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Use of Molecular Electrostatic Potential at the Carbene Carbon as a Simple and Efficient Electronic Parameter of N-heterocyclic Carbenes[†]

Jomon Mathew and Cherumuttathu H. Suresh*

Computational Modeling and Simulation Section, National Institute for Interdisciplinary Science and Technology CSIR, Trivandrum 695 019, India

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Topographical analysis of the molecular electrostatic potential (MESP) has been carried out for a variety of N-heterocyclic carbenes at the B3LYP, BP86, and M05 levels of density functional theory (DFT) using a 6-311++G** basis set. The electron rich character of the carbene carbon is assessed in terms of the absolute minimum of the MESP at the carbene lone pair region (V_{min}), as well as the MESP at the carbene nucleus (V_C). A linear relationship is established between the V_C and Tolman electronic parameter (TEP) which suggested the use of the former as a simple and efficient descriptor for the electron donating power of N-heterocyclic carbene ligands toward metal coordination. The V_{min} of the carbene also showed good correlation with TEP. However, the deviation from linearity was higher than V_C−TEP correlation, and the reason for this was attributed to the steric effect of N-substituents at the lone pair region. The greater coordinating power of N-heterocyclic carbenes over phosphines is explained on the basis of deeper V_{min} values obtained for the former, and in fact even the V_{min} of the least electron rich N-heterocyclic carbene is comparable to the highly electron rich phosphine ligands. Thus the MESP topographical approach presented herein offers quantification of the inherent electron donating power of a free N-heterocyclic carbene ligand.

Introduction

Accurate quantification of steric and electronic effects of ligands in organometallic chemistry is essential to the rapid development in the design and synthesis of homogeneous catalytic systems with optimum stereoelectronic features. The Tolman electronic parameter (TEP) and the Tolman cone angle (θ) are the first and the most widely used electronic and steric parameters of phosphine ligands.[1,2] The TEP is calculated on the basis of the ν(CO) stretching vibration A1 in the IR spectrum of the nickel complex $(R_3P)Ni(CO)_3$. As the electron donating power of the phosphine increases, the ν(CO) vibration decreases and that is attributed to the back-donation of electron density from the metal to the CO π^* orbital. The cone angle "θ" is calculated from a Corey−Pauling−Koltun model of the ligand with metal at the apex of the cone and the phosphorus atom placed at 2.28 Å from the metal. Other noteworthy advancements in the quantification of stereoelectronic properties of phosphine ligands use methods based on specific geometrical features of the metal complexes,[3] properties of redox couples,[4,5] and theoretically derived molecular quantities.[6−8] Previous work from our group showed that the absolute minimum of the molecular electrostatic potential (MESP) corresponding to the lone pair region of a phosphine is a good quantitative measure of the electronic effect of that ligand.[9−11] In recent years, a large variety of organometallic complexes have been synthesized with the use of strong σ-donating N-heterocyclic carbenes (hereafter the abbreviation NHC is used as an acronym for N-heterocyclic carbene) as two electron donors.[12−14] In many catalytic systems, the use of NHCs is found to be more effective than the previously used phosphines. The increased reactivity of second generation Grubb's catalyst $(PR_3)(NHC)Cl_2Ru=CHR$ compared to the phosphine coordinated first generation system $(PR_3)_2Cl_2Ru=CHR$ is a classical example of the impact of NHCs in catalysis.[15,16] The NHCs are attractive choice for the

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[†] Dedicated to Prof. Shridhar R. Gadre on the occasion of his 60th birthday.

*To whom correspondence should be addressed. E-mail: sureshch@gmail.com.

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fine-tuning of steric and electronic requirement of a catalyst through substitutions at the N-center or through proper modification of the conjugation features of the cyclic moiety. The lone pair in the sp^2 orbital of the carbon can be used for making strong coordination to late transition metals and heavy main group elements, and also to bind to early transition metals and the lanthanoids to produce divalent carbon(II) compounds.[17] Very recently, Frenking and co-workers[18−20] established the existence of a new class of carbon compounds named as carbones where the carbon atom carries two lone pairs rather than one and they yield divalent carbon(0) compounds. There are several attempts to quantify the stereoelectronic features of various types of NHCs. Cavallo et al.[21,22] introduced the buried volume ($\% V_{\mathrm{Bur}}$), a measure of the space occupied by the NHC ligand in the first coordination sphere of the metal center, as a parameter for the steric effect of NHCs. Nolan and co-workers[23,24] synthesized Ni, Ir, and Ru complexes of a variety of NHCs and generated a large quantity of structural data as well as TEP values for Ni and Ir complexes. They noticed that the dissociation energy of the metal-NHC carbene bond varies in accordance with the changes in the $\% V_{\mathrm{Bur}}$ values. Further, their TEP values showed that the NHCs have much higher electron donating capacity than the phosphines.[25,26] Recently, the TEP values of 76 NHCs have been calculated from $Ni(CO)_3NHC$ complexes by Gusev.[27] They introduced a parameter named **r** ("repulsiveness") for repulsiveness as a measure of steric effect of NHCs which is derived from the enthalpy change associated with the decarbonylation reaction of $Ni(CO)_4$. It may be noted that in all previous studies, the quantification of the electronic effect of NHCs is made by studying the properties of NHC-coordinated metal complexes. Herein, we show that it is not necessary to study the complex formation to describe the coordinating power of the NHC ligand instead, the knowledge about the electron rich character of the carbene center is good enough to describe its inherent coordinating ability to a metal center.

Methodology

(a). Topographical Analysis of the MESP. The MESP is a fundamental quantity, widely used to study chemical and biological reactivity[28,29] as well as the stereoelectronic properties of organic molecules and organometallic ligands.[9−11,30−33] This three-dimensional property of the molecule can be rigorously calculated by using eq 1

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

where Z_A is the nuclear charge of atom A with radius vector $\mathbf{R}_A$. $\rho(\mathbf{r}')$ is the electron density of the molecule, and $\mathbf{r}'$ is a dummy integration variable.[28,29] The MESP at nucleus A of a molecule V_A can be obtained by dropping out the nuclear contribution due to Z_A from the definition of the MESP, via eq 2

$$V_A = \sum_{B \neq A} \frac{Z_B}{|\mathbf{R}_B-\mathbf{R}_A|} - \int \frac{\rho(\mathbf{r}')\,\mathrm{d}^3\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|} \qquad (2)$$

Investigation of the topography of the MESP is an efficient way to understand the electronic distribution in molecules through critical points (CPs) at which all partial derivatives of the function vanish.[34−37] A CP is usually represented as an ordered pair of (*rank*, *signature*). The absolute minimum of the MESP (denoted as V_{min}) has a *rank* 3 and *signature* +3.[29] The V_{min} points are often located at lone-pair regions and π-bonded regions and they represent centers of negative charge on the molecule. We have used the UNIVIS program developed by Gadre and Limaye[38] to calculate the V_{min} on the lone pair region of the NHC.

It may be noted that there is no local maximum, a (3, −3) CP, in the MESP topography[39] and therefore the quantity V_A defined in eq 2 is often used as a convenient parameter to describe the local reactivity[40−44] of a molecule. The V_A value observed for the carbene carbon atom (designated as V_{C}) will be used in the present work as an electronic descriptor. The V_{C} values can be directly obtained from the Gaussian03[45] output of

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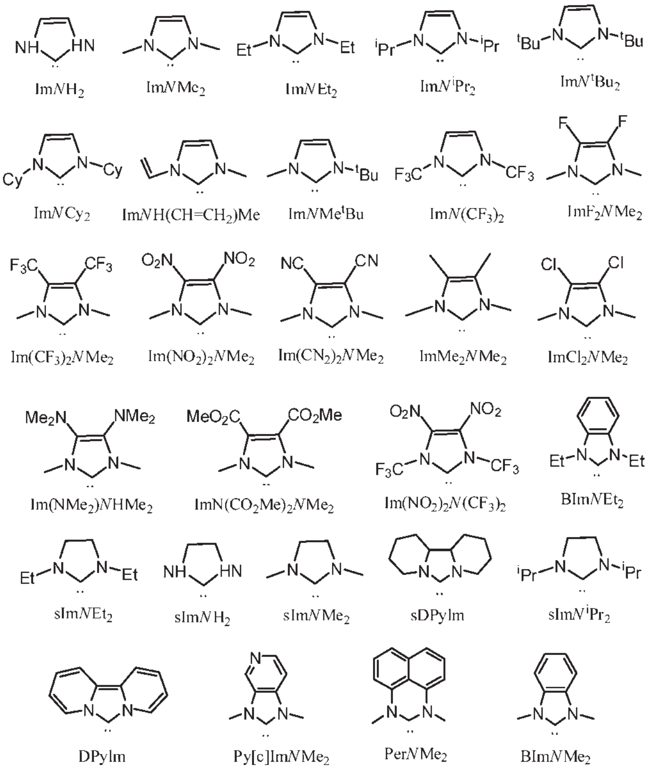

Figure 1. Schematic structures of the N-heterocyclic carbene ligands and the abbreviations used to represent them.

a MESP calculation. The $V_{\min}$ can also be calculated numerically by the 'cube' calculation in Gaussian03.

(b). Computational Methods. All the systems are optimized at B3LYP/6-311++G** level of density functional method[46,47] using Gaussian03 suite of programs,[45] and the wave function generated using the same method is used for the calculation of the MESP. For a comparison of the MESP results, all the systems are also optimized, and the MESP computed using a non hybrid functional BP86[48,49] and a hybrid meta functional M05.[50] At all the levels, a negative valued (3, +3) MESP minimum ($V_{\min}$) is located at the lone pair region of the NHC.

Results and Discussion

A set of 28 typically used NHC ligands are considered in the present study (Figure 1) to evaluate their $V_{\min}$ and V_C values. The abbreviations of the names of ligands used herein are the same as that used by Gusev.[27] MESPs of a representative set of six ligands are presented in Figure 2 wherein the $V_{\min}$, V_C, and a negative-valued MESP isosurface are depicted to indicate the lone pair region of the carbene. For the isosurface, the value −28.24 kcal/mol (−0.045 au) is chosen because it can show the progressive decrease in the negative character of the MESP when going from the electron rich to the electron poor ligands. The choice of the isosurface is arbitrary, and if we want to see the lone pair using the same isosurface value for all the molecules, we have to select a value available for the least electron rich ligand (the ligand showing the lowest negative character for $V_{\min}$). The $V_{\min}$ and V_C values at BP86/6-311++G** and M05/6-311++G** levels showed nearly the same trend to those calculated with the B3LYP functional. Compared to B3LYP, both BP86 and M05 level values showed ~3.00 kcal/mol less negative character for $V_{\min}$ and ~0.5% higher values for V_C. It may be noted that being a one electron property, the MESP is not significantly influenced by basis set effects and changes in methodology.[39,51] Therefore, the B3LYP functional is adequate enough for the analysis of $V_{\min}$ and V_C of all the NHC systems. The respective values are summarized in Table 1 (the values at BP86 and M05 levels are given in the Supporting Information).

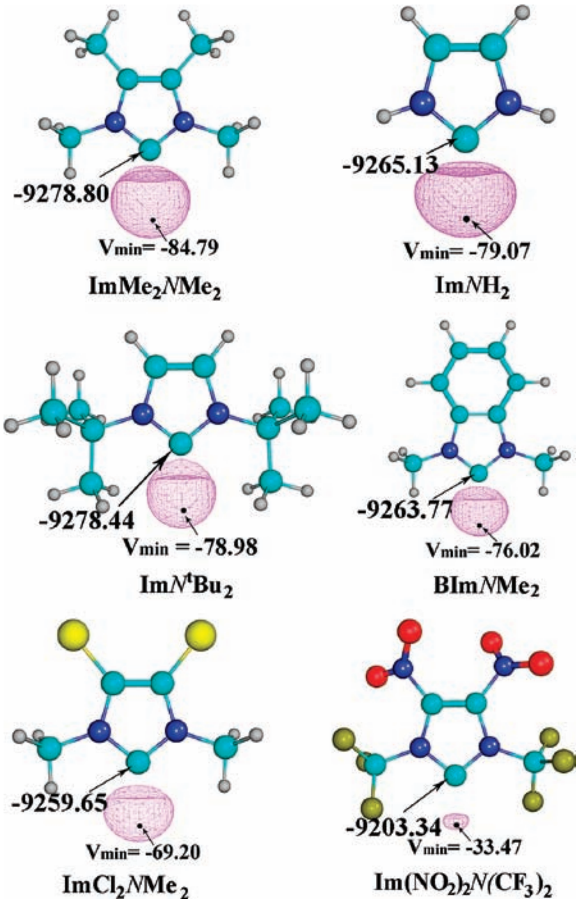

Figure 2. Representation of the MESP isosurface at −28.24 kcal/mol. $V_{\min}$ and V_C in kcal/mol.

The ligand Im(NO$_2$)$_2N$(CF$_3$)$_2$ showed the least negative $V_{\min}$ (−33.47 kcal/mol) while the deepest $V_{\min}$ is observed for Im(Me$_2$)$_2N$Me$_2$ (−84.79 kcal/mol). Similarly the V_C value is the least negative for Im(NO$_2$)$_2N$(CF$_3$)$_2$ (−9203.34 kcal/mol) and the most negative for Im(Me$_2$)$_2N$Me$_2$ (−9278.80 kcal/mol). When going from the electron deficient ImN(CF$_3$)$_2$ to the electron rich ImN^tBu$_2$, a gradual increase in the negative character of V_C, from −9232.49 kcal/mol to −9278.44 kcal/mol is observed (entries 1 to 7 in Table 1), and this reflects the increasing effect of inductive influence of the N-substituent toward electron donation. A very similar trend is also observed for the $V_{\min}$ values of entries 1 to 7, except for ImN^tBu$_2$. A lower $V_{\min}$ value of −78.98 kcal/mol for ImN^tBu$_2$ is observed compared to ImNMe$_2$ because in the

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Table 1. MESP Values of NHCs (V_{min} and V_{C}) and the Corresponding TEP Values

no.	system	V_{min} (kcal/mol)	V_{C} (kcal/mol)	TEP (cm^{-1})
1	$\mathrm{Im}N(\mathrm{CF}_3)_2$	−55.97	−9232.49	2072.0
2	$\mathrm{Im}N\mathrm{H}_2$	−79.07	−9265.13	2058.1
3	$\mathrm{Im}N\mathrm{Me}_2$	−80.43	−9273.06	2054.1
4	$\mathrm{Im}N\mathrm{Et}_2$	−81.01	−9274.32	2052.8
5	$\mathrm{Im}N{}^{\mathrm{i}}\mathrm{Pr}_2$	−81.68	−9275.36	2051.5
6	$\mathrm{Im}N\mathrm{Cy}_2$	−82.79	−9276.91	2049.7
7	$\mathrm{Im}N{}^{\mathrm{t}}\mathrm{Bu}_2$	−78.98	−9278.44	2050.6
8	$\mathrm{Im}N\mathrm{MetBu}$	−80.16	−9275.90	2051.7
9	$\mathrm{Im}N(\mathrm{CH{=}CH}_2)\mathrm{Me}$	−75.42	−9265.37	2058.1
10	$\mathrm{Im}(\mathrm{NO}_2)_2N(\mathrm{CF}_3)_2$	−33.47	−9203.34	2082.6
11	$\mathrm{Im}(\mathrm{CF}_3)_2N\mathrm{Me}_2$	−62.16	−9250.95	2063.9
12	$\mathrm{Im}(\mathrm{NO}_2)_2N\mathrm{Me}_2$	−50.75	−9235.71	2068.6
13	$\mathrm{Im}(\mathrm{CN})_2N\mathrm{Me}_2$	−54.80	−9241.25	2066.2
14	$\mathrm{ImF}_2N\mathrm{Me}_2$	−69.46	−9258.89	2059.1
15	$\mathrm{ImCl}_2N\mathrm{Me}_2$	−69.20	−9259.65	2059.0
16	$\mathrm{ImMe}_2N\mathrm{Me}_2$	−84.79	−9278.80	2051.7
17	$\mathrm{Im}(\mathrm{NMe}_2)_2N\mathrm{Me}_2$	−84.57	−9278.64	2050.2
18	$\mathrm{Im}(\mathrm{CO}_2\mathrm{Me})_2N\mathrm{Me}_2$	−71.79	−9262.24	2058.7
19	DPylm	−74.54	−9265.40	2055.9
20	$\mathrm{BIm}N\mathrm{Me}_2$	−76.02	−9263.77	2057.0
21	$\mathrm{BIm}N\mathrm{Et}_2$	−76.74	−9265.30	2055.2
22	$\mathrm{Per}N\mathrm{Me}_2$	−71.50	−9257.44	2058.5
23	sDPylm	−83.72	−9273.85	2051.3
24	$\mathrm{Py[c]Im}N\mathrm{Me}_2$	−73.48	−9259.11	2060.0
25	$\mathrm{sIm}N\mathrm{H}_2$	−80.87	−9266.10	2057.5
26	$\mathrm{sIm}N\mathrm{Me}_2$	−81.38	−9271.35	2054.7
27	$\mathrm{sIm}N\mathrm{Et}_2$	−81.70	−9272.50	2053.1
28	$\mathrm{sIm}N{}^{\mathrm{i}}\mathrm{Pr}_2$	−82.13	−9273.92	2051.9

former the bulky ${}^{\mathrm{t}}\mathrm{Bu}$ exert a significant through space effect which comes from the interaction of its C−H bonds and the lone pair electron density. The effect of substitution at the C4 and C5 position of the imidazole ring is showing a significant change in the electronic effect of NHCs (entries 10 to 18 in Table 1). The presence of electron donating Me substituents on C4 and C5, as well as at the N-centers, make the $\mathrm{Im(Me_2)_2}N\mathrm{Me_2}$ ligand the most electron rich among all while the $\mathrm{NO_2}$ substituents on C4 and C5 positions and $\mathrm{CF_3}$ substituents on N-centers bring down the electronic effect of $\mathrm{Im(NO_2)_2}N\mathrm{(CF_3)_2}$ ligand to the lowest. Ligands with saturated imidazole ring are slightly more electron donating compared to their unsaturated analogues.

The coordinating power of NHC ligands is assessed in terms of V_{min} as well as V_{C} by correlating these quantities with the TEP values. The correlation coefficient (R) for the V_{min} plot (TEP = $0.5939V_{\mathrm{min}} + 2101.3$) is 0.9638 (Figure 3) and that for the V_{C} plot (TEP = $0.4335V_{\mathrm{C}} + 6072.9$) is 0.9910 (Figure 4). In the case of V_{min} and V_{C} data obtained using the BP86 method, the slope, intercept and R values are 0.5917, 2099.7, and 0.9590, respectively for the V_{min}−TEP correlation whereas the corresponding values of the V_{C}−TEP correlation are 0.4465, 6195.4, and 0.9885. Similarly, using the M05 method, the calculated slope, intercept and R values are 0.6050, 2100.3, and 0.9629, respectively, for the V_{min}−TEP correlation while the corresponding values of the V_{C}−TEP correlation are 0.4449, 6180.1, and 0.9883 (Supporting Information). These correlations strongly suggest the use of the MESP-derived quantities as simple and efficient measure of the inherent tendency of an NHC ligand toward metal coordination. The V_{C}−TEP correlation is superior than the V_{min}−TEP correlation. The V_{min} is more sensitive than V_{C} to the subtle electronic variations in the region surrounding the lone pair and therefore, the values of V_{min} will be more influenced by bulky N-substituents ($\mathrm{Im}N{}^{\mathrm{t}}\mathrm{Bu}_2$) and N-substituents having lone pair centers ($\mathrm{Im(NO_2)_2}N\ \mathrm{(CF_3)_2}$). On the other hand, V_{C} will not be influenced significantly by such factors as the referred carbene nucleus is away from the substituent and moreover, the nuclear contribution from the carbene center is not considered in the definition of V_{C} (eq 2). We may also note that the lone pair electron density is utilized when the ligand is coordinated to a metal and therefore the through space effect of the N-substituent on the lone pair is insignificant in the complexed state of the ligand. The through space interactions will have a shielding effect on the lone pair which in turn will influence the preparation energy required for the ligand to go from the ground state electronic configuration to the configuration it adopts in the complex. Hence, we propose that the V_{min} is appropriate to use as a measure of the electron rich character of the free uncoordinated NHC ligand while V_{C} is more suited for the quantification of the coordinating power of the ligand.

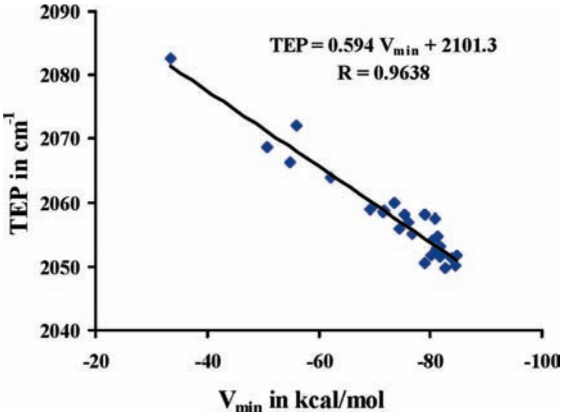

Figure 3. Correlation between V_{min} at the lone pair of N-heterocyclic carbene carbon and TEP.

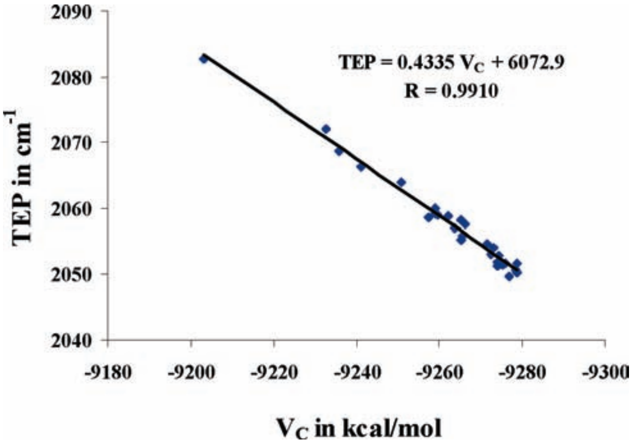

Figure 4. Correlation between MESP at the N-heterocyclic carbene carbon nucleus and TEP.

Our previous study[11] showed that $\mathrm{PCy_3}$ is one of the most electron donating phosphine ligands but the V_{min} value of this ligand (−42.56 kcal/mol at B3LYP/6-311++G**) is very close to the V_{min} value of some of the poorly electron donating NHC ligands (entries 1, 10, 12, and 13 in Table 1), suggesting that in general, the NHC ligands have much more metal-coordinating power than the phosphines. A similar conclusion was obtained earlier by Nolan et al.[21]

Conclusions

Three different DFT methodologies (B3LYP, BP86, and M05) have been used to study the topological properties of the MESP at the lone pair region of NHCs. The MESP showed very similar values and trends for V_{min} and V_{C} at the three DFT levels. Further, these quantities showed good linear relationship to the TEP, suggesting that the inherent electron donating power of the NHC to a metal center can be directly assessed from the electronic property of the uncoordinated ligand itself. On the basis of the strong correlation between V_{C} and TEP, we suggest the use of V_{C} as a simple and efficient measure of the electron donating power of the NHC. The use of V_{min} is more appropriate to compare the electron rich character of the lone pair of various carbenes which may also be affected by the through space interaction between the N-substituents and the lone pair electron density. The present MESP-based approach may find use in the fine-tuning of the electron donating power of the NHC ligands to design new organometallic catalysts.

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Supporting Information Available: Cartesian coordinates of all systems and MESP values at BP86 and M05 levels. This material is available free of charge via the Internet at http://pubs.acs.org.