

Novel *N*-heterocyclic Stannylenes (NHSns) Using DFT

A.H. Zamanzadeh^a, N. Mohebi^a, M.Z. Kassae^{a,b,*}, P.T. Cummings^b and K. Dong^{b,c}

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

^bChemical and Biomolecular Engineering, Vanderbilt University, Nashville, TN 37240

^cInstitute of Process Engineering, Chinese Academy of Sciences, Beijing, 100190

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Substitution effects are probed for novel *N*-heterocyclic stannylenes (NHSns), including 1,4-di(R)-tetrazole-5-stannylenes (1_R), and 1,3-di(R)-tetrazole-5-stannylenes (2_R), using B3LYP/6-311++G** level of theory. Nucleophilicity, multiplicity, and stability are calculated for 1_R and 2_R ; R = H, methyl, ethyl, *i*-propyl, *t*-butyl, Ph, OH, methoxy, NO₂, CN and CF₃. Asymmetric 2_H appears to be more nucleophilic ($N \sim 4$) than its corresponding symmetric 1_H isomer ($N \sim 3$), mostly due to the higher separation of charge in the former group. The *N* is more sensitive to electronic effects in 1_R stannylenes than those in the 2_R series. Electron donating R groups increase *N* with Hammett ρ constants of -3.3 and -2.7 for 1_R and 2_R , respectively. Stannylene 2_H is slightly more aromatic (NICS (1) = -10.31) than 1_H (NICS (1) = -10.25). All 1_R isomers are more stable than the corresponding 2_R . However, all 2_R structures are generally more nucleophilic and aromatic than the corresponding 1_R . In addition, the former is less electrophilic with a larger band gap and narrower stannylene bond angle. Substituent effects are probed on *N* by devising proper isodesmic reactions. The trend for *N* is: $2_{t\text{-butyl}} > 2_{iso\text{-propyl}} > 2_{ethyl} > 2_{methyl} > 2_{ph} > 2_{OMeth} > 1_{t\text{-butyl}} > 2_{OH} > 2_H > 1_{Ph} > 1_{iso\text{-propyl}} > 1_{OH} > 1_{ethyl} > 1_{methyl} > 1_{OMeth} > 1_H > 2_{CF_3} > 2_{NO_2} > 2_{CN} > 1_{CF_3} > 1_{CN} > 1_{NO_2}$.

Keywords: Nucleophilicity, N-Heterocyclic, Stannylenes, DFT

INTRODUCTION

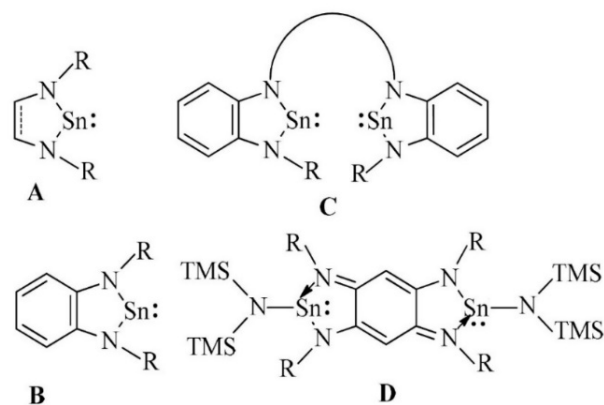
N-Heterocyclic stannylenes are a class of organotin (II) compounds that are analogues of *N*-heterocyclic carbenes (NHCs) and are mostly of interest as organocatalysts [1-7] and ligands in organometallic chemistry [8-11]. They are applied as spectator ligands [12-18], biologically relevant compounds [19-23], and in material sciences [24-27]. Unlike carbenes, which usually have a triplet ground state, stannylenes have a singlet ground state. So, in contrast to triplet H₂C:, the ground state of H₂Sn: is singlet [28-30]. This phenomenon is attributed to the valence orbitals of tin (Sn) that have less tendency to form hybrid orbitals and thus the electrons in 5s orbital are still paired up [31]. Free stannylenes stabilized by steric protection and adducts with

Lewis bases are acknowledged [32].

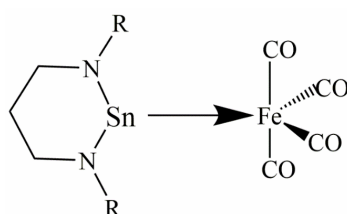
The coordination chemistry and synthesis of stannylene have been studied [33,34]. The NHSns are stabilized through coordination of π -electron-donating and electronegative heteroatoms to the Sn empty p-orbital [34]. The NHSns have the potential of replacing NHCs ligands in metal complexes. The type-A NHSns [35-37] may be used as ligands for transition metals [38-40] (Scheme 1). Similar to NHCs [12-14], NHSns may coordinate to metals and form active metal complexes (Scheme 2).

Here, we have chosen novel NHSns for their apparent compliance with the four criteria of aromaticity. Specifically, we have carried out the standard DFT calculations on normal (1_R) and abnormal (2_R), since they are cyclic, rather planar, and have six electrons that can be continuously conjugated while following the Hückel ($4n + 2$) rule (Fig. 1). Hence, thermodynamic parameters are assessed for stannylenes 1_R and 2_R ; R = H, methyl, ethyl,

*Corresponding author. E-mail: mohamad.z.kassae@vanderbilt.edu



Scheme 1. Examples of mono- and bi-dentate *N*-heterocyclic stannylenes A³⁵⁻³⁷, B⁴¹⁻⁴⁸, C⁴⁹⁻⁵¹ and D⁵³



Scheme 2. A possible example of an active metal complex of *N*-heterocyclic stannylene coordinated to a transition metal¹²⁻¹⁴

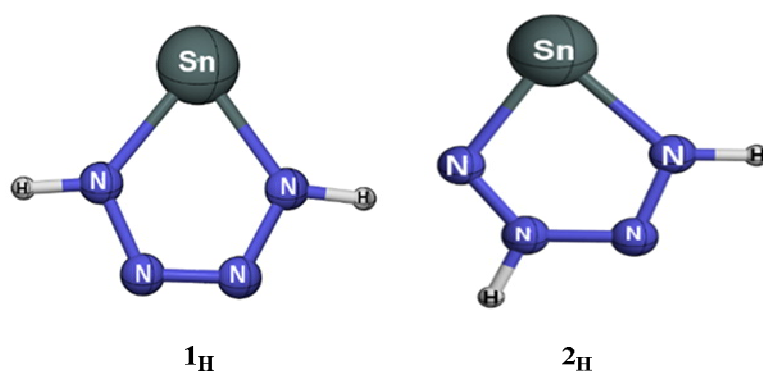


Fig. 1. Scrutinized normal 1,4-dihydro-tetrazastannole (1_H), and abnormal 1,3-dihydro-tetrazastannole (2_H), at DFT.

i-propyl, *t*-butyl, Ph, OH, methoxy, NO₂, CN and CF₃. In addition, steric effects are probed on *N* by devising proper isodesmic reactions.

COMPUTATIONAL METHODS

Geometry optimization were carried using B3LYP

hybrid functional [54,55], with 6-311++G(d,p) [56] in Gaussian 03 [57]. Minima and transition states appeared with zero and one imaginary frequency, respectively. Based on these measurements, Gibbs free energy, thermal correction, zero-point vibrational energy, enthalpy, and entropy at 298.15 K and 1.0 atm were measured.

The nucleophilicity index (*N*) [58] is measured as follows:

Table 1. The Highest Occupied Molecular Orbital Energies (E_{HOMO} /eV) and the Lowest Unoccupied Molecular Orbital Energies (E_{LUMO} /eV), along with HOMO-LUMO Energy Differences ($\Delta E_{\text{HOMO-LUMO}}$, kcal mol⁻¹), Singlet-triplet Energy Gaps ($\Delta E_{\text{S-T}}$, kcal mol⁻¹), Nucleophilicity (N), and Global Electrophilicity (ω) for the Singlet States of Scrutinized NHSns, at the B3LYP/6-311++G** Level

NHSns	E_{HOMO}	E_{LUMO}	$\Delta E_{\text{S-T}}$	$\Delta E_{\text{H-L}}$	N	ω
1 _H	-6.51	-2.06	51.07	102.4	2.99	-4.13
1 _{methyl}	-6.06	-1.94	43.95	95.00	3.44	-3.88
1 _{ethyl}	-6.02	-1.91	44.9	94.68	3.48	-3.83
1 _{iso-propyl}	-5.95	-1.85	44.47	94.66	3.55	-3.71
1 _{t-butyl}	-5.91	-1.80	45.84	94.74	3.59	-3.62
1 _{Ph}	-5.93	-2.47	38.73	79.75	3.56	-5.11
1 _{OH}	-5.95	-2.22	36.74	86.16	3.54	-4.47
1 _{OMeth}	-6.25	-2.22	38.5	92.72	3.25	-4.46
1 _{NO2}	-8.20	-4.13	50.66	93.92	1.29	-9.34
1 _{CN}	-7.99	-3.90	52.25	94.34	1.51	-8.63
1 _{CF3}	-7.88	-3.30	55.79	105.6	1.61	-6.83
2 _H	-5.93	-1.68	46.29	98.11	3.57	-3.40
2 _{methyl}	-5.61	-1.52	43.84	94.49	3.88	-3.10
2 _{ethyl}	-5.56	-1.48	43.93	94.10	3.94	-3.03
2 _{iso-propyl}	-5.48	-1.42	42.1	93.59	4.02	-2.93
2 _{t-butyl}	-5.47	-1.38	44.28	94.33	4.03	-2.87
2 _{ph}	-5.63	-2.02	39.23	83.14	3.87	-4.06
2 _{OH}	-5.92	-2.01	37.04	90.26	3.58	-4.02
2 _{OMeth}	-5.78	-1.88	37.39	89.97	3.72	-3.75
2 _{NO2}	-7.24	-3.65	36.21	82.90	2.26	-8.25
2 _{CN}	-7.37	-3.46	40.28	90.19	2.13	-7.50
2 _{CF3}	-6.98	-2.75	45.65	97.54	2.52	-5.59

$$N = E_{\text{HOMO(Nu)}} - E_{\text{HOMO(TCNE)}}$$

where HOMO(Nu) is that of NHSns and HOMO(TCNE) representing the reference tetracyanoethylene. In addition,

for determining global electrophilicity (ω) [59], the following formula is used:

$$\omega = (\mu^2/2\eta)$$

Table 2. Geometrical Parameters Including Stannylenes Bond Angles (N- $\hat{S}\hat{n}$ -N) (deg), and Dihedral Angle (Sn-N₁-N₂-N₃, D) in Degrees, at the B3LYP/6-311++G** Level of Theory

Normal NHSns	N- $\hat{S}\hat{n}$ -N	D	Abnormal NHSns	N- $\hat{S}\hat{n}$ -N	D
1 _H	72.21	0.000	2 _H	75.46	0.000
1 _{methyl}	73.52	0.001	2 _{methyl}	75.78	0.004
1 _{ethyl}	73.64	0.455	2 _{ethyl}	75.85	0.268
1 _{iso-propyl}	73.7	0.377	2 _{iso-propyl}	75.85	0.442
1 _{t-butyl}	73.97	0.007	2 _{t-butyl}	75.8	0.002
1 _{Ph}	73.46	0.861	2 _{Ph}	75.34	1.586
1 _{OH}	68.84	0.000	2 _{OH}	73.44	0.653
1 _{OMeth}	69.95	0.836	2 _{OMeth}	73.74	0.091
1 _{NO₂}	67.47	0.059	2 _{NO₂}	72.56	0.021
1 _{CN}	71.57	0.000	2 _{CN}	74.1	0.023
1 _{CF₃}	71.09	0.007	2 _{CF₃}	74.1	0.025

where μ ($\mu = (E_{\text{HOMO}} + E_{\text{LUMO}})/2$) is chemical potential and η ($\eta = (E_{\text{HOMO}} - E_{\text{LUMO}})$) is hardness [60].

RESULTS AND DISCUSSION

Theoretical measurements were employed to compare substitution effects on thermodynamic parameters of 1_R and 2_R at DFT. Optimized structure of 1_H and 2_H are shown as the examples (Fig. 1).

Here, we have calculated stability ($\Delta E_{\text{S-T}} = E_{\text{T}} - E_{\text{S}}$), nucleophilicity (N), electrophilicity (ω), and band gap ($\Delta E_{\text{HOMO-LUMO}}$), for stannylenes with various groups including R = H, methyl, *t*-butyl, ethyl, *i*-propyl, Ph, OH, methoxy, NO₂, CN, and CF₃.

The nucleophilicity index (N) was first reported by Domingo and colleagues [57]. Generally, all 2_R isomers

show a greater N compared to 1_R isomers (Table 1). As the results indicate, 2_{*t*-butyl} ($N = 4.03$ eV) shows a greater N in comparison with its 1_{*t*-butyl} isomer ($N = 3.59$ eV) (Table 1). This finding has many implications. First, asymmetric 2_R stannylenes exhibit more kinetic accessibility in comparison with their corresponding symmetric 1_R isomers, which have a greater steric hindrance. Second, stannylene angle for every 2_R exceeds that of the corresponding 1_R (Table 2). For instance, the stannylene angle is nearly 2.26° wider for 2_{methyl} compared to 1_{methyl} (Table 2). Third, for all 2_R (except for 2_{Ph} and 2_{OH}) structures, the band gap appears to be narrower than the corresponding 1_R (Table 1).

Fourth, all 2_R isomers exhibit less stability than the corresponding 1_R due to a smaller $\Delta E_{\text{S-T}}$. Fifth, every singlet 2_R emerges at a higher energy level than its corresponding 1_R. Sixth, every triplet 2_R has a lower energy than the

Table 3. The Nucleus Independent Chemical Shift (NICS) Calculated at 0.5, 1, 1.5 and 2 Å above the Ring Center for Singlet Stannylenes Normal (1_R) and Abnormal (2_R), at the B3LYP/6-311++G** Level of Theory

Normal NHSns	NICS (0)	NICS (0.5)	NICS (1)	NICS (1.5)	NICS (2)
1_H	-12.18	-12.41	-10.25	-6.794	-4.196
1_{methyl}	-9.54	-10.30	-9.01	-6.12	-3.80
1_{ethyl}	-9.13	-10.10	-9.28	-6.46	-3.95
$1_{\text{iso-propyl}}$	-8.09	-9.30	-8.76	-6.14	-3.76
$1_{\text{t-butyl}}$	-7.09	-8.20	-7.78	-5.55	-3.49
1_{Ph}	-7.43	-7.63	-6.45	-4.85	-3.41
1_{OH}	-12.20	-11.70	-8.96	-5.64	-3.34
1_{OMeth}	-11.90	-12.00	-9.68	-5.80	-3.15
1_{NO_2}	-8.01	-7.99	-6.55	-4.21	-2.41
1_{CN}	-11.10	-10.80	-8.36	-5.31	-3.18
1_{CF_3}	-8.33	-8.78	-7.37	-4.71	-2.76
Abnormal NHSns	NICS (0)	NICS (0.5)	NICS (1)	NICS (1.5)	NICS (2)
2_H	-11.37	-11.86	-10.31	-7.17	-4.58
2_{methyl}	-9.79	-10.60	-9.63	-6.89	-4.51
2_{ethyl}	-9.66	-10.50	-9.59	-6.93	-4.57
$2_{\text{iso-propyl}}$	-9.63	-10.60	-9.95	-7.10	-4.54
$2_{\text{t-butyl}}$	-10.40	-11.30	-10.20	-7.33	-4.86
2_{Ph}	-8.46	-8.36	-7.45	-5.59	-3.79
2_{OH}	-11.30	-10.90	-8.80	-6.02	-3.82
2_{OMeth}	-10.90	-11.60	-9.97	-6.70	-4.01
2_{NO_2}	-10.40	-9.87	-7.79	-5.37	-3.53
2_{CN}	-11.10	-11.20	-9.41	-6.51	-4.17
2_{CF_3}	-10.40	-10.90	-9.40	-6.48	-4.16

corresponding triplet 1_R .

All 2_R (except 2_H) species are more nucleophilic than the corresponding 1_R . In both 1_R and 2_R series, N increases

with an increase in the size of R. The π -electron-donating R groups exert more nucleophilicity than the electron-withdrawing groups. For instance, $2_{\text{t-butyl}}$ is the most

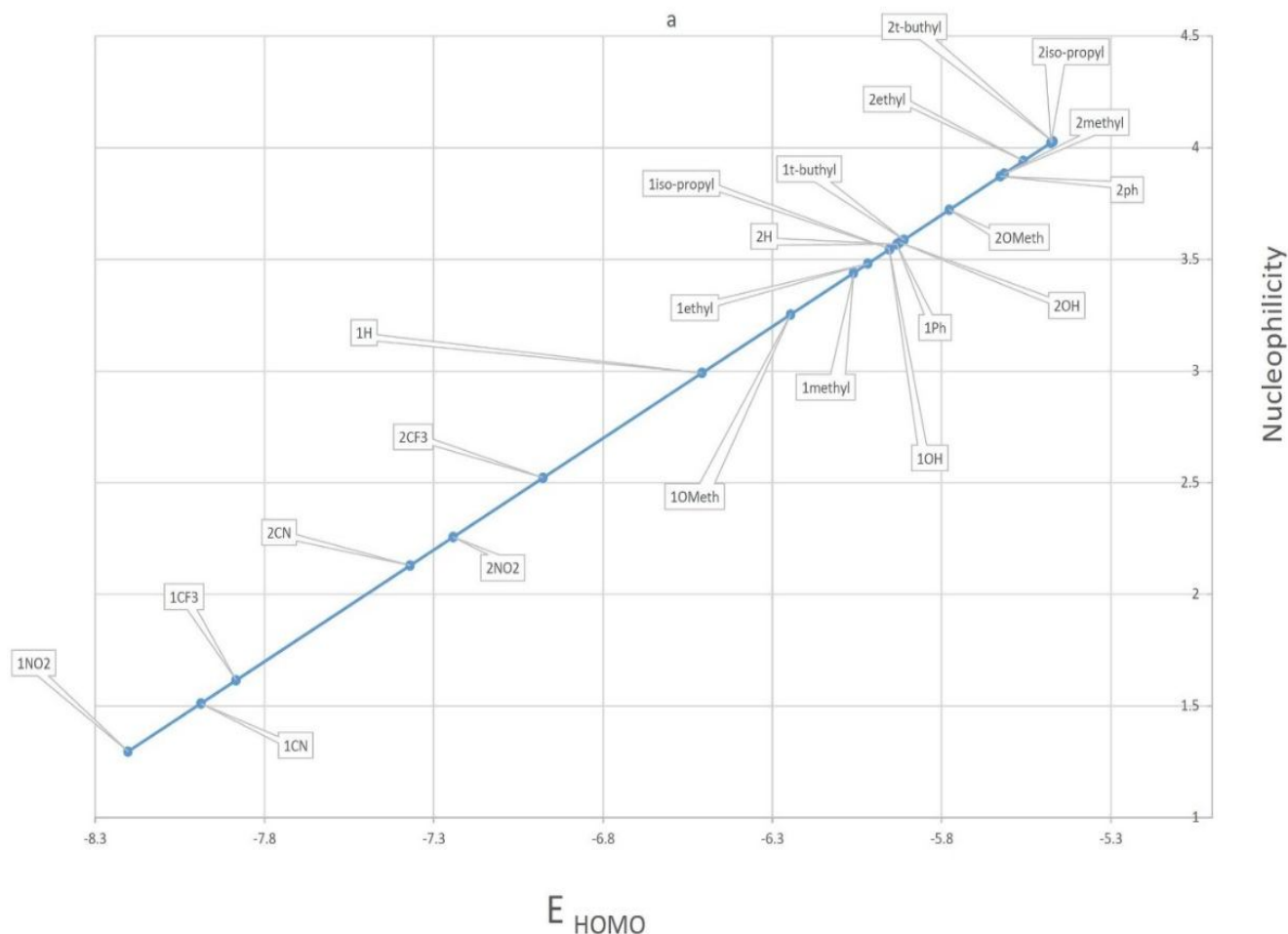


Fig. 2. Nucleophilicity for all the studied stannylenes appears as a function of E_{HOMO} with a correlation factor of one ($R^2 = 1$).

nucleophilic species ($N = 4.03$ eV), while 1_{NO_2} ($N = 1.29$ eV) is the opposite.

The measured global electrophilicity (ω/eV) followed an opposing trend from N . Electrophilicity of every 1_{R} is more than its corresponding 2_{R} isomer. For instance, 1_{NO_2} ($\omega = -9.34$ eV) shows the highest while $2_{\text{t-butyl}}$ ($\omega = -2.87$ eV) displays the lowest electrophilicity.

Stability ($\Delta E_{\text{S-T}}$) of every 1_{R} appeared to be more than that of 2_{R} . Hence, 1_{CF_3} ($\Delta E_{\text{S-T}} = 55.79$ kcal mol $^{-1}$) is more stable than 2_{CF_3} ($\Delta E_{\text{S-T}} = 45.65$ kcal mol $^{-1}$).

The trend of $\Delta E_{\text{HOMO-LUMO}}$ showed that every 1_{R} has a wider band gap than its corresponding 2_{R} . Also, our calculations showed the trend of $\Delta E_{\text{HOMO-LUMO}}$ to be indirectly proportional to N (Table 1).

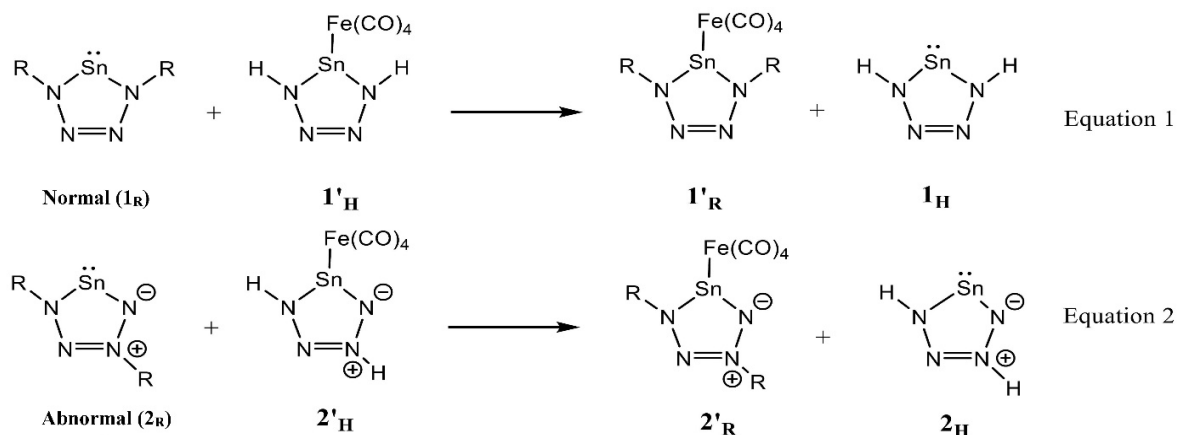
Our calculations indicate that every 2_{R} has a larger bond

angle and nucleophilicity relative to its corresponding 1_{R} . Also, 1_{NO_2} with a bond angle of 67.47° has the smallest bond angle in all scrutinized stannylenes (Table 2).

Nucleus-independent chemical shifts (NICS) were calculated at 0.5, 1, 1.5 and 2 Å above the ring center for every singlet stannylene 1_{R} and 2_{R} at the B3LYP/6-311++G** level of theory. Accordingly, every 2_{R} (except 2_{OH}) appears to be more aromatic than its corresponding 1_{R} (Table 3).

Our findings also revealed that N is in direct association with the HOMO energy (E_{HOMO}) for each species [61], showing a correlation factor of one ($R^2 = 1$) (Figs. 1 and 2).

The order of N values in our analyses is congruent with the trend of substituents σ -donor abilities. In fact, a higher N value is associated with a lesser σ Hammett substituent



Scheme 3. Isodesmic equation normal (1_R) and abnormal (2_R) stannylenes

Table 4. Substituent Effect Stabilization Energies (SESE) through Isodesmic Reactions for Normal (1_R) and Abnormal (2_R) Stannylenes

Equation	Isodesmic	reactions	SESE
Normal (1_R)			
1	1_{methyl}	+ $1'_H$ $\frac{3}{4}$	$1'_{\text{methyl}}$ + 1_H -0.000763
2	1_{ethyl}	+ $1'_H$ $\frac{3}{4}$	$1'_{\text{ethyl}}$ + 1_H 0.000555
3	$1_{\text{iso-propyl}}$	+ $1'_H$ $\frac{3}{4}$	$1'_{\text{iso-propyl}}$ + 1_H -0.000592
4	$1_{\text{t-butyl}}$	+ $1'_H$ $\frac{3}{4}$	$1'_{\text{t-butyl}}$ + 1_H -0.000193
5	1_{NO_2}	+ $1'_H$ $\frac{3}{4}$	$1'_{\text{NO}_2}$ + 1_H 0.003156
6	1_{CN}	+ $1'_H$ $\frac{3}{4}$	$1'_{\text{CN}}$ + 1_H 0.005067
7	1_{CF_3}	+ $1'_H$ $\frac{3}{4}$	$1'_{\text{CF}_3}$ + 1_H 0.003463
Abnormal (2_R)			
8	2_{methyl}	+ $2'_H$ $\frac{3}{4}$	$2'_{\text{methyl}}$ + 2_H -0.003855
9	2_{ethyl}	+ $2'_H$ $\frac{3}{4}$	$2'_{\text{ethyl}}$ + 2_H -0.005388
10	$2_{\text{iso-propyl}}$	+ $2'_H$ $\frac{3}{4}$	$2'_{\text{iso-propyl}}$ + 2_H -0.004675
11	$2_{\text{t-butyl}}$	+ $2'_H$ $\frac{3}{4}$	$2'_{\text{t-butyl}}$ + 2_H -0.004641
12	2_{NO_2}	+ $2'_H$ $\frac{3}{4}$	$2'_{\text{NO}_2}$ + 2_H 0.001995
13	2_{CN}	+ $2'_H$ $\frac{3}{4}$	$2'_{\text{CN}}$ + 2_H 0.002661
14	2_{CF_3}	+ $2'_H$ $\frac{3}{4}$	$2'_{\text{CF}_3}$ + 2_H 0.000728

constant. For example, $2_{t\text{-butyl}}$ and 1_{NO_2} exhibit N values of 4.03 and 1.29 with σ_p of -0.10 and 0.7, respectively (Table 1).

Also, we designed isodesmic reactions to examine steric effects of substituents on N of all the structures. Isodesmic reactions (Scheme 3) provide a measure of relative substituent effect stabilization energy (SESE) [62]. The SESE values indicate that a methyl group provides extra stabilization in 1_R (Table 4, Eq. (1)). Equation (9) shows a significant stabilization in 2_R (SESE -0.0054 kcal mol⁻¹), where 2_{ethyl} is the most nucleophilic structure. Also, every 2_R is more nucleophilic than 1_R because of the lower steric effect (Table 4). The results also indicate that electron-donating groups (EDG) enhance nucleophilicity, while electron-withdrawing groups (EWG) reduce it.

CONCLUSIONS

A comparison is made between N of 1,4-disubstituted tetrazastannole (1_R) and 1,3-disubstituted tetrazastannole (2_R) at the B3LYP/6-311++G** level, for R = H, methyl, ethyl, *i*-propyl, *t*-butyl, Ph, OH, methoxy, NO₂, CN and CF₃. All 2_R structures are more nucleophilic than the corresponding 1_R . In addition, N increases with electron donating groups, the $2_{t\text{-butyl}}$ and 1_{NO_2} appear as the most and the least nucleophilic species, respectively. Hence, among the species studied (1_R and 2_R), $2_{t\text{-butyl}}$ is the most nucleophilic structure. The trend of N for 2_R species is: $2_{t\text{-butyl}} > 2_{\text{iso-propyl}} > 2_{\text{ethyl}} > 2_{\text{methyl}} > 2_{\text{ph}} > 2_{\text{OMeth}} > 2_{\text{OH}} > 2_{\text{H}} > 2_{\text{CF}_3} > 2_{\text{NO}_2} > 2_{\text{CN}}$. The global electrophilicity (ω/eV) shows an opposite trend for N . Stabilities of 1_R and 2_R are presumed to be related to their ΔE_{S-T} . All 1_R (except 1_{ph} and 1_{OH}) species appear to be more stable, but less nucleophilic, than the corresponding 2_R isomers. Hence, N of an isomeric stannylene appears to be indirectly proportional to its ΔE_{S-T} . In another word, the less stable is a stannylene, the more nucleophilic it may be. According to our calculations, all 2_R (except 2_{OH}) isomers emerge more aromatic than the corresponding 1_R .

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REFERENCES

- [1] Biju, A. T.; Padmanaban, M.; Wurz, N. E.; Glorius, F., N-heterocyclic carbene catalyzed umpolung of michael acceptors for intermolecular reactions. *Angew. Chem. Int. Ed.* **2011**, *50*, 8412-8415, DOI: doi.org/10.1002/anie.201103555.
- [2] Biju, A. T.; Kuhl, N.; Glorius, F., Extending NHC-catalysis: Coupling aldehydes with unconventional reaction partners. *Acc. Chem. Res.* **2011**, *44*, 1182-1195, DOI: 10.1021/ar2000716.
- [3] Hirano, K.; Piel, I.; Glorius, F., Dual activation in N-heterocyclic carbene-organocatalysis. *Chem. Lett.* **2011**, *40*, 786-791, DOI: doi.org/10.1246/cl.2011.786.
- [4] Cohen, D. T.; Scheidt, K. A., Cooperative lewis acid/N-heterocyclic carbene catalysis. *Chem. Sci.* **2012**, *3*, 53-57, DOI: 10.1039/C1SC00621E.
- [5] Marion, N.; Díez-González, S.; Nolan, S. P., N-heterocyclic carbenes as organocatalysts. *Angew. Chem. Int. Ed.* **2007**, *46*, 2988-3000, DOI: doi.org/10.1002/anie.200603380.
- [6] Enders, D.; Niemeier, O.; Henseler, A., Organocatalysis by N-heterocyclic carbenes. *Chem. Rev.* **2007**, *107*, 5606-5655, DOI: 10.1021/cr068372z.
- [7] Nair, V.; Vellalath, S.; Babu, B. P., Recent advances in carbon-carbon bond-forming reactions involving homoenolates generated by NHC catalysis. *Chem. Soc. Rev.* **2008**, *37*, 2691-2698, DOI: doi.org/10.1039/C8CS00124C.
- [8] Poyatos, M.; Mata, J. A.; Peris, E., Complexes with poly(N-heterocyclic carbene) ligands: Structural features and catalytic applications. *Chem. Rev.* **2009**, *109*, 3677-3707, DOI: 10.1021/cr800501s.
- [9] Hahn, F. E.; Jahnke, M. C., Heterocyclic carbenes: Synthesis and coordination chemistry. *Angew. Chem. Int. Ed.* **2008**, *47*, 3122-3172, DOI: doi.org/10.1002/anie.200703883.
- [10] Bourissou, D.; Guerret, O.; Gabbai, F. P.; Bertrand, G. Stable Carbenes. *Chem. Rev.* **2000**, *100*, 39-92, DOI: 10.1021/cr940472u.
- [11] Dröge, T.; Glorius, F., The measure of all rings-N-heterocyclic carbenes. *Angew. Chem. Int. Ed.* **2010**,

- 49, 6940-6952, DOI: <https://doi.org/10.1002/anie.201001865>.
- [12] Herrmann, W. A., N-heterocyclic carbenes: A new concept in organometallic catalysis. *Angew. Chem. Int. Ed.* **2002**, *41*, 1290-1309, DOI: [doi.org/10.1002/1521-3773\(20020415\)41:8<1290::AID-ANIE1290>3.0.CO;2-Y](https://doi.org/10.1002/1521-3773(20020415)41:8<1290::AID-ANIE1290>3.0.CO;2-Y).
- [13] Nolan, S. P. E., N-Heterocyclic Carbenes in Synthesis. John Wiley & Sons, 2006, pp. 200-240.
- [14] Glorius, F. E., N-Heterocyclic Carbenes in Transition Metal Catalysis. Springer, 2007, p. 1-20
- [15] Kantchev, E. A. B.; O'Brien, C. J.; Organ, M. G., Palladium complexes of N-heterocyclic carbenes as catalysts for cross-coupling reactions-A synthetic chemist's perspective. *Angew. Chem. Int. Ed.* **2007**, *46*, 2768-2813, DOI: <https://doi.org/10.1002/anie.200601663>.
- [16] Wuertz, S.; Glorius, F., Surveying sterically demanding N-heterocyclic carbene ligands with restricted flexibility for palladium-catalyzed cross-coupling reactions. *Acc. Chem. Res.* **2008**, *41*, 1523-1533, DOI: [10.1021/ar8000876](https://doi.org/10.1021/ar8000876).
- [17] Monfette, S.; Fogg, D. E., Equilibrium ring-closing metathesis. *Chem. Rev.* **2009**, *109*, 3783-3816, DOI: [10.1021/cr800541y](https://doi.org/10.1021/cr800541y).
- [18] Díez-González, S.; Marion, N.; Nolan, S. P., N-heterocyclic carbenes in late transition metal catalysis. *Chem. Rev.* **2009**, *109*, 3612-3676, DOI: [10.1021/cr900074m](https://doi.org/10.1021/cr900074m).
- [19] Kascatan-Nebioglu, A.; Panzner, M. J.; Tessier, C. A.; Cannon, C. L.; Youngs, W. J., N-heterocyclic carbene-silver complexes: A new class of antibiotics. *Coord. Chem. Rev.* **2007**, *251*, 884-895, DOI: <https://doi.org/10.1016/j.ccr.2006.08.019>.
- [20] Hindi, K. M.; Panzner, M. J.; Tessier, C. A.; Cannon, C. L.; Youngs, W. J., The medicinal applications of imidazolium carbene-metal Complexes. *Chem. Rev.* **2009**, *109*, 3859-3884, DOI: [10.1021/cr800500u](https://doi.org/10.1021/cr800500u).
- [21] Li, Y.; Hindi, K.; Watts, K. M.; Taylor, J. B.; Zhang, K.; Li, Z.; Hunstad, D. A.; Cannon, C. L.; Youngs, W. J.; Wooley, K. L., Shell crosslinked nanoparticles carrying silver antimicrobials as therapeutics. *Chem. Commun.* **2010**, *46*, 121-123, DOI: [10.1039/B916559B](https://doi.org/10.1039/B916559B).
- [22] Ray, S.; Mohan, R.; Singh, J. K.; Samantaray, M. K.; Shaikh, M. M.; Panda, D.; Ghosh, P., Anticancer and antimicrobial metallopharmaceutical agents based on palladium, gold, and silver N-heterocyclic carbene complexes. *J. Am. Chem. Soc.* **2007**, *129*, 15042-15053, DOI: [10.1021/ja075889z](https://doi.org/10.1021/ja075889z).
- [23] Hickey, J. L.; Ruhayel, R. A.; Barnard, P. J.; Baker, M. V.; Berners-Price, S. J.; Filipovska, A., Mitochondria-targeted chemotherapeutics: The rational design of gold(I) N-heterocyclic carbene complexes that are selectively toxic to cancer cells and target protein selenols in preference to thiols. *J. Am. Chem. Soc.* **2008**, *130*, 12570-12571, DOI: [10.1021/ja804027j](https://doi.org/10.1021/ja804027j).
- [24] Boydston, A. J.; Williams, K. A.; Bielawski, C. W., A modular approach to main-chain organometallic polymers. *J. Am. Chem. Soc.* **2005**, *127*, 12496-12497, DOI: [10.1021/ja054029k](https://doi.org/10.1021/ja054029k).
- [25] Boydston, A. J.; Bielawski, C. W., Bis (imidazolylidene)s as modular building blocks for monomeric and macromolecular organometallic materials. *Dalton Trans.* **2006**, *0*, 4073-4077, DOI: [10.1039/B607696N](https://doi.org/10.1039/B607696N).
- [26] Tennyson, A. G.; Kamplain, J. W.; Bielawski, C. W., Oxidation of poly(enetetramine)s: a new strategy for the synthesis of conjugated polyelectrolytes. *Chem. Commun.* **2009**, *0*, 2124-2126, DOI: [10.1039/B902030F](https://doi.org/10.1039/B902030F).
- [27] Coady, D. J.; Khramov, D. M.; Norris, B. C.; Tennyson, A. G.; Bielawski, C. W., Adapting N-heterocyclic carbene/azide coupling chemistry for polymer synthesis: Enabling access to aromatic polytriazenes. *Angew. Chem. Int. Ed.* **2009**, *48*, 5187-5190, DOI: [10.1002/anie.200901046](https://doi.org/10.1002/anie.200901046).
- [28] Asay, M.; Jones, C.; Driess, M., N-heterocyclic carbene analogues with low-valent group 13 and group 14 elements: Syntheses, structures, and reactivities of a new generation of multitalented ligands. *Chem. Rev.* **2010**, *111*, 354-396, DOI: [10.1021/cr100216y](https://doi.org/10.1021/cr100216y).
- [29] Lappert, M. F.; Rowe, R. S., The role of group 14 element carbene analogues in transition metal chemistry. *Coord. Chem. Rev.* **1990**, *100*, 267-292, DOI: [https://doi.org/10.1016/0010-8545\(90\)85012-H](https://doi.org/10.1016/0010-8545(90)85012-H).

- [30] 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.
- [31] Sasamori, T.; Tokitoh, N., Encyclopedia of Inorganic Chemistry II. John Wiley & Sons, 2005, pp. 1698-1740.
- [32] Mizuhata, Y.; Sasamori, T.; Tokitoh, N., Stable heavier carbene analogues. *Chem. Rev.* **2009**, *109*, 3479-3511, DOI: 10.1021/cr900093s.
- [33] Zabula, A. V.; Hahn, F. E., Mono- and bidentate benzannulated N-heterocyclic germylenes, stannylenes and plumblyenes. *Eur. J. Inorg. Chem.* **2008**, *2008*, 5165-5179, DOI: <https://doi.org/10.1002/ejic.200800866>.
- [34] Mizuhata, Y.; Sasamori, T.; Tokitoh, N., Stable heavier carbene analogues. *Chem. Rev.* **2009**, *109*, 3479-3511, DOI: 10.1021/cr900093s.
- [35] Mansell, S. M.; Russell, C. A.; Wass, D. F., Synthesis and structural characterization of tin analogues of N-heterocyclic carbenes. *Inorg. Chem.* **2008**, *47*, 11367-11375, DOI: 10.1021/ic801479g.
- [36] Gans-Eichler, T.; Gudat, D.; Nieger, M., Tin analogues of "arduengo carbenes": Synthesis of 1,3,2λ2-diazastannoles and transfer of Sn atoms between a 1,3,2λ2-diazastannole and a diazadiene. *Angew. Chem. Int. Ed.* **2002**, *41*, 1888-1891, DOI: [https://doi.org/10.1002/1521-3773\(20020603\)41:11<1888::AID-ANIE1888>3.0.CO;2-O](https://doi.org/10.1002/1521-3773(20020603)41:11<1888::AID-ANIE1888>3.0.CO;2-O).
- [37] Gans-Eichler, T.; Gudat, D.; Nättinen, K.; Nieger, M., The transfer of tin and germanium atoms from N-heterocyclic stannylenes and germylenes to diazadienes. *Chem. Eur. J.* **2006**, *12*, 1162-1173, DOI: <https://doi.org/10.1002/chem.200500576>.
- [38] Mansell, S. M.; Herber, R. H.; Nowik, I.; Ross, D. H.; Russell, C. A.; Wass, D. F., Coordination chemistry of N-heterocyclic stannylenes: A combined synthetic and mössbauer spectroscopy Study. *Inorg. Chem.* **2011**, *50*, 2252-2263, DOI: 10.1021/ic101920x.
- [39] Heo, J.; Hock, A. S.; Gordon, R. G., Low temperature atomic layer deposition of tin oxide. *Chem. Mater.* **2010**, *22*, 4964-4973, DOI: 10.1021/cm1011108.
- [40] Kim, S. B.; Sinsermuksakul, P.; Hock, A. S.; Pike, R. D.; Gordon, R. G., Synthesis of N-heterocyclic stannylenes (Sn(II)) and germylene (Ge(II)) and a Sn(II) amidinate and their application as precursors for atomic layer deposition. *Chem. Mater.* **2014**, *26*, 3065-3073, DOI: 10.1021/cm403901y.
- [41] Braunschweig, H.; Gehrhus, B.; Hitchcock, P. B.; Lappert, M. F., Synthesis and characterisation of N,N'-disubstituted-1,2-phenylenebis(amido)tin(II) compounds; X-Ray structures of (tmeda). *ZAAC.* **1995**, *621*, 1922-1928, DOI: 10.1002/zaac.19956211115.
- [42] Heinicke, J.; Oprea, A.; Kindermann, M. K.; Karpati, T.; Nyulászi, L.; Veszprémi, T., Unsymmetrical carbene homologues: isolable pyrido[b]-1,3,2λ2-diazasilole, -germole and -stannole and quantum-chemical comparison with unstable pyrido[c] isomers. *Chem. Eur. J.* **1998**, *4*, 541-545, DOI: [https://doi.org/10.1002/\(SICI\)1521-3765\(19980310\)4:3<541::AID-CHEM541>3.0.CO;2-#](https://doi.org/10.1002/(SICI)1521-3765(19980310)4:3<541::AID-CHEM541>3.0.CO;2-#).
- [43] Hahn, F. E.; Wittenbecher, L.; Kühn, M.; Lügger, T.; Fröhlich, R., A zwitterionic carbene-stannylenes adduct via cleavage of a dibenzotetraazafulvalene by a stannylenes. *J. Organomet. Chem.* **2001**, *617*, 629-634, DOI: [https://doi.org/10.1016/S0022-328X\(00\)00700-2](https://doi.org/10.1016/S0022-328X(00)00700-2).
- [44] Hahn, F. E.; Wittenbecher, L.; Le Van, D.; Zabula, A. V., Benzimidazolin-2-stannylenes with N,N'-alkyl (Me and Et) and lewis base functional groups. *Inorg. Chem.* **2007**, *46*, 7662-7667, DOI: 10.1021/ic701064z.
- [45] Dickschat, J. V.; Urban, S.; Pape, T.; Glorius, F.; Hahn, F. E., Sterically demanding and chiral N,N'-disubstituted N-heterocyclic germylenes and stannylenes. *Dalton Trans.* **2010**, *39*, 11519-11521, DOI: 10.1039/C0DT01233E.
- [46] Krupski, S.; Pöttgen, R.; Schellenberg, I.; Hahn, F. E., Benzannulated N-heterocyclic germylenes and stannylenes with sterically demanding N,N'-substituents. *Dalton Trans.* **2014**, *43*, 173-181, DOI: 10.1039/C3DT51961A.
- [47] Zabula, A. V.; Rogachev, A. Y.; West, R., Self-assembly of N-heterocyclic derivatives of divalent germanium, tin, and lead. *Chem. Eur. J.* **2014**, *20*, 16652-16656, DOI: 10.1002/chem.201405062.

- [48] Krupski, S.; Schulte to Brinke, C.; Koppetz, H.; Hepp, A.; Hahn, F. E., Protic N-heterocyclic germlyenes and stannylenes: Synthesis and reactivity. *organometallics*. **2015**, *34*, 2624-2631, DOI: 10.1021/om5012616.
- [49] Zabula, A. V.; Pape, T.; Hepp, A.; Hahn, F. E., Coordination chemistry of bisstannylenes with platinum(0). *Dalton Trans.* **2008**, *0*, 5886-5890, DOI: 10.1039/B809878F.
- [50] Zabula, A. V.; Pape, T.; Hepp, A.; Hahn, F. E., Homoleptic complexes of bisstannylenes with nickel(0): Synthesis, X-ray diffraction studies, and ¹¹⁹Sn NMR investigations. *Organometallics*. **2008**, *27*, 2756-2760, DOI: 10.1021/om800096f.
- [51] Hahn, F. E.; Zabula, A. V.; Pape, T.; Hepp, A.; Tonner, R.; Haunschild, R.; Frenking, G., π -Bonding in complexes of benzannulated biscarbenes, -germylenes, and -stannylenes: An experimental and theoretical study. *Chem. Eur. J.* **2008**, *14*, 10716-10721, DOI: 10.1002/chem.200801128.
- [52] Zabula, A. V.; Pape, T.; Hepp, A.; Schappacher, F. M.; Rodewald, U. C.; Pöttgen, R.; Hahn, F. E., Trapping of tin(II) and lead(II) homologues of carbon monoxide by a benzannulated lutidine-bridged bisstanylene. *J. Am. Chem. Soc.* **2008**, *130*, 5648-5649, DOI: 10.1021/ja801000b.
- [53] Krupski, S.; Dickschat, J. V.; Hepp, A.; Pape, T.; Hahn, F. E., Synthesis and characterization of rigid ditopic N-heterocyclic benzobisgermylenes and -stannylenes. *Organometallics* **2012**, *31*, 2078-2084, DOI: 10.1021/om3000604
- [54] Becke, A. D., Density-functional thermochemistry. III. The role of exact exchange. *J. Chem. Phys.* **1993**, *98*, 5648-5652, DOI: <https://doi.org/10.1063/1.464913>.
- [55] Stephens, P.; Devlin, F.; Chabalowski, C.; Frisch, M. J., *Ab initio* calculation of vibrational absorption and circular dichroism spectra using density functional force fields. *J. Chem. Phys.* **1994**, *98*, 11623-11627, DOI: 10.1021/j100096a001.
- [56] Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A., Self-consistent molecular orbital methods. XX. A basis set for correlated wave functions. *J. Chem. Phys.* **1980**, *72*, 650-654, DOI: <https://doi.org/10.1063/1.438955>.
- [57] Frisch, M.; Trucks, G.; Schlegel, H.; Scuseria, G.; Robb, M.; Cheeseman, J.; Montgomery Jr, J.; Vreven, T.; Kudin, K.; Burant, J., Gaussian 03 software, Revision B. 02. Gaussian, Inc., Pittsburgh PA, Full author list at <http://www.gaussian.com>, 2003.
- [58] Domingo, L. R.; Chamorro, E.; Pérez, P., Understanding the reactivity of captodative ethylenes in polar cycloaddition reactions. A theoretical study. *J. Org. Chem.* **2008**, *73*, 4615-4624, DOI: 10.1021/jo800572a.
- [59] Parr, R. G.; Szentpaly, L. V.; Liu, S., Electrophilicity index. *J. Am. Chem. Soc.* **1999**, *121*, 1922-1924, DOI: 10.1021/ja983494x.
- [60] 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.
- [61] 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 pK_a of imidazolium cations in aqueous solution. *J. Am. Chem. Soc.* **2004**, *126*, 4366-4374, DOI: 10.1021/ja039890j.
- [62] Ramsden, C. A.; Oziminski, W. P., The relative stability of mesoionic and N-heterocyclic carbene tautomers: a computational study of substituent effects. *Tetrahedron*. **2015**, *71*, 6846-6851, DOI: 10.1016/j.tet.2015.07.024.