

*Phys. Chem. Res.*, Vol. 5, No. 4, 819-830, December 2017

DOI: 10.22036/pcr.2017.91172.1395

## N-Heterocyclic Plumbylenes (NHPbs) at Theoretical Levels

N. Mohebi and M.Z. Kassaee\*

Department of Chemistry, Tarbiat Modares University, P.O. Box: 14115-175, Tehran, Iran

(Received 3 July 2017, Accepted 26 August 2017)

Plumbylenes are reactive intermediates whose discovery and characterizations are of great significance. Here, ten novel plumbylenes are introduced and characterized. A comparison is made between novel 1,4-di(R)tetrazol-5-plumbylenes ( $I_R$ ) with their corresponding 1,3-di(R) isomers ( $II_R$ ), at DFT ( $R = H, Me, Et, i\text{-}Pro, \text{and } t\text{-}Bu$ ). Each of the plumbylene ( $I_R$  or  $II_R$ ) appears to be less stable, with a lower band gap ( $\Delta E_{HOMO-LUMO}$ ), and a higher nucleophilicity ( $N$ ) than its corresponding carbene ( $I'_R$  or  $II'_R$ ). For both  $I_R$  and  $II_R$  plumbylenes, the trend of  $N$  values emerges consistent with the size of substituents ( $t\text{-}Bu > i\text{-}Pro > Et > Me > H$ ). Every  $II_R$  shows a higher  $N$  than its corresponding  $I_R$ . Except  $II_H$ , each  $II_R$  shows more aromaticity than its counterpart  $I_R$ . The nucleophilicity index ( $N$ ) of both  $I_R$  and  $II_R$  appears to be directly proportional to the size of R, proton affinity (PA), and plumbylene bond angles ( $N-\widehat{Pb}-N$ ); while it is inversely proportional to electrophilicity ( $\omega$ ), and  $\Delta E_{HOMO-LUMO}$ .

**Keywords:** N-Heterocyclic plumbylenes, Nucleophilicity, Singlet-triplet energy gaps, Substituent effects, Density functional theory

### INTRODUCTION

Plumbylenes ( $PbR_2$ ) are the heaviest members of group 14 of divalents which appear to be more stable than carbenes [1,2]. Despite toxicity of lead, many reports on N-heterocyclic plumbylenes (NHPbs) have been presented [3,4]. The first examples were isolated after 1973 [5-14]. Evidently, steric protection by bulky substituents stabilize plumbylene by preventing attack on its electron-deficient center. In addition, heteroatoms adjacent to Pb induce stabilization through efficient  $p\pi-p\pi$  overlap between the heteroatom lone pairs and the vacant  $p$ -orbital of plumbylene [15]. Grimme and Hahn showed the binding of NHPbs to metals [16-20]. Lead compounds are used mainly in the formal oxidation state IV. Most of those with inorganic ligands appear with Pb(II). Divalent organolead compounds are rarely found [17-19].

We have already compared stability, in terms of singlet-triplet energy separations, for halogenated five-membered

cyclic conjugated plumbylenes  $I_X$  and  $II_X$  ( $X = H, F, Cl$  and  $Br$ ). Every 3-halo-substituted species ( $II_X$ ) appeared to be more stable than the corresponding 2-halosubstituted isomer ( $I_X$ ). Every singlet  $I_X$  or  $II_X$  showed a larger plumbylene angle ( $C-\widehat{Pb}-C$ ) than its corresponding triplet state (Fig. 1) [21]. Also, recently, one of us made a quest for Arduengo's type B-heterocyclic stable five membered ring 2,5-bis(halobora)cyclopentenplumbylene,  $III_X$ . Triplet  $III_X$  is assumed to have a planar geometry with a dihedral angle of about zero degree. In contrast, its corresponding singlet state showed a high tendency for puckering with dihedral angle of  $66^\circ$  (Fig. 1) [22].

Stability ( $\Delta E_{s-t}$ ) of propargylenic plumbylene  $H-C\equiv C-Pb-H$  was investigated at theoretical levels. Plotting MP2 relative energies of  $H-C\equiv C-Pb-H$  as a function of the plumbylene bond angle, ( $H-\widehat{Pb}-C$ ) gave a cross points between the singlet and triplet states at  $153^\circ$ . No significant contribution was found for lead valence d-orbital [23]. Considering the importance of NHPbs, in this work, steric effect on the nucleophilicity index ( $N$ ) of two series of them,  $I_R$  and  $II_R$ , are probed at DFT level.

\*Corresponding author. E-mail: [kassaem@modares.ac.ir](mailto:kassaem@modares.ac.ir)

## COMPUTATIONAL METHODS

Gaussian 98 program package was used for optimization of our compounds, at 6-311++G\*\* level of theory [24-25]. The latter is a B3LYP method which unites Becke's B3 with the LYP correlation [26,27]. The keyword "Extrabasis" is used in the Gaussian 98 (Using LANL2DZ, McGrath-Curtiss basis set for plumblylene) [28,29].

Frequency measurements presented thermodynamic data, including zero-point energy, thermal correction, Gibbs free energy, enthalpy, and entropy (298.15 K and 1.0 atm) [30]. The nucleophilicity index ( $N$ ) was measured as  $N = E_{\text{HOMO}(\text{Nu})} - E_{\text{HOMO}(\text{TCNE})}$ , where HOMO(Nu) denotes the highest occupied molecular orbital of nucleophiles and HOMO tetracyanoethylene (TCNE) represents the highest occupied molecular orbital of TCNE [31], TCNE is chosen as the reference with the lowest  $N$  for carbenes and their heavy analogous [32-39]. Moreover, global electrophilicity ( $\omega$ ) was measured as  $\omega = (\mu/2\eta)$  [40]. In this equation,  $\mu$  denoted the chemical potential ( $\mu = [E_{\text{HOMO}} + E_{\text{LUMO}}]/2$ ) and  $\eta$  represented chemical hardness ( $\eta = E_{\text{HOMO}} - E_{\text{LUMO}}$ ) [41].

## RESULTS AND DISCUSSION

Novel 1,4-(R)tetrazol-5-plumbylenes ( $I_R$ ) are compared and contrasted to their corresponding 1,3-(R)tetrazol-5-plumbylenes ( $II_R$ ), at B3LYP/6-311++G\*\*, where R is H, Me, Et, *i-Pro*, and *t-Bu* (Fig. 1). Changes of  $N$  (for  $I_R$  and  $II_R$ ) are studied as functions of: singlet-triplet energy gaps ( $\Delta E_{\text{S-T}} = E_{\text{T}} - E_{\text{S}}$ ), proton affinity (PA), nucleophilicity ( $N$ ), electrophilicity ( $\omega$ ), and band gap ( $\Delta E_{\text{HOMO-LUMO}}$ ) (Fig. 2).

### Changes of Nucleophilicity ( $N$ ) as a Function of R

A comparison between NHPbs and NHCs indicates that each NHPb is more nucleophilic than its corresponding NHCs (Table 1) [42]. Each  $II_R$  is more nucleophilic than its related  $I_R$  isomer (Table 1). For instance,  $II_{t-Bu}$  ( $N = 4.38$  eV) shows more nucleophilicity than  $I_{t-Bu}$  ( $N = 3.90$  eV) (Table 1).

Because of the steric hindrance, asymmetric  $II_R$  plumbylenes are kinetically more accessible than their symmetric  $I_R$  analogues. Plumbylene angle for every  $II_R$  is larger than its corresponding  $I_R$ . For instance, plumbylene angle for  $II_{i-Pro}$  is almost 2.89 degrees wider than  $I_{i-Pro}$  (Table

2). The band gap of each  $II_R$  appears to be narrower than its corresponding  $I_R$ . For instance,  $\Delta E_{\text{HOMO-LUMO}}$  of  $II_H$  is (3.64 kcal/mol) narrower than that of  $I_H$  (Table 1). The band gap of every NHPb is narrower than its corresponding NHC (Table 1).

Changes of  $N$  as a function of R is:  $I_H < I_{Me} < I_{Et} < I_{i-Pro} < I_{t-Bu} < II_H < II_{Me} < II_{Et} < II_{i-Pro} < II_{t-Bu}$ . Hence,  $N$  increases as the size of R increases (Fig. 3). Hence, each  $II_R$  has a higher  $N$  than its corresponding  $I_R$  (Table 1). The smaller is the Hammett substituent constant  $\sigma$ , the larger is  $N$ . For instance,  $II_{t-Bu}$  and  $I_H$  with  $\sigma_p$  values of -0.20 and 0.00 (Table S1) display  $N$  values of 4.38 and 3.37, respectively.  $N$  is relative to the energy of its HOMO ( $E_{\text{HOMO}}$ ) in each species (Table 1) [43].

Trend of the calculated global electrophilicity ( $\omega$ /eV) [40,41] is exactly opposite of that for  $N$  (Table 1). Each  $II_R$  is less electrophilic than its corresponding  $I_R$  isomer. For instance,  $II_{t-Bu}$  ( $\omega = -1.38$  eV) shows less electrophilicity than its corresponding  $I_{t-Bu}$  isomer ( $\omega = -1.78$  eV) (Table 2).

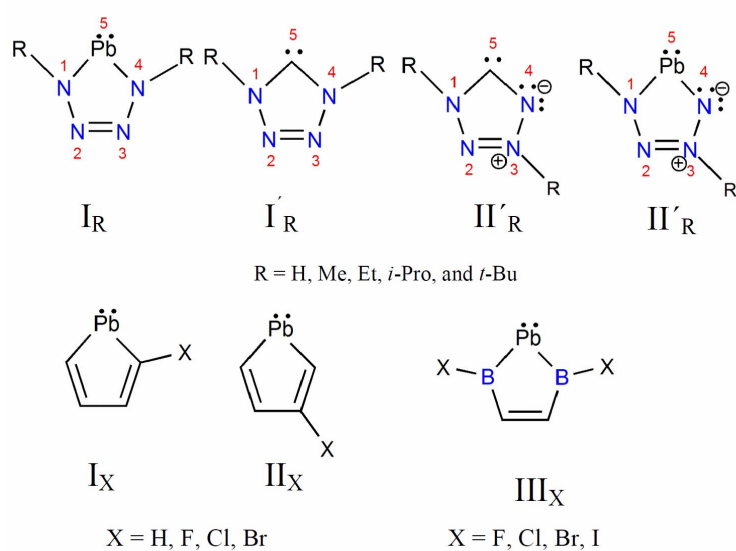
### Dihedral Angles ( $Pb^{\delta}-N_1-N_2-N_3$ , $D$ ) or Degrees of Puckering for $I_R$ and $II_R$ Plumbylenes

While puckering is known as a source of stability for many cyclic compounds, none of the rather aromatic species ( $I_R$  and  $II_R$ ), except  $II_{t-Bu}$ , showed any degree of puckering (Table 2).

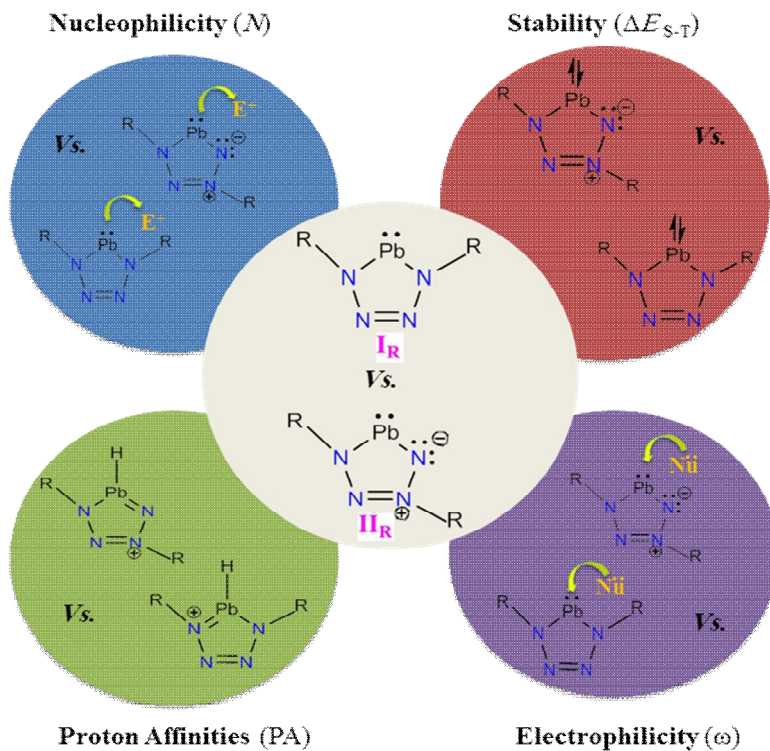
### Nucleophilicity ( $N$ ) vs. Plumbylene Bond Angle ( $N-Pb^{\delta}-N$ , $Deg$ )

The  $N-Pb^{\delta}-N$  is increased from  $I_R$  to  $II_R$  plumbylene (Table 2). Likewise,  $N$  as well as  $Pb-N_1$  bond lengths increase from  $I_R$  to their corresponding  $II_R$  plumbylenes (Fig. 1, Table 2).

With a smaller divalent angle, more p character is imposed on the covalent  $sp^2$  bonding orbitals. The greater s character of nonbonding  $\sigma$  orbital in plumbylene compensates for the change in bonding orbitals. Moreover, it reduces the  $\sigma$  orbital energy state and increases the  $\sigma-p_{\pi}$  gap, producing acceptable singlet and triplet (relatively unstable) states [44]. Therefore, the greater s character of  $\sigma$  orbital shortens the orbital and reduces nucleophilicity [45,46].



**Fig. 1.** Reported divalents:  $I_X$ ,  $II_X$  [21],  $III_X$  [22],  $I'_R$ ,  $II'_R$  [33] along with the ones scrutinized in this work including 1,4-(R)tetrazol-5-plumbylenes ( $I_R$ ), and 1,3-(R)tetrazol-5-plumbylenes ( $II_R$ ).



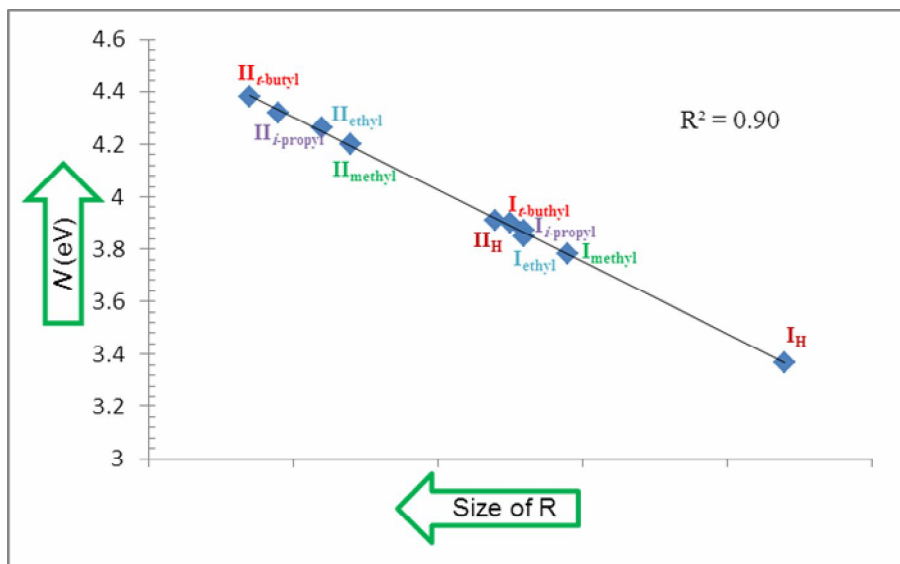
**Fig. 2.** A flow chart for scrutiny of normal vs. abnormal tetrazole-5-ylidenes ( $I_R$  and  $II_R$ , respectively), for R = H, Me, Et, *i*-Pro, and *t*-Bu.

**Table 1.** The Highest Occupied Molecular Orbital Energies ( $E_{\text{HOMO}}/\text{eV}$ ) and the Lowest Unoccupied Molecular Orbital Energies ( $E_{\text{LUMO}}/\text{eV}$ ), along with HOMO-LUMO Energy Differences ( $\Delta E_{\text{HOMO-LUMO}}$ , kcal mol<sup>-1</sup>), Singlet-triplet Energy Gaps ( $\Delta E_{\text{S-T}}$ , kcal mol<sup>-1</sup>) and Nucleophilicity ( $N$ , eV) for Singlet States of Scrutinized NHPbs and NHCs (Table 1 Top and Bottom Portions, Respectively) at B3LYP/6-311++G\*\*

NHPbs	$E_{\text{HOMO}}$	$E_{\text{LUMO}}$	$\Delta E_{\text{HOMO-LUMO}}$	$\Delta E_{\text{S-T}}$	$N$
I <sub>H</sub>	-6.10	-2.00	94.65	44.18	3.37
I <sub>Me</sub>	-5.69	-1.89	87.65	37.53	3.78
I <sub>Et</sub>	-5.62	-1.83	87.34	37.16	3.85
I <sub><i>i-Pro</i></sub>	-5.60	-1.82	87.28	38.38	3.87
I <sub><i>t-Bu</i></sub>	-5.57	-1.78	87.42	45.95	3.90
II <sub>H</sub>	-5.56	-1.61	91.01	40.02	3.91
II <sub>Me</sub>	-5.27	-1.47	87.65	37.82	4.20
II <sub>Et</sub>	-5.21	-1.44	86.92	37.63	4.26
II <sub><i>i-Pro</i></sub>	-5.14	-1.39	86.68	37.44	4.32
II <sub><i>t-Bu</i></sub>	-5.08	-1.34	86.28	37.41	4.38

NHCs	$E_{\text{HOMO}}$	$E_{\text{LUMO}}$	$\Delta E_{\text{HOMO-LUMO}}$	$\Delta E_{\text{S-T}}$	$N$
I' <sub>H</sub>	-7.37	-1.17	143.06	87.53	2.10
I' <sub>Me</sub>	-6.92	-0.93	138.1	87.28	2.55
I' <sub>Et</sub>	-6.84	-0.78	139.66	87.72	2.63
I' <sub><i>i-Pro</i></sub>	-6.75	-0.65	140.69	86.88	2.72
I' <sub><i>t-Bu</i></sub>	-6.56	-0.61	137.22	86.17	2.91
II' <sub>H</sub>	-6.54	-1.99	104.97	52.44	2.93
II' <sub>Me</sub>	-6.10	-1.54	105.07	54.77	3.37
II' <sub>Et</sub>	-6.00	-1.40	106.05	55.53	3.47
II' <sub><i>i-Pro</i></sub>	-5.93	-1.28	107.18	55.84	3.54
II' <sub><i>t-Bu</i></sub>	-5.80	-1.08	108.84	54.29	3.67



**Fig. 3.** Nucleophilicity ( $N$ ) as a function of substituent size for two series of plumbylene ( $I_R$  and  $II_R$ ).

**Table 2.** Geometrical Parameters Including Plumbylene Bond Angles ( $N-Pb-N$ , Deg), and Dihedral Angles ( $Pb-N_1-N_2-N_3$ , D) in Degrees, Carbenic Bond Lengths ( $\text{\AA}$ ), Proton Affinities (PA,  $\text{kcal mol}^{-1}$ ), and Global Electrophilicity ( $\omega$ ) at B3LYP/6-311++G\*\* Level of Theory

Plumbylenes	$N-Pb-N$	D	$N_4-Pb$	$Pb-N_1$	$\omega$	PA
$I_H$	70.39	0.01	2.131	2.131	-1.98	139.31
$I_{Me}$	71.58	0.01	2.137	2.137	-1.89	183.23
$I_{Et}$	71.40	0.00	2.145	2.145	-1.83	187.00
$I_{i-Pro}$	71.15	0.00	2.144	2.144	-1.82	190.13
$I_{t-Bu}$	71.95	0.01	2.145	2.145	-1.78	191.39
$II_H$	73.86	0.00	2.103	2.206	-1.63	178.84
$II_{Me}$	73.99	0.00	2.093	2.211	-1.49	197.66
$II_{Et}$	73.93	0.00	2.092	2.220	-1.47	200.80
$II_{i-Pro}$	74.04	0.09	2.093	2.217	-1.42	205.82
$II_{t-Bu}$	73.93	0.27	2.090	2.215	-1.38	210.84

### Nucleophilicity and Stability of Plumbylenes vs. their Corresponding Carbenes

Stability of carbenes and their heavy analogues are presumed to be related to their corresponding singlet-triplet energy gaps ( $\Delta E_{S-T} = E_T - E_S$ ). A higher stability for a singlet state is indicated by its positive  $\Delta E_{S-T}$ , while a negative value for the latter corresponds to a higher stability for the triplet state [47]. Stability for ten scrutinized plumbylenes are calculated at B3LYP/6-311++G\*\* level of theory (Table 1). Evidently, our singlet state NHPbs appear to be more stable than their corresponding triplet states.

Stability of plumbylenes  $I_R$  and  $II_R$  and their corresponding carbenes  $I'_R$  and  $II'_R$  (Fig. 1) are presumed to be related to their  $\Delta E_{S-T}$ . Interestingly, every plumbylene appears to be less stable, with a lower band gap ( $\Delta E_{HOMO-LUMO}$ ), and a higher  $N$  than its corresponding carbene, at B3LYP/6-311++G\*\* level of theory (Table 1). On the other hand, each  $II_R$  appears to be less stable, but more nucleophilic than its corresponding  $I_R$ . For instance, plumbylene  $II_{t-Bu}$  (with  $\Delta E_{S-T} = 37.41$  kcal mol<sup>-1</sup> and  $N = 4.38$  eV) is less stable but more nucleophilic than plumbylene  $I_{t-Bu}$  (with  $\Delta E_{S-T} = 45.95$  kcal mol<sup>-1</sup> and  $N = 3.90$  eV). Likewise, each  $II'_R$  appears to be less stable, but more nucleophilic than  $I'_R$ . For instance, carbene  $II'_{t-Bu}$  (with  $\Delta E_{S-T} = 54.29$  kcal mol<sup>-1</sup> and  $N = 3.67$  eV) is less stable but more nucleophilic than carbene  $I'_{t-Bu}$  (with  $\Delta E_{S-T} = 86.17$  kcal mol<sup>-1</sup> and  $N = 2.91$  eV).

### Nucleophilicity ( $N$ ) vs. Proton Affinity (PA)

The reaction induces the NHC catalyst formation from its salt through deprotonation; as a result, carbene basicity (salt acidity) greatly affects catalytic function. Overall, various experimental [48-53] and calculated [54-58] data have been reported regarding proton affinity and carbenes basicity.

Our calculated PA, kcal mol<sup>-1</sup> in  $I_R$  and  $II_R$  series takes on a trend with an exactly opposite direction from  $\Delta E_{HOMO-LUMO}$  (Table 1). The band gap of every  $II_R$  appears to be narrower than its corresponding  $I_R$ . The proton affinity of every  $II_R$  is more than its corresponding  $I_R$  and for  $II_R$  series the trend of proton affinity is similar to the nucleophilicity. This result indicates that every  $II_R$  plumbylene with narrower  $\Delta E_{HOMO-LUMO}$  and higher proton affinity is more reactive or nucleophilic than its corresponding  $I_R$ . For instance, in  $II_R$  series,  $II_{t-Bu}$  with ( $\Delta E_{HOMO-LUMO} = 86.28$

Kcal mol<sup>-1</sup>) and (PA = 210.84 kcal mol<sup>-1</sup>) is more reactive than others, and in  $I_R$  series,  $I_{t-Bu}$  with ( $\Delta E_{HOMO-LUMO} = 87.42$  kcal mol<sup>-1</sup>) and (PA = 191.39 kcal mol<sup>-1</sup>) is more reactive than others (Tables 1, 2).  $\Delta E_{HOMO-LUMO}$  for ten scrutinized plumbylene, appears to be a function of PA with a correlation factor of  $R^2 = 0.88$  (Table 3, Fig. 4).

### Nuclear Independent Chemical Shift (NICS)

For the assessment of aromaticity in molecules, magnetic criteria can be applied. Owing to its effectiveness and simplicity, nucleus-independent chemical shifts (NICS) parameter is now among aromaticity criteria [59,60]. NICS is a shielding constant of a virtual atom, situated near a molecule for probing the generated ring current. In the current study, the NICS-1 parameter was applied. This parameter is measured at 1 Å above the molecular ring center and is responsible for p-electron involvement; it is also free of s-electrons. In general, negative and positive NICS-1 values represent aromaticity and antiaromaticity, respectively.

For singlet plumbylenes  $I_R$  and  $II_R$ , NICS values are calculated at 0.5, 1, 1.5, 2, 2.5 and 3 Å above the ring center at B3LYP/6-311++G\*\* level of theory (Table 4). Each  $II_R$  (except  $II_H$ ) shows more aromaticity and nucleophilicity than its corresponding  $I_R$  isomer (Tables 1, 4).

### Atomic Charge Natural Bond Orbital (NBO)

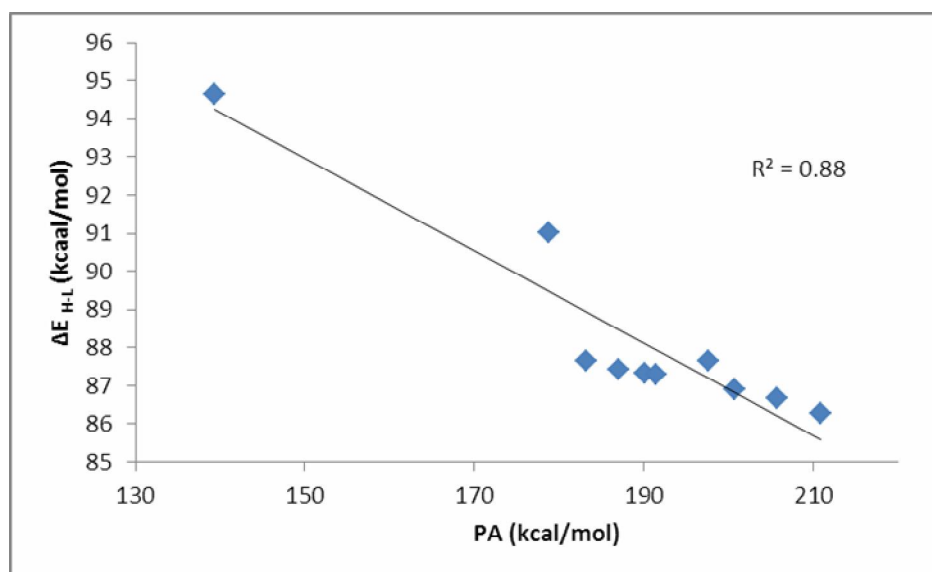
Natural bond orbital (NBO) analyses of our NHPbs were carried out at B3LYP/6-311++G\*\* (Table 5). Divalent Pb atoms display charges of +1.00 to +1.09, which appear in contrast to the reported atomic charges for their corresponding carbenes (-0.19 to -0.37) [30]. This may be attributed to the lower Pauling electronegativity of Pb (2.33) compared to that of C (2.55). Charges on Pb atoms of normal  $I_R$  are slightly higher than their corresponding abnormal  $II_R$  isomers.

### CONCLUSIONS

A comparison is made between nucleophilicity ( $N$ ), electrophilicity ( $\omega$ ), proton affinity (PA), substituent size ( $R$ ), plumbylene bond angle ( $N-Pb-N$ ), nucleus independent chemical shift (NICS, as a measure of

**Table 3.** Direct or Inverse Proportionality Correlations ( $R^2$ ) between the Main Thermodynamic and Structural Parameters of our Scrutinized Plumbylenes  $I_R$  and  $II_R$ , Including Nucleophilicity ( $N$ ), Substituent Size ( $R$ ), Proton Affinity (PA), Band Gap ( $\Delta E_{\text{HOMO-LUMO}}$ ), Electrophilicity ( $\omega$ ), and Bond Angle ( $N-\hat{p}\hat{b}-N$ ) at B3LYP/6-311++G\*\* 1 Level of Theory (See Supplementary Information Fig. S1)

Parameter <sub>1</sub>	vs. Parameter <sub>2</sub>	$R^2$	Proportionality
$N$	$R$	0.90	Direct
$N$	$\omega$	0.90	Inverse
$N$	PA	0.88	Direct
$N$	$N-\hat{p}\hat{b}-N$	0.77	Direct
$N$	$\Delta E_{\text{HOMO-LUMO}}$	0.60	Inverse
PA	$\Delta E_{\text{HOMO-LUMO}}$	0.88	Inverse
PA	$R$	0.66	Direct
PA	$\omega$	0.62	Direct
PA	$N-\hat{p}\hat{b}-N$	0.5	Direct
$\omega$	$R$	0.96	Inverse
$\omega$	$N-\hat{p}\hat{b}-N$	0.90	Direct
$N-\hat{p}\hat{b}-N$	$R$	0.83	Direct



**Fig. 4.** Bond gap ( $\Delta E_{\text{HOMO-LUMO}}$ ) of normal and abnormal tetrazol-5-plumbylene as a function of their proton affinity (PA,  $\text{kcal mol}^{-1}$ ) with a correlation factor of  $R^2 = 0.88$ .

**Table 4.** The Nucleus Independent Chemical Shift (NICS) Calculated at 0.5, 1, 1.5, 2, 2.5 and 3 Å above the Ring Center for Singlet Plumbylenes I<sub>R</sub> and II<sub>R</sub>, at B3LYP/6-311++G\*\* Level of Theory

NHPbs	I <sub>H</sub>	I <sub>Me</sub>	I <sub>Et</sub>	I <sub><i>i</i>-Pro</sub>	I <sub><i>t</i>-Bu</sub>
NICS (0)	-11.99	-8.79	-8.06	-8.26	-4.21
NICS (0.5)	-12.21	-9.53	-9.20	-8.53	-5.68
NICS (1)	-10.18	-8.48	-8.44	-6.68	-6.17
NICS (1.5)	-6.83	-5.89	-5.77	-4.37	-4.77
NICS (2)	-4.26	-3.75	-3.56	-2.67	-3.07
NICS (2.5)	-2.66	-2.34	-2.19	-1.66	-1.81
NICS (3)	-1.70	-1.49	-1.40	-1.04	-1.05

NHPbs	II <sub>H</sub>	II <sub>Me</sub>	II <sub>Et</sub>	II <sub><i>i</i>-Pro</sub>	II <sub><i>t</i>-Bu</sub>
NICS (0)	-11.14	-9.66	-9.57	-9.11	-8.10
NICS (0.5)	-11.53	-10.21	-10.52	-9.97	-9.22
NICS (1)	-10.05	-9.15	-9.76	-9.22	-8.95
NICS (1.5)	-7.16	-6.620	-7.22	-6.86	-7.15
NICS (2)	-4.71	-4.49	-4.87	-4.75	-5.25
NICS (2.5)	-3.03	-2.98	-3.18	-3.21	-3.60
NICS (3)	-1.97	-1.98	-2.07	-2.15	-2.38

aromaticity), band gap ( $\Delta E_{\text{HOMO-LUMO}}$ ), and singlet-triplet energy gap ( $\Delta E_{\text{S-T}}$ , assumed as a measure of stability) for a series of 1,4-(R), “normal”, tetrazol-5-plumbylenes (I<sub>R</sub>), vs. their corresponding 1,3-(R), “mesoionic<sub>a</sub> or abnormal”, isomers (II<sub>R</sub>), at the B3LYP/6-311++G\*\* level of theory, where R = H, Me, Et, *i*-Pro, and *t*-Bu. For every scrutinized plumpylyene, *N* appears directly proportional to its R, PA, and N- $\widehat{p\hat{b}}$ -N, while being indirectly proportional with  $\omega$ , and  $\Delta E_{\text{HOMO-LUMO}}$  with correlation factors ( $R^2$ ) = 0.90, 0.88, 0.77, 0.90 and 0.60, respectively. Changes of R directly affect on *N*, N- $\widehat{p\hat{b}}$ -N, and PA with  $R^2$  = 0.90, 0.83 and 0.66, respectively. The results of our calculations indicate that each II<sub>R</sub> is more nucleophilic than its corresponding I<sub>R</sub>

isomer for exhibiting a larger *N*. In addition, a comparison between NHPbs and NHCs indicates that the former is more nucleophilic than its corresponding NHCs. The trend of the calculated global electrophilicity ( $\omega$ ) is exactly opposite of that for *N*. The least stable in the II<sub>R</sub> is II<sub>*t*-Bu</sub> with more nucleophilicity. Except for II<sub>*t*-Bu</sub>, none of the rather aromatic species scrutinized (I<sub>R</sub> and II<sub>R</sub>), show any degrees of puckering. The N- $\widehat{p\hat{b}}$ -N is increased from I<sub>R</sub> to II<sub>R</sub> plumbylene. Likewise, nucleophilicity is increased from I<sub>R</sub> to II<sub>R</sub> plumbylene. The proton affinity of each II<sub>R</sub> is more than its corresponding I<sub>R</sub>. This result indicates that every II<sub>R</sub> plumbylene with narrower  $\Delta E_{\text{HOMO-LUMO}}$  and higher proton affinity is more active or nucleophilic than its corresponding



**Table 5.** NBO Atomic Charges on  $Pb_5$  and  $N_1-N_4$ , for Two Series of Plumbylene ( $I_R$  and  $II_R$ ), at B3LYP/6-311++G\*\* Level of Theory

Plumbylenes	$Pb_5$	$N_1$	$N_2$	$N_3$	$N_4$
$I_H$	1.09	-0.84	-0.08	-0.08	-0.84
$I_{Me}$	1.04	-0.64	-0.09	-0.09	-0.64
$I_{Et}$	1.02	-0.63	-0.89	-0.89	-0.63
$I_{i-Pro}$	1.03	-0.63	-0.09	-0.09	-0.63
$I_{i-Bu}$	1.05	-0.64	-0.10	-0.10	-0.64
$II_H$	1.02	-0.76	-0.12	-0.12	-0.78
$II_{Me}$	1.01	-0.57	-0.13	-0.01	-0.80
$II_{Et}$	1.00	-0.56	-0.12	-0.02	-0.80
$II_{i-Pro}$	1.00	-0.56	-0.13	-0.02	-0.80
$II_{i-Bu}$	1.00	-0.56	-0.14	-0.02	-0.80

$I_R$ . In  $II_R$  series,  $II_{i-Bu}$  ( $\Delta E_{HOMO-LUMO} = 86.28 \text{ kcal mol}^{-1}$  and  $PA = 210.84 \text{ kcal mol}^{-1}$ ) is more reactive than the other  $II_R$  series. In  $I_R$  series,  $I_{i-Bu}$  with  $\Delta E_{HOMO-LUMO} = 87.42 \text{ kcal mol}^{-1}$  and  $PA = 191.39 \text{ kcal mol}^{-1}$  is more reactive than its  $I_R$  analogs.  $\Delta E_{HOMO-LUMO}$  for ten scrutinized plumbylene, appears as a function of  $PA$ ,  $\text{kcal mol}^{-1}$  with a correlation factor of  $R^2 = 0.88$

## ACKNOWLEDGMENTS

Support from Tarbiat Modares University (TMU) is gratefully acknowledged.

## REFERENCES

- [1] Heitmann, D.; Pape, T.; Hepp, A.; Mück-Lichtenfeld, C.; Grimme, S.; Hahn, F. E., Palladium and platinum complexes of a benzannulated n-heterocyclic plumbylene with an unusual bonding mode. *J. Am. Chem. Soc.* **2011**, *133*, 11118-11120, DOI: 10.1021/ja204955f.
- [2] Arp, H.; Baumgartner, J.; Marschner, C.; Zark, P.; Müller, T., Coordination chemistry of cyclic disilylated stannylenes and plumbylenes to group 4 metallocenes. *J. Am. Chem. Soc.* **2012**, *134*, 10864-10875, DOI: 10.1021/ja301547x.
- [3] Charmant, J. P. H.; Haddow, M. F.; Hahn, F. E.; Heitmann, D.; Frohlich, R.; Mansell, S. M.; Russell, C. A.; Wass, D. F., Syntheses and molecular structures of some saturated N-heterocyclic plumbylenes. *Dalton Trans.* **2008**, *43*, 6055-6059, DOI: 10.1039/B808717B.
- [4] Gehrus, B.; Hitchcock, P. B.; Lappert, M. F., Crystalline (NN)C-M(NN) complexes: synthesis, structure, bonding and lability [M = Si, Ge, Sn or Pb; (NN) = 1,2-(ButCH<sub>2</sub>N)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>]. *J. Chem. Soc., Dalton Trans.* **2000**, *18*, 3094-3099, DOI: 10.1039/B005216G.
- [5] Barrau, J.; Rima, G., Stable germanium analogs of carbenes, imines, ketones, thiones, selones and tellones. *Coord. Chem. Rev.* **1998**, *178-180*, 593-622, DOI: 10.1016/S0010-8545(98)00076-9.
- [6] Tokitoh, N.; Okazaki, R., Recent topics in the chemistry of heavier congeners of carbenes. *Coord.*

- Chem. Rev.* **2000**, *210*, 251-277, DOI: 10.1016/S0010-8545(00)00313-1.
- [7] Kira, M., Isolable silylene, disilenes, trisilaallene, and related compounds, *J. Organomet. Chem.* **2004**, *689*, 4475-4486, DOI: 10.1016/j.jorganchem.2004.05.054.
- [8] Weidenbruch, M., Some silicon, germanium, tin, and lead analogues of carbenes, alkenes, and dienes. *Eur. J. Inorg. Chem.* **1999**, 373-381, DOI: 10.1002/(SICI)1099-0682.
- [9] Veith, M., Unsaturated molecules containing main group metals. *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 1-14, DOI: 10.1002/anie.198700013.
- [10] Kühl, O., N-heterocyclic germylenes and related compounds. *Coord. Chem. Rev.* **2004**, *248*, 411-427, DOI: 10.1016/j.ccr.2003.12.004.
- [11] Hill, N. J.; West, R., Recent developments in the chemistry of stable silylenes. *J. Organomet. Chem.* **2004**, *689*, 4165-4183, DOI: 10.1016/j.jorganchem.2004.09.012.
- [12] Gehrhus, B.; Lappert, M. F., Chemistry of thermally stable bis(amino)silylenes. *J. Organomet. Chem.* **2001**, *617-618*, 209-223, DOI: 10.1016/S0022-328X(00)00729-4.
- [13] Davidson, P. J.; Lappert, M. F., Stabilisation of metals in a low co-ordinative environment using the Bis(trimethylsilyl)methyl ligand; coloured SnII and PbII alkyls,  $M[CH(SiMe_3)_2]_2$ . *J. Chem. Soc. Chem. Commun.* **1973**, 317, DOI: 10.1039/C3973000317A.
- [14] Goldberg, D. E.; Harris, D. H.; Lappert, M. F.; Thomas, K. M., A new synthesis of divalent group 4B alkyls  $M[CH(SiMe_3)_2]_2$  ( $M = Ge$  or  $Sn$ ), and the crystal and molecular structure of the tin compound. *J. Chem. Soc. Chem. Commun.* **1976**, 261-262, DOI: 10.1039/C39760000261.
- [15] Izod, K.; Wills, C.; Clegg, W.; Harrington, R. W., Seven-membered cyclic dialkylstannylene and -plumbylene compounds stabilized by agostic-type B-H ··· E interactions [ $E = Sn, Pb$ ]. *Organometallics.* **2009**, *28*, 2211-2217, DOI: 10.1021/om801189h.
- [16] Bourissou, D.; Guerret, O.; Gabbai, F. P.; Bertrand, G., Stable carbenes. *Chem. Rev.* **2000**, *100*, 39-91, DOI: 10.1021/cr940472u.
- [17] Harrison, P. G., *Comprehensive Organometallic Chemistry*. Pergamon: Oxford, 1984, p. 629-674.
- [18] Harrison, P. G., *Comprehensive Organometallic Chemistry II*. Elsevier: Amsterdam: 1995; p. 305-319
- [19] Kaupp, M.; Schleyer, P. V. R., *Ab initio* study of structures and stabilities of substituted lead compounds. Why is inorganic lead chemistry dominated by PbII but organolead chemistry by Pb IV?. *J. Am. Chem. Soc.* **1993**, *115*, 1061-1073, DOI: 10.1021/ja00056a034.
- [20] Braunschweig, H.; Damme, A.; Dewhurst, R. D.; Hupp, F.; Jimenez-Halla, J. O. C.; Radacki, K.,  $\sigma$ -Donor- $\sigma$ -acceptor plumbylene ligands: synergic  $\sigma$ -donation between ambiphilic Pt0 and PbII fragments. *Chem. Commun.* **2012**, *48*, 10410-10412, DOI: 10.1039/C2CC35777A.
- [21] Kassae, M. Z.; Arshadi, S.; Acedy, M.; Vessally, E., Singlet-triplet energy separations in divalent five-membered cyclic conjugated  $C_5H_3X$ ,  $C_4H_3SiX$ ,  $C_4H_3GeX$ ,  $C_4H_3SnX$ , and  $C_4H_3PbX$  ( $X = H, F, Cl$ , and  $Br$ ). *J. Organometal. Chem.* **2005**, *690*, 3427-3439, DOI: 10.1016/j.jorganchem.2005.04.030.
- [22] Akbari, A.; Golzadeh, B.; Arshadi, S.; Kassae, M. Z., A quest for stable 2,5-bis(halobora)-cyclopentenylidene and its Si, Ge, Sn and Pb analogs at theoretical levels. *RSC Adv.* **2015**, *5*, 43319-43327, DOI: 10.1039/C5RA04911C.
- [23] Kassae, M. Z.; Musavi, S. M.; Ghambarian, M., Divalent propargylenic  $C_2H_2M$  group 14 elements: Structures and singlet-triplet energy splitting ( $M = C, Si, Ge, Sn$  and  $Pb$ ). *J. Mol. Struct.: THEOCHEM.* **2005**, *731*, 225-231, DOI: 10.1016/j.theochem.2005.06.033.
- [24] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C.

- Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. Gaussian 98, revision A.7; Gaussian, Inc.: Pittsburgh, PA, 1998.
- [25] Frisch, M. J.; Pople, J. A.; Binkley, J. S., Self consistent molecular orbital methods 25. Supplementary functions for Gaussian basis sets. *J. Chem. Phys.* **1984**, *80*, 3265-3269, DOI: 10.1063/1.447079.
- [26] Becke, A. D., Density-functional thermochemistry. III. The role of exact exchange. *J. Chem. Phys.* **1993**, *98*, 5648-5652, DOI: 10.1063/1.464913.
- [27] Lee, C.; Yang, W.; Parr, R. G., Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Phys. Rev. B: Condens. Mater.* **1988**, *37*, 785-789, DOI: 10.1103/PhysRevB.37.785.
- [28] Schlegel, H. B.; Frisch, M. J., Transformation between cartesian and pure spherical harmonic Gaussians. *Int. J. Quantum Chem.* **1995**, *54*, 83-87, DOI: 10.1002/qua.560540202.
- [29] Curtiss, L. A.; McGrath, M. P.; Blaudeau, J. P.; Davis, N. E.; Binning Jr. R. C.; Radom, L., Extension of Gaussian2 theory to molecules containing thirdrow atoms Ga-Kr. *J. Chem. Phys.*, **1995**, *103*, 6104-6113, DOI: 10.1063/1.470438.
- [30] Foresman, J. B. in: E. Frisch (Ed.), Exploring Chemistry with Electronic Structure Methods: a Guide to Using Gaussian. Gaussian Inc., Pittsburg, PA, 1996.
- [31] Domingo, L. R.; Chamorro, E.; Pérez, P. J., Understanding the reactivity of captodative ethylenes in polar cycloaddition reactions. A theoretical study. *J. Org. Chem.* **2008**, *73*, 4615-4624, DOI: 10.1021/jo800572a.
- [32] Kassae, M. Z.; Najafi, Z.; Shakib, F. A.; Momeni, M. R., Stable silylenes with acyclic, cyclic, and unsaturated cyclic structures: Effects of heteroatoms and cyclopropyl substituents at DFT. *J. Organometal. Chem.*, **2011**, *696*, 2059-2064, DOI: 10.1016/j.jorganchem.2010.10.065.
- [33] Momeni, M. R.; Shakib, F. A., Beyond conventional N-heterocyclic silylenes: A density functional approach toward structural features and catalytic applications. *Comput. Theoretical Chem.*, **2012**, *985*, 62-66, DOI: 10.1016/j.comptc.2012.01.040.
- [34] Kassae, M. Z.; Zandi, H.; Haerizade, B. N.; Ghambarian, M., Effects of  $\alpha$ -mono heteroatoms (N vs. P), and  $\beta$ -conjugation on cyclic silylenes. *Comput. Theoretical Chem.*, **2012**, *1001*, 39-43, DOI: org/10.1016/j.comptc.2012.10.005.
- [35] Amani, J.; Musavi, S. M.; Riazikia, M., Isomeric pyridylcarbenes and their Si and Ge heavier analogues at DFT: stabilization through  $\pi$ -p or n-p interaction. *Tetrahedron*, **2012**, *68*, 2061-2067, DOI: 10.1016/j.tet.2011.12.081.
- [36] Kassae, M. Z.; Zandi, H.; Momeni, M. R.; Shakib, F. A.; Ghambarian, M., Toward stable N-heterocyclic silylenes at theoretical levels. *J. Mol. Struct.: THEOCHEM*, **2009**, *913*, 16-21, DOI: 10.1016/j.theochem.2009.07.001.
- [37] Kassae, M. Z.; Zandi, H., P-Heterocyclic silylenes: a survey of stability with density functional theory. *J. Phys. Org. Chem*, **2012**, *25*, 50-57, DOI: 10.1002/poc.1867.
- [38] Amani, J.; Musavi, S. M.; Riazikia, M., Diazinylcarbenes and their heavier analogues at DFT: An intramolecular stabilization of singlet Si and Ge divalent centers. *Organometallics*, **2012**, *31*, 4157-4165, DOI: org/10.1021/om201264d.
- [39] Kassae, M. Z.; Momeni, M. R.; Shakib, F. A.; Ghambarian, M., Pyridine derived N-heterocyclic germlylenes: A density functional perspective. *J. Organometallic Chem.*, **2010**, *695*, 760-765, DOI: 10.1016/j.jorganchem.2009.12.013.
- [40] Parr, R. G.; Szentpaly, L.; Liu, S., Electrophilicity Index. *J. Am. Chem. Soc.* **1999**, *121*, 1922-1924, DOI: 10.1021/ja983494x.
- [41] Parr, R. G.; Pearson, R. G., Absolute hardness: companion parameter to absolute electronegativity. *J. Am. Chem. Soc.* **1983**, *105*, 7512-7516, DOI: 10.1021/ja00364a005.
- [42] Rezaee, N.; Ahmadi, A.; Kassae, M. Z., Nucleophilicity of normal and abnormal N-heterocyclic carbenes at DFT: steric effects on tetrazole-5-ylidenes. *RSC Adv.* **2016**, *6*, 13224-13233, DOI: 10.1039/C5RA21247B.

- [43] Amyes, T. L.; Diver, S. T.; Richard, J. P.; Rivas, F. M.; Toth, K., Formation and stability of N-heterocyclic carbenes in Water: the carbon acid pKa of imidazolium cations in aqueous solution. *J. Am. Chem. Soc.* **2004**, *126*, 4366-4374, DOI: 10.1021/ja039890j.
- [44] Kassaei, M. Z.; Shakib, F. A.; Momeni, M. R.; Ghambarian, M.; Musavi, S. M., A DFT study on pyridine-derived N-heterocyclic carbenes. *Tetrahedron.* **2009**, *65*, 10093-10098, DOI: 10.1016/j.tet.2009.09.043.
- [45] Sulzbach, H. M.; Bolton, E.; Lenoir, D.; Schleyer, P. V. R.; Schaefer, H. F., Tetra-tert-butylethylene: an elusive molecule with a highly twisted double bond. can it be made by carbene dimerization?. *J. Am. Chem. Soc.* **1996**, *118*, 9908-9914, DOI: 10.1021/ja960549r.
- [46] Liu, F.; Paton, R. S.; Kim, S.; Liang, Y.; Houk, K. N., Diels-Alder reactivities of strained and unstrained cycloalkenes with normal and inverse-electron-demand dienes: activation barriers and distortion/interaction analysis. *J. Am. Chem. Soc.* **2013**, *135*, 15642-15649, DOI: 10.1021/ja408437u.
- [47] Nemirowski, A.; Schreiner, P. R., Electronic Stabilization of Ground State Triplet Carbenes. *J. Org. Chem.*, **2007**, *72*, 9533-9540, DOI: 10.1021/jo701615x.
- [48] Alder, R. W.; Allen, P. R.; Williams, S. J., Stable carbenes as strong bases, *J. Chem. Soc. Chem. Commun.* **1995**, *12*, 1267-1268, DOI: 10.1039/C39950001267.
- [49] Kim, Y. -J.; Streitwieser, A., Basicity of a stable carbene, 1,3-Di-tert-butylimidazol-2-ylidene, in THF1. *J. Am. Chem. Soc.* **2002**, *124*, 5757-5761, DOI: 10.1021/ja025628j.
- [50] Chen, H.; Justes, D. R.; Cooks, R. G., Proton affinities of N-heterocyclic carbene super bases. *Org. Lett.* **2005**, *7*, 3949-3952, DOI: 10.1021/ol0514247.
- [51] Chu, Y.; Deng, H.; Cheng, J. -P., An acidity scale of 1,3-Dialkylimidazolium Salts in Dimethyl Sulfoxide Solution. *J. Org. Chem.* **2007**, *72*, 7790-7793, DOI: 10.1021/jo070973i.
- [52] Schroeder, M. A.; Makino, R. C., The relation between structure and reactivity in five-membered heteroaromatic compounds- II CND0/2 calculations on azolium cations and on the zwitterions resulting from their deprotonation. *Tetrahedron.* **1973**, *29*, 3469-3489, DOI: 10.1016/S0040-4020(01)93507-0.
- [53] Burke, A.; Balch, A. L.; Enemark, J. H., Palladium and platinum complexes resulting from the addition of hydrazine to coordinated isocyanide. *J. Am. Chem. Soc.* **1970**, *92*, 2555, DOI: 10.1021/ja00711a063.
- [54] Graham, D. C.; Cavell, K. J.; Yates, B. F., Dimerization mechanisms of heterocyclic carbenes. *J. Phys. Org. Chem.* **2005**, *18*, 298-309, DOI: 10.1002/poc.846.
- [55] Magill, A. M.; Cavell, K. J.; Yates, B. F., Basicity of nucleophilic carbenes in aqueous and nonaqueous solvents-theoretical predictions. *J. Am. Chem. Soc.* **2004**, *126*, 8717-8724, DOI: 10.1021/ja038973x.
- [56] Alder, R. W.; Blake, M. E.; Oliva, J. M., Diaminocarbenes; calculation of barriers to rotation about carbene-N bonds, barriers to dimerization, proton affinities, and <sup>13</sup>C NMR shifts. *J. Phys. Chem. A.* **1999**, *103*, 11200-11211, DOI: 10.1021/jp9934228.
- [57] Kassaei, M. Z.; Shakib, F. A.; Momeni, M. R.; Ghambarian, M.; Musavi, S. M., Carbenes with reduced heteroatom stabilization: a computational approach. *J. Org. Chem.* **2010**, *75*, 2539-2545, DOI: 10.1021/jo100022t.
- [58] Hollóczki, O.; Gerhard, D.; Massone, K.; Szarvas, L.; Németh, B.; Veszprémi, T.; Nyulászi, L., Carbenes in ionic liquids. *New J. Chem.* **2010**, *34*, 3004-3009, DOI: 10.1039/C0NJ00380H.
- [59] Chen, Z.; Wannere, C. S.; Corminboeuf, C.; Puchta, R.; Schleyer, P. V. R., Nucleus-independent chemical shifts (NICS) as an aromaticity criterion. *Chem. Rev.* **2005**, *105*, 3842-3888, DOI: 10.1021/cr030088+.
- [60] Schleyer, P. V. R.; Maerker, C.; Dransfeld, A.; Jiao, H.; Hommes, N. J. R. V. E., Nucleus-independent chemical shifts: a simple and efficient aromaticity probe. *J. Am. Chem. Soc.* **1996**, *118*, 6317-6318, DOI: 10.1021/ja960582d.