

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/236044650>

First Principles Studies towards the Design of Silylene Superbases: A DFT Study.

ARTICLE in THE JOURNAL OF PHYSICAL CHEMISTRY A · MARCH 2013

Impact Factor: 2.69 · DOI: 10.1021/jp401076j · Source: PubMed

CITATIONS

6

READS

44

3 AUTHORS:



Abul Kalam Biswas

Central Salt and Marine Chemicals Research I...

11 PUBLICATIONS 23 CITATIONS

SEE PROFILE



Rabindranath Lo

Academy of Sciences of the Czech Republic

27 PUBLICATIONS 127 CITATIONS

SEE PROFILE



Bishwajit Ganguly

Central Salt and Marine Chemicals Research I...

183 PUBLICATIONS 2,259 CITATIONS

SEE PROFILE

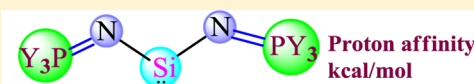
First Principles Studies toward the Design of Silylene Superbases: A Density Functional Theory Study

Abul Kalam Biswas, Rabindranath Lo, and Bishwajit Ganguly*

Analytical Discipline and Centralized Instrument Facility, Central Salt & Marine Chemicals Research Institute (Council of Scientific and Industrial Research), Bhavnagar, Gujarat, India 364 002

S Supporting Information

ABSTRACT: In this paper we have reported for the first time some designed silylene superbases using DFT calculations. These divalent Si(II) compounds can act as powerful neutral organic superbases in the gas phase and in the solvent phase. The DFT calculations performed with the B3LYP/6-311+G**//B3LYP/6-31+G* level of theory showed that one of the designed silylene derivatives :Si(N=PY₃)₂ [Y = -N=C(NMe₂)₂] (**8**) can fall in the range of hyperbase with gas phase proton affinity ~310 kcal/mol. In THF the calculated proton affinity of **8** was found to be 327.5 kcal/mol. The proton affinities computed at the B3LYP/6-311+G**//B3LYP/6-31+G* level for some simple silylenes have been found to be good agreement with the corresponding experimentally measured values. Phosphazene groups attached to the divalent silicon center of silylenes enhanced the basicity of the Si center significantly and further acted as a second protonation site. The calculated second proton affinity of the silylene derivative, **8** in THF was found to be 285.5 kcal/mol. We have shown that the dimerization and cyclization of such silylene superbases were less likely and the monomeric forms would be more stable than their corresponding dimers. The calculated proton affinities also showed a good correlation with the HOMO–LUMO energy gap and energy difference between the singlet and triplet states (ΔE_{S-T}) of the silylene systems. The isodesmic reactions have been employed to examine the stability of the silylene molecules by calculating the silylene stabilization energy (SiSE). The reactivity of silylene molecules has been presented in terms of the nucleophilicity, electronegativity, and hardness of such systems. The Lewis basic properties of these silylene systems have also been explored.



Y = Me, Me	278.0 (301.2)
Y = -N=CMe ₂ , -N=CMe ₂	286.4 (304.9)
Y = -N=C(NMe ₂) ₂ , -N=C(NMe ₂) ₂	309.2 (327.5)

The values in parantheses are in solvent phase.

1. INTRODUCTION

Uncharged organic superbases are important constituents in modern organic chemistry.^{1–7} The synthesis of organic superbases, their basicity in gas and solvent phases, and potential applications have been studied extensively in recent times.^{8,9} The advantages of organic superbases are based on the ease of their molecular variation, mild reaction conditions, better solubility in most organic solvents, and very good stability at lower temperature.^{10,11} Such useful advantages in reaction make organic superbases a better component than inorganic counterparts. Besides that, organic superbases showed the environment friendly recycling property, which makes them useful catalysts in green chemistry.^{12–14} The first organic superbase 1,8-bis(dimethylamino)naphthalene (DMAN) was reported by Alder et al.¹⁵ After that, various types of organic superbases containing amines, imines, guanidines, phosphazenes, and quinomines as building blocks have been reported.^{16–26} The extraordinary basicity of these compounds is attained by different strategies: strong lone-pair repulsion in these systems, relief of lone-pair repulsion in the protonated forms, a strong intramolecular hydrogen bonding in the resulting conjugate acids, and noncovalent interaction.^{24,25} To achieve the higher basicity, highly functionalized amines, imines, and phosphazenes are reported.^{16–20,23} Most of the organic superbases are designed with rigid molecular framework by forcing two or more basic centers in close proximity.^{8,9}

Besides different amines and imines, the divalent carbon(II) compounds also showed the higher proton affinity due to the presence of lone pair of electrons.²⁷

Simple carbene (:CH₂) possesses a higher proton affinity value than normal amines and imines.²⁸ A varieties of carbenes, stable at room temperature have been synthesized after the isolation of imidazol-2-ylidene carbene.²⁹ The experimental proton affinity of 1-ethyl-3-methyl-imidazol-2-ylidene is 251.3 ± 4 kcal/mol, which is the range of superbase.³⁰ Carbenes can be used as ligands in transition metal based catalysts³¹ and also in organic reactions as catalysts.³² Herein, we have designed some divalent silicon(II) compounds for accomplishing a new class of organo superbase. Silylene (:SiH₂), the heavier analogues of divalent neutral carbene, has a lone pair of electrons in singlet state.³³ Such a property of silylene is appropriate to design a new type of organic superbases based on divalent silicon(II) compounds. Silylenes are typically short-lived species with enormously high reactivity.³⁴ In the last two decades, organosilicon compounds have attracted a considerable interest in modern organic chemistry.³⁵ Silicon compounds act as catalysts or reagents in various organic reactions, e.g., synthesis of β -amino carbonyl compounds,

Received: January 30, 2013

Revised: March 11, 2013

Published: March 14, 2013



catalyst in Diels–Alder reactions, pyrolysis of propane–butane hydrocarbon mixture, and synthesis of alkene.^{36–39} Silylenes, the divalent silicon compounds, are the most essential reactive intermediate in these fields. Silylenes used as a catalyst for olefin polymerization, α -keto ester, can be converted into α -hydroxy acid metal-catalyzed silylene.⁴⁰

Several stable silylene systems have been isolated and were shown to be stable at room temperature under inert atmosphere.^{41–44} The first stable N-heterocyclic silylene (NHSi) at ambient temperature was synthesized by West and co-workers⁴¹ in 1994. After that, a number of stable divalent N-heterocyclic silylenes were synthesized^{41–44} and in all cases silicon is single bonded with nitrogen atoms. The first cyclic alkyl silylene, stable at low temperature, was reported by Kira.⁴⁵ The acyclic diaminosilylene $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Si}$: was synthesized by West and co-workers and is stable in solution at low temperature.⁴⁶ Recently, a new type of stable, acyclic, two-coordinated silylenes were reported, where silicon atom sits between two arylsulphur groups or a boron and nitrogen atom containing groups.^{41,47}

In this present article, we have chosen silylene ($:\text{SiH}_2$) as a basic scaffold for designing organosilicon superbases. Different substituents are introduced to make simple silylene from normal base to an organic superbase in the gas and solvent phases. The substituents have been located at appropriate positions to enhance the donor capability of such silylene systems. To examine the influence of solvent molecules, we have also calculated the proton affinities of the silylene molecules in THF. The calculated highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO) energy and difference between singlet and triplet state ($\Delta E_{\text{S,T}}$) energies of the silylene molecules also describes the superbasicity of these molecules well. The stability of the silylene systems is determined as the silylene stabilization energy (SISE) using isodesmic reactions. The Lewis basic properties of the silylene systems are also studied in donor–acceptor complexes with Lewis acid BH_3 .

2. COMPUTATIONAL METHODS

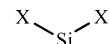
All calculations were performed with density functional theory (DFT) using Becke's three-parameter exchange functional with the correlation functional of Lee, Yang, and Parr (B3LYP).^{48,49} All systems were fully optimized with the 6-31+G* basis set,⁵⁰ and harmonic vibrational frequency calculations were used to confirm that the optimized structures were minima, as characterized by positive vibrational frequencies. Single-point calculations were carried out with the B3LYP/6-311+G** basis set. The proton affinity calculated at the B3LYP/6-311+G**//B3LYP/6-31+G* level of theory using the general equation: proton affinity (B) = (ΔE_{el}) , where $(\Delta E_{\text{el}}) = [E(\text{B}) - E(\text{BH})]$ is the electronic energy contributions to the proton affinity. Here B and BH^+ denote the examined base and its conjugate acid, respectively. The B3LYP/6-31+G* optimized geometries were used to calculate the solvation energies at the B3LYP/6-311+G** level employing polarizable continuum model (PCM)^{51–55} using united atom topological model (UAHF) atomic radii in tetrahydrofuran (THF) solvent ($\epsilon = 7.58$). The ionization potential (IP) was calculated as the energy difference between the nonoptimized cation-radical structure and the ground state structure, and the electron affinity (EA) was calculated as the energy difference between the anion-radical and ground state. The absolute electronegativity (χ) and the absolute hardness are calculated by the formula, $\chi = (\text{IP} + \text{EA})/$

2 and $\eta = (\text{IP} - \text{EA})/2$ respectively.^{56a} Isocontour maps of the ELF were plotted with CheckDen from WFN output files created with Gaussian.⁵⁷ All quantum chemical calculations were performed using Gaussian 03, Revision E.01 program.⁵⁸

3. RESULTS AND DISCUSSION

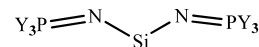
We have applied the density functional theory (DFT) at the B3LYP/6-311+G**//B3LYP/6-31+G* level of theory to calculate the gas phase proton affinity of silylene systems (Schemes 1 and 2). The proton affinity of silylene was first

Scheme 1



1. X = H, H
2. X = H, Me
3. X = Me, Me

Scheme 2



4. X = NMe_2 , NMe_2
5. X = $\text{N}(\text{iPr})_2$, $\text{N}(\text{iPr})_2$
6. Y = Me, Me
7. Y = $-\text{N}=\text{CMe}_2$, $-\text{N}=\text{CMe}_2$
8. Y = $-\text{N}=\text{C}(\text{NMe}_2)_2$, $-\text{N}=\text{C}(\text{NMe}_2)_2$

determined by Beauchamp and Shin using Fourier transform ion cyclotron resonance spectroscopy (CRS).⁵⁹ CRS determined proton affinity values enable us to benchmark the performance of the employed computational methods in predicting proton affinities for silylenes. The calculated proton affinities of these silylene systems have been compared with the experimental values (Table 1). The calculated gas phase proton affinity of simple silylene ($:\text{SiH}_2$) is 201.5 kcal/mol, which is very close to the reported experimental value (201 ± 3 kcal/mol)⁵⁹ (Table 1). The zero point vibrational energy (ZPVE) corrections applied to the proton affinity values seem to show larger differences with the available experimental results (Table 1). However, the uncorrected (ZPVE) PA values are in good agreement with the experimental results. The substitution of electron donating group such as methyl group can enhance the proton affinity value of the silylene system. The dimethyl substitution of silylene ($:\text{SiMe}_2$) shows the highest proton affinity in these series (Table 1). B3LYP/6-311+G**//B3LYP/6-31+G* calculated results show that these values are in good agreement to the experimentally determined results. The proton affinities of the silylene systems have further been calculated with post-Hartree–Fock level (MP2) and hybrid meta density functional M06-2X levels of theory.^{60,61} The proton affinities calculated with M06-2X and MP2 for 1–3 showed a larger difference in the PA values than the B3LYP results, when compared against the experimental data (Table 1).

The gas phase proton affinity values of silylene and its methyl substituted systems are in the range of normal base and lower than the proton affinity of organic superbases (compounds that have a proton affinity >1000 kJ/mol = 239 kcal/mol).^{15,62} To enhance the basicity of the silylene unit, the hydrogens were substituted with two $-\text{NMe}_2$ groups 4 (Scheme 2, Figure S1, Supporting Information). The silylene system $(\text{Me}_2\text{N})_2\text{Si}$: was reported extensively by different research groups and discussed

Table 1. Comparison of Experimental and Calculated Proton Affinities of Silylene Molecules 1–3 in the Gas Phase

compounds	proton affinity (kcal/mol)				
	experimental	calculated			
		B3LYP/6-311+G**//B3LYP/6-31+G*		MP2/6-311+G**//B3LYP/6-31+G*	M06-2X/6-311+G**//B3LYP/6-31+G*
		without ZPVE correction	with ZPVE correction		
1	201 ± 3	201.5	194.9	207.2	200.8
2	215 ± 3	216.5	210.5	219.9	214.5
3	231	228.8	222.8	230.1	225.3

the stability and dimerization ability of this silylene system.⁶³ The computed proton affinity of **4** was found to be 237.3 kcal/mol, which is close to the proton affinity of the organic superbase (Table 2).^{15,62} THF has been used as a solvent in

Table 2. B3LYP/6-311+G**//B3LYP/6-31+G* Calculated Proton Affinities (kcal/mol) of Different Silylene Molecules in the Gas Phase and Solvent Phase

compound	proton affinity		V_{\min} at Si atom ^a
	gas phase	solvent phase THF	
4	237.3	272.3	−32.2
5	250.6	279.6	−34.5
6	278.0	301.2	−52.1
7	286.4	304.9	−47.4
8	309.2	327.5	−65.7

^aThe calculated V_{\min} at the Si atom of different silylenes are given in kcal/mol.

this study because most of the reactions and synthesis of silylenes are reported in this solvent.^{41,42,63} In tetrahydrofuran solvent, compound **4** has a proton affinity value 272.3 kcal/mol, which is much higher than the gas phase proton affinity value for **4** (Table 2). The positively charged protonated form of silylene systems gains greater stabilizations in tetrahydrofuran solvent than the corresponding neutral forms.⁶⁴ In compound **4**, the lone pairs of nitrogen conjugate favorably with the empty 3p(Si)⁶⁵ and augment the nucleophilic character of central Si atom.⁶⁶ The calculated geometrical parameters of **4** describe well the effect of conjugation in the system. The calculated Si–N bond length (1.755 Å) in **4** is shorter than the normal Si–N bond length (1.78 Å) (Table 3).⁶⁷ The Si–N bond length (1.755 Å) and the N–Si–N bond angle (105.2°) are closer to the previous calculations (1.752 Å and 105.2°, respectively) using B3LYP/6-31G* level by Apeloig et al. (Table 3).^{65a} After protonation, the bond length of Si–N is greatly reduced from

Table 3. Bond Lengths (Å) and Bond Angles (deg) of the Optimized Molecules at the B3LYP/6-31+G* Level of Theory

compound	$r(\text{Si}\cdots\text{N})$	bond angle
4	1.755	105.2
4H ⁺	1.666	127.4
5	1.766	107.2
5H ⁺	1.671	128.1
6	1.720	103.8
6H ⁺	1.610	128.8
7	1.718, 1.714	103.1
7H ⁺	1.630, 1.633	121.7
8	1.712, 1.724	104.01
8H ⁺	1.621, 1.632	123.3

1.755 to 1.666 Å and the bond angle of N–Si–N changes from 105.2° to 127.4° (Table 3). The decrease of bond length and increase in the bond angle is due to the neutralized charge of the protonated form; i.e., more conjugation takes place in the protonated form than in the unprotonated form. Further, we have substituted the methyl group of (Me₂N)₂Si: with the more electron donating isopropyl group, **5** (Scheme 2). The bis(diisopropylamine)silylene can be prepared photochemically and was reported to be stable at room temperature in solution.⁶⁸ The gas phase proton affinity of the compound has been calculated to be 250.6 kcal/mol, which is in the range of the organic superbase and in tetrahydrofuran the proton affinity value is 279.6 kcal/mol (Table 2). The isopropyl groups attached to the Si atom in **5** enhance the basicity by 13 kcal/mol compared to the case for **4**. The higher proton affinity of the molecule is achieved due to the favorable conjugation between the lone pairs on nitrogen and vacant 3p(Si) orbital,⁶⁸ which increases the basic character of silylene. The Si–N bond length (1.766 Å) and N–Si–N bond angle (107.2°) are close to the previous calculated results 1.764 Å and 106.9°, respectively (Table 3).^{65a} In an earlier report, it was observed that these silylenes are singlets in the ground state due to their higher stability compared to that in the triplet ground state.³³ We have examined the stability of the singlet state silylene systems based on the singlet–triplet energy difference. To note that the singlet–triplet energy gap is method sensitive,⁶⁹ we have performed the ($\Delta E_{\text{S-T}}$) energy difference with B3LYP and post-Hartree–Fock (MP2) levels of theory. The B3LYP/6-311+G**//B3LYP/6-31+G* calculated singlet–triplet energy gap for **1** and **3** are 21.1 and 25.9 kcal/mol, respectively. These calculated results correlate well with the earlier report.⁶⁹ The calculated singlet–triplet energy difference ($\Delta E_{\text{S-T}}$) in **4** and **5** are 52.0 and 44.8 kcal/mol respectively, which is also in good agreement with the previous reports with different level of theory (Table 4).^{65a} Further, the singlet–triplet energy gap for **1** and **3** examined using MP2 level of theory also showed good agreement with the previous MP2 results (Table S1, Supporting Information).⁶⁹

In continuing the process to enhance the basicity, we have substituted –N=PMe₃ groups in the simplest silylene

Table 4. B3LYP/6-311+G**//B3LYP/6-31+G* Calculated Energy Difference ($\Delta E_{\text{S-T}}$, kcal/mol) between Singlet (¹A) and Triplet (³B) States of Different Silylene Molecules and the Stabilization Energies of These Systems

compound	$\Delta E_{\text{S-T}}$	stabilization energy
4	52.0	28.3
5	44.8	24.4
6	50.6	25.0
7	45.7	23.4
8	43.4	23.3

molecule (compound **6**, Scheme 2, Figure S1, Supporting Information). The iminophosphorane ligand is mainly used in superbases.^{70,71} In previous studies of organic superbases, the phosphazene units were mainly reported for involving as a proton binding sites; however, in the present study we have taken a different approach.⁷⁰ We have utilized the greater electron-releasing properties of the zwitterionic phosphazene groups to increase the basicity of silylene Si (II) center. The phosphazene groups placed in **6** give the proton affinity value of 278.0 kcal/mol, which is comparable to that for the highly basic organic molecules (Table 2).^{18e,71} In addition to that, we have also examined the probability for the protonation in the phosphazene units (Figure S2, Supporting Information). The calculated proton affinity values suggest that the phosphazene units are less preferable sites for the protonation than the Si center (Table 5).

Table 5. B3LYP/6-311+G**//B3LYP/6-31+G* Calculated Proton Affinities (kcal/mol) on the Nitrogen Atom of Different Silylene Molecules in the Gas Phase and Solvent Phase

compound	proton affinity	
	gas phase	THF
6	272.8	296.9
7	278.3	298.6
8	307.4	326.2

The phosphazene groups in the silylene system **6** enhance the proton affinity value by 27 kcal/mol compared to the case for **5**. The molecular electrostatic potential (MESP) isosurface calculated for these systems also rationalizes this behavior.⁷² The computed electrostatic potential shows that the V_{\min} value at the central Si atom for **6** is -52.1 kcal/mol, which is relatively much higher than that for **4** (-32.2 kcal/mol) and **5** (-34.5 kcal/mol) (Table 2). The Si–N bond length (1.720 Å) of **6** is greatly reduced compared to those for **4** and **5** as well as the normal Si–N single bond length (1.78 Å) (Table 3).⁶⁷ Furthermore, a shorter Si–N bond length (1.610 Å) occurs in the protonated form, which suggests a better π delocalization in the protonated form with the phosphazene unit than in the unprotonated form. Further, we have influenced the basicity of the silicon center through remote substitution effect. We have substituted the methyl group of phosphazene unit with $-\text{N}=\text{CMe}_2$ group in **7** to enhance the electron density at the Si atom (Scheme 2, Figure S1, Supporting Information). The calculated proton affinity in the gas phase was found to be 286.4 kcal/mol, which was 8.4 kcal/mol higher than **6** (Table 2). In tetrahydrofuran, the calculated proton affinity of **7** was 304.9 kcal/mol. The $-\text{N}=\text{CMe}_2$ unit in the phosphazene group arranged in such a way that it can avoid the steric repulsions (Figure S1, Supporting Information). The proton affinity calculated of the $-\text{N}=\text{CMe}_2$ unit in the phosphazene group is lower than that of the silicon center in **7** (Table S2, Supporting Information). The introduction of the $-\text{N}=\text{C}(\text{NMe}_2)_2$ group (compound **8**, Scheme 2, Figure S1, Supporting Information) shows the proton affinity value (Table 2), which falls in the range of hyperbases (compounds that have a proton affinity >300 kcal/mol).⁸ The solvent phase proton affinity of **8** was found to be 327.5 kcal/mol (Table 2). Compound **8** shows the highest V_{\min} value (-65.7 kcal/mol) in the series at the Si atom. The calculated V_{\min} values correlate well with the computed proton affinities for these systems (Figure 1). Furthermore, the

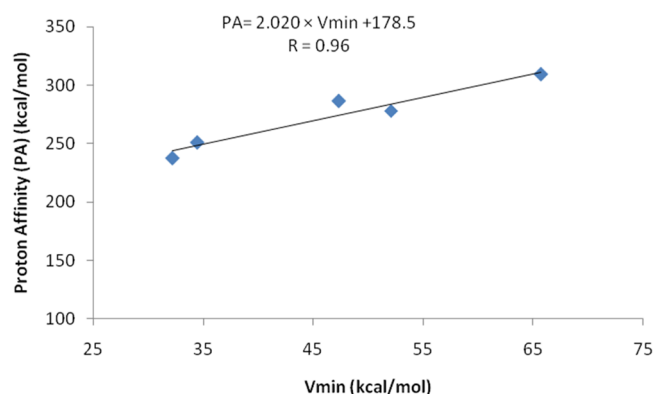
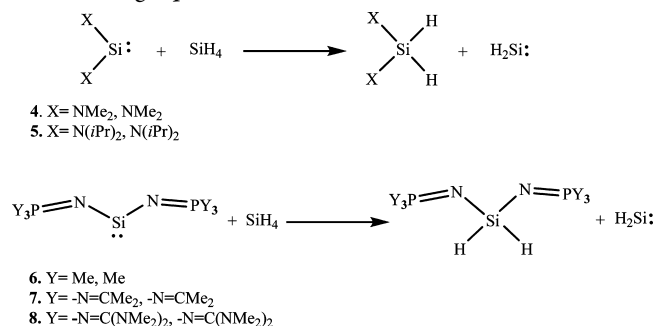


Figure 1. Relationship between the V_{\min} and the gas phase proton affinities for **4–8**.

isocontour maps of the electron localization function (ELF) are also plotted for these silylene systems (Figure S3, Supporting Information). The ELF isocounter maps show the electron localization on the silicon center as we observed with the location of V_{\min} values in MESP calculations. Further, we have examined the proton affinity value in the phosphazene unit for compound **8** (Figure S2, Supporting Information). The B3LYP/6-311+G**//B3LYP/6-31+G* calculated proton affinities in the phosphazene unit also showed the highest value in compound **8** compared to those of other studied systems (Table 5). The Mulliken charge analysis suggests that the nitrogen center of the phosphazene unit bears more negative charge in **8** (-1.263) than the corresponding nitrogen center in **6** (-0.917). Further, the arrangement of the bulky substituents can also induce secondary effects on the PA values in such cases. These phosphazene substituents in **6–8** can also be protonated along with the silicon divalent (II) center. We have examined the bis-protonation of compounds **6–8** at the same level of theory. The second proton affinity obtained in THF for the protonation of substituted phosphazene nitrogen center at **8** is 285.5 kcal/mol which is listed in Table S3 (Supporting Information). The $-\text{N}=\text{C}(\text{NMe}_2)_2$ unit in phosphazene group showed lower proton affinity than the silicon center in **8** (Table S2, Supporting Information).

The proton affinities calculated for the silylene systems **4–8** correlated well with the singlet–triplet energy gaps $\Delta E_{\text{S-T}}$ (Table 4).^{56a} For the silylene derivative **8**, we have found the lowest $\Delta E_{\text{S-T}}$ value of 43.4 kcal/mol and the highest proton affinity in the series.

Further, the stability of the silylene systems can be determined by calculating the silylene stabilization energy (SiSE).^{56a} The stabilization energy values were calculated using the following equations,



The silylene systems possess the silylene stabilization energy (SiSE) due to its extra stabilization compared to case of the

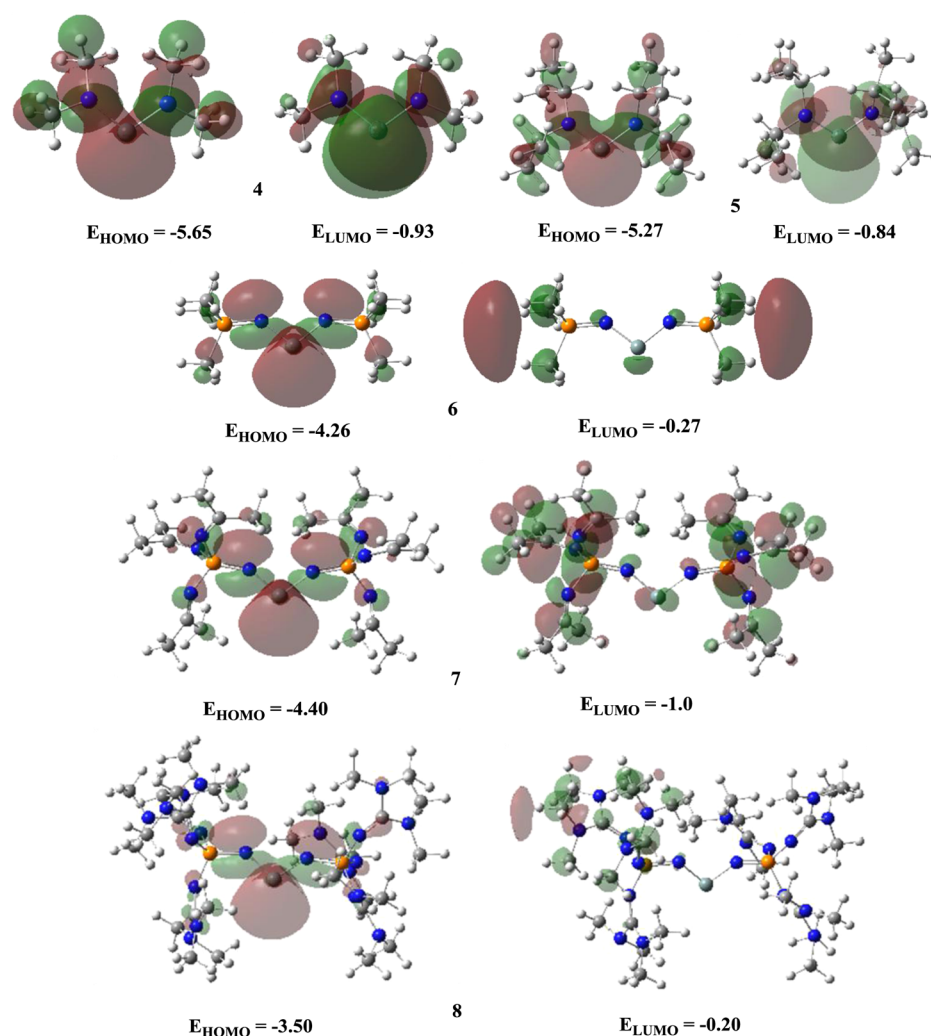


Figure 2. Frontier molecular orbitals of compounds 4–8 at B3LYP/6-311+G** level (energies in eV).

simplest silylene molecule ($:\text{SiH}_2$). The calculated results show that compound **4** has the highest value in the series, which implies its greater stability in the singlet state (Table 4). The silylene derivative **8** has the lowest stabilization energy and the highest proton affinity value in the series. However, the reactivity of **8** is greatly reduced due to the presence of bulky substituent groups and being elaborated in the later section. The calculated stabilization energy also follows the same trend as observed in the energy gap between the singlet and triplet state.

The energies of the frontier molecular orbitals in the silylene molecules also provide information about the possible reactivity of the Si atom. The contributions of molecular orbitals in singlet and triplet states are given in Figure 2 and Figure S4 (Supporting Information). All these studied silylene systems are in the singlet ground state. In the highest occupied molecular orbital (HOMO), the lone pair is localized on the central Si atom (Figure 2). The calculated HOMO energies are in the range -5.65 to -3.50 eV (Table 6). Compound **8** shows the highest HOMO energy in the series, and it is expected that this compound should be a better σ -donor than other studied silylene systems (Figure 2).⁵⁶ The calculated proton affinity values support this observation. A good relationship between calculated proton affinities and E_{HOMO} was observed with high correlation coefficient value of 0.99 (Figure 3). The HOMO–

Table 6. Energy of the Highest Molecular Orbital (E_{HOMO} , eV) and the Energy Differences between the Highest Occupied Molecular Orbital (HOMO) and the Lowest Unoccupied Molecular Orbital (LUMO) ($\Delta E_{\text{HOMO-LUMO}}$, eV) of Different Silylene Molecules in the Singlet State at the B3LYP/6-311+G** Level of Theory

compound	E_{HOMO}	$\Delta E_{\text{HOMO-LUMO}}$
4	-5.65	4.72
5	-5.27	4.43
6	-4.26	3.99
7	-4.40	3.40
8	-3.50	3.30

LUMO energy gap (HLG) is also an important parameter to calculate the reactivity of the silylene molecules. The HLG values decreases in the order of $4 < 5 < 6 < 7 < 8$, indicating compound **8** is more reactive than other systems.⁵⁶ The calculated proton affinities also show a good correlation with the HOMO–LUMO energy gap of the silylene systems (Figure 4).

The possibility of dimerization for the silylene systems are reported in earlier studies.⁵⁹ In the dimerization mechanism of singlet silylene systems, the filled σ orbital of each silylene is participated to interact with the empty p orbital for the

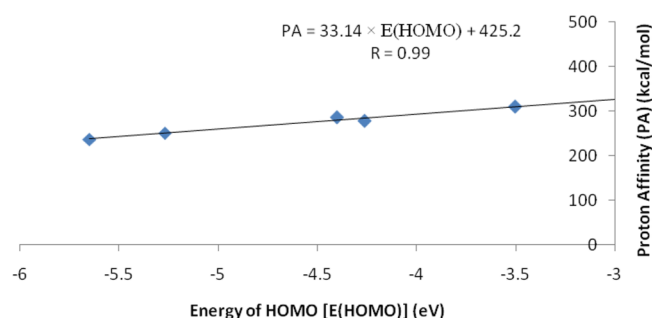


Figure 3. Relationship between the HOMO energy and the gas phase proton affinities for 4–8.

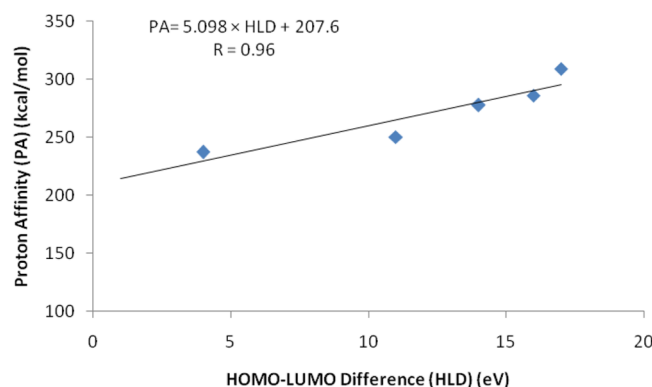


Figure 4. Relationship between the HOMO–LUMO energy difference and gas phase proton affinities for 4–8.

formation of Si=Si double bonded dimers. A cyclic bridged dimerization is also possible for these silylene systems.^{65a} These double bonded dimers are only possible when the sum of the ΔE_{S-T} values of two interacting silylenes is smaller than the corresponding double bond energy. For the compounds 6–8, we have examined the possibility for the formation of double bonded and cyclic dimerization compounds. In compound 6, the calculated double bond energy is relatively smaller than the sum of the ΔE_{S-T} values (Tables 4 and 7). The bonding

Table 7. Dimerization Energies (kcal/mol) to Si=Si Bonded Dimers ($E_{\text{dim}}(\text{Si}=\text{Si})$) and to the Cyclic Dimer ($E_{\text{dim}}(\text{cyclic})$)

compound	$E_{\text{dim}}(\text{Si}=\text{Si})$	$E_{\text{dim}}(\text{cyclic})$
6	−13.5	−3.6
7	−13.9	

parameter measured for this dimer shows that it has a very long Si–Si bond of 2.454 Å. This result suggests that 6 is less likely to dimerize from its monomers. Two bulky N=PMe₃ groups in compound 6 experiences strong steric crowding and minimizes the dimerization formation.^{65a} The cyclization energy for the formation of a bridged compound of 6 is also relatively smaller than the sum of ΔE_{S-T} values and suggests the inability of the dimerization process for this compound (Tables 4 and 7). Compound 7 also showed the analogous behavior for the dimerization process as observed with 6 (Table 7). The cyclic dimer form of 7 was not achieved due to the steric repulsions between the bulky substituent groups. Compound 8 fails to give the dimerization and cyclic dimer products, although it has the lowest silylene stabilization energy

compared to those of other studied silylene systems (Table 4).^{65a}

The silylene philicity can be determined by ionization potential (IP), electron affinity (EA), absolute electronegativity (χ), and absolute hardness (η) calculations (Table 8).^{21b,56a}

Table 8. Calculated Ionization Potential (IP, eV), Electron Affinity (EA, eV), Absolute Electronegativity (χ), and Absolute Hardness (η) of Free Silylene Molecules 4–8

molecules	IP	EA	χ	η
4	7.55	−0.57	3.49	4.06
5	6.93	−0.59	3.17	3.76
6	5.99	−0.48	2.76	3.24
7	5.84	−0.06	2.89	2.95
8	4.80	−0.48	2.16	2.64

The calculated results show that compound 8 has lower ionization potential in the series (Table 8). It implies that 8 has the highest nucleophilic character besides its higher proton affinity value. The lower absolute electronegativity value also supports this observation. The electron affinities calculated for 4–8 have negative values, suggesting that the addition of an electron is an endothermic process in these molecules. The calculated hardness values are decreases in the series from 4–8, which indicates the preference of soft metal complexes down the series (Table 8).

The Lewis basic properties of the silylene systems are also examined with the known Lewis acid BH₃. We have examined the bond dissociation energy for well-known donor–acceptor complex like NH₃–BH₃ at the same level of theory. The B3LYP/6-311+G**//B3LYP/6-31+G* calculated bond dissociation energy correlated well with available reported result.⁷³ The optimized complex geometries of the silylene systems 4–8 form stable donor–acceptor complexes compared to the case of normal base NH₃ (Table 9). The calculated high bond energies

Table 9. B3LYP/6-311+G**//B3LYP/6-31+G* Calculated Bond Dissociation Energy (kcal/mol) of Donor–Acceptor Complexes with the BH₃ Molecule

compound	dissociation energy
4	31.6
5	31.6
6	42.1
7	41.0
8	45.0
NH ₃	29.0 (31.0 ^a)

^aExperimental value.

for the BH₃ complexes indicate that the silylene–BH₃ complexes should be synthetically attainable. Compound 8 exhibits the highest Lewis basic property in the series due to its higher bond dissociation energy (45.0 kcal/mol) (Table 9). These calculated results suggest that the silylene systems can be used as valuable Lewis bases in donor–acceptor complexes with Lewis acids like BH₃.

4. CONCLUSIONS

We have reported for the first time some silylene superbases using DFT calculations at the B3LYP/6-311+G**//B3LYP/6-31+G* level of theory. The proton affinities of the silylene systems have further been calculated with post-Hartree–Fock

level (MP2) and hybrid meta density functional M06-2X levels of theory. The computed proton affinities of the silylenes at the B3LYP level have been found to be in better agreement with their experimentally measured proton affinity values. To enhance the basicity of simple silylene (:SiH₂), the hydrogen atoms were replaced with more electron donating -NMe₂ groups (4). The lone pairs of nitrogen conjugate favorably with the empty 3p(Si) and augment the proton affinity value to 237.3 kcal/mol. The substantial enhancement in the basicity was achieved with the -N=PMe₃ group coordinated to the Si center of the silylene unit. The proton affinity of 6 was found to be 278.0 kcal/mol. The introduction of the -N=C(NMe₂)₂ group (8) in the phosphazene groups enhanced the basicity, which falls in the range of the hyperbase, 309.2 kcal/mol. Interestingly, the phosphazene groups attached to the divalent silicon center of silylene can act as a bis-protonation site in such silylene derivatives and such examples are rare in the literature. The calculated second proton affinity of the silylene derivative 8 in THF is 285.5 kcal/mol. Isodesmic reactions have been performed to examine the stabilization of these systems using silylene stabilization energy (SiSE). Further, the DFT calculations show that the dimerization and cyclization of these silylene derivatives are not favored and they can primarily exist in monomeric forms. The calculated proton affinity also shows a good correlation with the HOMO–LUMO energy gap and energy difference between singlet and triplet state (ΔE_{S-T}) of the silylene systems. The silylene systems are characterized by Lewis basic properties and ligand binding energies in donor–acceptor complexes. These results will stimulate chemists to develop synthetic protocols to prepare this new family of superbase for their potential applications.

■ ASSOCIATED CONTENT

■ Supporting Information

MP2/6-31G** calculated energy differences, B3LYP/6-311+G** proton affinities, and B3LYP/6-31+G* optimized Cartesian coordinates of all the neutral and protonated silylene molecules. Figures of optimized geometries, ELF isocontour maps, and frontier molecular orbitals. This information is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*Fax: (+91)-278-2567562. Telephone: +91-278-2567760, ext 6770. E-mail: ganguly@csmcni.org.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

A.K.B. is thankful to UGC, New Delhi, India, for awarding a Junior research fellowship, R.L. is thankful to UGC, New Delhi, India, for awarding a Senior research fellowship, and B.G. thanks DST, New Delhi, and MSM, SIP, for financial support of this work. We are also thankful to the reviewers for their suggestions and comments that have helped us to improve the paper.

■ REFERENCES

- (1) (a) Alder, R. W. Strain Effects on Amine Basicities. *Chem. Rev.* **1989**, *89*, 1215–1223. (b) Alder, R. W. Intrabridgehead Chemistry. *Tetrahedron* **1990**, *46*, 683–713.
- (2) Llamas-Saiz, A. L.; Foces-Foces, C.; Elguero, J. Proton Sponges. *J. Mol. Struct.* **1994**, *328*, 297–323.

- (3) Staab, H. A.; Saupe, T. Proton Sponges” and the Geometry of Hydrogen Bonds: Aromatic Nitrogen Bases with Exceptional Basicities. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 865–879.

- (4) Raczynska, E. D.; Decouzon, M.; Gal, J.-F.; Maria, P.-C.; Gelbard, G.; Vielfaure-Joly, J. Gas-Phase Structural (Internal) Effects in Strong Organic Nitrogen Bases. *J. Phys. Org. Chem.* **2001**, *14*, 25–34.

- (5) Gal, J.-F.; Maria, P.-C.; Raczynska, E. D. Thermochemical Aspects of Proton Transfer in the Gas Phase. *J. Mass Spectrom.* **2001**, *36*, 699–716.

- (6) Alcamí, M.; Mó, O.; Yáñez, M. Computational Chemistry: A Useful (Sometimes Mandatory) Tool in Mass Spectrometry Studies. *Mass Spectrom. Rev.* **2001**, *20*, 195–245.

- (7) Alcamí, M.; Mó, O.; Yáñez, M. Modeling Intrinsic Basicities and Acidities. *J. Phys. Org. Chem.* **2002**, *15*, 174–186.

- (8) Maksić, J. V.; Kovačević, B.; Vianello, R. Advances in Determining the Absolute Proton Affinities of Neutral Organic Molecules in the Gas Phase and Their Interpretation: A Theoretical Account. *Chem. Rev.* **2012**, *112*, S240–S270.

- (9) *Superbases for Organic Synthesis*; Ishikawa, T., Ed.; Wiley: Chichester, West Sussex, 2009.

- (10) Tang, J.; Dopke, J.; Verkade, J. G. Decarboxylation of 2-Lactylthiazolium Cation. AM 1 and ab Initio MO/MP2 Studies. *J. Am. Chem. Soc.* **1993**, *115*, 1515–1519 and references therein.

- (11) Hibbert, F.; Hunte, K. P. P. Exceptional Basic Strength of 1,8-Bis(dimethylamino)- and 1,8-Bis(diethylamino)-2,7-dimethoxynaphthalenes: Kinetic and Equilibrium Studies of the Ionisation of the Protonated Amines in Me₂SO–H₂O Mixtures with Hydroxide Ion. *J. Chem. Soc. Perkin Trans. 2* **1983**, 1895–1899.

- (12) Schuchardt, U.; Vargas, R. M.; Gelbard, G. Transesterification of Soybean Oil Catalyzed by Alkylguanidines Heterogenized on Different Substituted Polystyrenes. *J. Mol. Catal. A: Chem.* **1996**, *109*, 37–44.

- (13) Gelbard, G.; Vielfaure-Joly, F. Polynitrogen Strong Bases as Immobilized Catalysts. *React. Funct. Polym.* **2001**, *48*, 65–74.

- (14) Ishikawa, T.; Isober, T. Modified Guanidines as Chiral Auxiliaries. *Chem.-Eur. J.* **2002**, *8*, 552–557.

- (15) Alder, R. W.; Bowman, P. S.; Steele, W. R.; Winterman, D. P. The Remarkable Basicity of 1,8-Bis(dimethylamino)naphthalene. *Chem. Commun.* **1968**, 723–724.

- (16) (a) Raczynska, E. D.; Maria, P.-C.; Gal, J.-F.; Decouzon, M. Superbases in the Gas Phase. Part II. Further Extension of the Basicity Scale Using Acyclic and Cyclic Guanidines. *J. Phys. Org. Chem.* **1994**, *7*, 725–733. (b) Howard, S. T.; Platts, J. A.; Coogan, M. P. Relationships Between Basicity, Structure, Chemical Shift and the Charge Distribution in Resonance-Stabilized Iminoamines. *J. Chem. Soc., Perkin Trans. 2* **2002**, 899–905. (c) Bachrach, S. M.; Wilbanks, C. C. Using the Pyridine and Quinuclidine Scaffolds for Superbases: A DFT Study. *J. Org. Chem.* **2010**, *75*, 2651–2660. (d) Maksić, Z. V.; Kovačević, B. Spatial and Electronic Structure of Highly Basic Organic Molecules: Cyclopropenimines and Some Related Systems. *J. Phys. Chem. A* **1999**, *103*, 6678–6684.

- (17) (a) Singh, A.; Chakraborty, S.; Ganguly, B. C₂-Chiral Substituted cis-1,3,5,7-Tetraazadecalins as Proton Sponges: A Computational Study. *Eur. J. Org. Chem.* **2006**, 4938–4942. (b) Singh, A.; Ganguly, B. DFT Studies toward the Design and Discovery of a Versatile Cage-Functionalized Proton Sponge. *Eur. J. Org. Chem.* **2007**, 420–422. (c) Singh, A.; Ganguly, B. Rational Design and First-Principles Studies toward the Remote Substituent Effects on a Novel Tetracyclic Proton Sponge. *J. Phys. Chem. A* **2007**, *111*, 6468–6471. (d) Singh, A.; Ganguly, B. Strategic Design of Small and Versatile Bicyclic Organic Superbases: A Density Functional Study. *New J. Chem.* **2008**, *32*, 210–213.

- (18) (a) Maksić, Z. V.; Kovačević, B. Absolute Proton Affinity of Some Polyguanides. *J. Org. Chem.* **2000**, *65*, 3303–3309. (b) Vianello, R.; Kovačević, B.; Maksić, Z. V. In Search of Neutral Organic Superbases—Iminopolyenes and Their Amino Derivatives. *New J. Chem.* **2002**, *26*, 1324–1328. (c) Kovačević, B.; Maksić, Z. V. The Proton Affinity of the Superbase 1,8-Bis(tetramethylguanidino)-naphthalene (TMGN) and Some Related Compounds: A Theoretical Study. *Chem. –Eur. J.* **2002**, *8*, 1694–1702. (d) Margetic, D.; Ishikawa,

- T.; Kumamoto, T. Exceptional Superbasicity of Bis(guanidine) Proton Sponges Imposed by the Bis(secododecahedrane) Molecular Scaffold: A Computational Study. *Eur. J. Org. Chem.* **2010**, 6563–6572.
- (e) Coles, M. P.; Aragón-Sàez, P. J.; Oakley, S. H.; Hitchcock, P. B.; Davidson, M. G.; Maksić, Z. V.; Vianello, R.; Leito, I.; Kaljurand, I.; Apperley, D. C. Superbasicity of a Bis-guanidino Compound with a Flexible Linker: A Theoretical and Experimental Study. *J. Am. Chem. Soc.* **2009**, 131, 16858–16868. (f) Peran, N.; Maksić, Z. B. Polycyclic Croissant-Like Organic Compounds are Powerful Superbases in the Gas Phase and Acetonitrile—A DFT Study. *Chem. Commun.* **2011**, 47, 1327–1329.
- (19) Koppel, I. A.; Schwesinger, R.; Breuer, T.; Burk, P.; Herodes, K.; Koppel, I.; Leito, I.; Mishima, M. Intrinsic Basicities of Phosphorus Imines and Ylides: A Theoretical Study. *J. Phys. Chem. A* **2001**, 105, 9575–9586.
- (20) (a) Maksić, Z. B.; Kovačević, B. Toward Organic Superbases: The Electronic Structure and the Absolute Proton Affinity of Quinodiiimines and Some Related Compounds. *J. Phys. Chem. A* **1998**, 102, 7324–7328. (b) Maksić, Z. B.; Glasovac, Z.; Despotović, I. Predicted High Proton Affinity of Poly-2,5-Dihydropyrrolimines—the Aromatic Domino Effect. *J. Phys. Org. Chem.* **2002**, 15, 499–508.
- (21) (a) Lo, R.; Ganguly, B. Exploiting Propane-1,3-Diimines as Building Blocks for Superbases: A DFT Study. *New J. Chem.* **2011**, 35, 2544–2550. (b) Lo, R.; Ganguly, B. Efficacy of Carbenes for CO₂ Chemical Fixation and Activation by Their Superbasicity/Alcohol: A DFT Study. *New J. Chem.* **2012**, 36, 2549–2554. (c) Lo, R.; Ganguly, B. Rational Design of a New Class of Polycyclic Organic Bases Bearing Two Superbasic Sites and Their Applications in the CO₂ Capture and Activation Process. *Chem. Commun.* **2012**, 48, 5865–5867.
- (22) Schwesinger, R.; Schlemper, H.; Hasenfratz, C.; Willaredt, J.; Dambacher, T.; Breuer, T.; Ottaway, C.; Fletschinger, M.; Boele, J.; Fritz, M.; Putzas, D.; Rotter, H. W.; Bordewell, F. G.; Satish, A. V.; Ji, G.-Z.; Peters, E.-M.; Peters, K.; von Schnering, H. G.; Walz, L. Extremely Strong, Uncharged Auxiliary Bases; Monomeric and Polymer-Supported Polyaminophosphazenes (P₂–P₅). *Liebigs Ann.* **1996**, 1055–1081.
- (23) (a) Kovačević, B.; Barić, D.; Maksić, Z. B. Basicity of Exceedingly Strong Non-Ionic Organic Bases in Acetonitrile—Verkade's Superbase and Some Related Phosphazenes. *New J. Chem.* **2004**, 28, 284–288. (b) Kovačević, B.; Maksić, Z. B. High Basicity of Tris-(tetramethylguanidinyl)-phosphine Imide in the Gas Phase and Acetonitrile—A DFT Study. *Tetrahedron Lett.* **2006**, 47, 2553–2555.
- (24) (a) Rodima, T.; Kaljurand, I.; Pihl, A.; Mäements, V.; Leito, I.; Koppel, I. A. Acid–Base Equilibria in Nonpolar Media. 2.¹ Self-Consistent Basicity Scale in THF Solution Ranging from 2-Methoxypyridine to EtP₁(pyrr) Phosphazene. *J. Org. Chem.* **2002**, 67, 1873–1881. (b) Kovačević, B.; Maksić, Z. B. High Basicity of Phosphorus–Proton Affinity of Tris-(tetramethylguanidinyl)-phosphine and Tris-(hexamethyltriaminophosphazeny)phosphine by DFT Calculations. *Chem. Commun.* **2006**, 1524–1526.
- (25) Schwesinger, R.; Hasenfratz, C.; Schlemper, H.; Walz, L.; Peters, E.-M.; Peters, K.; von Schnering, H. G. How Strong and How Hindered Can Uncharged Phosphazene Bases Be? *Angew. Chem., Int. Ed. Engl.* **1993**, 32, 1362–1363.
- (26) Bucher, G. DFT Calculations on a New Class of C₃-Symmetric Organic Bases: Highly Basic Proton Sponges and Ligands or Very Small Metal Cations. *Angew. Chem., Int. Ed.* **2003**, 42, 4039–4042.
- (27) (a) Magil, 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. (b) Lo, R.; Ganguly, B. First Principle Studies toward the Design of a New Class of Carbene Superbases Involving Intramolecular H... π Interactions. *Chem. Commun.* **2011**, 47, 7395–7397.
- (28) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D. Mallard, W. G. Gas-phase Ion and Neutral Thermochemistry. *J. Phys. Chem. Ref. Data.* **1988**, 17, 1–861.
- (29) Bourissou, D.; Guerret, O.; Gabbai, F. P.; Bertrand, G. Stable Carbenes. *Chem. Rev.* **2000**, 100, 39–91.
- (30) Chen, H.; Justes, D. R.; Cooks, R. G. Proton Affinities of N-Heterocyclic Carbene Super Bases. *Org. Lett.* **2005**, 7, 3949–3952.
- (31) Marion, N.; Nolan, S. P. Well-Defined N-Heterocyclic Carbenes-Palladium(II) Precatalysts for Cross-Coupling Reactions. *Acc. Chem. Res.* **2008**, 41, 1440–1449.
- (32) (a) Grasa, G. A.; Kissling, R. M.; Nolan, S. P. N-Heterocyclic Carbenes as Versatile Nucleophilic Catalysts for Transesterification/Acylation Reactions. *Org. Lett.* **2002**, 4, 3583–3586. (b) Izquierdo, J.; Huston, G. E.; Cohen, D. T.; Scheidt, K. A. A Continuum of Progress: Applications of N-Heterocyclic Carbene Catalysis in Total Synthesis. *Angew. Chem., Int. Ed.* **2012**, 51, 11686–11698.
- (33) Apeloig, Y.; Pauncz, R.; Karni, M.; West, R.; Steiner, W.; Chapman, D. Why Is Methylene a Ground State Triplet while Silylene Is a Ground State Singlet? *Organometallic* **2003**, 22, 3250–3256.
- (34) (a) Rekker, B. D.; Brown, T. M.; Fetting, J. C.; Tuononen, H. K.; Power, P. P. Isolation of a Stable, Acyclic, Two-Coordinate Silylene. *J. Am. Chem. Soc.* **2012**, 134, 6504–6507. (b) Bornemann, H.; Sander, W. Reactions of Methyl(phenyl)silylene With CO and PH₃—the Formation of Acid–Base Complexes. *J. Organomet. Chem.* **2002**, 641, 156–164.
- (35) (a) Lee, V. Y.; Sekiguchi, A. *Organometallic Compounds of Low Coordinate Si, Ge, Sn and Pb*; Wiley: New York, 2012. (b) Mizuhata, Y.; Sasamori, T.; Tokitoh, N. Stable Heavier Carbene Analogues. *Chem. Rev.* **2009**, 109, 3479–3511.
- (36) Azizi, N.; Baghi, R.; Ghafari, H.; Bolourtchian, M.; Hasemi, M. Silicon Tetrachloride Catalyzed Aza-Michael Addition of Amines to Conjugated Alkenes under Solvent-Free Conditions. *Synlett* **2010**, 3, 379–382.
- (37) Schmidt, R. K.; Müther, K.; Mück-Lichtenfeld, C.; Grimme, S.; Oestreich, M. Silylium Ion-Catalyzed Challenging Diels–Alder Reactions: The Danger of Hidden Proton Catalysis with Strong Lewis Acids. *J. Am. Chem. Soc.* **2012**, 134, 4421–4428.
- (38) Shekunova, V. M.; Didenkulova, I. I.; Tsygaova, E. I.; Aleksandrov, Y. A. Effect of Silicon Compounds on the Pyrolysis of Propane–Butane Hydrocarbon Mixture. *Russ. J. Gen. Chem.* **2012**, 82, 422–427.
- (39) Staden, L. F. V.; Gravestock, D.; Ager, D. J. New Developments in the Peterson Olefination Reaction. *Chem. Soc. Rev.* **2002**, 31, 195–200.
- (40) (a) West, R.; Daniel, M.; Michael, H. Silylene Catalyst for Olefin Polymerization. Pat. No. WO 02/28920 A1, 2002. (b) Howard, B. E.; Woerpel, K. A. Synthesis of Tertiary α -Hydroxy Acids by Silylene Transfer to α -Keto Esters. *Org. Lett.* **2007**, 9, 4651–4653.
- (41) Denk, M.; Ilenon, R.; Hayasi, R.; West, R.; Belyakov, A. V.; Verne, H. P.; Haaland, A.; Wagner, M.; Meltzer, N. Synthesis and Structure of a Stable Silylene. *J. Am. Chem. Soc.* **1994**, 116, 2691–2692.
- (42) Haaf, M.; Schmedake, T. A.; West, R. Stable Silylenes. *Acc. Chem. Res.* **2000**, 33, 704–714.
- (43) Denk, M.; Green, J. C.; Metzler, N.; Wagner, M. Electronic Structure of a Stable Silylene: Photoelectron Spectra and Theoretical Calculations of Si(NRCHCHNR), Si(NRCH₂CH₂NR) and SiH₂(NRCHCHNR). *J. Chem. Soc., Dalton Trans.* **1994**, 2405–2410.
- (44) West, R.; Denk, M. Stable Silylenes: Synthesis, Structure, Reactions. *Pure. Appl. Chem.* **1996**, 68, 785–788.
- (45) Kira, M.; Ishida, S.; Iwamoto, T.; Kabuto, C. The First Isolable Dialkylsilylene. *J. Am. Chem. Soc.* **1999**, 121, 9722–9723.
- (46) Lee, G.; West, R.; Müller, T. Bis[bis(trimethylsilyl)amino]-silylene, an Unstable Divalent Silicon Compound. *J. Am. Chem. Soc.* **2003**, 125, 8114–8115.
- (47) Protchenko, A. V.; Brijkumar, K. H.; Dange, D.; Schwarz, A. D.; Vidovic, D.; Jones, C.; Kaltsoyannis, N.; Mountford, P.; Aldrige, S. A Stable Two-Coordinate Acyclic Silylene. *J. Am. Chem. Soc.* **2012**, 134, 6500–6503.
- (48) Becke, A. D. Density-Functional Thermochemistry. III. The Role of Exact Exchange. *J. Chem. Phys.* **1993**, 98, 5648–5653.
- (49) 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* **1988**, 37, 785–789.

- (50) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab initio Molecular Orbital Theory*; Wiley: New York, 1988.
- (51) Tomasi, J.; Persico, M. Molecular Interactions in Solution: An Overview of Methods Based on Continuous Distributions of the Solvent. *Chem. Rev.* **1994**, *94*, 2027–2094.
- (52) Cossi, M.; Barone, V.; Cammi, R.; Tomasi, J. Ab Initio Study of Solvated Molecules: A New Implementation of the Polarizable Continuum Model. *Chem. Phys. Lett.* **1996**, *255*, 327–335.
- (53) Barone, V.; Cossi, M.; Tomasi, J. A New Definition of Cavities for the Computation of Solvation Free Energies by the Polarizable Continuum Model. *J. Chem. Phys.* **1997**, *107*, 3210–3221.
- (54) Barone, V.; Cossi, M.; Tomasi, J. Geometry Optimization of Molecular Structures in Solution by the Polarizable Continuum Model. *J. Comput. Chem.* **1998**, *19*, 404–417.
- (55) Cossi, M.; Barone, V. Analytical Second Derivatives of the Free Energy in Solution by Polarizable Continuum Models. *J. Chem. Phys.* **1998**, *109*, 6246–6254.
- (56) (a) Tukov, A. A.; Normand, A. T.; Nechaev, M. S. N-Heterocyclic Carbenes. *Dalton Trans.* **2009**, 7015–7028. (b) Kassae, M. Z.; Arshadi, A.; Acedy, M.; Vessally, E. Singlet–Triplet Energy Separations in Divalent Five-Membered Cyclic Conjugated C_3H_3X , C_4H_3SiX , C_4H_3GeX , C_4H_3SnX , and C_4H_3PbX ($X = H, F, Cl$, and Br). *J. Organomet. Chem.* **2005**, *690*, 3427–3439.
- (57) Pacios, L. F. CHECKDEN: A Computer Program to Generate 1D, 2D, and 3D Grids of Functions Dependent on the Molecular ab initio Electron Density. *Comput. Biol. Chem.* **2003**, *27*, 197–209.
- (58) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R. J.; Montgomery Jr., A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; et al. *Gaussian 03*, Revision E.01; Gaussian, Inc.: Wallingford, CT, 2004.
- (59) (a) Shin, S. K.; Beauchamp, J. L. Precise Determination of Stabilities of Primary, Secondary, and Tertiary Silicenium Ions from Kinetics and Equilibria of Hydride-Transfer Reactions in the Gas Phase. A Quantitative Comparison of the Stabilities of Silicenium and Carbonium Ions in the Gas Phase. *J. Am. Chem. Soc.* **1989**, *111*, 900–906. (b) Shin, S. K.; Beauchamp, J. L. Proton Affinity and Heat of Formation of Silylene. *J. Phys. Chem.* **1986**, *90*, 1507–1509.
- (60) Möller, C.; Plesset, M. S. Note on an Approximation Treatment for Many-Electron Systems. *Phys. Rev.* **1934**, *46*, 618–622.
- (61) Zhao, A.; Truhlar, D. G. Density Functionals with Broad Applicability in Chemistry. *Acc. Chem. Res.* **2008**, *41*, 157–167.
- (62) (a) Decouzon, M.; Gal, G. F.; Maria, P. C.; Raczynska, E. D. Superbases in the Gas Phase: Amidine and Guanidine Derivatives with Proton Affinities Larger than 1000 kJ mol^{-1} . *Rapid. Commun. Mass Spectrom.* **1993**, *7*, 599–602.
- (63) Xiong, Y.; Yao, S.; Driess, M. Versatile Conversion of N-Heterocyclic Silylene to Silyl Metal Compounds by Insertion of Divalent Silicon into Metal–Carbon and Metal–Hydrogen Bonds. *Chem.—Eur. J.* **2012**, *18*, 3316–3320.
- (64) Kovačević, B.; Maksić, Z. B. Basicity of Some Organic Superbases in Acetonitrile. *Org. Lett.* **2001**, *3*, 1523–1526.
- (65) (a) Müller, T.; Apeloig, Y. Possible Strategies toward the Elusive Tetraaminodisilene. *J. Am. Chem. Soc.* **2002**, *124*, 3457–3460. (b) Takahashi, M.; Tsutsui, S.; Sakamoto, K.; Kira, M.; Müller, T.; Apeloig, Y. Dimers of Diaminosilylenes: Doubly Bonded or Bridged? The Dimers of $(i\text{-PrN})_2\text{Si}$. *J. Am. Chem. Soc.* **2001**, *123*, 347–348.
- (66) (a) Oláh, J.; Veszprémi, T.; Proft, F. D.; Geerlings, P. Silylenes: A Unified Picture of Their Stability, Acid-Base and Spin Properties, Nucleophilicity, and Electrophilicity via Computational and Conceptual Density Functional Theory. *J. Phys. Chem. A* **2007**, *111*, 10815–10823. (b) Oláh, J.; Proft, F. D.; Veszprémi, T.; Geerlings, P. Hard-Soft Acid-Base Interactions of Silylenes and Germlyenes. *J. Phys. Chem. A* **2005**, *109*, 1608–1615.
- (67) Wiberg, N.; Schurz, K.; Reber, G.; Müller, G. Preparation and Structure of a Stable Molecule Containing a Silicon Nitrogen Double Bond and of its Tetrahydrofuran Adduct. *Chem. Commun.* **1986**, 591–592.
- (68) Tsutsui, S.; Sakamoto, K.; Kira, M. Bis(diisopropylamino)silylene and Its Dimer. *J. Am. Chem. Soc.* **1998**, *120*, 9955–9956.
- (69) Wang, Y.; Ma, J. Silylenes and Germlyenes: The Activation of H–H Bond in Hydrogen Molecule. *J. Organomet. Chem.* **2009**, *694*, 2567–2575.
- (70) Kovačević, B.; Maksić, Z. V. High Basicity of Phosphorus–Proton Affinity of Tris-(tetramethylguanidinyl)phosphine and Tris-(hexamethyltriaminophosphazeny)phosphine by DFT Calculations. *Chem. Commun.* **2006**, 1524–1526. (b) Kaljurand, I.; Kütt, A.; Sooväli, L.; Rodima, T.; Mäemets, V.; Leito, V.; Koppel, I. A. Extension of the Self-Consistent Spectrophotometric Basicity Scale in Acetonitrile to a Full Span of 28 $\text{p}K_a$ Units: Unification of Different Basicity Scales. *J. Org. Chem.* **2005**, *70*, 1019–1028.
- (71) (a) Kovačević, B.; Maksić, Z. V.; Vianello, R. The Proton Affinity of Some Extended π -Systems Involving Guanidine and Cyclopropanimine Subunits. *J. Chem. Soc., Perkin Trans. 2* **2001**, 886–891. (b) Raab, V.; Gauchenova, E.; Merkoulov, A.; Harms, K.; Sundermeyer, J.; Kovačević, B.; Maksić, Z. V. 1,8-Bis-(hexamethyltriaminophosphazeny)naphthalene, HMPN: A Superbasic Bisphosphazene “Proton Sponge”. *J. Am. Chem. Soc.* **2005**, *127*, 15738.
- (72) (a) Tomasi, J.; Bonaccorsi, R.; Cammi, R. *Theoretical Models of Chemical Bonding*; Maksić, R., Ed.; Springer: Berlin, 1990; p 230. (b) Murry, J. S.; Politzer, P. Statistical Analysis of the Molecular Surface Electrostatic Potential: An Approach to Describing Non-covalent Interactions in Condensed Phases. *THEOCHEM* **1998**, *425*, 107–114. (c) Suresh, C. H. Molecular Electrostatic Potential Approach to Determining the Steric Effect of Phosphine Ligands in Organometallic Chemistry. *Inorg. Chem.* **2006**, *45*, 4982–4986.
- (73) Haaland, A. Covalent versus Dative Bonds to Main Group Metals, a Useful Distinction. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 992–1007.