Lowcoordinated Silicon and Hypercoordinated Carbon

Structure and Stability of Silicon Analogs of Alkenes and Carbon Analogs of Silicates

ANDERS M. EKLÖF
Dissertation presented at Uppsala University to be publicly examined in C8:301, BMC, Husargatan 3 753 21, Uppsala, Saturday, October 25, 2008 at 10:15 for the degree of Doctor of Philosophy. The examination will be conducted in English.

Abstract

Quantum chemical studies on lowcoordinated group 14-16 compounds have been performed. This thesis focuses particularly on silenes influenced by reverse Si==C bond polarization. Hypercoordinated carbon compounds are also studied.

The geometries from calculations with several common computationally inexpensive methods have been tested against high level CCSD/cc-pVTZ geometries for a series of substituted silenes. Hybrid HF/DFT methods performed best among the inexpensive methods tested for silenes.

Heavy alkenes strongly influenced by reverse polarization are found to have less exothermic dimerization energies for both head-to-head and head-to-tail dimerizations, and to have higher activation energies for water addition than naturally polarized heavy alkenes.

We also investigated solvated lithium, magnesium and potassium silenolates and found that lithium and magnesium ions coordinate preferably to O, giving their SiC bond some double bond character.

Reverse polarized 2-siloxyl-, 2-thiosiloxyl-, and 2-(N-sila-N-methyl)-silenes could according to calculations be formed thermolytically from the corresponding tetrasilanes as transient species. It was, however, found that silenes highly influenced by π-conjugative reverse polarization have low barriers for the back-reaction, and thus these silenes are more difficult to form as stable species than naturally polarized silenes.

It is also found that conjugated 1-siladienes, formed by electrocyclic ring-opening of 1-silacyclobut-2-enes, which are highly influenced by π-conjugative reverse polarization, have higher barriers for electrocyclization back to starting material than naturally polarized 1-siladienes.

It is found that \( \text{CHE}_2^{\ddagger} \), \( \text{CHE}_2^{4\ddagger} \), \( \text{CNE}_2^{\ddagger} \), and \( \text{CNE}_2^{4\ddagger} \) are the closest carbon analogs of \( \text{SiH}_2^{\ddagger} \), \( \text{SiH}_2^{4\ddagger} \), \( \text{SiF}_2^{\ddagger} \) and \( \text{SiF}_2^{4\ddagger} \), respectively. However, due to their exothermic dissociation reaction, these very high-lying local minima will be impossible to reach experimentally.

Keywords: silenes, zwitterionic silenes, silenolates, reverse polarization, natural resonance theory, hypervalent carbon, hypercoordinated carbon, thermolysis, lowcoordinated silicon

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urn:nbn:se:uu:diva-9298 (http://urn.kb.se/resolve?urn=urn:nbn:se:uu:diva-9298)
EXPERIMENTALISTS THINK SILICON IS REALLY FUN TO USE
ITS PLACE IN NOVEL COMPOUNDS IS CERTAIN TO AMUSE
THEY SIT ALL DAY IN LABORATORIES MAKING ALL THIS SLUDGE
"LOADED WITH THE SILICON THEY SAY", TO ME IT LOOKS LIKE FUDGE.
FOR HAPPY THOUGH THEY BE WITH CRUD, I'D LIKE TO KNOW A LITTLE
ABOUT THE PI BONDS ON THE EDGE AND SIGMAS IN THE MIDDLE.

SO LETS DERIVE A WAVEFUNCTION.....6-31G*
USE AN OPTIMAL GEOMETRY AND SEE WHERE ELECTRONS ARE.
BUT WHAT OF CORRELATION? ASKS THE WIRY LITTLE SKEPTIC.
WE'LL THROW IN PERTURBATION AS AN ELECTRON ANTISEPTIC.
AND WHEN THE PROGRAM GIVES US ANSWERS IN THEM WE CAN TRUST
SINCE NOBODY CAN MAKE THE STUFF, WE HAVE NO CHOICE, WE MUST.

SO THEORY GUYS HAVE GOT IT MADE, IN ROOMS FREE OF POLLUTION.
INSTEAD OF PROBLEMS WITH THE REFLUX, THEY HAVE ONLY SOLUTIONS.
AND WHEN THE FEDS ANNOUNCE THE LIST OF CARCINOGENIC TERRORS,
THE THEORISTS SIT SAFELY AT THEIR TERMINALS FIXING ERRORS.
IN OTHER WORDS, EXPERIMENTALISTS WILL LIKELY DIE OF CANCER
FROM WORKING HARD YET FRUITLESSLY...TILL THEORY GIVES THE ANSWER.

-- THOMAS A. HOLME, 1983
List of Papers

This thesis is based on the following papers, referred to in the text by its roman numerals.

I


II

On the Role of the $\pi$-Contribution to Reverse Polarization for Structure and Stability of Heavy group 14-16 Alkene, Imine, and Carbonyl analogs. Anders M. Eklöf, Henrik Ottosson, Submitted manuscript.

III


IV


V


VI

The CNe$_5^{4+}$ and CNe$_6^{4+}$ ions: The Nearest Possible Carbon Analogs of Penta- and Hexafluorosilicate SiF$_5^-$ and SiF$_6^{2-}$. Anders M. Eklöf, Sebastien Villaume, Hui Tong, Henrik Ottosson, Manuscript.

Papers not included in this thesis:

Contribution Report

The Author wishes to clarify his contribution to the included papers I-VI:

I
The four authors equally shared the computational work and interpretation of the results.

II
Partly formulated the research project. Performed all computations involved and significant part of interpretation of the results, and writing of the manuscript.

III
Partly formulated the research project. Performed all computations and interpretation of the results. Wrote the manuscript.

IV
Performed the majority of the computational work involved and interpretation of the result. Significant part of the writing of the manuscript.

V
Partly performed computational work and interpretation of the results.

VI
Took active part in setting up the research project. The four authors equally shared the computational work, interpretation of the results, and writing of the manuscript.
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<tr>
<td>1-Ad</td>
<td>1-Adamantyl</td>
</tr>
<tr>
<td>6-31G(d)</td>
<td>Pople basis set</td>
</tr>
<tr>
<td>ANO-RCC</td>
<td>Atomic natural orbitals – relativistic correlation consistent</td>
</tr>
<tr>
<td>B3LYP</td>
<td>Becke-3 + LYP hybrid functional (method)</td>
</tr>
<tr>
<td>CC</td>
<td>Coupled Cluster (theory)</td>
</tr>
<tr>
<td>cc-pV(n)Z</td>
<td>Correlation Consistent Polarized Valence (n)-Zeta, (n) = level of contraction (basis set)</td>
</tr>
<tr>
<td>CCSD</td>
<td>Coupled Cluster Singles Doubles</td>
</tr>
<tr>
<td>CCSD(T)</td>
<td>Coupled Cluster Singles Doubles and perturbative Triples (method)</td>
</tr>
<tr>
<td>CGMT</td>
<td>Carter-Goddard-Malrieu-Trinquier (theory)</td>
</tr>
<tr>
<td>CI</td>
<td>Configuration Interaction (theory)</td>
</tr>
<tr>
<td>CISD</td>
<td>Configuration Interaction Singles Doubles (method)</td>
</tr>
<tr>
<td>(\Delta E)</td>
<td>Energy Difference</td>
</tr>
<tr>
<td>DFT</td>
<td>Density Functional Theory</td>
</tr>
<tr>
<td>ECP</td>
<td>Effective Core Potential (approximation)</td>
</tr>
<tr>
<td>GGA</td>
<td>Generalized Gradient Approximation</td>
</tr>
<tr>
<td>GTO</td>
<td>Gaussian-type Orbital Function</td>
</tr>
<tr>
<td>HF</td>
<td>Hartree-Fock (theory)</td>
</tr>
<tr>
<td>HK</td>
<td>Hohenberg-Kohn (anzats)</td>
</tr>
<tr>
<td>iPr</td>
<td>iso-Propyl</td>
</tr>
<tr>
<td>KS</td>
<td>Kohn-Sham (theory)</td>
</tr>
<tr>
<td>LCAO-MO</td>
<td>Linear Combination of Atomic Orbitals to Molecular Orbitals (approximation)</td>
</tr>
<tr>
<td>LDA</td>
<td>Local Density Approximation</td>
</tr>
<tr>
<td>LSDA</td>
<td>Local Spin Density Approximation</td>
</tr>
<tr>
<td>LYP</td>
<td>Lee, Yang and Parr (method)</td>
</tr>
<tr>
<td>MAD</td>
<td>Mean Absolute Deviation</td>
</tr>
<tr>
<td>MAX</td>
<td>Maximum Deviation</td>
</tr>
<tr>
<td>Me</td>
<td>Methyl</td>
</tr>
<tr>
<td>Mes</td>
<td>2,4,6-Trimethylphenyl</td>
</tr>
<tr>
<td>MO</td>
<td>Molecular Orbital</td>
</tr>
<tr>
<td>MP4(SDQ)</td>
<td>Möller-Plesset Perturbation Theory including Single, Double, and Quadruple excitations (method)</td>
</tr>
</tbody>
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1. Introduction

Heavy alkenes with one or both carbon atoms exchanged to the heavier elements of group 14, particularly the Si=C double bonded silenes, have been the subject of much research in the past decades.\(^1\) It has been found that the structure, reactivity and other properties of the heavy alkenes depend to large extent upon their substituents.\(^2\) Because of electronegativity difference, the SiC double bond in silenes is naturally polarized towards carbon and the weakness of this bond combined with its polarity makes it very reactive. Most silenes dimerize spontaneously in the absence of trapping reagents and they react with moisture very rapidly. It has been concluded from quantum chemical calculations, however, that \(\pi\)-electron donating substituents at C make the double bond less polar and this \(\pi\)-conjugative reverse polarization effect is the most important electronic factor to consider for stabilization and reduction of the reactivity of the SiC double bond.\(^3\)

Before 1961, when the first stable phosphaalkyne was synthesized,\(^4\) it was thought that elements outside the first row of the periodic table did not form multiple bonds, neither with themselves nor with other elements.\(^5\) This statement is known as “the double-bond rule” and was based on theoretical investigations by Pfitzer and Mulliken.\(^6,7\) They showed that multiple bonds between heavy elements should be weak, owing to the long distance in the case of multiple bonds between the same heavy element, and to size mismatch in the case of multiple bonds between different heavy elements.

The structures, reactivities, and electronic properties of silenes have been investigated ever since Gusel’nikov and Flowers reported evidence for the existence of a transient silene as an intermediate species in the pyrolysis of 1,1-dimethylsilacyclobutane in 1967 (2, Scheme 1).\(^8\) Some years later, in 1981, Brook and co-workers reported the preparation of the first isolable silene (5, Scheme 2) that was persistent at room temperature,\(^9\) and West and co-workers reported the isolation of the first disilene the same year (6, Scheme 3).\(^10\) These two persistent species have in common that their substituents are bulky and so shield the double bond from attack by nucleophiles and make the dimerization more difficult.
Recently, a new research direction focusing on applications of silenes in organic synthesis has emerged, even though already in 1980 Bertrand et al. pioneered this field by studying asymmetric induction at Si from prochiral silenes.\textsuperscript{11} Steel and co-workers have made publications on the use of silenes as novel reagents in stereoselective organic synthesis.\textsuperscript{12} It is for example known that silacyclohex-3-enes, the product of a Diels-Alder reaction between a silene and a diene, can be used to form $\delta$-lactones and 1,4-diols stereoselectively (Scheme 3).\textsuperscript{12c,e} Moreover, Diels-Alder reaction between silenes and dienes could make it possible to synthesize ring-systems where one or more C atoms have been replaced by Si atoms. For example, some silicon-containing bioactive molecules have been known for some time to exhibit higher biological activity and better pharmacokinetic profiles than other similar drugs.\textsuperscript{13,14,15} Other synthetically useful products have been made using silenes as intermediates.\textsuperscript{12c,16} In order to find silenes that can be applied to organic synthesis we need to understand substituent effects and find silenes that react selectively, are less air and moisture sensitive, that do not dimerize, and that are easily accessible.\textsuperscript{12,17}
In the first part of this thesis, the main qualitative models used to explain the chemical bonding in heavy alkenes will be discussed. Also, some generally important quantum chemical methods will be presented. Different computational methods will also be compared to each other with regard to their ability to reproduce structural properties of silenes and stannenes. It will later be shown computationally that reverse polarization is not only an important electronic factor for stabilizing silenes toward dimerization and nucleophile addition, but also for stabilizing other heavy alkenes, heavy imines, and heavy carbonyl compounds. The electrocyclic ring-opening of silacyclobut-2-enes to form a 1-siladienes was studied computationally and it will be concluded that reverse Si=C bond polarization is important also for stabilizing these species toward electrocyclization. The formation of silenes with varying degree of reverse polarization through thermolysis of acyltetrasilanes, carbamyltetrasilanes and thioacetyl tetrasilanes will be discussed computationally. Although this is fundamental research highlighting the important differences between C and Si, the facile formation of silenes that reacts more selectively is a prerequisite for introducing these compounds into organic synthesis. The first part of this thesis concerns tricoordinate compounds of silicon and other heavy elements in group 14, 15 and 16, while the last part concerns hypercoordinate carbon compounds. The final chapter in this thesis thus differs in the topic and it deals with the disability of C to form pentavalent and hexavalent compounds similar to e.g. SiF$_5^-$ and SiF$_6^{2-}$. It will be concluded that although it is theoretically possible to find stable compounds of this type \textit{in silico}, these are practically unreachable.
2. Bonding Models for Heavy Alkenes

To understand the bonding in heavy alkenes, one could split the heavy alkene into two heavy carbene fragments, or into one carbene fragment and one heavy carbene fragment. Because of differences in ground state multiplicity between carbenes and heavy carbenes, it is evident that the two heavy carbene fragments do not share their electron pairs in the resulting double bond as normal alkenes do. This difference in electronic structure will reflect the differences in geometric structure. In 1976, Lappert and co-workers isolated and characterized the first distannene (7, Scheme 4), which was found to have a non-planar trans-bent structure after analysis by X-ray crystal structure analysis.\(^{18}\) The origin of the difference in bonding between heavy alkenes and normal alkenes lies in the fact that while several carbenes are triplets at room temperature, most heavy carbenes are singlets.\(^{19}\) The qualitative bonding theories most commonly invoked to explain the bonding between a singlet and a triplet heavy carbene fragment, and between two singlet heavy carbene fragments, are Lappert’s original donor-acceptor model, the Carter-Goddard-Malrieu-Trinquier (CGMT) model, and models based on second-order Jahn-Teller (SOJT) distortion.

\[ \text{CH(SiMe}_3\text{)}_2 \quad \text{CH(SiMe}_3\text{)}_2 \]
\[ \text{(Me}_3\text{Si)}_2\text{HC} \quad \text{Sn} \quad \text{Sn} \quad \text{(Me}_3\text{Si)}_2\text{HC} \]

**Scheme 4**

Lappert interpreted the bonding in 7 in terms of a double donor-acceptor bond (A, Scheme 5) or a valence bond description (B).\(^{18,20}\) A doubly occupied sp\(^2\)-orbital on one fragment overlaps with an empty p(\(\pi\))-orbital on the other, giving rise to a trans-bent bond. One extreme case arises when strong \(\pi\)-donor groups on one fragment donate electrons to the p(\(\pi\))-orbital to such an extent that it becomes unavailable for bonding to the other fragment.
such cases, the heavy alkene is planar at one of the heavy atoms in the double bond, but strongly pyramidalized at the other (C).

\[ \text{Scheme 5} \]

Volland, Davidson, and Borden analyzed the dependence of the shape of the potential energy surface describing the simultaneous pyramidalization of the two C atoms in ethylene on second-order Jahn-Teller (SOJT) distortions (Scheme 6).\textsuperscript{21,22} The pyramidalization can lead to either cis- or trans-bent structures and, since reduction of the molecular symmetry allows mixing of empty \( \sigma^* \) and filled \( \pi \) MO’s, it provides for stabilization of the bonding orbitals involved, as a result of SOJT distortions. This mixing becomes more important as group 14 is descended because of the smaller energy gap between the orbitals involved.

\[ \text{Scheme 6} \]

A very useful way of analyzing double bonds in heavy alkenes was initialized by Carter and Goddard who related the variation in C=C bond strengths in substituted alkenes to the singlet-triplet energy splitting \( (\Delta E_{ST}) \) of the two interacting carbene fragments.\textsuperscript{23} It was found that the C=C bond strength equaled the dissociation energy of ethylene (172 ± 2 kcal/mol\textsuperscript{24}) minus the

\[ \text{Scheme 6} \]
sum of the singlet-triplet energy gaps, $\Sigma \Delta E_{ST}$, of the two carbenes involved. Trinquier and Malrieu developed this theory further and in particular, they focused on explaining when a heavy alkene adopts a planar structure and when it adopts a trans-bent structure. This theory is normally referred to as the Carter, Goddard, Malrieu and Trinquier (CGMT) theory. A non-substituted heavy alkene $H_2E=E'H_2$ was concluded to be trans-bent if $\Sigma \Delta E_{ST} > \frac{1}{2} E_{\sigma+\pi}$, where $E_{\sigma+\pi}$ is the total bond strength of the $E=E'$ double bond. For substituted heavy alkenes $X_2E=E'Y_2$ with four $\pi$-donor groups and consisting of two interacting fragments with singlet ground states, it was found that it is trans-bent when $\Sigma \Delta E_{ST} > \frac{1}{2} E_{\sigma+\pi}(1+(q_1+q_2)/2)+\alpha q_1 q_2$, where $q_1$ and $q_2$ are the partial charges of the $p(\pi)$-orbitals of the two (heavy) carbene fragments and $\alpha$ is a proportionality constant taken as 200 kcal/mol. The derivation was made from valence bond (VB) theory. Since the $\Delta E_{ST}$ of silylenes are positive while the same quantity often is negative for carbenes, and since it is very sensitive to substitution for both carbenes and silylenes, it is clear that the structure of substituted silenes vary extensively, ranging from classical planar to non-classical bent structures.

$$\Delta E_{TBE} = \Delta E_{\text{snap}} - \Delta E_{\text{prep}} = \Delta E_{\text{snap}} - \Delta E_{\text{prep}}^e - \Delta E_{\text{prep}}^g \quad \text{(eq 2.1)}$$

$$\Delta E_{\text{snap}} = \Delta E_{\text{elstat}} + \Delta E_{\text{pauli}} + \Sigma (\Gamma) \Delta E_{\text{int}} \quad \text{(eq 2.2)}$$

[Diagram of optimized singlet state geometry and bonding in $R_2E_2$]

Scheme 7

Jacobsen and Ziegler analyzed the bonding energy in the $E=E'$ double bond and decomposed it into various contributions as can be seen from the equations above and from Scheme 7. The energy required to form the triplet heavy carbenes and change their geometries to those optimal for the triplet...
species, $\Delta E_{\text{prep}}$, is subtracted from the energy gained by snapping them together, $\Delta E_{\text{snap}}$, in order to obtain the total bond energy $\Delta E_{\text{TBE}}$. The $\Delta E_{\text{prep}}$ consists of two parts, as shown in Scheme 7. The first corresponds to the vertical excitation from the singlet ground state of the heavy carbene to the triplet state. The second is a geometric part which corresponds to distortion from optimal singlet state to the geometry which the heavy carbene fragment will have in the heavy alkene formed. The $\Delta E_{\text{snap}}$ is composed of a term corresponding to electrostatic attraction/repulsion, $\Delta E_{\text{elstat}}$, a Pauli repulsion term, $\Delta E_{\text{Pauli}}$, and terms corresponding to attractive orbital interactions, $\Sigma(\Gamma)\Delta E_{\text{int}}^\Gamma$. Jacobsen and Ziegler concluded that a heavy alkene is expected to be stable as long as $\Delta E_{\text{snap}}$ is higher than $\Delta E_{\text{prep}}$.

Recently, Himmel and Schnöckel showed that when each H$_2$E fragment contributes one electron to the $\sigma$-bond and one electron to the $\pi$-bond in a singlet state, each fragment has a larger $\Delta E_{\text{prep}}$ for a singlet state heavy carbene than for a triplet state heavy carbene. The heavy alkene resulting from bonding between the two fragments then becomes planar. The opposite applies for trans-bent heavy alkenes, which have donor-acceptor bonds. They concluded that, while disilenes are trans-bent donor-acceptor species, alkenes are classically bonded. Silenes should thus be at the borderline and the outcome depends much on the nature of the substituents.

The Si=C double bond in a silene is normally polarized towards C due to the electronegativity difference between C and Si. Apeloig and Karni, and more recently Ottosson, have shown that $\pi$-electron donating substituents at Si counteracts this natural polarity of the Si=C double bond. This is called reverse polarization. For silenes strongly influenced by reverse polarization, R$_2$C=SiH$_2$, bonding mode C in Scheme 5 is important. The more bent the silene is, the more important is bonding mode C for describing its electronic structure, and the longer is the C-Si bond and Si-H bonds, as revealed by Cheng and Chu. According to these authors, this is because the Si-C bond develops to a weak one-way donor-acceptor interaction of type C while the s-character of the developing non-bonding orbital at Si increases. Also, the p($\pi$)-orbital at Si becomes more free for accepting electrons from the substituents and the C-R bonds thus shorten. Cheng and Chu found that the $\pi$-electron density is much more sensitive towards substitution than the $\sigma$-electron density. First-row $\pi$-electron donor substituents at C are the most effective for lowering the Si=C bond polarity because of better $\pi$-orbital overlap between two first-row elements.

$\pi$-Donors have high-lying lone-pairs and when these overlap with the empty p($\pi$)-orbital on the C atom of a carbene fragment, this orbital is raised in energy. This increases the $\Delta E_{\text{ST}}$ of the carbene fragment and causes the $\pi$-bond to become more polarized towards Si (Figure 1). It also brings the $\pi$-orbital closer to the Si=C $\sigma^*$-orbital in energy which provides a driving force for trans-bending since the $\pi$ and $\sigma^*$ orbitals can mix more effectively in line with Volland, Davidson, and Borden’s SOJT description. This is also
in line with CGMT theory which states that a larger $\Sigma \Delta E_{ST}$ as a result of a larger $\Delta E_{ST}$ of one of the fragments, given that the $\Delta E_{ST}$ of the other fragment is constant, leads to more trans-bending. The CGMT theory was originally derived for homonuclear heavy alkenes. However, it can easily be extended to heteronuclear heavy alkenes. In reverse polarized silenes only Si is pyramidalized due to the one-way donor-acceptor interaction of type C.

Figure 1: Orbital interactions for the formation of a $\pi$-bond from one triplet silylene and one triplet carbene. D₁ and D₂ are two $\pi$-donor groups.

In this thesis, we will use the total contribution from the reverse polarized resonance structures $\Phi_{II}$ and $\Phi_{III}$ as calculated by natural resonance theory (NRT) as a measure of the degree of reverse polarization (Scheme 8).

Indeed, a connection between the qualitative CGMT model and reverse polarization can also be derived. As reverse polarization of a silene increases the Si atom will gradually become more similar to a Si atom of a silyl anion. Ottosson found a good correlation between the charge at Si, $q$(Si), and the
\[ \Sigma \Delta E_{ST} \] of the two interacting fragments with their geometries frozen as in the silene.\textsuperscript{31} The resulting \( \pi \)-orbital becomes more and more localized at the Si atom of the silene, which means that the Si atom will gradually become more similar to a Si atom of a silyl anion.

It is important to realize that NRT only measures the \( \pi \)-component and not the \( \sigma \)-component of reverse polarization. Apeloig and co-workers have shown that also the electronegativity of the substituents plays an important role for reversing the polarity of a silene.\textsuperscript{34} For example, the authors show that silyl groups at Si diminishes the total charge on Si and thus make the silene more influenced by reverse SiC bond polarization. In most cases, however, it is possible to analyze the effects of reverse polarization by just studying its \( \pi \)-components. For 2-silenolates, which are studied in this thesis and which are found to be extensively influenced by reverse polarization, this does not always hold. In general, one has to be careful when interpreting results, particularly for systems highly or negligibly influenced by reverse polarization. The electronic structure of silenes influenced by \( \pi \)-conjugative reversed polarization are thus highly influence by resonance structure \( \Phi_{II} \) and \( \Phi_{III} \), where the Y and the X atoms, respectively, have a formal positive charge while the Si atom has a formal negative charge. They are therefore sometimes called zwitterionic silenes.
3. Quantum Chemical Methods

Ever since Heitler and London first used quantum mechanics to describe the H₂ molecule in 1927, the field we today call quantum chemistry has been constantly growing. One of the most fundamental equations in quantum chemistry is the time-independent Schrödinger equation (SE) (eq 3.1)

\[ H\Psi = E\Psi \]  (3.1)

an eigenvalue equation where \( H \) is the Hamiltonian operator, \( \Psi \) is the wavefunction of the system at hand, and \( E \) is the total energy of that system. It is a wave equation and the Hamiltonian operator for the total (kinetic and potential) energy of a system acts upon a wave function to generate its evolution in space. The outcome of the equation is the quantized energies of the system and the form of the wave function, which enables all other properties of the system to be calculated.

Unfortunately, the Schrödinger equation can only be solved exactly for systems containing no more than one electron. In order to solve the Schrödinger equation for many-electron systems, two approximations need to be employed. The first one is the decoupling of all interaction between different electronic states and is called the adiabatic approximation. The second one stems from recognizing the fact that since nuclei are much more heavy than electrons, the electrons will relax instantaneously after the nuclei have moved. This approximation is called the Born-Oppenheimer approximation and enables one to calculate the electronic energy for fixed nuclear coordinates and a potential energy surface can be constructed by calculating the electronic energy for different positions of the nuclei in space. For those who wish to read more about the \textit{ab initio} methods described in this chapter, the textbook by Szabo and Østlund is excellent and for those who wish to read more about DFT, the book by Koch and Holthausen is recommended.
3.1 The Hartree-Fock Method

Since the Schrödinger equation cannot be solved exactly for molecules, approximations need to be introduced and, with the exception of density functional theory (DFT), all these are based on the Hartree-Fock (HF) approximation. This approximation reduces the many-electron Schrödinger equation to a series of soluble one-electron equations. The main assumption is that every electron moves independently in the average field of all the other electrons.

Within the HF-approximation, the motion of electrons with the same spin is correlated. However, electrons with opposite spins are not correlated and thus, it overestimates the Coloumb repulsion between these electrons. The results are, among others, that bond lengths become too short, bond strengths are overestimated, and the absolute electronic energies at the basis set limits are slightly too high. The type of correlation discussed here is called dynamic electron correlation.

Another disadvantage with HF is its inability to deal with near degeneracy effects, the situation which arises when two electronic states are close to each other in energy. When that happens, static correlation needs to be introduced by mixing of HF configurations in the calculation.

3.2 Configuration Interaction

In order to include dynamic correlation, one can construct a different wave function consisting of a linear combination of the reference HF wave function and excited electron configurations, representing excitations from occupied to virtual orbitals, used as basis to describe the electron correlation. This can be written

\[ \Psi = c_0 |\Phi_{HF}\rangle + \sum_j c_j |\Phi_j\rangle \]  

(3.2)

where \( \Psi \) is the state wave function, \( \Phi \) are electron configurations and \( c \) are the coefficients of each electron configuration. When this wave function is used as a starting guess, the method is called configuration interaction.

Including all possible excitations results in a full CI and is exact within the Born-Oppenheimer approximation, but only possible for very small systems. Therefore, one truncates the CI expansion to include, for example, only singly and doubly excited determinants. This method is called CISD.
The main drawback of truncated CI is that it is not size-consistent, meaning that the larger the system studied, the less electron correlation is included in the calculation, making it impossible to compare molecules of different size. Today, CI is very seldomly used. However, it forms an instructive starting point for other electron correlated \textit{ab-initio} methods.

3.3 The Coupled-Cluster Method

A different approach to deal with electron correlation which solves the problem of size-inconsistency is coupled cluster theory. Here the coupled cluster wave function is written

\[ \Psi_{cc} = e^{\bar{T}} \Psi_{HF} \tag{3.3} \]

\( \bar{T} \) is the cluster operator and can be written

\[ \bar{T} = \bar{T}_1 + \bar{T}_2 + \bar{T}_3 + ... + \bar{T}_N \tag{3.4} \]

where each \( \bar{T}_j \) generates all possible excited determinants with \( j \) electrons excited from occupied to virtual orbitals, and \( N \) is the total number of electrons. If the cluster operator is not truncated, this method is the same as full CI. However, one must truncate and it is usually truncated after second order.

Brillouin’s theorem states that there is no interaction between the HF reference wave function and singly excited determinants. This means that \( t_1 \) should be zero. However, if the system has multireference character, that is, suffering from near-degeneracy effects, these coefficients are not exactly zero. In order to probe this, one can compute the \( T_1 \) diagnostic values, written as

\[ T_1 = \frac{|t_1|}{\sqrt{N}} \tag{3.5} \]

where \( N \) is the total number of electrons. A value of \( T_1 < 0.02 \) is considered good for a CCSD calculation, indicating that a single-reference method is sufficient.
Since the high-level CCSDT method is too computationally expensive to be feasible even for small systems, one can include disconnected triplets in a pertubative manner instead, which gives the CCSD(T) method.

3.4 Many-Body Perturbation Theory

Dynamic electron correlation can be treated as a perturbation, $U$, to a reference Hamiltonian, $H_0$. The total Hamiltonian for the system can then be written

$$H = H_0 + \lambda U$$  \hspace{1cm} (3.6)

where $\lambda$ is a parameter which is set to one at the end.

Many-body perturbation theory can be applied and the wave-function and the energy of the system can be expressed as the Taylor expansions

$$E = E_0 + \lambda E_1 + \lambda^2 E_2 + ... , \quad \Psi = \Psi_0 + \lambda \Psi_1 + \lambda^2 \Psi_2 + ...$$  \hspace{1cm} (3.7)

In Møller-Plesset perturbation theory (MP$n$, $n = 2, 3, ...$), where $n$ is the order at which the perturbation expansion is truncated, the Hamiltonian and perturbation can be written

$$H = H_0 + \lambda U$$ \quad and \quad $$U = \sum_{i}^{\text{occ}} \sum_{j < i}^{\text{occ}} \frac{1}{r_{ij}} - \sum_{i}^{\text{occ}} \sum_{j}^{\text{occ}} (J_{ij} - K_{ij})$$  \hspace{1cm} (3.8)

An MP2 calculation recovers about 80% of the correlation energy, and MP4(SDTQ) gives up to 95 - 98% of the correlation energy. In contrast to CISD, MP$n$ methods are size-consistent. However, the energies these methods produce tend to oscillate with the order $n$. 

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3.5 Density Functional Theory

Density functional theory (DFT) is built on the Hohenberg-Kohn (HK) theorems which state that any observable including the energy of a molecular system can be written as a functional of the ground state electron density.

The advantages of using the electron density instead of the wave function when deriving the energy for a molecular system is that it is a function of only three variables compared to the wave function, which is a function of $3n$ variables, where $n$ is the number of electrons. The reason why DFT has become so popular is that it gives reasonable results while still being not much more costly than an ordinary HF calculation.

In the so-called Kohn-Sham approach (KS), the total energy of the molecular system can be written

$$E[\rho(\vec{r})] = T[\rho(\vec{r})] + V[\rho(\vec{r})] + J[\rho(\vec{r})] + E_{xc}[\rho(\vec{r})]$$

(3.9)

where $T$ is the kinetic energy, $V$ is the potential energy due to electron-nuclear-interactions, $J$ is the energy contribution due to Coulomb repulsion and also takes care of the problem with self-interaction, and finally $E_{xc}$ is the term due to exchange-correlation and includes all contributions to the energy not taken care for by the other terms. If there was a systematic procedure to determine this term exactly, then the Schrödinger equation would be solved exactly too. Unfortunately, there is no such systematic procedure.

3.5.1 Exchange-Correlation Functionals

In DFT, functionals consist of an exchange part, which gives the exchange energy of the electrons and a correlation part which gives the correlation energy of the electrons. There are two main types of approximations used for construction of the functionals, namely the local density approximation (LDA) and the generalized gradient approximation (GGA).

In an LDA functional, the electron density is approximated as that of a uniform electron gas. The approximation is local in the sense that the functional depends only on the value of the density at each point in space and not on its derivatives. A GGA functional, on the other hand, does not only depend on the density itself, but also on its gradient. The most commonly used GGA functional is the classical functional by Lee, Yang and Parr (LYP).

The accuracy of the functional can be even more improved by the addition of some exact HF exchange, leading to functional of the general form

$$E_{XC}^{Hyb} = E_{XC}^{DFT} + c(E_X^{Exact} - E_X^{DFT})$$

(3.10)
This procedure forms the basis of the hybrid HF/DFT methods, such as B3LYP.

3.6 Basis Sets in *Ab Initio* and DFT Calculations

In chemistry, the most commonly used DFT method is Beckes 3-parameter hybrid functional.\(^{39}\) It was first developed by Becke as B3PW91, but the PW91 correlation functional was later replaced with LYP to form the B3LYP\(^{40}\) functional.

In order to build the wave function in an *ab initio* calculation and to properly describe the electron density in a DFT calculation, basis functions are used. These are atom-centered functions made to approximate atomic orbitals. Linear combinations of these are used to approximate molecular orbitals.

Linear combinations of primary GTOs (PGTOs) called contracted GTOs (CGTO) are used to approximate each STO and the contraction coefficients are normally chosen so that the overlap between the CGTO and the STO is maximized. There are two types of contractions, segmented contractions where all types of PGTOs are considered and general contractions where a selection of PGTOs are considered for each contraction.

The basis sets used in this thesis are Pople-type and correlation-consistent polarized valence triple-zeta (cc-pVTZ) basis sets. In Pople-type basis sets segmented contraction schemes are used where CGTOs approximate STOs. For example, in the common 6-311G(d) basis set, a contraction of six PGTOs is used to describe the core electrons and a contraction of three PGTOs combined with two PGTOs is used to describe the valence electrons. This results in a triple-zeta basis set. Finally, d-functions are added to all non-hydrogen atoms in order to describe their polarization. Because Truhlar and co-workers have found that the addition of diffuse basis functions in DFT is more important than going from a double-zeta to a triple-zeta basis set,\(^{41}\) single-point B3LYP/6-31+G(d) calculations were performed at all optimal geometries of silenes where the B3LYP functional is used.

3.6.1 Effective Core Potentials

For elements in period 4 and below in the periodic table, where the number of core electrons causes the calculations to be cumbersome and where relativistic effects are important, it is often convenient to use an effective core potential (ECP), or pseudopotential, instead of an explicit basis set to describe these electrons. ECPs are semi-empirically derived and the one most
used in this thesis is the Los Alamos ECP by Hay and Wadt\textsuperscript{42} included in the LACVP basis set, which we use for Ge, Sn, As, Sb, Se, and Te.

3.7 Natural Bond Orbital Analysis

The many-electron wave function from an \textit{ab initio} or a DFT calculation is often very complex and it is not easily interpretable. One way to analyze a wave-function which is of special interest for this thesis would be to transform it into a localized form which corresponds to the one-center ("lone pair") and two-center ("bond") elements of a Lewis structure. This is called natural bond orbital (NBO) analysis\textsuperscript{43} and the resulting NBOs are local block eigenfunctions of the one-electron density matrix. Furthermore, these functions form a complete orthonormal set of one-electron functions which can be used to form matrix representations of all one-electron operators. They also have optimal convergence properties for describing the electron density. The determinant of highly occupied NBOs is normally used as the “natural Lewis structure” of the molecular system. Delocalization effects are dealt with as weak departures from this Lewis structure.

3.7.1 Natural Resonance Theory

In natural resonance theory (NRT)\textsuperscript{44}, the molecular electron density is analyzed and resonance structures and weights are extracted from it. The reduced one-electron density operator, \( \Gamma \), is rewritten as a weighted sum of density operators, \( \{ \Gamma_i \} \), each of which corresponds to a Lewis resonance structure of the molecule according to

\[
\Gamma = \sum_i w_i \Gamma_i
\]

(3.11).

Natural resonance theory provides an excellent way to decompose the complex molecular wave function of a MO calculation and then read the Lewis structure and resonance weights directly from it.
4. On the Performance of Inexpensive Quantum Chemical Methods for the Calculation of Geometric Parameters of Silenes

All of the silenes which have been proven to be stable enough to be isolable have large and bulky substituents in order to prevent dimerization and reactions with nucleophiles. Sophisticated high-level quantum chemical calculations, e.g. CCSD, are too expensive for these relatively large systems and inexpensive methods incorporating electron correlation are needed instead. The methods of choice are MP2 and DFT. Allinger and Schaefer have shown that MP2 gives more accurate bond lengths than B3LYP for second-row saturated compounds. Both these methods are commonly applied to heavy alkenes, even though there has been no systematic investigation concerning which method is the best. In the study presented in paper I, several computationally inexpensive methods are applied to silenes and stannenes in order to investigate which method is the best choice for describing different geometric properties of these species. Since the calculations on stannenes were made by Dr. Tong Hui while the calculations on silenes were performed by the author of this thesis, this chapter will focus on the silenes.

CCSD/cc-pVTZ geometries was compared to those obtained at HF, MP2, MP3, MP4, BLYP, B3LYP, BHHLYP and PBE0 levels. The multireference character of the investigated species was also probed. CASPT2 calculations were performed for some of the silenes and stannenes with the highest degree of multireference character thus found. For the stannenes, the Stuttgart-Dresden-Bonn ECP was used. The CASPT2 calculations were performed with a numerical gradient using the MOLCAS 7.1 package. Since scalar relativistic effects are important for compounds containing second-row elements, the ANO-RCC basis sets were used. These calculations were made by Dr. Sebastien Villaume.

Focus is given to silenes and stannenes (E = C, E = Si or Sn) influenced by reverse polarization through \( \pi \)-donating substituents at their C-atom. The ability of the different methods to describe the \( E=C \) bond length \( r_{EC} \), and the pyramidalization angle, \( \Sigma \alpha(E) \), correctly, when evaluated against CCSD, was compared in this study.
The species selected were $\text{H}_2\text{E}=$CXY ($X, Y = \text{H, F, OH, NH}_2$ and SH). Thus, there are 15 silenes with a total of 26 different conformers and 15 stannenes with a total of 28 different conformers.

4.1. Different Methods and their Ability to Calculate the Structure of Silenes

Silenes follow the rule of CGMT theory mentioned earlier, and can thus have either planar or pyramidalized structure around the Si atom. This means that the accuracy by which a given computational methods can describe the singlet-triplet energy gaps of the interacting fragments and the SiC bond strength should correlate with the accuracy by which it describes the geometry of the corresponding silenes.

When probing the multiconfigurational character of the silenes through $T_1$ diagnostics, it was found that seven silenes with bond lengths in the range of 1.793 - 1.906 Å have multireference character. The silenes which are either the least or the most influenced by reverse polarization are not multireferent. Numerical CASPT2/ANO-RCC level optimizations were therefore carried out for the multireferent silenes, and the geometries of the silenes thus obtained did not deviate considerably from the MP2 geometries.

The CASSCF calculations indicated that the $(\pi^2 \pi^\ast)^2$ configuration was important for the multireference character of the silenes. One could therefore argue that a correlation could exist between the $T_1$ diagnostic values and the HOMO-LUMO gaps at the CCSD geometries. No such correlation was found, however. Some weak correlation existed for the stannenes. ($r^2 = 0.577$ for linear correlation).

At the CCSD/cc-pVTZ level of theory, the silene Si=C bond lengths are in the range of 1.702-1.946 Å. Based on a bond length criteria, twelve of the 26 silene conformers were found to be naturally polarized with bond lengths between 1.70-1.80 Å while four were found to be highly influenced by reverse polarization with bond lengths between 1.85-1.95 Å. The remaining silene conformers have bond lengths in between these intervals and these are expected to be most difficult to describe. In this analysis, the ability of a particular method to distribute the silene conformers among the different intervals was probed to evaluate its performance.

Both the (maximum deviation) MAX and the mean absolute deviation (MAD) values for silenes are larger at the HF/cc-pVTZ level than at any other of the investigated levels of theory (Table 1). The bond lengths at HF level are shorter for the naturally polarized silenes and longer for those influenced by reverse polarization. This is in line with the tendency of HF
theory to exaggerate bond polarization. The gap between the reverse polarized and naturally polarized silenes are slightly larger at the HF level than at the CCSD level.

Table 1. The MAD and MAX values for r(SiC) and Σα(Si) for the different methods studied here compared to the corresponding value at the CCSD/cc-pVTZ level.

<table>
<thead>
<tr>
<th>Method</th>
<th>MAD  (MAX) for r(SiC)</th>
<th>MAD  (MAX) for Σα(Si)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF/cc-pVTZ</td>
<td>0.051 (+0.178)</td>
<td>11.4 (-60.0)</td>
</tr>
<tr>
<td>MP2/cc-pVTZ</td>
<td>0.022 (-0.114)</td>
<td>7.3 (+41.2)</td>
</tr>
<tr>
<td>MP2/6-31G(d)</td>
<td>0.021 (-0.103)</td>
<td>5.8 (+35.6)</td>
</tr>
<tr>
<td>MP3/cc-pVTZ</td>
<td>0.008 (+0.038)</td>
<td>1.7 (+7.8)</td>
</tr>
<tr>
<td>MP4(SDQ)/cc-pVTZ</td>
<td>0.004 (+0.012)</td>
<td>1.2 (-5.8)</td>
</tr>
<tr>
<td>B3LYP/cc-pVTZ</td>
<td>0.017 (+0.052)</td>
<td>7.4 (-26.4)</td>
</tr>
<tr>
<td>B3LYP/6-311G(d,p)</td>
<td>0.016 (+0.055)</td>
<td>7.6 (-27.2)</td>
</tr>
<tr>
<td>B3LYP/6-31G(d)</td>
<td>0.019 (+0.064)</td>
<td>9.2 (-31.5)</td>
</tr>
<tr>
<td>BLYP/cc-pVTZ</td>
<td>0.033 (+0.084)</td>
<td>11.8 (-35.0)</td>
</tr>
<tr>
<td>PBE0/cc-pVTZ</td>
<td>0.016 (+0.046)</td>
<td>6.2 (-24.8)</td>
</tr>
<tr>
<td>BHHLYP/cc-pVTZ</td>
<td>0.016 (+0.041)</td>
<td>4.2 (-21.7)</td>
</tr>
</tbody>
</table>

*aΣα(Si) = Sum of valence angles around Si. Bond length differences in Å and angle differences in degrees.

While MP3 and MP4 are too time-consuming for calculating the large silenes synthesized and studied experimentally, MP2 is considered as inexpensive. The accuracy of the methods for describing the geometry and the properties of the silenes investigated increase in the expected order MP2, MP3 and MP4. The MAD at the MP2 level is reduced by 50 % for the silenes and the largest change in bond lengths is moderately reduced, in line with the fact that MP2 usually overcorrects the deficiency of the HF method. For naturally polarized silenes, MP2/cc-pVTZ gives very accurate results. However, while CCSD/cc-pVTZ places 18 silenes in this category, 21 silenes are naturally polarized at the MP2/cc-pVTZ level of theory. This trend is even more pronounced for stannenes. Seven stannenes have SnC bonds longer than 2.35 Å at the CCSD/cc-pVTZ(SDB) level of theory while none of the stannenes have bond lengths above this value at the MP2/cc-pVTZ(SDB) level of theory. For the stannenes, MP2 tend to sort them into one category with SnC bond lengths between 1.972 - 2.085 Å and another with SnC bond lengths in between 2.242 – 2.349 Å. This means that MP2 underestimates reverse E=C bond polarization and is particularly bad for reverse polarized silenes and stannenes. Replacing the cc-pVTZ with the 6-31G(d) basis set for silenes leads to some improvement which should be due to error cancellation.

For both silenes and stannenes, the hybrid DFT methods reproduce the CCSD geometries better than pure DFT methods in line with the finding that hybrid DFT methods are better than GGA methods for describing bond
length alternations of conjugated systems. For example, the hybrid functional B3LYP has a lower MAD deviation when compared to MP2, while the GGA functional BLYP has a higher MAD value than MP2. The bond lengths of the silenes at the B3LYP/cc-pVTZ level of theory is a little too long, as only thirteen silenes are naturally polarized at this level while six silenes are placed in the bond length interval between naturally and reverse polarized versus four at the CCSD/cc-pVTZ level of theory. PBE0 also places too few silenes in the naturally polarized category. However, the average bond length is the same as it is at the CCSD/cc-pVTZ level of theory, while it is longer by 0.006 Å at the B3LYP/cc-pVTZ level of theory. BHHLYP gives results close to the CCSD results, except that the average SiC bond length is too short. At the BLYP/cc-pVTZ level of theory, it is too long instead. While reducing the basis set from triple-zeta to double-zeta quality at the B3LYP level results in less accurate geometries, the performance is still better than at the MP2/cc-pVTZ level.

![Graph](image)

**Figure 2:** Comparison between the ability of MP2 and B3LYP when compared against CCSD(T)//CCSD to describe $\Sigma \Delta E_{ST}$ of the silenes correctly. Calculations with the cc-pVTZ basis set.
The better performance of B3LYP compared to MP2 in describing the geometry of silenes is reflected in their ability to describe the singlet-triplet gaps of the interacting carbene and silylene fragments correctly. It is found that MP2 always underestimate the sum of singlet-triplet gaps ($\Sigma \Delta E_{ST}$) for these fragments, while B3LYP is much closer to the CCSD(T)//CCSD results (Figure 2). This is in line with the tendency of MP2 to underestimate the extent of reverse polarization since CGMT theory states that silenes with lower values of $\Sigma \Delta E_{ST}$ also will have a lower degree of pyramidalization at Si, and thus be less influenced by reverse polarization. It is interesting to see that B3LYP performs worst for silenes which are in between naturally and reverse polarized as expected due to the partial multi-configurational character of these silenes.

When discussing pyramidalization we define that a silene is pyramidal if $\Sigma \alpha(Si) \leq 355^\circ$ and that it has an acute pyramidalization angle if $\Sigma \alpha(Si) \leq 320^\circ$. At the CCSD/cc-pVTZ level 15 silenes are pyramidal and of these 8 have acute pyramidalizations. The most pyramidal silene was H$_2$Si=CH$_2$ with a pyramidalization angle of 282.2°.

At the HF/cc-pVTZ level, all silenes are either planar or have acute pyramidalization angles. The number of bent silenes are only 13, compared to 15 at the CCSD level. This is in contrast to the stannenes where only one compound is planar at both the CCSD/cc-pVTZ(SDB) and the HF/cc-pVTZ(SDB) levels. While 18 of these have pyramidalization angles below 300° at the CCSD level of theory as many as 25 are that pyramidalized at the HF level. The MAD and MAX deviations are large.

The number of pyramidal silenes are the same at the MP2/cc-pVTZ and CCSD/cc-pVTZ levels of theory. However only four have acute pyramidalization angles at MP2 level versus eight at the CCSD level. The MAD and MAX deviations both decrease at the MP3 level compared to MP2, and these deviations are close to zero at the MP4(SDQ) level.

While BHHLYP tend to make the silenes either more planar or more pyramidal in analogy with HF, at the BLYP level the number of pyramidalized silenes are 21 vs. 15 at the CCSD level of theory and 12 of these have acute pyramidalization angles. Best is B3LYP according to which 16 are pyramidal and eight of these have acute pyramidalizations. The accuracies of both MP2 and the DFT methods investigated were found to be not basis set dependent.

### 4.2 Conclusions

For the majority of silenes, single-reference methods are sufficient to describe their geometry. Seven silenes in between naturally and reverse polarized had multireference character. However, this multireference does not
affect their geometry to any significant extent. It is also for the silenes in this group that the different methods give the largest variation. While HF exaggerates reverse polarization for the most reverse polarized silenes and exaggerates natural polarization for the most naturally polarized silenes, MP2 describe naturally polarized silenes reasonably well. However, MP2 results underestimate the influence of reverse polarization due to its tendency to overcorrect the HF results. Hybrid DFT methods like B3LYP, on the other hand, is best for reverse polarized silenes in contrast to MP2 which is better for naturally polarized silenes. As this thesis deals mostly with reverse polarized silenes, B3LYP will be used here.
5. The Effect of Reverse Polarization on the Structure and Stability of Heavy Alkene, Imine and Ketone analogs

So far, this thesis has focused mainly on silenes. However, most heavy alkenes other than silenes are also unstable with respect to dimerization or oligomerization. Besides silenes, phosphaalkenes are the only heavy alkenes that have been analyzed in terms of reverse polarization. According to a study by Markovskii et al., there are fundamental reactivity differences between reverse polarized phosphaalkenes, \( \text{RP} = \text{C(NMe}_2\text{)}_2 \), \( \text{R} = \text{H, TMS, alkyl, and aryl} \), and naturally polarized phosphaalkenes. For example, while the former have a nucleophilic P atom, the latter have a nucleophilic C atom. It should be noted that, in this thesis the term reverse polarization will be used although Markovskii et al. used the term inverse polarization for the same property.

The formally E=C double bonded compounds shown below (Scheme 9) will be investigated in the contexts of reverse polarization. It will be concluded that reverse polarization plays a fundamental role in determining both the geometry and reactivity of all these heavy alkene analogs. For each different E, a total of ten compounds were investigated, each corresponding to the minimum conformer of each species.

\[
\text{H}_m\text{E} = \begin{array}{l}
\text{A} = \text{H E8, SH E9, OH E10, NH}_2\text{ E11} \\
\text{B} = \text{H a, SH b, OH c, NH}_2\text{ d} \\
\text{m = 2; E = Si, Ge or Sn} \\
\text{m = 1; E = Pb, As or Sb} \\
\text{m = 0; E = S, Se or Te}
\end{array}
\]

Scheme 9

If we can find heavy alkenes that are stable with respect to both dimerization and reaction with water and that also react selectively, it is possible that these species can be used as novel reagents in organic reaction schemes. In this study, the effect of reverse polarization on thermodynamic stability to-
wards both head-to-head and head-to-tail dimerization of heavy alkenes will be examined as well as the kinetic and thermodynamic stability towards water addition. Before doing that, however, we will discuss how the E=C bond length, the pyramidalization angle around E, and the charge difference between C and E, $\Delta q(C=E)$, depend on the degree of reverse polarization.

The extent of reverse polarization, as measured by the total contribution from resonance structures $\Phi_{II}$ and $\Phi_{III}$ (Scheme 10), in the heavy alkenes investigated encompasses a very large range from zero percent in each parent species to 89.7 % in the 2,2-diaminosubstituted stannenes. When going down a group, it was found that the degree of reverse polarization increases and this trend is most pronounced for the diaminosubstituted species. When changing E from Si to Sn, the extent of reverse polarization increases from 70 % to 90 %, when changing E from P to As, it goes from 42 % to 56 %, and finally, when changing E from S to Te, it increases from 49 % to 62 %. This is most probably due to the higher polarizability of the heavier elements, causing easier mixing between the $\pi^-$ and $\sigma^*$-orbitals of the E=C bond as has been shown for silenes (see chapter 2).

![Scheme 10](image)

5.1 Effect of Reverse Polarization on Heavy Alkene Geometries and Charge Distribution

As expected, it is found that formally E=C double bonded species with a higher degree of reverse polarization have longer E=C bonds and a higher degree of pyramidalization around the E atom for Si$^8$ – 11, Ge$^8$ – 11, and Sn$^8$ – 11. The correlation coefficients, $r^2$, for the linear correlation between the E=C bond length and the extent of reverse polarization is in the range of 0.72 - 0.98 in all cases (Table 2). As the SOJT mixing between the $\pi^-$ and $\sigma^*$-orbitals of the E=C bond is increased, the E atom becomes more anionic, as has been shown earlier in the case for silenes (see chapter 2), and thus, this mixing becomes a driving force for pyramidalization. As the $\sigma^*$-orbital of the E=C bond becomes more populated, the E=C bond also lengthens. Both these effects increase when going down a group due to the increased polarizability of the element E.
Table 2. **Correlation coefficients for correlation between Φ_{II} + Φ_{III}^{a} and geometric parameters.**

<table>
<thead>
<tr>
<th>Group of species</th>
<th>Range in Φ_{II} + Φ_{III}^{d}</th>
<th>r(E=C) vs. Φ_{II} + Φ_{III}</th>
<th>Σα(E) vs. Φ_{II} + Φ_{III}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si8-11</td>
<td>0 – 69.9</td>
<td>0.921</td>
<td>2.96</td>
</tr>
<tr>
<td>Ge8-11</td>
<td>0 – 85.6</td>
<td>0.978</td>
<td>3.48</td>
</tr>
<tr>
<td>Sn8-11</td>
<td>0 – 89.7</td>
<td>0.981</td>
<td>3.85</td>
</tr>
<tr>
<td>P8-11</td>
<td>0 – 33.2</td>
<td>0.742</td>
<td>1.92</td>
</tr>
<tr>
<td>As8-11</td>
<td>0 – 40.6</td>
<td>0.717</td>
<td>2.02</td>
</tr>
<tr>
<td>Sb8-11</td>
<td>0 – 47.3</td>
<td>0.864</td>
<td>2.56</td>
</tr>
<tr>
<td>S8-11</td>
<td>0 – 44.6</td>
<td>0.758</td>
<td>1.28</td>
</tr>
<tr>
<td>Se8-11</td>
<td>0 – 51.4</td>
<td>0.850</td>
<td>1.76</td>
</tr>
<tr>
<td>Te8-11</td>
<td>0 – 62.5</td>
<td>0.860</td>
<td>2.09</td>
</tr>
</tbody>
</table>

^{a}Φ_{II} + Φ_{III} = extent of reverse polarization in percentage as determined by NRT at B3LYP/6-31G(d). ^{b} in Å/%. ^{c} in deg/%. ^{d} in %.

When studying the dependence of Δq(C=E) on the degree of reverse polarization, moderate or good linear correlations are found only for Si8 – 11, Ge8 – 11, and Sn8 - 11 (Table 3). The correlation is worst for the heavy ketone analogs. When going from Si8 to Sn8, Δq(C=E) is lowered from -0.1 e to -0.28 e, the negative end being on C. This is in line with both theoretical and experimental findings relating to the reactivity of silenes and germenes towards nucleophiles.34,2a,59 For the thio-, seleno- and telluroketones, the negative end is on the E atom. The reason for the gradually worsened correlation between Δq(C=E) and the degree of reverse polarization as one goes to the right in the periodic table could possibly be the gradually smaller electronegativity differences between the E and C atoms. This should cause the effect to disappear among other effects.

Table 3. **Correlation coefficients for correlation between percentage contribution of reverse polarization and the charge difference between C and E.**

<table>
<thead>
<tr>
<th>Group of species</th>
<th>Δq(C=E) vs. Φ_{II} + Φ_{III}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>r$^2$</td>
</tr>
<tr>
<td>Si8-11</td>
<td>0.651</td>
</tr>
<tr>
<td>Ge8-11</td>
<td>0.721</td>
</tr>
<tr>
<td>Sn8-11</td>
<td>0.722</td>
</tr>
<tr>
<td>P8-11</td>
<td>0.271</td>
</tr>
<tr>
<td>As8-11</td>
<td>0.307</td>
</tr>
<tr>
<td>Sb8-11</td>
<td>0.536</td>
</tr>
<tr>
<td>S8-11</td>
<td>0.179</td>
</tr>
<tr>
<td>Se8-11</td>
<td>0.233</td>
</tr>
<tr>
<td>Te8-11</td>
<td>0.170</td>
</tr>
</tbody>
</table>

^{a} in e/%. 
5.2. Effect of Reverse Polarization on the Thermodynamic Stability Towards Dimerization

To investigate the effect of reverse polarization on the dimerization energies for heavy alkenes, the contribution of reverse polarization was plotted against the dimerization energies for both head-to-head and head-to-tail dimerizations, which we designate $\Delta E_{\text{hth-dim}}$ and $\Delta E_{\text{htt-dim}}$, respectively. It is important that no intramolecular hydrogen bonds are present in the dimer because differences in hydrogen bond strengths between the different heavy elements could otherwise influence the results. Thus, the lowest conformer which obeyed this criterion was chosen in each case. The resulting graphs are shown in Figure 3 for stannenes and similarly good linear correlation are found for the other heavy alkenes (Table 4).

Table 4. Correlation coefficients for the correlation between $\Phi_{II} + \Phi_{III}$ and $\Delta E_{x\text{-dim}}$ ($X = \text{htt or hth}$) and the range for $\Delta E_{x\text{-dim}}$

<table>
<thead>
<tr>
<th>Group of species</th>
<th>$\Delta E_{\text{hth-dim}}$ $a$ vs. $\Phi_{II} + \Phi_{III}$</th>
<th>Range $d$</th>
<th>$\Delta E_{\text{htt-dim}}$ $b$ vs. $\Phi_{II} + \Phi_{III}$</th>
<th>Range $d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si8-11</td>
<td>0.815 0.616 -67.4 - (-13.9) 0.837 0.649 -81.7 - (-24.7)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ge8-11</td>
<td>0.799 0.649 -69.1 - (-0.3) 0.891 0.712 -71.2 - 0.4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sn8-11</td>
<td>0.799 0.651 -82.2 - 16.2 0.811 0.915 -80.5 - 22.9</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P8-11</td>
<td>0.902 1.314 -40.1 - 15.3 0.939 1.335 -36.5 - 9.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>As8-11</td>
<td>0.955 1.215 -47.3 - 12.5 0.988 1.235 -38.3 - 18.7</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sb8-11</td>
<td>0.902 1.189 -60.2 - 6.8 0.924 1.255 -47.6 - 20.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S8-11</td>
<td>0.651 1.455 -28.7 - 45.8 0.724 1.196 -27.0 - 35.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Se8-11</td>
<td>0.921 1.745 -40.8 - 47.8 0.895 1.289 -30.4 - 38.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Te8-11</td>
<td>0.945 1.617 -55.3 - 39.8 0.971 1.589 -41.2 - 59.2</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$$\Delta E_{\text{hth-dim}}$ = head-to-head dimerization energy in kcal/mol. $^b$$\Delta E_{\text{htt-dim}}$ = head-to-tail dimerization energy in kcal/mol. $^c$k is in kcal/(mol%).

**Figure 3:** Relationships between $\Phi_{II} + \Phi_{III}$ and $\Delta E_{x\text{-dim}}$ ($X = \text{htt or hth}$) for $E = \text{Sn}$. 
A higher degree of reverse polarization causes both head-to-head and head-to-tail dimerization to become increasingly less exothermic for all heavy alkenes investigated (Table 4). The dimerization of the species highly influenced by reverse polarization in each type of heavy E=C double bonded compound, such as the diaminosubstituted species are even endothermic.

This means that computational support has been presented here for the conclusion that reverse polarization is a generally important electronic feature for stabilizing all types of main group heavy alkenes, imines and ketones toward dimerization. These results are in line with earlier experimental and computational findings on silenes,\textsuperscript{17} as well as findings on phosphaalkenes.\textsuperscript{54} In addition of introducing $\pi$-donating groups at the C atom of the heavy alkenes, an even higher degree of reverse polarization can be achieved by adding $\sigma$-donating groups to the E atom as has been shown for silenes.\textsuperscript{60}

It is interesting to see that the slope of the plots increases as one goes down a group and to the right in the $p$-block in the periodic table. The dimerization energies of the selenoketones and telluroketones are the most sensitive to the effect of reverse polarization among all formally E=C double bonded compounds investigated here. That is, reverse polarization is even more important for stabilizing these compounds than for stabilizing for example silenes.

5.3. Effect of Reverse Polarization on Kinetic and Thermodynamic Stability of Heavy Alkenes toward Addition of Water

Naturally polarized silenes react readily with alcohols according to a well known mechanism.\textsuperscript{2a} Since these silenes are highly polarized with the negative end on carbon, the reaction is very regiospecific. A $\sigma$-bonded complex is formed and the reaction proceeds by a unimolecular or bimolecular proton transfer from the O atom to the C atom. Recently, evidence has been found that this complex may not form during the reaction and such a complex was non-existent according to our calculations.\textsuperscript{61} Bendikov and co-workers also showed in a kinetic experiment that a hydrogen-bonded dimer of alcohol molecules was present in the TS for alcohol addition to silenes.\textsuperscript{61} However, the study indicated that the activation energy for this addition increased as the degree of reverse SiC bond polarization increased. In the present study, a single water molecule will be used to model a nucleophile. If a hydrogen-bonded dimer of water molecules were used instead in the calculations, this simply amount to a change of nucleophile and the trends shown in this chapter will presumably still hold.
Since we emphasize general trends in this chapter, we only computed the activation energy for the heavy alkenes representing three of the four corners of the rectangle formed by the elements E in the periodic table. Thiocarbonyl compounds were not calculated since nothing in the literature indicates that they react with water.

When our formal E=C double bonded compound reacts with water, two possible adducts could form, namely \(H_2(OH)E-CHR_2\) or \(H_3E-C(OH)R_2\). Both these have been included in our calculations. The correlation coefficients for the correlation between the degree of reverse polarization influence and both the reaction energy and the activation energy for Si8-11, Sn8-11 and Te8-11 for the C-hydroxylated products can be found in Table 5, together with the slope of the corresponding plots and the range of the reaction and activation energies.

Table 5. Correlation coefficients for the correlation between \(\Phi_{II} + \Phi_{III}\) and both \(\Delta E_{H_2O(C)}^a\) as well as \(\Delta E_{H_2O(C)}^b\) and the ranges for \(\Delta E_{H_2O(C)}^a\) and \(\Delta E_{H_2O(C)}^b\).

<table>
<thead>
<tr>
<th>Group of species</th>
<th>(\Delta E_{H_2O(C)}^a)</th>
<th>Range (\Delta E_{H_2O(C)}^a)</th>
<th>(\Delta E_{H_2O(C)}^b) vs. (\Phi_{II} + \Phi_{III})</th>
<th>Range (\Delta E_{H_2O(C)}^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si8-11</td>
<td>0.003</td>
<td>-9</td>
<td>-41.7 - (-29.1)</td>
<td>0.005</td>
</tr>
<tr>
<td>Ge8-11</td>
<td>0.482</td>
<td>172</td>
<td>-36.1 - (-10.8)</td>
<td>0.742</td>
</tr>
<tr>
<td>Sn8-11</td>
<td>0.659</td>
<td>272</td>
<td>-32.4 - 1.2</td>
<td>0.835</td>
</tr>
<tr>
<td>P8-11</td>
<td>0.683</td>
<td>363</td>
<td>-17.8 - (-3.3)</td>
<td>0.935</td>
</tr>
<tr>
<td>As8-11</td>
<td>0.717</td>
<td>341</td>
<td>-15.5 - 0.1</td>
<td>0.962</td>
</tr>
<tr>
<td>Sb8-11</td>
<td>0.645</td>
<td>304</td>
<td>-17.0 - 1.1</td>
<td>0.976</td>
</tr>
<tr>
<td>S8-11</td>
<td>0.828</td>
<td>660</td>
<td>-20.1 - 14.3</td>
<td>0.976</td>
</tr>
<tr>
<td>Se8-11</td>
<td>0.935</td>
<td>594</td>
<td>-18.1 - 13.3</td>
<td>0.976</td>
</tr>
<tr>
<td>Te8-11</td>
<td>0.962</td>
<td>539</td>
<td>-19.2 - 13.5</td>
<td>0.976</td>
</tr>
</tbody>
</table>

The relevant plots of the reaction energies for Sn8 - 11 are shown below (Figure 4). Increased influence by reverse polarization causes the reaction to become increasingly less exothermic, and raises the activation energies for water addition to the C atom for Sn8 – 11 and Te8 – 11. For the heavy ketone analogs, which are highly influenced by reverse polarization, it is even endothermic. The lack of correlation for the reaction energies for silenes and germines is presumably caused by the relatively low spread in these values. It can also be seen in Table 4 that the activation energies for water addition to C are relatively high the silenes, indicating that these do not react with water to form C-hydroxylated products. For the telluroketones, the activation energies increase with increasing influence of reverse polarization and the
correlation is good. Similarly good correlation is expected for the thioke-tones and selenoketones.

![Figure 4: Plots showing the relationship between $\Phi_{II} + \Phi_{III}$ and $\Delta E_{H2O(C)}$ as well as $\Delta E_{H2O(Sn)}$.](image)

The plots of the activation energies for Sn8-11 can be found in Figure 5. Note that the only conclusion that can be drawn here is that species heavily influenced by reverse polarization are more stable towards the type of water addition reaction studied here. If another mechanism for water addition is operative, these species may still react readily with water. This could be the case for the thioketones and telluroketones whose chemistry most probably resembles that of carbonyl compounds rather than that of silenes. Still, it can be concluded that Apeloig and Karni’s findings on the dependence of reverse polarization on the addition of nucleophiles to silenes can be extended to other heavy alkenes as well.

The correlation coefficients and slope of the corresponding plots for the correlation between $\Phi_{II} + \Phi_{III}$ on $\Delta E_{H2O(E)}$ and $\Delta E'_{H2O(E)}$ can be found in Table 6 along with the ranges in the activation energies for Si8-11, Sn8-11 and Te8-11.
Table 6. Correlation coefficients for the correlation between $\Phi_{II} + \Phi_{III}$ and both $\Delta E_{H2O(E)}$ as well as $\Delta E_{H2O(Si)}^t$ and ranges for $\Delta E_{H2O(E)}$ and $\Delta E_{H2O(Si)}^t$.

<table>
<thead>
<tr>
<th>Group of species</th>
<th>$\Delta E_{H2O(E)}$ a vs. $\phi_{II} + \phi_{III}$ Range $\Delta E_{H2O(Si)}$</th>
<th>$\Delta E_{H2O(E)}^b$ b vs. $\phi_{II} + \phi_{III}$ Range $\Delta E_{H2O(Si)}^t$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si8-11</td>
<td>$r^2$ 0.488 $k^c*10^{-3}$ $[-77.5 - (-51.5)]$</td>
<td>$r^2$ 0.640 $k^c$ $[-11.2 - 22.6]$</td>
</tr>
<tr>
<td>Ge8-11</td>
<td>$r^2$ 0.860 $k^c$ $[-62.6 - (-27.2)]$</td>
<td>$r^2$ 0.817 $k^c$ $[-6.5 – 15.2]$</td>
</tr>
<tr>
<td>Sn8-11</td>
<td>$r^2$ 0.824 $k^c$ $[-67.5 - (-17.5)]$</td>
<td>$r^2$ 0.817 $k^c$ $[-6.5 – 15.2]$</td>
</tr>
<tr>
<td>P8-11</td>
<td>$r^2$ 0.858 $k^c$ $[-38.0 - (-9.9)]$</td>
<td>$r^2$ 0.817 $k^c$ $[-6.5 – 15.2]$</td>
</tr>
<tr>
<td>As8-11</td>
<td>$r^2$ 0.919 $k^c$ $[-33.4 - (-3.0)]$</td>
<td>$r^2$ 0.817 $k^c$ $[-6.5 – 15.2]$</td>
</tr>
<tr>
<td>Sb8-11</td>
<td>$r^2$ 0.844 $k^c$ $[-41.2 - (-8.2)]$</td>
<td>$r^2$ 0.817 $k^c$ $[-6.5 – 15.2]$</td>
</tr>
<tr>
<td>S8-11</td>
<td>$r^2$ 0.809 $k^c$ $[-12.7 - 28.2]$</td>
<td>$r^2$ 0.817 $k^c$ $[-6.5 – 15.2]$</td>
</tr>
<tr>
<td>Se8-11</td>
<td>$r^2$ 0.951 $k^c$ $[-15.8 – 27.2]$</td>
<td>$r^2$ 0.817 $k^c$ $[-6.5 – 15.2]$</td>
</tr>
<tr>
<td>Te8-11</td>
<td>$r^2$ 0.925 $k^c$ $[-27.5 – 15.1]$</td>
<td>$r^2$ 0.817 $k^c$ $[-6.5 – 15.2]$</td>
</tr>
</tbody>
</table>

$^a\Delta E_{H2O(E)} =$ reaction energy in kcal/mol for the addition of water to the heavy alkene leading to the E-hydroxylated product. $^b\Delta E_{H2O(E)}^t =$ activation energy in kcal/mol for addition of water to the heavy alkene leading to the E-hydroxylated product. $^ck$ is in kcal/(mol%).

Moreover, it is assumed that a linear correlation between reverse polarization and the properties studied exists, and there is no physical argument for neither a linear, quadratic nor exponential correlation. Other types of correlation may operate instead.

During the calculation of the reactions with water, it was found that the stannenes with one or two amino substituents as well as the dihydroxy substituted stannene dissociate instead of forming adducts. This is in line with Grützmacher’s description of the azastannallene $R_2Sn=C=NMes$ ($R = 2,4,6-(CF_3)_3C_6H_2$) as a weak carbene-stannylene $\pi$-complex. The Sn=C bond
length was found to be 2.397 Å. The authors found that it formed R₂Sn(Ot-Bu)₂ and :C=NMes upon reaction with tert-butanol, i.e. the products to be expected upon dissociation of the formal double bond.⁶² The bond length of the most reverse polarized stannenes were 2.322 - 2.328 Å, significantly longer than normal SnC single bonds of 2.13 - 2.20 Å.⁶³ This indicates that also these stannenes could be described as a weak π-complex between a carbene and a stannylene.

It can finally be concluded that reverse polarization is very important for stabilizing heavy alkenes towards both modes of dimerization and towards addition of nucleophiles. An increased degree of reverse polarization influence can be realized through introduction of π-donating substituents at the C atom and further by introducing σ-donating substituents at the E atom. The dimerization reactions can be made even more endothermic by exchanging OH or NH₂ for the even bulkier OMe or NMe₂. Another important conclusion is that the reactivity of the selenoketones and the telluroketones are the most sensitive to reverse polarization. The selenoketones, telluroketones, and stannenes most influenced by reverse polarization will dissociate upon water addition due to their weak formal E=C bond. The species with a degree of reverse polarization influence of around 80% appear to be the most stable towards water. The same goes for the arsaalkenes and stibaalkenes. In the reminder of this thesis, the formation of reverse polarized silenes will be discussed as well as the effect of reverse polarization on the stability of substituted siladienes.
6. The Effect of Substituents and Counterions on the Geometry and Electronic Properties of Silenolates

It is noteworthy that none of the silenes studied in the previous chapter were found to have a degree of $\pi$-conjugative reverse polarization above 70% according to NRT. In order to find such SiC double bonded species, more strongly $\pi$-donating groups than NMe$_2$ are needed. Silen-2-olates have a negatively charged oxygen bound to the C atom and thus satisfy this criterion. Unfortunately, their chemistry are not known equally well as the rich chemistry of enolates.\(^{64}\)

The formation of lithium silenolates was first observed by Biltueva, Bravo-Zhivotovskii and co-workers in 1989.\(^{65}\) A few years later, in 1993, a further study was made by Bravo-Zhivotovskii and Apeloig. In the subsequent ten years, a few more reports by Bravo-Zhivotovskii, Apeloig, Ishikawa, and Ohshita were published.\(^{66}\) Lithium silenolates with bulky alkyl and aryl substituents were found to dimerize and undergo further reactions at room temperature. However, Ishikawa and Ohshita found that these could be characterized by NMR spectroscopy at low temperatures.

Potassium silenolates are significantly more stable than lithium silenolates, as found by Ottosson and co-workers, who characterized the first isolable silenolates, [TMS$_2$SiC(=O)Bu]K([18]-crown-6) by X-ray crystallography.\(^{67}\) This silenolate did not degrade when stored in an inert atmosphere at room temperature for three months, but decomposed instantly when exposed to air. The potassium ion is coordinated to both the O and the Si atom and the O-K distance was a bit shorter than the Si-K distance. The long SiC bond length of 1.926 Å and the small pyramidalization angle (317.8°) showed that this silene was strongly influenced by reverse polarization.

In 2003, Ottosson also calculated a large number of silene and uncoordinated silenolates including the parent silen-2-olate at the B3LYP level and found that these were best described as acyl substituted silylanions.\(^{31}\) This could be explained in terms of the $\pi$-contribution to reverse SiC bond polarization. If we take the parent silenolate as an example, resonance structure $\phi_B$ dominates the electronic structure as shown in Ottosson's study (Scheme 11).
Scheme 11

Group A (Z = H):
Y = SiH$_3$ 12, TMS 13, H 14, tBu 15, Me 16, OMe 17, NMe$_2$ 18

Group B (Y = H):
Z = TMS 19, Me 20, Ph 21, H 22, SiH$_3$ 23, F 24

\[ M^1 = : ; M^2 = : \text{a (}: = \text{lone pair)} \]
\[ M^1 = : ; M^2 = \text{Li b} \]
\[ M^1 = \text{Li} ; M^2 = : \text{c} \]
\[ M^1 = : ; M^2 = \text{MgCl d} \]
\[ M^1 = \text{MgCl} ; M^2 = : \text{e} \]
\[ M^1 = \text{K} M^2 = : \text{f} \]

Group C:
Y = tBu; Z = Me 25, TMS 26
Y = OMe 27, NMe$_2$ 28; Z = TMS

Scheme 12

For lithium silenolates, Ishikawa, Ohshita and co-workers found, using variable temperature $^1$H-NMR spectroscopy, indication of partial double bond character for the central SiC bond in the [TMS$_2$SiC(=O)Mes]Li silenolate.$^{66b}$ The authors suggested an activation energy of 14.3 kcal/mol for the SiC bond rotation. In order to bring some clarity to these marked differences
between lithium and potassium silenolates, a number of lithium, potassium and magnesium silenolates will be compared with regard to differences in geometry and electronic properties. For the lithium and magnesium silenolates, two isomers will be discussed, one where the metal ion is coordinated to the O atom and one where it is coordinated to the Si atom. For the potassium silenolates, these two collapse into one structure where the potassium ion is coordinated to both atoms. Before starting, two groups of free silenolates, one group within which the substituent at C will be changed and one group within which the substituents at Si will be changed, will be analyzed with regard to the effect of reverse polarization on their geometry and charge distribution. Thus, three distinct groups of silenolates will be discussed (Scheme 12).

6.1 Analysis of the Uncoordinated Silenolates

The group A silenolates showed the same excellent linear correlation between the total contribution from reverse polarized resonance structures, \( \Sigma \phi_B \), and both the SiC bond length, \( r(\text{SiC}) \) \( (r^2 = 0.854) \) and the pyramidalization angle around Si, \( \Sigma \text{Si} \), \( (r^2 = 0.945) \) as the silenes studied in chapter 5 did. The correlation between \( \Sigma \phi_{RP} \) and \( \Delta q(\text{CSi}) \) was also excellent \( (r^2 = 0.918) \).

The main difference between the silenolates and the silenes mentioned in chapter 5 was that the silenolates were generally more influenced by reverse SiC bond polarization \( (86.6 - 94.3 \%) \). The SiC bond length ranged from 1.912 to 1.984 Å, that is longer than a typical SiC single bond \( (1.87 \text{ Å}^{68}) \) and the more influenced by reverse polarization a silenolate was, the longer was \( r(\text{SiC}) \). The pyramidalization angle around Si ranged from 287.3 to 293.4° and \( \Delta q(\text{CSi}) \) ranged from -0.40 to 0.45 e. These geometric data support that these species could be treated as acyl substituted silyl anions and that resonance structures \( \phi_B \) and \( \phi_C \) dominate their electronic structure. While 18, with a strongly \( \pi \)-donating \( \text{NMe}_2 \) group at C, had the highest value of \( \Sigma \phi_{RP} \), the longest \( r(\text{SiC}) \) and the smallest value of \( \Sigma \text{Si} \), the opposite applied for 12, which had a slightly \( \pi \)-accepting group at C. The trend seen was also that the more influenced by reverse polarization a group A silenolates was, the higher its \( \Delta q(\text{CSi}) \).

For the group B silenolates, the substituents at Si were varied instead of the substituent at C. Since the \( \pi \)-component of reverse polarization mainly determines the \( \pi \)-component of the total charge at Si, and since the \( \sigma \)-component of the charge at Si is mainly determined by the inductively donating/withdrawing ability of the substituents at Si, the correlation between \( \Sigma \phi_{RP} \) and both \( \Sigma \text{Si} \) \( (r^2 = 0.506) \) and especially \( \Delta q(\text{CSi}) \) \( (r^2 = 0.362) \) were much poorer than for the group A silenolates. The correlation between \( \Sigma \phi_{RP} \)
and \( r(\text{SiC}) \) was still excellent, however \( (r^2 = 0.903) \). Even though the substitute at C was not changed, \( \Sigma \phi_{\text{RP}} \) nevertheless ranged from 88.9 – 95.9 %. This could be because electronegative substituents tend to stabilize resonance structures of type \( \phi_B \) by stabilizing the negative charge at Si. The SiC bond lengths ranged from 1.917 to 1.981 Å and \( \Sigma \text{Si} \) ranged from 293.8 to 306.5°. The group B silenolates with the lowest value of \( \Sigma \phi_{\text{RP}}, 19 \), had the shortest SiC bond length, while 24, which had the highest value of \( \Sigma \phi_{\text{RP}} \) had the longest.

The trend seen was that the more influenced by reverse polarization a group B silenolate is, the smaller is its pyramidalization angle around Si and the lower was its \( \Delta q(\text{Si}) \). The value of \( \Delta q(\text{Si}) \) ranged -1.06 to 0.15 e. It was interesting that the least reverse polarized group B silenolates was found to have the most reverse polarized charge differences. This is because \( q(\text{Si}) \) depends on the inductive effect and of the polarizability of the substituents at Si.

For the group C silenolates, \( \Sigma \phi_{\text{RP}} \) varied between 89.5 and 94.5 %, \( r(\text{SiC}) \) varied between 1.954 – 1.978 Å, and \( \Sigma \text{Si} \) varied between 298.7 and 312.6°. The degree of reverse polarization was found to correlate very modestly with both \( r(\text{SiC}) \) \( (r^2 = 0.544) \) and \( \Sigma \text{Si} \) \( (r^2 = 0.727) \). No correlation was observed between \( \phi_B \) and \( \Delta q(\text{SiC}) \) \( (r^2 = 0.321) \), as was the case for the group B silenolates.

### 6.2 Analysis of the Solvated Metal Silenolates

The group C silenolates were also coordinated to solvated lithium, magnesium and potassium counterions in order to assess the effect of the counterion on their geometries and charge distributions. It was found that adding more than three THF molecules to the lithium counterion caused one of them to leave during the geometry optimization. The corresponding number for the magnesium and potassium silenolates were four and five, respectively.

There are only two potassium silenolates that have been analyzed by X-ray crystallography so far. Both have been found by the Ottosson group and the first is 26f, but with a [18]-crown-6 ether instead of five THF molecules. The second is 28f, but with a piperidyl group instead of a dimethylamino group and without any solvent molecules. In both the two crystal structures and in our calculated structures, the potassium ion were coordinated to both the Si atom and the O atom with a somewhat closer contact to the O atom. The calculated of 26f reproduced the SiC bond length and \( \Sigma \text{Si} \) of the crystal structure very well (1.939 Å and 317.4° in 26f vs. 1.926 Å and 317.8° in the corresponding crystal structure). However, while the SiC bond length in 28f was calculated to be 1.992 Å, it was 1.933 Å in the corresponding crystal structure. The reason for this deviation could be the undercoordi-
nation of the potassium ion in the crystal structure causing stronger coordination between the potassium ion and the silenolate. Actually, \([\text{TMS}_2\text{SiC}(-\text{O})\text{pip}K]_n\) oligomers were present in the crystal.\(^{69}\)

The maximum change was only 0.10 Å in \(r(\text{SiC})\) (Table 1) and 40° in \(\Sigma \text{Si}\) (Table 7) when changing the solvated counterion from \(\text{Li(THF)}_3^+\) to \(\text{MgCl(THF)}_4^+\) or \(\text{K(THF)}_5^+\), or changing the coordination site between \(\text{O}\) and \(\text{Si}\). Changing the substituents at \(\text{Si}\) from methyl to TMS does not affect the SiC bond length.

When the solvated metal counterion is coordinated to the \(\text{O}\) atom of the silenolate, the inductively electron withdrawing ability of the oxygen is increased, leading to more influence from resonance structures of type \(\phi_A\). This leads in turn to more double-bond character for the central SiC bond and shorter SiC bond length when compared with the corresponding free silenolate. If, on the other hand, the solvated counterion is coordinated to the Si atom of the silenolates, the influence of resonance structures of type \(\phi_B\) increases instead since a negative charge at Si is stabilized by the metal counterion. This leads to longer SiC bond lengths when compared with the corresponding free silenolate. Both these effects are less pronounced for the silenolates with \(\pi\)-donor groups at \(\text{C}\) and the latter effect is even reversed in some cases.

Since the Mg-O and Mg-Si bonds have more covalent character than the Li-O and Li-Si bonds, respectively, both effects mentioned above are stronger for the magnesium silenolates. It is interesting to note that Brook’s silene which has \(M_2^2 = \text{TMS}\), \(i.\ e.\) a fully covalent M-O bond, has an even shorter SiC bond length than the magnesium silenolates.

Since the potassium ion is in slightly closer contact with the \(\text{O}\) atom than the \(\text{Si}\) atom of the silenolates, the SiC bond length is equally long or a bit shorter than in the corresponding free silenolates.

### Table 7: Bond lengths in Å for the lithium, magnesium and potassium silenolates studied.

<table>
<thead>
<tr>
<th>Silenolates</th>
<th>25</th>
<th>26</th>
<th>27 (Conformer 1)(^a)</th>
<th>27 (Conformer 2)(^a)</th>
<th>28</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>1.954</td>
<td>1.958</td>
<td>1.947</td>
<td>1.978</td>
<td>1.992</td>
</tr>
<tr>
<td>b</td>
<td>1.879</td>
<td>1.879</td>
<td>1.934</td>
<td>1.926</td>
<td>1.983</td>
</tr>
<tr>
<td>c</td>
<td>1.966</td>
<td>1.965</td>
<td>1.946</td>
<td>1.966</td>
<td>1.977</td>
</tr>
<tr>
<td>d</td>
<td>1.852</td>
<td>1.851</td>
<td>1.913</td>
<td>1.912</td>
<td>1.948</td>
</tr>
<tr>
<td>e</td>
<td>1.983</td>
<td>1.974</td>
<td>1.952</td>
<td>1.972</td>
<td>1.979</td>
</tr>
<tr>
<td>f</td>
<td>1.939</td>
<td>1.941</td>
<td>1.947</td>
<td>1.945</td>
<td>1.994</td>
</tr>
</tbody>
</table>

\(^a\) In conformer 1, the O-Me bond and the C=O bond is syn to each other, in conformer 2, the O-Me bond and the C=O bond is anti to each other.

The pyramidalization angle around Si increases for all solvated metal ion coordinated silenolates when compared with the corresponding free si-
lenolates (Table 8). For the silenolates where the counterion is coordinated to the O atom, this is in line with the shorter SiC bond length in these silenolates. Changing the substituents at Si from methyl to TMS causes the pyramidalization angle to increase due to the larger steric bulk of the TMS group when compared with a methyl group. The pyramidalization angle around Si is increased for the potassium silenolates when compared with the corresponding free silenolates.

Table 8: Pyramidalization around Si (ΣSi) for the lithium, magnesium and potassium silenolates studied.

<table>
<thead>
<tr>
<th>Silenolates</th>
<th>25 (Conformer 1)</th>
<th>26 (Conformer 1)</th>
<th>27 (Conformer 1)</th>
<th>27 (Conformer 2)</th>
<th>28 (Conformer 2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>312.6</td>
<td>300.2</td>
<td>302.1</td>
<td>298.7</td>
<td>296.3</td>
</tr>
<tr>
<td>b</td>
<td>333.2</td>
<td>322.7</td>
<td>308.2</td>
<td>311.9</td>
<td>317.5</td>
</tr>
<tr>
<td>c</td>
<td>317.1</td>
<td>310.7</td>
<td>309.6</td>
<td>311.3</td>
<td>312.8</td>
</tr>
<tr>
<td>d</td>
<td>351.7</td>
<td>330.7</td>
<td>314.2</td>
<td>324.6</td>
<td>316.8</td>
</tr>
<tr>
<td>e</td>
<td>314.4</td>
<td>310.1</td>
<td>306.5</td>
<td>315.9</td>
<td>314.8</td>
</tr>
<tr>
<td>f</td>
<td>321.7</td>
<td>309.2</td>
<td>304.4</td>
<td>317.4</td>
<td>317.4</td>
</tr>
</tbody>
</table>

a In conformer 1, the O-Me bond and the C=O bond is syn to each other, in conformer 2, the O-Me bond and the C=O bond is anti to each other.

As mentioned above, a counterion coordinated to the O atom of the silenolate causes increasing influence of resonance structures of type φ by increasing the effective electronegativity of the O atom, while a counterion coordinated to the Si atom of the silenolates causes increasing influence of reverse polarized resonance structures by stabilizing a negative charge at Si. This is very well reflected in the values of Δq(CSi) for the solvated metal ion coordinated silenolates (Table 9). The silenolates where the counterion is coordinated to the O atom have smaller values of Δq(CSi) than the corresponding free silenolate, while the opposite applies for the silenolates where the counterion is coordinated to the Si atom. The lithium ester silenolates have a larger value of Δq(CSi), and thus a larger value of q(Si), than the alkyl substituted lithium silenolates, in line with the observations by Ohshita that the former give no O-silylated product upon reaction with Et$_3$SiCl, indicating a higher anionic charge at Si for these silenolates. The negative end of the SiC dipole is on C for the methyl substituted silenolates and on Si for the TMS substituted silenolates, in line with the observations by Bendikov et al. that TMS substituents have this effect on silenes. The values of Δq(CSi) for the potassium silenolates do not differ to an appreciable extent from those of the free silenolates.
Table 9. The charge on C minus the charge on Si, $\Delta q(CSi)$, for the lithium, magnesium and potassium silenolates studied.

<table>
<thead>
<tr>
<th>Silenolates</th>
<th>25</th>
<th>26</th>
<th>27 (Conformer 1)$^a$</th>
<th>27 (Conformer 2)$^b$</th>
<th>28</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>0.39</td>
<td>-0.48</td>
<td>0.64</td>
<td>0.74</td>
<td>0.62</td>
</tr>
<tr>
<td>b</td>
<td>0.18</td>
<td>-0.81</td>
<td>0.68</td>
<td>0.63</td>
<td>0.60</td>
</tr>
<tr>
<td>c</td>
<td>0.63</td>
<td>-0.39</td>
<td>0.84</td>
<td>0.90</td>
<td>0.77</td>
</tr>
<tr>
<td>d</td>
<td>0.04</td>
<td>-0.96</td>
<td>0.58</td>
<td>0.57</td>
<td>0.52</td>
</tr>
<tr>
<td>e</td>
<td>0.66</td>
<td>-0.37</td>
<td>0.87</td>
<td>0.91</td>
<td>0.75</td>
</tr>
<tr>
<td>f</td>
<td>0.45</td>
<td>-0.52</td>
<td>0.73</td>
<td>0.71</td>
<td>0.66</td>
</tr>
</tbody>
</table>

$^a$ In conformer 1, the O-Me bond and the C=O bond is *syn* to each other, in conformer 2, the O-Me bond and the C=O bond is *anti* to each other.

The calculated association energies of the lithium, magnesium or potassium silenolates show that O coordination is preferred over Si coordination (Table 10). This means that lithium silenolates generally should have shorter SiC bond length than potassium silenolates and this is in line with the studies by Ishikawa and Ohshita which show that the central SiC double bond of lithium silenolates has some double bond character.$^{66b,c}$

Table 10. The association energies in kcal/mol of the lithium, magnesium and potassium silenolates studied.

<table>
<thead>
<tr>
<th>Silenolates</th>
<th>25</th>
<th>26</th>
<th>27 (Conformer 1)$^a$</th>
<th>27 (Conformer 2)$^a$</th>
<th>28</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>-83.4</td>
<td>-95.3</td>
<td>-83.5</td>
<td>-89.4</td>
<td>-86.2</td>
</tr>
<tr>
<td>b</td>
<td>-79.1</td>
<td>-89.4</td>
<td>-82.1</td>
<td>-79.4</td>
<td>-79.4</td>
</tr>
<tr>
<td>c</td>
<td>-76.3</td>
<td>-92.1</td>
<td>-79.0</td>
<td>-88.7</td>
<td>-77.5</td>
</tr>
<tr>
<td>d</td>
<td>-68.5</td>
<td>-88.5</td>
<td>-73.0</td>
<td>-67.5</td>
<td>-70.6</td>
</tr>
<tr>
<td>e</td>
<td>-68.6</td>
<td>-79.5</td>
<td>-70.2</td>
<td>-72.4</td>
<td>-70.4</td>
</tr>
<tr>
<td>f</td>
<td>-83.4</td>
<td>-95.3</td>
<td>-83.5</td>
<td>-89.4</td>
<td>-86.2</td>
</tr>
</tbody>
</table>

$^a$ In conformer 1, the O-Me bond and the C=O bond is *syn* to each other, in conformer 2, the O-Me bond and the C=O bond is *anti* to each other.

The potassium silenolates have the lowest association energies of all the metal ion coordinated silenolates investigated by 7-17 kcal/mol. This causes the potassium silenolates to be more similar to acyl anions than lithium silenolates, which are instead more similar to silenes. The potassium silenolates should thus be more stable towards dimerization and it can be postulated that this effect will be even more pronounced for rubidium silenolates. Moreover, a strongly chelating agent like HMPA or DMPU could perhaps be added to the lithium silenolates in order to lower the association energies and thus increase their stabilities towards dimerization.
7. How Reverse Polarization Affects the Reaction Profile for Thermolytic Formation of Silenes

Because carbon is more electronegative than silicon, most silenes have a dipole moment that points towards C. These silenes are called naturally polarized silenes. When \( \pi \)-donating groups are attached to C, this polarity can be lowered through influence of the reverse polarized resonance structures \( \Phi_{\text{II}} \) and \( \Phi_{\text{III}} \) (Scheme 10 with \( E = \text{Si} \)).

It has been recognized that silenes influenced by reverse polarization (RP) reacts more slowly with water and alcohols than naturally polarized silenes in cases when the O atom of H\(_2\)O/ROH adds to the Si.\(^{61}\) Indeed, the Ottosson group has found that some 2-amino-2-siloxy silenes both can be formed thermally from carbamylsilanes and further reacted with dienes in the presence of both air and moisture without any significant loss in yield.\(^{17,70}\) This raises the important question whether this approach for formation of reverse polarized silenes is general or not.

The Brook-type silenes can be formed thermally from acyltetrasilanes, whereby a [1,3]-silyl shift from silicon to oxygen occurs during the reaction (see Figure 1). These 2-siloxy silenes are considered to be influenced by reverse polarization due to the \( \pi \)-donating siloxy substituents at C,\(^{3b}\) even though the present NRT study reveals only a small influence. The other group at C in the silenes generated thermolytically so far has been either CH=CMe\(_2\), Me, 1-Ad, Mes, Ph, \( t \)-Pr, \( t \)-Bu, CH\(_2\)CH\(_2\)C(=O)Si(SiMe\(_3\))\(_3\) or NR\(_1\)R\(_2\) (R\(_1\), R\(_2\) = Ph or Me) and the temperature required are in the range of 65-180 °C.\(^{17,71,72,73,74,75,76,77,78}\) The influence of reverse polarization is the highest in the 2-amino-2-siloxy silenes.\(^{17,31}\) For TMS\(_2\)SiC(OTMS)rBu, the total contribution of \( \Phi_{\text{II}} \) and \( \Phi_{\text{III}} \) was calculated to be 7.4 %.

A problem encountered in this study with the formation of silenes strongly influenced by reverse polarization is that the [1,3]-silyl shift is reversible and that the barrier for this back-reaction is low. Lickiss and Brook tried to form the 1,1-bis(trimethylsilyl)-2-(\( N,N \)-dimethylamino)-2-(trimethylsiloxy)silene through photolysis of \( \text{tris} \)(trimethylsilyl)-\( N,N \)-dimethylsilaacetamide without success.\(^{79}\) The Ottosson group generated this silene thermally, and it was found to be 17.5 kcal/mol less stable than the starting silane and the activation energy for the back-reaction was 10.7 kcal/mol at the B3LYP/6-
31G(d) level of theory. This made it impossible to detect silene formation using regular techniques at the elevated temperatures used.\textsuperscript{17} The silene was instead trapped with 2,3-dimethyl-1,3-butadiene.

Given this knowledge, it should be interesting to explore the dependence of the reaction profile for silene formation on the properties of the silanes and silenes formed thermolytically through [1,3]-silyl shifts. It was reasoned that if the temperature required for thermolysis could be lowered, this method of formation of silenes could potentially have wide applicability since reverse polarized silenes also are less air and moisture sensitive and react selectively with dienes to form exclusively [4+2]-cycloadducts.\textsuperscript{17}

A prerequisite for the usage of silenes influenced by RP in organic synthesis is their facile formation. For studying the reaction profile, the B3LYP hybrid DFT method was used combined with the 6-31G(d) valence double-zeta basis set by Pople and Harirahan.\textsuperscript{80} In addition to the model systems shown in Scheme 13, for some silenes the SiH\textsubscript{3} groups were replaced with SiMe\textsubscript{3} groups so as to build systems that could potentially be generated experimentally. For benchmarking purposes, some selected systems were calculated at the CCSD(T)/cc-pVTZ//CCSD/6-31G(d) level of theory while replacing two silyl groups with H atoms to reduce the computational cost. Finally, the effects of dialkylsubstitution at Si on the reaction profile were investigated.

\begin{center}
\begin{align*}
&\begin{array}{c}
\text{H}_3\text{Si}\text{Si}\text{Si} \\
\text{H}_3\text{Si} \\
\text{H}_3\text{Si} \\
\end{array}
\begin{array}{c}
X \\
Y \\
\Delta \\
\end{array}
\rightarrow
\begin{array}{c}
\text{H}_3\text{Si} \\
\text{H}_3\text{Si} \\
\text{H}_3\text{Si} \\
\end{array}
\begin{array}{c}
\text{SiH}_3 \\
\text{SiY} \\
\text{SiX} \\
\end{array}
\end{align*}
\end{center}

\begin{center}
\begin{align*}
&\begin{array}{c}
\text{H}_3\text{Si} \\
\text{H}_3\text{Si} \\
\text{H}_3\text{Si} \\
\end{array}
\begin{array}{c}
X \\
Y \\
\Delta \\
\end{array}
\rightarrow
\begin{array}{c}
\text{CH}_3 \\
\text{CH}_3 \\
\text{CH}_3 \\
\end{array}
\begin{array}{c}
\text{SiH}_3 \\
\text{SiY} \\
\text{SiX} \\
\end{array}
\end{align*}
\end{center}

\begin{center}
\textbf{Scheme 13}
\end{center}

The reason behind the choice of model systems for this study was that both Brook-type silenes and 2-amino-2-siloxy-silenes have silyl groups at Si. Other studies have also shown that silyl substituents at Si help reduce the natural polarity of the Si=C bond.\textsuperscript{81} These studies illuminate the fact that there is a $\sigma$- and a $\pi$-component to reverse polarization. The NRT method calculates
the $\pi$-conjugative reverse polarization and its effect on the charge distribution, geometry and reaction profile were studied. Finally, the effect of exchanging the silyl groups for methyl groups was investigated.

7.1 Effects of Reverse Polarization on Silene Geometries

The parent silene $\text{H}_2\text{Si} = \text{CH}_2$ was found to have a SiC bond length of 1.7039 Å as measured by Bailleux et al. using millimeter wave spectroscopy,\textsuperscript{81} to be compared to a typical SiC single bond length of 1.87-1.89 Å.\textsuperscript{82} Among the model silenes chosen, the SiC bond lengths encompass this entire spectrum. It can be argued that silenes influenced by $\pi$-conjugative reverse polarization should have longer SiC bond lengths than naturally polarized silenes and thus have a lower barrier for rotation about the SiC bond (Table 11). This should allow reverse polarized silenes to more easily adopt the conformation required for the [1,3]-silyl shift. This is also reflected in the excellent correlation between the degree of $\pi$-conjugative RP and both bond length and bond order. Silenes with higher degree of $\pi$-conjugative RP have longer SiC bonds and smaller pyramidalization angles than naturally polarized silenes, and they also have smaller SiC charge differences and more negative charge at Si. The modest correlation between the degree of $\pi$-conjugative RP and $\Delta q(\text{Si-C})$, $q(\text{Si})$ and $\Sigma \text{Si}$ is a result of the influence by the inductively electron donating/withdrawing ability of the groups bonded to C and Si on these properties. Note that only the $\pi$-component to reverse polarization is studied here. Herein, the degree of $\pi$-conjugative reverse polarization in each of the silenes was determined by NRT, as given by the sum of contributions from resonance structures $\Phi_{II}$ and $\Phi_{III}$.

Table 11. Correlation coefficients for correlation between total contribution of resonance structures $\Phi_{II} + \Phi_{III}$ and a series of different properties.

<table>
<thead>
<tr>
<th>Property</th>
<th>S29A – S31D</th>
</tr>
</thead>
<tbody>
<tr>
<td>$r_{\text{SiC}}$</td>
<td>0.957</td>
</tr>
<tr>
<td>$\eta_{\text{SiC}}$</td>
<td>0.946</td>
</tr>
<tr>
<td>$\Delta q(\text{Si-C})$</td>
<td>0.625</td>
</tr>
<tr>
<td>$q(\text{Si})$</td>
<td>0.760</td>
</tr>
<tr>
<td>$\Sigma (\text{Si})$</td>
<td>0.546</td>
</tr>
<tr>
<td>$\Delta E(\text{silane} \rightarrow \text{silene})$</td>
<td>0.097</td>
</tr>
<tr>
<td>$\Delta E^i(\text{silane} \rightarrow \text{silene})$</td>
<td>0.214</td>
</tr>
<tr>
<td>$\Delta E^i(\text{silene} \rightarrow \text{silane})$</td>
<td>0.623</td>
</tr>
</tbody>
</table>
The total contributions of $\Phi_{II}$ and $\Phi_{III}$ for the different silenes follow the order expected from the difference in $\pi$-donor capacity of the various groups at C (Table 12). As can be seen from the data in Tables 11 and 12, there is a strong correlation between degree of $\pi$-conjugative RP and both SiC bond lengths and SiC bond orders.

Table 12. Atomic charges, charge differences, percental contribution of $\Phi_{II}$ and $\Phi_{III}$, SiC bond lengths and bond orders of silenes S29A - S31D at the B3LYP/6-31+G(d)//B3LYP/6-31G(d) level.

<table>
<thead>
<tr>
<th>Silene</th>
<th>q(Si)</th>
<th>q(C)</th>
<th>$\Delta$q(Si-C) $^a$</th>
<th>$\Sigma(\Phi_{II} + \Phi_{III})$ $^b$ [%]</th>
<th>$r_{Si-C}$ (Å)</th>
<th>$n_{Si-C}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>S29A</td>
<td>0.08</td>
<td>0.03</td>
<td>0.05</td>
<td>25.2</td>
<td>1.852</td>
<td>1.46</td>
</tr>
<tr>
<td>S29B</td>
<td>0.03</td>
<td>0.20</td>
<td>-0.18</td>
<td>36.7</td>
<td>1.870</td>
<td>1.39</td>
</tr>
<tr>
<td>S29C</td>
<td>0.30</td>
<td>-0.48</td>
<td>0.79</td>
<td>17.2</td>
<td>1.796</td>
<td>1.67</td>
</tr>
<tr>
<td>S29D</td>
<td>0.18</td>
<td>-0.20</td>
<td>0.38</td>
<td>21.7</td>
<td>1.820</td>
<td>1.58</td>
</tr>
<tr>
<td>S30A</td>
<td>-0.04</td>
<td>0.25</td>
<td>-0.29</td>
<td>46.9</td>
<td>1.920</td>
<td>1.23</td>
</tr>
<tr>
<td>S30B</td>
<td>0.08</td>
<td>0.30</td>
<td>-0.22</td>
<td>22.0</td>
<td>1.838</td>
<td>1.66</td>
</tr>
<tr>
<td>S30C</td>
<td>0.29</td>
<td>-0.36</td>
<td>0.65</td>
<td>14.6</td>
<td>1.782</td>
<td>1.77</td>
</tr>
<tr>
<td>S30D</td>
<td>0.27</td>
<td>-0.11</td>
<td>0.38</td>
<td>11.0</td>
<td>1.774</td>
<td>1.84</td>
</tr>
<tr>
<td>S31A</td>
<td>0.19</td>
<td>-0.41</td>
<td>0.61</td>
<td>22.1</td>
<td>1.819</td>
<td>1.57</td>
</tr>
<tr>
<td>S31B</td>
<td>0.21</td>
<td>-0.26</td>
<td>0.47</td>
<td>17.5</td>
<td>1.801</td>
<td>1.74</td>
</tr>
<tr>
<td>S31C</td>
<td>0.53</td>
<td>-1.01</td>
<td>1.54</td>
<td>10.4</td>
<td>1.757</td>
<td>1.84</td>
</tr>
<tr>
<td>S31D</td>
<td>0.53</td>
<td>-0.75</td>
<td>1.28</td>
<td>6.3</td>
<td>1.746</td>
<td>1.89</td>
</tr>
</tbody>
</table>

It is known that the pyramidalization at Si, given as the sum of valence angles around Si, increases as the SiC bond length increases. This trend is reproduced in the calculations (Table 12). The charge difference between C and Si also correlates well with the degree of reverse polarization (Table 11).

7.2 Effects of Reverse Polarization on Reaction Profile

The activation and reaction energies for silene formation via [1,3]-silyl shifts are shown in Table 13.

As expected, silenes highly influenced by $\pi$-conjugative reverse polarization have the lowest barriers for the back-reaction and these silenes also have the longest SiC bond lengths. A moderate correlation was found between the barrier for the reverse reaction and both the total contribution of reverse polarized resonance structures ($r^2 = 0.623$) and bond lengths ($r^2 = 0.642$). This is in line with findings by Ohshita et al. on Brook-type silenes with $X = O$ and $Y = i$-Pr, $t$-Bu, 1-Ad, 2,6-xylyl or Mes. Two factors that also influence the potential energy surface for the reaction could be differences in steric bulk and differences in bond strengths of the bonds involved in the reaction coordinate. Note that assuming an exponential correlation between the de-
gree of reverse polarization influence and the barrier for the back reaction gave r² as 0.685. There is no physical or chemical argument supporting or not supporting either a linear or exponential correlation here. Nevertheless, a linear correlation can be assumed here and for the studies presented in earlier chapters, it has proved to be a reasonably good model.

Table 13. Reaction and activation energies for the thermolytic [1,3]-silyl shift at the B3LYP/6-31+G(d)/B3LYP/6-31G(d) level. a

<table>
<thead>
<tr>
<th>Silene</th>
<th>ΔE [silene - silane]</th>
<th>ΔE ‡ [silane → silene]</th>
<th>ΔE ‡ [silene → silane]</th>
</tr>
</thead>
<tbody>
<tr>
<td>S29A</td>
<td>11.0</td>
<td>11.8</td>
<td>0.8</td>
</tr>
<tr>
<td>S29B</td>
<td>8.1</td>
<td>11.3</td>
<td>3.2</td>
</tr>
<tr>
<td>S29C</td>
<td>14.9</td>
<td>21.4</td>
<td>6.5</td>
</tr>
<tr>
<td>S29D</td>
<td>20.0</td>
<td>23.5</td>
<td>3.5</td>
</tr>
<tr>
<td>S30A</td>
<td>25.0</td>
<td>25.7</td>
<td>0.7</td>
</tr>
<tr>
<td>S30B</td>
<td>24.0</td>
<td>35.0</td>
<td>11.0</td>
</tr>
<tr>
<td>S30C</td>
<td>21.8</td>
<td>32.0</td>
<td>10.2</td>
</tr>
<tr>
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<td>13.8</td>
<td>31.0</td>
<td>17.2</td>
</tr>
<tr>
<td>S31A</td>
<td>21.9</td>
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<td>4.4</td>
</tr>
<tr>
<td>S31B</td>
<td>11.6</td>
<td>26.5</td>
<td>14.9</td>
</tr>
<tr>
<td>S31C</td>
<td>16.1</td>
<td>28.8</td>
<td>12.7</td>
</tr>
<tr>
<td>S31D</td>
<td>6.8</td>
<td>28.2</td>
<td>21.4</td>
</tr>
</tbody>
</table>

a Energies in kcal/mol. Values in italics are from IEF-PCM calculations with the dielectric constant set to that of acetonitrile.

The [1,3]-silyl shifts are all endothermic and the reaction energies range from 6.8 kcal/mol (S31D) to 25.0 kcal/mol (S30A). However, these reaction energies do not correlate with the degree of reverse polarization (r² = 0.097). The methyl substituted silenes S30D and S31D have the highest barriers for the reverse reaction in their respective group and only S31D has a barrier above 20 kcal/mol, a result which is in line with the finding that Brook’s silene with X = O and Y= 1-Ad is a relatively stable and isolable silene. The conclusion was that the thermolytic formation of silenes from acylsilanes through a [1,3]-silyl shift will probably not be a good way to generate isolable silenes highly influenced by reverse polarization. The barrier for the reverse reaction would then be so low that the silene is undetectable by conventional means. As already seen, it needs instead to be trapped by dienes, with which they react selectively forming [4+2]-adducts. A possible way to form isolable silenes strongly influenced by RP could perhaps be through treatment of the silanes investigated with potassium tert-butoxide in order to synthesize anionic species instead, a method already used to form potassium silenolates. 

Now, a few of the systems were calculated in which silyl groups were replaced by TMS groups. The systems chosen were those corresponding to model silenes S29A, S30A, S31A, S29D, S30D and S31D. These were named as FS29A, FS30A, FS31A, FS29D, FS30D and FS31D. It was found that the total contributions from resonance structures Φ II and Φ III were 3-23
% less for these systems than for the corresponding model systems. A likely reason for this is that the steric bulk of the TMS group prevent optimal alignment of the lone pair orbital of the heteroatom bound to C with the π- and π*-orbitals of the SiC bond. However, the FS29A, FS30A and FS31A were more influenced by reverse polarization than FS29D, FS30D and FS31D, a trend also seen for the model systems.

A strong correlation was present between the SiC bond lengths of the full systems and both the total contributions ΦII and ΦIII of (r² = 0.944) and the bond orders (r² = 0.929). As for the model systems, the barrier height for the back-reaction also correlated well with bond length (r² = 0.822), and moderately with the total contribution of ΦII and ΦIII (r² = 0.539). The correlation between the degree of π-conjugative reverse polarization and Δq(Si-C) was found to be moderate (r² = 0.720).

Due to larger steric repulsion in the transition state for silene formation, the reaction barriers are higher for the TMS-substituted systems than for the model systems. Also, due to the result that the reaction is less endothermic for the TMS substituted systems than for the model systems, the barriers for the back-reactions are about 10 kcal/mol higher than for the model systems. For this reason, it was proposed that silenes FS30B, FS30C, FS31B and FS31C, which should have activation barriers in the range of 20-25 kcal/mol, would be experimentally observable. Note that the total contribution of ΦII and ΦIII will probably only be 10-15 %. Since the activation barriers for FS30D and FS31D was calculated to be 29-34 kcal/mol, it was postulated that these are templates for isolable silenes. A strong indication of this is that FS30D is a small Brook-type silene. A bulkier R-group than methyl, like for example 1-Ad, is needed or else these silenes will still dimerize quickly.

Since the thermolysis reaction, like other organic reactions, are carried out in a solvent, we performed single-point calculations using Tomasi’s polarized continuum model in the integral equation formalism (IEF-PCM)⁸⁴ on the TMS-substituted silenes. The solvent used was acetonitrile (ε = 37), however, the trends did not change due to the introduction of a polar solvent and no additional trends could be found for describing the effect of the solvent. The activation energies for the back-reaction were found to be very similar or lower in a polar solvent.

In order to probe an experimentally observed system, Brook’s silene with three TMS groups and one t-Bu group was calculated (BS30D). The SiC bond length was found to be 1.784 Å, i.e. longer than that of Brook’s silene with R = 1-Ad (1.764 Å).⁹ The activation energy for its formation from the corresponding acylsilane was endothermic by 12.0 kcal/mol, i.e. more endothermic than the corresponding reaction for FS30D, and the reaction barrier was 33.9 kcal/mol. The barrier for the back-reaction was calculated to be approximately 22 kcal/mol, i.e. lower than for FS30D. The reason for these results is the larger steric strain in BS30D when compared to FS30D due to
the \textit{t}-Bu group. Steric factors are required in order to hinder dimerization and reactions with nucleophiles. However, the steric strain caused by the \textit{t}-Bu group also prevents the oxygen lone-pair orbital to align properly with the SiC \(\pi^*\)-orbital and, as a result, for \textbf{BS30D} the total contribution of \(\Phi_{\text{II}}\) and \(\Phi_{\text{III}}\) is only 7.4 \%.

In order to simulate the effect of two alkyl substituents at Si, the systems with two methyl groups at Si instead of silyl groups were calculated. The reactions were all more endothermic than the corresponding reactions for the model systems with silyl substituents and the SiC bond lengths in the silenes were all shorter for \textbf{S32} – \textbf{S34} than for \textbf{S29} – \textbf{S31}. The latter result are in line with our previous findings,\textsuperscript{17} and is also seen from comparison of Wiberg’s and Apeloig’s isolable silenes.\textsuperscript{85,86}

The degree of \(\pi\)-conjugative reverse polarization was lower for \textbf{S32} – \textbf{S34} than for \textbf{S29} – \textbf{S31}, but the activation energies for the back-reaction to the corresponding acyilsilanes are higher. This was due to the shorter SiC bond length of \textbf{S32} – \textbf{S34}, which causes the barrier for rotation about the SiC bond to increase. More energy is thus needed for the silene to adopt the required conformation for the back-reaction to occur and this is reflected in the activation energies. Even though \textbf{S32} – \textbf{S34} are more stable with regard to the back-reaction than \textbf{S29} – \textbf{S31}, the silenes with alkyl substituents at Si will most probably dimerize more quickly due to their shorter SiC bond length and larger SiC bond dipoles.

In conclusion, our NRT calculations have shown that there is a moderate correlation between the degree of \(\pi\)-conjugative reverse polarization and the barrier for the back-reaction from silene to silane via the [1,3]-shift. Silenes strongly influenced by \(\pi\)-conjugative reverse polarization have lower barriers for the back-reaction and are thus more difficult to isolate than naturally polarized silenes. They need instead to be trapped by \textit{e.g.} dienes.
In this thesis, the properties of both naturally and reversed polarized silenes have been discussed. In chapter 7, one route for synthesizing reverse polarized silenes was studied computationally. Except for aryl-substituted silenes, few studies have been performed on conjugated silenes corresponding to linear polyenes such as 1,3-butadiene. Earlier in this thesis, the formation of silenes from thermolysis of acyltetrasilanes has been studied. Other methods for silene formation also exist, for example sila-Peterson-olefination. However, none of these yield silabutadienes.

In this chapter, a method for preparation of silabutadienes through thermal or photochemical ring-opening reaction of silacyclobut-2-enes will be discussed. The 1-silabutadienes formed are always higher in energy than the corresponding silacyclobut-2-enes. They are also higher in energy than products resulting from subsequent transformation. Silacyclobut-2-enes have previously been synthesized, using the electrocyclization of 1-silabutadiene. Ishikawa and Yoshizawa have also proposed a 1-silabutadiene as a highly reactive intermediate in the thermal rearrangement of silacyclobut-2-ene to a silacyclopentene.

Here, a computational analysis of the effects of the substituents on the thermal retrocyclization of silacyclobut-2-enes will be presented. Silyl substituents were chosen at Si over other known alkyl, aryl and alkoxy substituents due to their ability to lower the polarity of the Si=C bond, which could lower the electrophilicity of the 1-silabutadiene. The 1,1-disilylsilacyclobut-2-enes investigated (Scheme 14) had X as H (a), CF$_3$ (b), SiH$_3$ (c), CN (d), OCH$_3$ (e), OH (f) or NH$_2$ (g). The names were preceded by a prefix 2-, 3- or 4- indicating the position of the substituent on the ring. Both s-cis and s-trans isomers as well of E- and Z-isomerism were taken care of and all possible isomers were calculated.
Our goal was to achieve as low barrier and endothermicity as possible by altering both the type of substituents as well as their positions on the ring. It is well known that silabutadienes can be trapped by alcohols or suitable die-nophiles. They could also form silyl substituted cyclopropanes. Silacyclohex-3-enes, products of [4+2] cycloaddition of silabutadienes with alkenes have been reported. Also alkynes and ketones should react in the same way.

Calculations at the B3LYP/6-31G(d) level of theory shows that 36a is a conjugated diene at its optimal geometry (Figure 6) as the Si=C and C=C bonds are longer than the Si=C bonds in silaethylene (1.710 Å) and ethylene (1.331 Å), respectively,

\[ \text{H}_3\text{Si}-\text{SiH}_3 \]

\[ \text{H}_3\text{Si}-\text{SiH}_3 \]

\[ \text{NH}_2 \]

\[ \text{NH}_2 \]

Figure 6: Optimal bond lengths (Å) of some selected 1,1-disilyl-1-silabutadienes. Values at the B3LYP/6-31G(d) level and CCSD/6-311G(d) level (italics).
while the single bond in the middle is shorter than the corresponding single bond in 1,3-butadiene (1.444 Å for the s-trans-conformer and 1.470 Å for s-cis conformer). Moreover, in s-cis 36a, the Si=C-C=C dihedral angle was calculated to be 33.2°, which is to be compared to the corresponding dihedral angle in s-cis 1,3-butadiene (30.2°). At the CCSD/6-311G(d) level of theory, the Si=C and C=C bonds are shorter while the central C-C bond is longer than at the B3LYP/6-31G(d) level of theory by approximately 0.015 Å. The conclusions made above are still valid, however.

There are two ring-opening reactions for the 4-substituted 1,1-disilylsilacyclobut-2-enes, one “inward” and one “outward” process leading to two different isomers of 1,1-disilyl-1-silabutadienes according to Scheme 15. The “inward” isomer is shown to the left and the “outward isomer to the right. Our calculations show that the outward product is always kinetically favored and this is more pronounced for the species with π-donor group at the 4-position. These results are in line with the findings of Houk and coworkers on the torqueselectivity of substituted cyclobutenes.

![Scheme 15](image)

The barrier for the ring-opening reaction of 35a was 28.9 kcal/mol at the B3LYP/6-31G(d) level of theory, and the reaction is endothermic by 10.2 kcal/mol for the formation of the s-trans conformer and 13.9 kcal/mol for the formation of the s-cis conformer. This makes the reaction possible only at higher temperatures and the 1-silabutadienes formed will only be transient and easily revert back to starting material. The difference is only 1.2 kcal/mol between results at the CCSD(T)/cc-pVTZ and B3LYP/6-31G(d) levels of theory. The conclusions drawn is consistent with the fact that the s-trans conformer is more stable than the s-cis conformer for 1,3-butadiene.

While substitution at the 2- or 3-position in the silacyclobut-2-enes leads to more endothermic ring-opening reactions, substitution at the 4-position contrastingly leads to less endothermic reactions when compared to the ring-opening of 35a.

The results of our calculations (Table 14) shows that while σ-acceptor groups (CF₃) leads to higher reaction barriers for the retrocyclization and makes the reaction more endothermic, σ-donor groups (SiH₃) lowers the same barriers and makes the reaction less endothermic. Another interesting result is that both π-donor (OCH₃, OH, NH₂) and, to a lesser extent, π-acceptor (CN) groups at the 4-position lowers the barrier for the retrocycliza-
tion reaction substantially and the reaction becomes less endothermic. For 4- amino-1,1-disilylsilacyclobut-2-ene, the retrocyclization is even exothermic. And the activation energy at the B3LYP/6-31+G(d)//B3LYP/6-31G(d) level of theory, the barrier is only 14.8 kcal/mol, only somewhat lower than the CCSD(T)/6-311G(d)//CCSD/6-311G(d) result of 18.8 kcal/mol.

Table 14. Free energies of activation and change in free energies during the retro-
cyclization of the substituted 1,1-disilylsilacyclobut-2-enes at 298 K (kcal/mol).

<table>
<thead>
<tr>
<th>Substituent X Position</th>
<th>ΔG‡</th>
<th>ΔGcis</th>
<th>ΔGtrans</th>
</tr>
</thead>
<tbody>
<tr>
<td>H (a)</td>
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<td>13.9</td>
<td>10.2</td>
</tr>
<tr>
<td>CF₃ (b)</td>
<td>2</td>
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<td>18.0</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>30.7</td>
<td>15.9</td>
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<tr>
<td></td>
<td>4 (outward)</td>
<td>28.3</td>
<td>13.9</td>
</tr>
<tr>
<td></td>
<td>4 (inward)</td>
<td>33.7</td>
<td>18.1</td>
</tr>
<tr>
<td>CN (c)</td>
<td>2</td>
<td>27.7</td>
<td>15.2</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>30.7</td>
<td>16.4</td>
</tr>
<tr>
<td></td>
<td>4 (outward)</td>
<td>24.5</td>
<td>9.4</td>
</tr>
<tr>
<td></td>
<td>4 (inward)</td>
<td>28.5</td>
<td>10.5</td>
</tr>
<tr>
<td>SiH₃ (d)</td>
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<td>28.2</td>
<td>16.4</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>29.4</td>
<td>15.9</td>
</tr>
<tr>
<td></td>
<td>4 (outward)</td>
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<td>11.8</td>
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<tr>
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<td>3</td>
<td>33.1</td>
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<td></td>
<td>4 (inward)</td>
<td>33.9</td>
<td>5.0</td>
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<td>OH (f)</td>
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<td>30.7</td>
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<td>NH₂ (g)</td>
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<td>28.0</td>
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<tr>
<td></td>
<td>4 (inward)</td>
<td>31.2</td>
<td>2.1</td>
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</table>

As can be seen from Figure 5, the C(2)-C(3) bond is significantly shorter in both s-cis and s-trans 36g than those in both s-cis 36a and s-trans 36a.
Moreover, the C(4)-N bond also shortens significantly when the retrocyclization of s-trans (s-cis) 4-36g takes place. The one feature which 1,1-disilylsilacyclobut-2-enes with \( \pi \)-conjugative substituents at the 4-position have in common is reverse polarization. The influence of resonance structure III below (Scheme 16), in which the lone-pairs on N donate electrons into the \( \pi \)-system extends the conjugation. This diminishes the partial positive charge at Si and makes it easier for the Si atom to bind to the partially positively charged C atom bearing the X substituent, and thus lowers the reaction barrier for the retrocyclization reaction. In the 2-substituted species the extended conjugation is much shorter and in the 3-substituted species, it is virtually non-existent and the corresponding retrocyclization is much more endothermic for 2-substituted 1,1-disilyl-1-silacyclobut-2-enes and even more so for the 3-substituted species.

![Scheme 16](image)

We also investigated an important side-reaction which possibly competes with retrocyclization, namely the formation of 3-bis(silyl)silylcyclopropene isomers with the substituent X at the silyl group (Scheme 17). These can be formed directly from the 1,1-disilylsilacyclobut-2-enes through a 1,2-shift and their formation was first observed in thermolysis reactions by Ishikawa and Yoshizawa. However, it was found that the barrier between 35a and 37a was 73.0 kcal/mol while the barriers for formation of 37e and 37g from 4-35e and 4-35g was 39.5 and 49.5 kcal/mol, respectively. Thus, this rearrangement will not occur during the formation of the 1,1-disilyl-1-silabutadienes or compete with trapping reactions.

![Scheme 17](image)
Substituents at the 4-position were shown to both stabilize the 1,1-disilylsilabutadienes and the transition state for their formation. It was therefore natural to investigate the 4,4-disubstituted 1,1-disilyl-1-silabutadienes. It was found that two \( \pi \)-donors or \( \pi \)-acceptors at the 4-position increased the degree of reverse polarization and \( \pi \)-conjugation even further and thus both the products and transition states were even more stabilized (Table 15). At the B3LYP level, the retrocyclization reaction of the 4,4-diaminosubstituted species are significantly exothermic and the barrier for the retrocyclization reaction can be as low as 14.8 kcal/mol. At the CCSD(T) level, the reactions are slightly endothermic, but the 4,4-diamino-1,1-disilylsilacyclobut-2-enes are still the most stable isomers. The transition state energy was 22.3 kcal/mol at the CCSD(T)/6-311G(d)//CCSD/6-311G(d) level of theory, lower than the corresponding CCSD(T) energy for 35a (31.1 kcal/mol), but higher than the corresponding B3LYP energy.

Table 15. Free energies of activation and change in free energies during the retrocyclization of the 4,4-disubstituted 1,1-disilylsilacyclobut-2-enes at 298 K (kcal/mol).

<table>
<thead>
<tr>
<th>Substituent X</th>
<th>( \Delta G^\ddagger )</th>
<th>( \Delta G_{\text{cis}} )</th>
<th>( \Delta G_{\text{trans}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>28.9</td>
<td>13.9</td>
<td>10.2</td>
</tr>
<tr>
<td>CF(_3)</td>
<td>28.9</td>
<td>15.8</td>
<td>6.8</td>
</tr>
<tr>
<td>SiH(_3)</td>
<td>28.2</td>
<td>15.2</td>
<td>8.3</td>
</tr>
<tr>
<td>CN</td>
<td>22.1</td>
<td>5.8</td>
<td>0.5</td>
</tr>
<tr>
<td>OCH(_3)</td>
<td>20.9</td>
<td>0.3</td>
<td>-2.1</td>
</tr>
<tr>
<td>OH</td>
<td>22.9</td>
<td>1.5</td>
<td>0.4</td>
</tr>
<tr>
<td>NH(_2)</td>
<td>14.8</td>
<td>-4.2</td>
<td>-8.7</td>
</tr>
</tbody>
</table>

At the end, we also performed calculations on the corresponding 1,1-dimethyl-1-silacyclobut-2-enes and found that the retrocyclization reactions were more endothermic for these systems. Our final conclusion is that reverse polarization is not just the key to stabilize isolated silenes, but also for a class of conjugated silenes. By employing silyl groups at Si and two \( \pi \)-conjugative substituents at the 4-position, it should be possible to generate persistent silabutadienes.
9. Hypervalent Carbon Compounds

So far in this thesis, heavy analogs of unsaturated carbon compounds like alkenes, imines and ketones have been discussed. Ethene is for example a stable compound while the corresponding silene is a transient species. However, there are compounds, like SiF$_5^-$ (38), which are stable silicon compounds whereas CF$_5^-$ (39) is a transition state for the S$_2$N$_2$ substitution of one fluoride ion for another. In the final chapter of this thesis, we will discuss the potential existence of stable carbon compounds with a formal number of valence electron pairs at C above four. In particular, we will search for the true carbon analogs to 38, SiH$_5^-$ (40), SiF$_6^{2-}$ (41) and SiH$_6^{2-}$ (42) and show that these will be impossible to reach experimentally.

9.1. Hypervalency

The term hypervalency was introduced by J. I. Musher in 1969.\textsuperscript{105} He proposed that hypervalent compounds are group 15-18 compounds whose Lewis structure cannot be written without assigning more than eight electrons to the central atom. This definition of hypervalency was revised in 1980 by Perkins \textit{et al.} to include also groups 1, 2, 13 and 14. The designation N-X-L was introduced where $N$ is the number of formally assigned electrons in a valence shell belonging to the central atom X, and $L$ is the number of ligands around X.\textsuperscript{106} Already in 1951, Pimentel and Rundle attempted to explain how more than eight electrons can be held within a valence-shell by introducing the idea of three-centre-four-electron bonds.\textsuperscript{107} This idea means that two bonding electrons are delocalized over three centers while the other two electrons are in a non-bonding orbital. In this way, the two ligands are assigned a formal charge of almost -0.5 each, and a formal charge of almost +1.0 is assigned to the central atom. That is, extra electrons are localized on the ligands resulting in an actual number of electron pairs around the central atom of less than four. The octet rule is thus obeyed. It should be noted, however, that Weinhold and Curtiss recently performed NRT calculations at the B3LYP level of theory showing that among the compounds considered the only compound to be truly hypervalent are SF$_6$ (43).
When stating that the octet rule is obeyed, it is important to note that Lewis never discussed three-center-four-electron bonds and considered 43 and PF₅ (44) to disobey his octet rule. An atom in a molecule is sometimes said to obey the octet rule if the number of electrons formally assigned to it is fewer than or equal to eight. While all non-hypervalent atoms in a molecule obey this modified octet rule, hypervalent atoms only do so if the ligands are electronegative enough. These electrons can be fully shared, partially shared or unshared depending on the bonding situation. Lewis originally stated that this number of electrons should be exactly eight. In this thesis, Lewis original definition will be used when regarding a molecule to be hypervalent.

It is today known that it is possible to describe 44, a hypervalent compound according to Lewis, by employing only the valence s- and p-orbitals of the central atom. The P atom can be regarded to be sp²-hybridized with an empty p-orbital that interacts with the filled pₓ-orbitals of two F atoms. In this way, we obtain three equal equatorial bonds and a three-center-four-electron bond. The molecule still has five covalent bonds, however, and thus does not obey the Lewis octet rule. Gillespie and Robinson proposed in 1995 that the above description of 44 employing three-center-four-electron bonds is inconsistent with the small difference in bond length between the axial and equatorial bonds (1.577 Å and 1.543 Å, respectively). The concept hypervalency should according to these authors be removed completely and replaced by a duet rule for period 1 elements, an octet rule for period 2 elements, and a duodecet rule for period 3 and 4 elements. Both CF₄ (45) and 43 thus obey the octet rule and duodecet rule, respectively, while BF₃ (46) and SF₅ (47) disobey them. The hypovalency of BF₃ explains its Lewis acid character. Reed and Schleyer calculated natural bond orders for a large number of hypervalent molecules at HF/6-31G(d) level. The highest total bond order to the central atom was 3.98 for H₃PS and it was lowest for F₃PO (1.95). Noury et al. have found, using the electron localization function (ELF), that the total valence shell population of the central atom depends on the electronegativity of the ligands. If the ligands are weakly electronegative compared to the central atom, the valence shell population approaches 10 and 12 for a group 15 and a group 16 central atom, respectively. These molecules cannot be said to obey the Lewis octet rule. The authors found no difference between the bonds of these molecules and those of non-hypervalent molecules.

Very recently, the group of Bickelhaupt analyzed hypervalency in terms of a Ball-in-a-box model. The authors compared the D₃h-symmetric [Cl-CH₃-Cl⁻] (48), a transition state for the replacement of one chlorine atom for another, with the D₃h-symmetric [Cl-SiH₃-Cl⁻] (49), which is a minimum on the potential energy surface. The model emphasizes the importance of steric factors and size of the central atom for hypervalency. The authors show that while the Si atom in 49 perfectly fits into the “box” formed by the
five substituents, the C atom is too small and can therefore not bind strongly to both the axial substituents at the top and bottom of the box. The boxes [Cl-H3-Cl] (50 and 51) of 48 and 49 were optimized at the BP86/TZ2P level with the H3 moiety frozen as in 48 and 49, respectively while constrained to C$_{3v}$-symmetry. The authors found these boxes to have optimum distances between the center and each Cl atom of 2.408 and 2.317 Å, respectively. This is very close the essentially identical distances in 48 (2.352 Å) and 49 (2.359 Å). This showed that the optimum box size was close to the actual box size in 48 and 49. The distance from the center to each of the Cl atoms in 48 and 49 was then compared to the corresponding distance in [Cl-C-Cl]$^+$ (52) and [Cl-Si-Cl]$^+$ (53), respectively. Carbon was found to be too small to fit in the box formed by the five substituents and thus it binds more strongly to one of the axial substituent than to the other, resulting in pyramidalization of the CH$_3$ moiety and a very weak C$_{3v}$-complex.

In a somewhat later study, the same group reported the hypervalency of [X-CH$_3$-X]$^+$ (X = He (54) or Ne (55)). Compound 55 has been observed by Dopfer et al. using infrared photodissociation spectroscopy, and Bickelhaupt calculated the structure of 54 using $ab$ initio calculations. The authors performed (ZORA-)OLYP/TZ2p calculations and found that the stabilization energy gained when going from D$_{3h}$ symmetry to a C$_{3v}$-symmetric complex in 54 and 55 is not enough to surmount the barrier for pyramidalization of CH$_3^+$. For X = Ar (56), this situation was found not to occur again a weak C$_{3v}$ complex between CH$_3$Ar$^+$ and Ar was formed. In 54 and 55, The relatively strongly bound CH$_3^+$ moiety could be seen as a “disk” between two “balls” of noble gas atoms and not as a ball in a box. It should be noted that the C-Ng bond lengths of 54 and 55 were 2.047 Å and 2.261 Å, respectively, at the CCSD(T)/6-311++G** level of theory. These are much longer than the corresponding C-Ng-distances in the hypervalent compounds described in this chapter.

In this chapter, we will search for the closest carbon analogs of 38, 40, 41, and 42.

9.2. Hypervalent First-Row Compounds

To our knowledge, the true C analogs of 38, 40, 41, and 42 have yet not been identified. In order to be true analogs, the CL$_5$ and CL$_6$ species should be local minima on the PES with a D$_{3h}$ or O$_h$ structure, respectively, the bond lengths should not differ very much from those of normal single bonds and for CL$_5$, the ratio of the bond lengths to the equatorial bond lengths ($r_{ax}/r_{eq}$) should not be far above one. For example, $r_{ax}/r_{eq}$ is 1.035 in 38. The bond lengths, $r_{ax} = 1.646$ and $r_{eq} = 1.591$ Å, are longer than the normal Si-F bond.
in SiF\textsubscript{4} (1.550 Å)\textsuperscript{119} by 6.2 and 2.6 %, respectively.\textsuperscript{120} The Si-F bond in K\textsubscript{2}SiF\textsubscript{6} (56) of 1.683 Å\textsuperscript{121} is 8.6 % longer than the Si-F bonds in SiF\textsubscript{4}. The dianion CF\textsubscript{6}\textsuperscript{2-} (57) was found to be a local minimum on the PES 150 kcal/mol above 45 + 2F.\textsuperscript{122} The C-F bonds calculated at the MP2/6-31+G(d) level (1.582 Å) were 19 % longer than those of 45 (1.333 Å) at the same level of theory, indicating that this is not completely analogous to 38. In 1998, Bettinger et al. found the dissociation of the D\textsubscript{3h} symmetric NF\textsubscript{5} (58) into NF\textsubscript{3} (59) and F\textsubscript{2} to be exothermic by 42 kcal/mol at the CCSD(T)/cc-pVTZ//CCSD/DZP level of theory.\textsuperscript{123} The molecule itself was found to be a minimum on the PES. However, it was found to have two three-centre-two-electron bonds and three normal bonds. Its metastable nature was attributed to the weakly ionic character of the N-F bonds and the short F-F distances. The axial N-F bond lengths (r\textsubscript{ax} = 1.568 and r\textsubscript{eq} = 1.384 Å) are much longer than the N-F bonds in NF\textsubscript{3} (1.367 Å), ruling out this species as a full analog of 44. Also, r\textsubscript{ax}/r\textsubscript{eq} = 1.133 is significantly above one.

The discussion about hypervalent carbon compounds has been ongoing for years and many authors have claimed to synthesize the compounds in question. Forbas and Martin performed a \textsuperscript{1}H- and \textsuperscript{19}F-NMR spectroscopic study observing compounds 60a – c in 1979.\textsuperscript{124} Many other analogous compounds have also been synthesized (Scheme 18).\textsuperscript{125,126,127,128,129,130,131} The hypercoordinated compound 61 was synthesized and characterized by Yamamoto et al. (Figure 1).\textsuperscript{132} However, this compound is probably not a carbon analog to SiF\textsubscript{5} since r\textsubscript{ax}/r\textsubscript{eq} is too large (r\textsubscript{ax}/r\textsubscript{eq} = 1.91) due to its unusually long axial bonds of 2.43 and 2.45 Å. Yamamoto et al. also synthesized 62, in which the C-O distances was 2.64-2.75 Å, significantly shorter than the sum of the van der Waals radii of C and O (3.25 Å), but longer than a typical C-O single bond of 1.43 Å. The hypervalency of the TBP Si\textsubscript{2}(CH\textsubscript{3})\textsubscript{7}\textsuperscript{+} (63) by Abboud et al. can be ruled out due to its far too long and weak Si-C bonds (Figure 1).\textsuperscript{134} The apparently hexavalent compound CLI\textsubscript{6} was observed by Kudo in a mass spectroscopic experiment (Figure 1).\textsuperscript{135} Ten years earlier Schleyer and co-workers had found computationally that the extra electrons in CLI\textsubscript{5} (64) and CLI\textsubscript{6} (65) were involved in Li-Li-bonding causing the C-Li bonds to lengthen.\textsuperscript{136} Thus, Reed et al. determined using natural population analysis that the central C atom had less than an octet of electrons.\textsuperscript{137} Our NRT calculation now show that 56 has not even four electron pairs associated with the central C atom, and the leading resonance structure (67.9 %) had three covalent bonds between C and Li and a Li-Li bond between the two free Li atoms. For 65, our calculations gave inconsistent results given the O\textsubscript{h} symmetry. Exner and Schleyer studied 66 computationally and found that the number of electrons associated with its C atom do not exceed eight.\textsuperscript{138} It should also be mentioned that Naumkin computed the intermolecular charge-transfer metal-fluorocarbon complexes M:F\textsubscript{3}C-C(F\textsubscript{3})F, 67 and found that some of these could potentially have pentavalent C atoms.\textsuperscript{139} For this compound, r\textsubscript{ax}/r\textsubscript{eq} is only 1.056. The compound is how-
ever only hypercoordinated if the alkali metal ion is coordinated to the backside of the trifluoromethyl group. In this way it increases the effective electronegativity of the trifluoromethyl group.

\[
\begin{align*}
\text{52a: } X &= \text{CH}_3, R = \text{H} \\
\text{52b: } X &= \text{CH}_3, R = \text{t-Bu} \\
\text{52c: } X &= \text{F}, R = \text{H}
\end{align*}
\]

\[
\begin{align*}
\text{54} & \quad \text{55} & \quad \text{56} \\
\text{57} & \quad \text{58}
\end{align*}
\]

Scheme 18

Three-center-four-electron bonds are highly polar and most of the electron density resides at the substituents. Therefore electronegative substituents
facilitate coordination expansion at Si, P, and S. For the more electronegative central atom C to form hypervalent compounds, even more electronegative atoms or groups than F are needed in order to create a sufficiently large electronegativity difference. Both the He$^+$ and the Ne$^+$ ions have electronegativities above that of F and they are isoelectronic with H and F, respectively. For example, the Ne ion has been assigned an electronegativity of 4.79 compared to 4.19 for F in the scale of Allen. In this present study, the structure and electronic properties of CX$_5^{4+}$ was studied at the B3LYP/cc-pVTZ and CCSD(T)/cc-pVTZ levels of theory. Both the TBP CHe$_5^{4+}$ (68) and the octahedral CHe$_6^{4+}$ (69) are minima on the PES at the CCSD(T)/cc-pVTZ level of theory (Table 1). The $r_{ax}/r_{eq}$ value in 68 of 1.060 is close to one and the C-He bonds are only longer than normal C-H bonds by 0.15-0.22 Å (Table 1). For the TBP CNe$_5^{4+}$ (70), which is a stable minimum, the $r_{ax}/r_{eq}$ value is 1.062 (Table 1). As expected, 39 is a transition state for the S$_{N}$2-displacement reaction at the same level of theory with an axial bond length of 1.657 Å and a significantly shorter equatorial bond length of 1.344 Å. Thus $r_{ax}/r_{eq}$ = 1.233. For 68 and 69, the C-He bonds are longer than those of CHe$_4$ by 2.9, 9.1 and 8.4 %, respectively. The corresponding values when comparing 40 and 42 with SiH$_4$ are 3.9, 9.1 and 11.0 %, respectively. For 39, the bonds are elongated by 25.6 % when compared to 45. Moreover, if we compare the V$_X$ values in Table 1, we see that it is similar for 68 and 40, for 69 and 42, for 70 and 38, and finally for CNe$_6^{4+}$ (71) and 41. It can thus be concluded that 68 is the closest possible analog of 40 and 69 is the closest possible analog of 38 for which $r_{ax}/r_{eq}$ = 1.023. NRT calculations have been performed at the B3LYP/cc-pVTZ level of theory for 68 and 69, and they show that although the bond orders are in the range of 0.8-1.0, there are more than four electron pairs associated with the central C atom (Table 1). The leading resonance structure of 68 contributes with 70.8 % to the total electronic structure while that of 69 has a total contribution of 43.6 %. For 70, the leading resonance structure (58.1 %) has two equatorial bonds with lower bond orders and that of 71 has also two bonds with lower bond orders.

It can thus be concluded that 70, 68, 71, and 69 are the closest possible carbon analogs to 38, 40, 41, and 42, respectively.
Table 16. Geometric parameters and NRT results for the hypercoordinated species investigated.

<table>
<thead>
<tr>
<th>Species</th>
<th>Sym</th>
<th>$r_{X,L}$ (Å)</th>
<th>$p_{\text{val}}$(NPA)</th>
<th>$n_\text{X(NRT)}$</th>
<th>$V_\text{X(NRT)}$</th>
</tr>
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<tbody>
<tr>
<td>CF$_5^-$ (39)</td>
<td>D$_{3h}$</td>
<td>1.657 (ax)</td>
<td>C: 2.87</td>
<td>0.61 (eq)</td>
<td>3.85</td>
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<td></td>
<td></td>
<td>1.344 (eq)</td>
<td>F$_{\text{ax}}$: 7.58</td>
<td>0.88 (ax)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>F$_{\text{eq}}$: 7.34</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NF$_5^-$ (58)</td>
<td>D$_{3h}$</td>
<td>1.568 (ax)</td>
<td>N: 4.17</td>
<td>0.59 (ax)</td>
<td>3.70</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.383 (eq)</td>
<td>F$_{\text{ax}}$: 7.29</td>
<td>0.84 (eq)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>F$_{\text{eq}}$: 7.09</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiH$_5^-$ (40)</td>
<td>D$_{3h}$</td>
<td>1.618 (ax)</td>
<td>Si: 3.54</td>
<td>0.83 (ax)</td>
<td>4.46</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.532 (eq)</td>
<td>F$_{\text{ax}}$: 1.37</td>
<td>0.93 (eq)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>F$_{\text{eq}}$: 1.24</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiF$_5^-$ (38)</td>
<td>D$_{3h}$</td>
<td>1.671 (ax)</td>
<td>Si: 1.63</td>
<td>0.52 (ax)</td>
<td>3.91</td>
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<tr>
<td></td>
<td></td>
<td>1.634 (eq)</td>
<td>F$_{\text{ax}}$: 7.69</td>
<td>0.96 (eq)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>F$_{\text{eq}}$: 7.66</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiH$_6^2^-$ (42)</td>
<td>O$_h$</td>
<td>1.646</td>
<td>Si: 3.74</td>
<td>0.84</td>
<td>5.03</td>
</tr>
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<td></td>
<td></td>
<td></td>
<td>H: 1.38</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiF$_6^2^-$ (41)</td>
<td>O$_h$</td>
<td>1.717</td>
<td>Si: 1.33</td>
<td>0.76</td>
<td>3.93</td>
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<td></td>
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<td>F: 7.73</td>
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<tr>
<td>PF$_5$ (44)</td>
<td>D$_{3h}$</td>
<td>1.584 (ax)</td>
<td>P: 2.35</td>
<td>0.90 (ax)</td>
<td>3.82</td>
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<tr>
<td></td>
<td></td>
<td>1.546 (eq)</td>
<td>F$_{\text{ax}}$: 7.55</td>
<td>0.67(eq)</td>
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<tr>
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<td></td>
<td></td>
<td>F$_{\text{eq}}$: 7.51</td>
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<tr>
<td>CHe$_5^{4+}$ (68)</td>
<td>D$_{3h}$</td>
<td>1.308 (ax)</td>
<td>C: 2.90</td>
<td>0.83 (ax)</td>
<td>4.41</td>
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<tr>
<td></td>
<td></td>
<td>1.234 (eq)</td>
<td>He$_{\text{ax}}$: 1.44</td>
<td>0.92 (eq)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>He$_{\text{eq}}$: 1.39</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CNe$_5^{4+}$ (70)</td>
<td>D$_{3h}$</td>
<td>1.618 (ax)</td>
<td>C: 2.65</td>
<td>0.67(ax)</td>
<td>3.68</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.524 (eq)</td>
<td>Ne$_{\text{ax}}$: 7.50</td>
<td>0.78 (eq)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Ne$_{\text{eq}}$: 7.45</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CF$_6^2^-$ (57)</td>
<td>O$_h$</td>
<td>1.560</td>
<td>C: 3.00</td>
<td>0.62</td>
<td>3.75</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>F: 7.50</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CHe$_6^{4+}$ (69)</td>
<td>O$_h$</td>
<td>1.300</td>
<td>C: 3.26</td>
<td>0.82</td>
<td>4.90</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>He$_{\text{ax}}$: 1.44</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CNe$_6^{4+}$ (71)</td>
<td>O$_h$</td>
<td>1.622</td>
<td>C: 2.88</td>
<td>0.62</td>
<td>3.70</td>
</tr>
<tr>
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<td></td>
<td></td>
<td>Ne$_{\text{ax}}$: 7.52</td>
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</table>

* Optimized geometries at CCSD(T)/cc-pVTZ level.

bPopulation of the valence orbitals at each atom according to NPA calculations at B3LYP/cc-pVTZ.

c Bond orders according to NRT calculations at B3LYP/aug-cc-pVTZ level.

d Central atom valency according to NRT calculations at B3LYP/aug-cc-pVTZ level.

e Transition state structure.
9.3 The Prospect of Formation and Possible Existence of CX$_5^{4+}$ and CX$_6^{4+}$ (X = He, Ne)

While He$^+$ and Ne$^+$ can be generated by electron impact ionization,$^{141,142}$ the ions have been detected in both the radiation belt of the earth’s ionosphere and in the intergalactic medium.$^{143,144}$ One could speculate that 68 and 70 could be formed when C collides with He$^+$ and Ne$^+$ ions, which could be formed by electron-impact ionization.$^{145}$ However, our calculations show that the CX$_5^{4+}$ and CX$_6^{4+}$ ions are not global minima on the PES but are instead local minima of very high energy. The global minima correspond instead to a dissociated geometry where one or several noble gas atoms have left the central C atom. For example, at the (U)CCSD(T)/CC-pVTZ level of theory, the energy released for the departure of a He$_2^+$ ion from 68 to form CHe$_3^{3+}$ was 281.1 kcal/mol. This shows that the carbon equivalents to 38, 40, 41, and 42 most likely will be impossible to reach experimentally.
This thesis deals mainly with the similarities and differences in bonding configurations between the two elements carbon and silicon. In particular, ways to stabilize the unstable sila-analogs of alkenes and the unstable C analogs of the silicates SiF$_5^-$ and SiF$_6^{2-}$ are studied.

The SiC double bond is polarized towards carbon which makes the silenes prone to dimerization, moisture sensitive and unselective in reaction with dienes forming [2 + 2]- and ene-adducts in addition to [4 + 2]-adducts. The polarization of the SiC double bond also facilitates the electrocyclic ring-closure of 1-siladienes forming 1-silacyclobut-2-enes making these difficult to synthesize. These issues can be partially resolved by introducing so-called reverse SiC bond polarization through π-donating substituents at C and by using sterically bulky substituents both at Si and at C.

In the first chapter of this thesis, several computational methods for calculating different geometric and electronic properties of silenes and stannenes have been compared and among the inexpensive methods studied, the hybrid DFT functionals proved to be the best. This method is therefore by far the most used method throughout the studies in this thesis.

Previous studies have shown that silenes highly influenced by reverse polarization are less prone to dimerize, less reactive towards nucleophiles and react more selectively in for example Diels-Alder reactions. Quantum chemical calculations in this thesis have indicated that also other heavy alkenes, heavy imines and possibly also heavy ketone analogs from periods 3-5 in the periodic table are stabilized through reverse polarization towards both head-to-head and head-to-tail dimerization as well as towards reaction with nucleophiles.

One way to form isolated silenes from acyltetrasilanes and related derivatives is through a [1,3]-silyl shift. It has been found that silenes strongly influenced by reverse polarization more easily reverts back to starting material. They instead need to be trapped by for example dienes. However, our computational studies indicate that the silenes (SiH$_3$)$_2$Si=C(OSiH$_3$)(Me) and (SiH$_3$)$_2$Si=C(SSiH$_3$)(Me) have high enough barriers for the back-reaction to be isolable if the silyl groups are replaced by TMS groups and the methyl group by a larger alkyl group. The latter modification increase steric bulk and thus prevent dimerization and reactions with nucleophiles further. This is in line with Brook’s silene being stable at room temperature.
Formation of 1,1-disilyl-1-siladienes from electrocyclic ring-opening of 1,1-disilylsilacyclobut-2-enes are also facilitated by introducing reverse polarization through π-electron donating substituents at the 4-position. The activation energy for the reaction becomes lower and it also becomes less endothermic as the degree of reverse polarization is increased.

The final chapter in this thesis deals with the search for C analogs to SiF$_5^-$ and SiF$_6^{2-}$. Quantum chemical calculations confirm that more electronegative ligands than fluorine are required for carbon to formally accommodate more than four electron pairs in its valence shell. The trigonal bipyramidal molecules CNe$_5^{4+}$ is the closest possible carbon analog of SiF$_5^-$ while the octahedral molecules CNe$_6^{4+}$ is the closest analog of SiF$_6^{2-}$. However, these species correspond to local minima on the potential energy surface and they are of extremely high relative energy. Thus, there is very little prospect that one ever can form true carbon analogs to the silicates SiF$_5^-$ and SiF$_6^{2-}$. 
11. Acknowledgements

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And most of all, my girlfriend Maria, and my parents Mona and Christer.

Kisel, som står rakt under kol i periodiska systemet utgör 25,7 vikt-% av jordskorpan och är därmed det vanligaste grundämnet i jordskorpan efter syre. Det är ett kristallint ämne med en grå metallisk färg. Precis som glas är det starkt men skört. Den mest förekommande isotopen är $^{28}\text{Si}$ (92 %). Rent kisel kan inte hittas i naturen, utan förekommer istället i form av sand, kvarts, granit och lera som består av kiseloxider. Kisel har en viktig roll i växternas metabolism, men djur och människor behöver ämnet endast i små mängder.

Kisel är en halvledare som används, dopad med andra ämnen, i kretskort, hårdiskar, solceller, transistorer och dioder, och grundämnet är och har varit en förutsättning för den snabba datorutveckling som skett under de senaste årtiondena. En lättmetall-legering av kisel och aluminium har hög hållfasthet och används i bland annat bilar. Vidare ingår kisel i glas, cement och kera-
miska material. När professor Kipping vid universitetet i Nottingham i England år 1930 försökte tillverka kisel-syre dubbelbundna föreningar (Si=O), så kallade silikon eller kiselketoner, uppstod det näst största användningsområdet för kisel. Istället för kiselketoner bildades långa polymerer, så kallade polysiloxaner, som nu bär trivialnamnet silikon. Dessa utgör silikon som nu används bland annat i implantat, för att täta fogar och i kontaktlinser.

I en atom finns elektronerna i s-, p- och d-atomorbitaler. Dessa orbitaler har olika energi och form. Vidare kan de kombineras på olika sätt när molekylorbitaler bildas. En dubbelbindning består av två överlappande sp²-orbitaler, bestående av en s-orbital och två p-orbitaler, som bildar en så kallad σ-bindning och två överlappande p-orbitaler, som bildar en så kallad π-bindning. Det finns både stora likheter och skillnader mellan de molekylära strukturer som kol och kisel vanligtvis ingår i. Vissa strukturer som är vanliga för kol är ovanliga för kisel och omvändt (Tabell 1). Precis som kol binder kisel gärna fyra atomer eller atomgrupper runt sig och kan ocksåilda långa kedjor, så kallade silaner, och polymerer. Till skillnad från kol-kol bindningen är dock kisel-kisel bindningen lättare att kväva med om det bestrålas. Medan kol bildar stabila föreningar innehållande dubbelbindningar (C=C) och trippelbindningar (C≡C) med både sig själv och andra ämnen i andra perioden i det periodiska systemet, är motsvarande kiselöreningar instabila intermedier. I disilener (Si=Si) är det dålig överlappning mellan de två p-orbitalerna på kislet och π-bindningen är dålig svag och reagerar med både syre och vatten. Silener (Si=C) har också en svag π-bindning på grund av storleksskillnaden mellan kolens 2p- och kislets 3p-orbital. Dessutom är bindningen polär, på grund av elektronegativitetsskillnaden mellan kol och kisel. Silener reagerar därför med luftens fukt och syre, och både disilener och silener dimeriserar gärna och bildar 1,3-disilacyklobutaner i frånvaro av andra reagens (Figur 1).

Tabell 1: Skillnader i bindningsförhållanden mellan kol och kisel.

<table>
<thead>
<tr>
<th></th>
<th>Stabila föreningar</th>
<th>Instabila föreningar</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kol, C</td>
<td>C≡C</td>
<td>C≡C</td>
</tr>
<tr>
<td>Kisel, Si</td>
<td>Si≡Si</td>
<td>Si≡C</td>
</tr>
</tbody>
</table>

Figur 1: En generell reaktionsformel för sileners dimerisering varvid 1,3-
disilacyklobutaner bildas.

År 1981 bevisade Brook et al. och West existensen av silener och disilener. Genom stora, bulkiga grupper hindrade de molekylerna från att dimerisera och från att reagera med nukleofiler, dvs. ämnen med fria elektronpar.


En kemisk förening där en centralatom binder fler än fyra ligander kallas för hyperkoordinerad. Ibland talar man också om hypervalens, som vanligtvis innebär att centralatomen har fler än åtta elektroner i yttersta skalet. Så är dock inte fallet för många hyperkoordinerade kiselföreningar, som SiF\textsubscript{5}\textsuperscript{-} och SiF\textsubscript{6}\textsuperscript{2-}, enligt kvantkemiska beräkningar av Professor Frank. A. Weinhold och C. R. Landis. Iställt är de extra elektronerna lokaliserade till liganderna, vilket ger färre än åtta elektroner kring kisel.

En del forskare menar att begreppet hypervalens ska ersättas med en två-elektronregel i första perioden, en åtta-elektronregel i andra perioden och en 18-elektronregel i tredje perioden i det periodiska systemet. I den här avhandlingen letar vi efter de hyperkoordinerade kolföreningar som mest liknar SiH\textsubscript{5}\textsuperscript{-}, SiF\textsubscript{5}\textsuperscript{-}, SiH\textsubscript{6}\textsuperscript{2-} och SiF\textsubscript{6}\textsuperscript{2-}. För dessa kolföreningar ska ungefär samma antal elektroner tillskrivas kol som tillskrivs kisel i mostvarande kiselföreningar. Skillnaden mellan de axiella och de ekvatoriella bindningarna får inte vara alltför stor (\textit{r}_{ax}/\textit{r}_{eq} ≈ 1) och bindningarna får inte skilja sig alltför mycket från normala enkelbindningslängder mellan liganden och centralatomen, vilket är fallet för de fyra kiselföreningarna ovan. Vi har upptäckt att kolföreningarna vi söker är CHe\textsubscript{5}\textsuperscript{4+}, CNe\textsubscript{5}\textsuperscript{4+}, CHe\textsubscript{6}\textsuperscript{4+} och CNe\textsubscript{6}\textsuperscript{4+}.

Det forskningsprojekt som presenteras i denna avhandling hör till den grundläggande forskningen som har till huvudsyfte att öka vår förståelse av och kunskap om hur naturen fungerar. Avhandlingen ger en ökad förståelse för likheter och skillnader mellan kol och kisel. Speciellt kommer metoder
att stabilisera silener och hypervalenta kolföreningar att diskuteras. Den första studien som omnämns jämför olika beräkningsmetoder för att beräkna olika elektroniska och strukturella egenskaper hos silener och stannener (C=Sn dubbelbundna föreningar).


\[
\begin{array}{ccc}
   & X & Y \\
I & Si & Si \\
   & Y & X \\
II & Si & Si \\
   & Y & X \\
III & Si & Si \\
\end{array}
\]

Figur 2: De tre mest dominerande resonansstrukturerna för en silen med π-elektronondonerande grupper på C.

Naturligt polariserade silener reagerar med diener och bildar då [4+2]-addukter, [2+2]-addukter och/eller en-addukter (Figur 3). För att en reaktion ska kunna bli intressant för organisk syntes är det viktigt att en produkt bildas i högt utbyte.

\[
\begin{align*}
   & Si=X & Y \\
   & Si=X & Y \\
   & Si=X & Y \\
\end{align*}
\]

Figur 3: De olika produkter som kan bildas då en silen reagerar med en dien.

Omvänt polariserade silener är mindre reaktiva gentemot luftens fukt och syre än naturligt polariserade silener och de har mindre tendens att dimerisera. Med hjälp av kvantkemiska beräkningar har vi funnit att detsamma gäller för andra tunga alkener, tunga iminer (C=X; X = P, As eller Sb) och tunga ketoner (C=X; X = S, Se eller Te). Silener influerade av omvänt polarisering reagerar också mer selektivt med diener och ger högre andel [4+2]-addukter. Experimentella studier inom gruppen har visat att framställning av omvänt polariserade silener genom upphettning av karbamyltetrasilaner i närvaro av diener ger Diels-Alder addukter utan att man behöver utesätta luft eller
använda vattenfria lösningsmedel. I denna avhandling undersöker vi vilka egenskaper hos silener som påverkar aktiveringsenergin och den relativa energin hos silener som bildas termolytiskt genom en omlagring (Figur 4). Vi studerade även hur silenernas geometri påverkades av substituenterna.

\[ \begin{align*}
\text{Si} & \text{H}_3 \text{Si} - \text{Si} - \text{Si} - \text{Si} \text{H}_3 \\
\text{R} & \text{X} \quad \Delta \\
\text{Si} & \text{H}_3 \text{Si} - \text{Si} - \text{Si} - \text{Si} \text{H}_3 \\
\text{R} & \text{X}
\end{align*} \]

\( X = \text{NMe}, \text{O or S}; Y = \text{NMe}_2, \text{OMe, SME or Me} \)

\( R = \text{reaktant}; S = \text{Silen} \)

**Figur 4:** Figur som visar hur en silan omlagras till en silen via termolys.

Starkt omvänt polariserade silener har betydligt lägre aktiveringsenergi för att omlagras tillbaka till startmaterialet. De bör dock kunna ge Diels-Alder addukter om de bildas i närvaro av diener. I en annan beräkningskemisk studie angående syntesen av 1-silabutadiener genom elektrocyklisk ringöppning av silacyklobut-2-ener fann vi att aktiveringsenergin för framställning av omvänt polariserade 1-siladiener var lägre än för naturligt polariserade silener (Figur 5). Silenernas energi var också lägre i förhållande till start materialet för dessa silener.

\[ \begin{align*}
\text{H}_2\text{N} \quad \text{R} \quad \text{Si} & \text{R} \\
\text{R} \quad \text{Si} & \text{H}_2\text{N} \quad \text{R} \\
\text{s-cis} & \text{s-trans}
\end{align*} \]

**Figur 5:** Figur som visar ringöppningen av 1-silacyklobut-2-ener. Till 1-siladiener samt den kemiska jämvikten mellan s-cis och s-trans form hos dessa silener.

Omvänd polarisering är alltså nyckeln för att stabilisera de bindningsförhållanden som är stabila för kol, men instabila för kisel. Elektronegativitet visar sig vara nyckeln för att stabilisera de bindningsförhållanden som är instabila för kol, men stabila för kisel. Eftersom vi sett ovan att en stor del av elektronätheten ligger på liganderna i ett pentakoordinerat eller hexakoordinerat system går de från att vara sadelpunkter till att vara minima på potentialenergiytan när ligandernas elektronegativitet ökar. Vi har funnit med hjälp av kvantkemiska beräkningar att kol teoretiskt kan bilda föreningar med koordinationstalen 5 och 6 om elektronegativa ligander som He⁺ och Ne⁺ används.
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