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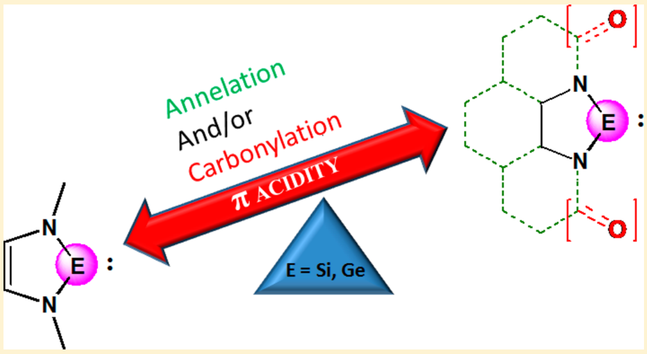
Theoretical Study on the Effect of Annelation and Carbonylation on the Electronic and Ligand Properties of *N*-Heterocyclic Silylenes and Germylenes: Carbene Comparisons begin To Break Down

Ankur Kanti Guha[§] and Ashwini K. Phukan*[,†,‡]

[†]Department of Chemical Sciences, Tezpur University, Napaam 784028, Assam, India
[‡]Institut für Anorganische Chemie, Julius-Maximilians-Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany
[§]Department of Chemistry, Dibrugarh University, Dibrugarh 786004, Assam, India

Supporting Information

ABSTRACT: Quantum chemical calculations have been carried out to investigate the effect of annelation and carbonylation on the electronic and ligand properties of *N*-heterocyclic silylenes and germylenes. The thermodynamic stability of these ligands has been found to increase with annelation, while the reverse is true for carbonylation. This is in sharp contrast to N-heterocyclic carbenes (NHCs) where annelation leads to a decrease in their thermodynamic stabilities. Compared to nonannelated derivatives, annelated and carbonylated ones are found to be weaker σ donors but better π acceptors. The effect of carbonylation is more pronounced than annelation toward increasing the π acidity of these ligands. Carbonylation at the α-position with respect to the N atom attached to the Si/Ge center has been found to be the most effective way of enhancing the π acidity of these ligands. The computed natural charges reveal that electrophilicity increases upon both annelation and carbonylation. The calculated values of ^{31}P NMR chemical shifts of corresponding phosphinidene adducts of these ligands have been found to correlate well with the π acidity of these Si/Ge centers.



1. INTRODUCTION

The donation and acceptance ability of ligands are key to the catalytic efficiency of various transition-metal complexes. One prominent class of ligands are divalent group 14 element containing compounds as *N*-heterocyclic carbenes (NHC),[1a] silylenes (NHSi),[1b] and germylenes (NHGe).[1c,d] Since their isolation, NHCs have served as superior ligands compared to some of the classical two-electron donor ligands, such as amines and phosphines.[2] Many experimental[3] and theoretical[4] studies have been devoted toward exploring the stability and σ donation abilities of these heterocyclic ligands. However, evidence of non-negligible π accepting properties of these ligands in their transition-metal complexes has recently accumulated.[5] This has opened up another possibility as moderate-to-strong π-accepting properties of carbenes, silylenes, and germylenes may be useful in some catalytic applications. Remarkably, Fürstner et al. have shown that the outcomes of gold-catalyzed reactions are influenced by the π acceptor property of carbenes.[6]

The electronic properties of carbenes are different from those of their heavier analogues. For example, both NHSi and NHGe show lower basicity and higher acidity compared to NHCs.[7a,b,8] The symmetry of the highest occupied molecular orbital (HOMO) also changes from σ in NHCs to π in NHSis or NHGes; the σ-symmetric lone pair orbital becomes more stable for these heavier analogues.[9b,4f] This partly explains the lower basicity of the Si/Ge center for these heavier analogues.

Although the σ donation ability of NHSis and NHGes has received some attention,[10] studies related to their π-accepting ability are scarce.[10c] Kühl et al.[10b] have calculated the molecular electrostatic potential (MEP) of some annelated germylenes and correlated them with the Tolman electronic parameter (TEP).[11] The ligating properties so obtained mostly revealed their net donation abilities. However, quantification of the π-accepting ability is somewhat difficult using these approaches as suggested by Kühl et al.[10c] Heinicke and co-workers reported the isolation of various benzo-, pyrido-, and naphtho-annelated NHSis[7] and NHGes.[12] They found that annelation results in an increase in the π-acceptor strength of these ligands by virtue of their electron-withdrawing ability. Thus, it is expected that introduction of pyrido-, pyrazino-, or quinoxalino-ring systems will further increase the π-acidity of these species. In fact, the strongest annelation effect was observed in quinoxaline-annelated NHEs (E = C−Sn) as reported by Heinicke et al.[13] Another strategy to increase the π accepting ability of

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Scheme 1

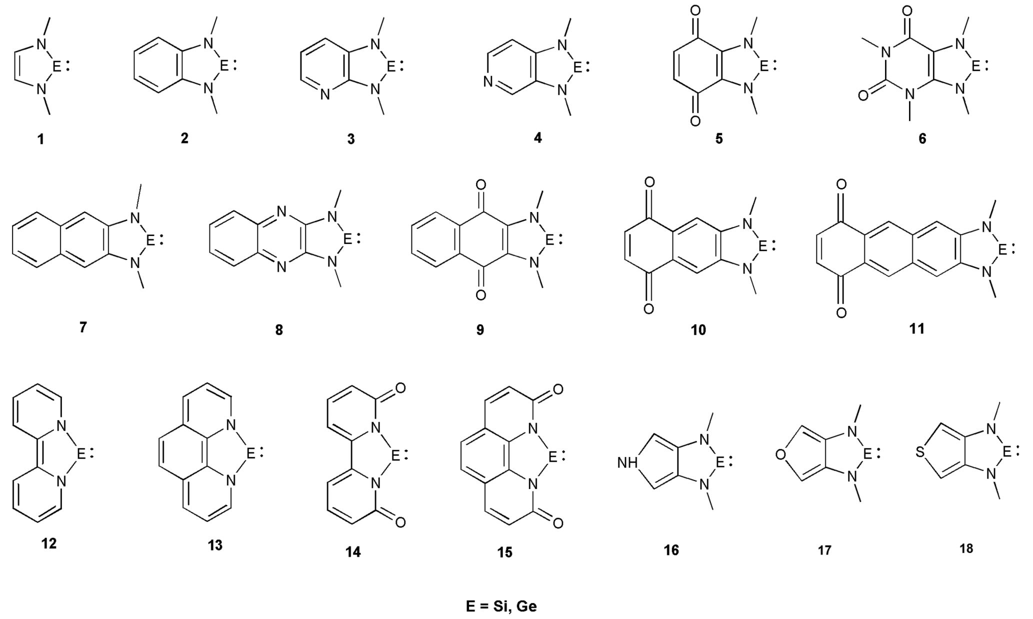


Table 1. PBE1PBE/6-31+G*-Calculated Selected Geometric Parameters of 1−18[a]

molecule	r_{N-Si}	<N−Si−N	molecule	r_{N-Ge}	<N−Ge−N
1Si	1.772 (1.753)[22a]	86.5 (90.5)[22a]	**1Ge**	1.845 (1.859)[22b]	84.5 (84.8)[22b]
2Si	1.765 (1.752)[7b]	87.7 (88.2)[7b]	**2Ge**	1.837 (1.857)[22c]	85.8 (84.4)[22c]
3Si	1.766/1.772	87.9	**3Ge**	1.846/1.838 (1.860/1.866)[21b]	85.6 (84.6)[21b]
4Si	1.774/1.762	87.9	**4Ge**	1.843/1.835	86.0
5Si	1.775	87.1	**5Ge**	1.843	85.2
6Si	1.744/1.800	87.3	**6Ge**	1.817/1.868	84.9
7Si	1.764	88.0	**7Ge**	1.839	85.7
8Si	1.772	88.4	**8Ge**	1.845	86.2
9Si	1.774	87.0	**9Ge**	1.847	84.9
10Si	1.770	87.6	**10Ge**	1.845	85.3
11Si	1.767	87.8	**11Ge**	1.840	85.8
12Si	1.797	84.6	**12Ge**	1.868	82.5
13Si	1.815	85.3	**13Ge**	1.883	83.8
14Si	1.817	83.8	**14Ge**	1.890	81.2
15Si	1.823	84.9	**15Ge**	1.890	83.1
16Si	1.772	89.4	**16Ge**	1.842	87.4
17Si	1.772	89.7	**17Ge**	1.843	87.7
18Si	1.770	89.0	**18Ge**	1.842	87.0

[a] Bond lengths are in angstroms and angles are in degrees. Experimental values are given within parentheses.

NHEs would be to introduce carbonyl groups into the NHE scaffold. Carbonyl groups (C═O), being good acceptors, can withdraw electron density from the p orbital of the "ene" center, making it more electrophilic. This has been demonstrated experimentally by Bielawski et al. for NHCs.[14] Thus, it could be rewarding to study the effect of annelation and carbonylation on the electronic and ligating properties of NHE **1**−**18** (Scheme 1, E = Si or Ge) with a special emphasis on their π-accepting abilities as it has been recently shown that dialkylgermylenes and plumbylenes activate dihydrogen and C−Cl bonds.[15] The activation of the H_2 molecule by germylene follows from the initial attack of the σ bond of H_2 molecule at the empty 4p orbital of germanium resulting in the formation of a stable intermediate.[15a] Thus, it seems that the π-acidity of these molecules is an important parameter in the activation of small molecules. The extent and pattern of annelation were varied by annelating the parent NHEs with ligands like benzene, pyridine, pyrrole, etc. so as to get a better understanding of the most effective way of increasing the electrophilicity of these NHEs.

2. COMPUTATIONAL DETAILS

All the structures were fully optimized without any geometry constraints using the hybrid PBE1PBE exchange-correlation functional.[16] We have used the 6-31+G* basis set for all the elements. Frequency calculations were performed at the same level of theory to characterize the nature of the stationary point. All structures were found to be minima on the potential energy surface with real frequencies. This level of theory was found to be adequate in dealing with similar systems as reported recently.[17,18] Natural bonding analyses were performed with the natural bond orbital (NBO) partitioning scheme[19] as implemented in the Gaussian 09 suite of programs.[20]

Table 2. PBE1PBE/6-31+G*-Computed Singlet−triplet (ΔE_{S-T}, kcal mol^{-1}) and HOMO−LUMO (ΔE_{H-L}, eV) Gaps of 1−18

molecule	ΔE_{S-T}	ΔE_{H-L}	molecule	ΔE_{S-T}	ΔE_{H-L}	molecule[a]	ΔE_{S-T}	ΔE_{H-L}
1Si	52.1	4.8	**1Ge**	46.9	4.5	**1C**	81.3	6.5
2Si	59.0	4.7	**2Ge**	54.6	4.4	**2C**	75.5	5.7
3Si	58.6	4.7	**3Ge**	54.2	4.4	**3C**	71.5	5.4
4Si	60.9	4.8	**4Ge**	56.6	4.6			
5Si	28.7	3.1	**5Ge**	27.7	2.9			
6Si	49.8	4.5	**6Ge**	45.9	4.2			
7Si	53.8	4.2	**7Ge**	52.2	4.0	**7C**	54.4	4.6
8Si	56.3	4.3	**8Ge**	53.1	4.1	**8C**	59.6	4.6
9Si	35.9	3.3	**9Ge**	34.8	3.2	**9C**	46.7	3.5
10Si	46.0	3.5	**10Ge**	45.0	3.4			
11Si	46.9	3.4	**11Ge**	46.2	3.3			
12Si	30.2	3.3	**12Ge**	27.0	3.1			
13Si	14.7	2.5	**13Ge**	14.3	2.4	**13C**	21.6	3.0
14Si	42.8	3.1	**14Ge**	28.9	3.0			
15Si	52.8	3.8	**15Ge**	45.8	3.7	**15C**	35.7	3.8
16Si	56.2	4.6	**16Ge**	52.0	4.4			
17Si	56.2	4.6	**17Ge**	57.0	4.3			
18Si	58.9	4.7	**18Ge**	54.4	4.5			

[a] Values of structurally similar NHCs (E = C) calculated at the same level of theory[17a] are also included.

Isotropic ^{31}P chemical shifts were calculated using the gauge independent atomic orbital scheme (GIAO) at the PBE1PBE/6-31+G(d) level of theory relative to H_3PO_4. The same level of theory was also used for calculating the absolute isotropic chemical shift of H_3PO_4 (σ_{iso} = 374.0).

3. RESULTS AND DISCUSSION

3.1. Geometries. The selected geometrical parameters of **1**−**18** are collected in Table 1. It is evident from Table 1 that the geometrical parameters of the molecules are very close to the experimental X-ray data[7b,21b,22] with a deviation in E−N (E = Si or Ge) bond lengths of ≈0.02 Å. All the molecules have perfectly planar five-membered rings containing the silylene and germylene center with two equal E−N bonds. However, due to the unsymmetrical backbone in **3**, **4**, and **6**, the two E−N bonds are not equal (Table 1). Table 1 reveals that the E−N distances of **1**−**11** as well as **16**−**18** are not very different; however, molecules **14** and **15** have the longest E−N distances, respectively, of all the NHSis and NHGes considered in this study. This implies that annelation or carbonylation have no dramatic effect on the geometrical parameters of NHSis or NHGes, although carbonylation at the α-position with respect to the N atom adjacent to the Si/Ge center leads to weakening, and hence elongation, of the E−N bonds. This might be due to the electron-withdrawing ability of the adjacent CO group into its π^* orbital from the N lone pairs. As a result, N can donate less electron density to the formally vacant p_π orbital of Si and Ge centers, respectively, and hence, the E−N bonds in **14** and **15** lengthen considerably. However, this effect is not pronounced when the CO group is away from the N atoms as in **5**, **6**, **9**, **10**, and **11**.

Similar to the E−N bonds, the angles ∠N−E−N (E = Si or Ge) do not vary significantly for **1**−**11** and **16**−**18**. However, the angles become more acute for **14** and **15**. This is because these molecules have weaker E−N bonds, and as a result, the E−N bonds acquire more p character. The involvement of more p character leads to a reduction of the ∠N−E−N angles.

3.2. Singlet−Triplet and HOMO−LUMO Gaps. The stabilities of these silylenes and germylenes can be judged from their respective singlet−triplet (ΔE_{S-T}) and HOMO−LUMO (ΔE_{H-L}) gaps.[23] In general, the higher the value of ΔE_{S-T} and ΔE_{H-L}, the higher the stability of these molecules in the singlet state. The calculated values of ΔE_{S-T} and ΔE_{H-L} are collected in Table 2. Both experimental and theoretical studies revealed that annelation decreases the singlet−triplet and HOMO−LUMO gaps[9,14,17a] of NHCs, which in turn are believed to facilitate small molecule activation. We have included the calculated values of ΔE_{S-T} and ΔE_{H-L} gaps at the same level of theory[17a] for structurally similar NHCs in Table 2 for a quick comparison. It is evident from Table 2 that, unlike NHCs, annelation of NHSi or NHGe does not decrease the ΔE_{S-T}; rather, it increases in most cases. This is in tune with experimental observations where annelation was found to increase the stability of these heavier analogues of NHCs.[21a] Interestingly, like NHCs, carbonylation of the NHSi or NHGe scaffolds decreases the singlet−triplet and HOMO−LUMO gaps. Thus, it appears that while both annelation and carbonylation decrease the stability of NHCs,[9,17] annelation of the heavier analogues increases the same and carbonylation decreases it. Among all the heterocyclic silylenes considered in this study, **4Si** and **13Si** are found to have the highest and lowest singlet−triplet gap respectively; for the germylenes, **17Ge** has the highest singlet−triplet gap whereas **13Ge** has the lowest. The lower value of singlet−triplet as well as HOMO−LUMO gap for **5** and **9** may be due to the presence of the annelated quinine moiety, whereas the lower values of **12** and **13** may be attributed to the higher π accepting ability of 2,2′-bipyridine and 1,10-phenanthroline moiety. This is in tune with previous observations[24] that π acceptor substituents attached to the silylene or germylene center stabilize the triplet state. We obtained reasonable correlation between the singlet−triplet and HOMO−LUMO gaps of these molecules (see Figure S1, Supporting Information).

3.3. Ligating Properties. The σ donation ability of these ligands has been well explored,[3,4,10] and recent reports have provided evidence of their non-negligible π accepting properties.[5] In this perspective, the nature and energies of the *key* frontier orbitals of NHEs (E = Si or Ge) are very important as these orbitals dictate the reactivity and ligating properties of these molecules. Table 3 contains the energies of the σ-

Table 3. Summary of Different Parameters Calculated at the PBE1PBE/6-31+G* Level of Theory

molecule	E_σ[a]	E_{π^*}[b]	occ(p_π)[c]	q_{Si}[d]	molecule	E_σ[a]	E_{π^*}[b]	occ(p_π)[c]	q_{Ge}[d]
1Si	−6.7	−0.6	0.506	0.935	**1Ge**	−6.9	−0.7	0.532	0.897
	IP[e] = 8.2[4f]					IP[e] = 8.70[4f]			
2Si	−7.0	−1.1	0.423	1.108	**2Ge**	−7.2	−1.3	0.438	0.986
	IP[e] = 8.55[7d]								
3Si	−7.2	−1.4	0.407	1.035	**3Ge**	−7.4	−1.5	0.422	1.005
	IP[e] = 8.98[7d]								
4 Si	−7.4	−1.5	0.404	1.038	**4Ge**	−7.6	−1.6	0.416	1.009
5 Si	−7.4	−1.4	0.439	1.016	**5Ge**	−7.5	−1.5	0.455	0.985
6 Si	−7.3	−1.3	0.462	1.000	**6Ge**	−7.3	−1.4	0.488	0.964
7 Si	−7.2	−1.5	0.393	1.048	**7Ge**	−7.4	−1.6	0.407	1.019
8 Si	−7.5	−0.7	0.357	1.087	**8Ge**	−7.8	−2.1	0.367	1.066
9 Si	−7.3	−0.8	0.436	1.018	**9Ge**	−7.4	−0.8	0.454	0.991
10 Si	−7.5	−1.8	0.392	1.055	**10Ge**	−7.7	−1.9	0.406	1.029
11Si	−7.6	−2.1	0.371	1.000	**11Ge**	−7.8	−2.2	0.387	1.046
12Si	−7.2	−1.2	0.619	0.853	**12Ge**	−7.4	−1.2	0.661	0.805
13Si	−7.1	−1.1	0.646	0.827	**13Ge**	−7.3	−1.2	0.686	0.788
14Si	−7.4	−3.4	0.174	1.289	**14Ge**	−7.5	−3.4	0.161	1.298
15Si	−7.3	−3.1	0.237	1.222	**15Ge**	−7.3	−3.1	0.231	1.226
16Si	−6.7	−0.8	0.440	1.000	**16Ge**	−6.8	−0.9	0.456	0.965
17Si	−7.0	−1.2	0.397	1.040	**17Ge**	−7.2	−1.3	0.409	1.014
18Si	−7.0	−1.3	0.400	1.040	**18Ge**	−7.3	−1.4	0.412	1.013

[a] Energy of the σ-symmetric lone pair orbital (E_σ in eV). [b] Energy of the π-symmetric unoccupied orbital (E_{π^*} in eV) concentrated on the central atom E (E = Si,Ge) of **1**-**16**. [c] Natural atomic orbital occupancy of the out-of-plane p orbital at the Si/Ge center. [d] q_E represents the natural charge at the Si/Ge center. [e] Experimental ionization potentials (in eV) assigned to the transitions originating from the σ-symmetric lone pair orbital.

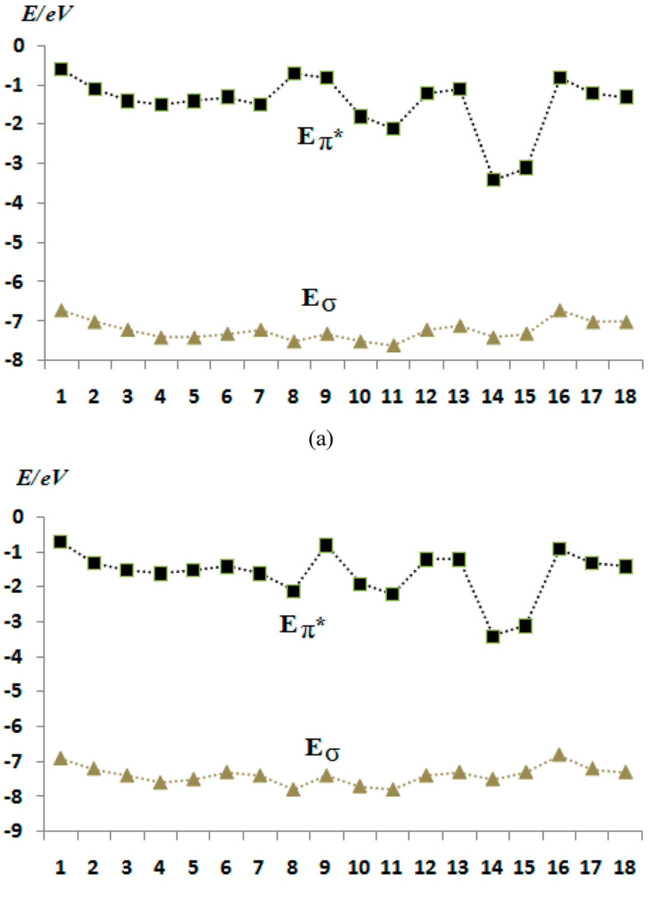
symmetric lone pair and π-symmetric unoccupied MO concentrated on the Si/Ge center of **1**−**18**, and Figure 1 shows the energies of these orbitals.

It is evident from Table 3 and Figure 1 that there is lowering in the energies of both σ-symmetric electron donor and π-symmetric acceptor orbitals as a result of annelation and carbonylation. This implies that annelation and carbonylation of the NHE scaffold decreases and increases the σ donation and π acceptance abilities, respectively. The calculated orbital energies are in agreement with the experimental ionization potentials assigned to the transitions originating from the σ-symmetric lone pair orbital.[4f,7d] It should be noted that the experimental ionization potentials follow a similar trend to that of the orbital energies calculated at PBE1PBE/6-31+G* level of theory.[16] This implies that the orbital energies calculated at this level of theory are adequate for a discussion of the trend in their donation/acceptance abilities. It is also clear from Table 3 that compared to their effect on σ donation abilities, annelation or carbonylation has a dramatic effect on the π accepting ability of these NHEs with carbonylation being the most dominant. The most dramatic effect is obtained for **14** and **15**. This might be due to the fact that carbonyl (C═O) groups are attached to the α-position with respect to the heteroatom N. CO, being a good π acceptor, can withdraw electron density from the nitrogen lone pair (N_{LP}). As a result, the delocalization from the N_{LP} to the formally vacant p orbital of the Si/Ge center decreases, making the Si/Ge center electron deficient. This electron deficiency results in higher π acidity of the molecules. The noncarbonylated compounds **12** and **13** have lower π acidity compared to their carbonylated analogues **14** and **15**. This further proves the effect of carbonylation toward increasing the π acidity of these derivatives. In general, annelation increases the π-acidity of these NHEs to some extent; however, carbonylation near to the Si/Ge center appears to be more effective in increasing the π-acidity, which in turn may find wide applicability in various fields.[25−27] In this regard, the recent report of Driess et al. which provided a hint for the use of silylene ligands for σ-metathesis reactions[28] (believed to be caused by the σ, π- synergism of the metal—silylene complex) is very promising.

We were surprised by the enhanced π-accepting ability of compound **10** than **9** even though the electron-withdrawing carbonyl groups were further away from the N atom in **10**. We reasoned that this difference might arise from more extended π conjugation to the carbonyl groups in **10** compared to **9**. Also, the resonance structure obtained upon donation of the N_{LP} into the carbonyl group is stabilized to a greater extent in **10** than in **9**. Hence, the donation of the N_{LP} into the Si/Ge center becomes stronger in **9**, and as a result, the π acidity decreases. To further probe this hypothesis, we have introduced an additional phenyl ring between the NHE (E = Si, Ge) ring and the quinoid moiety (**11**). Indeed, **11** exhibits even better π-accepting ability, thereby lending support to our reasoning.

There is no appreciable change in the ligand properties of the parent silylenes and germylenes as a result of annelation by the electron-rich pyrrole molecule. However, annelation by furan and thiophene has similar effects as annelation with benzene. The electrophilicity increases in the order **16** < **17** < **18**, which is in agreement with the relative inductive electron-withdrawing ability of these heterocycles.[29]

Table 3 also contains the occupancies of the formally vacant p_π orbital of the Si/Ge center obtained using the NBO method. The occupancies decrease upon annelation and/or carbonylation of the NHE scaffolds. A significant decrease in occupancy is obtained for **14** and **15**, which are found to be the most acidic among the studied NHEs. In general, a good correlation is obtained between the energy of the π-accepting orbital and the occupancies of the formally vacant p_π orbital (Figure S2, Supporting Information). This means that annelation/carbonylation decreases the p_π−p_π conjugation



(a)

(b)

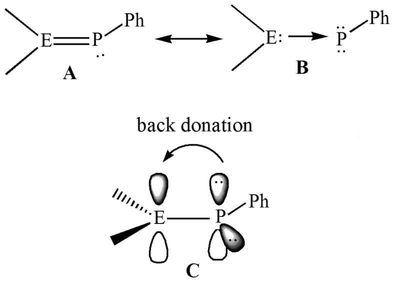
Figure 1. Plot of the energies of the σ-symmetric lone pair (donor) orbital (E_σ) and the π symmetric unoccupied (acceptor) orbital (E_π*) concentrated on the Si/Ge center of (a) NHSis **1Si-18Si** and (b) NHGes **1Ge-18Ge**.

from the lone pair of the adjacent N atoms to the vacant p_π orbital at the Si/Ge center. This decrease in conjugation makes the Si/Ge center electron deficient and results in a lowering of the energy of the π-accepting orbital at the Si/Ge center. As a result, the acidity of these Si/Ge centers increases.

An analysis of the computed natural charges shows that all the annelated and carbonylated ligands have greater positive charge at the Si/Ge center than that of nonannelated **1**. This implies that all the annelated and carbonylated derivatives are more electrophilic than **1**. Significantly higher positive charges are obtained for **14** and **15** which have higher π acidity implying that charge at the Si/Ge center varies almost linearly with the π acidity of these ligands even though we did not obtain one-to-one correlation for all the molecules.

3.4. ^{31}P NMR Spectroscopy. Recently, the use of ^{31}P NMR spectroscopy as a tool for evaluating the π-acidity of carbenes has been demonstrated by Bertrand et al.[30] and theoretically substantiated by our group.[17] We now turn our attention toward the use of ^{31}P NMR spectroscopy for the heavier analogues of NHC, thus quantifying their π-accepting ability by evaluating the ^{31}P NMR chemical shifts of silylene (and germylene)−phosphinidene adducts. In Scheme 2, the resonance form A dominates over B with the increasing π acidity of these ligands. The orbital interaction involving the backdonation of the phosphorus lone pair to the formally vacant p_π orbital at the Si/Ge center is depicted in C. This backdonation reduces the electron density at the phosphorus atom which results in a downfield shift of the ^{31}P signal of the respective phosphinidine adduct. Thus, the change in electron density at the phosphorus center can be monitored in terms of their ^{31}P NMR shifts, providing a quantitative assessment of the π acidity of these ligands.

Scheme 2. Resonance Forms of Silylene (and Germylene)−Phosphinidene Adducts (E = Si or Ge)[a]



[a] Resonance form **A** dominates over **B** with increasing π acidity of these ligands. **C** represents the orbital interaction involved in back donation from the phosphorus center to the formally vacant p orbital at the Si/Ge center.

This approach appears to be quite adequate in quantifying the π-acidity of the Si/Ge centers as very few competing factors are there which may otherwise complicate the outcome. Recently, Cui et al.[31] have reported the synthesis of the first aminophosphasilene, $[Ar(Me_3Si)N]HSi{=}PAr'$ (Ar = 2,6-iPr$_2$C$_6$H$_3$, Ar′ = 2,6-Mes$_2$C$_6$H$_3$), which was characterized by X-ray crystallography and ^{31}P NMR spectroscopy confirming the existence of a Si═P π bond. Table 4 contains the E−PPh bond lengths and ^{31}P NMR chemical shifts of NHE−PPh adducts (E = Si or Ge). The P−C$_{Ph}$ bonds are not coplanar (Figure 2) with the NHE ring, ensuring that the phosphorus lone pair is only delocalized with the vacant p orbital of the Si/Ge center rather than with the phenyl ring. The calculated E−PPh bond length of the annelated and carbonylated NHEs are shorter than that of the nonannelated one implying higher π

Table 4. Calculated E−PPh (r_{E-P}) Bond Distances (in Å) and ^{31}P NMR Chemical Shifts for the Adducts NHE−PPh (E = Si or Ge)

molecule	r_{Si-P}	δ^{31}P	molecule	r_{Ge-P}	δ^{31}P
1Si	2.107	−244.7	**1Ge**	2.182	−147.8
2Si	2.095	−166.0	**2Ge**	2.159	−90.6
3Si	2.092	−161.7	**3Ge**	2.157	−88.1
4Si	2.092	−161.5	**4Ge**	2.156	−87.3
5Si	2.094	−158.9	**5Ge**	2.160	−77.8
6Si	2.097	−158.5	**6Ge**	2.166	−86.3
7Si	2.092	−148.5	**7Ge**	2.156	−79.6
8Si	2.081	−222.0	**8Ge**	2.151	−72.4
9Si	2.095	−246.8	**9Ge**	2.176	−153.9
10Si	2.089	−145.6	**10Ge**	2.154	−75.8
11Si	2.088	−146.4	**11Ge**	2.153	−81.9
12Si	2.104	−163.0	**12Ge**	2.213	205.3
13Si	2.138	−15.6	**13Ge**	2.224	277.5
14Si	2.048	−75.2	**14Ge**	2.147	82.0
15Si	2.050	−108.7	**15Ge**	2.149	33.7
16Si	2.098	−151.6	**16Ge**	2.180	−141.3
17Si	2.092	−154.3	**17Ge**	2.156	−81.6
18Si	2.092	−158.1	**18Ge**	2.156	−85.6

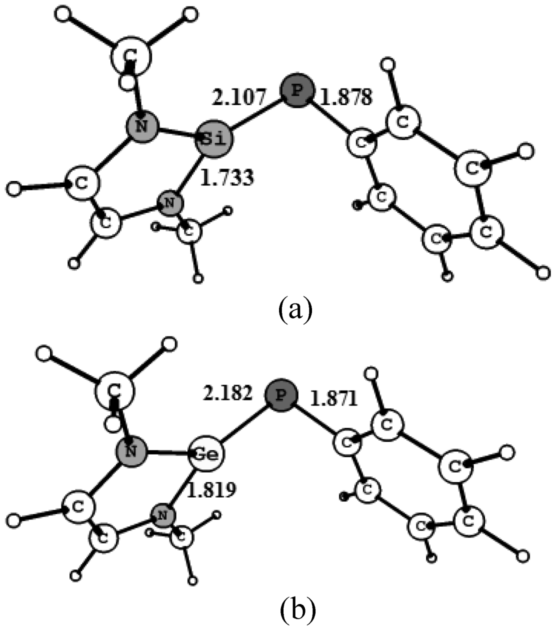


Figure 2. Optimized geometries along with the computed bond lengths (Å) of the PPh adducts of (a) **1Si** and (b) **1Ge**.

acidity for these annelated and carbonylated derivatives. Significantly shorter E−PPh bonds are found for **14** and **15** which can be traced to their higher π acidity. Thus, any change in electron density at the phosphorus center may be traced to the relative π acidity of the NHSi or NHGe. Also, any change in electron density at the phosphorus center will be reflected in the ^{31}P NMR chemical shifts of the adducts. In general, the higher the π acidity of these ligands, the more downfield the chemical shift of the phosphorus nucleus in the adducts will be. For example, molecules **14** and **15** are found to have higher π acidity and consequently their ^{31}P chemical shifts are significantly downfield compared to other ligands. In fact, a good correlation (R^2 = 0.70 for NHSi omitting the point corresponding to **13Si**, and 0.90 for NHGe omitting the points corresponding to **12Ge** and **13Ge**, Figure 3) has been obtained between the energy of the π symmetric unoccupied MO ($E_{\pi*}$) centered at the Si/Ge center of the NHEs and their ^{31}P chemical shifts.

4. CONCLUSION

The last few decades have seen tremendous growth in the chemistry of carbenes, especially the understanding of their σ-donation abilities and, lately, of their π accepting abilities. In comparison, the corresponding chemistry of silylenes and germylenes is developed to a much lesser extent. In this respect, we have undertaken a systematic quantum chemical study on the effect of annelation and carbonylation toward the ligating properties of silylenes and germylenes. Calculations suggest that annelation increases the thermodynamic stability of these heavier analogues, in stark contrast to that of carbenes, whose stability is found to decrease upon annelation.[9,17] Thus, the comparison of the thermodynamic stability of carbenes with their heavier analogues breaks down for the annelated derivatives. However, carbonylation of these heterocyclic silylenes and germylenes is found to exert a similar influence to that of NHCs, i.e., thermodynamic stability decreases on carbonylation. Both annelation and carbonylation are found to decrease the σ-donation abilities of these ligands to some extent but increase the π-acidities significantly. The most dramatic increase in π-acidity of the Si/Ge center is found when the α-position with respect to the N atom attached to the Si/Ge center is carbonylated as in **14** and **15**. The π acidities of these ligands have been further assessed by evaluating the ^{31}P NMR chemical shifts of the respective phosphinidene adduct of these ligands. The calculated ^{31}P chemical shifts values as well as the E−PPh (E = Si, Ge) bond lengths of the phosphinidene adducts have been found to have a good correlation with the π acidity of these Si/Ge centers.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

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

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: ashwini@tezu.ernet.in.

Notes

The authors declare no competing financial interest.

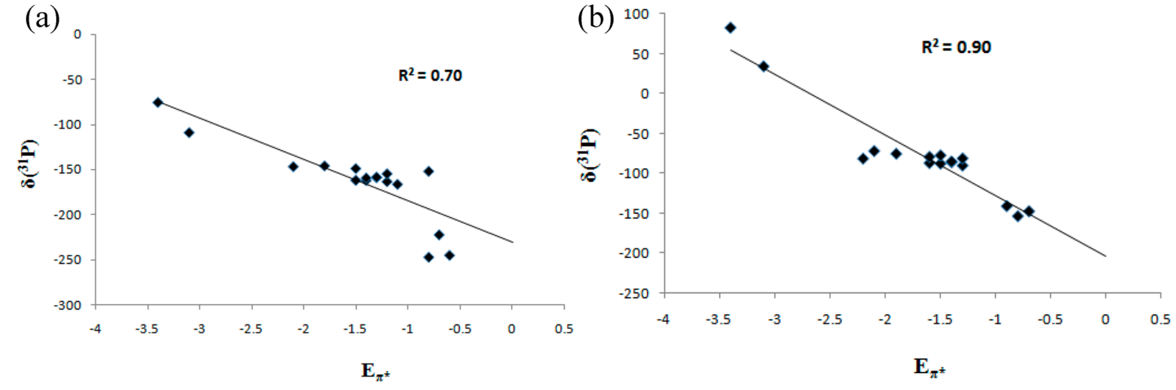


Figure 3. Correlation plots of the energy of the π-symmetric unoccupied MO ($E_{\pi*}$) and ^{31}P chemical shifts (δ^{31}P) of the (a) NHSi−phosphinidene and (b) NHGe−phosphinidene adducts.

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