP minimum (V_{min}) in the lone pair region. The value of V_{min} itself acts as a quantitative measure of the lone pair strength. Linear correlations of (V_{min}, pK_a), (V_{min}, ν-CO), (V_{min}, ΔE), (V_{min}, $\Delta H°$), and (V_{min}, $E°$) confirm this fact. Compared to the V_{min} value of PH_3 (−28.22 kcal/mol), the ligands P(t-Bu)$_3$, PCy_3, P(i-Bu)$_3$, P(i-Pr)$_3$, P(n-Bu)$_3$, PEt_3, P(n-Pr)$_3$, PMe_3, PEt_2Ph, PMe_2Ph, PCy_2H, P(n-Bu$_2$)H, P(NMe$_2$)$_3$, $PMePh_2$, P(i-Bu)H$_2$, P(n-Bu)H$_2$, P(CHCH$_2$)$_3$, PPh_3, P(CHCH$_2$)Ph$_2$, P(p-C$_6$H$_4$F)Ph$_2$, $PHPh_2$, P(m-C$_6$H$_4$F)Ph$_2$, P(o-Tol)$_3$, and P(p-C$_6$H$_4$F)$_3$ have shown more negative

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(23) Fernandez, A. L.; Lee, T. Y.; Reyes, C.; Prock, A.; Giering, W. P. *Organometallics* **1998**, *17*, 3169.

character to V_{min}, which suggests the electron-donating ability of the substituents of phosphorus. On the other hand, the substituents of the ligands such as $P(OEt)_3$, $P(m\text{-}C_6H_4F)_3$, $P(OMe)_3$, $PClPh_2$, $P(OPh)_3$, $P(OCH_2CH_2Cl)_3$, PCl_2Ph, and $P(OCH_2CCl_3)_3$ are electron withdrawing because in these cases the V_{min} values are less negative than the V_{min} value of PH_3. The V_{min} based approach for quantifying the electronic effect of PR_3 could be more advantageous and straightforward than the approaches based on ν-CO or pK_a values because here we need to look to the property of only the ligand and not to its complex or to its protonated form. It is hoped that V_{min} could be used as the σ-donating power of the phosphine ligand to a metallic moiety. The interaction energy between the metallic moiety and the phosphine ligand would be proportional to the V_{min} value if there is no significant π-back-bonding from the metal to the phosphine.

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Supporting Information Available: Cartesian coordinates of the optimized geometries and total energies of PR_3, $Ni(CO)_3$, $Ni(CO)_3PR_3$, ScH_3, ScH_3PR_3 MnH_3NH_3, and $MnH_3NH_3PR_3$ systems at the levels of theory mentioned in the text. This material is available free of charge via the Internet at http://pubs.acs.org.

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