# CHAPTER-2

## Tuning the Electronic and Ligand Properties of Remote Carbenes

**Abstract:** The effect of annulation and carbonylation on the electronic and ligating properties of remote *N*-heterocyclic carbenes (rNHCs) has been studied quantum-chemically. The thermodynamic stability of these complexes has been assessed on the basis of their hydrogenation and stabilization energies, while HOMO−LUMO gaps are used to measure the kinetic stabilities. Annulated/carbonylated rNHCs are found to be weaker σ donors but better π acceptors compared with the parent rNHCs. The reactivity of these rNHCs has been studied by evaluating their nucleophilicity and electrophilicity indices. The nucleophilicity values are in good agreement with the σ basicities of all of the rNHCs. The $^{31}$P NMR chemical shifts of the corresponding rNHC-phosphinidene adducts have been calculated and found to correlate well with the π-acidities of these rNHCs.

**[2.1] Introduction**

$N$-Heterocyclic carbenes (NHCs) have found a great deal of attention after their isolation by Arduengo in 1991 and have grown extensively in the past few years because of the remarkable catalytic activity of the corresponding transition metal complexes [1]. The excellent catalytic activity shown by transition-metal complexes having NHCs as ligands is considered to be due to the NHCs' high σ-donation ability and almost zero π-accepting ability [2]. However, several theoretical and experimental studies have suggested that NHCs have not only strong σ-donating ability but also non-negligible π-accepting ability [3,4].

In addition to these normal NHCs, more recently the chemistry of another type of NHCs, called remote NHCs (rNHCs), in which the heteroatom is away from the carbenic carbon atom, has been explored [5]. The singlet state of normal NHCs is stabilized mainly by attaching nitrogen atoms to the ylidene center, while the stabilization of rNHCs is largely attributed to aromatic delocalization [6]. Delocalization through the enamine π system provides the necessary aromatic stabilization [7]. To date, however, no rNHC has been isolated in its free state, whereas palladium and nickel complexes of five and six-membered rNHCs derived from pyrazole, pyridine, and quinoline have been reported [8,9]. These complexes exhibit high efficiency in many catalytic transformations. Ni(II) complexes of the type [Ni(rNHC)(PPh$_3$)$_2$(Cl)][BF$_4$] have been reported as highly efficient catalyst in Kumada-Corriu-type cross-coupling reactions, whereas Pd(II) complexes containing a pyrazole-derived rNHC ligand exhibit high catalytic efficiency in aqueous Suzuki-Miyaura coupling reactions [10]. The highly efficient catalytic behavior of these complexes is believed to be due to the extremely strong σ-donor ability of the rNHC systems. In a comparison study, Pd(II)-rNHC-mediated C-C coupling reactions were found to be more effective than the reactions using precatalysts derived from normal NHCs [11a]. Theoretical studies by Schneider et al. [11] suggested that since rNHCs have better σ-donating as well as π-accepting abilities compared with classical NHCs, they are useful for certain catalytic transformations. Thus, tuning the ligating properties of rNHCs may help in developing novel catalysts of particular interest.

Several attempts to increase their π-accepting abilities have been made, such as annulation and/or carbonylation of the NHC ligands, and indeed, these ligands have been found to have higher π-accepting abilities compared with non-annulated and non-carbonylated NHCs [12,13]. This is because annulation and carbonylation remove

electron density from the adjacent nitrogen atoms, thereby making the carbene carbon electrophilic in nature. Thus, it is expected that annulated and carbonylated rNHCs may also possess higher π acidity compared with non-annulated/carbonylated ones. However, to the best of our knowledge, there exists no systematic study, either theoretical or experimental, on tuning of the ligand properties of remote carbenes. We present here a systematic theoretical investigation of the effect of annulation and carbonylation on the electronic and ligating properties of five-membered mesoionic and six-membered remote NHCs (Scheme 2.1).
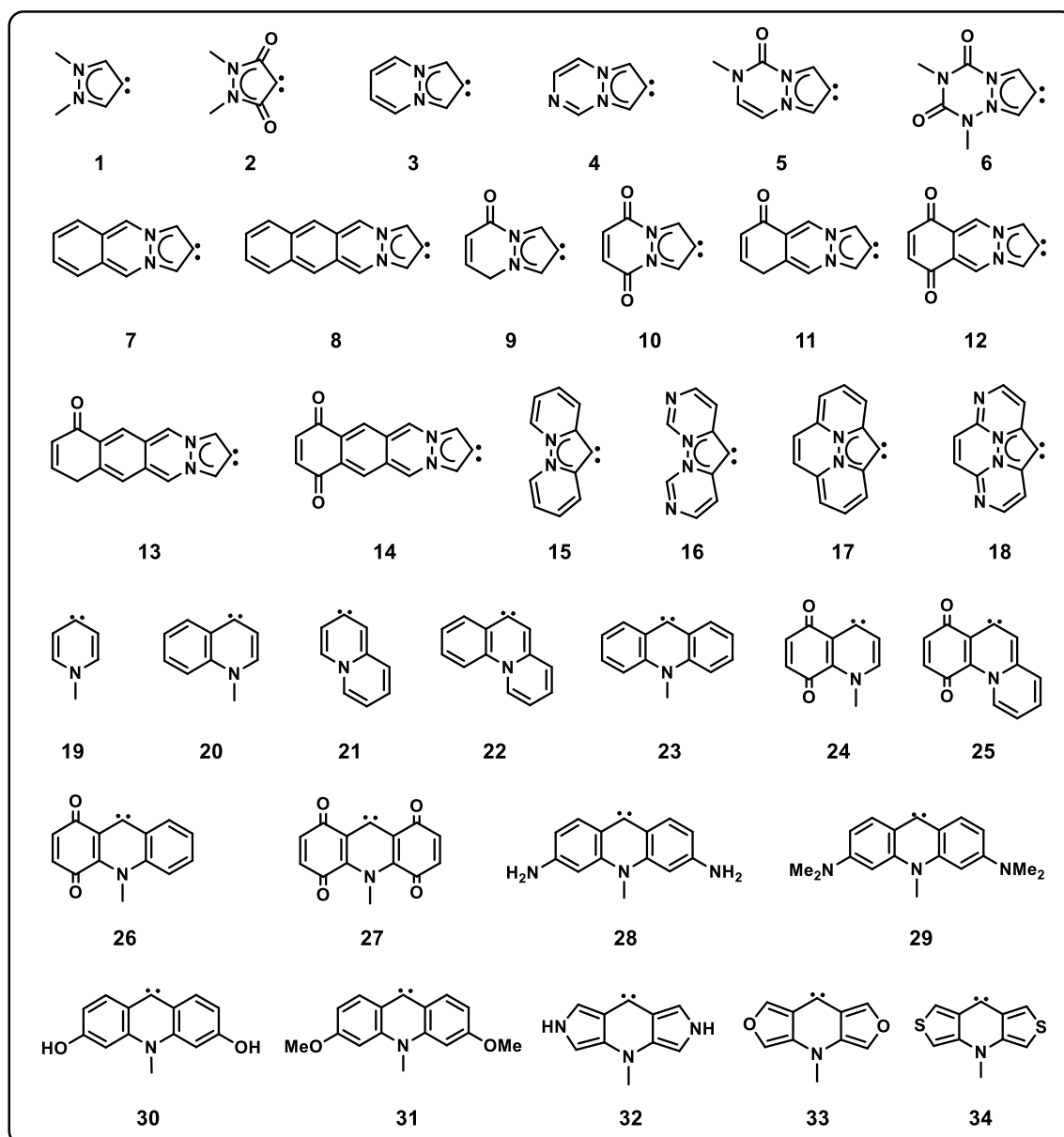


**Scheme 2.1**: Schematic representation of the mesoionic (**1−18**) and remote NHCs (**19−34**) considered in this study.

**[2.2] Computational Details**

All of the structures were fully optimized without any geometry constraints using the PBE0 hybrid exchange-correlation functional [14] and the 6-31+G* basis set [15]. Frequency calculations were performed at the same level of theory to characterize the nature of the stationary point. All of the structures were found to be minima on the potential energy surface with real frequencies. This level of theory was found to be adequate in dealing with similar systems as reported recently [16,17]. Natural bonding analyses were performed with the natural bond orbital (NBO) partitioning scheme [18] as implemented in the Gaussian 03 suite of programs [19]. We calculated the electrophilicity and nucleophilicity indices with reference to tetracyanoethylene (TCNE), which was optimized at the same level of theory. Isotropic $^{31}$P chemical shifts were calculated relative to $H_3PO_4$ at the same level of theory at which the geometry of all the molecules were optimized. The same level of theory was also used to calculate the absolute isotropic chemical shift of $H_3PO_4$ ($\sigma_{iso} = 374.0$).

**[2.3] Results and Discussion**

**[2.3.1] Molecular Geometries**

The optimized geometries of all of the five-membered rNHCs are perfectly planar in their singlet states, except for molecules **6** and **9** (Figure 2.1). Optimization of **2** resulted in a broken geometry, and thus, this molecule is not considered for further discussion. Important geometrical parameters for all of the optimized molecules are given in Table 2.1. Our calculated C−$C_C$ bond lengths and C−$C_C$−C bond angles (where $C_C$ stands for carbenic carbon) for the five-membered rNHCs are in the ranges of 1.370−1.408 Å and 99.6−101.1°, respectively, in their singlet states. These calculated values are in good agreement with the experimentally observed values for metal−rNHC complexes (1.373−1.422 Å and 104.3−107.4°, respectively) [8,10]. The small variation may come from the fact that our calculations considered the free carbene whereas the experimental structures were obtained with the metal complexes. The majority of the five-membered rNHCs (except **7**, **8**, **13**, and **17**) have larger C−$C_C$−C bond angles in the triplet state than in the singlet state, which is consistent with triplet carbenes having larger central bond angles than the corresponding singlet carbenes [20]. Consequently, the $C_C$−C bond lengths of triplet carbenes are shorter than those of singlet carbenes. However, for the molecules with unsymmetrical backbones (i.e., **4−6**, **9**, **11**, and **13**), the $C_C$−C bond lengths on each side of the central carbon atom are not equal. It may be
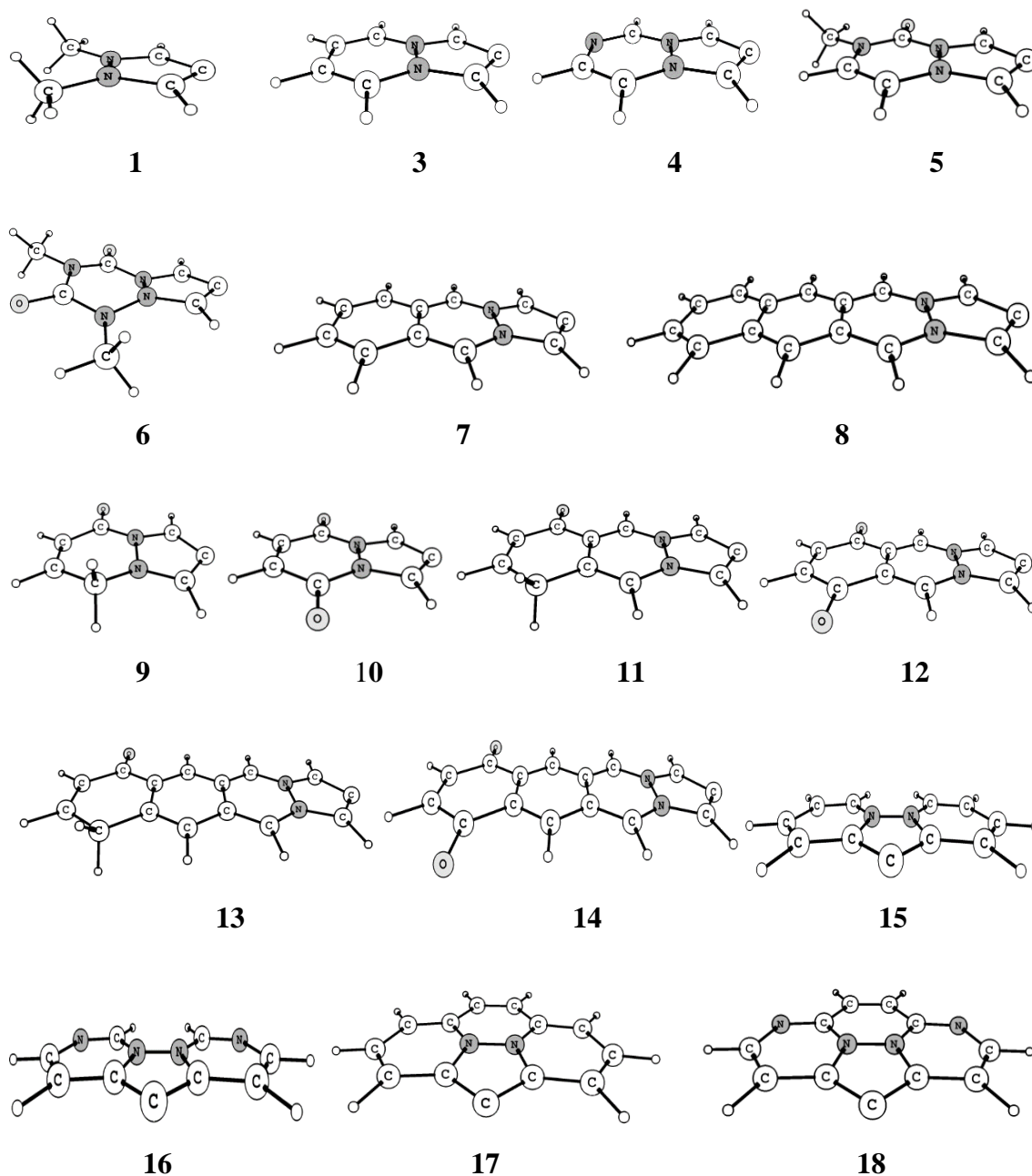
**Figure 2.1**: Optimized singlet state geometries for the mesoionic NHCs (**1**−**18**).

noted that even though **7**, **8**, **13**, and **17** have smaller C−C$_C$−C angles in their triplet states, the difference is not very large compared with the corresponding angle in their respective singlet states. Accordingly, the calculated C−C$_C$ bond lengths in the triplet states change very little compared with the singlet states. Table 2.1 reveals that for five-membered rNHCs, there are no significant differences in C$_C$−C bond lengths and C−C$_C$−C bond angles in the stable singlet states as a result of annulation or carbonylation. This indicates that annulation or carbonylation have no dramatic effect on the geometrical parameters of the five-membered rNHCs.

**Table 2.1**: PBE0/6-31+G* calculated C−C$_C$−C bond angles (in degrees) and C$_C$−C bond lengths (in Å) of **1−34** for both singlet and triplet states.

| Molecule | ∠C−C$_C$−C | r(C$_C$−C) | Molecule | ∠C−C$_C$−C | r(C$_C$−C) |
|---|---|---|---|---|---|
| **1S** | 99.6 | 1.396 | **18T** | 110.3 | 1.393 |
| **1T** | 111.4 | 1.370 | **19S** | 110.9 | 1.424 |
| **3S** | 100.5 | 1.397 | **19T** | 121.8 | 1.401 |
| **3T** | 109.1 | 1.378 | **20S** | 111.6 | 1.413/1.440 |
| **4S** | 100.6 | 1.404/1.393 | **20T** | 124.5 | 1.385/1.410 |
| **4T** | 109.8 | 1.387/1.370 | **21S** | 110.6 | 1.436/1.403 |
| **5S** | 100.4 | 1.401/1.394 | **21T** | 125.8 | 1.419/1.339 |
| **5T** | 112.8 | 1.374/1.370 | **22S** | 111.6 | 1.448/1.391 |
| **6S** | 100.9 | 1.408/1.385 | **22T** | 125.7 | 1.420/1.352 |
| **6T** | 112.4 | 1.374/1.396 | **23S** | 112.4 | 1.428 |
| **7S** | 100.8 | 1.398 | **23T** | 126.1 | 1.397 |
| **7T** | 100.1 | 1.392 | **24S** | 112.3 | 1.419/1.409 |
| **8S** | 101.0 | 1.399 | **24T** | 126.3 | 1.378/1.366 |
| **8T** | 100.3 | 1.394 | **25S** | 118.2 | 1.397/1.365 |
| **9S** | 99.8 | 1.406/1.391 | **25T** | 126.6 | 1.384/1.352 |
| **9T** | 110.8 | 1.381/1.370 | **26S** | 112.4 | 1.428/1.414 |
| **10S** | 100.1 | 1.396 | **26T** | 126.9 | 1.400/1.350 |
| **10T** | 110.0 | 1.377 | **27S** | 117.8 | 1.386 |
| **11S** | 100.6 | 1.403/1.393 | **27T** | 126.5 | 1.370 |
| **11T** | 110.0 | 1.384/1.370 | **28S** | 112.5 | 1.423 |
| **12S** | 100.6 | 1.397 | **28T** | 125.9 | 1.379 |
| **12T** | 111.3 | 1.373 | **29S** | 112.3 | 1.423 |
| **13S** | 100.9 | 1.401/1.396 | **29T** | 125.6 | 1.397 |
| **13T** | 100.2 | 1.395/1.390 | **30S** | 112.4 | 1.425 |
| **14S** | 100.8 | 1.398 | **30T** | 125.8 | 1.398 |
| **14T** | 111.9 | 1.372 | **31S** | 112.4 | 1.425 |
| **15S** | 100.9 | 1.396 | **31T** | 125.8 | 1.398 |
| **15T** | 109.3 | 1.395 | **32S** | 108.1 | 1.421 |
| **16S** | 100.7 | 1.394 | **32T** | 121.1 | 1.404 |
| **16T** | 110.6 | 1.389 | **33S** | 107.1 | 1.425 |
| **17S** | 101.1 | 1.400 | **33T** | 120.8 | 1.401 |
| **17T** | 100.9 | 1.424 | **34S** | 109.2 | 1.426 |
| **18S** | 101.1 | 1.399 | **34T** | 123.3 | 1.397 |

In the case of six-membered rNHCs, the singlet-state structures of **19−21** and **32−34** are found to be planar, but **22** and **24−27** show non-planar structures in the optimized singlet states and **23** and **28−31** exhibit slightly arched conformations (Figure 2.2). Like the five-membered rNHCs, the calculated C−$C_C$ bond length (1.424 Å) and C−$C_C$−C bond angle (110.9°) of the parent six-membered rNHC were found to be close
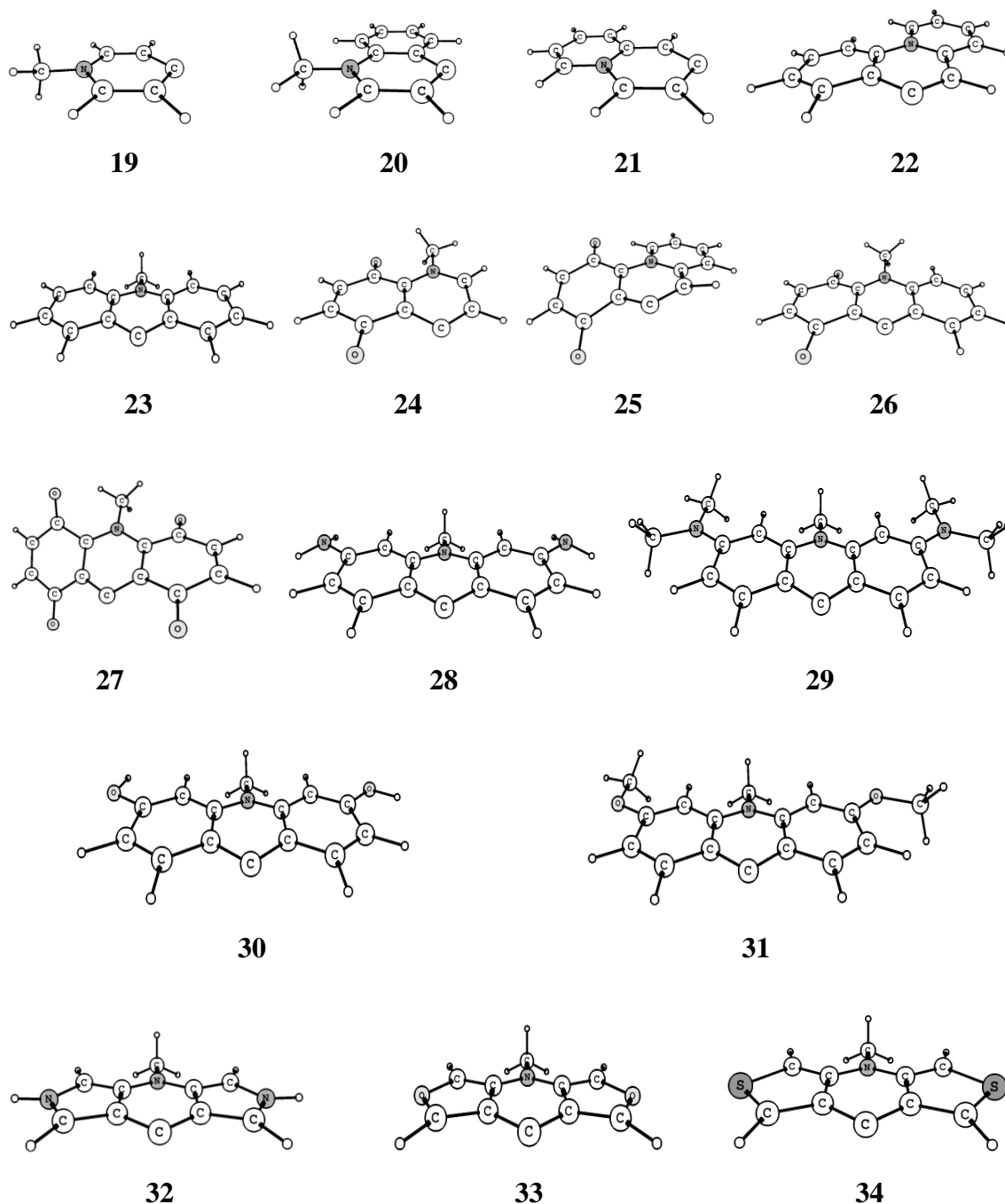
**19**  **20**  **21**  **22**

**23**  **24**  **25**  **26**

**27**  **28**  **29**

**30**  **31**

**32**  **33**  **34**

**Figure 2.2**: Optimized singlet state geometries for the six-membered remote NHCs (**19−34**)

to the C–$C_C$ bond length (1.402 Å) and C–$C_C$–C bond angle (114.9°) of the corresponding experimentally observed Ni(II) complex [11b]. Similarly, there is a good agreement between the calculated geometrical parameters of **22** (C–$C_C$ bond length of 1.391 Å and C–$C_C$–C bond angle of 111.6°) with the experimentally observed values in the corresponding metal complexes (C–$C_C$ bond length of 1.372 Å and C–$C_C$–C bond angle of 117.4°) [7]. For all of the six-membered rNHCs, the triplet states have larger C–$C_C$–C bond angles and shorter $C_C$–C bond lengths than the corresponding singlet states. For molecules **20−22** and **24−26**, the $C_C$–C bond lengths on each side of the central carbon atom are not equal because of the unsymmetrical backbone. The geometrical parameters of the six-membered rNHCs change significantly upon annulation/carbonylation. For molecules **23** and **28−31**, both the $C_C$–C bond lengths and C–$C_C$–C bond angles are almost similar, indicating a negligible effect of the substituents on the annulated rings. The central C–$C_C$–C angles for six-membered rNHCs are found to be wider than those of five-membered rNHCs. Schoeller and co-workers reported that a smaller central carbene angle favors effective complexation to a metal [21,22] and accordingly, the five-membered rNHCs considered in this study should be more suitable for transition-metal catalysts compared with the six-membered rNHCs.

**[2.3.2] Singlet−Triplet and HOMO−LUMO Gaps**

The stabilities of these rNHCs can be gauged from their respective singlet−triplet ($\Delta E_{S-T}$) and HOMO−LUMO ($\Delta E_{H-L}$) gaps [23]. In principle, the higher the values of $\Delta E_{S-T}$ and $\Delta E_{H-L}$, the higher will be the stabilities of these molecules in the singlet state. The calculated values of $\Delta E_{S-T}$ and $\Delta E_{H-L}$ for all of the molecules are given in Table 2.2. It is evident from Table 2.2 that benz-annulation of the parent five-membered rNHC (**3**) increases the singlet-triplet separation, while annulation with larger aromatics (**7** and **8**) decreases the $\Delta E_{S-T}$ value, which follows the order **3** > **7** > **8**. Introduction of benzene rings on both sides of the parent rNHC (**15**) also results in an increase in the $\Delta E_{S-T}$ value. In the case of normal NHCs, both benz- and naphtho-annulated NHCs have lower $\Delta E_{S-T}$ values compared with the non-annulated NHCs [16a], but for five-membered rNHCs, benz- (**3**) and naphtha-annulated (**7**) rNHCs have higher and lower $\Delta E_{S-T}$ values, respectively, compared with the non-annulated ones. Molecules **4** and **16**, which are the aza-substituted variants of molecules **3** and **15**, respectively, have smaller $\Delta E_{S-T}$ values compared with the parent ones. But this is not the case for **18**, which has a higher $\Delta E_{S-T}$ value compared with the parent rNHC **17**. Overall, aza-substitution leaves the

**Table 2.2**: PBE0/6-31+G* computed singlet-triplet ($\Delta E_{S\text{-}T}$, in kcal mol$^{-1}$) and HOMO-LUMO ($\Delta E_{H\text{-}L}$, in eV) gaps of **1-34**.

| Molecule | $\Delta E_{S\text{-}T}$ | $\Delta E_{H\text{-}L}$ | Molecule | $\Delta E_{S\text{-}T}$ | $\Delta E_{H\text{-}L}$ |
|----------|-------------------------|-------------------------|----------|-------------------------|-------------------------|
| 1 | 36.7 | 4.4 | 19 | 18.2 | 3.4 |
| 3 | 42.8 | 3.5 | 20 | 11.7 | 3.1 |
| 4 | 39.7 | 3.5 | 21 | 18.2 | 2.7 |
| 5 | 36.7 | 3.7 | 22 | 11.7 | 2.5 |
| 6 | 28.0 | 3.7 | 23 | 7.1 | 2.9 |
| 7 | 23.3 | 2.7 | 24 | -3.2 | 1.7 |
| 8 | 10.3 | 2.2 | 25 | -5.3 | 2.2 |
| 9 | 26.5 | 2.7 | 26 | -3.5 | 1.8 |
| 10 | 5.0 | 1.7 | 27 | -4.2 | 2.2 |
| 11 | 32.5 | 2.7 | 28 | 13.6 | 3.1 |
| 12 | 22.8 | 2.1 | 29 | 14.3 | 3.1 |
| 13 | 20.2 | 2.4 | 30 | 12.0 | 3.1 |
| 14 | 32.6 | 2.2 | 31 | 11.9 | 3.1 |
| 15 | 38.0 | 3.5 | 32 | 17.0 | 3.5 |
| 16 | 36.8 | 3.4 | 33 | 9.9 | 3.3 |
| 17 | 18.9 | 2.8 | 34 | 7.0 | 3.0 |
| 18 | 23.6 | 2.8 | | | |

HOMO−LUMO gap unaffected while marginally shifting the singlet-triplet gap. However, carbonylation of the annulated rNHCs does not follow a particular trend. For example, for the benz-annulated rNHC **3**, carbonylation with one (**9**) and two (**10**) carbonyl groups decreases $\Delta E_{S–T}$ in the order **3** > **9** > **10**. However, carbonylation of the anthro-annulated rNHC **8** follows the reverse trend, **8** < **13** < **14**. On the other hand, carbonylation of the naphtho-annulated rNHC **7** follows the order **11** > **7** > **12**. We could not find any specific reason for such discrepancies. Comparison of **10**, **12**, and **14** shows that $\Delta E_{S–T}$ increases as the carbonyl groups are moved away from the parent rNHC scaffold. In other words, introduction of more benzene rings between the quinoid moiety and the rNHC scaffold stabilizes the singlet state, and $\Delta E_{S–T}$ follows the order **10** < **12** < **14**. Among all of the five-membered rNHCs, **3** and **10** were found to have the highest and lowest values of $\Delta E_{S–T}$, respectively.

The $\Delta E_{S–T}$ values of the six-membered rNHCs decrease as a result of annulation and carbonylation of the rNHC scaffold and were found to be lower than those of the

five-membered rNHCs. This is because there is one less electronegative nitrogen atom in the six-membered rNHCs. For carbonylated rNHCs **24−27**, the triplet state becomes the ground state, and it may be anticipated that these molecules will exhibit reactivity typical of triplet carbenes. In other words, rNHCs **24−27** are likely to react via their triplet states. Accordingly, these molecules were not considered for further discussion, as the main focus of the present work is on tuning the σ-donor and π-acceptor abilities of rNHCs in their stable singlet states. The lower $\Delta E_{S-T}$ values of **24−27** may arise from the presence of the quinine moiety [16c]. It is seen from Table 2.2 that the $\Delta E_{S-T}$ values for **19** and **21** are the same (18.2 kcal mol$^{-1}$), as is the case with **20** and **22** (11.7 kcal mol$^{-1}$). These results indicate that annulation of **19** at the 1- and 2-positions does not change the singlet-triplet separation. Upon annulation of both sides of the parent rNHC (**23**), the $\Delta E_{S-T}$ value decreases significantly ($\Delta E_{S-T}$ = 7.1 kcal mol$^{-1}$), but introduction of electron-donating groups such as NH$_2$, NMe$_2$, OH, and OMe on the annulated rNHC scaffold (molecules **28−31**) increases the singlet-triplet separation. Annulation of the parent six-membered rNHC with the electron-rich pyrrole molecule decreases $\Delta E_{S-T}$ by 1.2 kcal mol$^{-1}$, while the introduction of furan and thiophene moieties significantly decreases the same. Among the six-membered rNHCs, the highest $\Delta E_{S-T}$ value was obtained for **19** and **21** and the lowest value was obtained for **25**.

The HOMO−LUMO gap is used to measure the kinetic stability of carbenes [23b]. Both annulation and carbonylation of the five-membered rNHC scaffold result in decreases in $\Delta E_{H-L}$, implying a decrease in kinetic stability. Among the five-membered rNHCs considered in this study, **1** and **10** were found to be kinetically the most and least stable, respectively. Similarly, annulated/carbonylated six-membered rNHCs (except **32**) were found to have lower kinetic stabilities compared to the parent ones. rNHCs **32** and **24** were found to have the highest and lowest kinetic stabilities, respectively, among all of the six-membered rNHCs.

### [2.3.3] Hydrogenation and Stabilization Energies

The thermodynamic stabilities of the rNHCs were further assessed by evaluation of their hydrogenation and stabilization energies with the help of equations (2.1) and (2.2), respectively, and the results are given in Table 2.3.
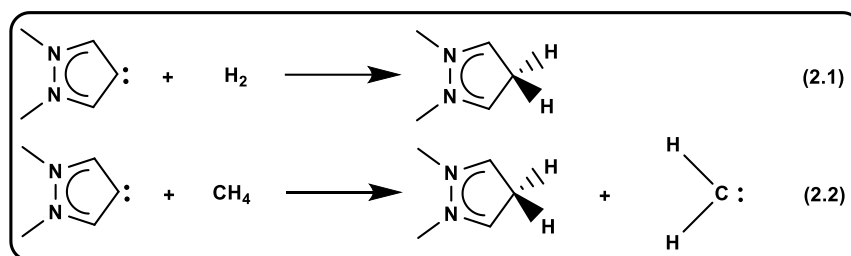
**Table 2.3**: PBE0/6-31+G* computed hydrogenation energies ($E_{hydro}$, in kcal mol$^{-1}$) and stabilization energies (SE, in kcal mol$^{-1}$) of **1-34** (excluding **2** and **24-27**).

| Molecule | $E_{hydro}$ | SE | Molecule | $E_{hydro}$ | SE |
|:---:|:---:|:---:|:---:|:---:|:---:|
| **1** | 2.3 | 130.6 | **17** | -27.7 | 100.5 |
| **3** | -10.1 | 118.2 | **18** | -24.0 | 104.3 |
| **4** | -13.1 | 115.2 | **19** | -56.1 | 72.2 |
| **5** | -4.9 | 123.4 | **20** | -61.8 | 66.5 |
| **6** | -34.1 | 94.2 | **21** | -52.7 | 75.6 |
| **7** | -21.6 | 106.7 | **22** | -57.5 | 70.8 |
| **8** | -28.3 | 99.9 | **23** | -70.4 | 57.8 |
| **9** | -4.7 | 123.6 | **28** | -63.4 | 64.8 |
| **10** | -12.8 | 115.5 | **29** | -62.7 | 65.5 |
| **11** | -16.0 | 112.3 | **30** | -65.9 | 62.3 |
| **12** | -17.9 | 110.3 | **31** | -65.8 | 62.4 |
| **13** | -24.9 | 103.3 | **32** | -62.6 | 65.7 |
| **14** | -26.5 | 101.8 | **33** | -71.1 | 57.2 |
| **15** | -17.6 | 110.6 | **34** | -71.4 | 56.8 |
| **16** | -14.7 | 113.5 | | | |

In the case of five-membered rNHCs, all of the molecules except for **1** have negative hydrogenation energies. The lower the negative value, the higher will be the stability of the parent system. It is apparent from Table 2.3 that both annulation and carbonylation of the five-membered rNHC scaffold result in a decrease in thermodynamic stability. However, the introduction of nitrogen atoms in the annulated rings (except **4**) was found to increase the thermodynamic stability. It is observed that with an increase in the number of annulated rings, the hydrogenation energy becomes more negative (*e.g.*, **3** > **7** > **8**), implying a decrease in the thermodynamic stability. The carbonylated derivatives also show an additive effect in decreasing the thermodynamic stability of the five-membered rNHCs, as with an increase in the number of carbonyl groups from one to two the hydrogenation energy becomes more negative. The stabilization energies of the five-membered rNHCs obtained using equation (2.2) also

show trends similar to those for the hydrogenation energies. However, the thermodynamic stabilities predicted from calculations of the hydrogenation and stabilization energies do not go in parallel with those obtained from an evaluation of the singlet-triplet gaps of the respective molecules. For example, while the $\Delta E_{S-T}$ values of **10**, **12**, and **14** increase in the order **10** < **12** < **14**, the hydrogenation energies follow the reverse order, *i.e.*, **10** > **12** > **14**. From the calculated values of both the hydrogenation and stabilization energies, **1** and **6** were found to have the highest and lowest thermodynamic stabilities, respectively.

Similarly, in case of six-membered rNHCs, annulation results in a decrease in the thermodynamic stability. Except for **21**, the hydrogenation energies of all of the rNHCs are more negative than those of the parent molecule **19**. A comparison of the hydrogenation and stabilization energies of the six-membered rNHCs shows that the thermodynamic stability decreases with an increase in the number of annulated rings, *e.g.*, **19** > **20** > **23**. As is the case with singlet-triplet separation, substitution with electron-donating groups increases the thermodynamic stabilities of bis-annulated rNHCs (**28**−**31**) compared with the parent bis-annulated carbene (**23**). Among all of the six-membered rNHCs, **21** and **34** were found to be the most and least thermodynamically stable, respectively. This result is consistent with the corresponding $\Delta E_{S-T}$ values. Thus, while for five-membered rNHCs, the $\Delta E_{S-T}$ values do not vary linearly with the respective hydrogenation energies, the calculated hydrogenation energies follow a similar trend as the $\Delta E_{S-T}$ values for six-membered rNHCs. Indeed, we obtained a reasonable correlation between the calculated hydrogenation energies and $\Delta E_{S-T}$ values for the six-membered rNHCs (Figure 2.3).
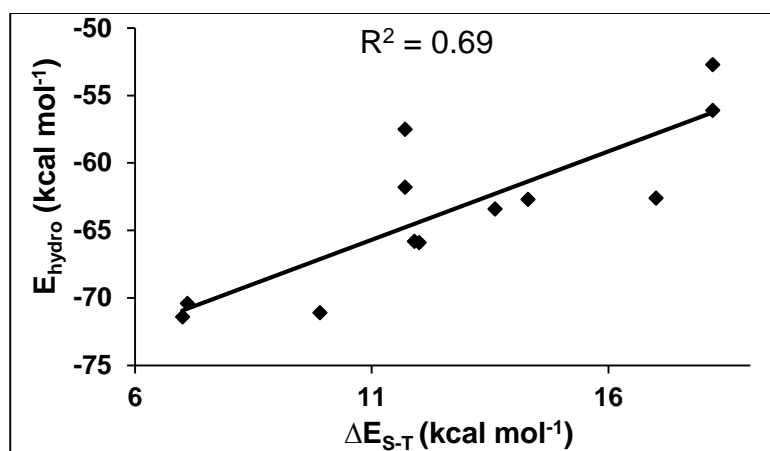


**Figure 2.3**: Correlation plot between hydrogenation energies ($E_{hydro}$) and singlet-triplet gaps ($\Delta E_{S-T}$) of six-membered rNHCs.

**[2.3.4] Ligand Properties**

Both theoretical and experimental reports support the strong σ-donating and non-negligible π-accepting properties of NHCs [2-4,16a]. The reactivity [24] and ligating properties [25] of carbenes depend on the nature and energies of the key frontier molecular orbitals. In order to find out the energies of these frontier orbitals, we performed NBO analysis [18]. The calculated energies of the σ-symmetric lone pair and π-symmetric unoccupied molecular orbital concentrated on the central carbon atom are listed in Table 2.4 and graphically represented in Figure 2.4.
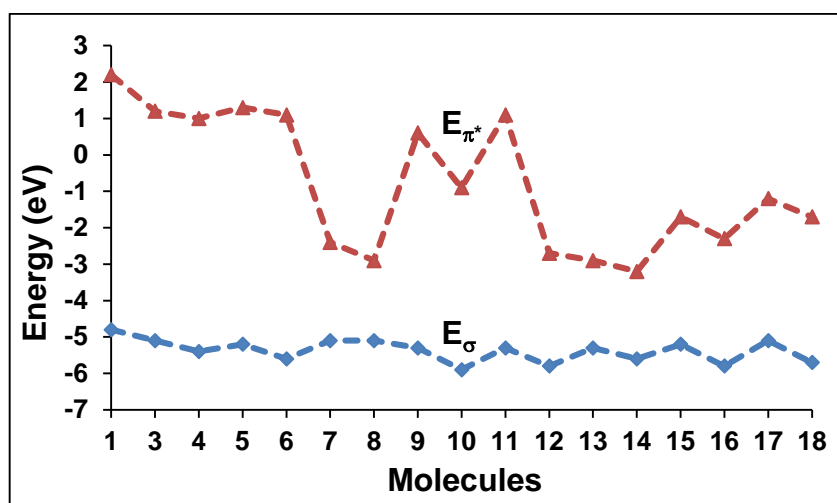


(a)
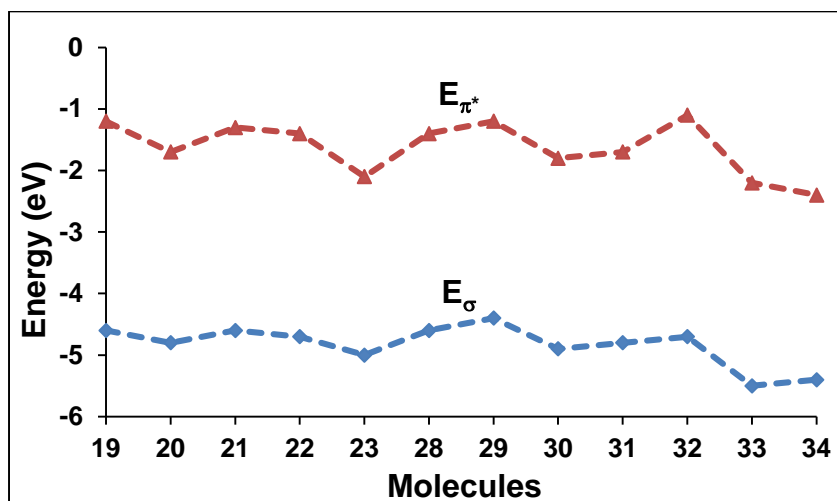


(b)

**Figure 2.4**: Plots of the energies of σ-symmetric lone pair orbitals ($E_\sigma$) and π-symmetric unoccupied orbitals ($E_{\pi*}$) concentrated on the central carbon atom of (a) five-membered rNHCs (**1**, **3-18**) and (b) six-membered rNHCs (**19-23**, **28-34**).

**Table 2.4**: PBE0/6-31+G* calculated energies of σ-symmetric lone pair orbital ($E_\sigma$ in eV) and π-symmetric unoccupied orbital ($E_{\pi*}$ in eV) concentrated on the carbenic carbon atom ($C_C$) as well as natural charge at $C_C$ ($q(C_C)$) of **1-34** (excluding **2** and **24-27**).

| Molecule | $E_\sigma$ | $E_{\pi*}$ | $q(C_c)$ |
|---|---|---|---|
| 1 | -4.8 | 2.2 | -0.421 |
| 3 | -5.1 | 1.2 | -0.377 |
| 4 | -5.4 | 1.0 | -0.365 |
| 5 | -5.2 | 1.3 | -0.389 |
| 6 | -5.6 | 1.1 | -0.383 |
| 7 | -5.1 | -2.4 | -0.358 |
| 8 | -5.1 | -2.9 | -0.347 |
| 9 | -5.3 | 0.6 | -0.398 |
| 10 | -5.9 | -0.9 | -0.388 |
| 11 | -5.3 | -2.6 | -0.366 |
| 12 | -5.8 | -2.7 | -0.356 |
| 13 | -5.3 | -2.9 | -0.351 |
| 14 | -5.6 | -3.2 | -0.344 |
| 15 | -5.2 | -1.7 | -0.343 |
| 16 | -5.8 | -2.3 | -0.340 |
| 17 | -5.1 | -1.2 | -0.358 |
| 18 | -5.7 | -1.7 | -0.349 |
| 19 | -4.6 | -1.2 | -0.222 |
| 20 | -4.8 | -1.7 | -0.167 |
| 21 | -4.6 | -1.3 | -0.245 |
| 22 | -4.7 | -1.4 | -0.198 |
| 23 | -5.0 | -2.1 | -0.104 |
| 28 | -4.6 | -1.4 | -0.124 |
| 29 | -4.4 | -1.2 | -0.143 |
| 30 | -4.9 | -1.8 | -0.117 |
| 31 | -4.8 | -1.7 | -0.115 |
| 32 | -4.7 | -1.1 | -0.104 |
| 33 | -5.5 | -2.2 | -0.052 |
| 34 | -5.4 | -2.4 | -0.062 |

It may be noted that the electronic structure of rNHC **1** differs from that of its isomeric Arduengo carbene (AC). For example, the σ-symmetric lone pair orbital at the carbenic carbon ($C_C$) has more s character in AC ($LP_{hybrid}$ = s(51.6%) + p(48.3%)) than in **1** ($LP_{hybrid}$ = s(38.7%) + p(61.2%)). Accordingly, the carbene center of AC is more electrophilic than that of **1**. This is also reflected in the computed natural charges at $C_C$ for AC and **1** (0.105 and −0.421, respectively) and the populations of the formally vacant p orbital at $C_C$ (0.672 and 0.793, respectively). Furthermore, the carbene center of **1** lies in the nodal plane of the lowest π antibonding orbital, while this is not the case with AC. Thus, the σ-symmetric occupied molecular orbital (*i.e.*, the σ-symmetric lone pair orbital of **1**) lies at a higher energy than that of AC, thereby making it a better donor than AC. Indeed, similarly annulated/carbonylated remote carbenes have better σ-donor ability than the corresponding Arduengo carbenes. For example, the σ-donating abilities of remote carbenes **3**, **6**, **7** and **17** are higher than those of their normal analogues (vide infra) [16a].

It is clear from Table 2.4 and Figure 2.4 that annulation and carbonylation decreases the energies of both the σ-symmetric lone pair orbitals and π-symmetric unoccupied orbitals of five-membered rNHCs **3−18** compared to the parent rNHC **1**. This indicates the decrease in σ-donation ability and increase in π-accepting ability of five-membered rNHCs as a result of annulation/carbonylation. It may be noted that unlike in Arduengo-type carbenes (i.e., normal NHCs), where two nitrogen atoms are present next to the carbenic carbon atom ($C_C$), in the carbenes considered in this study the nitrogen atoms are further away from $C_C$ (by one and two atoms for the five- and six-membered rNHCs, respectively). Consequently, while there is effective delocalization of the nitrogen lone pair ($N_{LP}$) into the formally vacant p orbital of the carbenic carbon in NHCs, such direct overlap is not possible in the carbene compounds considered for the present study. Indeed, NBO analysis did not show any direct delocalization of $N_{LP}$ to the formally vacant p orbital of $C_C$. However, electron delocalization from the neighboring C=C or C=N bonds to the formally vacant p orbital of $C_C$ does take place. Both annulation and carbonylation of the rNHC scaffold were found to make $C_C$ more electrophilic, thereby increasing the π-accepting ability. The increase in electrophilicity of $C_C$ is evident from the decrease in the natural charge at $C_C$ (Table 2.4). In fact, we obtained a reasonable correlation ($R^2$ = 0.70) between the energies of the unoccupied π-symmetric molecular orbital ($E_{\pi*}$) of the molecules with their respective natural charge values (Figure 2.5). Analysis of Table 2.4 indicates that with an increase in the degree
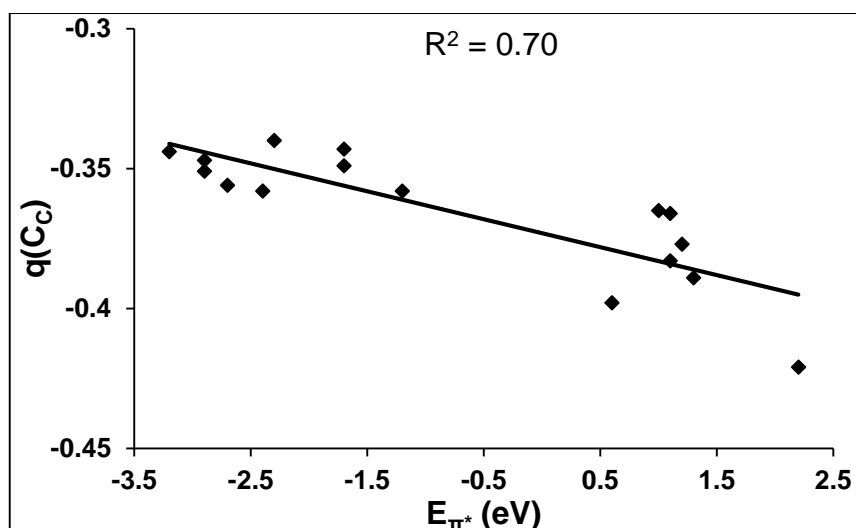
**Figure 2.5**: Correlation plot between the energies of the π-symmetric unoccupied MO ($E_{\pi*}$) and the values of natural charge at carbenic carbon (q($C_C$)) of five-membered rNHCs (omitting the point corresponding to **10**).

of annulation and the number of carbonyl groups in the rNHC scaffold, the value of $E_{\pi*}$ decreases, *i.e.*, the π-accepting ability increases. Therefore, annulation and carbonylation have an additive effect in increasing the π-accepting ability. For example, the π-accepting abilities of **3**, **7**, and **8**; **3**, **9**, and **10**; **7**, **11**, and **12**; and **8**, **13**, and **14** increase in the orders **3** < **7** < **8**; **3** < **9** < **10**; **7** < **11** < **12**; and **8** ≈ **13** < **14**, respectively. Comparison of **15** with **16** and **17** with **18** shows that aza substitution lead to an increase in the π-accepting ability. We were surprised by the increase in π-accepting abilities of compounds **10**, **12** and **14** in the order **10** < **12** < **14** even though the carbonyl groups were moved away from the rNHC scaffold. We reasoned that this difference may arise from the increase in the extension of π conjugation to the carbonyl groups in the order **10** < **12** < **14**. Among all of the five-membered rNHCs, **14** was found to have the highest π-accepting ability.

For six-membered remote carbenes, barring a few exceptions (**29** and **32**), annulation was found to decrease and increase the σ-donor and π-acceptor abilities, respectively. The increase in π-accepting ability is also evident from the calculated natural charge at $C_C$, and we obtained a reasonable correlation ($R^2$ = 0.77) between the $E_{\pi*}$ and q($C_C$) values (Figure 2.6). However, the increase in π acidity of the six-membered rNHCs is less dramatic than that of the five-membered rNHCs. There is no appreciable change in the ligand properties of the parent rNHC **19** as a result of
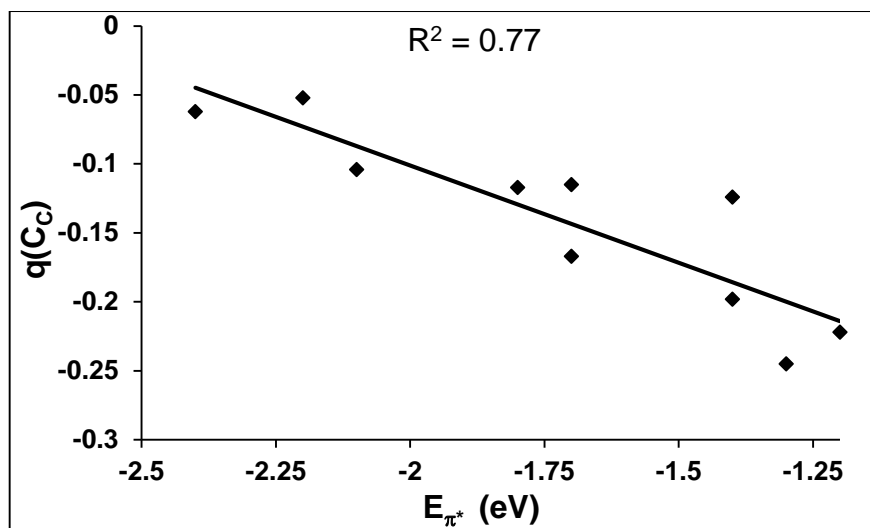
**Figure 2.6**: Correlation plot between the energies of the $\pi$-symmetric unoccupied MO ($E_{\pi*}$) and the values of natural charge at carbenic carbon ($q(C_C)$) of six-membered rNHCs (omitting the points corresponding to **29** and **32**).

annulation with the electron-rich pyrrole molecule. The $\pi$-accepting abilities increase in the order **32** < **33** < **34**, which is in agreement with the relative inductive electron-withdrawing abilities of these heterocycles [26]. Among all of the six-membered rNHCs, **34** was found to have the highest $\pi$ acidity.

### [2.3.5] Nucleophilicity and Electrophilicity

In order to determine the respective basicities and acidities of these rNHCs, we evaluated their nucleophilicity ($N$) and electrophilicity ($\omega$) indices. The nucleophilicity index was calculated using the equation $N = E_{HOMO} - E_{HOMO(TCNE)}$, considering tetracyanoethylene (TCNE) as the reference [27a]. The global electrophilicity was calculated using the expression $\omega = \mu^2/2\eta$, where $\mu$ is the chemical potential ($\mu \approx (E_{HOMO} + E_{LUMO})/2$) and $\eta$ is the chemical hardness ($\eta = E_{HOMO} - E_{LUMO}$) [27b−d]. The calculated values of $N$ and $\omega$ are listed in Table 2.5.

The nucleophilicity index values ($N$) for five-membered rNHCs **1−18** were found to be in the range of 3.8−4.8 eV. These values are in accordance with the respective $\sigma$-donating abilities of the rNHCs (Table 2.4 and Figure 2.4). We obtained an excellent correlation between $E_\sigma$ and $N$ ($R^2 = 0.99$; Figure 2.7). All of the annulated and carbonylated five-membered rNHCs were found to be more electrophilic than the parent rNHC **1**. This indicates higher $\pi$ acidity of the annulated/carbonylated rNHCs compared with the parent one. However, we did not get a one-to-one correlation between the $E_{\pi*}$

**Table 2.5**: PBE0/6-31+G* calculated nucleophilicity indices ($N$, in eV) and electrophilicity indices ($\omega$, in eV) for **1**-**34** (excluding **2** and **24**-**27**).

| Molecule | $N$ | $\omega$ | Molecule | $N$ | $\omega$ |
|----------|-----|----------|----------|-----|----------|
| **1** | 4.8 | 0.7 | **17** | 4.5 | 2.5 |
| **3** | 4.5 | 1.6 | **18** | 3.9 | 3.3 |
| **4** | 4.1 | 1.9 | **19** | 5.0 | 1.2 |
| **5** | 4.4 | 1.6 | **20** | 4.8 | 1.7 |
| **6** | 4.0 | 1.9 | **21** | 5.0 | 1.9 |
| **7** | 4.5 | 2.6 | **22** | 4.9 | 2.2 |
| **8** | 4.5 | 3.6 | **23** | 4.6 | 2.2 |
| **9** | 4.3 | 2.9 | **28** | 5.0 | 1.4 |
| **10** | 3.8 | 7.0 | **29** | 5.2 | 1.2 |
| **11** | 4.3 | 2.8 | **30** | 4.7 | 1.8 |
| **12** | 3.8 | 5.3 | **31** | 4.8 | 1.7 |
| **13** | 4.3 | 3.5 | **32** | 4.9 | 1.1 |
| **14** | 4.0 | 4.6 | **33** | 4.0 | 2.2 |
| **15** | 4.4 | 1.7 | **34** | 4.2 | 2.5 |
| **16** | 3.8 | 2.3 | | | |
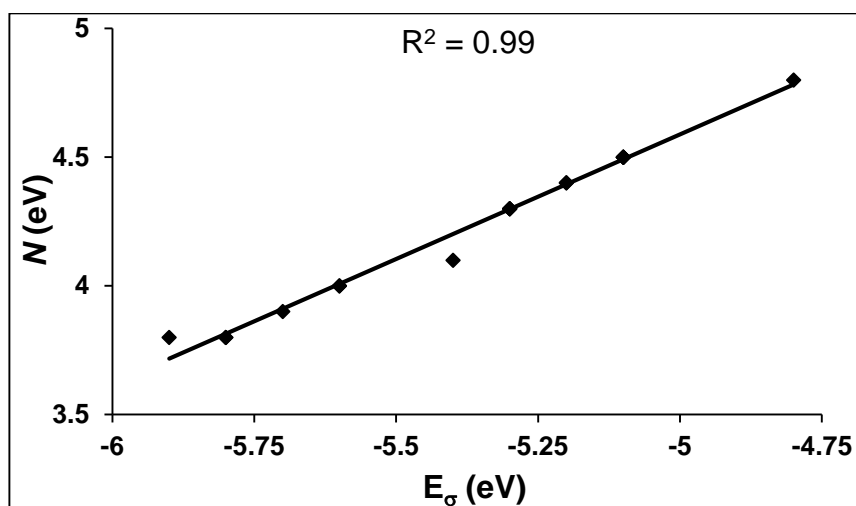


**Figure 2.7**: Correlation plot between the energies of the σ-symmetric lone pair orbital ($E_\sigma$) and the values of nucleophilicity index ($N$) of five-membered rNHCs.

values of these molecules and their respective electrophilicity indices. The highest value of $\omega$ was obtained for **10** (7.0 eV). The nucleophilicity indices of rNHCs **3**, **7** and **8** are

the same ($N = 4.5$ eV), but the electrophilicity indices were found to increase in the order **3** < **7** < **8**. This indicates almost similar σ-donating abilities of **3**, **7** and **8** but increasing π-accepting abilities in the order **3** < **7** < **8**. Comparison of **3** with its mono- (**9**) and dicarbonylated (**10**) derivatives shows that carbonylation marginally decreases the nucleophilicity but significantly enhances the electrophilicity. Similar results were also obtained for **7**, **11**, **12** and **8**, **13**, **14**. It can also be concluded that the effect of carbonylation on both nucleophilicity and electrophilicity is additive in nature.

The values of $N$ for the six-membered rNHCs **19**−**34**, lie in a higher range (4.0−5.2 eV) than for the five-membered ones. This is in tune with the stronger basicities of the six-membered rNHCs compared with the five-membered ones. The $N$ values are in excellent agreement with the respective $E_\sigma$ values ($R^2 = 0.99$; Figure 2.8(a)). Like the five-membered rNHCs, the values of the electrophilicity index for all of the annulated six-membered rNHCs (except **32**) are higher than that for the parent molecule **19**, indicating an increase in π acidity as a result of annulation. In fact, a good correlation between the values of $\omega$ and $E_{\pi*}$ was obtained ($R^2 = 0.85$; Figure 2.8(b)). Annulation of **19** with one (**20**) or two (**23**) benzene rings has an additive effect on both the nucleophilicity and electrophilicity. The $N$ and $\omega$ values for **19**, **20** and **23** decrease and increase in the orders **19** > **20** > **23** and **19** < **20** < **23** respectively. Comparison of **23** with **28**−**31** shows that installation of electron-donating groups increases and decreases the nucleophilicity and electrophilicity, respectively, compared with those of the parent cyclic aromatic remote carbene **23**. There is no appreciable change in the nucleophilicity and electrophilicity compared with **19** as a result of annulation with the electron-rich pyrrole molecule (**32**). However, annulation with furan (**33**) and thiophene (**34**) decreases the nucleophilicity but increases the electrophilicity. This is in agreement with the respective σ-donating and π-accepting abilities of the molecules (Table 2.4). The highest value of $\omega$ for six-membered rNHCs was obtained for **34** (2.5 eV). It should be noted that the highest π acidity among the six-membered rNHCs was also obtained for **34** (Table 2.4 and Figure 2.4).
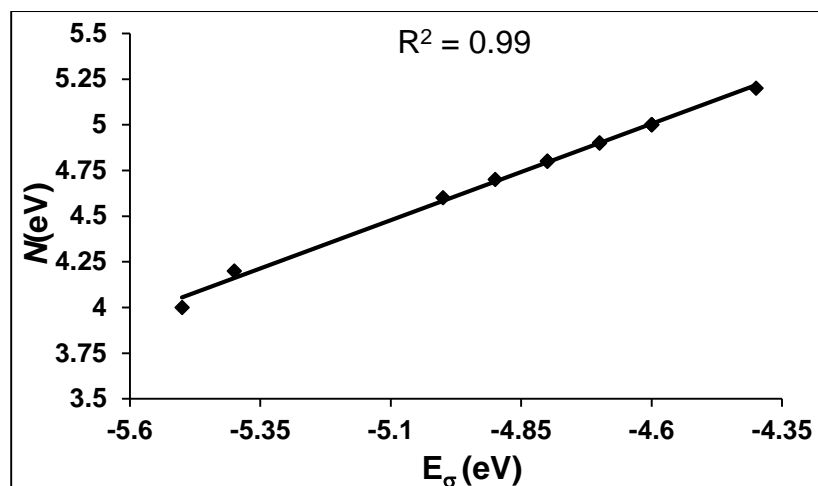
(a)
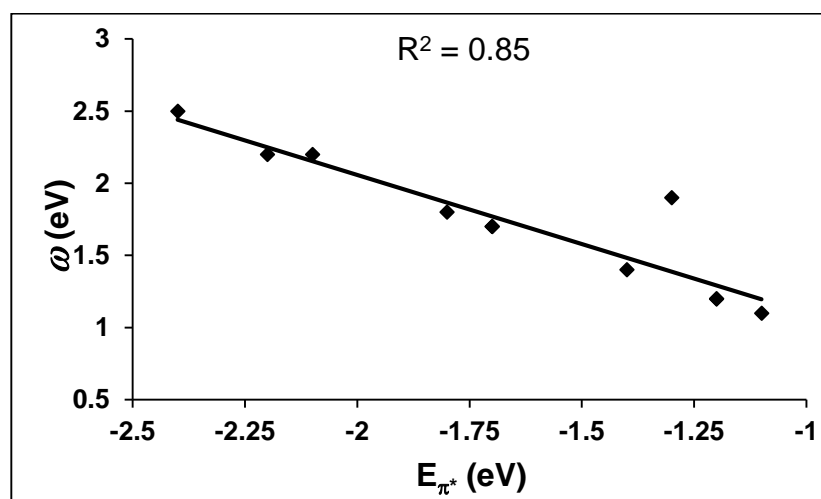


(b)

**Figure 2.8**: Correlation plot between the (a) energies of the σ-symmetric lone pair orbital ($E_\sigma$) and nucleophilicity index values ($N$) and (b) energies of the π-symmetric unoccupied molecular orbital ($E_{\pi*}$) and electrophilicity index values ($\omega$) for six-membered rNHCs.

### [2.3.6] $^{31}$P NMR Spectroscopy

The use of $^{31}$P NMR chemical shifts of carbene-phosphinidene adducts to understand the ligating properties of normal NHCs has been reported previously by various research groups [16a,28,29]. In Scheme 2.2, **A** and **B** represent the two resonance forms of carbene-phosphinidene adducts, in which resonance form **A** dominates over **B** with increasing π acidity of the carbene ligand. Thus, the higher the π acidity of the carbene, the higher will be the back-donation from the phosphorus lone
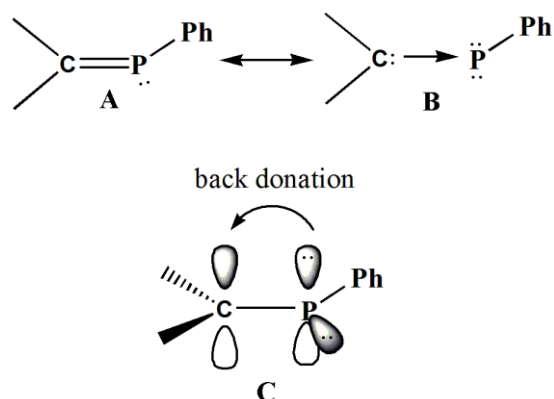
**Scheme 2.2**: Resonance forms of carbene-phosphinidene adducts [28]. Resonance form **A** dominates over **B** with increasing $\pi$ acidity of carbenes. **C** represents the orbital interaction involved in back donation from the phosphorus center to the formally vacant p orbital at the carbenic carbon atom.

pair orbital to the formally vacant carbene $p_\pi$ orbital (**C**). As a result, the chemical shift of the phosphorus center in the carbene-phosphinidene adduct will be further downfield. Thus, it was expected that $^{31}$P NMR spectroscopy would also be useful for evaluating the $\pi$-acidities of rNHCs. Therefore, we calculated the $^{31}$P chemical shift ($\delta(^{31}$P)) of the rNHC-phosphinidene adducts to determine the relative $\pi$ acidities of **1**−**34**. The $\delta(^{31}$P) values of the rNHC−PPh adducts as well as the $C_C$−P and P−$C_{Ph}$ bond lengths are listed in Table 2.6.

The optimized geometry of the phosphinidene adduct of **1** is shown in Figure 2.9 as a representative case. In all of the rNHC-PPh adducts, the P−$C_{Ph}$ bond is not coplanar
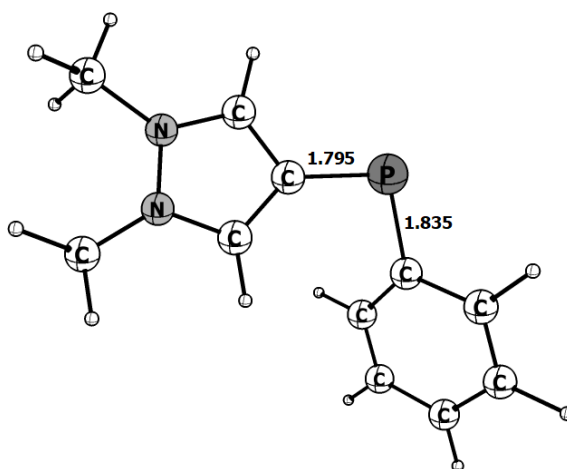


**Figure 2.9**: Optimized geometry and key bond lengths (in Å) of the **1**-PPh adduct.

**Table 2.6**: PBE0/6-31+G* calculated $C_C$-P and P-$C_{Ph}$ bond lengths (in Å) and $^{31}$P NMR chemical shifts ($\delta(^{31}$P)) for the adducts L-PPh (L=**1-34**, excluding **2** and **24-27**).

| Molecule | $C_C$-P | P-$C_{Ph}$ | $\delta^{31}$P |
|---|---|---|---|
| 1 | 1.795 | 1.835 | -31.2 |
| 3 | 1.771 | 1.839 | -12.6 |
| 4 | 1.767 | 1.841 | -2.3 |
| 5 | 1.777 | 1.842 | -36.9 |
| 6 | 1.794 | 1.831 | -24.3 |
| 7 | 1.764 | 1.836 | 37.7 |
| 8 | 1.760 | 1.833 | 79.8 |
| 9 | 1.795 | 1.828 | 14.9 |
| 10 | 1.813 | 1.795 | 159.8 |
| 11 | 1.767 | 1.835 | 24.5 |
| 12 | 1.763 | 1.838 | 28.7 |
| 13 | 1.762 | 1.835 | 66.3 |
| 14 | 1.759 | 1.834 | 78.9 |
| 15 | 1.780 | 1.834 | 16.6 |
| 16 | 1.776 | 1.837 | 22.5 |
| 17 | 1.787 | 1.836 | 28.6 |
| 18 | 1.797 | 1.816 | 90.3 |
| 19 | 1.733 | 1.841 | 111.3 |
| 20 | 1.732 | 1.840 | 131.1 |
| 21 | 1.737 | 1.840 | 102.4 |
| 22 | 1.738 | 1.840 | 108.8 |
| 23 | 1.715 | 1.836 | 206.9 |
| 28 | 1.723 | 1.837 | 160.6 |
| 29 | 1.737 | 1.837 | 137.8 |
| 30 | 1.720 | 1.837 | 176.0 |
| 31 | 1.720 | 1.837 | 178.4 |
| 32 | 1.725 | 1.841 | 123.9 |
| 33 | 1.713 | 1.837 | 179.4 |
| 34 | 1.715 | 1.836 | 197.3 |

with the rNHC ring. In addition to this, the $C_C$−P bond is shorter than the P−$C_{Ph}$ bond in all of the rNHC−PPh adducts (except **10**−PPh). Both of these facts indicate that the phosphorus lone pair is delocalized only into the vacant p orbital of the rNHC rather than

to the phenyl ring. Therefore, the $^{31}$P chemical shift of the rNHC-phosphinidene adduct will vary as a function of the relative $\pi$ acidity of the remote carbene. Table 2.6 shows that with increasing $\pi$ acidity of the rNHC ligand, the $\delta(^{31}$P) value of the adduct is shifted further downfield.

Among the five-membered rNHCs, **8** and **14** were found to have higher $\pi$ acidity (Table 2.4) and consequently, the $\delta(^{31}$P) values of the corresponding PPh adducts appear significantly downfield compared with those of the other ligands. In addition, the $C_C$−P bond in the **14**−PPh adduct was found to be the shortest. In fact, we obtained a good correlation ($R^2 = 0.79$, omitting the points corresponding to **10** and **18**) between $E_{\pi*}$ and the $^{31}$P NMR chemical shift of the phosphorus center (Figure 2.10(a). However, the correlation is somewhat poor in case of the six-membered rNHCs ($R^2 = 0.67$; Figure 2.10(b)). The additive effect of annulation is also evident from the $\delta(^{31}$P) values. The $\delta(^{31}$P) values for **19**, **20** and **23** increase in the order **19** < **20** < **23**, which is in tune with their respective $\pi$-accepting abilities and electrophilicities. Comparison of the $\delta(^{31}$P) values for the cyclic aromatic remote carbenes **23** and **28**−**31** shows that $\delta(^{31}$P) varies linearly with the relative $\pi$ acidity and electrophilicity for these molecules. Similar results were also obtained for **32**−**34**. However, it was found that like normal NHCs, annulation or carbonylation of the rNHC scaffold results in a downfield shift of the $^{31}$P NMR signal. The $^{31}$P NMR signals for remote carbenes having a central six-membered ring were found to be further downfield than those for the five-membered rNHCs.
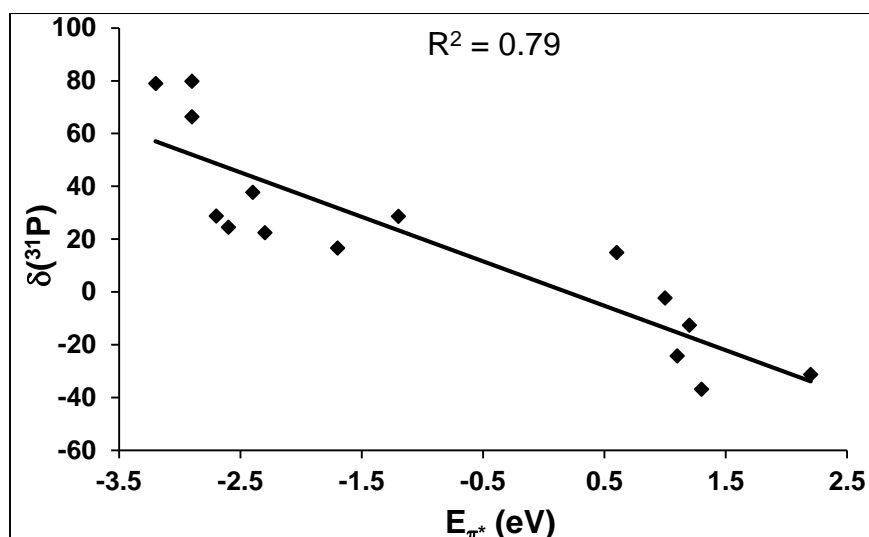
(a)
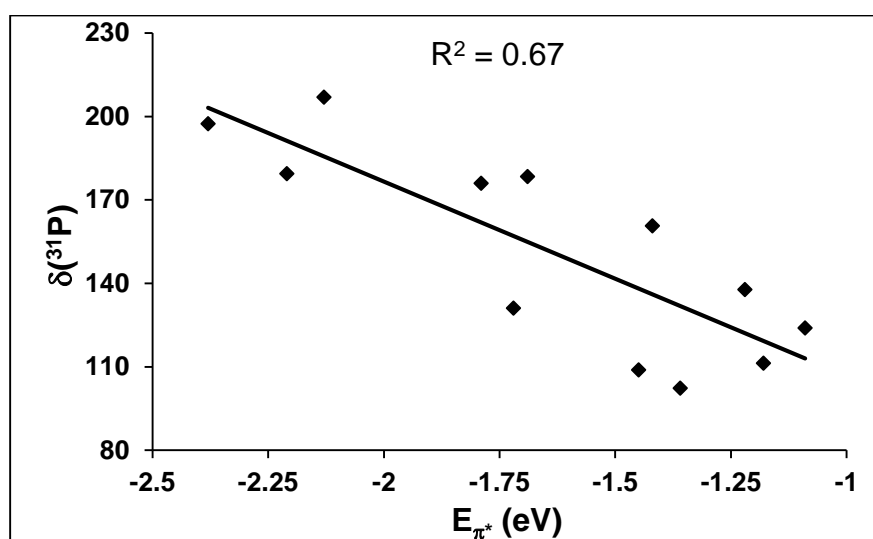


(b)

**Figure 2.10**: Correlation plots between the energy of the $\pi$-symmetric unoccupied MO ($E_{\pi^*}$) and $^{31}P$ chemical shifts ($\delta^{31}P$) of the phosphinidene adducts of (a) five- and (b) six-membered rNHCs.

### [2.4] Conclusions

Quantum-chemical calculations have been carried out to investigate the effect of annulation and carbonylation on the electronic and ligating properties of rNHCs (Scheme 2.1). This study suggests that annulation and carbonylation of five-membered rNHCs results in decreases in thermodynamic and kinetic stability. Similar results were obtained for annulated six-membered rNHCs, and the thermodynamic stabilities of six-membered rNHCs were found to be lower than those of the five-membered ones. Both annulation

and carbonylation result in a decrease in σ-donating ability but a significant increase in π-accepting ability. The degree of increase in π acidity was found to be greater for the five-membered rNHCs (**1−18**) than for the six-membered rNHCs (**19−34**). The calculated values of the nucleophilicity index are in accordance with the σ-donating ability of the respective NHCs. The electrophilicity of the rNHCs is found to increase with increasing π acidity. The π acidities of these rNHCs were further assessed by calculation of the $^{31}$P chemical shift values of the corresponding rNHC-phosphinidene adducts. The chemical shift values also indicate an increase in the π-accepting abilities of rNHCs upon annulation and carbonylation. A good correlation between the energies of the π-symmetric unoccupied orbital of five-membered rNHCs and the $^{31}$P chemical shifts of the corresponding rNHC-PPh adducts was obtained.

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