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**Theoretical study on the structure, reactivity and
stability of silylenes and silenes**

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Ph.D. thesis

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Introduction

Low coordinated organosilicon compounds have been the subject of intensive theoretical and experimental research since the 1980s when the first stable silicon double bonded species (silenes and disilenes) were synthesized. Silylenes are divalent silicon compounds, in general, short-lived reactive intermediates. It was only in 1994, when the first, bottleable silylene was isolated. The aim of my work was get some insight into the properties of silylenes and silenes by computational chemistry. In the first part of my work I studied the structure, stability and reactivity of silylenes. With the help of DFT derived chemical concepts, such as hardness, softness, electrophilicity, spin-philicity/spin-donicity etc. I studied the Lewis acid and base character of silylenes and germylenes. I explored the properties of the spin-philicity, spin-donicity and spin hardness indices on a large set of carbenes, silylenes and germylenes. I investigated the relationship between the stability and dimerization ability of silylenes and finally I applied the previous results in the design of new, possibly stable species. In order to obtain systematic information on silylenes, all silylenes substituted by first and second elements (HSiR , where $\text{R}=\text{H}$, Li , BeH , CH_3 , NH_2 , OH , F , Na , MgH , AlH_2 , SiH_3 , PH_2 , SH , Cl) were studied. The set included disubstituted species as well (R_1SiR_2 , where R_1 , $\text{R}_2=\text{NH}_2$, OH , F , SH , Cl) and some already synthesized ring compounds.

The second part of my thesis considered the reaction mechanism of water addition to silafulvenes with special attention given to their possible aromatic character. Silafulvenes are special silenes, which contain a conjugative double bond system enclosed in a ring with an extra exo double bond. These molecules shift their π -electrons in the ground state due to influence of dipolar aromatic resonance structures. As a consequence, the polarity of the Si=C double bonds of silafulvenes differs markedly from other silenes. Experiments showed that 4-silatriafulvene derivatives possess a different reactivity pattern toward alcohols than other silenes. In order to have a better understanding of the 4-silatriafulvene alcohol addition reaction, we investigated the water addition of various substituted silene compounds.

Computational methods

Quantum chemical calculations were performed with the B3LYP hybrid functional and at the MP2 level of theory, using various basis sets. In order to obtain reliable reaction energies CBS-Q/CBS-QB3 calculations were performed and analytical second derivatives were used to characterize the optimized stationary points on the PES. IRC calculations were performed for all path at the B3LYP/6-31G(d) to confirm the reaction coordinates from transition states to stable product. NPA charges were obtained with the NBO program as implemented in Gaussian 98.

Results

I. Spin-philicity and spin-donicity of carbenoid compounds

1. A thorough investigation of spin-philicity, spin-donicity and spin hardness indices of carbenes, silylenes, germylenes and stannylenes substituted by first and second row elements, disubstituted species and ring compounds was given. The spin hardness values only slightly change with the different substituents, but increase with the atomic number of the central atom for a given substituent. The spin-philicity and spin-donicity indices are relevant to two neighboring spin states and can describe both ground state and excited state properties. The spin-philicity and spin-donicity indices decrease linearly with the vertical singlet-triplet energy separation of the molecule. The analogy with the electrophilicity index has been discussed in detail. A very good linear correlation has been found between the energy difference estimated on the basis of the sum of the spin potentials and the vertical triplet energy gaps independent of the ground state of the molecule and the atomic number of the central atom. The maximal spin acceptance and spin release values in the case of molecules with large vertical energies may be helpful in the investigation of the spin catalysis phenomenon.

2. The spin-philicity, spin-donicity and spin hardness indices were used to obtain information on the similarity of molecular groups. The spin

hardness turned out to give the most reliable information of the three indices. Sound evidence was obtained for the similarity of nitrenes and phosphinidenes and silylenes and germylenes and it was also demonstrated that substitution changes the spin hardness of these molecules in a similar manner. The indices correctly indicated the experimentally established similarity of nitrenes and carbenes.

3. Comparison of the spin-philicity and spin-donicity indices of carbenoids, nitrenes, phosphinidenes and diatomic compounds with the adiabatic singlet-triplet gap of the molecules reveals the uniform behavior of these indices (Figure 1).

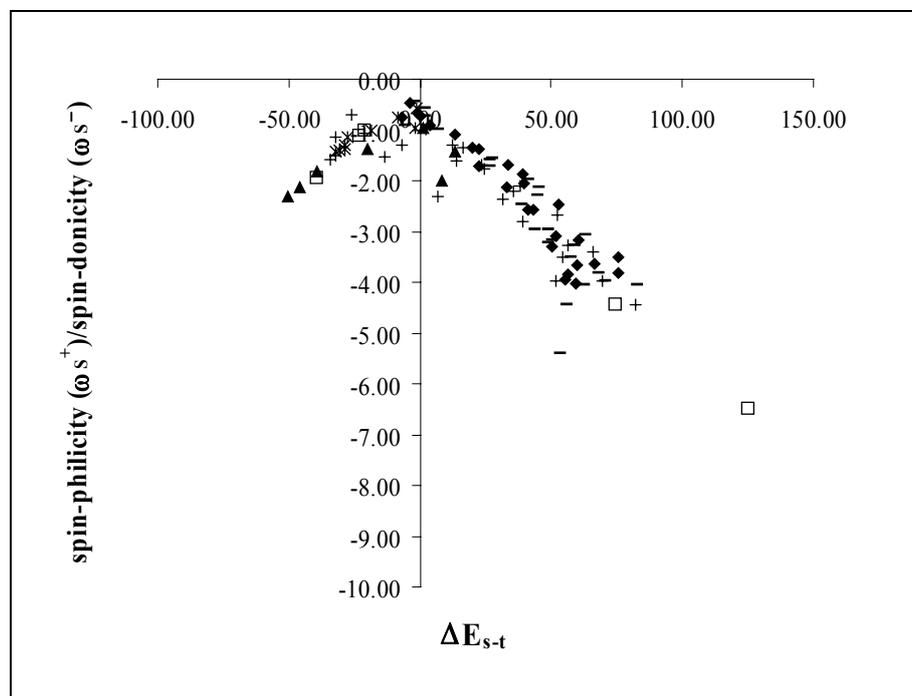
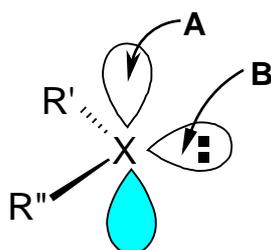


Figure 1. Spin-philicity ω_s^+ and spin-donicity ω_s^- vs. the adiabatic singlet-triplet gap ΔE_{s-t} for carbenes (+), silylenes (♦), germylenes (-), nitrenes (▲), phosphinidenes (*) and diatomic molecules (□).

On the basis of this result it can be concluded that these indices are universal, whose behavior depends only on the singlet-triplet energy separation of the molecules. Correlation has been found between the spin-philic and electrophilic character of silylenes.

II. Electrophilic and nucleophilic character of silylenes and germylenes

4. We applied conceptual DFT indices to assess the Lewis acid and base character of silylenes and germylenes. The reaction of silylenes and germylenes with Lewis acids and bases is essentially charge controlled and the interaction with hard bases is preferred. The electrostatic potential calculated 2\AA above the plane of the silylene/germylene (Point A in Scheme 1) is a good measure of local hardness and the electrophilicity index correctly predicts the electrophilicity of the differently substituted molecules.



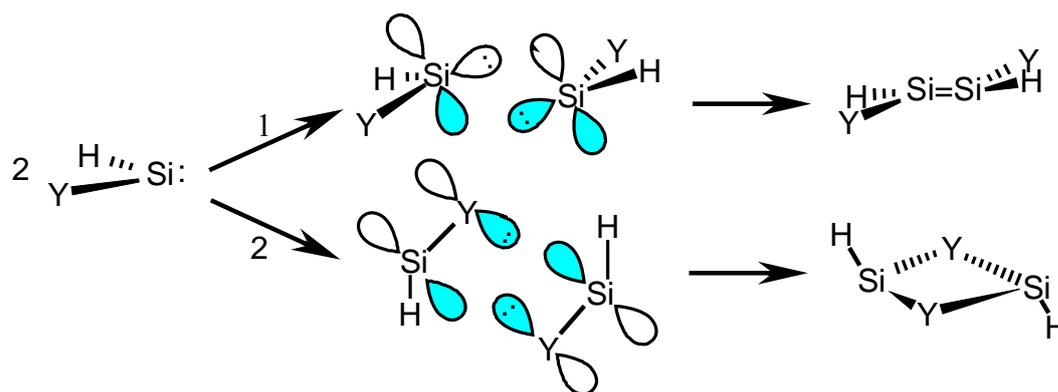
Scheme 1

5. The nucleophilicity of nucleophilic silylenes is proportional to the minimum of the electrostatic potential in the lone pair region (Point B in Scheme 1), but this quantity alone is not enough to predict the

nucleophilicity. Only those silylenes show nucleophilic character, which are not electrophilic. Electrophilic silylenes prefer the formation of a bridged silylene-BH₃ molecule instead of the conventional Lewis acid-base adduct. Our results are in accordance with the experimental findings.

III. Relationship between the thermodynamic stability and dimerization ability of silylenes

6. I studied the relationship between the thermodynamic stability and dimerization ability of silylenes. Dimerization of silylenes can lead either to a disilene (Si=Si double bonded compound) or to a cyclic, four membered ring dimer (Scheme 2).



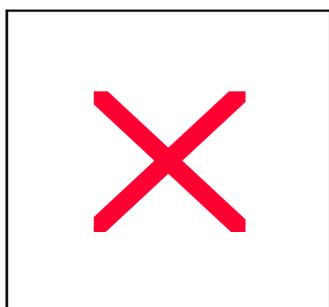
Scheme 2

A linear correlation was found between the isodesmic reaction energies and dimerization energies in the $4 < \Delta E_i < 35 \text{ kcal/mol}$ region along Path 1. The

singlet-triplet energy differences also correlate well with the dimerization energies, but in the case of the highly stable silylenes ($\Delta E_{s-t} < 60$ kcal/mol) the curves become flat (Path 1). It can be concluded that both the isodesmic reaction energy and the singlet-triplet energy separation could be used to predict the chemical stability of silylenes. No correlation, however, has been found between the dimerization energy of the bridged dimer formation and the isodesmic reaction energy or the singlet-triplet energy separation of silylenes (Path 2).

IV. Design of a new silylene with a novel structure

7. We designed a new type of silylene by using the N=S=N-S fragment to enclose the divalent Si in a ring (Scheme 3).



Scheme 3

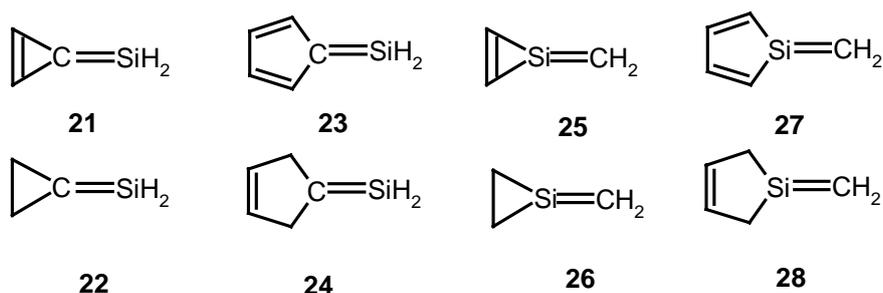
The isodesmic reaction energy of the molecule predicts it to be a stable compound, which is further proved by its nucleophilic character. The stability of the compound is increased by its considerable aromatic

stabilization, which, according to NICS(1) index, is larger than that of benzene.

8. Study of the constitutional isomers of SiN_2S_2 led to the conclusion, that the triplet state of silylenes can be stabilized by using substituents that allow for the delocalization of spin. This effect lowers the singlet-triplet gap of silylenes. Calculations on the silylene containing the $\text{N}=\text{S}=\text{S}=\text{N}$ fragment show that it is stabilized both in its singlet and triplet state, and as a consequence it has a small $\Sigma\Delta E_{s-t}$, but it does not dimerize. This is an important exception to our earlier findings.

V. Water addition reaction of silenes

9. The water addition reaction of the following silenes (Scheme 4) were examined:



Scheme 4

The water addition can be regarded as a model to study the addition of alcohols. I studied two different reaction channels: the *normal* and the *abnormal* additions. In *normal* addition of alcohols and silenes alkoxy silanes are produced. The reaction is highly exothermic (~ -60

kcal/mol) and has a small energy of activation (~10 kcal/mol). In the *abnormal* addition carbon-substituted silanes are produced. This reaction is only moderately exothermic (~-15 kcal/mol). and its energy of activation is very high (~50 kcal/mol) In general the *abnormal* channel cannot compete with the *normal* addition.

10. The reaction starts by the formation of an initial van der Waals complex. Depending on the interaction between the silene and water, the complex can be characterized as electrophilic or nucleophilic. From the van der Waals complexes cyclic transition states lead to the different products.

11. In the case of 4-silatriafulvene only one electrophilic and in the case of 6-silapentafulvene only one nucleophilic van der Waals complex were found. These complexes keep the aromaticity of the reactant. Loss or maintaining of aromaticity at the transition state influences the activation energy of the *normal* and *abnormal* channels to a great extent (Figure 2).

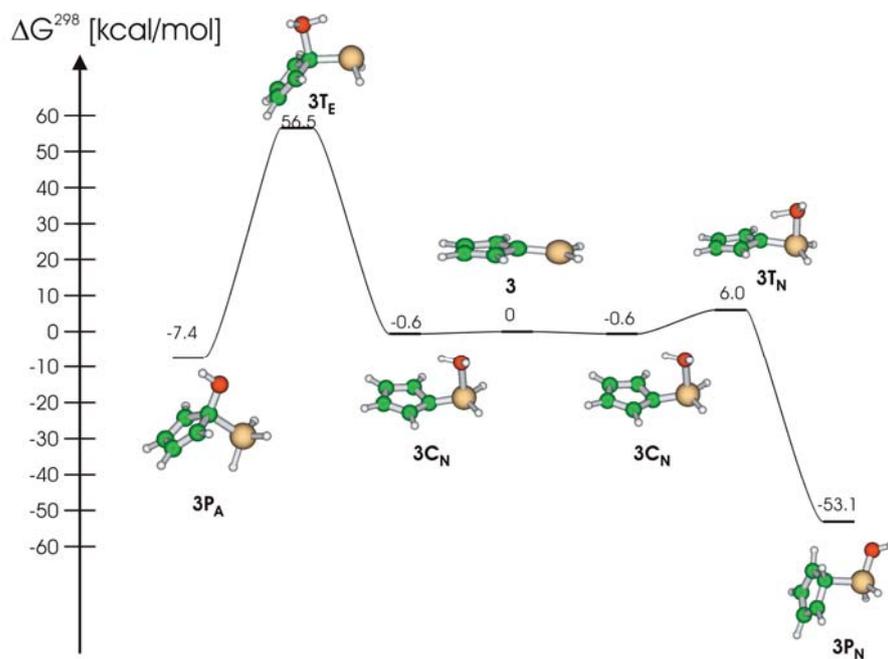
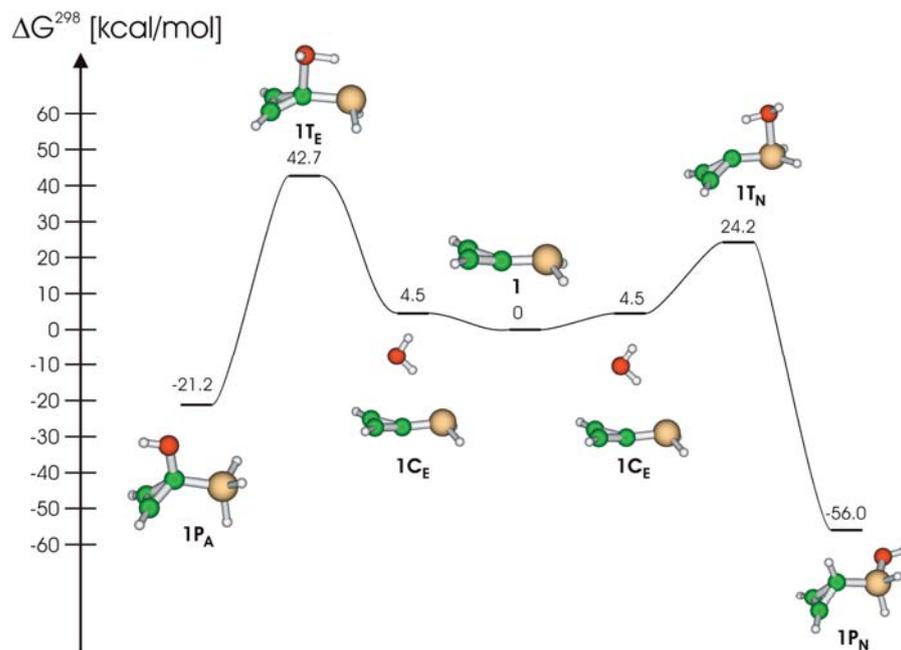


Figure 2. Comparison of the free energy diagram at the CBS-QB3 level for the reaction channels of 4-silatriafulvene + water and 6-silapentafulvene + water reactions

List of Publications

- (1) **Oláh J.**, De Proft F., Veszprémi T., Geerlings P. *J. Phys. Chem. A* **108**, **2004**, 490-499, Spin-Philicity and Spin-Donicity of Substituted Carbenes, Silylenes, Germylenes, and Stannylenes
- (2) **Oláh J.**, Veszprémi T., Nguyen M. T. *Chem. Phys. Lett.* **301**, **2005**, 337-341 Spin-philicity and spin-donicity of simple nitrenes and phosphinidenes
- (3) **Oláh J.**, De Proft F., Veszprémi T., Geerlings P. *J. Phys. Chem. A* **109**, **2005**, 1608-1615 Hard-soft acid-base interactions of silylenes and germylenes
- (4) **Oláh J.**, De Proft F., Veszprémi T., Geerlings P. *J. Mol. Struct. (THEOCHEM)*, *submitted* Relationship between electrophilicity and spin-philicity of divalent and monovalent species of group 14 and 15 elements
- (5) **Oláh J.**, Veszprémi T., *J. Organomet. Chem.* **686**, **2003**, 112-117, Relationship between stability and dimerization ability of silylenes
- (6) Water addition reaction of Si=C double bonds attached to ring substituents, *in preparation*

Publications not included in the thesis:

- (7) **Oláh J.**, Van Alsenoy C, Sannigrahi A. B. *J. Phys. Chem. A* **106**, **2002**, 3885-3890 Condensed Fukui functions derived from stockholder charges: Assessment of their performance as local reactivity descriptors
- (8) Csonka GI, Ruzsinszky A, **Oláh J.**, Van Alsenoy C, *J. Mol. Struct. (THEOCHEM)* **589-590**, **2002**, 1-5, Organizing atomic partial charges into a database
- (9) **Oláh J.**, Veszprémi T, *J. Mol. Struct. (THEOCHEM)* **620**, **2003**, 157-163, Molecular structure and internal rotation potential of perfluoro (2,4-dimethyl-3-oxa-2,4-diazapentane), (CF₃)₂N-O-N(CF₃)₂
- (10) **Oláh J.**, Van Alsenoy, C., Veszprémi T., *J. Phys. Chem. A* **108**, **2004**, 8400-8406, NaSCN: Striking differences between its gas-phase and crystal-phase structure: A theoretical study
- (11) Tersago, K., **Oláh, J.**, Martin, J.M.L., Veszprémi, T., Van Alsenoy, C., Blockhuys F. *Chem. Phys. Lett.* **413**, **2005**, 440-444, Towards a satisfactory description of the molecular structure of Roesky's ketone
- (12) **Oláh, J.**, Blockhuys, F. Veszprémi, T., Van Alsenoy, C. *Eur. J. Inorg. Chem* *accepted*, On the usefulness of overlap populations and bond orders to chalcogen-nitrogen systems