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Molecular Electrostatic Potential Approach to Determining the Steric Effect of Phosphine Ligands in Organometallic Chemistry[†]

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A two-layer ONIOM(B3LYP/6-31G(d,p):UFF) quantum mechanics (QM)–molecular mechanics (MM) optimization of PR_3 ligands, where the QM layer is always constructed as PH_3, followed by molecular electrostatic potential (MESP) analysis of the QM layer is suggested as a simple and effective method for evaluating the steric effect of PR_3 ligands. The subtle variations in the electron distribution that arise as a result of the steric bulkiness as well as the conformational changes in the substituent groups is well reflected in the value of the MESP minimum (V_{min}) located in the QM region. In general, a sterically bulky group has always shown a more negative V_{min} than a sterically less bulky group. The difference between the V_{min} value of free PH_3 and the V_{min} value at the QM region of PR_3 is used as a measure of the steric effect of the PR_3 ligand. This value, designated as $MESP_{steric}$, showed a good linear correlation with the cone angle values as well as the average of the intervalence HPH angles found in the QM layer. Further, the difference between the V_{min} value at the QM region of PR_3 (an indicator of the steric effect) and the V_{min} value of the completely optimized PR_3 ligand (an indicator of the combined effect of steric and electronic effects) showed a good linear correlation with the Hammett $\sum\sigma_p$ constants, which further confirmed the present approach to understanding the steric effect separately from the electronic effect.

Introduction

Phosphine ligands are widely used for the fine-tuning of the electronic and steric effects that control the reactivity and catalytic property of an organometallic complex.[1-8] This feature enables them to find many applications in the field of homogeneous catalysis.[9-16] It is therefore essential to quantify the electronic as well as the steric effect of a phosphine ligand. Tolman in his famous *Chemical Review* article[1] noted that electronic effects are mainly associated with the electron transmission along chemical bonds while the steric effects are often associated with nonbonded interactions between parts of a molecule. However, in any molecule, because of the intimate connection between these two effects, it is nearly impossible to separate them in totality.[1] For steric effects, the Tolman cone angle (θ) developed in 1970, based on the Corey−Pauling−Koltun (CPK) model of ligand−metal complexes, is the most widely used measure.[1,17] The cone angle is calculated from a CPK model of the ligand with the phosphorus atom placed at 2.28

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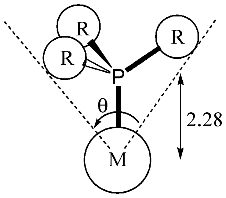
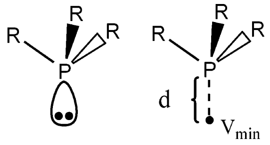


Figure 1. Tolman method for measuring the cone angle.



	$\mathbf{V_{min}}$ (kcal/mol)	d (Å)
R=H	-28.22	1.850
R=Cy	-44.99	1.741
R=Ph	-34.85	1.816

Figure 2. Lone pair of a phosphine ligand and the corresponding V_{min} value observed at distance *d* from the phosphorus atom. Compared to PH_3, an electron-donating group will increase the negative value of V_{min} and an electron-withdrawing group will decrease it. Values are taken from ref 37.

Å from the metal (Figure 1).[1,3] This method, though very simple and crude, was found to be very useful in interpreting and quantifying the dependence of the ligand steric properties on the chemical behavior of a system.[18−20] Several attempts to improve the Tolman model[21−27] were also based on the geometry parameters, either obtained from the crystallographic structure or from a quantum mechanically calculated structure of the ligand−metal complex. The most recent work in this category is reported by Boeré and Zhang[28,29] on the steric shielding and steric pressure in extremely bulky aromatic phosphine ligands. The only exception to the geometric models is the ligand repulsive energy parameter (E_R) of Brown and co-workers, which they calculated based on a molecular mechanics (MM) model.[30,31] In fact, a proper interpretation of the Tolman cone angle data in terms of a quantum mechanically derived quantity (except the calculated structure-based data) for the steric effect is lacking[3] in the literature.

Among the experimental measures of electronic parameters of phosphine ligands, the methods based on (i) IR frequencies corresponding to the carbonyl and nitrosyl groups of transition-metal complexes (Tolman approach),[1] (ii) the rate of ligand-exchange reactions,[32] (iii) ^{13}C NMR chemical shift parameters,[33] (iv) basicity of the phosphine ligands,[34] and (v) the QALE approach of Giering et al.[6,12] are the prominent ones. Several theoretical measures for the quantification of the electronic effects of the phosphine ligands have also been designed.[35−37] Recently, Suresh and Koga suggested that the molecular electrostatic potential (MESP) minimum (designated here as V_{min}) observed at the lone-pair region of a phosphine ligand is a good measure of the net electron-donating ability of a phosphine ligand[37] (Figure 2). Giering et al.[38] have argued that a one-parameter V_{min}-based correlation for the electron-donating ability may not be accurate for a variety of phosphine ligands. In a very recent review, Kühl[39] compared several approaches used for predicting the net electron-donating ability of phosphine ligands and commented that V_{min} values of the MESP are useful for calculating the electron-donating ability of a broad range of phosphine ligands. He also noted that the V_{min}-based approach for PR_3 ligands required the least effort in terms of required software, hardware, and computer time. In this work, we will illustrate that if we can treat the steric effect of a substituent separately from the electronic effect, the MESP-based approach can be extended to quantify the steric effect also.

Method

In the recent years, "integrated molecular orbital molecular mechanics" (IMOMM) computational schemes have been used to understand the steric effects in chemistry.[40−43] The advantage of such methods is the use of a MM force field to incorporate the steric effect of a part of a molecule while treating the rest of the molecule in quantum mechanical ways. The ONIOM method of Morokuma and co-workers[44,45] incorporated in the *Gaussian03* package[46] is a very useful IMOMM technique. In this work, we use a two-layer ONIOM method for optimization of the phosphine ligands (Figure 3). The outer layer contains the substituent R groups, which are treated with the MM method utilizing the universal force field (UFF).[47] R groups in the outer layer are connected to the inner layer via the link hydrogen atoms. Therefore, the inner layer comprises a PH_3 ligand, and it is treated with a density functional theory method at the B3LYP/6-31G(d,p) level.[48,49]

The MESP of a molecule is a real physical property, and that can be determined experimentally by X-ray diffraction

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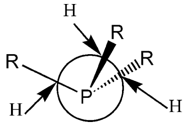

Figure 3. Two-layer ONIOM scheme used in the present study. The link hydrogen atoms shown via arrows define the inner layer as PH_3 (inside the circle).

techniques or 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 $\mathbf{R}_A$.[50,51] The MESP is used widely for understanding molecular reactivity, intermolecular interactions, molecular recognition, electrophilic reactions, and a variety of chemical phenomena.[52−57] Visualization of MESP is a good way to see the charge distribution within a molecule. Local minima of the MESP (V_{min}) are often observed at the lone-pair region of a molecule because of the larger value of the electronic term in eq 1 as compared to the nuclear term, and these V_{min} points represented centers of negative charge on the molecule.[51] At these minima, ∇V will be zero and the Hessian matrix of $V(\mathbf{r})$ will have three positive eigenvalues.

Here we report the MESP results of a variety of PR_3 ligands in which the P−R connections are all through P−C or P−H bonds. For every ONIOM-optimized geometry of PR_3 ligands, a cube file containing the MESP is generated for the inner layer using a fine grid of dimension 100 × 100 × 100 at the B3LYP/6-31G(d,p) level using the *Gaussian03* program.[46] For the visualization of the MESP, the freely available *MOLEKEL* program is used.[58] From just visual inspection of the MESP data, the most negative-valued MESP point (V_{min}) in the lone-pair region can be obtained. If a guess point near V_{min} is used along with the Prop = (potential, opt) keyword in *Gaussian03*, the exact location and the value of V_{min} can be obtained from a rigorous calculation. It may be noted that the numerical calculation is adequate because the V_{min} value obtained from a fine grid will be nearly identical with the value obtained from a rigorous topography calculation.[59]

Results and Discussion

In the ONIOM-level geometry optimization, because we use the MM method for the outer layer, the arrangement of hydrogen atoms in the inner layer, PH_3, will be governed by the steric effects exerted between the R groups. In other words, as compared to the H−P−H angles in the free PH_3, the H−P−H angles of PH_3 in the inner layer of the ONIOM-level-optimized geometry will be different. Compared to a small R group, a bulky R group is expected to widen the intervalence H−P−H angles. Electronically, this means that the sp^3-hybridized lone-pair orbital on the phosphorus atom will have increasingly more p character or more Lewis basic character as the bulkiness of the R group increases. It is felt that these subtle changes in the p character of the phosphorus atom will be well reflected in the MESP around its lone-pair region, and therefore a quantification of the steric effect in terms of the MESP may be feasible.

For the ONIOM-optimized geometries of the PR_3 ligands, the MESP results for the inner layer are presented in Table 1 along with the available cone angle data. In general, the V_{min} value of a PR_3 becomes more negative when compared to V_{min} of PH_3 as the Tolman cone angle increases, which is attributed to the more p character of its lone-pair electrons. The important point is that the V_{min} values spanning a range of −28.22 kcal/mol for the smallest (PH_3) to −43.67 kcal/mol for the largest ligand $[P(2,4,6\text{-}CH_3C_6H_2)_3]$ suggest that it is very sensitive to the steric influence of the substituents. Also note that, according to the definition in eq 1, the MESP, $V(\mathbf{r})$, is the energy required to bring a unit test positive charge from infinity to a point $\mathbf{r}$, which means that the V_{min} value is the maximum attractive interaction energy between a test positive charge and the ligand system. As the steric size of the substituent R increases, this attractive interaction energy also increases. Therefore, compared to the V_{min} value of PH_3, the observed increase in the negative value of V_{min} of a PR_3 ligand can be attributed to the steric bulkiness of its substituents. This means that the quantification of the steric effect in terms of the quantum chemically derived quantity of the MESP is possible. Using eq 2, we define this quantity as $MESP_{steric}$,

$$MESP_{steric} = V_{min}(PH_3) - V_{min}(ONIOM\_PR_3) \qquad (2)$$

where $V_{min}(PH_3)$ is the V_{min} value of the PH_3 ligand and V_{min}-$(ONIOM\_PR_3)$ is the V_{min} value of the PH_3 unit in the inner

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Table 1. MESP Results (in kcal/mol) of the PR_3 Ligands, Cone Angles, and ∠HPH Angles (in degrees) and Hammett $\Sigma\sigma_p$ Constants[a]

ligand	V_{min}	$MESP_{steric}$	θ	θ_{MESP}	V_{min}(real)	$\Sigma\sigma_p$	∠HPH
PH_3	−28.22	0.00	87	87	−28.22	0.00	93.46
PH_2Ph	−28.63	−0.41	101	91	−31.05[b]	−0.01	93.69
PMe_3	−30.62	−2.40	118	108	−43.02	−0.51	96.07
PMe_2Ph	−32.83	−4.61	122	128	−40.41	−0.35	98.01
PMe_2CF_3	−31.44	−3.22	124	115	−26.46[b]	0.20	96.92
$PHPh_2$	−30.78	−2.56	128	110	−32.88	−0.02	95.64
PEt_3	−33.35	−5.13	132	132	−43.51	−0.45	98.98
PEt_2Ph	−33.01	−4.79	136	129	−40.76	−0.31	98.31
$PMePh_2$	−32.47	−4.25	136	125	−36.76	−0.19	98.89
$P(m\text{-}C_6H_4F)_3$	−33.82	−5.19	145	133	−27.77	0.30	98.97
$P(CF_3)_3$	−33.68	−5.46	137	135	−5.95[b]	1.62	99.15
$PEtPh_2$	−35.12	−6.90	140	148	−37.23[b]	−0.17	100.30
PPh_3	−34.62	−6.40	145	144	−34.85	−0.03	99.37
$PPh_2(i\text{-}Pr)$	−34.12	−5.90	150	139	−37.62[b]	−0.17	99.31
$P(i\text{-}Pr)_3$	−37.34	−9.12	160	168	−44.47	−0.45	103.19
PCy_3	−37.83	−9.61	170	172	−44.99	−0.45	103.53
$PPh_2(t\text{-}Bu)$	−36.58	−8.36	157	161	−38.86[b]	−0.22	101.99
$PMe(CF_3)_2$	−32.27	−4.05		123	−12.26[b]	0.91	97.95
$P(o\text{-}Tol)_3$	−39.88	−11.66	194	190			102.99
$P(o\text{-}i\text{-}PrC_6H_4)_3$	−40.65	−12.43	212[60]	197			103.72
$P(o,m,p\text{-}(CH_3)_3C_6H_2)_3$	−42.35	−14.13	212	212			107.16

[a] Cone angles and the Hammett constant are taken mainly from refs 1 and 61, respectively. [b] V_{min}(real) values calculated in the present study. The remaining ones are taken from ref 37.

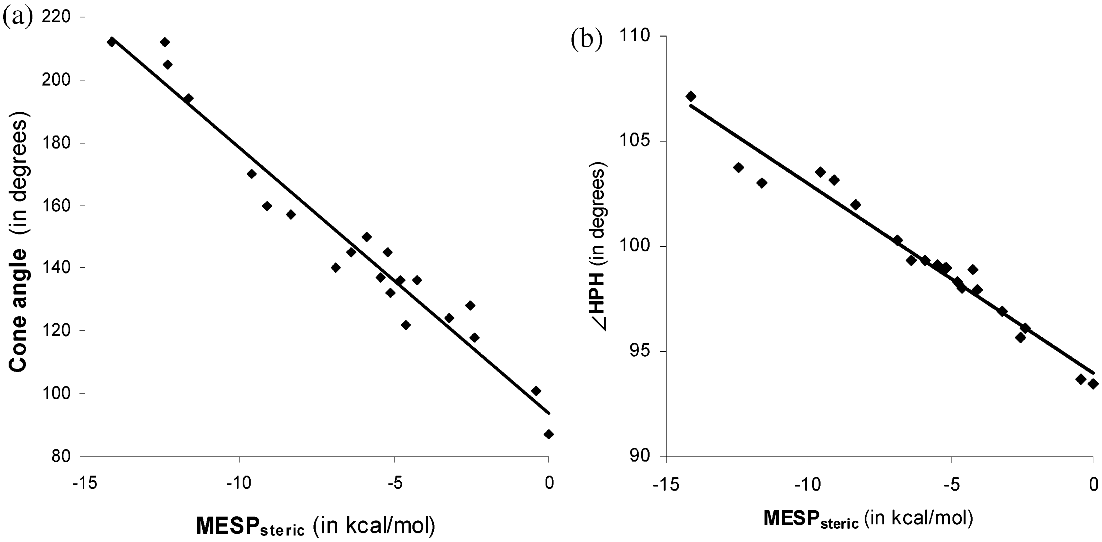

Figure 4. Correlation between the $MESP_{steric}$ and (a) the cone angle and (b) the average of the intervalence H−P−H angles (∠HPH).

layer of the ONIOM-level-optimized PR_3 ligand. A good linear correlation between the $MESP_{steric}$ and Tolman cone angle values is obtained (Figure 4a), which supports the present approach to the steric effect (correlation coefficient = 0.976).

For all of the systems, the average value of the intervalence H−P−H angles (∠HPH) observed for the quantum mechanics (QM) layer is also depicted in Table 1. Because H is used as the link atom in the two-layer ONIOM model, ∠HPH and the average of the intervalence angles in the PR_3 ligand (mainly the average of the C−P−C angles) represent the same quantities. It is already mentioned that the large negative V_{min} value observed for a bulky PR_3 may be due to the increase in the intervalence H−P−H angle (in the QM layer), leading to an enhancement in the p character of the phosphorus lone pair. This is indeed true because the values of ∠HPH reported in Table 1 show, in general, a gradual increase when the bulkiness of the substituent R group is increased. A good linear correlation between $MESP_{steric}$ and ∠HPH (correlation coefficient = 0.980) is also obtained (Figure 4b), which not only gives additional support and validity to the present approach to the steric effect of the phosphine ligands but also accounts for the origin of the correlation between the MESP and the Tolman cone angle. Further, the linear correlation depicted in Figure 4b suggests that the quantity ∠HPH can also be used as a measure of the ligand steric effect. However, like the Tolman cone angle data, the ∠HPH data can only be considered as a purely structural parameter. On the other hand, based on eq 1, the $MESP_{steric}$ can be interpreted as purely an electronic quantity for the ligand steric effect.

For those who prefer to use the popular cone angle data rather than another quantity for the steric effect, we propose

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(59) For the systems studied here, the V_{min} value obtained via numerical calculation and rigorous calculation differed at the maximum by only 0.5 kcal/mol and, therefore, even without a sophisticated program, V_{min} can be obtained.

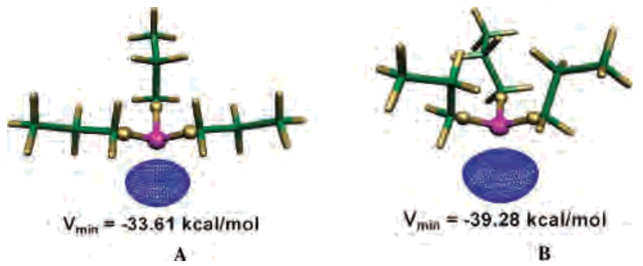

Figure 5. Two different conformations A and B obtained for P(n-Pr)$_3$ using two-layer QM−MM ONIOM optimization. The MESP isosurface is plotted for the −18.83 kcal/mol value. The QM level consists of PH_3, which is shown as a ball-and-stick model.

a cone angle θ_{MESP}, derived based on the $MESP_{steric}$. This is done by first obtaining a linear equation given in eq 3 for the $MESP_{steric}$ (x variable) and the cone angle (y variable) from the data of two ligands, viz., PH_3 and P(2,4,6-$CH_3C_6H_2$)$_3$, which are the smallest and largest ligands reported by Tolman, respectively, and then fitting the remaining $MESP_{steric}$ values to this equation. The θ_{MESP}

$$\theta_{MESP} = -8.8464(MESP_{steric}) + 87 \tag{3}$$

values are also presented in Table 1. In general, θ and θ_{MESP} show good agreement between each other.

We feel that the $MESP_{steric}$ is a more reliable quantity than the cone angle parameter for comparing the steric effect of different ligands, particularly their different conformations because the former quantity is very sensitive to the subtle variations occurring in the electron distribution due to changes in the steric bulkiness as well as changes in the conformations of the substituent groups. For instance, in the case of a flexible ligand P(n-Pr)$_3$, the conformer A given in Figure 5 is the one observed in its free state and also in most of its metal complexes. The V_{min} value of this conformer is −33.61, which suggests a steric effect very close to that of PEt_3. However, if this ligand exists as conformer B in any complex, it would exert a much larger steric effect, and this is indeed reflected in its V_{min} value of −39.28 kcal/mol.

In Table 1, we also depict the V_{min} value corresponding to the fully optimized PR_3 ligands at the B3LYP/6−31(d,p) level, which is denoted as V_{min}(real). It is to be noted that V_{min}(real) is an indicator of the combined effect of both the electronic and steric effects, while V_{min} obtained at the QM layer of the ONIOM-optimized PR_3 ligand is an indicator of its steric effect only. Therefore, the difference between the V_{min}(real) and V_{min} values would reflect the variations in the electronic effect of various R substituents. The best parameter that quantifies the electronic effect of a substituent R is its Hammett σ_p constant.[61] Because the electronic effects of the substituents are mostly additive in nature, $\sum\sigma_p$ is used as a measure of the total electronic effect of all of the R groups in PR_3. It is found that the quantity V_{min}(real) − V_{min} is linearly proportional (correlation coefficient = 0.986) to $\sum\sigma_p$, and this linear relationship shown in Figure 5 further confirms the validity of the present approach to understanding the steric effect separately from the electronic effect.

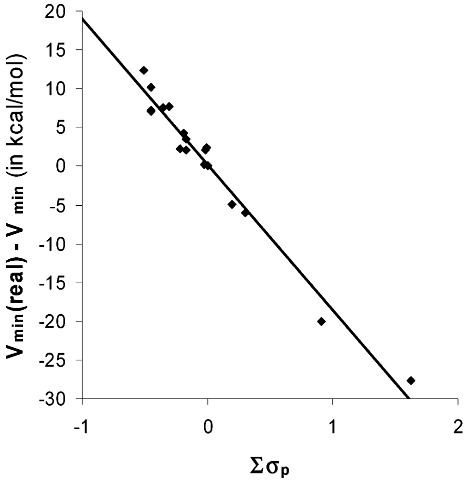

Figure 6. Correlation between Hammett $\sum\sigma_p$ and V_{min}(real) − V_{min}.

Conclusion

In conclusion, the theoretical study presented in this work suggests that the $MESP_{steric}$ value calculated from the V_{min} value of a two-layer QM−MM geometry of the PR_3 ligand is a good measure of the steric effect of that ligand. Although the correlation coefficients of 0.976, 0.980, and 0.986 calculated for the linear plots given in Figures 4a,b and 6 are quite impressive, one may consider them as a “broad-brush” approach[39] to correlations because it is rather difficult to explain the deviations of the points from the correlation line [e.g., points corresponding to P(o-i-PrC_6H_4)$_3$ in Figure 4a, PMe(CF_3)$_2$ in Figure 4b, and P(o-Tol)$_3$ and P(o-i-PrC_6H_4)$_3$ in Figure 6]. The difficulty arises because of the less precise nature of the Tolman cone angle data as well as the approximations in the ONIOM approach. Even then, the three good linear correlations obtained in this work are supportive of the ONIOM-based QM−MM approach utilizing the UFF force field in the outer layer as a reasonable method for separating the steric effect from the electronic effect of the substituent R groups. The proposed method is very simple and inexpensive in terms of computational cost, and hence the steric effect of the bulky ligands as well as their various conformations can be studied in real time for practical purposes. It may be noted that $MESP_{steric}$ is the first quantum mechanically derived electronic quantity for the steric effect of the PR_3 ligands that interpreted the cone angle data. It is hoped that the ONIOM-based technique adopted in this work would be a valuable tool for the analysis of interesting stereoelectronic features in chemical systems, particularly organometallic complexes such as metathesis catalysts. Further conformational studies and the expansion of the ligands into other classes are underway.

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Supporting Information Available: Computed geometries of the PR_3 ligands optimized at the ONIOM(B3LYP/6-31G(d,p):UFF) level. This material is available free of charge via the Internet at http://pubs.acs.org.

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