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Electronic and Ligand Properties of Annelated Normal and Abnormal (Mesoionic) *N*-Heterocyclic Carbenes: A Theoretical Study

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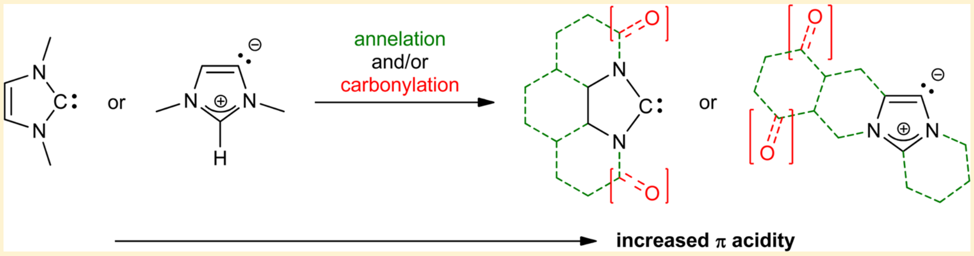

ABSTRACT: The effect of annelation and carbonylation on the electronic and ligating properties of N-heterocyclic carbenes (NHCs) has been studied quantum chemically. The thermodynamic and kinetic stability of these NHCs have been assessed on the basis of their singlet−triplet and HOMO−LUMO gaps respectively. Both annelation and carbonylation have been found to decrease the stability of NHCs. Compared to nonannelated carbenes, annelated and carbonylated carbenes are found to be weaker σ donors but better π acceptors. However, the effect of carbonylation is more pronounced than annelation toward increasing the π acidity of the NHCs. The reactivity of these carbenes has been discussed in terms of nucleophilicity and electrophilicity indices. The calculated values of the relative redox potential and ^{31}P NMR chemical shifts of corresponding carbene-phosphinidene adducts have been found to correlate well with the π acidity of the NHCs.

1. INTRODUCTION

The discovery of stable N-heterocyclic carbenes (NHC, **1**, Scheme 1) has opened up a new avenue in organometallic chemistry due to their superior σ donation ability compared to conventional two-electron donors such as amines and phosphines.[1] This superior ligating property of NHCs has led to numerous breakthroughs in a range of chemical transformations.[1,2]

Many experimental[3] and theoretical[4] studies have been devoted to exploring the stability and σ donation abilities of NHCs, as the latter was postulated to be responsible for the excellent catalytic activity of transition metal NHC complexes. However, evidence has recently accumulated of non-negligible π accepting properties of NHCs in their transition metal complexes.[5] This has opened up another possibility, as moderate-to-strong π accepting properties of NHCs may be useful in some catalytic applications. Remarkably, Fürstner et al. have shown that the outcomes of gold-catalyzed reactions are influenced by the π acceptor property of carbenes.[6a] Moreover, based on the difference in reactivity observed between NHC−gold and acyclic diaminocarbene (ADC)−gold complexes, Hong et al. hypothesized that the reactivity of ADCs might be attributed to their higher π accepting ability.[6b] Thus, it seems reasonable that tuning the π acceptor property of NHCs may help in controlling the outcome of many catalytic reactions.

Various strategies have been adopted to increase the π accepting ability of carbenes. Recently, Bertrand et al. have shown that pyramidalization of one nitrogen atom of an NHC considerably increases its π accepting ability.[7] A recent theoretical study from our group has revealed that substitution of boron atoms into the ring framework of five-, six-, and seven-membered NHCs dramatically increases the π accepting ability of the carbenes.[5f] Heinicke et al. have observed that the extension of the π system of NHCs by annelation also increases their π accepting ability.[8] Thus, stronger π acidity is expected for benzo-,[9a] pyrido-,[9b] quinoxilane,[9d] quinine,[5d] and naphtho-annelated[8] NHCs as these NHCs possess lower π electron density at the divalent carbon atom, due to withdrawal of π electron density from the adjacent nitrogen atoms by the extended π system. Another strategy to increase the π accepting ability of carbene would be to introduce carbonyl groups into the NHC scaffold. Carbonyl groups (C=O), being good acceptors, can withdraw electron density from the carbene p orbital, making the carbenic carbon electron-poor. As a result, the carbene center will become more electrophilic. In fact, Bielawski et al. have shown that introduction of carbonyl groups into NHC scaffolds broadens their chemical reactivity by increasing their π accepting ability.[10] The above observations

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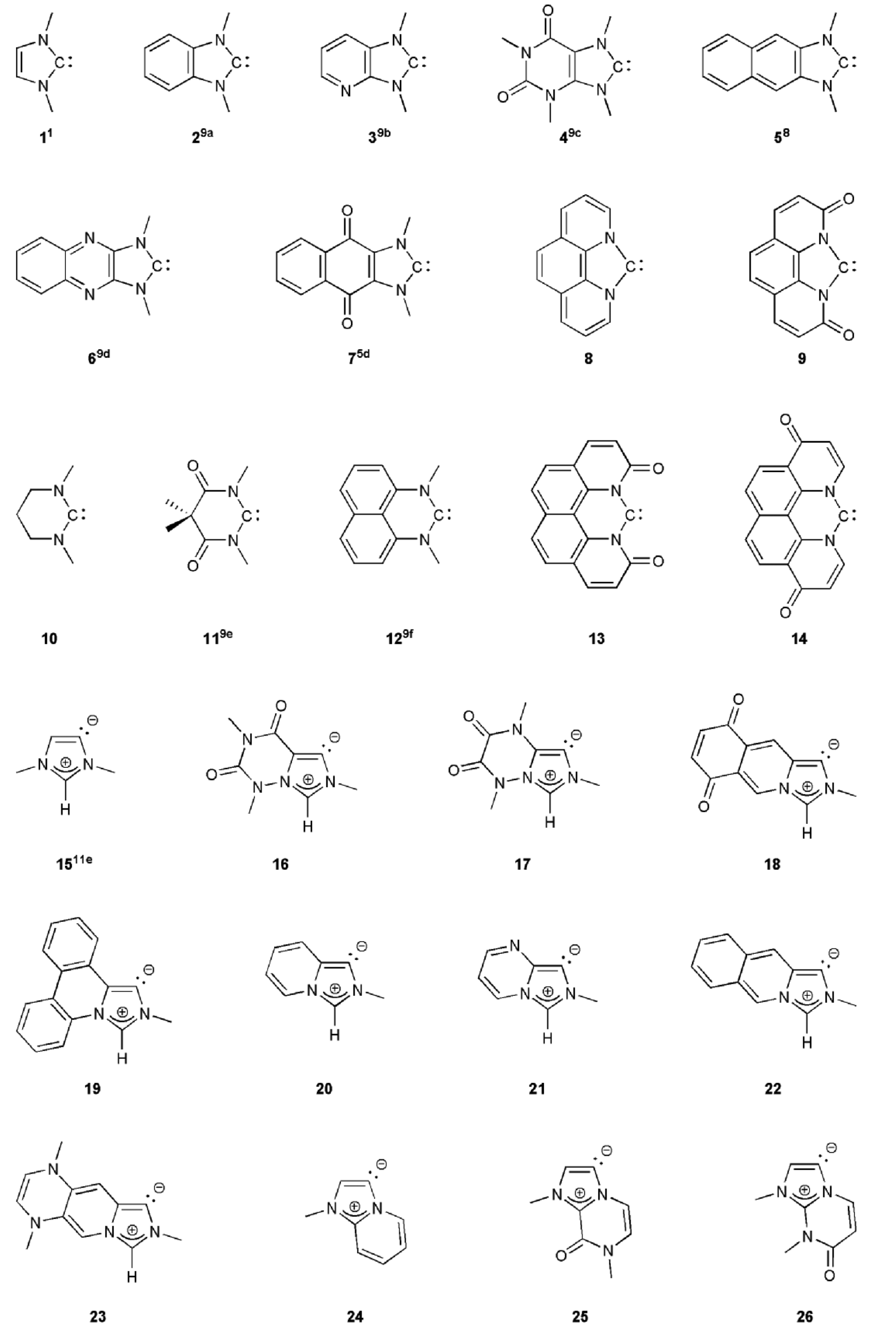
Scheme 1. Schematic Representation of the Range of NHCs Considered in This Study



prompted us to investigate the ligation ability of annelated NHCs (Scheme 1) with a special emphasis on their π accepting ability. Herein, we present a systematic theoretical investigation on the effect of annelation, as well as introduction of carbonyl groups to the carbene scaffold, on the electronic and ligating properties of carbene. The so-called "abnormal" counterparts of NHCs (**15**–**26**)[11] have also been included in this study. To the best of our knowledge, prior to this report, there is no systematic study, either theoretical or experimental, on the effect of annelation on the electronic and ligand properties of abnormal (mesoionic) carbenes.

2. COMPUTATIONAL DETAILS

All the structures were fully optimized without any geometry constraint using the hybrid PBE1PBE exchange-correlation functional.[12] We have used the 6-31+G* basis set for main group elements and the SDD basis set with Stuttgart-Dresden relativistic effective core potential for the rhodium atom.[13] Frequency calculations were performed at the same level of theory to characterize the nature of the stationary point. All structures were found to be minima on the potential energy surface with real frequencies. Natural bonding analyses were performed with the natural bond orbital (NBO) partitioning scheme[14] as implemented in the Gaussian 03 suite of programs.[15]

For calculating the standard redox potential, we employed the protocol of the Born–Haber cycle (Scheme 2). The same protocol has been applied in our recent paper on boron-substituted carbenes.[5f] The standard Gibbs free energy of the redox half reaction, $\Delta G_{\mathrm{sol}}^{0,\mathrm{redox}}$, consists of free energy changes in the gas and solution phase of the oxidized and reduced species.[16] Solvent effects (CH_2Cl_2) have been estimated in single-point calculations on gas-phase-optimized structures using the polarizable continuum model, PCM.[17] The values

Scheme 2. Born–Haber Cycle

$$\begin{tikzcd}
\mathbf{Ox}_{g} + \mathbf{e}^{-}_{\mathbf{g}} \arrow[r, "\Delta G\mathbf{gas}^{0,\mathbf{redox}}"] \arrow[d, "\Delta G\mathbf{s}^{0}(\mathbf{Ox})"'] & \mathbf{Red}_{g} \arrow[d, "\Delta G\mathbf{s}^{0}(\mathbf{Red})"] \\
\mathbf{Ox}_{solv} + \mathbf{e}^{-}_{\mathbf{g}} \arrow[r, "\Delta G\mathbf{sol}^{0,\mathbf{redox}}"] & \mathbf{Red}_{solv}
\end{tikzcd}$$

obtained from the Born–Haber cycle have been used to calculate the standard free energy (kcal mol^{-1}) of the overall reaction in solution according to eq 1.

$$\Delta G_{\text{sol}}^{0,\text{redox}} = \Delta G_{\text{gas}}^{0,\text{redox}} + \Delta G_{\text{s}}^{0}(\text{Red}) - \Delta G_{\text{s}}^{0}(\text{Ox}) \qquad (1)$$

The standard one-electron redox potential, E^0 (in V), is then calculated using the Nernst equation (eq 2),

$$\Delta G_{\text{sol}}^{0,\text{redox}} = -FE^{0}{}_{\text{calc}} \qquad (2)$$

where F is the Faraday constant and is equal to 23.06 kcal mol^{-1} V^{-1}.

We have used the PBE1PBE functional for standard redox potential calculation as it provides accurate results for several early, middle, and late transition metals.[16] All the calculated values were referenced to the calculated absolute half cell potential of ferrocene at the same level of theory. Isotropic ^{31}P chemical shifts were calculated relative to H_3PO_4 at the same levels of theory at which the geometry of the molecules were optimized. The same level of theory was also used for calculating the absolute isotropic chemical shift of H_3PO_4 ($\sigma_{\text{iso}} = 374.0$).

3. RESULTS AND DISCUSSION

3.1. Geometries. The optimized geometries of all the molecules are planar except **10** and **11** due to the presence of an sp^3 carbon atom. Table 1 contains the calculated geometrical parameters of all the molecules. The calculated geometrical parameters of the molecules are in good agreement with the available X-ray data.[1a,5d,9f,11e] Among the normal carbenes **1**–**14**, the shortest and longest C_c–N (C_c = carbene carbon) distance is found for **4** and **9** respectively. The C–N bond lengths of the abnormal carbenes **15**–**26** are found to be longer than those of normal carbenes.

The central NCN angles for all the normal carbenes featuring a five-membered central ring (**1**–**9**) containing the carbene center are found to be comparable. Similar behavior is obtained for six-membered carbenes (**10**–**14**). However, the central NCN angles for **10**–**14** are found to be wider than those of **1**–**9**. Like normal carbenes, there is no appreciable change in the central NCC angle of all the abnormal carbenes **15**–**26**.

3.2. Singlet–Triplet and HOMO–LUMO Gaps. The singlet–triplet ($\Delta E_{\text{S-T}}$) and HOMO–LUMO ($\Delta E_{\text{H-L}}$) gaps of these NHCs provide a measure of their respective thermodynamic and kinetic stabilities.[18] In general, the higher the value of $\Delta E_{\text{S-T}}$ and $\Delta E_{\text{H-L}}$, the higher the stability of the singlet carbenes. The calculated values of $\Delta E_{\text{S-T}}$ for **1** (81.3 kcal mol^{-1}, Table 2) are in very good agreement with previous calculations at different levels of theory (80.0,[19a] 79.3,[19b] 84.5[19c] kcal mol^{-1}). It is seen from Table 2 that annelation or carbonylation of the NHC scaffold decreases the $\Delta E_{\text{S-T}}$ of these molecules, implying that both of these factors decrease the thermodynamic

Table 1. PBE1PBE/6-31+G* Calculated C–N Bond Lengths (Å), NCE Angles (E=N, C) (in degrees) of Carbenes 1–26[a]

molecule	annelated	carbonylated	C–N	∠NCE
"normal" NHCs				
1	–	–	1.363 (1.367)[1a]	102.0 (102.1)[1a]
2	X	–	1.365	103.5
3	X	–	1.369	103.8
4	X	X	1.345	103.6
5	X	–	1.364	103.8
6	X	–	1.370	104.5
7	X	X	1.368 (1.392)[5d]	103.0
8	X	–	1.387	100.4
9	X	X	1.390	101.3
10	–	–	1.346	115.6
11	–	X	1.358	115.7
12	X	–	1.353 (1.359)[9f]	115.2 (114.3)[9f]
13	X	X	1.364	114.6
14	X	X	1.363	113.9
"abnormal" (mesoionic) NHCs				
15	–	–	1.402 (1.417)[11e]	100.6 (101.0)[11e]
16	X	X	1.385	101.0
17	X	X	1.390	100.4
18	X	X	1.380	100.8
19	X	–	1.387	100.8
20	X	–	1.377	100.8
21	X	–	1.377	100.8
22	X	–	1.365	100.8
23	X	–	1.385	100.7
24	X	–	1.410	99.9
25	X	X	1.395	99.6
26	X	X	1.421	99.7

[a] Experimental values are given within parentheses.

Table 2. PBE1PBE/6-31+G* Computed Singlet-Triplet ($\Delta E_{\text{S-T}}$, kcal mol^{-1}) and HOMO−LUMO ($\Delta E_{\text{H-L}}$, eV) Gap of Carbenes 1−26

molecule	annelated	carbonylated	$\Delta E_{\text{S-T}}$	$\Delta E_{\text{H-L}}$
"normal" NHCs				
1	–	–	81.3	6.5
2	X	–	75.5	5.7
3	X	–	71.5	5.4
4	X	X	67.1	5.6
5	X	–	54.4	4.6
6	X	–	59.6	4.6
7	X	X	46.7	3.5
8	X	–	21.6	3.0
9	X	X	35.7	3.8
10	–	–	58.0	5.7
11	–	X	45.0	4.7
12	X	–	55.7	4.6
13	X	X	28.5	3.7
14	X	X	51.2	4.0
"abnormal" (mesoionic) NHCs				
15	–	–	57.4	5.1
16	X	X	56.1	5.0
17	X	X	52.1	4.6
18	X	X	34.5	3.1
19	X	–	49.9	4.3
20	X	–	49.2	4.6
21	X	–	44.2	4.2
22	X	–	28.1	3.3
23	X	–	49.9	4.2
24	X	–	50.9	4.2
25	X	X	52.8	4.3
26	X	X	58.8	4.3

stability of NHCs. Based on $\Delta E_{\text{S-T}}$ values, among all the NHCs, **1** and **8** are found to have the highest and lowest thermodynamic stabilities, respectively. The decreasing thermodynamic stability (or $\Delta E_{\text{S-T}}$) in the series non- (**1**), benzo- (**2**), and naphtho-annelated NHC (**5**) has been previously observed by Heinicke et al.[9d] This decrease in thermodynamic stability of NHCs upon annelation or carbonylation is caused by the removal of electron density from the adjacent nitrogen atom by the extended π system or the π^* orbital of CO.

The thermodynamic stabilities of the abnormal counterparts of NHCs (**15**−**26**) are calculated to be lower than those of their normal counterparts (**1**−**14**). This might be due to the absence of one adjacent nitrogen atom in the abnormal carbenes. This absence of one π donating heteroatom lowers the π delocalization between the nitrogen atom and the carbene p_π orbital which is responsible for the stability of the singlet ground state. As a result, the stability of the singlet ground state of abnormal carbenes is lower than their normal counterparts. The effect of annelation as well as carbonylation in decreasing the $\Delta E_{\text{S-T}}$ values is also observed for these abnormal carbenes. Among the abnormal carbenes, **26** is found to have the highest thermodynamic stability while naphtho-annelated abnormal carbene **22** has the lowest.

The calculated values of the HOMO−LUMO gap ($\Delta E_{\text{H-L}}$), a measure of kinetic stability,[18b] of these NHCs follow the same trend as the singlet−triplet gap ($\Delta E_{\text{S-T}}$) (Figure S1) implying that the thermodynamically stable carbenes are also kinetically stable and vice versa.

3.3. Ligating Properties.

The σ donation ability of NHCs has been well explored,[3,4] and recent reports have provided evidence of their non-negligible π accepting properties.[5,6] From this perspective, the nature and energies of the *key* frontier orbitals of NHCs are very important as these orbitals dictate the reactivity[20] and ligating properties[21] of NHCs. Thus, we performed NBO[14] analysis to obtain the energies of these key frontier molecular orbitals (MOs). Table 3 contains the energies of the σ-symmetric lone pair and π-symmetric unoccupied MO concentrated on the central carbon atom of **1**−**26**. These energies have been graphically represented in Figure 1.

Table 3. PBE1PBE/6-31+G* Calculated Energies of σ-Symmetric Lone Pair Orbital (E_σ in eV), and the π-Symmetric Unoccupied Orbital (E_{π^*} in eV) Concentrated on the Central Carbon Atom of 1−26

molecule	annelated	carbonylated	E_σ	E_{π^*}
"normal" NHCs				
1	–	–	−6.1	0.8
2	X	–	−6.3	1.3
3	X	–	−6.5	0.8
4	X	X	−6.7	0.4
5	X	–	−6.4	0.2
6	X	–	−6.7	−0.1
7	X	X	−6.7	−0.2
8	X	–	−6.5	0.4
9	X	X	−7.1	−3.3
10	–	–	−5.4	0.6
11	–	X	−6.6	−1.9
12	X	–	−6.2	−0.5
13	X	X	−6.4	−2.7
14	X	X	−7.6	−2.8
"abnormal" (mesoionic) NHCs				
15	–	–	−5.2	1.4
16	X	X	−6.1	0.7
17	X	X	−6.1	1.1
18	X	X	−6.3	0.2
19	X	–	−5.6	0.5
20	X	–	−5.6	0.9
21	X	–	−5.7	0.8
22	X	–	−5.7	0.7
23	X	–	−5.2	0.6
24	X	–	−5.5	1.6
25	X	X	−5.7	1.2
26	X	X	−5.8	1.3

It is evident from Table 3 and Figure 1a that, compared to the nonannelated NHCs (**1** and **10**), the energies of the σ-symmetric lone pair orbital of the annelated/carbonylated carbenes are lower. This implies that annelation or carbonylation of the NHC scaffold decreases the σ donation abilities of carbenes. Even though both annelation and carbonylation affect the π accepting ability of the carbenes, carbonylation is found to significantly enhance the same. For example, a closer look at Table 3 shows that the energies of the π^* orbitals of **9**, **11**, **13**, and **14** are significantly lower, implying the enhanced π acidity or π acceptor ability of these molecules. This might be due to the fact that CO, being a good π acceptor, can withdraw electron density from the nitrogen lone pair. As a result, the delocalization from the nitrogen lone pair to the formally vacant p orbital of the carbene carbon decreases, making the

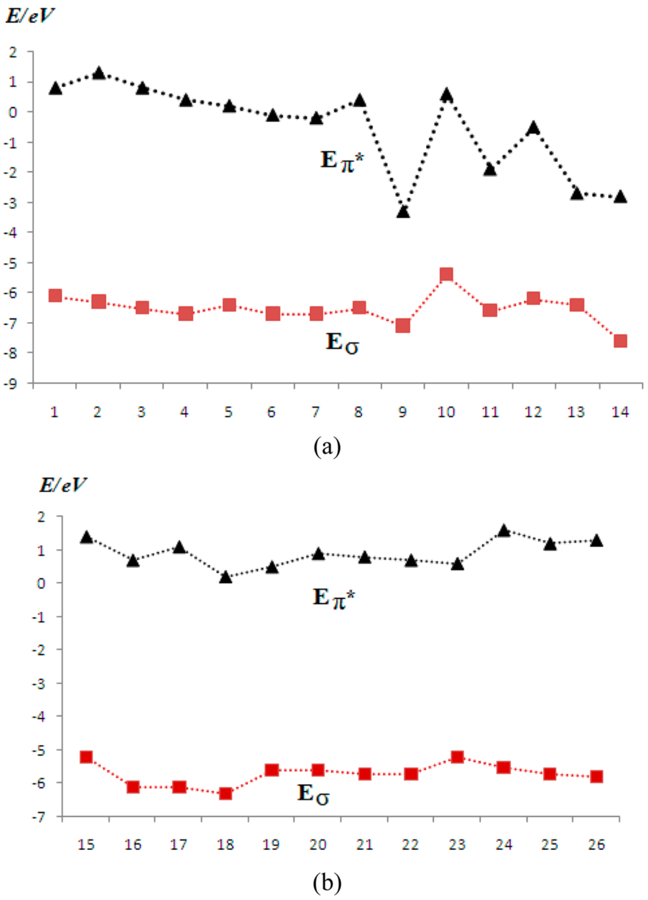


Figure 1. Plot of the energies of the σ-symmetric lone pair orbital (E_σ) and the π symmetric unoccupied orbital ($E_{\pi*}$) concentrated on the central carbon atom of (a) normal carbenes **1**−**14** and (b) abnormal carbenes (**15**−**26**).

Table 4. PBE1PBE/6-31+G* Calculated Nucleophility Index, *N*, and Electrophilicity Index, ω[a]

molecule	annelated	carbonylated	*N*	ω
"normal" NHCs				
1	–	–	3.6	0.6
2	X	–	3.3	1.0
3	X	–	3.2	1.3
4	X	X	3.1	1.2
5	X	–	3.7	1.4
6	X	–	2.9	2.2
7	X	X	2.9	3.5
8	X	–	4.5	2.2
9	X	X	2.5	3.7
10	–	–	4.2	0.5
11	–	X	3.1	1.9
12	X	–	4.2	1.1
13	X	X	3.3	2.8
14	X	X	2.9	2.8
"abnormal" (mesoionic) NHCs				
15	–	–	4.4	0.7
16	X	X	3.6	1.3
17	X	X	3.5	1.6
18	X	X	3.4	3.6
19	X	–	4.1	1.4
20	X	–	4.1	1.1
21	X	–	4.5	1.8
22	X	–	5.3	0.7
23	X	–	5.2	0.7
24	X	–	4.2	1.4
25	X	X	3.9	1.5
26	X	X	3.9	1.5

[a] All values are in eV.

carbene center electron-deficient. This electron deficiency results in the higher π acidity of the carbenes. Among the normal carbenes **1**−**14**, the highest and lowest π accepting abilities are obtained for **9** and **2**, respectively.

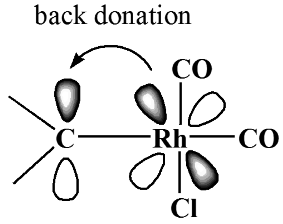
As expected,[11] the abnormal carbene **15** has higher σ basicity compared to **1**. Both annelation and carbonylation in **16**−**26** decrease the σ basicity; however, their π acidity is higher than that of **15**. Annelation at the 1,5 position (**16**−**23**) significantly enhances the π acidity of these abnormal carbenes; however the same is not true for annelation at the 2,3 position (**24**−**26**).

3.4. Nucleophilicity and Electrophilicity. Nucleophilicity and electrophilicity are two important parameters of a ligand, which in turn provide a measure of the basicity and acidity of a ligand, respectively. Thus, we have calculated the nucleophilicity index, *N*, using a method similar to that reported by Domingo et al.[22a] In this method, *N* is calculated as $N = E_{\mathrm{HOMO}} - E_{\mathrm{HOMO(TCNE)}}$, where tetracyanoethylene (TCNE) is considered as the reference. In addition, the global electrophilicity, ω, is computed by employing the expression $\omega = (\mu^2/2\eta)$, where μ is the chemical potential ($\mu \approx (E_{\mathrm{HOMO}} + E_{\mathrm{LUMO}})/2$) and η is the chemical hardness ($\eta = (E_{\mathrm{HOMO}} - E_{\mathrm{LUMO}})$.[22b−d] The calculated values of *N* and ω are collected in Table 4.

The value of *N* for the normal carbenes **1**−**14** lies in the range of 2.5−4.5 eV, with the highest being found for **8** and the lowest for **9**. On the other hand, the value of *N* for the abnormal carbenes **15**−**26** lies in a higher range (3.5−5.3 eV) than their normal counterparts. This is in accordance with the higher basicity of the abnormal over normal carbenes. The calculated values of the electrophilicity, ω, of all the annelated/carbonylated carbenes are higher than the parent carbenes (**1** and **10**). This is in accordance with the π acidity of these ligands (Table 3 and Figure 1a). On the other hand, the highest value of ω for abnormal carbenes is found for **18** (3.6 eV). It should be noted that the highest π acidity among the abnormal carbenes is also found for **18**. Thus, both the nucleophilicity and electrophilicity of **1**−**26** follow the same trend as their relative σ donating and π accepting abilities. However, it is difficult to obtain a *one-to-one* correlation between the ligand properties and reactivity indices of these carbenes. This is because the ligand properties are evaluated by computing the absolute energies of the respective σ donor and π acceptor orbitals whereas the evaluation of the nucleophilicity index involves a reference molecule (tetracyanoethylene) and that of electrophilicity index involves computation of the sum and difference of the energies of the frontier occupied (HOMO) and unoccupied (LUMO) orbitals.

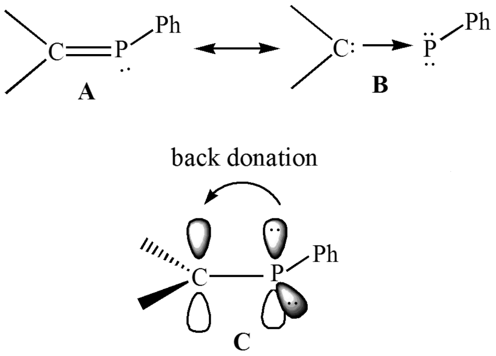
3.5. Electrochemistry and ^{31}P NMR Spectroscopy. The relative π acidity of the carbenes is further assessed from the relative redox potential ($\Delta E_{1/2}$) of their corresponding $\mathrm{Rh(CO)_2Cl}$ complexes (Scheme 3). The higher the π acidity of a carbene, the more it can withdraw electron density from the metal center, which in turn lowers the energy of the highest occupied molecular orbital (HOMO, concentrated at the metal center) of the **L**−$\mathrm{Rh(CO)_2Cl}$ complex (**L** = **1**−**26**). As a result, the first ionization energy or the relative $\Delta E_{1/2}$ values of the **L**−$\mathrm{Rh(CO)_2Cl}$ complex increase. Thus, $\Delta E_{1/2}$ values may be taken

Scheme 3. Possible Backdonation in Transition Metal Complexes of Carbenes 1−26



as a measure of the π acidity of the carbenes. The use of $\Delta E_{1/2}$ values in assessing the relative π acidity of carbenes has been recently highlighted by our group.[5f] In addition, a recent paper by Bertrand et al.[23] has demonstrated the use of ^{31}P NMR chemical shifts of carbene−phosphinidene adducts (Scheme 4) in evaluating the π acidity of carbenes. The utility of both ^{31}P NMR and redox potential in understanding the electron-donating or -accepting abilities of a particular NHC ligand is also highlighted by Nolan et al. in a recent review.[24] While this manuscript was under review, we came across an article where the π-acceptor strengths of NHCs were measured by evaluating the ^{77}Se NMR chemical shifts of their selenium adducts.[25] The carbene−phosphinidene adducts may be represented by two resonance forms, **A** and **B**, in which resonance form **A** will dominate with the increasing π acidity of the carbene. Thus, in principle, the higher the π acidity of the carbene, the more it can withdraw electron density from the lone pair of phosphorus. As a result, the chemical shift of the phosphorus center in the adducts will be further downfield. In Scheme 4, **C** represents the orbital interaction involving "backdonation" from the phosphorus lone pair to the carbene p orbital. Thus, ^{31}P chemical shifts may also be taken as an indication of the relative π acidity of the carbene.

Scheme 4. Resonance Forms of Carbene−Phosphinidene Adducts[23a]



[a]Resonance form **A** dominates over **B** with increasing π acidity of carbenes. **C** represents the orbital interaction involved in back donation from the phosphorus center to the formally vacant p orbital at the carbenic carbon atom.

Table 5 contains the relative redox potential ($\Delta E_{1/2}$) of the $LRh(CO)_2Cl$ complexes. The calculated values of $\Delta E_{1/2}$ are in the range of other NHC-supported $[M(CO)_2Cl]$ complexes (0.88−1.60 V).[10,26] The calculated values of $\Delta E_{1/2}$ are found to be a function of the relative π acidity of the carbenes. For example, carbenes **9**, **11**, **13**, and **14** have higher π acidity (Table 3) and consequently their $\Delta E_{1/2}$ values are high. The highest value of $\Delta E_{1/2}$ is calculated for carbene **9** (1.45 V), and it is 650 mV higher than that of nonannelated carbene **1**. Moreover, we obtained a reasonable correlation (R^2 = 0.78) between the energy of the π-symmetric unoccupied MO and the $\Delta E_{1/2}$ values (Figure 2) for the molecules **1−26**. Both annelation and carbonylation have increased the $\Delta E_{1/2}$ values of the carbenes compared to the nonannelated examples. All the calculated transition metal complexes are found to be quite stable as indicated by their binding energies which are in the range of 39.9−69.3 kcal mol^{-1} (Table S1).

Table 5. Relative Redox Potential ($\Delta E_{1/2}$, in volts) Values of $LRh(CO)_2Cl$ (L = 1−26) Complexes and ^{31}P NMR Chemical Shifts for the Adducts L−PPh (L = 1−26)

L	annelated	carbonylated	$\Delta E_{1/2}$ (V)	δ^{31}P
"normal" NHCs				
1	–	–	0.80	−46.1
2	X	–	0.94	−43.8
3	X	–	0.99	−29.1
4	X	X	0.88	−37.6
5	X	–	0.96	−16.9
6	X	–	0.93	20.2
7	X	X	1.21	−14.1
8	X	–	0.83	−35.2
9	X	X	1.45	153.1
10	–	–	0.82	−9.9
11	–	X	1.26	86.9
12	X	–	0.92	11.2
13	X	X	1.29	91.3
14	X	X	1.42	150.7
"abnormal" (mesoionic) NHCs				
15	–	–	0.94	−44.9
16	X	X	0.95	−4.3
17	X	X	0.77	−31.2
18	X	X	0.88	17.6
19	X	–	0.99	−21.0
20	X	–	0.88	−28.8
21	X	–	0.61	10.8
22	X	–	0.80	3.5
23	X	–	0.91	−37.7
24	X	–	0.75	−43.7
25	X	X	0.69	−32.1
26	X	X	0.72	−75.5

Table 5 also contains the ^{31}P NMR chemical shifts of carbene−phosphinidene (**L**−PPh) adducts. The optimized geometry of the **1**−PPh adduct is shown in Figure 3 as a representative one. The calculated C_C−P bond length is reasonably close to the experimental value. Moreover, the P−C_{Ph} bonds are not coplanar with the NHC ring, which is in accordance with the recent report by Bertrand et al.[23] This noncoplanarity ensures that the phosphorus lone pair is only delocalized into the vacant p orbital of the NHC rather than to the phenyl ring. This is also supported by the fact that the C_C−P bond is significantly shorter than the P−C_{Ph} bond. Thus, any change in electron density at the phosphorus center may be traced to the relative π acidity of the carbenes. Also, any change in electron density at the phosphorus center will be reflected in the ^{31}P NMR chemical shift for the adducts. In general, the higher the π acidity of the carbene, the more downfield the chemical shift of the phosphorus nucleus in the adducts will be. In fact, a good correlation (R^2 = 0.89, Figure 4) has been obtained between the energy of the π symmetric unoccupied MO ($E_{\pi*}$) centered at the central carbon atom of NHCs and

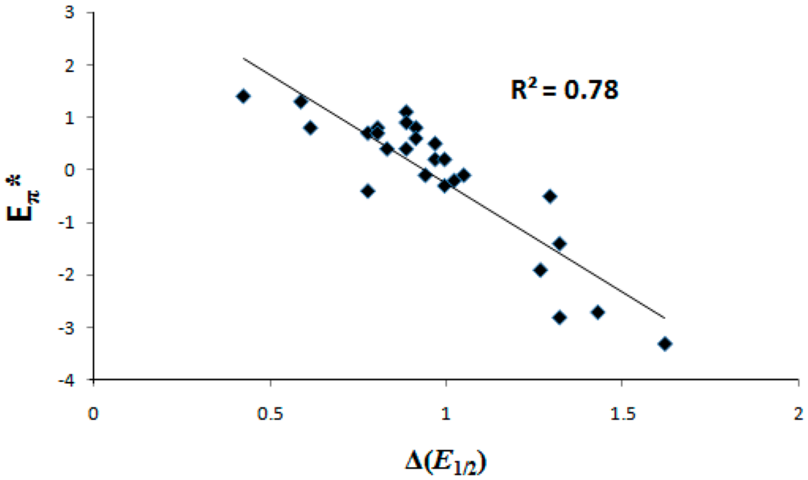


Figure 2. Correlation plot between the energy of the π symmetric unoccupied MO ($E_{\pi*}$ in eV) and the $\Delta E_{1/2}$ (in volts) values.

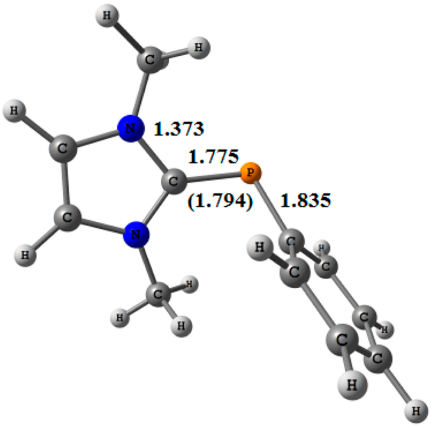


Figure 3. Optimized geometry and bond lengths (Å) of the **1**−PPh adduct. The experimental C_C−P bond length (Å) is shown in parentheses.[22]

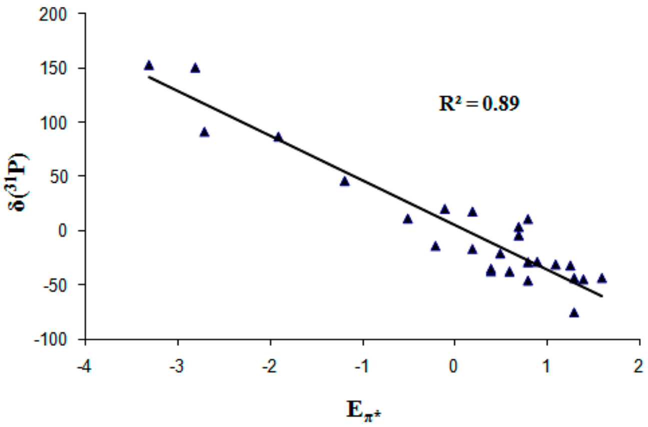


Figure 4. Correlation plot between the energy of the π-symmetric unoccupied MO ($E_{\pi*}$) and ^{31}P chemical shifts (δ^{31}P) of the carbene−phosphinidene adducts.

their ^{31}P chemical shifts. The calculated C_C−P bond lengths are also in good agreement with the π acidity of the carbenes. For example, the higher π acidity is found for carbenes **9**, **11**, **13**, and **14**. Consequently, the C_C−P bonds in their PPh adducts are shorter (**9**·PPh 1.720 Å, **11**·PPh 1.733 Å, **13**·PPh 1.721 Å, and **14**·PPh 1.721 Å) compared to the PPh adduct of nonannelated carbene **1** (**1**·PPh 1.775 Å), which has a lower π acidity.

Similar trends in C_C−P bond lengths are also obtained for abnormal carbenes. For example, the π acidity of **18** is significantly higher than that of **15** and **24**. Accordingly, the C_C−P bond length of the phosphinidene adduct of **18** (1.761 Å) is shorter than those of **15** (1.795 Å) and **24** (1.799 Å).

Barring a few exceptions, the ^{31}P NMR signal for carbenes (**10**−**14**) featuring a central six-membered ring are found downfield compared to the five-membered ring carbenes (**1**−**9**). Carbonylation or annelation also resulted in a downfield shift of the ^{31}P NMR signal. This has also been observed previously by Heinicke et al.[8]

4. CONCLUSION

Quantum chemical calculations have been performed to investigate the effect of annelation and carbonylation of the NHC scaffold on the electronic and ligating properties of NHCs (Scheme 1) with a special emphasis on their π accepting ability. Annelation and carbonylation decrease the thermodynamic as well as kinetic stability of NHCs which is in accord with experimental findings.[9d] Both annelation and carbonylation decrease the σ donation abilities of NHCs. However, both these effects increase the π accepting ability of the carbenes although carbonylation of the NHC scaffold results in a dramatic increase in the π accepting ability of NHCs. The degree of increase in π acidity has been found to be more for the normal carbenes (**1**−**14**) compared to the abnormal ones (**15**−**26**). The reactivity of these carbenes has been assessed by calculating their nucleophilicity and electrophilicity, which were found to follow the same trend as their relative σ donation and π accepting abilities. The π acidities of the carbenes have been further assessed by evaluating the relative redox potentials of the LRh(CO)$_2$Cl complexes and ^{31}P NMR chemical shifts of the carbene−phosphinidene adducts. Both the calculated values of the relative redox potential and ^{31}P chemical shifts have been found to have a good correlation with the π acidity of the carbenes.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Cartesian coordinates of all the molecules along with their total energies including zero point vibrational correction. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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