J Mol Model (2013) 19:5327–5341
DOI 10.1007/s00894-013-2027-1

ORIGINAL PAPER

Changes in ligating abilities of the singlet and triplet states of normal, abnormal and remote N-heterocyclic carbenes depending on their aromaticities

Resul Sevinçek · Hande Karabıyık · Hasan Karabıyık

Received: 17 July 2013 / Accepted: 1 October 2013 / Published online: 25 October 2013

Abstract Quantum chemical calculations at B3LYP/aug-cc-pVTZ level about singlet N-heterocyclic carbene (NHC) ligands, imidazol-2-ylidene, imidazol-4-ylidene, pyrazol-3-ylidene and pyrazol-4-ylidene, and their protonated analogues show that they are considerably aromatic except for pyrazol-3-ylidene. This result is experimentally verified by approximately five thousand NHC transition metal complexes retrieved from the Cambridge Structural Database (CSD). CSD search discloses that NHCs can participate in π-stacking interactions, albeit scarce. Geometry-based HOMA and electronic aromaticity index FLU rather than NICS provide a satisfactory description of the bonding situations in NHC ligands. Singlet state of the normal NHC has electron-deficient aromaticity as compared to those of the abnormal and remote NHCs. Depending on the transition from the singlet to triplet state, NHCs become electron-deficient ligands except for remote NHC. Computational studies regarding electronic nature of free NHC ligands show that the π-electronic population of the formally vacant p_π orbital on the carbene atoms in abnormal and remote NHC is occurred as a result of the aromaticity of NHCs, not as a result of the direct electron donation from LP-orbitals of N atoms to carbene atom according to putative push-pull effect used in understanding the electronic stabilization of normal NHC. Increase in the aromaticity raises σ-donating ability of both imidazol- and pyrazol-based NHC ligands. Free abnormal and remote NHC ligands have higher σ-donation ability than normal NHC ligands. The lack of σ-donating ability of normal NHC is compensated by its relatively high π-accepting ability, whereas π-back donation abilities of abnormal and remote NHCs are prohibited by their almost fully occupied π-orbitals. Aromaticities of the triplet NHC ligands are higher than that of the lowest-lying triplet state of benzene. Increase in the aromaticity of NHC ligands decreases van der Waals shortening in TM-NHC bonds mainly due to diminishing dative character of these bonds.

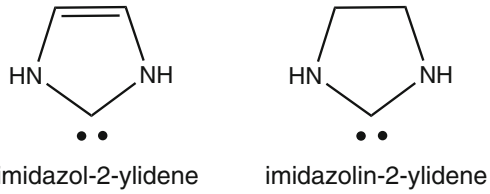
Keywords Abnormal NHC · Aromaticity · CSD search · FLU · HOMA · N-Heterocyclic carbene (NHC) · Remote NHC · Triplet state

Introduction

N-heterocyclic carbenes (NHCs) are defined as cyclic chemical species containing a neutral divalent C atom that bears two nonbonding electrons. These nonbonding electrons are spin-paired locating at the σ-lone pair (LP) of carbene C atom (C_c) in the singlet state, $^1A_1(\sigma^2)$, whereas they are spin-unpaired locating at different orbitals of C_c in the triplet state, $^3B_1(\sigma^1p^1{}_\pi)$, obtained by excitation from the doubly occupied σ-LP into the formally vacant p_π orbital of C_c orthogonal to the ring plane. The first solid-state isolation of metal-free singlet NHC in 1991, imidazol-2-ylidene (normal NHC-*n*NHC) in Scheme 1, by Arduengo and co-workers [1–3] has initiated a vast series of both experimental and theoretical investigations, since NHCs include divalent C atom which was regarded as elusive until those days. The foremost factor which makes NHCs an intriguing research topic is their unusual stabilities. On the other hand, singlet NHCs have become widely used chemical species in organometallic [2, 4, 5] and heteroatom chemistry [6–11] as well as in transition-metal-mediated catalysis [12–15] and organocatalysis [16–18] due to their versatile applications. The ground state electronic

Electronic supplementary material The online version of this article (doi:10.1007/s00894-013-2027-1) contains supplementary material, which is available to authorized users.

R. Sevinçek · H. Karabıyık (✉) · H. Karabıyık
Department of Physics, Dokuz Eylül University, 35160, Tınaztepe, İzmir, Turkey
e-mail: hande.karabiyik@deu.edu.tr



imidazol-2-ylidene imidazolin-2-ylidene

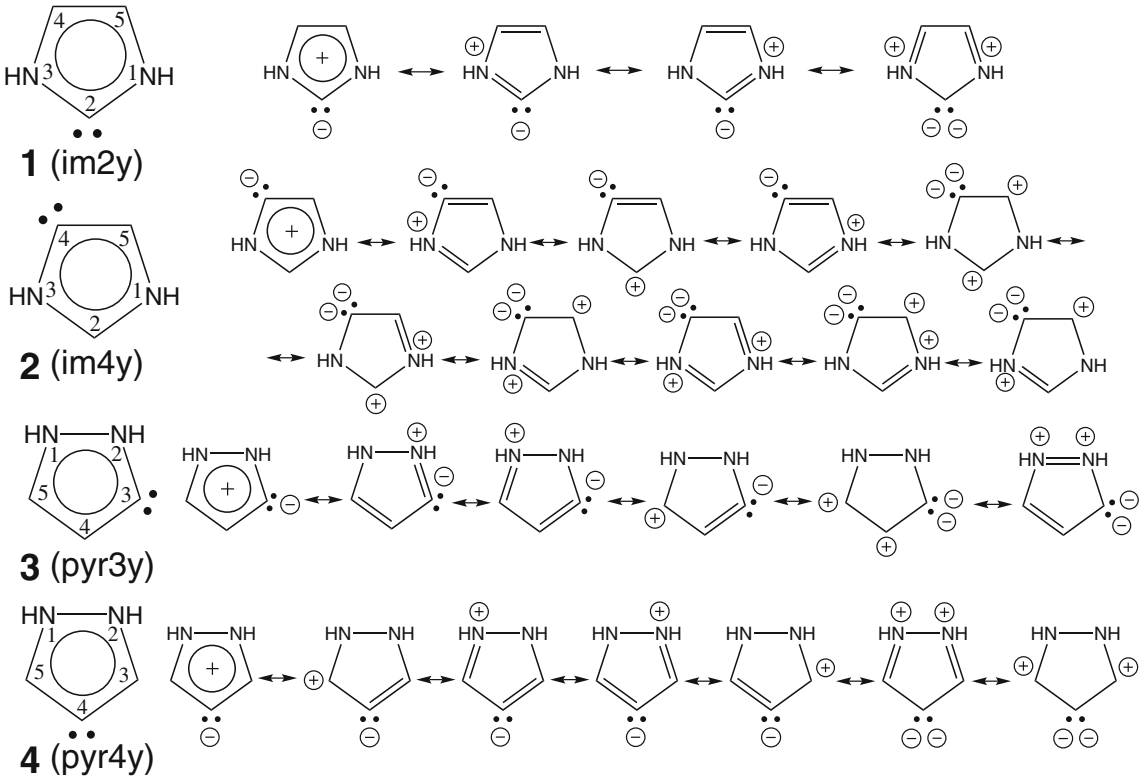
Scheme 1 Unsaturated and saturated Arduengo-type (normal) NHCs

configuration of imidazol-2-ylidene ($C_3N_2H_4$) is singlet, with a singlet-triplet energy gap in the range of 65–85 kcal mol^{-1} [19]. Since triplet carbenes are much more difficult to stabilize relative to their singlet analogues, the crystallographic characterization of a triplet carbene has not been achieved yet. Therefore, synthesis of the triplet carbenes, in particular their cyclic analogues such as triplet NHC, is still a worthwhile challenge [20, 21].

According to a generally accepted view, unusual stability of the singlet *n*NHC is explained by the electron donation from the nitrogen LPs into the formally empty p_π orbital of the C_c [19, 22]. Theoretical and experimental studies have also suggested that there is a cyclic electron stabilization overall ring, emphasizing partial aromatic character of the imidazol-2-ylidenes [23]. After the first isolation of the imidazolin-2-ylidene in 1995 including CH_2–CH_2 group instead of CH= CH as shown in Scheme 1, which is the saturated analogue of imidazol-2-ylidene (im2y), it was proposed that electron donation from two neighboring N atoms to divalent C_c atom would be necessary and sufficient for stabilizing the free carbene and also, cyclic 6π-electron delocalization overall the im2y ring provides additional stability of 26 kcal mol^{-1} relative to imidazolin-2-ylidene [19, 24], of which 6 kcal mol^{-1} is provided by 4π-electron delocalization in N–C_c–N subunit. Coexistence of local electronic delocalization in N–C_c–N unit involving 4π-electrons through three centers and unsaturated C=C bond results in a cyclic delocalization overall im2y ring [19, 22, 25]. According to IUPAC, cyclically delocalized molecular entity with stability significantly greater than that of its hypothetical localized structure (e.g., Kekulé structure) is said to possess aromatic character [26]. Aromaticity of im2y was experimentally evidenced by Raman spectroscopy [27]. By definition, even though aromaticity can be partially ascribed to im2y ring, quantitative results reported about its aromaticity were based on substantially magnetic aromaticity quantifiers such as nucleus independent chemical shift (NICS) [19, 22]. These avant-garde studies in 1996 indicated that aromaticity of im2y is appreciably smaller than that of reference systems such as benzene or imidazolium salts and a crucial factor in the unusual stabilization of im2y [19, 25]. However, the extent of aromaticity of im2y remains somewhat controversial [2, 19].

Recent progress in NHC chemistry introduce us to abnormal and remote NHCs (or mesoionic carbenes-MICs) [28]. Abnormal NHCs (*a*NHCs) contain only one N atom in α-positions relative to the carbene carbon atom, while remote NHC (*r*NHC) does not contain any N atom in α-positions [12, 29] as shown in Scheme 2. The first isolation of one of free singlet *a*NHCs, imidazol-5-ylidene or equivalently imidazol-4-ylidene, was successfully carried out in 2009 by Bertrand and coworkers [30]. In the literature, the studies regarding cyclic delocalization or aromaticities of NHCs are not interested in *a*NHCs, *r*NHC and their triplet analogues. They consider only singlet im2y and its germylenes, silylenes analogues [19, 22, 24]. In addition, aromaticities of NHCs and its analogues in these studies were evaluated by NICS, whereas the use of NICS for quantifying local aromaticity is very problematic as discussed elaborately in ref. [31] and its magnitude does not directly reflect the aromaticity [32]. One of the reasons for the use of NICS values in describing aromaticities of Arduengo-type NHCs may be regarded as an inadequate development of aromaticity indices used in the 1990s. Up to now, different criteria based on electron delocalization measures have been defined for the purpose of quantitative evaluation of aromaticity [33, 34]. In principle, the use of delocalization indices for investigating aromaticity is an efficient way, since they refer directly to the idea of electron delocalization underlying the concept of aromaticity [34]. Recent developments regarding aromaticity indices, in particular electronic ones, have continued and many different indices from distinct origins have been defined. Electronic aromaticity indices such as para delocalization index (PDI) [35], average two-center index (ATI) [36] and aromatic fluctuation index (FLU) [37], have become widespread.

Abnormal and remote NHCs are characterized by significantly lower heteroatom stabilization as compared to the normal NHC, which causes intriguing changes in the ligand donor properties and hence the reactivity of carbene atom. In this study, our primary interest will be addressed to examine aromaticities of both singlet and triplet states of normal, abnormal, and remote NHCs (**1**, **2**, **3** and **4** in Scheme 2) besides their singlet protonated analogues in order to gain some insights into their ligating abilities and electronic properties. Another purpose is also to provide reference values for their aromaticities, bond orders and natural atomic p_π populations, which will be likely to be used in analysis of the bonding situations of NHC transition metal (TM) complexes. Keeping in mind that the stabilization of triplet carbenes has been a current research topic, such information may guide studies to be designed by the related scientific community. Examination of the electronic properties of NHCs using reliable contemporary tools developed to describe aromaticity with the aid of electronic and geometry-based indices is of importance and provides useful reference values. In addition, we quest an answer to the question whether NHCs can participate in π-stacking interactions. Since 1996, there have been several articles notifying that im2y may be regarded as aromatic at least in part [19, 22, 24]. One of the reasons why aromaticity of the *n*NHC,



Scheme 2 Possible resonance structures of normal (Arduengo-type **1**), abnormal (**2** and **3**) and remote (**4**) NHC showing their localized zwitterionic and doubly-zwitterionic forms: **1**, imidazol-2-ylidene (im2y); **2**, imidazol-4-ylidene (im4y); **3**, pyrazol-3-ylidene (pyr3y), and **4**, pyrazol-4-ylidene (pyr4y). Atomic centers were numbered in accordance with chemical name of the associated NHC

*a*NHCs and *r*NHC in Scheme 2 is regarded as a suspicious phenomenon is the lack of any articles about π-stacking interactions involving NHCs. Most authors have incorrectly supposed that aromaticity and π-stacking interactions are directly interconnected with each other, whereas this is not true as much as thought. In this study, we have firstly reported the presence of such interactions, thus structural objection to aromaticity of NHCs will be gotten rid of. On the other hand, our ultimate purpose is to examine variations in aromaticities depending on endocyclic positioning of C_c atom in NHCs with regard to their singlet and triplet electronic states.

Computational procedures

Geometry optimizations of the singlet and triplet electronic states of all NHCs in Scheme 2 were performed without constraints at the B3LYP [38, 39] level with the Gaussian09 program [40]. All atoms were described with the correlation consistent aug-cc-pVTZ basis set [41, 42]. Vibrational analyses on the optimized geometries of all structures and their protonated counterparts confirm that these structures represent minima on the associated PESs. To be able to examine bonding situations and electronic populations in certain atomic orbitals, natural bond orbital (NBO) analyses [43] were carried out at the same level of theory give the natural population analysis (NPA). The π-electron population of closed shell systems is obtained from the occupancy of the p_π natural atomic orbitals (NAO). For open-shell triplet states, the π-populations are obtained from the difference between α-spin and β-spin NPA atomic charges or p_π NAO occupancies, respectively. In order to quantitatively describe aromaticities of NHCs in Scheme 2, topological parameters were computed in the framework of the quantum theory of atoms in molecules (QTAIM) [44]. Wavefunction sets for all structures and triplet NHCs are obtained by Kohn-Sham molecular orbitals. Then, they are used as input data in AIMAll Pro software [45] to perform topological analyses on the electron density distribution ρ(r) and critical point searches. Bond order calculations were performed by Mayer's scheme [46] via AOMix software [47].

Assessment of aromaticities of NHCs and CSD survey

Due to the lack of a proper definition of aromaticity [31], many different aromaticity indices, i.e., numerical descriptors for aromaticity, have been introduced up to now [33, 34]. These indices put emphasis on one of the characters of aromaticity such as geometry-based structural [48], magnetic

[49], energetic [50], electronic [33, 34], and chemical reactivity property [51]. Among these indices from different aspects of aromaticity, the geometry-based ones are easily accessible and reliable. Therefore, in this study, we have used a geometry-based structural aromaticity index called harmonic oscillator model for aromaticity (HOMA) [52] to describe aromaticities of NHC rings retrieved from Cambridge Structural Database (CSD). HOMA index describes the average squared deviation of bond lengths from their optimal value in fully aromatic ring systems as follows:

$$\mathrm{HOMA} = 1-\left(\frac{1}{\mathrm{n}}\sum\nolimits_{i=1}^{n}\alpha_i\left(R_i-R_{opt}\right)^2\right), \quad (1)$$

where n is the number of bonds taken into the summation (here equal to 5), R_t stands for a running individual bond length, α_t regarded as a normalization constant is equal to 257.7 for C-C and 93.52 for C-N bonds, fixed to give HOMA=0 for non-aromatic Kekulé systems and HOMA=1 for purely aromatic systems with all bonds equal to the optimal value R_{opt}=1.388 Å for C-C, R_{opt}=1.334 Å for C-N [52]. Molecular fragments whose HOMA is greater than 0.5 can be regarded as conventionally aromatic [53]. In addition, since parameterization used in the definition of HOMA index was obtained by quantum-chemical calculations, it can be applied to both the calculated and crystallographically observed molecular geometries [53].

Electronic aromaticity indices such as FLU [37], were used to describe quantitatively aromaticity of im2y, im4y, pyr3y and pyr4y in Scheme 2. FLU index express quantitatively the fluctuation of the amount of sharing electronic charge between adjacent atoms in a given ring. If a molecular fragment is aromatic, the electron transfer from one atom to another one which is covalently bonded to the first atom and the reverse electron flow between these atoms must be equal or strictly speaking, fluctuation of electronic delocalization indices are close to zero in an ideally aromatic system [37]. It is obvious that the values of the FLU index deviated from zero indicate a decrease in aromaticity of the relevant molecular fragment. An increase in FLU means an increase in the order of electronic charge distribution or in other words, a decrease of aromaticity due to prominence of a particular resonance structure. The higher values of FLU index of a ring system, the lower the aromaticity of the ring. The aromaticity indices including reference parameters such as HOMA and FLU should not be used for the analysis of aromaticity changes in chemical reactions, since those parameters are determined by considering stable aromatic species [34, 54]. However, all NHCs examined in this study are stable chemical species. Therefore, FLU and HOMA indices having different origins, i.e., geometric and electronic, can be reliably used to observe aromaticity changes in NHCs under discussion.

Geometric details of NHC rings which variously substituted were retrieved from CSD [55, 56] with the following restrictions: (i) the searches were performed for arbitrarily substituted normal, abnormal and remote NHC-TM complexes in which carbene atom is directly bonded to metal center; (ii) the searches were restricted to structure determinations with an R factor<7.5%; (iii) error-free coordinates according to the criteria used in the CSD system; (iv) no polymeric structures. Although decision of a unique (or predominant) resonance form of normal, abnormal and remote NHCs (Scheme 2) is difficult, natural resonance theory (NRT) provides valuable information about description of the chemical bonding in NHCs when canonical Lewis structure cannot be drawn precisely [57]. Nonetheless, their localized resonance structures of NHCs are generally favored by the chemical community in spite of their ability to accommodate nonzwitterionic resonance structures [29]. For instance, it is not preferred that im2y is presented so as to possess completely electronic delocalization due to the fact that its aromaticity is somewhat controversial, whereas partial delocalization over N-C_c-N subunit in im2y is frequently pointed out by chemists without any hesitation. Therefore, all possible resonance structures and different partial resonance structures in Scheme 2 were considered in CSD searches. CSD hits were filtered by geometry-based aromaticity index, HOMA. Ones of which HOMA values are negative or almost zero were excluded in the examination due to better zwitterionic charge separation abilities indicating their reduced aromaticity. On the other hand, participation in π-stacking interactions of NHCs can be regarded as evidence for their aromatic character. In CSD searches, it has also been investigated in CSD whether NHCs are involved in π-staking interactions. It was considered that a π-stacking interaction existed if the dihedral angle between the mean planes of two NHC rings is less than 10°, the distance between the centroids of the involving NHC rings is less than 3.8 Å, and the angle between the normal to the NHC ring and the line that connects the centers of two NHC rings, β, is less than 30°.

Results and discussion

Electronic nature and ligating abilities of NHCs

The calculations at B3LYP/aug-cc-pVTZ level reveal that *a*NHCs and *r*NHC have higher energy values than *n*NHC. Normal NHC (im2y) is about 19 kcal mol^{-1} more stable than its abnormal analogue (im4y) [58] and our calculations also support this result. Pyrazol-based NHCs have a more pronounced energetic destabilization as compared to that of im4y as shown in the second row of Table 1. Heretofore, it has been generally accepted that the singlet-triplet splittings of the saturated and unsaturated normal NHCs are in the range of

Table 1 Relative energies of the free singlet, triplet and protonated NHCs in kcal mol^{-1} and their aromaticities quantified by electronic (FLU) and geometry-based (HOMA) indices. Chemical potential (μ) and electronegativity (χ) is defined by $\mu = -\chi = (\varepsilon_{HOMO}+\varepsilon_{LUMO})/2$, hardness is considered as $\eta = \varepsilon_{LUMO} - \varepsilon_{HOMO}$ and electrophilicity index is calculated by $\omega = \mu^2/2\eta$ [59, 60]. These quantities are expressed in eV. EA stands for electron affinity calculated by $EA = -(2\mu+\eta)/2$. Mayer's bond orders [46] of the free singlet, triplet, and protonated NHCs are in Scheme 2. Values in the association with the bonds including carbene carbon atom were italicized. Atomic centers were numbered in accordance with chemical name of the associated NHC. Topological *ion*/*cov* parameters defined as $|\lambda_1|/\lambda_3$, where λ_1 and λ_3 are eigenvalues of the Hessian matrix of the electron density calculated at the relevant bond critical point, are given in parentheses below the associated bond orders. Natural populations are given in *e* unit

	1 $^1A_1(\sigma^2)$	**1** $^3B_1(\sigma^1p^1_\pi)$	**1** (H^+)	**2** $^1A_1(\sigma^2)$	**2** $^3B_1(\sigma^1p^1_\pi)$	**2** (H^+)	**3** $^1A_1(\sigma^2)$	**3** $^3B_1(\sigma^1p^1_\pi)$	**3** (H^+)	**4** $^1A_1(\sigma^2)$	**4** $^3B_1(\sigma^1p^1_\pi)$	**4** (H^+)
ΔE †	0	85.10	−260.23	0	61.21	−279.17	0	52.28	−271.44	0	51.71	−287.55
ΔE ‡	0	85.10	−260.23	18.93	80.14	−260.23	33.75	86.03	−237.69	49.86	101.57	−237.69
FLU	0.0074	0.0096	0.0057	0.0054	0.0135	0.0058	0.0167	0.0201	0.0083	0.0103	0.0181	0.0084
HOMA (calc.)	0.784	0.370	0.873	0.827	0.449	0.865	0.356	−0.445	0.742	0.694	0.151	0.740
HOMA (exp.)*	0.729	-	-	0.744	-	0.804	-	-	-	-	-	-
HOMA (CSD)#	0.723	-	0.810	0.777	-	-	0.543	-	-	0.550	-	0.582
μ (=−χ)	−3.239	−1.739	−6.863	−3.011	−2.092	−9.363	−3.199	−2.066	−9.877	−2.988	−1.558	−9.879
η	5.639	2.716	5.648	4.502	3.231	6.679	4.701	3.460	6.723	3.803	2.001	6.722
ω	0.930	0.556	4.170	1.007	0.677	6.563	1.089	0.617	7.256	1.174	0.606	7.258
EA	0.419	0.381	4.039	0.760	0.477	6.023	0.850	0.336	6.516	1.087	0.557	6.517
Bond orders and (*ion*/*cov*) ratios												
1-2	*1.125* *(1.123)*	*0.901* (*2.035*)	*1.275* (*1.412*)	1.265 (1.378)	0.947 (1.960)	1.275 (1.410)	0.597 (0.817)	0.502 (0.679)	0.659 (0.964)	0.713 (0.956)	0.671 (0.844)	0.659 (0.962)
2-3	*1.125* *(1.123)*	*0.901* (*2.035*)	*1.275* (*1.412*)	1.206 (1.718)	0.930 (3.573)	1.275 (1.410)	*1.345* (*0.766*)	*0.954* (*1.897*)	*1.449* (*0.969*)	1.339 (0.962)	1.074 (1.474)	1.449 (0.968)
1-5	0.967 (1.703)	0.875 (1.831)	1.039 (1.283)	1.097 (1.162)	0.975 (1.637)	1.038 (1.289)	1.308 (1.098)	0.857 (1.864)	1.450 (0.968)	1.339 (0.962)	1.074 (1.474)	1.449 (0.969)
3-4	0.967 (1.703)	0.875 (1.831)	1.039 (1.283)	*0.877* (*1.022*)	*0.942* (*1.634*)	*1.039* (*1.288*)	*0.539* (*2.028*)	*1.142* (*2.987*)	*1.002* (*2.891*)	*1.095* (*2.599*)	*1.193* (*3.106*)	*1.002* (*2.891*)
4-5	1.370 (3.813)	1.319 (3.918)	1.266 (3.626)	*0.954* (*2.996*)	*1.225* (*3.573*)	*1.266* (*3.647*)	1.139 (3.138)	1.166 (2.806)	1.001 (2.881)	*1.095* (*2.600*)	*1.193* (*3.106*)	*1.002* (*2.891*)
Natural p_π populations of the atomic centers												
1	1.393	1.360	1.384	1.535	1.636	1.511	1.631	1.618	1.549	1.599	1.742	1.550
2	*0.645*	*0.644*	*0.788*	1.014	1.153	0.916	1.601	1.615	1.549	1.599	1.742	1.550
3	1.393	1.360	1.384	1.530	1.649	1.511	*0.631*	*1.034*	*0.914*	0.988	1.216	0.914
4	1.084	1.076	1.083	*0.741*	*0.931*	*1.019*	1.119	1.085	1.049	*0.793*	*1.013*	*1.049*
5	1.084	1.076	1.083	1.144	1.081	1.019	0.987	1.105	0.914	0.988	1.216	0.914
Σp_π	5.599	5.516	5.722	5.965	6.452	5.976	5.970	6.457	5.977	5.967	6.928	5.977
Hybrid. of C_c	$s^{1.31}p^{2.56}$	$s^{0.41}p^{0.67}$	$s^{0.91}p^{2.80}$	$s^{1.27}p^{2.86}$	$s^{0.37}p^{0.95}$	$s^{0.97}p^{3.04}$	$s^{1.28}p^{2.74}$	$s^{0.62}p^{1.91}$	$s^{0.97}p^{2.94}$	$s^{1.26}p^{3.09}$	$s^{0.60}p^{1.76}$	$s^{1.00}p^{3.25}$

† The values are separately expressed energy values of the singlet, triplet, and protonated NHCs among themselves

‡ Relative energy values of NHCs with respect to the energy of the most stable NHC, singlet im2y

* The values in this row are calculated with respect to firstly isolated geometry of im2y [1], im4y and its protonated analogue [30]

Average values of HOMA index are calculated for 4620 TM complexes of im2y, for 45 protonated imidazolium structures, for 124 TM complexes of im4y, for 27 TM complexes of pyr3y, for 16 TM complexes of pyr4y, for the protonated pyr4y deposited under ref. code JOXNUF

65–85 kcal mol^{-1} [19], whereas the overall singlet-triplet gap in different NHCs vary from ~52 kcal mol^{-1} (for pyr4y) to ~85 kcal mol^{-1} (for im2y). In addition, the first proton affinities of NHCs are in good-agreement with their previously reported values [29]. The singlet-triplet energy gap of *n*NHC is significantly larger than those of *a*NHCs and *r*NHC as shown in the first row of Table 1. More importantly, the singlet-triplet gap in imidazolylidene ligands (**1** and **2**) is more sensitive to endocyclic positioning of the carbene atom than that in pyrazolylidene ligands (**3** and **4**). Saying that the larger singlet-triplet gap indicates higher stability of NHC is somewhat disputable, because the stabilities of NHCs arise from different origins such as thermodynamic, kinetic, electronic, or energetic. Nonetheless, some aspects draw attention. For example, according to the above idea, imidazol-based NHCs are, in general, more stable than pyrazol-based ones probably due to their enhanced aromaticity as mentioned below. The absence of heteroatoms adjacent to the carbene center reduces the energetic stability of the free singlet NHC ligands.

According to the results in Table 1, aromaticity levels of imidazolylidene ligands (**1** and **2**) are higher than those of pyrazolylidene (**3** and **4**). Aromaticities of imidazol-based NHCs are obviously more pronounced than that of pyrazol-based ones. In all cases, aromaticity level of the singlet states is higher than that of the triplet states and furthermore protonation of the carbene atom makes the aromaticity of the associated ring greater. Geometry-based HOMA and electronic FLU indices verify this inference. This point deserves further investigation. Aromaticity level calculated by HOMA and FLU indices increases in the order **3** < **4** << **1** < **2**. In addition, variation in the position of carbene atom in pyrazolylidene ligands (**3** and **4**) leads to a more dramatic change in aromaticity level than that of imidazolylidene ligands (**1** and **2**). These results can be understood with the aid of the results from natural resonance theory (NRT). Höltzl and co-workers demonstrated that probabilities of the principal resonance structures of im4y (**2**) are more evenly distributed than those of the other NHCs [57]. This explains the reason why the most aromatic NHC is im4y. As already mentioned, prominence of a resonance structure reduces the relevant ring aromaticity. In addition, there is no relation between the identities of the atoms neighboring C_c atom and the aromaticity of the ring.

The calculated HOMA values regarding different kinds of free singlet NHC ligands except for pyr3y (**3**) are at comparable level with those of polycyclic aromatic hydrocarbons. A common belief in pursuit of the avant-garde studies [19, 22] has stated that aromaticity level of im2y (**1**) is approximately 60% level of reference species such as benzene [19, 22, 24], whereas HOMA values of singlet im2y (**1**) and im4y (**2**) in Table 1 suggest that **1** and **2** are considerably aromatic as compared to that of benzene (HOMA=0.999) and their aromaticities are not low as much as supposed. It can be better understood when one keeps in mind that aromaticity of linear and angular poliacenes varies from 0.624 to 0.999 [48]. FLU index values of chemical moieties accepted as remarkably aromatic are lower than 0.02 [37]. Consequently, both structural and electronic aromaticity indices indicate that NHCs are considerably aromatic except for pyr3y. FLU index also produces the same aromaticity hierarchy among NHCs. In addition, aromaticity levels of the optimized geometries of NHCs are increased depending on the protonation of carbene atom. This observation is, at least in part, verified by taking account of the firstly isolated experimental geometries of **1**, **2** and **2**($\mathbf{H}^+$) in Table 1. As mentioned before, the use of NICS to describe aromaticity of NHCs and their metal complexes is a common scientific habit. Indeed, NICS does not reflect properly aromaticity levels of NHCs and produces unacceptable results. Aromaticity levels of neutral NHCs in Scheme 2 having regard to the calculated NICS values reported in ref. [57] increase in the order **3** < **1** < **2** < **4**. This sequencing is not even close to that of structural and electronic aromaticity indices. As shown in the later, the aromaticity order prescribed by HOMA and FLU indices can be rationalized by further analysis, whereas the order by NICS could not.

The amount of the population of formally vacant p_π orbitals on carbene centers seems to be increased by transition from singlet to triplet states. However, this is illusive due to the fact the triplet states of NHCs have seven π-electrons, while the singlet states have six π-electrons. In an ideally aromatic electronic configuration, carbene atoms in the singlet and triplet states would have 1.20 (6/5) and 1.40 (7/5) π-electrons, respectively. Considering hybridization of carbene centers in Table 1, im4y and pyr4y are more aromatic than im2y and pyr3y due to the relatively enhanced p-electron character in hybridization of the carben atom, respectively. This is consistent with the above order of aromaticity. However, some authors have drawn a conclusion about aromaticity or π-delocalization strength within NHC ligands by examining only the p_π population of carbene atoms or N atoms. As known, aromaticity is a global (nonlocal) property of a molecular moiety and it is problematic to trying to understand variations in aromaticity with the aid of the changes in a local property of a molecule such as LP-population on N centers. Increase in the p_π population of carbene atoms is due to π-donation from LP orbital of nitrogen atoms [19, 22]. At first glance, while such an electronic charge donation to carbene atom is reasonable in im2y, im4y and pyr3y, it is complicated in pyr4y due to the fact that N atoms in pyr4y are not directly bonded to the carbene atom, suggesting remote π-donation. While the N atom at position 2 in pyr3y can directly donate π-electrons from its LP orbital to carbene atom, nitrogen atoms in pyr4y cannot. Since such a donation in pyr4y can be carried out

through π-delocalized path, it is facilitated by the aromaticity. This consideration explains that pyr4y is more aromatic than pyr3y. It can be stated that donation from the nitrogen atom of the neighboring carbene center is more pronounced than that of the other nitrogen atom in pyr3y. Nonetheless, it is generally observed that an increase in π-electron donation from LP-orbitals of N atoms to cyclic delocalization increases the aromaticities of NHCs as shown in Fig. 1a.

Aromaticities of the considered NHCs are decreased by transition from singlet to triplet state due to dramatic structural changes such as pyramidalization of the endocyclic nitrogen centers and weakening of N−C_c and N−N bonds. The extent of pyramidalization of endocyclic nitrogen atoms which is directly bonded to the carbene atom can be evaluated with the improper torsion angle C(N for **3**)−N−C_c−H, describing angular deviation of N−H bond from C(N for **3**)−N−C_c plane. It is worth noting that pyramidalization is not observed in pyr4y, **4**. Pyramid-like geometry around N atoms is flattened as pyramidalization angle increase. Pyramidalization angle is 139.45° for im4y (**2**), 132.75° for im2y (**1**), and 118.52° for pyr3y (**3**). This result is in agreement with the order of aromaticities of the relevant rings. This geometric analysis emphasizes that nitrogen atoms favor a flattening of the pyramid-like geometry depending on increase in aromaticities of NHCs. The loss of aromaticity causes pyramidalization on N centers adjacent to carbene atom, since one of the well-known manifestations of aromatic fragments is their planarity. Another reason for reducing aromaticity of the triplet states of NHCs is weakening of N−C_c and N−N bonds, which are explicitly observed in Mayer's bond order values in Table 1. In addition, bond angles X_α−C_c−Y_α in the triplet NHC ligands are wider than those in the singlet analogues. This widening arises from the weakening of the bond between the atoms in β positions relative to carbene atom as shown in Table 1. Depending on the transition from the singlet to triplet state, the openings of X_α−C_c−Y_α angle in pyrazol-based NHCs are more pronounced than those in imidazolylidene ligands. Further geometric details (bond lengths and angles) in NHCs are found in Supporting information document. The widening on electronic transition from the singlet to triplet state is 4.91° for im2y, 5.73° for im4y, 11.16° for pyr3y, and 12.28° for pyr4y. On the other hand, even though transition from the singlet to triplet state of NHCs occurs at the expense of aromaticity of the singlet states, aromaticity levels of the triplet NHCs are remarkably higher than that of the lowest-lying triplet state of benzene (FLU=0.033) [61]. Relatively high aromaticity of the triplet states of NHCs as compared to the lowest-lying triplet state of benzene plays an important role in their electronic stabilizations.

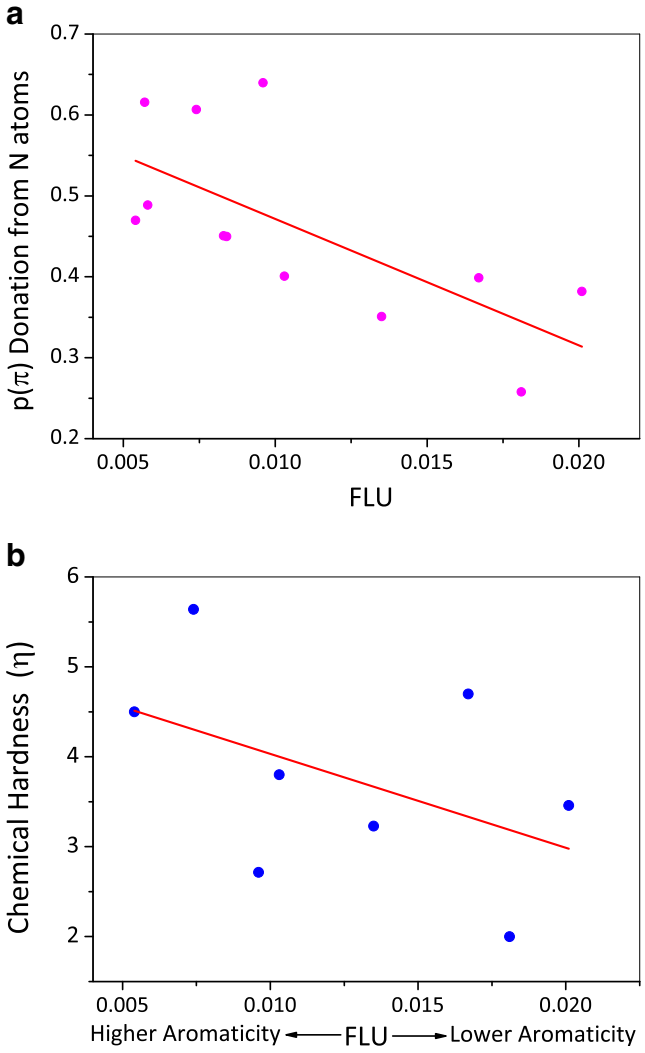


Fig. 1 (**a**) Linear correlation between the amount of π-donation from N atoms and aromaticity of the singlet, triplet free NHC ligands and their protonated variants. (**b**) Linear correlation between the calculated chemical hardness and aromaticity of free singlet and triplet NHC ligands

Chemical potential (μ), i.e., negative of the electronegativity (χ) [59, 60], increases depending on excitation from singlet to triplet state. An increase in chemical potential makes NHC ligand binding to metal center difficult due to reduction in their basicity. This can be easily shown by electron affinity (EA) values in Table 1. EA values of the triplet states are lower than those of the singlet states, therefore addition of an electron is facilitated by transition from singlet to triplet states. As a result of this electronic transition, acidity of NHC ligands is enhanced. The enhanced acidity of NHC ligands corresponds to a decrease in their basicity, i.e., electron donating ability. This inference is supported by total valence electron population at C_c atom. While total valence electron populations of carbene atoms in the singlet NHCs are calculated as 3.874 for im2y, 4.133 for im4y, 4.022 for pyr3y and 4.350 for pyr4y, their respective values in triplet states are obtained as 3.716 for im2y, 3.774 for im4y, 3.698 for pyr3y and 3.852 for pyr4y. Since total valence electron population of carbene carbon is formally equal to 4, it is inferred from these results that the triplet states of NHCs are remarkably electron deficient chemical species. Furthermore, abnormal and remote

singlet NHC ligands (**2**, **3**, and **4**) have higher σ-donating ability due to excess valence electrons on their carbene atoms. According to total valence population of the carbene carbons, σ-donating strengths of NHCs increase in the order **1** < **3** < **2** < **4**. In addition, transition from the singlet to triplet states of free NHC ligands reduces the amount of the total valence electrons or equivalently the capability of σ-donation. The order of σ-donating ability of the triplet states, **3** < **1** < **2** < **4**, is quite similar to that of the singlet states. The most efficient σ-donating NHC ligand is pyr4y when both the singlet and triplet ligands are under discussion. This order is very interesting to propose a guiding rule about σ-donating strength of NHC ligands and can be explained by electronegativity of the atoms in α-position relative to carbene atom. Two electronegative nitrogen atoms in im2y (**1**) pull electrons away from the carbene center much more than that of pyr3y (**3**) and im4y (**2**), which include one nitrogen in α-position, and pyr4y (**4**) not including nitrogen atom in α-position. The absence of any electronegative atom in α-position of pyr4y (**4**) facilitates to preserve electronic population at carbene center or at least, hinder to move electrons away from carbene center. Thus, one can say that σ-donating ability of NHC ligands decreases as the number of nitrogen atoms directly attached to carbene center increases.

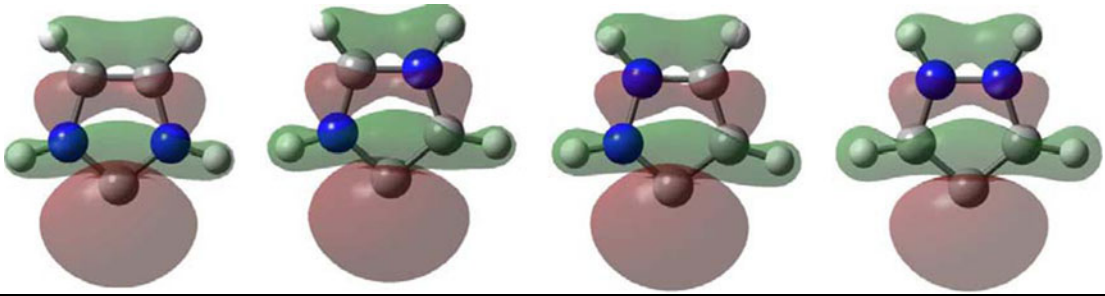
Transition from the singlet to triplet state makes chemical hardness (η) of the free NHC ligands smaller. The hardness corresponds to the gap between the HOMO and LUMO orbital energies and has been qualitatively associated with the stability of a chemical system [59, 60]. As known, hardness is correlated with heteroaromaticity [62]. The calculated hardness value of benzene at B3LYP/aug-cc-pVTZ level is 6.612 eV [63]. Hardness values of the singlet NHCs in Table 1 is at a comparable level than that of benzene. The values of hardness for the considered NHCs vary from 58% (for pyr4y) to 85% (for im2y) of that of benzene. Hardness values in Table 1 also suggest that the triplet states of NHCs are less stable than their singlet counterparts. Generally, the values of chemical hardness of free NHCs ligands exhibit the same trend with their aromaticity as shown in Fig. 1b. This result is convenient with the fact that aromaticity of a chemical moiety is related to its stability. The absence of heteroatoms adjacent to the carbene carbon generally reduces the stabilities of the free singlet NHC ligands. Even though chemical hardness values of free NHC ligands are generally increased with increasing aromaticities as shown in Fig. 1b, there is no one-to-one correspondence between the order of their aromaticities and hardness values. This case deserves an explanation. The sequencing of the hardness values for the singlet (**1** > **3** > **2** > **4**) and triplet (**3** > **2** > **1** > **4**) NHC ligands are opposite to the above orders about σ-donating strengths of the singlet and triplet NHC ligands. Although hardness seems to be an energetic concept, it is essentially related to chemical reactivity of a ligand [64]. Thus, reverse orders between the hardness values and σ-donating strengths of both singlet and triplet NHCs can be understood, because the ligands having lower hardness are more reactive in the sense of σ-donation than ligands having higher hardness.

Electrophilicity index (ω) describes the electrophilic power of a ligand, namely its propensity to accept electrons [59]. Electrophilicity index is also decreased by transition from the singlet to triplet states of NHC ligands. All these results suggest that transition from the singlet to triplet states of free NHC ligands decreases both of their electron donating and accepting ability. These features are of importance in order to understand ligating abilities of *n*NHC, *a*NHCs, and *r*NHC. NHCs in organometallic chemistry act as L→M (metal) σ- and π-donors besides M→L π-acceptors via π*-backdonation mechanism [65]. A decrease both in their electrophilicity index and in their capability of electron donation depending on transition from singlet to triplet state reduces π*-backdonation from TM to NHC and σ- and π-donating abilities of NHCs, respectively. These results explain that up to now no triplet NHC transition metal complexes have been observed. More importantly, ligating abilities of free NHCs, in particular their electron donating and accepting properties, are finely tunable by aromaticity of the free ligands.

The highest occupied molecular orbital (HOMO) describes the carbene carbon σ-lone pair (σ-LP) and the energy levels of the carbene σ lone-pair orbitals are associated with the σ-donating abilities of the free singlet ligands [29, 58]. This fact is explicitly shown in MOs in the higher band of Table 2. HOMOs which are energetically low-lying make σ-donating ability of the relevant NHC difficult. Therefore, the σ-donating strength of NHCs ligands or σ-basicity of carbene atom is in agreement with the order **1** < **3** < **2** < **4**. This order based on energetic sequencing of HOMOs is the same as one inferred from total valence population on the carben atoms in NHCs. As seen from this result in Table 2, *a*NHCs and *r*NHC have higher σ-donating ability than that of Arduengo-type normal NHC, im2y. Experimental studies [66, 67] have also suggested that σ-donating strengths of abnormal NHC ligands are superior to that of normal NHCs. Based on ^{31}P NMR shifts [68], it was shown that donor power of NHCs is increased in the order **1** < **2** < **4**. This sequencing is fully in agreement with our calculations. It is obviously seen that the higher the aromaticity of an imidazol- or pyrazol-based NHC ligand, the higher the σ-donating strength of the ligand.

In addition, the absence of heteroatoms adjacent to the carbene carbon enhances significantly σ-donating ability of free singlet NHC ligands due to the reduced inductive effects of the heteroatoms [69]. This is reminiscent of push-pull mechanism proposed to explain distinctive stability of free im2y ligand by Arduengo and coworkers [70]. According to push-pull effect, nitrogen LPs in *n*NHC would push electron density into formally empty p_π orbital on carbene atom,

Table 2 HOMOs representing σ-LP on carbene atoms in free singlet NHC ligands



(ε_{HOMO}= -6.059 eV)	(ε_{HOMO}=-5.262 eV)	(ε_{HOMO}=-5.550 eV)	(ε_{HOMO}=-4.890 eV)
im2y (**1**)	im4y (**2**)	pyr3y (**3**)	pyr4y (**4**)

leading to π-stabilization, while electronegative nitrogens pull electron density away from the carbene center, giving rise to σ-stabilization. The natural atomic p_π populations of carbene atoms in Table 1 indicate that this idea cannot produce a consistent estimation about p_π population on the carbene atoms in *a*NHCs and *r*NHC. If it had been true, the highest and lowest p_π population on carbene would have been observed for im2y and pyr4y, respectively. This guess cannot be verified by $p_\pi(C_c)$ populations in Table 1. Populations of $p_\pi(C_c)$ for im4y (including one nitrogen in α position) and pyr4y (not including nitrogen in α position) are more pronounced than those of im2y (including two nitrogen atoms in α position) and pyr3y (including one nitrogen in α position). Hence, the kind of atom neighboring C_c is of no significance in order to understand the population of $p_\pi(C_c)$. In fact, the aromaticity of free NHC ligands is more decisive on the spatial confinement of π-electronic population into formally vacant p_π orbital of carbene atom rather than the kind of atoms neighboring C_c. This case is explicitly shown in pyr4y, which has the highest $p_\pi(C_c)$ population in spite of the fact that there is no N atom neighboring carbene atom. Since both C atoms adjacent to the carbene atom in pyr4y do not have any π-donating LP orbitals, π-stabilization of carbene in pyr4y can be essentially achieved by its aromaticity. Similar thoughts are valid for *a*NHCs.

Singlet and triplet carbenes are formally sp^2- and sp-hybridized respectively. The results in Table 1 show that both s- and p-character in hybridization of carbene are increased in singlet NHCs relative to canonical sp^2 hybridization. These indicate that σ-donating strength of carbene centers in singlet NHCs increases as s-character in hybridizations of carbene atoms decreases, giving rise to the same order formerly obtained from total valence electrons of carbene atom and energy values of the HOMOs. However, there is a distinctive behavior in hybridization scheme of carbene atom in imidazolylidenes and pyrazolylidenes upon transition to triplet state as compared to canonical sp hybridization. While both s- and p-character in hybridization of carbene decrease in triplet imidazolylidene ligands, s-character decreases as p-character increases in triplet pyrazolylidenes.

The p_π populations of carbenes in Table 1 are enhanced by protonation just as aromaticity. Additional p_π electronic population in the protonated NHCs is not due to π*-backdonation, since proton does not have any π-electron on itself. Then, increase in p_π population of carbene depending on the protonation is related to stronger π-donation from LP orbitals on nitrogen atoms and slightly enhanced aromaticity of NHCs as shown in Table 1 and Fig. 1a. Slight increase in aromaticity of NHCs after the protonation of the carbene center is not only due to the extra π-donation from LP-orbitals on nitrogens to cyclically conjugated electrons in NHC rings, but also due to rearrangement in bonding situations of NHCs as shown by bond order values in Table 1. The orders of bonds involving carbene atom are increased by the protonation in free imidazolylidene ligands and pyr3y, while they are slightly decreased in pyr4y, *r*NHC.

The bond orders of free NHC ligands produce some surprising results. For instance, N−N bond orders in both pyrazol-based NHCs are remarkably reduced relative to formal single bond, implying considerable electronic charge depletion between the associated atomic centers at first glance. However, examination having regard to only bond orders may be illusive, because there is another possibility to explain this case. At this point, topological *ion*/*cov* parameters reveal the formation character of a bond. It is less than 1 for closed shell (ionic or dative covalent) interactions and greater than 1 for shared (covalent) interactions [71]. To better understand bonding situations, one should take into account both the order and *ion*/*cov* parameter of a bond. It is inferred from *ion*/*cov* parameters of N−N bonds in pyrazol-based NHCs that they possess substantial dative character depending on zwitterionic or doubly-zwitterionic resonance structures shown in Scheme 2.

An increase in the order of $N-C_c$ bond of pyr3y (1.345) indicates an electronic charge concentration relative to formal single bond between the associated atomic centers. However,

the formation of this bond is also dative according to its *ion*/*cov* value (0.766). Different from the other NHC ligands, the orders of the bonds involving carbene atom in pyr4y decrease by the protonation of carbene atom. This does not stem from electronic charge depletion in the region $C{-}C_c{-}C$. On the contrary, electronic charge concentration comes about in the relevant region. What the orders of bonds in $C{-}C_c{-}C$ subunit of pyr4y reduce comes into prominence of its zwitterionic resonance forms in Scheme 2. Another distinctive behavior is observed for $C{-}C_c$ bond in pyr3y. The order and *ion*/*cov* ratio of this bond are 0.539 and 2.028, respectively. Although this bond has significantly dative character due to doubly-zwitterionic resonance structure with regard to only its bond order, there is an electronic charge concentration at a remarkable extent along its bond path according to its *ion*/*cov* value. Considering only the orders of the bonds involving carbene atom in the most aromatic singlet NHC ligand (im4y), one may conclude that these bonds are dative, whereas their *ion*/*cov* ratios indicate the electronic charge concentration along these bonds. Although possible variations in resonance structures of im4y are much more notable than those of the other NHCs as shown in Scheme 2, charge separation property of these resonance structures is obscured by the effect from π-electronic delocalization within the ring due to its enhanced aromaticity. As a result of this, *ion*/*cov* parameter of the bonds $N{-}C_c$ and $C{-}C_c$ in im4y become greater than 1. Depending on transition from singlet to triplet states, essentially dative bond formations of which both its order and *ion*/*cov* ratio are less than 1 are under discussion only for pyrazol-based NHCs. If a dative bond with the order less than 1 allows electronic charge concentration, this charge condensation is only explained by electron flow through the remaining part of the ring, qualitatively suggesting electronic delocalization within the ring system.

The bonding situations NHCs indicate that imidazolylidene ligands are more aromatic than pyrazolylidene ligands due to the fact that dative bond formations in the latter are more evident than those of the former. This explains aromaticity hierarchy between imidazolylidene and pyrazolylidene ligands and indicates that dative bond formations perturb aromatic character of NHCs. In addition, ionic character of the dative bonds in pyr3y, $N\text{-}C_c$ and N-N, is more pronounced than those of pyr4y. Since the prominence of a charge-separated resonance structure of a ring decreases its aromaticity, it is understandable that pyr4y is more aromatic than pyr3y. These inferences about the bonding situations support the aromaticity order of NHCs obtained by FLU and HOMA indices. NICS index suggests that the most aromatic NHC ligand is pyr4y [57], whereas the above discussion reveals that this is not reasonable. Therefore, relevant scientific community should avoid the use of magnetic aromaticity indices and bond orders to describe electronic delocalization level of NHCs.

The π-accepting (acidity) and π-donating (basicity) properties of NHC ligands are determined by their total p_π population. Considering total p_π populations of the five atomic centers given in Table 1, it can be stated that π-deficiency of normal (im2y) free NHC ligand is more pronounced than those of abnormal and remote NHCs, since π-orbitals in the singlet abnormal and remote NHCs are almost fully occupied. As a result of this, π-accepting abilities of *a*NHCs and *r*NHC, i.e., the capability of π*-backdonation, are even less than that of *n*NHC. It is worth noting that remarkable π-deficiency of im2y (**1**) remains after the protonation of its carbene atom. This result obviously indicates that π*-backdonation mechanism in *n*NHC is more probable than those in *a*NHCs and *r*NHC, suggesting that *n*NHC ligands may act as π-acceptors [65]. The abnormal and remote NHCs hardly ever behave as π-acceptors [12]. In addition, σ-donating ability of *n*NHC is much less than those of *a*NHCs and *r*NHC as mentioned before. Thus, it can be stated that the lack of σ-donating ability of *n*NHC is compensated by its relatively high π-accepting ability. Normal (**1**) and abnormal NHCs (**2** and **3**) in the triplet state behave as less π-accepting ligands, whereas triplet state of the *r*NHC (**4**) is still very weak π-accepting ligand. Consequently, the capability of π*-backdonation in the triplet NHCs, in particular *n*NHC, will provide an additional stabilization factor in formation of its TM complexes as a future prospect. Total p_π populations in Table 1 also show that stabilization of the triplet *r*NHC ligand by accepting π-electrons from TM center is too hard to occur.

Addition of the proton to the anionic carbene atom in free ligands **1** and **2** results in the formation of identical imidazolium cations, just as protonation to carbene atom in **3** and **4** leads to the formation of identical pyrazolium cations. The protonated NHCs can be regarded as model compounds to understand NHC-TM complexes, since π-backbonding mechanism (NHC←TM) occurs generally at a small extent in *n*NHC-TM complexes [25, 72, 73] and almost never in *a*NHC-TM and *r*NHC-TM complexes. Protonation of carbene carbon atom cannot lead to NHC←H π-backbonding due to the absence of any π-electron on the proton. The protonated NHCs show different behavior from their free singlet analogues with regard to their aromaticities. While the aromaticities of singlet im4y (**2**) and pyr4y (**4**) are higher than that of im2y (**1**) and pyr3y (**3**) respectively, the aromaticity order related to imidazol- and pyrazol-based NHCs becomes reversed separately after the protonation, i.e., $\mathbf{2}>\mathbf{1} >>\mathbf{4}>\mathbf{3}\rightarrow\mathbf{1}(\mathbf{H}^+)>\mathbf{2}(\mathbf{H}^+) >>\mathbf{3}(\mathbf{H}^+) \approx \mathbf{4}(\mathbf{H}^+)$. In spite of this, aromatic hierarchy between imidazolylidenes and pyrazolylidenes remains unchanged on the protonation, namely the protonated imidazolylidenes are still more aromatic than the protonated pyrazolylidenes. Protonation of carbene atom increases the hardness of free singlet ligands in any case, just as aromaticities of NHCs are increased by the

protonation of carbenic center. This finding can be understood with the aid of the maximum hardness principle [74], which states that molecules will arrange themselves to be as hard as possible. Even though imidazol- and pyrazol-based NHC ligands become identical after protonation of carbene atom, i.e., $\mathbf{1}(\mathbf{H}^+)=\mathbf{2}(\mathbf{H}^+)$ and $\mathbf{3}(\mathbf{H}^+)=\mathbf{4}(\mathbf{H}^+)$, the protonated imidazolylidenes, $\mathbf{1}(\mathbf{H}^+)$ and $\mathbf{2}(\mathbf{H}^+)$, are quite different from each other (particularly their hardness), whereas identicalness between the protonated pyrazolylidenes, $\mathbf{3}(\mathbf{H}^+)$ and $\mathbf{4}(\mathbf{H}^+)$, is more than that of the formers. Since the amounts of changing in hardness depending on the protonation of the *a*NHCs are more pronounced than that of *n*NHC ligand, it can be stated that *a*NHCs and *r*NHC complexes are hard to generate.

C_c−H activation (or C_c−H bond cleavage) leads to oxidative addition of the carbene ligand to the metal center. C−H activation levels of the different sites in NHC rings are different, i.e., C_2 and C_4 activation in imidazolylidene or C_3 and C_4 activation in pyrazolylidene. C−H bond orders and their *ion*/*cov* parameters were calculated to gain some insight into C−H bond activation in the protonated NHCs, since the strength of a bond and the amount of electron in a bond can be described by its order and *ion*/*cov* parameter, respectively. The bond orders (and *ion*/*cov* parameters) of C_2−H and C_4−H in the protonated imidazolylidenes, $\mathbf{1}(\mathbf{H}^+)$ and $\mathbf{2}(\mathbf{H}^+)$, are 0.611 (1.725) and 0.720 (1.740), while the bond orders (and *ion*/*cov* parameters) of C_3−H and C_4−H are 0.566 (1.719) and 0.884 (1.737), in the protonated pyrazolylidenes, $\mathbf{3}(\mathbf{H}^+)$ and $\mathbf{4}(\mathbf{H}^+)$, respectively. These results clearly indicate that C_4−H is stronger than C_2−H in the protonated imidazolylidenes and, C_4−H is stronger than C_3−H in the protonated pyrazolylidenes. An increment in the order (or electronic density) of a bond makes its cleavage difficult. Thus, the synthetic routes using direct metallation at carbene atom via C−H bond activation (or cleavage) can be achieved by protection of C_2 (in imidazolylidenes) [69] and C_3 (in pyrazolylidenes). In other words, C_2-bound imidazolylidenes are more favorable than their C_4-bound analogues, just as C_3-bound pyrazolylidenes are more favorable than their C_4-bound pyrazolylidenes. The difference between C−H activation levels in the protonated pyrazolylidenes is more pronounced than that of the protonated imidazolylidenes due to better zwitterionic charge separation abilities arising from their reduced aromaticity as mentioned before. This implies the presence of zwitterionic resonance forms as a ground state in different pyrazolylidene complexes [75].

CSD survey about NHCs depending on their aromaticity

Aforementioned quantum chemical considerations between the electronic effects in NHCs and their aromaticities require to be verified by experimental results. One of the useful geometric parameters to describe ligating abilities of NHCs is the van der Waals (vdW) shortening in TM-C_c bond defined as the difference between the length of TM-C_c bond and the sum of the covalent radii of the associated atoms. Here we used the covalent van der Waals radii revised in 2008 [76]. For approximately five thousands NHC TM complexes retrieved from CSD, %vdW shortenings are calculated and illustrated against the aromaticity of the associated NHC rings as shown in Fig. 2. It is generally accepted that TM-C_c bond is of dative character [77]. There are two reasons for vdW shortening in TM-C_c bonds: (i) electronic charge concentration along TM-C_c bond arising from π-donating strength of carbene atom and π*-backbonding mechanism from TM to C_c, (ii) prominent dative character of TM-C_c bond. While all of these mechanisms in TM complexes derived from *n*NHC ligands have an influence on the shortening of their TM-C_c bonds, only dative character of TM-C_c bonds plays a role in the shortening of TM-C_c bonds of TM complexes derived from *a*NHCs and *r*NHC, since σ-donating property of carbene atom is primarily responsible for the formation of TM-C_c bond, not for reinforcement of this bond. In addition, electronic nature of the coordination sphere, i.e., electron-rich or electron-poor, may also play an important role in such a shortening.

HOMA values of imidazol-based NHC rings in their TM-complexes are accumulated in the range of 0.6-0.9 as shown in Fig. 2, while maximum HOMA values of pyrazol-based NHCs in their TM-complexes could hardly have reached the average HOMA values of the formers. This behavior can be explained by the fact that aromaticity of imidazolylidenes are greater than that of pyrazolylidenes, indicated by average HOMA values retrieved from CSD in Table 1. Variations in aromaticities of NHCs in their TM complexes are not only due to endocyclic delocalization effects as comprehensively

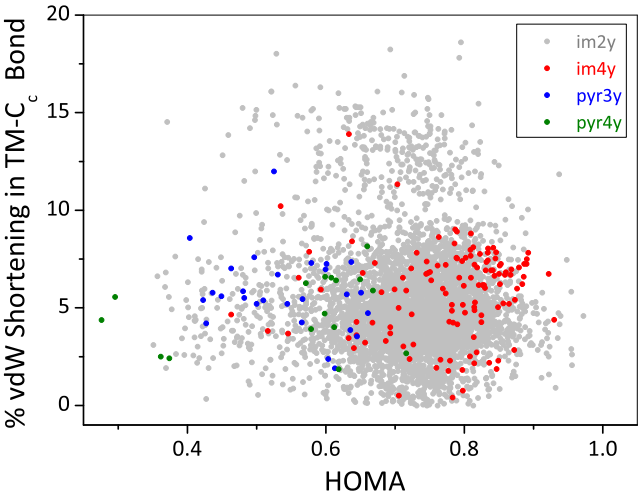


Fig. 2 Scattergram for van der Waals shortenings in TM-C_c bonds of NHC-TM complexes retrieved from CSD against their aromaticities: im2y (**1**) by gray-filled circles, im4y (**2**) by red-filled circles, pyr3y (**3**) by blue-filled circles and pyr4y (**4**) by green-filled circles

discussed in Electronic nature and ligating abilities of NHCs, but also exocyclic delocalization effects from electronic nature of the substituents attached to NHC (π-electron withdrawing or donating) [78]. Figure 2 shows that complexation with TMs does not change aromaticity hierarchy among free NHCs: aromaticities of pyrazol-based NHC ligands are still lower than those of imidazol-based NHC ligands after complexation. In addition, %vdW shortening values of the complexes involving pyrazolylidene ligands are generally lower than those of the complexes involving imidazolylidene ligands due to variety in the contributions to the shortening in TM-C_c bond. Furthermore, %vdW shortenings in TM-C_c bond of the complexes derived from pyr3y can be more than those of pyr4y as shown in Fig. 2. This observation implies that the enhanced aromaticities of NHC ligands reducing charge separation property and dative character of the resulting TM-C_c bond lessen vdW shortening in TM-C_c bond. Thus, it can be stated that vdW shortening in NHC-TM complexes of pyr3y is essentially due to dative character of TM-C_c bond.

The data in Fig. 2 for NHC-TM complexes including 26 different TM elements are much dispersed due to multifarious coordination environments and the presence of various substituents attached to NHC ring, in particular for *n*NHCs. Therefore, one needs further analyses about the data in order to conclude certain guiding rules. Figure 3 shows scatterplots of average %vdW shortening in TM-C_c bonds against average HOMA indices of the associated NHC ligands retrieved from CSD with respect to TM elements. Distribution of the points suggests that %vdW shortening in TM-C_c bonds for all NHC ligands generally decreases as aromaticity of NHC ligands increases. Average %vdW shortenings in TM-C_c bonds comply with the order **3** (5.92%)>**2** (5.76%)>**1** (4.45%)>**4** (4.10%). This order is in general agreement with the order of C-H activation level in NHCs: C_3 (**3**)>C_2 (**1**)>C_4 (**2**)>C_4 (**4**). One may ask why %vdW shortenings in **1** are more than those of **4**, though the aromaticity of **1** is considerably higher than that of **4**. This case is originated from the enhanced π-donating and π*-accepting abilities through TM-C_c bond in *n*NHC complexes, whereas such additional mechanisms resulting in the contraction of TM-C_c bond are disabled in the TM complexes of *r*NHC. Diminishing tendency in %vdW shortenings with the aromaticities of the NHC ligands is evident for the complexes including TMs in period 4 and 5. It is worth noting that aromaticities of NHC-TM complexes of period 6 are spread out in a narrower interval than those of period 4 and 5, which can be ascribed to the presence of very diffuse d-orbitals in TMs of period 6. Presence of the more diffused d-orbitals at metal center makes π-electron flow through TM-C_c bond difficult due to less spatial overlap between p_π orbital of carbene and d_π orbitals of TM center. As a result of this, aromaticity levels of NHCs ligated with TMs in period 6 remain somewhat higher than those of period 4 and 5, since protection of π-electron delocalization levels of NHC ligands in TM complexes of period 6 is more pronounced than those of period 4 and 5. Another important effect is observed in %vdW shortenings depending on the period of TM. %vdW shortenings gradually decrease on going from period 4 to period 6, because both NHC→TM π-donation and TM→NHC π*-backdonation are decreased by the presence of diffuse d-orbitals.

Due to the lack of any article about π-stacking interactions involving NHC ligands, aromaticity of NHCs seems to be suspicious in structural sense as well, even though evidence from vibrational spectroscopy are available [27]. The presence of bulky substituents of NHC rings leading to a clash makes the observation of such π-stacking interactions difficult, even though it is necessary for kinetic stabilization of NHCs [79]. Therefore, prevalence of such interactions in crystal structures of NHC-TM complexes is very low (approximately 1%). CSD

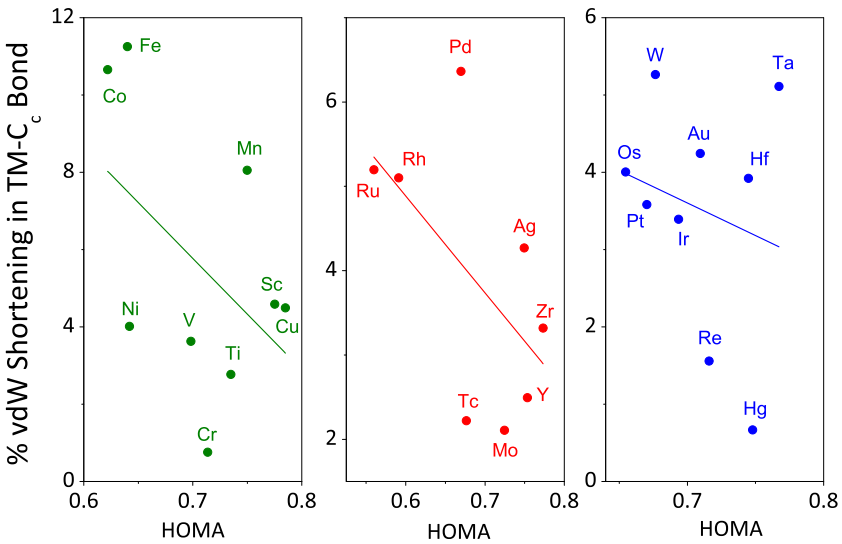


Fig. 3 Side-by-side view of the variations of average %vdW shortenings in TM-C_c bonds against aromaticities of NHC ligands in TM complexes of period 4 (leftmost), period 5 (middle) and period 6 (rightmost) showing the associated linear fits. Data for period 4, 5 and 6 have been colored by green, red and blue, respectively

search regarding π-stacking interactions involving NHCs results in 48 hits for im2y, one hit for im4y, three hits for pyr3y and one hit for pyr4y complexes. The centroid-centroid separation is decreased as slippage angle increases. Diversity in the total aromaticity of the interacting NHCs can be explained by various exocyclic substituents of NHCs. It has been recently reported that aromaticity of a ring system is not a *sine qua non* condition for participation to π-stacking interactions [80]. As shown in Scheme 2, free NHC ligands are weakly polarized ligands due to their considerable aromaticities. At this point, one should keep in mind π-deficient aromaticities of NHCs in particular im2y (*vide supra*) corresponding to 90% of these interactions. For polarized π-systems, favorable stacking interaction requires both a π-deficient atom (N and C_c) leading to π-polarization and a positively charged atom (N and non-carbene C atoms) leading to σ-polarization [81].

Although the aromaticity is not an additive quantity, the summation of the individual aromaticities of the rings participating in the interactions is used to describe the amount of π-electron involving the interaction. The interactions of which the summation of HOMA indices is more than 1 are referred to as π-rich, ones of which total HOMA values are less than 1 are qualified as π-deficient. The interactions between less aromatic NHC rings are stronger than the interactions involving more aromatic NHCs, because Cg⋯Cg distances of π-rich (more aromatic) NHCs are extended in a broader interval than those of π-deficient (less aromatic) as shown in the relevant histogram of Fig. 4. Although the centroid-centroid distances of both π-rich and π-deficient interactions involving NHCs are accumulated in the same region (3.3-3.4 Å), Cg⋯Cg distances of the former can reach a longer region in order to reduce π-π repulsion between the rings, perturbing the stability of the interaction. In general, Cg⋯Cg distance of the interactions is decreased as its β slippage angle increases as shown in the upper band of Fig. 4, and therefore displacement angles of π-rich interactions are accumulated in somewhat smaller region (15-20°) than those of π-deficient interactions (20-25°).

Conclusions

The calculations about the free singlet NHC ligands at B3LYP/aug-cc-pVTZ level predict that im2y is 18.93 kcal mol^{-1} more stable than its abnormal isomer im4y, which in turn is 14.82 kcal mol^{-1} lower in energy than the pyr3y and is 30.93 kcal mol^{-1} lower in energy than the pyr4y. Energetic stabilities of *a*NHCs and *r*NHC are less than that of *n*NHC. Aromaticity of imidazol-based NHCs is obviously more pronounced than that of pyrazol-based ones. Aromaticities of the singlet NHCs are higher than those of their triplet counterparts due to dramatic

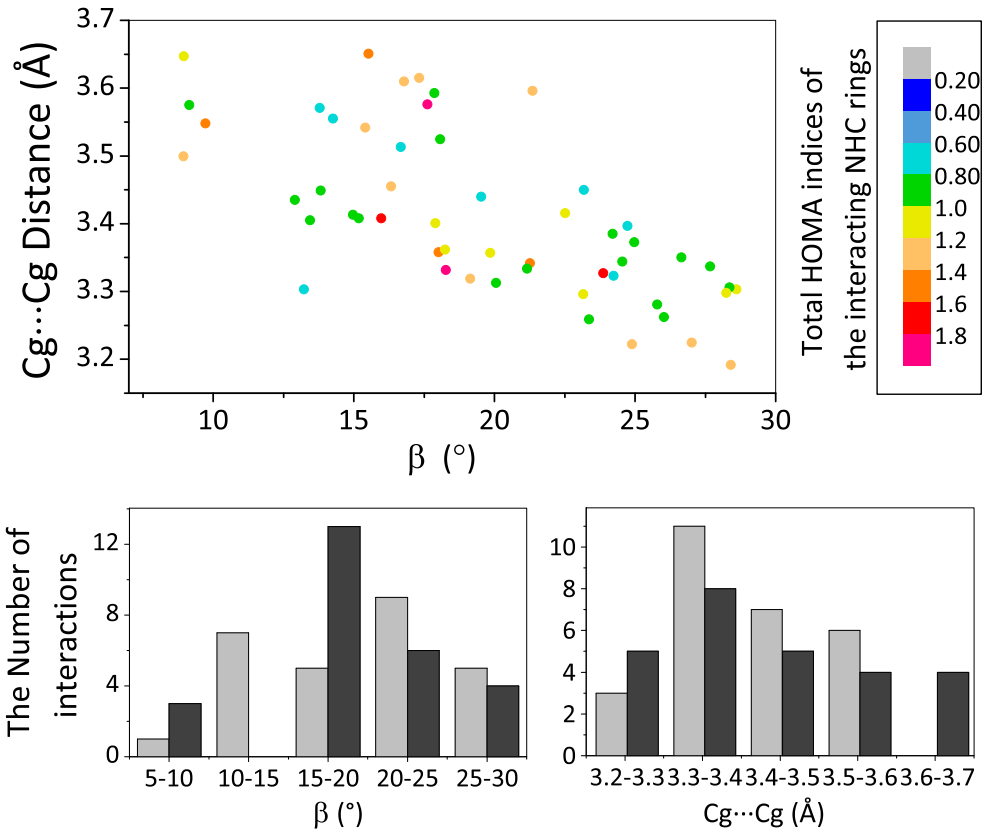


Fig. 4 Scattergram for the correlation between the centroid-centroid separation (Cg⋯Cg) and β-slippage (or displacement) angle in the upper band. Filled circles are colored according to the total HOMA indices of NHC rings involved in π-stacking interactions. Lower band includes a side-by-side view of histograms showing the distributions of (Cg⋯Cg) distances and of the slippage angles. Light gray columns correspond to π-deficient NHC ring pairs, while dark-gray columns represent π-rich NHC ring pairs

structural changes such as pyramidalization of the endocyclic nitrogen centers and weakening of N-C_c and N-N bonds. Bond angles X_α–C_c–Y_α in the triplet NHC ligands become wider than those in the singlet analogues due to the weakening of the bond between the atoms in β-positions. In addition, the protonation of the carbene atom makes the aromaticity of the associated NHC ligand slightly greater. Aromaticities of the singlet NHC ligands suggested by HOMA and FLU indices increase in the order pyr3y<pyr4y<< im2y<im4y. Structural (HOMA) and electronic aromaticity (FLU) indices show that NHCs except for pyr3y are considerably aromatic. The aromaticity sequencing of NHCs suggested by HOMA and FLU indices can be rationalized by quantum chemical considerations about the electronic nature of NHC ligands, whereas the aromaticity order determined by NICS could not. We therefore propose that NICS or other local magnetic quantifiers for aromaticity should no longer be used to describe aromaticities of NHCs.

The well-known push-pull mechanism [70] prevalently used in understanding the electronic stabilization of carbene atom in *n*NHC cannot explain π-electronic population of the formally vacant p_π orbital on C_c atoms of *a*NHCs and *r*NHC in a consistent manner. Aromaticity of NHCs rather than the effect from N atoms neighboring carbene center is more decisive on π-stabilization of the carbene atoms in *a*NHCs and *r*NHC. Therefore, putative scenario about π-electronic stabilization of carbene atom in NHCs should be revised. Push-pull mechanism is only valid for stabilization of the saturated *n*NHC. Instead of mentioning the direct electron donation from LP orbitals on N atoms to formally vacant p_π orbital on the carbene atom in *a*NHCs and *r*NHC, it would be more accurate to mention electron donation to π-delocalization within the ring system of *a*NHCs and *r*NHC. Figure 1a showing that an increase in aromaticity of NHC ligands and their protonated analogues corresponds to increase in p_π donation from LPs of N atoms also supports this inference. Arduengo-type NHCs (*n*NHCs) can be classified into saturated (nonaromatic) and unsaturated (aromatic) as shown in Scheme 1, whereas *a*NHCs and *r*NHC cannot. In structural regard, aromaticity of *a*NHCs and *r*NHC is an inseparable part of their functionality. As pointed out in ref. [28], abnormal binding chemistry of NHCs will soon be well-understood. Similar foresight is valid for the triplet states of NHC ligands. Our calculations indicate that their aromaticities play a key role in understanding the stabilization of triplet NHCs complexes to be synthesized in the future. Aromaticities of the triplet NHC ligands are higher than that of the lowest-lying triplet state of benzene. More importantly, it is allowed to donate π-electron donation from TM to the triplet NHC ligands due to their considerable π-electron deficiency except for the *r*NHC.

Abnormal and remote singlet NHCs have higher σ-donating ability than that of normal NHC in agreement with the order im2y<pyr3y<im4y<pyr4y, implying that σ-donating ability of NHC ligands decreases as the number of N atoms in α-positions increases. Increase in the aromaticity raises σ-donating ability of both imidazol- and pyrazol-based NHC ligands. The lack of σ-donating ability of *n*NHC as compared to *a*NHCs and *r*NHC is compensated by the relatively high π-accepting ability of *n*NHC. An increase in π-electron donation from LP-orbitals of N atoms to cyclic delocalization raises the aromaticity of the ring even in *r*NHC. Although NHC ligands are overall donor, *n*NHC can accept π-electronic charge from TM, whereas *a*NHCs and *r*NHC cannot accept excess π-electronic charge due to their almost fully occupied p_π orbitals.

These quantum chemical considerations were questioned by means of the CSD searches to gain structural insights. Bulkiness of the substituents groups of NHC ligands necessary for kinetic stabilization would sterically hinder their participation in π-stacking interactions. Increase in the aromaticity of NHC ligands decreases van der Waals shortening in TM-C_c bond mainly due to diminishing dative character of the bond. This effect is more pronounced for NHC complexes of TMs in period 4 and 6. The more diffused d-orbitals of TMs in period 6 make π-electron flow through TM-C_c bond difficult due to less spatial overlap between carbene p_π orbital and d_π orbitals of TM center. Inhibition of mutual π-electron interchange between NHC ligand and TM center facilitates protection of the aromaticity level of NHC ligand.

Acknowledgments This work was supported by TÜBİTAK (The Scientific and Technological Research Council of Turkey) under the allocation 112T636.

References

1. Arduengo AJ III, Harlow RL, Kline MJ (1991) Am Chem Soc 113: 361–363
2. Herrmann WA, Köcher C (1997) Angew Chem Int Ed Engl 36:2162–2187
3. Arduengo AJ III (1999) Acc Chem Res 32:913–921
4. Hahn FE, Jahnke MC (2008) Angew Chem Int Ed 47:3122–3172
5. Öfele K, Tosh E, Taubmann C, Herrmann WA (2009) Chem Rev 109:3408–3444
6. Wang Y, Robinson GH (2011) Inorg Chem 50:12326–12337
7. Al-Rafia SMI, Malcolm AC, Liew SK, Ferguson MJ, Rivard E (2011) J Am Chem Soc 133:777–779
8. Curran DP, Solovyev A, Makhlouf Brahmi M, Fensterbank L, Malacria M, Lacote E (2011) Angew Chem Int Ed 50:10294–10317
9. Wang Y, Robinson GH (2012) Dalton Trans 41:337–345
10. Kinjo R, Donnadieu B, Celik MA, Frenking G, Bertrand G (2011) Science 333:610–613
11. Martin D, Soleilhavoup M, Bertrand G (2011) Chem Sci 2:389–399
12. Schuster O, Yang L, Raubenheimer HG, Albrecht M (2009) Chem Rev 109:3445–3478
13. Nolan SP (2011) Acc Chem Res 44:91–100
14. Correa A, Nolan SP, Cavallo L (2011) Top Curr Chem 302:131–155
15. Valente C, Calimsiz S, Hoi KH, Mallik D, Sayah M, Organ MG (2012) Angew Chem Int Ed 51:3314–3332
16. Marion N, Diez-Gonzalez S, Nolan SP (2007) Angew Chem Int Ed 46:2988–3000

17. Biju AT, Kuhl N, Glorius F (2011) Acc Chem Res 44:1182–1195
18. Bugaut X, Glorius F (2012) Chem Soc Rev 41:3511–3522
19. Heinemann C, Müller T, Apeloig Y, Schwarz H (1996) J Am Chem Soc 118:2023–2038
20. Tomioka H (1997) Acc Chem Res 30:315–321
21. Hirai K, Itoh T, Tomioka H (2009) Chem Rev 109:3275–3332
22. Boehme C, Frenking G (1996) J Am Chem Soc 118:2039–2046
23. Lehmann JF, Urquhart SG, Ennis LE, Hitchcock AP, Hatano K, Gupta S, Denk MK (1999) Organometallics 18:1862–1872
24. Frison G, Sevin A (1999) J Phys Chem A 103:10998–11003
25. Diez-Gonzalez S, Nolan SP (2007) Coord Chem Rev 251:874–883
26. Muller P (1994) Pure Appl Chem 66:1077–1184
27. Leites LA, Magdanurov GI, Bukalov SS, Nolan SP, Scott NM, West R (2007) Mendeleev Commun 17:92–94
28. Arnold PL, Pearson S (2007) Coord Chem Rev 251:596–609
29. Huynh HV, Frison G (2013) J Org Chem 78:328–338
30. Aldeco-Perez E, Rosenthal AJ, Donnadieu B, Parameswaran P, Frenking G, Bertrand G (2009) Science 326:556–559
31. Lazzeretti P (2004) Phys Chem Chem Phys 6:217–223
32. Gomes JANF, Mallion RB (2001) Chem Rev 101:1349–1383
33. Bultinck P, Rafat M, Ponec R, van Gheluwe B, Carbo-Dorca R, Popelier P (2006) J Phys Chem A 110:7642–7648
34. Feixas F, Matito E, Poater J, Solà M (2008) J Comput Chem 29: 1543–1554
35. Poater J, Fradera X, Duran M, Solà M (2003) Chem Eur J 9:400–406
36. Bultinck P, Ponec R, Van Damme SJ (2005) Phys Org Chem 18:706–718
37. Matito E, Duran M, Solà M (2005) J Chem Phys 122:014109–8
38. Becke AD (1993) J Chem Phys 98:5648–5652
39. Lee CT, Yang WT, Parr RG (1988) Phys Rev B 37:785–789
40. Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Scalmani G, Barone V, Mennucci B, Petersson GA, Nakatsuji H, Caricato M, Li X, Hratchian HP, Izmaylov AF, Bloino J, Zheng G, Sonnenberg JL, Hada M, Ehara M, Toyota K, Fukuda R, Hasegawa J, Ishida M, Nakajima T, Honda Y, Kitao O, Nakai H, Vreven T, Montgomery JA Jr, Peralta JE, Ogliaro F, Bearpark M, Heyd JJ, Brothers E, Kudin KN, Staroverov VN, Kobayashi R, Normand J, Raghavachari K, Rendell A, Burant JC, Iyengar SS, Tomasi J, Cossi M, Rega N, Millam JM, Klene M, Knox JE, Cross JB, Bakken V, Adamo C, Jaramillo J, Gomperts R, Stratmann RE, Yazyev O, Austin AJ, Cammi R, Pomelli C, Ochterski JW, Martin RL, Morokuma K, Zakrzewski VG, Voth GA, Salvador P, Dannenberg JJ, Dapprich S, Daniels AD, Farkas O, Foresman JB, Ortiz JV, Cioslowski J, Fox DJ (2009) Gaussian 09, Revision C01. Gaussian, Inc, Wallingford, CT
41. Dunning TH (1989) J Chem Phys 90:1007–1023
42. Woon DE, Dunning TH (1993) J Chem Phys 98:1358–1371
43. Glendening ED, Landis CR, Weinhold F (2012) WIREs Comput Mol Sci 2:1–42
44. Bader RFW (1994) Atoms in Molecules: A Quantum Theory. Oxford University Press, USA
45. Keith TA (2012) AIMAll (Version 12.09.23, Professional), TK Gristmill Software, Overland Park KS, USA, (aim.tkgristmill.com)
46. Mayer I (2007) J Comput Chem 28:204–221
47. Gorelsky SI, AOMix: Program for Molecular Orbital Analysis, http://www.sg-chem.net/, University of Ottawa, version 6.5, 2011
48. Krygowski TM, Cyrański MK (2001) Chem Rev 101:1385–1419
49. Chen ZF, King R (2005) Chem Rev 105:3613–3642
50. Cyrański MK (2005) Chem Rev 105:3773–3811
51. Ciesielski A, Krygowski TM, Cyrański MK, Dobrowolski MA, Balaban AT (2009) J Chem Inf Model 49:369–376
52. Krygowski TM (1993) J Chem Inf Comput Sci 33:70–78
53. Frizzo CP, Martins MAP (2012) Struct Chem 23:375–380
54. Matito E, Poater J, Duran M, Solà M (2005) J Mol Struc Theo chem 727:165–171
55. Bruno IJ, Cole JC, Edgington PR, Kessler M, Macrae CF, McCabe P, Pearson J, Taylor R (2002) Acta Crystallogr B58:389–397
56. Groom CR, Allen FH (2011) WIREs Comput Mol Sci 1:368–376
57. Holtzl T, Ngan VT, Nguyen MT, Veszprémi T (2009) Chem Phys Lett 481:54–57
58. Tonner R, Heydenrych G, Frenking G (2007) Chem Asian J 2:1555–1567
59. Parr RG, Von Szentpály L, Liu SB (1999) J Am Chem Soc 121: 1922–1924
60. Minkin VI (1999) Pure Appl Chem 71:1919–1981
61. Feixas F, Vandenbussche J, Bultinck P, Matito E, Solà M (2011) Phys Chem Chem Phys 13:20690–20703
62. De Proft F, Geerlings P (2001) Chem Rev 101:1451–1464
63. Torrent-Sucarrat M, Luis JM, Duran M, Solà M (2002) J Chem Phys 117:10561–10570
64. Pearson RG (2005) J Chem Sci 117:369–377
65. Jacobsen H, Correa A, Poater A, Costabile C, Cavallo L (2009) Coord Chem Rev 253:687–703
66. Appelhans LN, Zuccaccia D, Kovacevic A, Chianese AR, Miecznikowski JR, Macchioni A, Clot E, Eisenstein O, Crabtree RH (2005) J Am Chem Soc 127:16299–16311
67. Crabtree RH (2013) Coord Chem Rev 257:755–766
68. Iglesias M, Albrecht M (2010) Dalton Trans 39:5213–5215
69. Albrecht M (2009) CHIMIA 63:105–110
70. Arduengo AJ, Dias HVR, Dixon DA, Harlow RL, Klooster WT, Koetzle TF (1994) J Am Chem Soc 116:6812–6822
71. Krygowski TM, Palusiak M, Plonka A, Zachara-Horeglad JE (2007) J Phys Org Chem 20:297–306
72. Frenking G, Solà M, Vyboishchikov SF (2005) J Organomet Chem 690:6178–6204
73. Heydenrych G, von Hopffgarten M, Stander E, Schuster O, Raubenheimer HG, Frenking G (2009) Eur J Inorg Chem 1892–1904
74. Parr RG, Chattaraj PK (1991) J Am Chem Soc 113:1854–1855
75. Heckenroth M, Neels A, Garnier MG, Aebi P, Ehlers AW, Albrecht M (2009) Chem Eur J 15:9375–9386
76. Cordero B, Gómez V, Platero-Prats AE, Revés M, Echeverría J, Cremades E, Barragán F, Alvarez S (2008) Dalton Trans 21:2832–2838
77. Baba E, Cundari TR, Firkin I (2005) Inorg Chim Acta 358:2867–2875
78. Fernandez I, Dyker CA, DeHope A, Donnadieu B, Frenking G, Bertrand G (2009) J Am Chem Soc 131:11875–11881
79. Bourissou D, Guerret O, Gabbai FP, Bertrand G (2000) Chem Rev 100:39–91
80. Martinez CR, Iverson BL (2012) Chem Sci 3:2191–2201
81. Janiak C (2000) J Chem Soc Dalton Trans 21:3885–3896