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Assessment of Stereoelectronic Factors That Influence the CO_2 Fixation Ability of N-Heterocyclic Carbenes: A DFT Study

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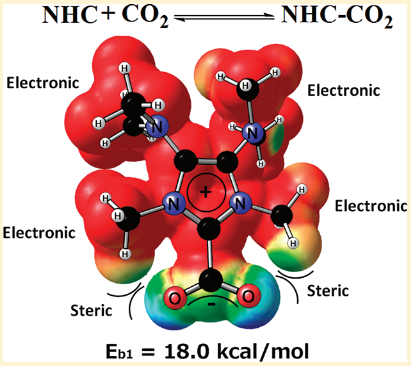
Supporting Information



ABSTRACT: The CO_2 fixation ability of N-heterocyclic carbenes (NHC) has been assessed on the basis of electronic and steric properties of the N- and C-substituents, measured in terms of molecular electrostatic potential minimum, observed at the carbene lone pair region of NHC (V_{min1}) as well as at the carboxylate region of the NHC−CO_2 adduct (V_{min2}). Both V_{min1} and V_{min2} are found to be simple and efficient descriptors of the stereoelectronic effect of NHCs. The V_{min}-based analysis also proved that the stereoelectronic effect of N- and C-substituents is additive. When only C-substituents are present in NHC, its CO_2 affinity solely depends on the electronic effect, whereas if the N-center bears the substituents, the steric factor plays a major role in the carboxylation/decarboxylation process. For standard substituents, maximum CO_2 binding energy of 18.0 kcal/mol is observed for the most electron-donating combination of NMe_2 as the C-substituent and Me as the N-substituent. Introduction of ring strain through five-membered ring fusion at the NC bond slightly increased the electron-rich character of the carbene lone pair and also enhanced the CO_2 binding energy to 20.9 kcal/mol. To further improve the CO_2 fixing ability of NHCs, we have proposed the use of CH_2OH, $CH_2NHCOMe$, and CH_2NHPh as N-substituents, as they participate in intramolecular hydrogen bond interaction with the carboxylate. With the new strategy, considerable improvement in the CO_2 binding energy (26.5 to 33.0 kcal/mol) is observed.

INTRODUCTION

The chemistry surrounding N-heterocyclic carbenes (NHC) has become a prominent area of research for the past two decades due to versatile utilization of these ligands in producing a large variety of metal complexes, uses as reagents in organic reactions, and identification of these molecules as efficient organocatalysts.[1−14] A large variety of NHCs with structural and electronic diversities have been reported.[12,14−19] Despite the high unsaturation of the carbene carbon, NHCs show high stability due to the mesomeric interaction of the lone pair electrons on the nitrogen atoms with the vacant p orbital of the sp^2 hybridized carbene. Further, the ability to tune the stereoelectronic features of the ligand through substituents on C4 and C5 positions as well as N-centers make them attractive for the design of homogeneous catalysts.[11] A number of attempts have been carried out in the past to characterize reliable steric and electronic parameters for these systems.[20−39] Huynh et al.[20] proposed that the ^{13}C chemical shift of the carbene carbon in NHC complexes are useful to characterize the donor strength of NHC ligands in palladium(II)−benzimidazolylidene complexes. Lever et al. used electrochemical E_0 value (Lever electronic parameter, LEP) for various redox couples in a series of Ru^{III}/Ru^{II} complexes containing the ligands of interest.[21−23] Tolman electronic parameter (TEP)[24] which measures the fundamental CO stretching frequencies of $Ni(CO)_3(NHC)$ complexes is a widely used parameter to evaluate the electron donor ability of the NHC ligands. The TEP approach was built upon the pioneering work by Strohmeier et al.[40] and Bigorgne et al.[41] which makes use of the fact that the electron density from the ligand not only passed on to the metal but also to the anti-bonding orbital of CO ligands. Further, a large quantity of structural data have been generated by various groups to correlate the TEP values obtained for a large variety of NHCs in different metal carbonyl complexes.[25−30] Gusev[31] used a diverse group of representative NHC ligands to quantify electron-donor properties by means of TEP and steric properties by a parameter called "repulsiveness" which is a measure of direct repulsive interaction between the NHC and carbonyl ligands of $Ni(CO)_3(NHC)$. Herrmann et al. examined and classified the relative σ-donor/π-acceptor quality of various NHC ligands by means of IR spectroscopy at the corresponding $Rh(CO)_2I(NHC)$ complexes.[42] A systematic investigation of the electronic and steric properties of various 4,5-dialkylated NHCs was reported by Glorius et al.[43] Recently studies from our laboratory[32] showed that molecular electrostatic potential (MESP) at the carbene lone pair or at the nucleus of the carbene carbon can be used as a simple and efficient electronic parameter of NHCs and showed good correlation with TEP. Though the core of the NHC is largely planar, bulky substituents on the N-centers can exert a large steric effect upon coordination to a metal, and the proper

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quantification of such an effect is of great interest in catalyst design. An approach based on the critical features of the molecular electrostatic potential is also developed for the quantification of steric and electronic properties of NHCs in Grubbs second-generation olefin metathesis catalysts.[44] Liu et al. studied NHC steric contours to understand the effects of NHC ligands on the reversal of regioselectivity in Ni-catalyzed reductive couplings of alkynes and aldehydes.[45] The buried volume method developed by Cavallo et al.[34−37,46] quantifies the steric demand of various NHCs by means of a single parameter called percent buried volume ($\%V_{\mathrm{bur}}$) which is defined as the percent of the total volume of a sphere of definite radius occupied by a ligand with a metal center at its core. The bond dissociation energy of NHC ligands in metal complexes reflects the relative strength of the metal−NHC bond which can also be dependent on the steric properties of the NHC ligands.[35,37,47]

Interestingly, all the previous quantifications of structural and electronic parameters of NHCs are based on treating NHC as a ligand in various metal complexes. Because NHCs are also used as versatile catalysts for organic transformations, to describe the stereoelectronic properties of the 'NHC catalyst', an organic model could be more useful than an organometallic model. Therefore, we propose that the formation of the NHC−CO_2 adduct offers a simple and elegant model to describe and quantify the electronic and steric properties of NHC catalyst. Louie et al. studied factors influencing the decarboxylation of 1,3-disubstituted-2-imidazolium carboxylates, and their results indicate that the steric bulkiness on the N-substituent increases the ability of NHC−CO_2 to decarboxylate and extra electron density on the imidazolium ring enhances the stability of NHC−CO_2 adducts.[48] The usefulness of NHC−CS_2 adducts had also been proposed by Delaude et al. for assessing the steric and electronic properties of NHC ligands.[49] Most of the NHC-mediated organocatalysis includes the formation of covalent, active intermediates by their addition to double bonds as the key step, leading to nucleophilic incorporation of the carbonyl functional group.[50−52] Such a σ-donor character of NHCs has also been applied to CO_2 capture, and the resulting imidazolium-2-carboxylates are identified as the typical NHC−CO_2 adducts.[53−56] It is assumed that a dynamic equilibrium of the NHC−CO_2 adduct, free CO_2, and the corresponding NHCs exists in the organic solution of NHC−CO_2 adducts. Hence, the dissociation energy, E_{b1}, of the NHC−CO_2 adduct can serve as a good energetic parameter to describe the nucleophilic behavior of NHCs in organic transformations. Further, the CO_2 capture reaction by NHC enables us to understand the atmospheric CO_2 fixation by various NHCs. This in turn can help in the designing of distinct NHC architectures of desirable electronic and steric demand for new organocatalytic transformations.

COMPUTATIONAL DETAILS

We have selected four sets of unsaturated NHCs for the present study in which some NHCs are structurally characterized compounds and some others are possessing features that can be of interest for future investigation. Set A includes NHCs with substituents only on the carbon atoms, set B includes substituents only on the nitrogen atoms, set C includes substituents on both carbon and nitrogen atoms, and set D consists of some miscellaneous NHCs with ring fusions (Figure 1). All the NHC geometries and their CO_2 adducts were optimized using density functional theory at the MPWB1K/6-31++G(d,p) level[57−59] using Gaussian03 suite of programs,[60] and the wave function generated from the same method is used for the molecular electrostatic potential (MESP) analysis.[61,62] The MESP of a molecule is a real physical property, and that can be determined experimentally by X-ray diffraction techniques or calculated rigorously from the electron density, $\rho(\mathbf{r})$, distribution using eq 1, where Z_A is the charge on nucleus A located at $\mathbf{R}_A$ and $\mathbf{r}'$ is a dummy integration variable.

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

MESP at the carbene lone pair region (V_{min1}) and the MESP at the carboxylate moiety of the NHC−CO_2 adduct (V_{min2}) are calculated by the cube calculation in Gaussian 03. MESP has been widely used as an efficient electronic descriptor to quantify substituent effects in several organic systems.[63−74] The energy released due to the bonding interaction between NHC and CO_2 (E_{b1}) is calculated using the supermolecular approach. According to the supermolecular approach, E_{b1} is evaluated as the difference between the energy of the NHC−CO_2 adduct and sum of the energies of its subsystems (NHC and CO_2).

RESULTS AND DISCUSSION

All the NHCs show a negative-valued MESP minimum, V_{min1}, at the lone pair region while the NHC−CO_2 adducts show a negative-valued V_{min2} at the oxygen lone pair region. Considering $ImNH_2$ as the unsubstituted reference system (all N- and C- substituents are H; $V_{\mathrm{min1}} = -83.1$ kcal/mol), the difference between the V_{min1} of a ligand and V_{min1} of the reference system (ΔV_{min1}) is used as a measure of the combined effect of the C- and N-substituents. In the case of ligands in set A, ΔV_{min1} gives the combined effect of the C4 and C5 substituents. For instance, the V_{min1} values −87.2, −87.5, and −52.5 kcal/mol calculated, respectively, for $ImEt_2$, $Im(NMe_2)_2$, and $Im(NO_2)$ suggest that the effects of C-substituents Et, NMe_2, and NO_2 are −4.1, −4.4, and 30.7 kcal/mol, respectively (Table 1). In the case of NHC−CO_2 adducts, the relative value of the V_{min2} with respect to the reference system (ΔV_{min2}) is useful to assess the substituent effect. Both V_{min1} and V_{min2} (Table 1) follow almost the same trend in the relative order of the values and show a strong linear correlation between them, indicating that the substituents exert almost the same stereoelectronic effect in both free and complexed NHCs.

The MESP painted on the van der Waals surface is presented in Figure 2 for a representative set of NHC−CO_2 adducts which shows strong charge separation in the systems; the carboxylate moiety is negatively charged while the rest of the molecule is positively charged. These pictures also indicate that the carbene lone pair is donated to the CO_2 carbon and the bonding is very similar to a ligand−metal 2e coordination bond observed in organometallic complexes. In the NHC−CO_2 adduct, the negative charge is delocalized on the CO_2 moiety while the positive charge is delocalized on the NHC ring. Figure 3 shows V_{min1} of a representative set of NHC ligands taken from set A and set B as well as the V_{min2} of the corresponding CO_2 adducts. For set A and set B ligands, Table 1 also depicts the energy released due to the coordinate bonding interaction between NHC and CO_2 (E_{b1}), the distance between carbene carbon and the carbonyl carbon (d_{cc}), and angle between the plane of NHC and CO_2 of the NHC−CO_2 adduct (θ).

In general, when V_{min1} is more negative, more energy (E_{b1}) is released during NHC−CO_2 adduct formation. Electron-donating C-substituents always show a high value for E_{b1}, the highest being 21.0 kcal/mol for $Im(NMe_2)_2$. On the other hand, CO_2 binding is weak when the C-substituent is electron withdrawing, and the lowest value of E_{b1} (1.9 kcal/mol) is

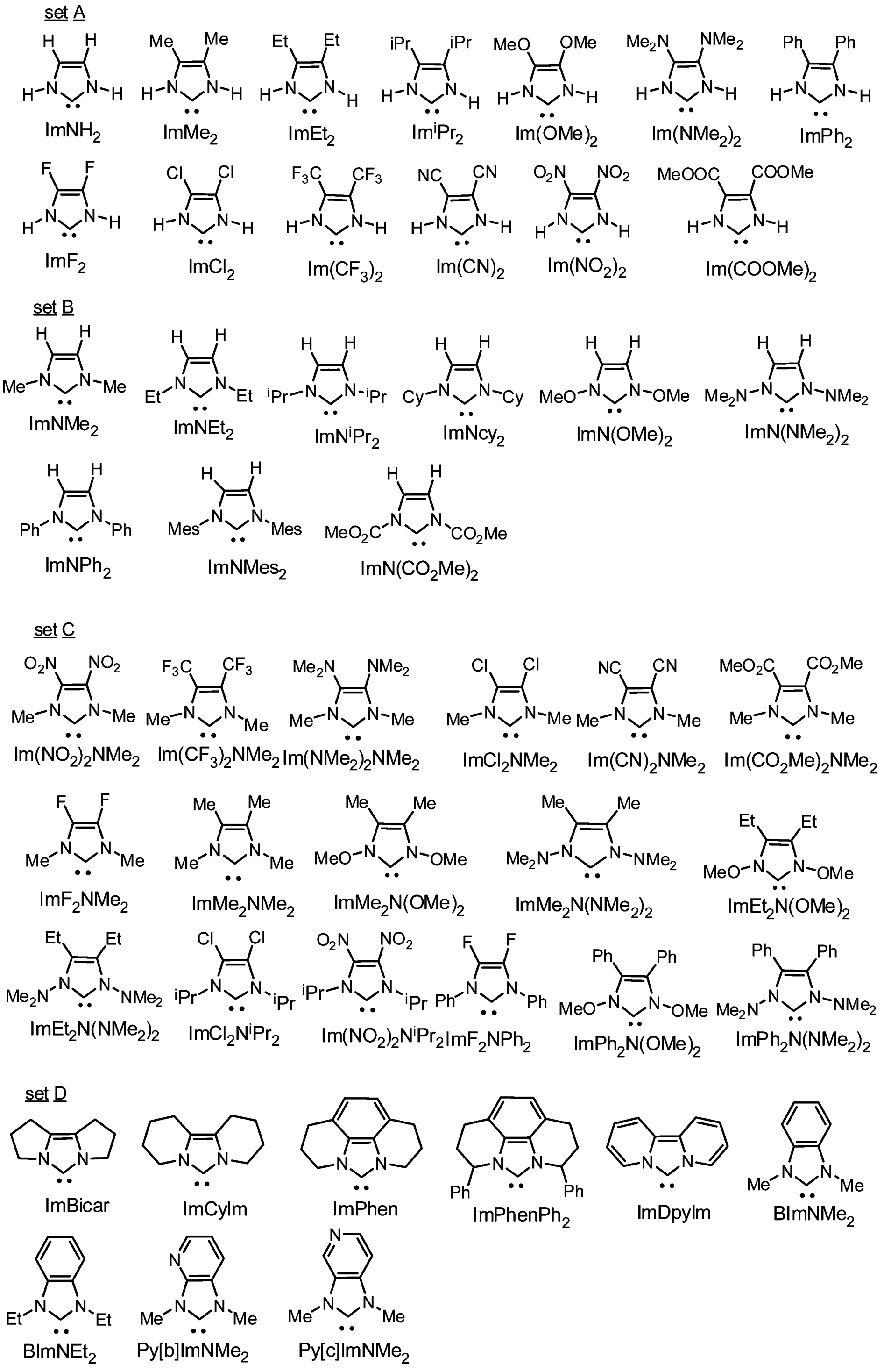

Figure 1. The selected NHCs with typical abbreviations.[31]

obtained for $Im(NO_2)_2$. A good correlation between V_{min1} and E_{b1} (correlation coefficient is 0.99) exists for set A systems (Figure 4). This suggests that the CO_2 binding energy of set A systems solely depends on the electronic effects of the C-substituents. The value of θ is zero or close to zero for set A systems, which also indicates that the CO_2 binding is not sterically affected by the C4 and C5 substituents. Hence, V_{min1} can be treated as a convenient electronic parameter to describe the substituent effect in NHCs which in turn can explain the binding efficiency of CO_2 though a 2e coordination bond from the carbene. The more electron-rich the carbene, the stronger the coordination bond. This fact is also reflected in the CC bond distance (d_{cc}) of the NHC adduct (Table 1). The shortening of the CC bond occurs with increase in the electron-donating nature of the NHC and results in weakening of the CO bond.

It is believed that the substituents at the nitrogen atoms significantly contribute to the steric demand of the carbene carbon and they also affect the stability of the NHC−CO_2 adducts. Both V_{min1} and V_{min2} show less negative values for set

B systems than for set A systems. This suggests that electronically, substitution at the N-positions is less effective for making electron-rich carbene than substitution at C-positions. The binding distance of CO_2 with NHC (d_{cc}) is also increased in the case of N-substituted systems compared to C-substituted systems. This can be attributed to a decrease in the electron-rich character of set B systems as well as increase in the steric effect. The θ values give a good indication of the steric effect which falls in the range of 18–90° for all the N-substituted systems except the $ImNMe_2-CO_2$. In the case of $ImNMe_2-CO_2$, θ observed for the crystal structure[48] is 29.0° whereas the calculated structure showed a value of 0.0°. Calculation also showed that $ImNMe_2-CO_2$ can exist in a twisted conformation (θ = 26.4°) which is less stable than the planar conformation by 0.8 kcal/mol. These results suggest that N-substituents significantly hinder the coplanarity of the carboxylate moiety and imidazolium ring. The V_{min1} of set B systems are significantly deviated from the correlation line obtained for set A systems (Figure 4). Since the correlation line of set A systems is free from steric influence, the deviation of V_{min1} points of set B systems from set A line is considered as due to steric influence of the N-substituents. From the analysis of V_{min1} of set A and set B systems, it is clear that alkyl substitution at the C- and N-positions can significantly increase the negative MESP around the carbene lone pair. The C-substitution with NMe_2 is also very effective for making an electron-rich carbene while the same at N-positions will not be effective.

Table 1. V_{min1} of Free NHCs and V_{min2}, E_{b1}, d_{cc}, and θ of $NHC-CO_2$ Adducts of Set A and Set B NHCs

system	V_{min1} (kcal/mol)	V_{min2} (kcal/mol)	E_{b1} (kcal/mol)	d_{cc} (Å)	θ (deg)
$ImNH_2$	−83.1	−82.3	16.4	1.532	0.0
$ImMe_2$	−87.2	−86.0	18.9	1.528	0.0
$ImEt_2$	−87.2	−86.3	19.4	1.527	0.0
Im^iPr_2	−87.5	−87.1	19.9	1.527	0.0
$Im(OMe)_2$	−83.8	−84.7	17.3	1.522	0.0
$Im(NMe_2)_2$	−87.5	−88.5	21.0	1.522	1.3
$ImPh_2$	−81.6	−85.8	17.1	1.529	0.4
ImF_2	−71.1	−74.4	11.3	1.537	0.0
$ImCl_2$	−70.4	−76.4	11.1	1.538	0.0
$Im(CF_3)_2$	−62.6	−71.1	7.3	1.542	0.5
$Im(CN)_2$	−54.8	−66.1	4.2	1.546	0.0
$Im(NO_2)_2$	−52.5	−64.1	1.9	1.553	0.0
$Im(CO_2Me)_2$	−72.9	−78.7	11.4	1.538	1.8
$ImNMe_2$	−84.8	−85.8	16.3	1.540	0.0
$ImNEt_2$	−85.0	−84.3	18.2	1.544	18.6
$ImNiPr_2$	−86.0	−84.0	17.2	1.543	32.6
$ImNcy_2$	−86.8	−85.5	17.5	1.544	34.3
$ImN(OMe)_2$	−69.7	−79.8	6.0	1.559	45.4
$ImN(NMe_2)_2$	−75.6	−78.4	10.2	1.545	45.1
$ImNPh_2$	−75.5	−82.0	7.9	1.545	90.7
$ImNMes_2$	−83.9	−84.8	15.6	1.536	80.7
$ImN(CO_2Me)_2$	−57.4	−68.7	0.8	1.568	89.9

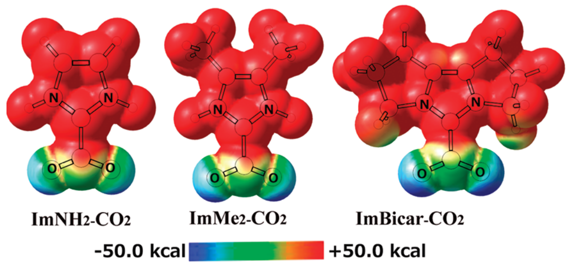

Figure 2. The MESP mapped on to the van der Waals surface of a representative set of $NHC-CO_2$ adducts.

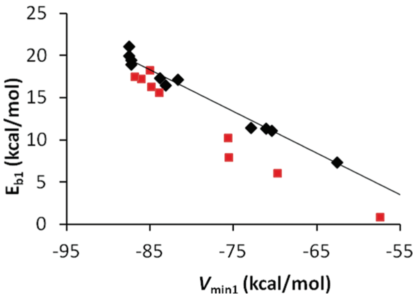

Figure 4. Correlation between V_{min1} and E_{b1} of the NHCs given in set A (black) and set B (red).

Set C and set D systems carry both N-and C-substituents wherein the former has well-defined substituents while the latter has saturated/unsaturated ring fusions at the C–N bonds. Figure 5 shows the V_{min1} of a representative set of NHC ligands

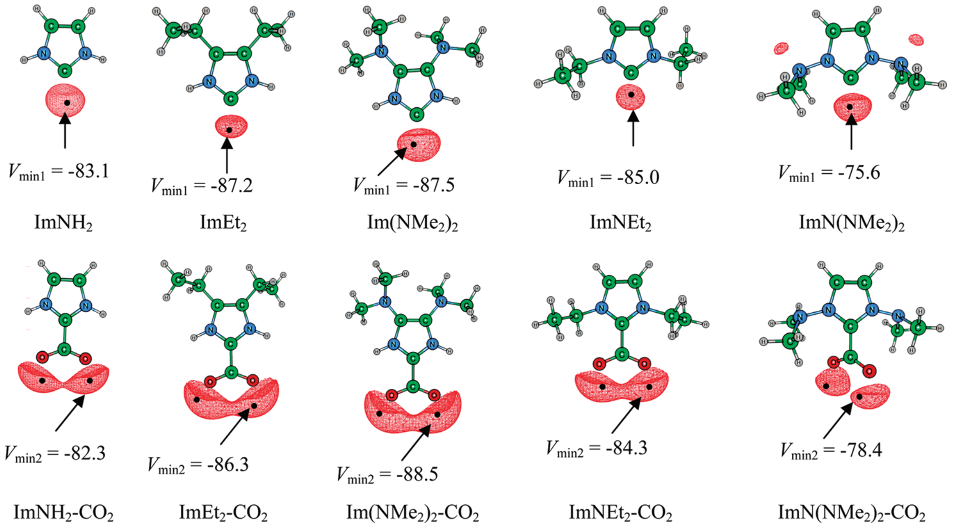

Figure 3. Representation of the MESP isosurface of some set A and set B NHCs. V_{min} values are given in kcal/mol.

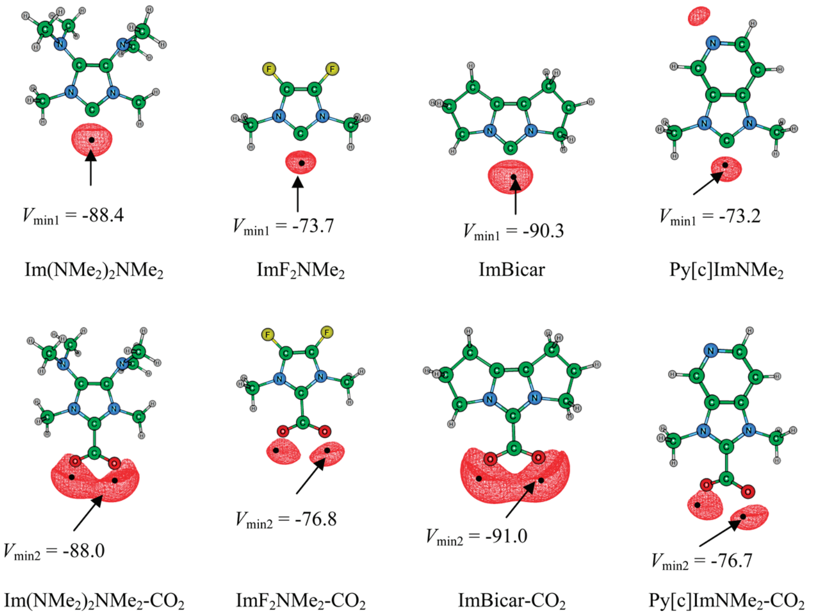

Figure 5. Representation of the MESP isosurface of some set C and set D NHCs. V_{min} values are given in kcal/mol.

Table 2. V_{min1} of Free NHCs and V_{min2}, E_{b1}, d_{cc}, and θ of NHC−CO$_2$ Adducts of Set C and Set D NHCs

system	V_{min1} (kcal/mol)	V_{min2} (kcal/mol)	E_{b1} (kcal/mol)	d_{cc} (Å)	θ (deg)
Im(NO$_2$)$_2$NMe$_2$	−54.7	−65.6	1.8	1.569	33.7
Im(CF$_3$)$_2$NMe$_2$	−66.6	−73.5	7.1	1.557	29.3
Im(NMe$_2$)$_2$NMe$_2$	−88.4	−88.0	18.0	1.549	27.8
ImCl$_2$NMe$_2$	−72.9	−77.4	10.7	1.561	26.2
Im(CN)$_2$NMe$_2$	−58.4	−67.1	4.8	1.567	30.0
Im(CO$_2$Me)$_2$NMe$_2$	−75.1	−79.9	10.0	1.557	35.4
ImF$_2$NMe$_2$	−73.7	−76.8	11.0	1.560	18.5
ImMe$_2$NMe$_2$	−88.2	−86.5	17.7	1.550	26.4
ImMe$_2$N(OMe)$_2$	−73.6	−83.3	8.4	1.555	45.5
ImMe$_2$N(NMe$_2$)$_2$	−78.5	−80.8	12.5	1.542	45.7
ImEt$_2$N(OMe)$_2$	−73.3	−83.4	8.3	1.555	45.4
ImEt$_2$N(NMe$_2$)$_2$	−77.4	−80.8	12.3	1.543	50.4
ImPh$_2$N(OMe)$_2$	−73.7	−82.9	7.1	1.556	48.5
ImPh$_2$N(NMe$_2$)$_2$	−73.4	−79.6	10.5	1.542	53.3
ImCl$_2$N^{i}Pr$_2$	−74.2	−78.3	10.6	1.553	45.9
Im(NO$_2$)$_2$N^{i}Pr$_2$	−56.9	−67.6	4.2	1.558	42.7
ImF$_2$NPh$_2$	−67.7	−77.7	4.4	1.552	90.6
ImBicar	−90.3	−91.0	20.9	1.530	0.6
ImCylm	−89.9	−90.0	20.1	1.540	14.9
ImPhen	−83.3	−86.7	17.5	1.540	5.8
IMPhenPh$_2$	−83.7	−87.1	14.7	1.540	34.8
ImDpylm	−77.9	−85.9	17.6	1.530	0.0
BImNMe$_2$	−79.3	−80.8	13.2	1.552	34.0
BImNEt$_2$	−79.4	−81.5	14.9	1.547	30.9
Py[b]ImNMe$_2$	−75.9	−80.6	11.8	1.551	25.6
Py[c]ImNMe$_2$	−73.2	−76.7	10.8	1.554	35.7

of sets C and D and V_{min2} of the corresponding CO$_2$ adduct. The V_{min1} of free NHCs and V_{min2}, E_{b1}, d_{cc}, and θ of NHC−CO$_2$ adducts of set C and D systems are given in Table 2.

In Figure 6, (V_{min1}, E_{b1}) points are plotted for set C and D systems along with V_{min1} versus E_{b1} correlation line for set A systems. This plot shows that set C and D systems agree with the general observation that CO$_2$ binding energy increases with an increase in the electron-rich character of the carbene lone pair. Because the correlation line for set A systems occupy steric free area, the deviation of (V_{min1}, E_{b1}) points from this line can be attributed to the steric effect. In general, the steric effect decreases the affinity of NHC toward CO$_2$. The trends observed in d_{cc} and θ are very similar to that observed in the cases of set A and set B systems. Sterically demanding substituents increase both θ and d_{cc}.

Because substituent effects are mostly additive in organic systems, the ligands in set C with substituents on both the ring nitrogen atoms and ring carbon atoms are expected to show the combined effect on the MESP at the carbene lone pair. Applying additivity of substituent effect, V_{min1} or V_{min2} of

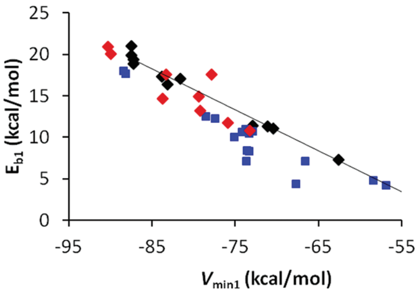

Figure 6. Correlation between V_{min1} and E_{b1} of the NHCs given in set A (black), set C (blue), and set D (red).

set C systems can be predicted by adding the contributions (ΔV_{min} values) of the C-substituents from set A systems and N-substituents from set B systems to the corresponding V_{min1} or V_{min2} of the unsubstituted $ImNH_2$ system (Supporting Information). All the systems follow additivity to a large extent (Figure 7), as the predicted V_{min1} and V_{min2} values are approximately ±3% deviated from the actual values for most of the systems. However, the ImF_2NPh_2 and $ImPh_2N(OMe)_2$ systems show a deviation of 6.3% and 7.6%, respectively, for V_{min1}, and the $ImF_2NPh_2{-}CO_2$ system shows a deviation of 4.7% for V_{min2}. The most electron-rich NHC is $Im(NMe_2)_2NMe_2$, as it contains the most electron-donating NMe_2 substituent at the C-position and Me at the N-position.

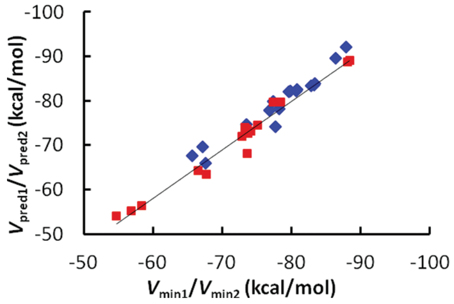

Figure 7. Correlation between actual V_{min} and predicted V_{min} using additivity of substituent effect. Red squares correspond to V_{min1} and V_{pred1}, and blue squares correspond to V_{min2} and V_{pred2}.

Substitution in ImBicar can be compared with the $ImMe_2NMe_2$ given in set C because the C- and N-positions of both systems are connected to saturated hydrocarbon moieties. Importantly, V_{min1} (−90.3 kcal/mol) and V_{min2} (−91.0 kcal/mol) of ImBicar are, respectively, 2.1 and 4.5 kcal/mol more negative than $ImMe_2NMe_2$. This means that the ring fusion and the ring strain associated with the additional five-membered ring in ImBicar can enhance the electron density at the carbene lone pair. Very similar observation of V_{min} is observed for ImCylm where the N- and C-substitutions are filled with saturated hydrocarbon portions. Among all the NHC systems studied herein, MESP features suggest that the most electron-rich systems are ImBicar and ImCylm, and they show the highest CO_2 binding affinity of 20.9 and 20.1 kcal/mol, respectively. The C- and N-positions of ImPhen, $IMPhenPh_2$, $BImNMe_2$, $BImNEt_2$, $Py[b]ImNMe_2$, and $Py[c]ImNMe_2$ are connected to sp^2- and sp^3-hybridized carbon atoms, respectively and therefore the V_{min} of these systems can be compared with $ImPh_2NMe_2$. Similarly, V_{min} of ImDpylm can be assessed on the basis of the V_{min} of $ImPh_2NPh_2$ system. These comparisons clearly indicate that, the ring-fused structures show slightly more negative character for V_{min} in both free and CO_2 complexed systems. A connection to sp^2 carbon will decrease the electron density on the carbene. In general, ring fusion at the CC and CN bonds of the NHC system as well as ring strain due to additional five-membered ring is good for increasing the electron-rich character of the carbene lone pair as well as its CO_2 affinity.

On the basis of the MESP-based analysis of the carbene center of NHC, we can see that the combined effect of alkyl and NMe_2 substitution can at the most increase the binding energy to a value of 18.0 kcal/mol, which is 1.6 kcal/mol more than unsubstituted NHC (16.4 kcal/mol). For standard experimental conditions, even the most negative E_{b1} value (20.9 kcal/mol) observed for ImBicar is not enough to make stable $NHC{-}CO_2$ complexes. Therefore, to enhance the binding energy, we propose the use of N-substituents with hydrogen bond formation ability with the incoming CO_2 moiety, and such systems (set E) are presented in Figure 8.

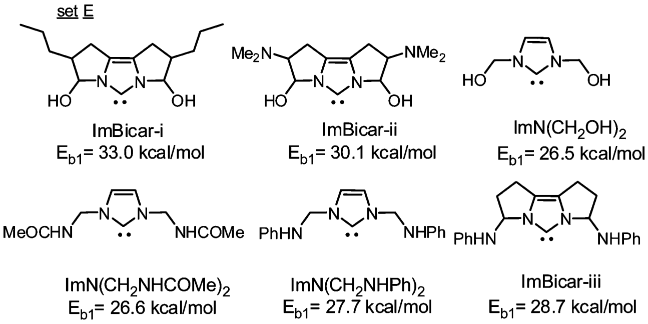

Figure 8. Selected new designs of NHCs. The CO_2 binding energy is also depicted.

The selected N-substituents are CH_2OH, $CH_2NHCOMe$, CH_2NHPh, and related ring-fused substituents. The incorporation of amino/amido groups on the N-positions is already reported in the literature.[75,76] All the systems in set E show considerable improvement (6−14 kcal/mol) in the binding energy from the most stable $ImBicar{-}CO_2$ system.

In Figure 9, the structures of the $NHC{-}CO_2$ complexes of set E are presented which show the formation of hydrogen

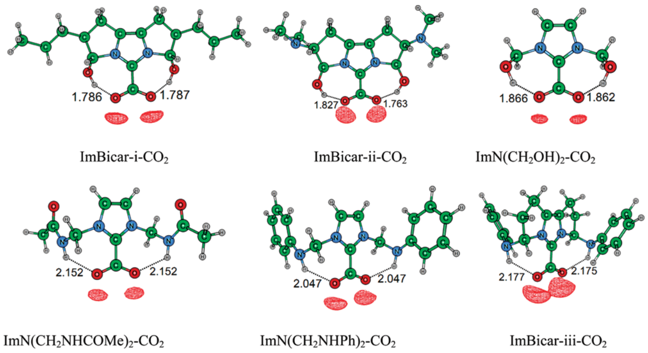

Figure 9. Representation of the MESP isosurface and geometrical parameters of set E $NHC{-}CO_2$ adducts. Bond lengths are given in angstroms.

Table 3. V_{min1} of Free NHCs and V_{min2}, E_{b1}, d_{cc}, and θ of NHC−CO_2 Adducts of Set E NHCs

system	V_{min1} (kcal/mol)	V_{min2} (kcal/mol)	E_{b1} (kcal/mol)	d_{cc} (Å)	θ (deg)
ImBicar-i	−69.3	−73.6	33.0	1.515	0.2
ImBicar-ii	−70.5	−74.0	30.1	1.516	0.4
$ImN(CH_2OH)_2$	−72.2	−68.7	26.5	1.529	0.5
$ImN(CH_2NHCOMe)_2$	−75.0	−71.2	26.6	1.531	17.3
$ImN(CH_2NHPh)_2$	−64.8	−73.9	27.7	1.535	6.7
ImBicar-iii	−79.2	−80.0	28.7	1.517	10.4

bond interaction between the carboxylate group and the N-substituents (Table 3). ImBicar-i and ImBicar-ii show good binding affinity (33.0 and 30.1 kcal/mol, respectively) due to the combined effect of electron-donating substituents, ring strain, and hydrogen bonding interactions. Substitution of the *N*-amino group also stabilizes the NHC−CO_2 adduct via hydrogen bonding interactions. $ImN(CH_2NHCOMe)_2$ shows a binding affinity (E_{b1}) of 26.6 kcal/mol whereas $ImN(CH_2NHPh)_2$ and ImBicar-iii shows 27.7 and 28.7 kcal/mol, respectively.

■ CONCLUSIONS

In this study, we have used topological features of MESP to evaluate the stereoelectronic properties of NHC as well as the NHC−CO_2 adduct. In general, the electron-rich character of the carbene center is well reflected on the V_{min1} value observed for the carbene lone pair. The C-substituents exert electronic effect on the carbene center while N-substituents contribute significantly through steric effects. For the combination of standard substituents given in set C, the most electron-rich NHC is $Im(NMe_2)_2NMe_2$, as it contains the most electron-donating NMe_2 substituent at the C-position and Me at the N-position. V_{min1} or V_{min2} of set C systems can be predicted by applying the additivity of substituent effect. It is also observed that the ring fusion at the CC and CN bonds of the NHC system and the associated ring strain in the structure is good for increasing the electron-rich character of the carbene lone pair. In addition, the use of an N-substituent such as CH_2OH, $CH_2NHCOMe$, and CH_2NHPh substantially improve the CO_2 fixing ability of NHCs.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Cartesian coordinates and thermodynamic parameters of all the geometries. This material is available free of charge via the Internet at http://pubs.acs.org/.

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■ REFERENCES

(1) Arduengo, A. J. III. *Acc. Chem. Res.* **1999**, *32*, 913.

(2) Connor, E. F.; Nyce, G. W.; Myers, M.; Möck, A.; Hedrick, J. L. *J. Am. Chem. Soc.* **2002**, *124*, 914.

(3) Fürstner, A.; Ackermann, L.; Gabor, B.; Goddard, R.; Lehmann, C. W.; Mynott, R.; Stelzer, F.; Thiel, O. R. *Chem.—Eur. J.* **2001**, *7*, 3236.

(4) Garber, S. B.; Kingsbury, J. S.; Gray, B. L.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2000**, *122*, 8168.

(5) Stauffer, S. R.; Lee, S.; Stambuli, J. P.; Hauck, S. I.; Hartwig, J. F. *Org. Lett.* **2000**, *2*, 1423.

(6) Trnka, T. M.; Grubbs, R. H. *Acc. Chem. Res.* **2001**, *34*, 18.

(7) Enders, D.; Balensiefer, T. *Acc. Chem. Res.* **2004**, *37*, 534.

(8) Enders, D.; Niemeier, O.; Henseler, A. *Chem. Rev.* **2007**, *107*, 5606.

(9) Alcarazo, M.; Stork, T.; Anoop, A.; Thiel, W.; Fürstner, A. *Angew. Chem., Int. Ed.* **2010**, *49*, 2542.

(10) de Frémont, P.; Marion, N.; Nolan, S. P. *Coord. Chem. Rev.* **2009**, *253*, 862.

(11) Dröge, T.; Glorius, F. *Angew. Chem., Int. Ed.* **2010**, *49*, 6940.

(12) Hahn, F. E.; Jahnke, M. C. *Angew. Chem., Int. Ed.* **2008**, *47*, 3122.

(13) Kirmse, W. *Angew. Chem., Int. Ed.* **2010**, *49*, 8798.

(14) Radius, U.; Bickelhaupt, F. M. *Coord. Chem. Rev.* **2009**, *253*, 678.

(15) Poyatos, M.; Mata, J. A.; Peris, E. *Chem. Rev.* **2009**, *109*, 3677.

(16) Prades, A.; Poyatos, M.; Mata, J. A.; Peris, E. *Angew. Chem., Int. Ed.* **2011**, *50*, 7666.

(17) Nemcsok, D.; Wichmann, K.; Frenking, G. *Organometallics* **2004**, *23*, 3640.

(18) Tonner, R.; Frenking, G. *Chem. Commun.* **2008**, 1584.

(19) Tonner, R.; Heydenrych, G.; Frenking, G. *Chem. Asian J.* **2007**, *2*, 1555.

(20) Huynh, H. V.; Han, Y.; Jothibasu, R.; Yang, J. A. *Organometallics* **2009**, *28*, 5395.

(21) Fielder, S. S.; Osborne, M. C.; Lever, A. B. P.; Pietro, W. J. *J. Am. Chem. Soc.* **1995**, *117*, 6990.

(22) Lever, A. B. P. *Inorg. Chem.* **1990**, *29*, 1271.

(23) Lever, A. B. P. *Inorg. Chem.* **1991**, *30*, 1980.

(24) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

(25) Chianese, A. R.; Li, X.; Janzen, M. C.; Faller, J. W.; Crabtree, R. H. *Organometallics* **2003**, *22*, 1663.

(26) Fürstner, A.; Alcarazo, M.; Krause, H.; Lehmann, C. W. *J. Am. Chem. Soc.* **2007**, *129*, 12676.

(27) Leuthäußer, S.; Schwarz, D.; Plenio, H. *Chem.—Eur. J.* **2007**, *13*, 7195.

(28) Peris, E.; Crabtree, R. H. *Coord. Chem. Rev.* **2004**, *248*, 2239.

(29) Vorfait, T.; Leuthäußer, S.; Plenio, H. *Angew. Chem., Int. Ed.* **2009**, *48*, 5191.

(30) Wolf, S.; Plenio, H. *J. Organomet. Chem.* **2009**, *694*, 1487.

(31) Gusev, D. G. *Organometallics* **2009**, *28*, 6458.

(32) Mathew, J.; Suresh, C. H. *Inorg. Chem.* **2010**, *49*, 4665.

(33) Clavier, H.; Nolan, S. P. *Chem. Commun.* **2010**, *46*, 841.

(34) Dorta, R.; Scott, N. M.; Costabile, C.; Cavallo, L.; Hoff, C. D.; Nolan, S. P. *J. Am. Chem. Soc.* **2005**, *127*, 2485.

(35) Hillier, A. C.; Sommer, W. J.; Yong, B. S.; Petersen, J. L.; Cavallo, L.; Nolan, S. P. *Organometallics* **2003**, *22*, 4322.

(36) Kelly, R. A. III; Clavier, H.; Giudice, S.; Scott, N. M.; Stevens, E. D.; Bordner, J.; Samardjiev, I.; Hoff, C. D.; Cavallo, L.; Nolan, S. P. *Organometallics* **2008**, *27*, 202.

(37) Scott, N. M.; Dorta, R.; Stevens, E. D.; Correa, A.; Cavallo, L.; Nolan, S. P. *J. Am. Chem. Soc.* **2005**, *127*, 3516.

(38) Díez-González, S.; Nolan, S. P. *Coord. Chem. Rev.* **2007**, *251*, 874.

(39) Fey, N. *Dalton Trans.* **2010**, *39*, 296.

(40) Strohmeier, W.; Muller, F. J. *Chem. Ber.* **1967**, *100*, 2812.

(41) Bouquet, G.; Loutellier, A.; Bigorgne, M. *J. Mol. Struct.* **1968**, *1*, 211.

(42) Herrmann, W. A.; Schütz, J.; Frey, G. D.; Herdtweck, E. *Organometallics* **2006**, *25*, 2437.

(43) Urban, S.; Tursky, M.; Fröhlich, R.; Glorius, F. *Dalton Trans.* **2009**, 6934.

(44) Mathew, J.; Suresh, C. H. *Organometallics* **2011**, *30*, 3106.

(45) Liu, P.; Montgomery, J.; Houk, K. N. *J. Am. Chem. Soc.* **2011**, *133*, 6956.

(46) Cavallo, L.; Correa, A.; Costabile, C.; Jacobsen, H. *J. Organomet. Chem.* **2005**, *690*, 5407.

(47) Singh, S.; Kumar, S. S.; Jancik, V.; Roesky, H. W.; Schmidt, H. G.; Noltemeyer, M. *Eur. J. Inorg. Chem.* **2005**, 3057.

(48) Van Ausdall, B. R.; Glass, J. L.; Wiggins, K. M.; Aarif, A. M.; Louie, J. *J. Org. Chem.* **2009**, *74*, 7935.

(49) Delaude, L.; Demonceau, A.; Wouters, J. *Eur. J. Inorg. Chem.* **2009**, 1882.

(50) Nair, V.; Varghese, V.; Paul, R. R.; Jose, A.; Sinu, C. R.; Menon, R. S. *Org. Lett.* **2010**, *12*, 2653.

(51) Nair, V.; Bindu, S.; Sreekumar, V. *Angew. Chem., Int. Ed.* **2004**, *43*, 5130.

(52) Nair, V.; Vellalath, S.; Babu, B. P. *Chem. Soc. Rev.* **2008**, *37*, 2691.

(53) Zhou, H.; Zhang, W. Z.; Liu, C. H.; Qu, J. P.; Lu, X. B. *J. Org. Chem.* **2008**, *73*, 8039.

(54) Riduan, S. N.; Zhang, Y.; Ying, J. Y. *Angew. Chem., Int. Ed.* **2009**, *48*, 3322.

(55) Kayaki, Y.; Yamamoto, M.; Ikariya, T. *Angew. Chem., Int. Ed.* **2009**, *48*, 4194.

(56) Ajitha, M. J.; Suresh, C. H. *Tetrahedron Lett.* **2011**, *52*, 5403.

(57) Lynch, B. J.; Fast, P. L.; Harris, M.; Truhlar, D. G. *J. Phys. Chem. A* **2000**, *104*, 4813.

(58) Lynch, B. J.; Zhao, Y.; Truhlar, D. G. *J. Phys. Chem. A* **2003**, *107*, 1384.

(59) Mohan, N.; Vijayalakshmi, K. P.; Koga, N.; Suresh, C. H. *J. Comput. Chem.* **2010**, *31*, 2874.

(60) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A. T. V.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03, Revision E.01*, Gaussian, Inc., Wallingford, CT, 2004.

(61) Politzer, P.; Truhlar, D. G. *Chemical applications of atomic and molecular electrostatic potentials: reactivity, structure, scattering, and energetics of organic, inorganic, and biological systems*; Plenum Press: New York, 1981.

(62) Gadre, S. R.; Shirsat, R. N. *Electrostatics of Atoms and Molecules*; Universities Press: Hyderabad, India, 2000.

(63) Galabov, B.; Ilieva, S.; Schaefer, H. F. III *J. Org. Chem.* **2006**, *71*, 6382.

(64) Politzer, P.; Murray, J. S. *Theor. Chem. Acc.* **2002**, *108*, 134.

(65) Gadre, S. R.; Suresh, C. H. *J. Org. Chem.* **1997**, *62*, 2625.

(66) Suresh, C. H.; Gadre, S. R. *J. Am. Chem. Soc.* **1998**, *120*, 7049.

(67) Suresh, C. H. *Inorg. Chem.* **2006**, *45*, 4982.

(68) Suresh, C. H.; Gadre, S. R. *J. Phys. Chem. A* **2007**, *111*, 710.

(69) Mathew, J.; Thomas, T.; Suresh, C. H. *Inorg. Chem.* **2007**, *46*, 10800.

(70) Sayyed, F. B.; Suresh, C. H. *New J. Chem.* **2009**, *33*, 2465.

(71) Sayyed, F. B.; Suresh, C. H.; Gadre, S. R. *J. Phys. Chem. A* **2010**, *114*, 12330.

(72) Deshmukh, M. M.; Gadre, S. R.; Tonner, R.; Frenking, G. *Phys. Chem. Chem. Phys.* **2008**, *10*, 2298.

(73) Gross, K. C.; Seybold, P. G.; Peralta-Inga, Z.; Murray, J. S.; Politzer, P. *J. Org. Chem.* **2001**, *66*, 6919.

(74) Pinjari, R. V.; Gejji, S. P. *J. Phys. Chem. A* **2008**, *112*, 12679.

(75) Li, C. Y.; Kuo, Y. Y.; Tsai, J. H.; Yap, G. P. A; Ong, T. G. *Chem. Asian J.* **2011**, *6*, 1520.

(76) Spencer, L. P.; Fryzuk, M. D. *J. Organomet. Chem.* **2005**, *690*, 5788.