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Silylenes: A Unified Picture of Their Stability, Acid−Base and Spin Properties, Nucleophilicity, and Electrophilicity via Computational and Conceptual Density Functional Theory

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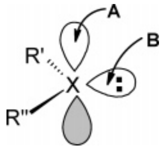
Conceptual DFT gives sharp definitions for many long-known, but rather vaguely defined chemical concepts. In this study DFT-based reactivity indices are applied to silylenes in order to elucidate the relationships among their properties: stability, acid−base, and spin properties, nucleophilicity and electrophilicity. On the basis of a detailed, comparative analysis of previously published data, it is shown that the properties of simple silylenes can be tuned by varying one single factor, the π-electron donating ability of the substituents of the silicon atom leading to well-characterized and systematic changes in the stability/reactivity pattern of the molecule. In order to test the model a series of new compounds are studied: including CH_3SiR (where R = CH_3, NH_2, OH and SH), $Si(Si(CH_3)_3)_2$, $Si(CF_3)_2$ and benzo-, pyrido-, pyridazo-, and pyrimido-anellated-1,3,2λ^2-diazasiloles.

Introduction

The relationship between the reactivity and stability of compounds has been intriguing scientists for long. In this paper, we try to shed light on this question by studying silylenes, divalent silicon compounds.[1−3] Silylenes form a perfect playground for such a study as their stability varies on a large scale according to both experimental and theoretical studies. While most silylenes are only known as reactive intermediates whose existence is proved by their adducts with trapping agents, several stable species have been isolated and were shown to be stable for months at room temperature under inert atmosphere.[4−9] It is an experimental fact that the stability and reactivity of silylenes are strongly related: unstable species show a strong electrophilic character while the stable compounds are highly nucleophilic and not electrophilic.[10] As a consequence, stable and unstable species can be characterized with a completely different reactivity pattern. In all cases, the reactive center of the molecule is the divalent silicon atom. Despite the intensive efforts to synthesize a triplet ground state silylene, almost all silylenes observed and studied so far possess a singlet ground state. Scheme 1 depicts their structure in general and it demonstrates the two regions that participate in electrophilic and nucleophilic reactions. Region **A** corresponds to the empty $3p_z$ orbital of the silicon atom, which is responsible for the electrophilic character of the molecule. Singlet silylenes possess a lone pair that is located in region **B**, provoking the nucleophilic character of stable silylenes.

SCHEME 1: Electrophilic (A) and Nucleophilic Regions (B) around the Central Silicon Atom



The fact that the reactivity of the same center within a molecule is affected by the stability of the molecule to this extent raises fundamental questions on the connections between stability and reactivity. Silylenes are ideal candidates for the investigation of such relationships as the separation of the electrophilic and nucleophilic regions in the molecule is ensured by the structure of the molecule, thus they can be independently analyzed.

Since the 1980s large number of theoretical studies have dealt with the problem of predicting the stability of silylenes and with the identification of factors that stabilize the divalent silicon compounds.[11−14] These factors include the nature of the substitutents on the divalent silicon and the aromaticity of the compound. Two different concepts of stability can be considered in chemistry. In a chemist's mind stability indicates the preservability of a compound. In quantum chemistry, stability means the depth of the minima on the potential energy surface. The first is a kinetic factor, which can be studied and quantified by the reactivity of the compound. The latter is a thermodynamic factor which can be calculated by quantum chemical methods.

Two useful ways have been introduced to estimate the thermodynamic stability of silylenes. On the one hand the singlet−triplet energy separation of silylenes turned out to be a reliable measure: increasing stability of the molecules increases the singlet−triplet energy separation. On the other hand isodesmic reaction energies were used to set up a scale for the relative stability of substituted silylenes.[12,13] In this method the energy of a substituted silylene-silane pair is compared to the energy of the unsubstituted silylene−silane system, as shown in eq 1.

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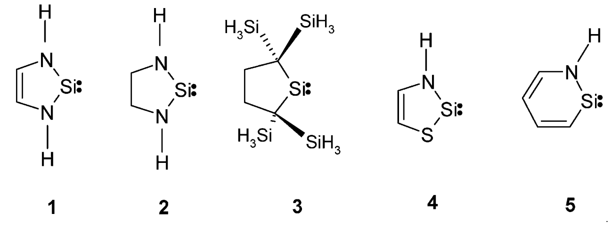
$$RR'Si: + SiH_4 \rightarrow RR'SiH_2 + H_2Si: \quad \Delta H_i \qquad (1)$$

Application of both methods led to the same conclusion: π-electron donating substitutents stabilize the divalent silicon center, and the largest stabilization is caused by the NH_2, SH and OH groups, while electropositive or π-electron acceptor substituents stabilize the triplet state.[12,13,15]

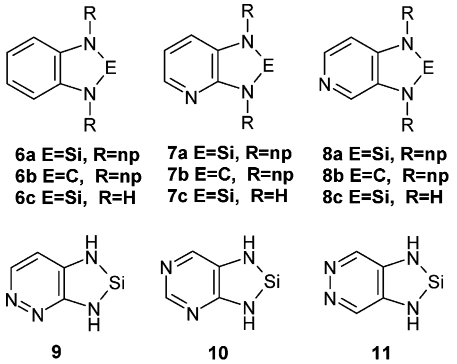
Most silylenes are known to be extremely short-lived due to their ability to dimerize, but the bottleable, stable silylenes do not dimerize.[4] Therefore, their ability to dimerize can be regarded as a method of quantification of their preservability and their kinetic stability. With decreasing ability to dimerize, the stability of the silylene increases and vice versa. It was shown theoretically that the presence of π-electron donating substitutents (e.g., NH_2, SH, and OH groups) on the silicon reduces the ability to dimerize and the reactivity of the compound. From this it follows that in the case of silylenes there is a strong relationship between their thermodynamic and kinetic stability which was confirmed by the linear correlation between the dimerization energy and the singlet−triplet energy separation[16] and the isodesmic reaction energy[17] of the molecules. This strong relationship between the thermodynamic and kinetic stability of silylenes makes it possible to speak in general terms about the "stability" of silylenes and the three proposed ways of estimating the stability of the compound have a common root and show exactly the same tendencies.

What kind of tools does a chemist have for the characterization of the reactivity of molecules? The obvious choice is to carry out relevant reactions in vitro or compute them in silico and to highlight the relevant characteristics of the compound on the basis of these reactions. Conceptual DFT[18,19,20] supplies us with simple, but sharp definitions for long-known, rather vaguely defined chemical properties, which enable the quantification of chemical reactivity and the easy comparison of compounds. In our previous work we have successfully applied the electrophilicity index,[21] and the electrostatic potential as a measure of local hardness, calculated in different regions around the molecule, to predict and quantify the electrophilic and nucleophilic character of silylenes.[22] We concentrated on simple monosubstituted silylenes involving first and second row elements (HSiR, where R = H, Li, BeH, CH_3, NH_2, OH, F, Na, MgH, AlH_2, SiH_3, PH_2, SH, Cl), disubstituted species (RSiR′, where R and R′ = NH_2, OH, F, SH, Cl), and model compounds of some well-known already synthesized compounds (see Scheme 2.) **1** and **2** are the model compounds of the first synthesized stable silylene,[4] and its saturated analogue,[5] **3** is the only isolated stable alkyl substituted silylene.[9] The carbene analogue of **4** was the first non-diamino-substituted synthesized carbene. Finally **5**, which was predicted by computational means to be stable,[23] was recently observed.[24]

SCHEME 2: Cyclic Silylenes Investigated in Our Previous Studies



SCHEME 3: Anellated Silylenes and Carbenes (np = Neopentyl)



The aim of the present study is to combine our earlier results in order to draw a general picture on the relationship between the reactivity and stability of silylenes as reflected in their electrophilic and nucleophilic nature, their ability to dimerize, their spin-philicity, and their Lewis acid and base character as finally governed by the nature of the substituents. The structure of the paper is as follows. First, we give a general picture on the reactivity of silylenes based upon our previous calculations. In the next part of the paper we apply our model to a series of new silylenes and discuss our results. As the predictive power of any model can only be judged by applying it to a new set of compounds, not included for the set up of the model, we decided to investigate the performance of our model on a set of 12 compounds. Four of the compounds (CH_3−Si−CH_3, NH_2−Si−CH_3, OH−Si−CH_3, SH−Si−CH_3) contain a combination of substituents that we studied in our previous works;[17,22,25] therefore, if our model is valid, it is expected to predict the properties of these compounds reliably. Eight of the 12 compounds differ in structure from our previously studied molecules, which gives us the possibility to test whether our model is applicable to new types of compounds. $Si(CF_3)_2$ and $Si(Si(CH_3)_3)_2$ contain substituents with different electronic properties, especially in the σ-system. In an early computational study Dixon studied carbenes containing CF_3-substituents and showed that CF_3-groups affect the singlet−triplet gap and geometry of carbenes in a manner very similar to that seen for hydrogen.[26] Alkyl−silyl-substituted silylenes received a lot of attention recently as they possess very small singlet−triplet energy gaps and may provide a route to synthesize triplet ground state silylenes.[15,27] Furthermore, trapping of $Si(Si(CH_3)_3)_2$ with antracene gave evidence for its dimerization.[28] The CF_3 and $Si(CH_3)_3$ substituents are expected to exert their effect mainly in the σ-system of the compound, thereby influencing the σ-type orbital corresponding to the silicon lone pair and they do not donate electrons in to the empty Si $3p_z$ orbital. The test set included six anellated compounds (**6c**, **7c**, **8c**, **9**−**11**) which are shown in Scheme 3. A very recent work by one of us on the analogous carbenes called our attention to the apparent differences between the stability of asymmetrically anellated carbenes and their higher homologues.[29] While carbenes **6b**, **7b**, and **8b** were isolated and proved to be stable,[29] only silylenes **6a**[30] and **7a**[31] could be synthesized and the unsuccessful attempts to synthesize **8a** were attributed to kinetic factors.[31] While non-anellated and benzo-anellated species with a symmetric π-charge density are stable, it is argued that the stability of anellated species decreases with increasing asymmetry of the π-charge density in the HOMO of the molecules. This effect is small in the case of **7c** as its HOMO contains a nodal plane through the pyridine-N atom, but leads to the destabilization of **8c**. It was shown that the electrophilicity of the divalent silicon center in **7a** is strongly reduced and it has a low tendency to form Lewis-base-complexes. Therefore, we performed calculations on silylenes **6c**−**11** with 0, 1, or 2 nitrogen atoms in the anellated

TABLE 1: Calculated Molecular Properties, Units, the Covered Range, and Reference to the Original Paper

property	unit	range[a]	ref
electrophilicity (ω)	au	*0.06* to 0.13	22
electrostatic potential in region **A** (V_A)	kcal/mol	*2.51* to 44.55	22
isodesmic reaction energy (ΔH_i)	kcal/mol	−16.9 to *51.47*	17
Lewis acidity (reaction with NH_3) (ΔE_{NH_3})	kcal/mol	−26.99 to *−0.56*	22
Lewis basicity (reaction with BH_3) (ΔE_{BH_3})	kcal/mol	*−46.24* to −21.77	22
nucleophilicity (electrostatic potential in region B) (V_{min})	kcal/mol	*−61.50* to −6.28	22
dimerization energy (ΔE_{dim})	kcal/mol	−115.0 to *−0.6*	17
singlet−triplet gap (Δ_{s-t})	kcal/mol	−23.8 to *75.6*	17
spin-philicity (ω_s^+)	eV	*−4.03* to −0.9	25

[a] The italic values correspond to silylenes with strongly π-electron donating substituents (see text)

TABLE 2: Isodesmic Reaction Energies (ΔH_i), Singlet−Triplet Gaps (ΔE_{s-t}), Dimerization Energies (ΔE_{dim}) and Estimates of Dimerization Energy Based on ΔH_i($\Delta E_{dim}^{\Delta H_i}$) and ΔE_{s-t}($\Delta E_{dim}^{\Delta E_{s-t}}$) for the Compounds Investigated in This Study[a]

compound	ΔH_i	ΔE_{s-t}	ΔE_{dim}	$\Delta E_{dim}^{\Delta H_i}$	$\Delta E_{dim}^{\Delta E_{s-t}}$
$Si(CH_3)_2$	1.73	24.93	−52.74	−57.90	−51.00
NH_2SiCH_3	21.86	42.34	−18.08[a]	−18.25	−23.32
$OHSiCH_3$	16.24	43.06	−24.78	−29.31	−22.17
$SHSiCH_3$	18.78	35.98	−25.99	−24.31	−33.42
$Si(CF_3)_2$	2.87	26.86	−47.98	−55.66	−47.92
$Si(SiMe_3)_2$	−0.34	2.34	−73.60	−61.97	−86.92
6c	45.49	63.68	no dimer	28.31	10.63
7c	44.08	63.18	no dimer	25.54	9.82
8c	44.23	65.78	no dimer	25.82	13.96
9	42.17	66.64	no dimer	21.77	15.33
10	42.79	65.24	no dimer	22.99	13.10
11	43.35	68.60	no dimer	24.08	18.45

[a] All values were calculated at the B3LYP/6-31G(d) level and are given in kcal/mol. $\Delta E_{dim}^{\Delta H_i}$ is calculated as $\Delta E_{dim}^{\Delta H_i} = 1.97\Delta H_i - 61.31$ (see ref 17). $\Delta E_{dim}^{\Delta E_{s-t}}$ is calculated as $\Delta E_{dim}^{\Delta E_{s-t}} = 1.59\Delta E_{s-t} - 90.63$ (see ref 17). Both *cis* and *trans* dimers were optimized and the lowest energy conformation was taken, although the two conformers lie very near in energy. For $NH_2-Si-CH_3$ and $OH-Si-CH_3$ the *cis* dimer and for $SH-Si-CH_3$ the *trans* dimer was found to be more stable.

ring in order to test the effect of symmetric/asymmetric substitution on the electrophilicity and nucleophilicity of the compounds.

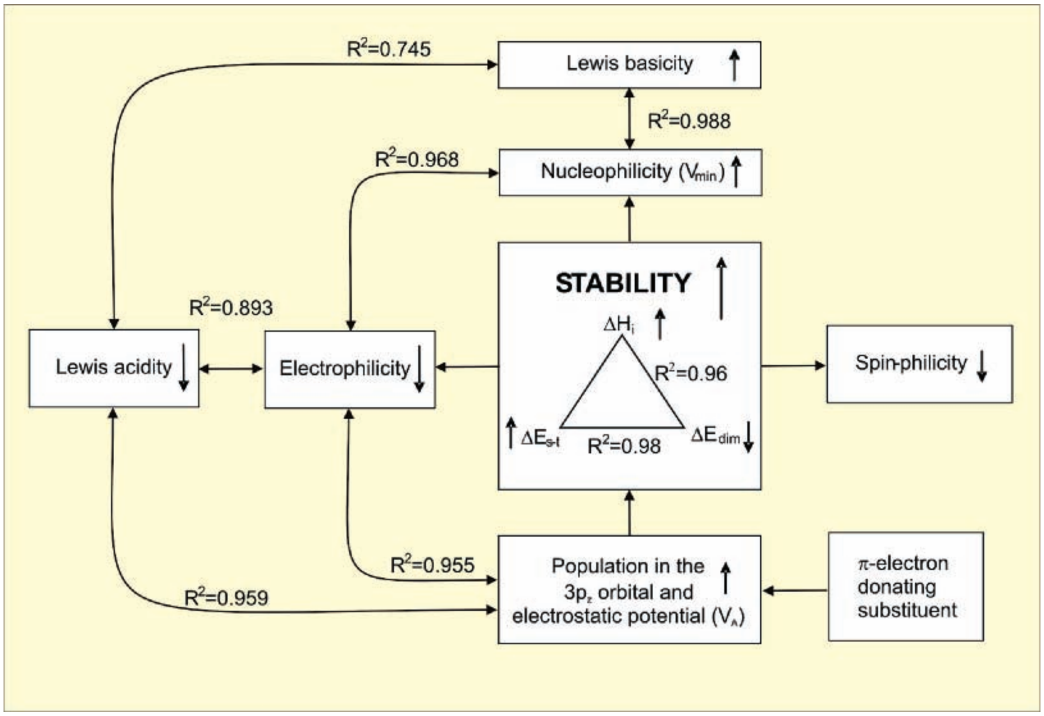
Computational Data

Part of the numerical data used in this work were taken from refs 17, 22, and 25. In Table 1, the revisited molecular properties are collected with the appropriate ranges and the exact references. The underlined values correspond to the cases with strong π-electron donating substituents, e.g., compounds **1** and **2**, whereas the other end of the scale for a given property mostly corresponds to monosubstituted silylenes involving atoms or groups with low electronegativity, e.g., Li, BeH, AlH_2. In all cases, calculations were performed using the Gaussian 03 program package[32] within the context of DFT using the B3LYP functional and the 6-311+G(d,p) basis set. The geometries of the molecules were optimized and second-derivative calculations were performed to ensure that the structures are minima on the PES. Conceptual DFT indices were calculated as it is discussed in ref 22. NPA charges were calculated at the at the same level of theory by the NBO program[33] as implemented in Gaussian 03.[34] The electrostatic potential in region **A** (V_A) was calculated by placing a ghost atom 2 Å above the Si atom perpendicular to the plane of the silylenes (point **A** in Scheme 1). In region **B**, which corresponds to the lone pair region of the silicon, the minimum of the electrostatic potential (V_{min}) was determined.[22] Furthermore, as we want to compare the calculated isodesmic reaction energies, dimerization energies and singlet−triplet energy gaps with previously published data we performed additional calculations at the B3LYP/6-31G(d) level of theory adopted in ref 17. We optimized the geometry of all singlet and triplet silylenes, silanes and disilenes using the 6-31G(d) basis set and verified by second derivative calculations that all structures were minima on the PES. Comparison of the data in Table 2 and Table S1 shows that changing the basis set from 6-31G(d) set to 6-311+G(d,p) has only a slight effect on the isodesmic reaction energies, dimerization energies and singlet−triplet gaps.

Results and Discussion

1. Establishing a Unified Picture. Both the stability and reactivity of silylenes are primarily determined by the substituents of the divalent silicon. As, with the exception of one or two very recently observed triplet silylenes,[35,36] all silylenes have singlet ground states, we will concentrate only on singlet species. In silylenes, the divalent silicon center possesses only six valence electrons, which in most cases leads to a strongly electron-deficient and electrophilic center in the molecule. When π-electron donor substitutents are bonded to the divalent silicon, the lone pair, or any other appropriately oriented π-orbital, of the substituent can overlap with the empty $3p_z$ orbital of the silicon atom, which is perpendicular to the plane of the molecule. This at first will decrease the electron-deficiency of the silicon atom in region **A**, as indicated by the decrease of the electrostatic potential. This shift of electrons profoundly influences the reactivity and stability of the whole molecule. The delocalization of the lone pair into the empty $3p_z$ orbital leads to a stabilization of the molecule. On the other hand the decrease of the electron-deficiency of silicon leads to a decrease of the electrophilicity of the molecule (see Scheme 4.). The direct relationship between the electrostatic potential (V_A) and the electrophilicity (ω) of the molecule is demonstrated by the correlation coefficient of the linear fit between the two values ($R^2 = 0.955$), in the case of π-electron donating substituents.[22] The electrophilicity of the molecules is strongly related to their Lewis acidity as investigated through their reactions with Lewis bases, NH_3, PH_3, and AsH_3.[22] Indeed, the reaction energy of the silylene + Lewis base complex formation correlates very well: the more electrophilic the compound, the larger its Lewis acidity. ($R^2 = 0.893$ for the global electrophilicity of the silylene and the reaction energy with NH_3 (ΔE_{NH_3}).[22] Intuitively there should be an inverse relationship between the electrophilic and nucleophilic character of molecules, which is indeed found in the case of silylenes. Most silylenes show only electrophilic and some of them only nucleophilic character.[10] This is confirmed by our results, which demonstrate that when the electrophilicity of the silylenes becomes smaller than a certain threshold value they suddenly become nucleophilic.[22] The disappearance of the electrophilic and appearance of nucleophilic character is well-observed for NH_2, SH, and OH disubstituted silylenes which

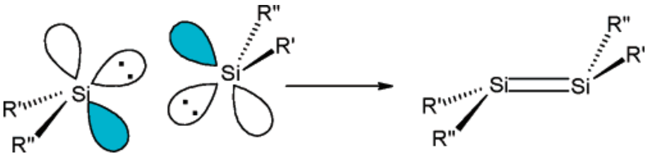
SCHEME 4: Relationships between Reactivity Indices and Stability for Silylenes in Their Singlet State[a]



[a] In the stability box the reaction enthalpy for the isodesmic reaction **1** ΔH_i, the dimerization energy ΔE_{dim}, and also the singlet−triplet energy difference ΔE_{s-t} are given. Arrows indicate the behavior of the property (increasing ↑ or decreasing ↓ upon Introduction of a π-electron-donating substituent.

turned out to be ambiphilic on the basis of our calculations. We used the minimum of the electrostatic potential (V_{min}) in the lone pair region (region **B**) of the silicon as a measure of nucleophilicity. We have shown that if no other interactions play a role during the reaction of silylenes with Lewis acids, this quantity correctly predicts the nucleophilicity of the compounds. In the case of the ambiphilic silylenes, we found a good linear correlation between their electrophilicity as measured by V_A or ω and their nucleophilicity as measured by V_{min} ($R^2 = 0.968$). In this way the inverse relationship between nucleophilicity and electrophilicity is supported theoretically. The nucleophilicity of the compounds is expected to be strongly coupled with their Lewis basicity, therefore we studied the reactions of silylenes with BH_3 and AlH_3. As expected, highly electrophilic silylenes did not form Lewis acid−base complexes, while silylenes with very low electrophilicity formed conventional Lewis acid−base complexes with these Lewis acids. The electrophilic silylenes formed H-bridged adduct with BH_3. Bharatam et al. showed that these electron-deficient H-bridged systems are associated with the strong donation of the B−H σ-electron density to the empty $3p_z$ orbital on silylenes.[37] The NBO analysis showed that in the bridged SiH_2-BH_3 adduct the second-order stabilization energies $E^{(2)}$ associated with $\sigma_{B-H} \rightarrow$ Si $3p_z$ delocalization is 285.9 kcal/mol at the MP2(full)/6-31+G(d) level. This suggests that the H-bridged complexes are stabilized by $\sigma_{B-H} \rightarrow$ Si $3p_z$ delocalizations.[37] Stable silylenes, and the NH_2, SH, and OH disubstituted species, formed conventional Lewis acid−base complexes with BH_3, in which the silicon acts as a Lewis base. In these complexes, due to the large saturation of the Si $3p_z$ orbital with electrons the $\sigma_{B-H} \rightarrow$ Si $3p_z$ delocalization does not take place. We found a very good linear correlation between the nucleophilicity (as measured by V_{min}) and the Lewis basicity of silylenes (as measured by the reaction heat of complex formation withBH$_3$ (ΔE_{BH_3} , $R^2 = 0.988$). On the basis of the above ideas there should be a direct correlation between the Lewis acidity and Lewis basicity of molecules. This relationship was indeed found, albeit with a smaller correlation coefficient ($R^2 = 0.745$) than the correlation between electrophilicity and nucleophilicity ($V_A - V_{min}$).

SCHEME 5: Non-Least-Motion-Path Dimerization of Two Singlet Silylenes



So far we have discussed the electrophilic and nucleophilic properties of silylenes separately. Still, the most typical reaction of silylenes, the dimerization incorporates both elements. Scheme 5. depicts the general way of dimerization of singlet silylenes along the non-least motion path, in which the lone pair of the first molecule overlaps with the empty $3p_z$ orbital of the second silylene to form a double bonded disilene with a trans-bent geometry. In this reaction both partners react as nucleophiles and electrophiles at the same time. The experimental results clearly indicate that only unstable silylenes dimerize, while stable species do not. By theoretical means, it was also shown that the singlet−triplet energy separation of silylenes was strongly related to their energy of dimerization. Apeloig et al. reported that with increasing singlet−triplet energy separation, the energy of dimerization linearly decreases.[16] If we combine these results with the CGMT model,[38,39,40] which states that Si=Si double bonds are expected to be formed when the sum of the singlet−triplet energy separations of the silylene fragments is smaller than the total bond energy of the Si=Si double bond, we find that the stability, the singlet−triplet gap, the ability of silylenes to dimerize and the stability of the Si=Si double bond are strongly related. Unstable species have small singlet−triplet energy separations, they are expected to dimerize, and the dimer will be stable. From this, it follows that those substituents that destabilize the silylene fragment will stabilize the Si═Si double bond and the dimer will be favored over the silylenes. π-Electron-donating substituents stabilize the silylene and destabilize the Si═Si double bond; therefore, the silylene is favored over the dimer. This model is capable of predicting the dimerization ability of silylenes, but it does not explain the main character of the interaction. We showed above that the electrophilicity of silylenes continuously decreases with their increasing stability and below a certain electrophilicity level (i.e., above a certain level of stability), their nucleophilic character emerges. This is exactly the opposite for the dimerization ability of silylenes. Therefore, we may conclude that the electrophilicity of the molecules drives the dimerization process, and although the presence of an unshared pair on the silicon is the prerequisite of the dimerization, its role is minor as compared to that of the silicon $3p_z$ orbital.

The reactivity indices discussed above did not consider the spin of the molecules. Spin-related DFT descriptors were developed with the aim to give insight into properties and processes which involve changes in spin state of the molecules.[41,42,43,44] The spin-philicity index, (ω_s^+)[45] is relevant for two neighboring spin states (e.g., for singlet and triplet) and a linear correlation was reported between the spin-philicity of singlet molecules and their vertical singlet−triplet energy separation (i.e., the energy difference between the singlet and triplet states calculated at the same geometry).[25] It was also shown that the largest part of the singlet−triplet energy separation (i.e., the energy difference between the lowest lying singlet and triplet states at optimized geometries) is due to the vertical singlet−triplet energy gap and only a small part of it arises as a consequence of geometry relaxation.[25] This suggests a relationship between the stability (i.e., singlet−triplet energy separation) and the spin-philicity index of the molecules. With increasing singlet−triplet energy separation of the molecules their spin-philicity values become more and more negative, which means that they become less and less spin-philic indicative for an increasing stability of the singlet state.

In Scheme 4 an overview is given of the various relationships discussed above which can most easily be read starting from the π-electron donating character of the substitutents (bottom right of the scheme). Increasing π-donating capability of the substitutents increases the population of the Si $3p_z$ orbital leading to a less positive electrostatic potential in the lone pair region yielding lower electrophilicity and Lewis acidity of the silicon atom (interactions along the z-axis perpendicular to the molecular plane). Decreasing electrophilicity in this region is accompanied by an increasing nucleophilicity in the lone pair (in plane) region yielding and increased Lewis basicity. Increasing $3p_z$ electron population reflects the larger overlap of this orbital with the substituent π-orbitals, hereby increasing the stability of the considered (singlet) silylene with lower tendency to dimerize and increasing singlet−triplet gap finally resulting in a lower spin-philicity.

A word of caution should be inserted here. σ-effects were not considered up to now in the model proposed. The structure and stability of carbenes and silylenes were investigated thoroughly during the last 30 years. As early as 1968, Roald Hoffmann concluded that the stability of these compounds depended on the π-donor substituents.[46] From that time on several authors studied the substituent effect[1,11−14] and recognized the largely predominant importance of the π-donation on the geometry, charge distribution, orbital ordering, singlet−triplet gap and electronic structure. Still the question remains whether σ-effects have an important influence on the reactivity and stability of these compounds. Therefore, it is important to investigate whether our assumption that the σ-donor/acceptor nature of the substituents plays only a minor role in the reactivity of silylenes, is acceptable or not. For this reason $Si(Si(CH_3)_3)_2$, and $Si(CF_3)_2$, containing substituents with different electron-donating and withdrawing properties in the σ-system, were included in our test set.

2. Testing the Model. In order to test the model that we described above, we decided to calculate the properties of 12 new compounds and to predict their ability to dimerize and their heats of reaction with ammonia and BH_3 from simple quantities and reactivity indices. In Table 2. the isodesmic reaction energies (ΔH_i), singlet−triplet gaps (ΔE_{s-t}), dimerization energies (ΔE_{dim}) of these molecules are collected together with the estimates of the dimerization energy based on ΔH_i and ΔE_{s-t}. As a strong correlation was found between the isodesmic reaction heat and singlet−triplet energy gap, we used the fitted equations from ref 17 to estimate the energy of dimerization from these two quantities. The estimated dimerization energies are in good agreement with the calculated ones. For the six acyclic molecules, the energy of dimerization falls between the two estimated values. For the six ring compounds (**6c**−**11**) very large, positive dimerization energies are predicted, which is in accordance with the fact that no dimer was found on the PES. This result gives further support for our model, and shows the strong relationship between these quantities.

As we intend to study how substituents via the σ-system influence the reactivity and stability of silylenes it is worth comparing H_2Si, $Si(CH_3)_2$, $Si(Si(CH_3)_3)_2$, and $Si(CF_3)_2$, as none of them contain π-donor substituents. It follows from eq 1 that ΔH_i of H_2Si is zero, and for the three other silylenes, the calculated ΔH_i is very close to zero indicating that none of these groups stabilizes or destabilizes the divalent silicon center compared to hydrogen significantly. The singlet−triplet gaps of $Si(CH_3)_2$ and $Si(CF_3)_2$ are slightly larger than that of H_2Si (20.1 kcal/mol at the same level),[25] but this increase is much smaller than when the compound includes π-donor substituents. The effect of the $Si(CH_3)_3$ substituent on the singlet−triplet gap of the molecule is much larger, decreasing the gap close to zero. This originates from (1) an electronic effect, as it was shown that electropositive substituents decrease ΔE_{s-t} (2) a steric factor, due to the presence of the bulky $Si(CH_3)_3$ group, the Si−Si−Si angle increases from around 90° in SiH_2 to around 100°, which results in the destabilization of the singlet state relative to the triplet state.[15,27]

In Table 3, the calculated conceptual DFT indices are collected, together with the interaction energies with NH_3 and BH_3. In a similar manner as above, we estimated the reaction heats with NH_3 from the electrophilicity (ω) of the silylene, from the local electrophilicity on the silicon (ω_{Si}^+) and from the electrostatic potential (V_A). For the mono and disubstituted silylenes, studied in our previous works (ref 22), the estimated interaction energies with NH_3 are presented as Supporting Information in Table S2. For the six acyclic compounds the electrostatic potential performs the best (the difference between the accurate and the estimated value is less than 1.3 kcal/mol, 3 kcal/mol for $Si(Si(CH_3)_3)_2$). The local electrophilicity gives an estimate 3 kcal/mol lower than the accurate value for the NH_2, OH, and SH substituted species, but it performs poorly for $Si(CH_3)_2$, $Si(Si(CH_3)_3)_2$, and $Si(CF_3)_2$ as well as for HSi−CH_3 (see Table S2.) The performance of the global electrophilicity is the poorest of all, seriously under- or overestimating the complexation energy. For compounds **6c**−**11**, the local

TABLE 3: Electrostatic Potential Calculated at Point A (V_A) and Point B (V_{min}), Fukui Function for Nucleophilic Attack on the Silicon (f_{Si}^{+}), Electronic Chemical Potential (μ), Hardness (η), Global Electrophilicity (ω) and Local Electrophilicity on the Silicon (ω_{Si}^{+}). Calculated Interaction Energy with NH_3 (ΔE_{NH_3}), and Its Estimates from Global ($\Delta E_{NH_3}^{\omega}$) and Local ($\Delta E_{NH_3}^{\omega^{Si+}}$) Electrophilicties and from V_A ($\Delta E_{NH_3}^{V_A}$), Charge on Ammonia (δ^{NH_3}) and Si−N Distance (d_{Si-N}) in the Complex, and Interaction Energy with BH_3 (ΔE_{BH_3}) and Its Estimate from V_{min} ($\Delta E_{BH_3}^{V_{min}}$)[a]

compound	V_A	V_{min}	f_{Si}^{+}	μ	η	ω	ω_{Si}^{+}	ΔE_{NH_3}	$\Delta E_{NH_3}^{V_A}$	$\Delta E_{NH_3}^{\omega}$	$\Delta E_{NH_3}^{\omega^{Si+}}$	δ^{NH_3}	d_{Si-N}	ΔE_{BH_3}	$\Delta E_{BH_3}^{V_{min}}$
$Si(CH_3)_2$	0.0525	−0.0496	0.816	−0.158	0.143	0.087	0.071	−18.44	−17.71	−9.99	−10.94	0.20	2.10	*c*	
NH_2SiCH_3	0.0290	−0.0495	0.779	−0.145	0.162	0.065	0.051	−7.45	−6.54	−1.67	−4.05	0.16	2.20	*c*	
$OHSiCH_3$	0.0452	−0.0363	0.823	−0.158	0.157	0.080	0.066	−12.95	−14.24	−7.14	−9.05	0.18	2.13	*c*	
$SHSiCH_3$	0.0467	−0.0297	0.728	−0.168	0.151	0.094	0.068	−14.93	−14.94	−12.49	−10.00	0.19	2.13	*c*	
$Si(CF_3)_2$	0.0938	*b*	0.447	−0.236	0.152	0.183	0.082	−38.38	−37.36	−45.63	−14.40	0.24	2.03	*c*	
$Si(SiMe_3)_2$	0.0579	−0.0460	0.045	−0.162	0.106	0.125	0.006	−23.32	−20.29	−23.92	11.10	0.22	2.10	*c*	
6c	0.0172	−0.0297	0.639	−0.138	0.146	0.065	0.042	−1.30	−0.89	−1.65	−0.99	0.06	2.80	−24.24	−23.28
7c	0.0236	−0.0247	0.596	−0.148	0.147	0.075	0.044	−2.21	−3.97	−5.23	−1.94	0.08	2.56	−23.65	−21.59
8c	0.0276	−0.0211	0.642	−0.153	0.151	0.077	0.050	−2.39	−5.86	−6.25	−3.69	0.08	2.63	−23.35	−20.37
9	0.0367	−0.0142	0.583	−0.167	0.151	0.092	0.054	−4.08	−10.19	−11.70	−5.02	0.11	2.46	−22.62	−18.03
10	0.0346	−0.0157	0.607	−0.174	0.162	0.093	0.057	−3.56	−9.19	−12.17	−5.99	0.10	2.50	−22.70	−18.53
11	0.0387	−0.0115	0.652	−0.164	0.151	0.089	0.058	−3.67	−11.16	−10.52	−6.43	0.10	2.52	−22.22	−17.13

[a] All values were calculated at the B3LYP/6-311+G(d,p) level of theory. V_A, V_{min}, f_{Si}^{+}, μ, η, ω, and ω_{Si}^{+} values are in au, $\Delta E_{NH_3}^{\omega}$, $\Delta E_{NH_3}^{\omega^{Si+}}$, $\Delta E_{NH_3}^{V_A}$, ΔE_{BH_3}, and $\Delta E_{BH_3}^{V_{min}}$ are in kcal/mol, δ^{NH_3} is given in electrons, and d_{Si-N} is in Å. $\Delta E_{NH_3}^{\omega}$ is calculated as $\Delta E_{NH_3}^{\omega} = (0.06069 - \omega)/0.00267$, $\Delta E_{NH_3}^{\omega^{Si+}}$ is calculated as $\Delta E_{NH_3}^{\omega^{Si+}} = (0.03868 - \omega_{Si}^{+})/0.00298$, $\Delta E_{NH_3}^{V_A}$ is calculated as $\Delta E_{NH_3}^{V_A} = (0.0153 - V_A)/0.0021$, and $\Delta E_{BH_3}^{V_{min}}$ is calculated as $\Delta E_{BH_3}^{V_{min}} = 338.876V_{min} - 13.2183$. All equations were fitted in ref 22. [b] No minimum was found [c] The molecule does not form a Lewis acid−base complex with BH_3.

electrophilicity index performs by far much better than the electrostatic potential and the global electrophilicity index, predicting the interaction energy within 3 kcal/mol difference, which follows the trend as observed for the four compounds above. However, the poor performance of the electrostatic potential is very surprising if we consider its performance for the six acyclic compounds. Although with increasing electrostatic potential the interaction energy increases (as our model predicts), but the increase in the interaction energy is much smaller than could be expected on the basis of the differences in V_A. Therefore, we studied these complexes in more detail. Table 3 gives the distance between the silicon atom and the nitrogen atom of NH_3 in the complexes, and the amount of charge transfer. The charge transfer is calculated by summation of the NPA charges on the atoms of NH_3 in the silylene−ammonia complex. As expected, ammonia acts as a nucleophile, and charge is transferred from ammonia to the silylenes. For the acyclic compounds the amount of charge transferred is about 0.2 e, while in the case of compounds **6c**−**11**, the charge transfer is only half as large. Further important difference is that while, for compounds with a considerable charge transfer the characteristic Si−N distance is about 2.1 Å, for the anellated compounds, the Si−N distance is much longer and with increasing Si−N distance, the charge transfer decreases. Therefore, we assume that these ammonia-silylene complexes cannot be regarded as Lewis acid−base complexes, but only as van der Waals complexes, where both the interaction energy and the charge transfer are much smaller. Van der Waals complexes have already been found in similar cases. For example, the addition of nucleophiles and electrophiles to Si═Si, Si═C, and C═C containing compounds, starts by the formation of electrophilic or nucleophilic complexes.[47,48] The nonexistence of Lewis acid−base complexes in the case of **6c**−**11** with ammonia is in agreement with the experimental results that the electrophilicity of **7a** is strongly reduced and has a low tendency to form Lewis-base complexes.[31] Here we would like to point out, that in the case of **1**, the model of the experimentally most stable silylene isolated so far, no electrophilic van der Waals complex or Lewis acid−base complex were found on the PES indicating a complete lack of electrophilic character. Further electrophilic van der Waals complexes have been found for **2** (d_{Si-N} = 2.75, δ^{NH_3} = 0.06, ΔE_{NH_3} = −0.70), for **4** (d_{Si-N} = 2.45, δ^{NH_3} = 0.11, ΔE_{NH_3} = −2.29) and for **5** (d_{Si-N} = 2.36, δ^{NH_3} = 0.13, ΔE_{NH_3} = −1.98). The fact that the charge transfer and Si−N distance found for the complex of **6c** is most similar to **2** is in agreement with the findings of Pause et al.[49] They studied compounds **1**, **6c**, and **7c** and concluded that the aromatic stabilization in **6c** and **7c** is very small, thus their properties should resemble more closely the saturated compound **2** than the aromatic compound **1**. In Table S2. we have given the Si−N distances and the charge on the ammonia in the complex for the molecules studied in our previous work. Figure 1. shows the dependence of charge transfer on the Si−N distance in the complex (molecules of Table 3 and Table S2 are included). It can be seen that in those complexes in which the Si−N distance is about 2.1 Å the charge transfer from ammonia is about 0.2 e, which almost linearly decreases with the Si−N distance. As intuitively expected the diagram suggests, that in those case when the Si−N distance increases above 3 Å, the charge transfer will diminish, and the interaction energy will become zero, as shown in Figure 2. In Table 3, we compared the interaction energies with BH_3 (nucleophilic complexes) with the interaction estimated from the minimum of electrostatic potential in region **B** (V_{min}). From our previous studies it became clear that those

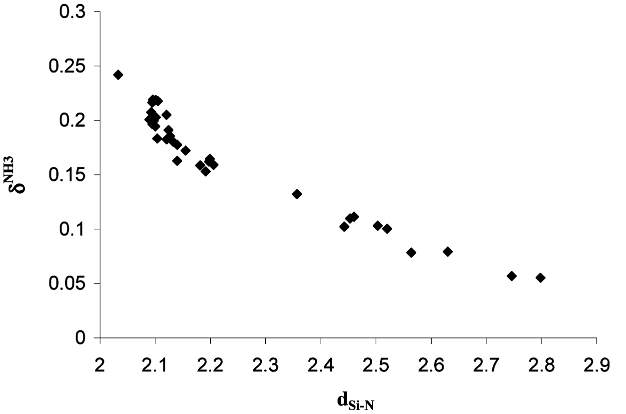


Figure 1. Charge on ammonia (δ^{NH_3} in e) in the studied complexes (compounds in Table 3 and Table S2) vs the Si−N distance (d_{Si-N}, in Å) in the complex.

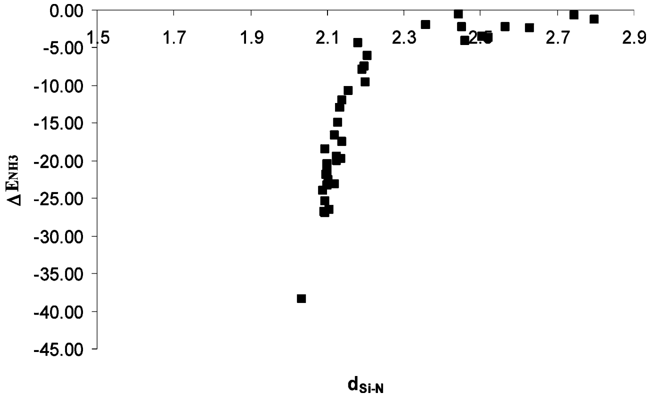


Figure 2. Interaction energy with NH_3 (ΔE_{NH_3}, in kcal/mol) vs the Si−N distance (d_{Si-N}, in Å) in the ammonia complex of compounds in Table 3 and Table S2.

silylenes which form Lewis acid−base complexes with NH_3 did not form a complex with BH_3. As expected, in the case of all acyclic molecules instead of the conventional Lewis acid−base complex with BH_3, bridged structures were found. In these structures one of the H atoms of BH_3 is in bridging position between silicon and boron,[22] and the structure is stabilized by the $\sigma_{B-H} \rightarrow$ Si $3p_z$ delocalization.[37] This interaction is only favorable when the Si $3p_z$ orbital is not filled with electrons. The formation of the bridged structure is in complete accordance with the finding that these acyclic molecules are highly electrophilic, the electrostatic potential (V_A) is large above the silicon and they form Lewis acid−base complexes with NH_3. It can also be noted that independent of the effect of the substituent in the σ-system (i.e., all of $Si(CH_3)_2$, $Si(Si(CH_3)_3)_2$, $Si(CF_3)_2$ $HSiCH_3$, and SiH_2) form similar bridged adducts with BH_3. Compounds **6c**−**11** form complexes with BH_3 and the estimated interaction energies (from V_{min}) follow the correct trend when compared with the calculated energy. However, the best agreement is found for **6c** and with increasing number of nitrogen atoms in the anellated ring, the difference between the estimated and calculated values increases. This phenomenon strongly resembles our results in the case of disubstituted silylenes (RSiR′where R and R′ = NH_2, OH, SH), for which it was found that the interaction energy with BH_3 depended much less on the electrostatic potential.[22] In Figure 3, V_{min} is plotted vs V_A for the ambiphilic species. The overall tendency discussed in section 1 is regained, confirming our model, but two almost parallel curves appear, one for the disubstituted species and another one for the anellated compounds. **2** and **4** seem to belong to the group of disubstituted species based on their V_{min} and V_A values.

From the reactions with BH_3 and NH_3 we may conclude that both the electrophilic and nucleophilic character of silylenes are governed by the population of the formally empty Si $3p_z$ orbital, and that is why the σ-donor or acceptor property of the substituent influences the reactivity of silylenes to a much smaller extent and explains why σ-effects received very little attention in the literature in the case of silylenes. It is easy to see that the presence of a π-donor substituent will increase the π-electron population of the Si $3p_z$ orbital and as a consequence ΔE_{NH_3} will decrease. The effect on nucleophilicity is exerted via the possible donation of the B−H electron density into the empty Si $3p_z$ orbital and when this interaction is not favorable the nucleophilic character of the silylenes will emerge.[37] In Table S3, we collected the orbital energies of the MOs corresponding to the silicon lone pair for the 12 compounds studied in this work. The results show that the σ-donor/acceptor property of the substituent influences the lone pair energy level considerably, e.g., in the case of the strong electron-withdrawing CF_3 group the orbital energy (−0.30 a.u.) is much lower than in the case of $Si(CH_3)_{3b}$ (−0.20 au). However, we have shown above that if the Si $3p_z$ orbital is empty, the most important interaction between BH_3 and the silylene will be the delocalization of the B−H electron density into the Si $3p_z$ orbital and not the interaction between the Si lone pair and the boron empty orbital. We only observe a Lewis acid−base complex of the two molecules when the Si $3p_z$ orbital is considerably filled with electrons, e.g., in the case of the anellated species or the stable compounds. Therefore, we may conclude that the primary factor determining the nucleophilicity and Lewis basicity of the silylenes is the Si $3p_z$ population. We would like to note here, that in the case of the anellated compounds a very good linear correlation is found between V_A and the lone pair energy level ($R^2 = 0.98$) showing that with increasing Si $3p_z$ population (decreasing V_A) the lone pair energy level rises resulting in a more favorable interaction with σ-type Lewis acids.

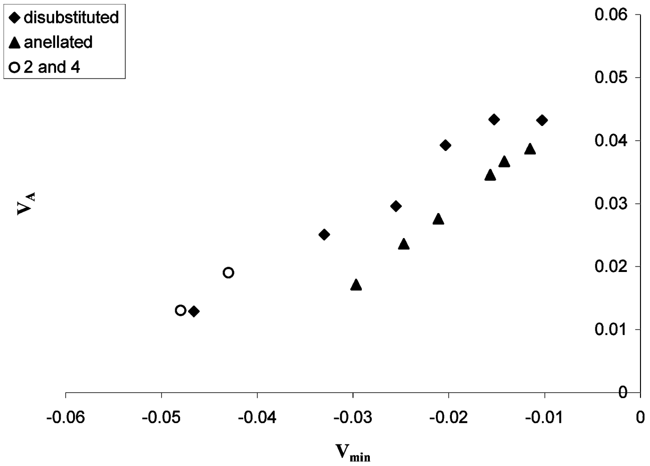


Figure 3. Relationship between the minimum of the electrostatic potential calculated in the lone pair region (V_{min}) of silylenes vs the electrostatic potential calculated in the region of the empty orbital of the silicon (V_A). In the diagram the ambiphilic species are included (NH_2, OH and SH disubstituted species, anellated molecules (**6c**−**11**) and compounds **2** and **4**.

On the basis of our results we propose that silylenes could be classified in three groups. *Group 1.* Silylenes with no or a single π-electron-donating group will only show electrophilic character and form Lewis acid−base complexes with Lewis bases. The characteristic Si−N distance in the ammonia complexes was found to be about 2.1 Å and the charge-transfer considerably large, above 0.16 e. For these molecules, the electrostatic potential can be used to predict the interaction energy with NH_3. These complexes do not show nucleophilic character and do not form Lewis acid−base complexes with BH_3, instead a bridged compound exist on the PES of silylene+BH_3, which is stabilized by $\sigma_{B-H} \rightarrow$ Si $3p_z$ delocalization. *Group 2.* When the empty orbital of silicon is filled to a larger extent (e.g., in the case of silylenes disubstituted with π-electron-donating groups or the anellated species(**6c**−**11**), **2b**, **4**, and **5**) the molecule does not form Lewis acid−base complexes with Lewis bases, but a van der Waals complex exists on the PES, in which the silylene acts as the electrophilic partner. The characteristic Si−N distance in these complexes varies between 2.2 and 2.8 Å and the amount of charge transferred from ammonia to the silylenes depends on the distance between the fragments, but is in all cases considerably smaller than in *Group 1*. The interaction energy with ammonia can most readily be estimated from the local electrophilicity index on the silicon atom. These silylenes are nucleophilic and form complexes with BH_3. Between their electrophilic and nucleophilic ($V_A - V_{min}$) and Lewis acid−Lewis base characters (ΔE_{NH_3} and ΔE_{BH_3}) a strong relationship was found, with decreasing electrophilicity of the compound its nucleophilicity increases. However, as seen from Figure 3, to describe $V_A - V_{min}$ or (ΔE_{NH_3} and ΔE_{BH_3}) relationships quantitatively no unique equation exists. In the case of these molecules with increasing $3p_z$ orbital population, the energy level of the Si lone pair increases resulting in a more favorable interaction with σ-type Lewis acids, such as BH_3. *Group 3* includes those silylenes, which do not act as an electrophile toward NH_3 and do not form Lewis acid−base or Van der Waals complexes with it, e.g., **1**. which besides the π-donation from the nitrogen atoms is further stabilized by the aromaticity of the molecule.[50]

All in all the scheme presented in section 1 and the new results presented in the present section show that electrophilicity/nucleophilicity, Lewis acidity/basicity, spin-philicity and stability are related in this type of compounds; DFT reactivity descriptors are clearly able to account for this unique situation when two different regions around a single atom show a fundamentally different behavior toward perturbation from a substituent resulting in an inverse reactivity tendency toward a given type of reactants.

Conclusions

We presented a detailed account on the relationship between various DFT-based reactivity indices used to study silylenes. It was shown that a change in one single factor, the π-electron donating ability of the substituents of the silicon atom, leads to changes of all reactivity indices, which can be interpreted in a chemically appealing way, indicating that the properties of silylenes can be tuned by changing the substituents. Our results further imply that on the basis of the stability of the silylene its chemical properties can be predicted, including its nucleophilic and electrophilic properties, Lewis acidity and basicity, spin-philicity and dimerization ability. The validity of the model proposed on the basis of previously obtained numerical results is successfully tested in the case of CH_3SiR (where R = CH_3, NH_2, OH, and SH) $Si(Si(CH_3)_3)_2$, $Si(CF_3)_2$, and benzo-, pyrido-, pyridazo-, and pyrimido-anellated 1,3,2λ^2-diazasiloles.

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Supporting Information Available: Table S1, showing isodesmic reaction energies (ΔH_i), singlet−triplet gaps (ΔE_{s-t}), dimerization energies (ΔE_{dim}), and estimates of dimerization energy based on ΔH_i ($\Delta E_{dim}^{\Delta H_i}$) and ΔE_{s-t} ($\Delta E_{dim}^{\Delta E_{s\text{-}t}}$) for the compounds investigated in this study, where all values were calculated at the B3LYP/6-311+G(d,p) level and are in given kcal/mol, Table S2, showing electrostatic potential calculated at point **A** (V_A) and point **B** (V_{min}), Fukui function for nucleophilic attack on the silicon (f_{Si}^{+}), global electrophilicity (ω), and local electrophilicity on the silicon (ω_{Si}^{+}) and the calculated interaction energy with NH_3 (ΔE_{NH_3}), and its estimates from global ($\Delta E_{NH_3}^{\omega}$) and local ($\Delta E_{NH_3}^{\omega^{Si+}}$) electrophilicities and from V_A ($\Delta E_{NH_3}^{V_A}$), charge on the ammonia (δ^{NH_3}) and the Si−N distance (d_{Si-N}) in the complex, interaction energy with BH_3 (ΔE_{BH_3}) and its estimate from V_{min} ($\Delta E_{BH_3}^{V_{min}}$), where all values were calculated at the B3LYP/6-311+G(d,p) level of theory, and the values of V_A, V_{min}, f_{Si}^{+} , ω, ω_{Si}^{+} , ΔE_{NH_3} and ΔE_{BH_3} are taken from ref 22, and Table S3, showing the identity and orbital energy of the Si lone pair at the B3LYP/6-311+G(d,p) level for the 12 compounds investigated in the present study. This material is available free of charge via the Internet at http://pubs.acs.org.

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