ALIEN MOLECULES ON EARTH

PhD dissertation

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Hálás köszönettel tartozom témavezetőmnek, Dr. Veszprémi Tamásnak a kimeríthetetlen türelméért, magyarázataiért, tanácsaiért és kutatómunkám irányításáért.


Köszönöm feleségemnek, Skara Gabriellának, hogy mindig mellettem állt és mindig, mindenben támogatott.

Hálás vagyok szüleimnek és testvéreimnek, hogy mindig hittek bennem és, mint egy biztos pont, nyugodt légkört teremtettek körülöttem.

Az együtt eltöltött évekért, a közös kutatómunka fáradását, beszélgetéseinkért és a rengeteg segítségért hálás vagyok Olasz Andrásnak.

Dr. Zsombok Györgynek köszönöm a humoros és családi hangulat megteremtését a tanszéken valamint a kérdésemre adott építő jellegű válaszait.

Köszönöm a csoport jelenlegi és volt diákjainak, Okinak, Dinónak, Tomának, Julinak, Gábornak, Tibinek, Hidrinek, Klárinak, Kingának és Tibinek a jó hangulatot, segítséget, tanítást, élményeket, ebédeket és pókerjátékmákat.
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1 INTRODUCTION

“Where shall I start, please your majesty?” he asked.

“Begin at the beginning,” the king said gravely,

“and go on till you come to the end: then stop.”

Lewis Carroll

It is well-known that, by today, computational/quantum chemistry has reached the reliability and accuracy of experimental methods and it could help in all branches in chemistry; it can be used to analyze spectra, design drugs, reveal reaction mechanisms, provide thermodynamically data and so on and even to understand atmospheric chemistry processes.

For very long, silicon chemistry has been one of the leading research fields of the Department of Inorganic Chemistry of the Budapest University of Technology and Economics. Accordingly, our group deals with a special branch of silicon chemistry; with hypovalent silicon/germanium/phosphorous compounds. This is how I got involved in the calculation of silylenes and disilenes.

I got my first research project in 2001 as a second year student, just after Sekiguchi’s group reported the isomerization of 1-disilagermirene* into 2-disilagermirene. With the supervising of prof. Tamás Veszprémi and collaboration of András Olasz our primary aim was the exploration of the mechanism of this extraordinary reaction. This project resulted a prize in the Scientific Student Conference and a Schay prize and finally our results were published in two articles.

My second project related to silicones came into light when a new carbene, cyclopronelylidene, was synthesized in 2006. Our goal was twofold; to explore the stabilizing factors in the new

structure and to determine whether the identical silicon and germanium molecules are synthesizable.

Cyclopropenylidene was first identified by Thaddeus et al. in 1985 in various sources [1a], including Orion A and in diffuse molecular clouds. It has also been observed in extragalactic sources, such as NGC 5128 [1b] and NGC 253 [1c], and is now the most abundant cyclic hydrocarbon observed in interstellar space. On Earth cyclopropenylidene is highly reactive, and acts as an intermediate in numerous organic chemical reactions. All previous efforts to isolate it in the laboratory have failed until 2006, when Bartrand’s group managed to stabilize cyclopropenylidene by attaching amino groups. The new molecule was commented in a short report as „Chemists bring alien molecule down to Earth” [2]. This inspired me to change the original „Hypovalent three-membered ring compounds containing Group 14 elements” title of this thesis to “Alien molecules on Earth”.

My thesis includes six chapters. Chapter 2 gives an overview of achievements in silylene/carbene, cyclotrimetallene and bridged compound chemistry. I shortly introduce the base of quantum chemistry and few special theories within it in Chapter 3. In the Result part (Chapter 4) I explain the prominent stability of cyclopropenylidene (4.1), discuss the synthesizability of “heavy weight” alien molecules (4.2 and 4.3), explore the mechanism of cyclotrimetallene rearrangements (4.4) and analyze bridged structures (4.5). Summary and references are given in Chapters 5 and 6, respectively.

For numbering the molecules and structures the set of four characters is used in this thesis, viz. bold lowercase fonts, bold uppercase fonts, Arabic and Roman numerals. a, b… are used in the Literature survey part (Chapter 2) to distinguish the general molecular skeletons. In these cases, for a given molecule the substituents are specified in brackets in the text. For instance hexamethylcyclopropane is a (R=Methyl). Unfortunately, I run out of single letters and I had to introduce the double characters, such as aa, bb, etc. Since there are molecules which are referred many times through the text, for the sake of simplicity, these are highlighted by Roman digits (I, II, etc.). In the Result section (Chapter 4) the isomers are signed and numbered sequentially from 1 to 101. For the sake of lucidity all the investigated molecules and their numbers are shown in bookmark enclosed for the thesis. The suffixes H and NH₂ are used to distinguish the hydrogen and diamino substituted species in the text. For instance 1-H represents the cyclopropenylidene,
while $\textbf{1-NH}_2$ is the diamino-cyclopropenylidene. Bold capital letters (A, B, etc.) represent different resonance structures or ring frameworks always specified for the actual use. The skeletal atoms are distinguished by the $\alpha$, $\beta$ and $\gamma$ symbols.
2 LITERATURE SURVEY

Life's too short; eat dessert first.

Snoopy

The main keywords of this thesis are divalent\(^*\), unsaturated and bridged three-membered ring compound of group 14. Accordingly, this chapter contains three main sections dealing with the literature of divalent, unsaturated and bridged structures. The common skeletal in the investigated molecules is, however, the three-membered ring containing carbon, silicon or germanium atoms. Hence, it is worth to start this chapter with a brief introduction of the chemistry of the parent saturated three-membered ring compounds.

2.1 Saturated three-membered rings

The smallest cycloalkane, cyclopropane (\(\text{a}\)) is discussed in every elementary organic chemistry books. It is the simplest example in which the two different kinds (angle and torsional) of ring strain can be easily introduced. Angle strain arises when the C-C-C bonds of the ring depart from the ideal tetrahedral angle preferred for sp\(^3\) carbon while torsional strain arises when bonds are not ideally staggered. Since the C-C-C angles are forced to be 60 degree and all of the C-C bonds are eclipsed in a, the evolving ring strain is expected to be large. Accordingly, from heats of combustion measurements the estimated total ring strain in cyclopropane is 28 kcal/mol [3]. Destabilization caused by ring strain is reflected in the reactivity of cyclopropane. Although it is still easily isolated and stored, much more reactive than acyclic alkanes and other cycloalkanes such as cyclopentane or cyclohexane.

\(^*\) Having a valence of two. The number of bonds an atom forms corresponds to its valence. The Columbia Encyclopedia, Sixth Edition
Of the ten possible variations for cyclotrimetallane rings (See in Scheme 1, a-j) made of C, Si, and Ge, all have been synthesized to date. The silacyclopropane (b, silirane) chemistry began with the synthesis of hexamethylsilirane (b, R=CH$_3$) in 1975 [4]. It is stable under inert atmosphere and it can be kept at 0 degree for prolonged periods of time and at room temperature for at least 9 days. The un-, mono- and di-substituted (considering the substituents on the ring carbons) siliranes are also known [5]. Their polarized Si$^{+}$–C$^{-}$ bonds are highly reactive towards polar reagents in vigorous and exothermic reactions [6]. Comparing the stability of cyclopropane and silacyclopropane it turns out that the latter is less stable because of the lack of stabilization through σ–electron delocalization due to poor orbital energy and size mismatch [7]. The calculated ring strain is also higher in the heterocycle (38 kcal/mol) than in the carbon ring (27 kcal/mol) [8]. The synthesis of the corresponding stable germanium analogues (c) was also achieved [9], however, germiranes having no substituents on the ring carbons appear mostly as short lived intermediates [10].

As early as 1976 the first evidence of the formation of a disilacyclopropane (d, disilirane) was reported by Seyferth and Duncan [11]. It is surprising that up to now only four other disilacyclopropanes have been isolated [12], two of them were characterized by X-ray crystallographic analysis. Analogously to the silicon species, only a few stable digermacyclopropanes (e, digermirane) are known. The representatives of both groups are moderately persistent to air and moisture. Their curious utility is the functionalization of fullerene; the addition of both disiliranes and digermiranes with C$_{60}$ takes place and occurs via the intermediacy of an exciplex [13]. Interestingly, the silicon analogues provide 1,2-cycloadduct [13a] while the germanium analogues give 1,4-cycloadduct [13b]. The formation and several reaction of the only existing silagermirane (f, C-Si-Ge ring) were reported by Gaspar and co-workers in 1997 [14].
Cyclotrisilanes (g) and cyclotrigermanes (h) have attracted considerable attention due to their unusual chemical reactivity; they undergo photochemical or thermal ring cleavage to afford disilenes, digermenes (Scheme 2) [15, 16]. Their syntheses are severely limited by a critical dependence on the size of the applied substituent. If the substituents are not very bulky (for example, methyl or phenyl), four- or higher-membered ring is obtained during the reductive cyclization [17]. If the substituents are too large, disilene [18] (digermene [19]) may be formed directly. Despite much research in the area of cyclosilanes and -germanes, only a limited number of saturated three-membered ring compounds containing both silicon and germanium are known: to date there are two stable siladigermiranes (i) [20] and less than a dozen stable disilagermiranes (j) [21].

2.2 Low coordinated three-membered rings I. Three-membered rings containing divalent atom

2.2.1 Synthesis of carbenes and silylenes

Elements of Group 14 exist mainly in tetravalent form in their compounds, however, the heavier members are suitable to form hypovalent structures. Indeed, the divalent lead compounds are usually more stable than the corresponding tetravalent lead compounds. Nevertheless, compounds which contain divalent carbon atom are known for a long time and found to be very reactive intermediates. The presence of carbene intermediates were assumed in certain reactions by Buchner and Curtis already in the end of the 19th century [22]. Their result came into interest when Hine suggested CCl₂ intermediates in the alkali base hydrolysis of chloroform [23]. In spite of their short lifetime, carbenes play an important role in synthetic organic chemistry.
The first carbene, which was stable under standard conditions, was synthesized in 1991 by Arduengo’s group (k, R₁=Adamantly, R₂=H) [24]. It shows astonishing thermal stability, its colorless crystals are melting at 240 °C and are persistent in the absence of air at room temperature. Related carbenes with various substituents (R₁=t-Butyl, R₂=H; R₁=t-Tolyl, R₂=H; R₁=Methyl, R₂=Methyl; etc.) were also reported [25]. So, the doctrine that carbenes were only transient species disappeared and a new and exciting field of research was developed for synthetic chemists. Up to now, from then, a number of milestones reflect (Scheme 3) the intense research of carbenes; the saturated analogue of Arduengo carbene was isolated in 1995 [26] (l, R₁=Mesityl, R₂=H), the first stable open-chain carbene, bis-diizopropylcarbene was synthesized in 1996 [27] (m, R=i-Pr), thiazol-2-ylidene (n, R=Dipp) which did not contain two stabilizing amino groups was bottled in 1997 [28] and the preparation of o (R=N(i-Pr)₂) and p (R=i-Pr) which feature only one heteroatom substituent were also reported [29]. The carbene, which has no heteroatom substituent directly linked to the carbene center (q, R=N(i-Pr)₂) was even isolated in 2006 [30].

\[ ^{\dagger}\text{Dipp}=\text{diisopropylphenyl} \]
Similarly to the carbenes, most of the divalent silicon compounds have short lifetime. Silylenes were investigated in argon and hydrocarbon matrices already in the 70’s [31]. At higher temperature, however, these silylenes went under dimerization. The first stable silylene, the silicon analogue of Arduengo carbene (r, \( R_1=\text{-Butyl}, R_2=\text{H} \)), was synthesized by Denk et al. in 1994 (Scheme 4) [32]. The preparation of r was followed by the synthesis of its saturated analogue, s (\( R_1=\text{-Butyl}, R_2=\text{H} \)) [33] and the preparation of the benzo and (t, \( R=\text{Np} \)) pyrido-fused (u, \( R=\text{Np} \)) silylenes [34, 35]. All of these molecules are stabilized by two nitrogen atoms bonded to the divalent center. More recently, Kira et al. have isolated a silylene, (v, \( R=\text{SiMe}_3 \)) with no such nitrogen stabilization [36]. As a matter of fact the chemistry of silylenes is evolving parallel to that of carbenes and is girt by increasing interest to this day.

### 2.2.2 Stabilization of carbenes and silylenes

From the electronic point of view the ground state of \( \text{CH}_2 \) is triplet, while that of \( \text{SiH}_2 \) and most of the silylene derivatives is singlet (Scheme 5). Thermodynamically, the singlet state can be stabilized by electronegative groups while triplet state can be stabilized by electropositive substituents. Using correlated ab initio methods the singlet-triplet energy gaps for \( \text{CH}_2 \) and \( \text{SiH}_2 \) are ca. -10 and 20 kcal/mol, respectively.
It is obvious, that the criterion of synthesizability of these divalent compounds is the appropriate stabilization of the singlet state. There are two ways to stabilize the singlet state [37,38], first using bulky groups around the reactive center (kinetic stabilization), second stabilizing the electron configuration via appropriate substituents (thermodynamic stabilization).

The electron configuration of molecules has an effect on their geometries. For instance, the bond lengths are always shorter in triplet than in singlet state. Bond angles for carbenes and silylenes respectively are around 90 and 100 degree in singlet and around 120 and 130 degree in triplet state [39]. Accordingly, the bigger the bond angle the more stable the triplet state of the silylene compound [40]. It was predicted by Apeloig and co-workers that triisopropylsilyl iPr$_3$Si substituents would be the smallest that would open the bond angle to the ‘crossover angle’ for bis-silylsilylenes (singlet-triplet energy difference is 1.7 kcal/mol) [41]. Finally, the efforts to synthesize triplet silylene brought success in 2001 with tri-tert-butylsilyl (triisopropylsilyl)silylene ($t$Bu)$_3$Si-Si-Si(iPr)$_3$ [42].

Scheme 5. Schematic representation of the singlet and triplet states of carbenes, silylenes and germynes.

Scheme 6 shows the main stabilization effect of these hypovalent structures. Singlet carbenes and silylenes have a lone pair in the plane of the molecule and an empty p orbital perpendicular to the plane. Functional groups which have occupied p orbital parallel to that of divalent center and liable to donate this electron pair to the empty p of C or Si stabilize the singlet electron configuration. Thus, the singlet molecule is stabilized by a pπ-pπ conjugation (Scheme 6, blue).
compared to both the triplet and the first excited singlet state [43]. Such stabilizing substituents are the amino (NH$_2$), hydroxyl (OH), thio (SH) and halide functional groups. The effect of electronegativity also plays an important role in the stabilization (Scheme 6, red). For instance, connecting a methyl group to the Si(II) center instead of hydrogen (the electronegativity of carbon is slightly higher than that of hydrogen) increases the singlet triplet energy gap only by 5 kcal/mol. If hydrogen is substituted by electropositive Li or BeH the triplet state is stabilized in the same way as in the case of MgH and AlH$_2$ substituents. In contrast the fluorine substitution extremely increases the singlet-triplet separation, the singlet lies 57 kcal/mol lower than the triplet state. $\pi$-acceptors, such as CN, HCO also destabilize the singlet state of carbenes and silylenes.

Pople et al. investigated the effects of functional groups deriving from the first row elements of the periodic table on the geometry, energy and electron configuration of silylenes and carbenes [44]. Using ab initio methods and bond-separation (a special isodesmic reaction) techniques they found that the amino and hydroxyl groups cause the highest stabilization (22.3 and 15.0 kcal/mol). Other studies lead to similar conclusions: the most efficient substituents to stabilize the divalent silicon (or carbon) center are the NH$_2$ [43] followed by SH [45] and OH groups. The stabilization has been attributed to the interaction between the empty p-type orbital of the carbon/silicon center and the lone pair of the neighboring group, by forming a dative $\pi$-bond. Disubstitution by these groups increases the stability of the silylene, but the effect of the second substituent is smaller than that of the first one [46]. This has been attributed to the saturation of the empty 3p orbital of the silicon with electrons.

2.2.3 Stable carbenes and silylenes. Imidazol-2-ylidene derivatives

Contrary to the usual expectation, the imidazol-2-ylidenes (k) show high stability and can be handled under inert atmosphere. Since the extraordinary stabilization in the five-membered imidazol-2-ylidenes and their silicon analogues (r) could not be ascribed only to the effect of substituents, their electronic structures have already been thoroughly investigated in both experimental and theoretical manner. The major conclusions are summarized in Table 1.
<table>
<thead>
<tr>
<th>Year</th>
<th>Property studied</th>
<th>Method</th>
<th>Conclusion</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>1991</td>
<td>electronic structure of ( k ) in the lowest singlet and triplet states; proton affinity</td>
<td>correlated ab initio calculations</td>
<td>bonding character carbenic rather than ylidic; ( \pi )-delocalization important in imidazolium cation but not in the carbene</td>
<td>[47]</td>
</tr>
<tr>
<td>1993</td>
<td>electronic structure of ( k ): bond orders, atomic charges, localized natural orbitals</td>
<td>correlated ab initio calculations</td>
<td>stabilization of singlet ground state by ( \sigma )-back-donation along C-N bonds; ( \pi )-delocalization plays only a minor role in ( k ), but a major role in imidazolium cation</td>
<td>[48]</td>
</tr>
<tr>
<td>1994</td>
<td>electronic structure of aminocarbenes: singlet-triplet splittings, Mulliken populations, barriers for 1,2-rearrangements to imines</td>
<td>correlated ab initio calculations</td>
<td>singlet-triplet splitting in ( k ) is 15 kcal/mol higher than in ( l ); consequently smaller propensity of the former towards dimerization; ( k ) kinetically stable toward rearrangement to imidazole</td>
<td>[49]</td>
</tr>
<tr>
<td>1994</td>
<td>chemical shielding tensor of ( k )</td>
<td>solid-state NMR, correlated ab initio and DFT calculations</td>
<td>dominance of carbenic over ylidic resonance structures in ( k )</td>
<td>[50]</td>
</tr>
<tr>
<td>1994</td>
<td>photoelectron spectra of ( k ) and ( r )</td>
<td>photoelectron spectroscopy; density-functional calculations</td>
<td>degree of interaction between the ( \pi )-electrons of the five-membered ring and the divalent atom higher in ( r ) than in ( k )</td>
<td>[51]</td>
</tr>
<tr>
<td>1994</td>
<td>electron distribution in a substituted ( k )</td>
<td>X-ray and neutron diffraction, DFT calculations</td>
<td>( \pi )-delocalization not dominant in ( k ), its stability is kinetic in origin</td>
<td>[52]</td>
</tr>
<tr>
<td>1996</td>
<td>electronic structure of stable carbenes, silylenes, and germynes</td>
<td>correlated ab initio calculations</td>
<td>( \pi )-delocalization more extensive in ( k ) compared to ( l ); ( k ) has partial aromatic character; similar conclusions for isostructural silylenes and germynes</td>
<td>[53]</td>
</tr>
</tbody>
</table>
### Alien Molecules on Earth

<table>
<thead>
<tr>
<th>Year</th>
<th>Topic</th>
<th>Methods</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>1996</td>
<td>thermodynamic, structural, and magnetic criteria, the properties of the charge distributions, and low-energy ionization processes in ( k )</td>
<td>correlated ab initio calculations</td>
<td>planar amino substituents stabilize singlet carbenes significantly, aromaticity of ( k ) is about 60% of that of benzene</td>
</tr>
<tr>
<td>1996</td>
<td>aromaticity of 6( \pi )-electron heterocyclic ring carbenes</td>
<td>correlated ab initio calculations</td>
<td>aromatic stabilization ranging from 7.6 to 25.5 kcal/mol. The most highly stabilized system is ( k )</td>
</tr>
<tr>
<td>1999</td>
<td>inner shell electron energy loss spectra of 1,2,3,4,5,6</td>
<td>inner shell electron energy loss spectroscopy and ab initio calculations</td>
<td>strong N-E-N delocalization in all species, aromaticity is a factor in explaining the exceptional stability of ( k )</td>
</tr>
<tr>
<td>2007</td>
<td>vibrational and electronic spectra and electronic structure of ( k )</td>
<td>Raman, IR and UV spectroscopy, correlated ab initio calculations</td>
<td>high ( \pi )-conjugation</td>
</tr>
<tr>
<td>2008</td>
<td>intermolecular hydrogen bonds in crystalline ( k )</td>
<td>IR spectroscopy, X-ray diffraction analysis</td>
<td>hydrogen bonds found for ( k ) form a chain throughout its crystal lattice.</td>
</tr>
</tbody>
</table>

### Silylenes

<table>
<thead>
<tr>
<th>Year</th>
<th>Topic</th>
<th>Methods</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>1994</td>
<td>gas-phase structure and solution-phase NMR, theoretical heats of hydrogenation for ( r ) and ( s )</td>
<td>electron diffraction; correlated ab initio calculations</td>
<td>( r ) benefits from aromatic stabilization</td>
</tr>
<tr>
<td>1994</td>
<td>photoelectron spectra of ( r ) and ( s ); rotational barriers in Si(( \text{NH}_2 ))(_2) and C(( \text{NH}_2 ))(_2)</td>
<td>photoelectron spectroscopy; correlated ab initio calculations</td>
<td>significant ( \pi p-\pi p ) interaction between divalent center and amino substituent; aromatic resonance structures contribute significantly in ( r )</td>
</tr>
<tr>
<td>1996</td>
<td>chemical shifts and anisotropies in aminosilylenes</td>
<td>correlated ab initio calculations</td>
<td>significant degree of 6( \pi )-aromaticity in ( r )</td>
</tr>
<tr>
<td>1996</td>
<td>synthesis, electronic structure and reactions of ( r ) and ( s )</td>
<td>X-ray crystallography, proton NMR, correlated ab</td>
<td>some degree of aromatic delocalization in ( r ), greater ( \pi )-donation is expected for ( s )</td>
</tr>
</tbody>
</table>
It has been shown that the main stabilization factor in both unsaturated species (k and r) is the π-electron donation of the amino groups to the empty 2p and 3p orbital of the carbon and silicon [66], respectively. Since the molecule of k contains six π-electrons in a planar cycle, it obeys the Hückel rule. It can be seen from the table, however, that there has been a long debate on the extent and role of aromaticity in k and in the related systems. Arduengo supposed that k is a true carbene (A in Scheme 7) with only negligible importance of π-delocalized ylidic resonance structures; in particular, the stability of carbenes k was regarded as kinetic and explained by electron density accumulation around the carbene center, which protects the molecules from an attack by nucleophiles.
On the other hand, different methods lead to diverse conclusions regarding the extent of aromaticity. The aromaticity of \( \mathbf{k} \) was discussed and confirmed using energetic, chemical, structural and magnetic criteria. There is an agreement in the literature that the isostructural silylenes \( \mathbf{r} \) do in fact benefit from aromatic 6\( \pi \)-electron delocalization. However, the existence of stable imidazolyn-2-ylidene (\( \mathbf{l} \)) and the related silylene derivative \( \mathbf{s} \) proved that it had no essential role in the stabilization, although, these molecules slowly isomerize or dimerize.

### 2.2.4 A new stable carbene. Cyclopropenylidene derivatives

Profiting the advantages of the cyclic structure, carbene and silylene chemistry become fruitful fields for organic and organometallic chemists. Accordingly, most of the synthesized compounds have an imidazol-like five membered-ring skeletal. That is why the synthesis of bis(diisopropylamino)cyclopropenylidene (\( \mathbf{q} \)) in 2006 gave a new twist to the story of carbenes [30]. The new carbene is a stable, yellow crystal with a melting point between temperatures of 107° to 109°C. The same compound was mentioned to be transient carbene so far in 1997. The previous attempts to isolate cyclopropenylidene have failed, however, but its complexes with transition metals and main group elements have been known for many years. Nevertheless, one year after the first isolation the synthesis of bis[bis(R-1-phenylethyl)amino]cyclopropenylidene, a chiral cyclopropenylidene derivative was also reported [67].

The parent cyclopropenylidene (\( \mathbf{q} \), \( \text{R=H} \)) prepared first by high-vacuum flash pyrolysis was detected in 1984 [68]. Its significant abundance in outer space was also shown while its further investigation was achieved by matrix isolation procedures and in low-density plasma [1]. Many authors dealt with the aromaticity of \( \mathbf{q} \). Gleiter and Hoffmann have already predicted that it has singlet ground state stabilized by the interaction between the carbene center and the unsaturated part of the molecule [69]. One of the early studies written by Simons \textit{et al.} stated that the effect of cyclic delocalization is an important factor in the electronic configuration [70]. Further, Pople
and co-workers attributed the stability of cyclopropenylidene to the aromaticity [71]. Two additional C₃H₂ isomers, vinylidenecarbene [72] and propargylene [73], are also known and the interconversion among the three isomers was demonstrated [74].

The silicon analogue, i.e. the silacyclopropenylidene (z), and further 14 higher lying singlet C₂SiH₂ isomers were theoretically investigated by Frenking et al. [75] while the infrared spectra of several of these isomers were experimentally observed by Maier et al. using a matrix-spectroscopic technique [76]. The effect of different halogen substituents [77], the ionization potentials, the electron affinities [78] and the triplet isomers [79] were also studied for this system. The study of the related germanium compounds involving germacyclopropenylidene belongs to a less explored field of chemistry. Only one paper was published about this system in which Kassae et al. predicted the switching of global minima for the GeC₂HX (X=H, F, Cl, Br) system: instead of the ring analogue the acyclic germoproapargylene becomes the global minimum of the corresponding PES using electronegative halogen substituents [80].

Considering the synthesizability of carbenes, silylenes and germynes one has to take also into account their kinetic stability. The reactivity of divalent compounds can be sorted into three classes: electrophilic, nucleophilic and radical reactivity. The triplet state of the species is liable for the latter property. Since the singlet-triplet energy gap is high for stable carbenes and silylenes, i.e. the triplet state is high in energy, no radical-like reactivity can be observed for stable divalent species. The nucleophilic and electrophilic reactivity evolve by virtue of the lone pair electrons and the empty p orbital in the singlet state, respectively. Carbenes and silylenes are known to be nucleophilic and take place in many reactions as a nucleophilic reagent. Using appropriate solvent and inert atmosphere these reactions can be avoided.

Scheme 8. The orientation of the approaching carbene monomers during dimerization

On the other hand, three types of self-reaction can hinder the isolation of carbenes: dimerization, isomerization and insertion. Both the nucleophilic and electrophilic properties are responsible for
the dimerization while isomerization and insertion were attributed only to the electrophilic reactivity. When carbenes undergo dimerization with formation of homonuclear double bond the carbene monomers are approaching in perpendicular planes (Scheme 8) and the interaction may be described as the attack of the lone pair of the first monomer on the empty p orbital of the second monomer. It has been shown that stabilized carbenes do not dimerize and that the singlet-triplet splitting are related to the dimerization energy of carbenes [81]. Generally, two major mechanisms are relevant for the dimerization reaction of silylenes and germynes; the „classical“ disilene formation (Scheme 9, blue) [82] and a donor-acceptor adduct which is produced via the overlap of a substituent’s lone pair and the p orbital of the divalent center (“bridge” way) (Scheme 9, red) [83]. The relationship between stability, dimerization ability and singlet-triplet energy gap of silylenes was investigated and described by Oláh et al. [65]. Competition between the routes and temperature dependence were observed by Takahashi et al. [84]. Further complications, such as steric hindrance in the case of Denk silylene, can modify the mechanism of the dimerization [85].

Scheme 9. The classical (left) and bridge (right) dimerization ways of silylenes

The tautomerization and the electrophilic reactivity (modeling with hydride ion addition) of k and r were investigated Böhme and Frenking [53]. They found that the reluctance of stable carbenes to participate in these reactions is kinetic in origin. The systematic study of the electrophilic and nucleophilic character of silylenes and germynes was also presented investigating their complexation ability with Lewis acids and bases. It was shown that stable silylenes and germynes do not form stable complex because the electron donating substituents decrease their electrophilicity. As a main consequence, the vacant p orbital of stable divalent compounds is pumped up by electrons due to the delocalization, causing considerable electron repulsion against any incoming nucleophile thereby preventing against any self-reaction.
2.3 Low coordinated three-membered rings II. Three-membered rings containing double bond

Another type of low coordinated three-membered ring compounds is three-membered rings with double bonds, i.e. the cyclopropene (Scheme 10, aa) and its heavy analogues (bb-hh) (cyclotrimetallenes). Cyclopropene, the smallest unsaturated cyclic alkene, together with its derivatives, represents one of the most important classes of organic compounds because of its enhanced reactivity caused by the large ring strain. Very recently, it was demonstrated that the heavy elements of Group 14 are also capable of forming such unsaturated three-membered ring systems. Undoubtedly, heavy cyclopropenes are very unusual molecules, since they possess the attributes of both a highly strained three-membered skeleton and a highly reactive endocyclic heavy metal-metal double bond. Therefore, one can reasonably expect unusual properties in such compounds, including structural characteristics, photochemical behavior, and enhanced reactivity. Before the presentation of the special features of cyclotrimetallenes it is worth to briefly introduce the evolution of the chemistry of double bonded silicon, germanium, tin and lead compounds.

As little as a few decades ago the chemistry of the main-group elements was governed, beside the octet rule, by the multiple-bond rule, often simply referred to as the double-bond rule. According to this rule elements of the first period but not those of the higher periods are able to form multiple bonds. This rule is based on experimental observations [86] and theoretical investigations [87, 88]. The double bond rule was finally disproved in 1976, when the first stable
compound with Sn=Sn double bond was synthesized by Lappert et al. [93]. Since then impressive progress has been made in this field resulting in a wide diversity of double and triple bonded compounds (Table 2). By today, stable double bonded compounds are known of almost all elements of Group 13, 14, 15 and 16. Very recently, the first compounds containing Si-Si triple bond was also synthesized [89].

It was found that the geometry around the double bond (R₂X=XR₂) in most heavy analogues (X=Si, Ge, Sn, Pb) is not classical planar but rather a trans-bent structure, with pyramidalization of both XR₂ groups. According to the CGMT model, suggested independently by Carter and Goddard [90] and Malrieu and Trinquier [91], X=Y double bonds are expected to be formed only when the sum of the singlet-triplet separations (ΣΔE_s-t) of the carbenoid fragments is smaller than the total X=Y bond energy (E_σ+π). The product has a trans-bent geometry if ΣΔE_s-t is larger than ½ E_σ+π. This rule gives an acceptable explanation for the increasing deviation from planarity in the disilene<digermene<distannene series.

Similarly to the divalent species, there are two ways to stabilize these reactive species; kinetic stability can be achieved using bulky substituents to protect the reactive center while thermodynamic stability can be achieved by incorporating the double bond in a ring. The efficiency of this method is well demonstrated by the existence of a large amount of cyclic species [92]. The main stabilization factor of these cyclic compounds is the delocalization of the double bond, while ring strain has an impact of destabilization on the system.
Table 2. The development of the unsaturated bonds and functions between heavy elements

<table>
<thead>
<tr>
<th>Type of bond /function</th>
<th>Year</th>
<th>Ref.</th>
<th>Theor. invest.</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn=Sn</td>
<td>1976</td>
<td>Lappert [93]</td>
<td>Pb=Pb</td>
<td>[94]</td>
</tr>
<tr>
<td>P=C</td>
<td>1978</td>
<td>Bickelhaupt [95]</td>
<td>Sn=Sn</td>
<td>[96]</td>
</tr>
<tr>
<td>Si=C</td>
<td>1981</td>
<td>Brook [99]</td>
<td>Si=Si</td>
<td>[100]</td>
</tr>
<tr>
<td>Si=Si</td>
<td>1981</td>
<td>West [101]</td>
<td>Si=C</td>
<td>[102]</td>
</tr>
<tr>
<td>As=As</td>
<td>1983</td>
<td>Cowley [103]</td>
<td>Si=P</td>
<td>[104]</td>
</tr>
<tr>
<td>Si=P</td>
<td>1984</td>
<td>Bickelhaupt [105]</td>
<td>Si=N</td>
<td>[106]</td>
</tr>
<tr>
<td>Si=N</td>
<td>1985</td>
<td>Wiberg [107]</td>
<td>P=P</td>
<td>[104]</td>
</tr>
<tr>
<td>Si=As</td>
<td>1992</td>
<td>Driess [110]</td>
<td>Si=Si=Si</td>
<td>[111]</td>
</tr>
<tr>
<td>Si=C=C</td>
<td>1993</td>
<td>West [112]</td>
<td>Si≡Si</td>
<td>[113]</td>
</tr>
<tr>
<td>Si=S</td>
<td>1994</td>
<td>Okazaki [114]</td>
<td>X=X</td>
<td>[115]</td>
</tr>
<tr>
<td>Ge\Ge</td>
<td>1995</td>
<td>Sekiguchi [116]</td>
<td>X=Si, Ge</td>
<td></td>
</tr>
<tr>
<td>Si=Si\Si=Si</td>
<td>1997</td>
<td>Weidenbruch [119]</td>
<td>Ga=Ga</td>
<td>[118]</td>
</tr>
<tr>
<td>Si=Se</td>
<td>1998</td>
<td>Okazaki [120]</td>
<td>In=In</td>
<td>[118]</td>
</tr>
<tr>
<td>Si=C</td>
<td>1999</td>
<td>Apeloig [121]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si\Si=Si</td>
<td>1999</td>
<td>Kira [122]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P=C=Si</td>
<td>1999</td>
<td>Escuidé [123]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sn=Sn=Sn</td>
<td>1999</td>
<td>Wiberg [124]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>szilabenzol</td>
<td>2000</td>
<td>Okazaki [125]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pb=Pb</td>
<td>2000</td>
<td>Power [126]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ge\Si≡Si</td>
<td>2000</td>
<td>Sekiguchi [127]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ge=C</td>
<td>2001</td>
<td>Couret [128]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si=Si=Si</td>
<td>2003</td>
<td>Kira [129]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si≡Si</td>
<td>2004</td>
<td>Sekiguchi [89]</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
2.3.1 Synthesized cyclotrimetallenes

Historically, cyclotrigermenes (cc) were the first stable heavy cyclopropanes; the synthesis of the first unsaturated three-membered ring system consisting of Ge atoms (cc1, Scheme 11) and its structural characterization with X-ray crystallography was reported in 1995 by Sekiguchi and co-workers [116]. To date, 11 cyclotrigermenes have been prepared and isolated, and eight of them have been structurally characterized [130]. Almost all the cyclotrigermenes were obtained as air- and photosensitive dark red crystals corresponding to the $\pi - \pi^*$ electronic transition due to the Ge=Ge double bond. Their structures can be determined by X-ray crystallography and $^1$H, $^{13}$C, and $^{29}$Si NMR spectroscopy in liquid and in solid states. Using these techniques $C_{2v}$ symmetry and completely planar geometry around the Ge=Ge double bond was observed for the first cyclotrigermenes. This planarity was somewhat unusual, since all previous digermenes were reported as having a trans-bent configuration of the Ge=Ge double bond, with folding angles ranging from $12^\circ$ to $36^\circ$ [131].

Shortly after the discovery of the first cyclotrigermenes, a cyclotrigermenium cation (I) was prepared by the oxidation of cc1 (Scheme 12), as the first germyl cation with an aromatic two $\pi$ electron system [132]. Such a stable cation was found to be a very convenient source for the synthesis of new, unsymmetrically substituted cyclotrigermenes. Thus, alkyl-, aryl-, silyl-, and germyl-substituted cyclotrigermenes were prepared in good yields by the reaction of the cyclotrigermenium salt with the corresponding nucleophiles (Scheme 13).
X-ray analysis of their crystals revealed that the geometry around the Ge=Ge double bond strongly depends on the substituents. In contrast to the planar arrangement in \textit{cc1}, a \textit{trans}-bent geometry around the Ge=Ge double bond was found in \textit{cc2} (Scheme 14) with bending angles of 6.8° and 4.3° and a Ge=Ge double bond length of 2.2680(4) Å. Such geometry is in agreement with the previous findings that digermenes exhibit \textit{trans}-bent arrangement. On the other hand, changing the substituent from mesityl to the tris(trimethylsilyl)silyl group a \textit{cis} geometry around the double bond was observed with bending angles of 12.5° and 4.4° for sp² Ge atoms and a Ge=Ge bond length of 2.264(2) Å (\textit{cc3}). Theoretical calculations confirmed the \textit{cis} geometry with angle values of 8.8° and 5.8°, respectively.

Due to the lack of a suitable stable silylene the synthesis of the first cyclotrisilene was achieved more than four years after the appearance of cyclotrigermenes. First, the preliminary preparation of the appropriate silylene precursors, which can generate silylenes in situ, was required for the successful synthesis of cyclotrisilenes. Finally, in 1999 Kira’s and Sekiguchi’s groups independently reported the synthesis of two cyclotrisilenes with different substituents (\textit{bb}, R=SiMe₂Bu, on X₁, R₃= (SiMe₂Bu)₃ [122] and \textit{bb}, R=SiMe₂Bu₂ [133]). The existence of Si=Si double bond in both compounds was proven by $^{29}$Si NMR spectroscopy: the downfield signals (depending on the substituents it modulates around +90 ppm) correspond to the unsaturated silicon atoms, while the upfield signal at -127.3 ppm was attributable to the sp³ silicon atom in a
three-membered ring system. The X-ray analysis of the orange-red crystals showed a *trans*-bent geometry around the Si=Si double bond with a bending angle of 31.9(2)° and bond length of 2.138(2) Å, which was recognized as one of the shortest distances among the Si=Si double bond lengths reported so far.

![Scheme 15.](image)

Up to date only three stable cyclotrisilenes have been synthesized, the third of them, an unusual spirostructure, tetrakis[tri(tert-butyldimethylsilyl)silyl]spiropentasiladiene (Scheme 15) was observed as a by-product during the preparation of bb [134]. Although spiropentasiladiene is sensitive to air, it is thermally very stable; it melts at 216° to 218°C without decomposition. X-ray single-crystal analysis shows that the two three-membered rings in spiropentasiladiene are not perpendicular to each other but are slightly twisted with a dihedral angle of 78.26(0)°. The bathochromic shift in the UV spectra provides evidence for the possible through-space conjugation between the two remote Si=Si double bonds. While the elongation of the Si=Si double bond compared with that in cyclotrisilene cc was attributed to the phenomenon of $\pi-\sigma^*$ conjugation (described later).

The only cyclotristannene (dd, R=Si(tBu)$_3$) analogue synthesized so far has dark red-brown crystals [124]. The two sets of signals in the $^1$H, $^{13}$C, and $^{29}$Si NMR spectra are in accordance with the symmetrical structure of the molecule. The $^{119}$Sn NMR spectrum was the most informative, showing both upfield (-694 ppm) and downfield (+412 ppm) resonances. The latter is typical of doubly bonded tin atoms whereas the former was assigned to the endocyclic Sn atom in a three-membered ring system. It has a planar environment around the Sn=Sn double bond ($r=2.59$ Å), whereas all previously reported distannenes have a trans-bent configuration. One of the most important findings concerning the last step of the synthesis of the tin analogue was the discovery of the intermediately formed tristannaallene. However, it was thermally unstable and gradually rearranged to the isomeric cyclotristannane at room temperature.
As the next step after the isolation of cyclotrisilene, cyclotrigermene, and cyclotristannene the synthesis of the heteronuclear disilagermirenes) was reported in 2000 [127]. Moreover, due to an extraordinary 1,2-migration (see below) it immediately provided the appearance of two types of disilagermirenes, \(3H\)-disilagermirene (\(ee\), \(R=\text{SiMe}(\text{tBu})_2\)) and \(1H\)-disilagermirene (\(ff\), \(R=\text{SiMe}(\text{tBu})_2\)) [127]. Two other representatives of unsaturated ring compounds containing two different group 14 elements, \(1H\)-siladigermirene (\(gg\), \(R=\text{SiMe}(\text{tBu})_2\)) [135] and disilacyclopropene (\(hh\), \(R=\text{Si}(\text{tBu})_3, R=\text{Adamantyl on X}\)) [136] were reported in 2007. Since the synthesis of these hybrid compounds are not evident only the above mentioned four examples have been prepared so far (see also Table 3).

<table>
<thead>
<tr>
<th>Structure</th>
<th>Name</th>
<th>Color</th>
<th>MP (°C)</th>
<th>Length of the double bond (Å)</th>
<th>Geometry around the double bond</th>
<th>Extra</th>
</tr>
</thead>
<tbody>
<tr>
<td>ee</td>
<td>(1H)-disilagermirene</td>
<td>dark red</td>
<td>205-207</td>
<td>2.146(1)</td>
<td>trans-bent, 37.0(2)</td>
<td>isomerization to (ff)</td>
</tr>
<tr>
<td>ff</td>
<td>(3H)-disilagermirene</td>
<td>bright red</td>
<td>194-196</td>
<td>n.d.</td>
<td>trans-bent, 40.3(5)</td>
<td>extreme thermodynamic stability</td>
</tr>
<tr>
<td>gg</td>
<td>(1H)-siladigermirene</td>
<td>dark red</td>
<td>n.d.</td>
<td>2.2429(6)</td>
<td>trans-bent 51.0(2)</td>
<td>monoclinic crystals</td>
</tr>
<tr>
<td>hh</td>
<td>disilacyclopropene</td>
<td>yellow</td>
<td>n.d.</td>
<td>1.745(2)</td>
<td>nearly planar, 4.5(2)</td>
<td>air stable</td>
</tr>
</tbody>
</table>

In 2003 Sekiguchi and Lee wrote that „there is a very limited number of methods for cyclotrimeallene synthesis, which are not general and are usually more complicated than in the case of cyclotrimeallanes” [130c]. Since then, a few other heavy cyclopropene derivatives were isolated but even now, no universal protocol exists for their synthesis. In the following lines, however, I outline three classes (as a first step of generalization) of procedures resulting cyclotrimeallenes: nucleophilic addition to the corresponding three-membered cation, Würtz-type reductive coupling and reductive coupling with dilithiosilane.

As it was mentioned above the cyclotrigermanium ion (I) was a perfect precursor for producing unsymmetrically substituted cyclotrigermenes. Very recently, cyclotrisilenylum \(\text{R}_3\text{Si}_3^+\) (2005) and disilacyclopropenylium \(\text{R}_3\text{Si}_2\text{C}^+\) (2007) ions were reported [137, 136] which seem to be promising candidates as the starting material for new, unsymmetrically substituted unsaturated \(\text{Si}_3\) and \(\text{Si}_2\text{C}\) rings, respectively.
The Würtz type reductive coupling was a successful tool in the preparation of 3H-disilagermirene (Scheme 16) [127] and cyclotrisilene [133]. With appropriate in situ generated doubly bonded precursors it also can be a convenient method for the preparation of unsaturated heavy three-membered rings.

\[
2 \text{R-SiBr}_3 + \text{R}_2\text{GeCl}_2 \xrightarrow{\text{Na / toluene, r.t. 6 h}} \text{Ge-Si-Si-R} \\
\text{R} = \text{SiMe}_2\text{Bu}_2
\]

**Scheme 16.**

The chemistry of dilithiosilane was developed by Sekiguchi’s group [138]. It offered a straightforward method for the synthesis of dimetallenes of the type >Si=E< (E = B [139d], Al [139c], Ga [139c], Si [139a], Ge [139a], Sn [139b], Hf [139e]) and two unsaturated heavy three membered rings (gg [135] and hh [136]) by a coupling reaction of (tBu₂MeSi)₂SiLi₂ with the appropriate dihalogenated compounds (Scheme 17). Thus, dilithiosilane (dilithiogermane) is also a promising reagent for the synthesis of hitherto unknown unsaturated silicon compounds including homo- and heteronuclear cyclopropene derivatives.

\[
\text{tBu}_2\text{MeSiGeCl}_2\text{-GeCl}_2\text{SiMe}^3\text{Bu}_2 + \text{tBu}_2\text{MeSi}_2\text{SiLi}_2 \xrightarrow{\text{toulene, - LiCl}} \text{Me}^3\text{Bu}_2\text{Si}_{\text{llllllll}}\text{SiMe}^3\text{Bu}_2 \\
\text{Me}^3\text{Bu}_2\text{Si}_{\text{llllllll}}\text{Ge}_{\text{llllllll}}\text{SiMe}^3\text{Bu}_2
\]

**Scheme 17.**

The reactivity of cyclotrimetallenes, which combines the chemical properties of both cyclotrimetallanes and dimetallenes, was found to be very diverse and unique. Addition with haloalkanes and alcohols takes place easily, even at low temperature, to form the corresponding trans-1,2-disubstituted derivatives.

Based on model calculations, it was found that the addition of CCl₄ proceeds via a two-step abstraction-recombination path which explains the selectivity for the trans- product [140]. [2+2] (with phenylacetylene, aldehydes and ketones) and [2+4] (with 1,3-dienes) cycloadditions are also characteristic reactions of cyclotrimetallenes. Obviously, these reactions occur by means of the reactivity of the double bond.
Hereinafter I will focus on the more extraordinary reactions, such as halogen atom migration over the ring skeleton, isomerisation, and ring expansion reactions. The reaction of cyclotrimercury ion (I) with potassium halides KX (X= Cl, Br, I) provided also an efficient route to halogen substituted cyclotrigermenes [130b]. One of the most interesting features of these compounds is the migration of the halogen atoms over the three-membered ring skeleton (Scheme 18).

![Scheme 18.](image)

The activation energy was found to be independent of the concentration and solvent polarity, suggesting that the halogen atom migrates intramolecularly without intermediate. On the other hand, theoretical calculations predicted two-step reactions with great differences between the energy levels of the intermediates: 12.5 kcal/mol for F migration, 7.8 kcal/mol for Cl migration, and only 4.0 kcal/mol for Br migration (Scheme 19). This is in complete accord with the general tendencies of increasing polarizability and decreasing strength of the Ge-X bond on going from F to Br atoms, which provides the flexibility necessary for the 1,2-migration in highly strained three-membered ring systems.
A similar phenomenon was observed for disilagermirene by Sekiguchi et al. [127] (Scheme 20). Under irradiation a bulky group from the saturated atom (Ge) migrates to one of the unsaturated silicones. The isomerization of 3H-disilagermirene (II) to 1H-disilagermirene (III) can also be performed under thermal conditions. 1,2-substituent migration, also, was found in the case of the cyclotrisilene ring due to photochemical excitation [141]. In the case of the tin analogue the rearrangement of cyclotristannene apparently implies the migration of one silyl substituent followed by cyclization [124].

Several examples are known for ring expansion reactions. For example, compounds ce and gg readily react with an excess of CH₂Cl₂ at room temperature to produce the new four-membered-ring compounds (Scheme 21). It was shown that the ring-expansion reaction with CH₂Cl₂ is general for all heavy cyclopropene analogues of the type R₄YX₂ (R= SiMetBu₂; Y, X=Si, Ge).
Thus, the previously reported $1H$-trisilirene ($R_4Si_3$) as well as the $3H$- and $1H$-disilagermirenes (II and III) smoothly react with $\text{CH}_2\text{Cl}_2$ to produce the isostructural four-membered rings.

\[
\begin{align*}
\text{Scheme 21.}
\end{align*}
\]

2.4 Bridged structures

Hydrogen-bridged structures are known for a long time in chemistry. Its classic school-book example is diborane with a $D_{2h}$ structure containing four terminal and two bridging hydrogen atoms (Scheme 22). Later other dibridged structures on the $X_2H_6$ PESs were found, like digallane [142] and most recently in 2003 Andrews et al. could detect the $\text{H}_2\text{Al}-\text{H}_2\text{-AlH}_2$ dimer in soft hydrogen matrix at 6.5 K [143]. The $X_2H_2$ PES was also analyzed with Group 13 elements ($X=$B, Al, Ga, In, Tl) [144]. In all cases but boron, the global minimum is found to be the dibridged structure.

\[
\begin{align*}
\text{Scheme 22. Structure of diborane.}
\end{align*}
\]

Similar hydrogen bridges are also known among the compounds made of heavier Group 14 elements. The small silicon hydrides are of interest because of their potential applications in semiconductors and optoelectronics and their likely existence in the interstellar spaces of evolved carbon stars [145]. Already, in 1983 Lischka and Köhler demonstrated that the singlet potential energy surface of $\text{Si}_2\text{H}_2$ is very different from that of $\text{C}_2\text{H}_2$ [146]. For instance, the acetylene-like linear structure is a second-order saddle point on the PES. The energetically lowest lying form of $\text{Si}_2\text{H}_2$ was found to be the doubly hydrogen-bridged butterfly structure ii (Scheme 23). Two other minima, having vinylidene and trans-bent (kk) geometry, were
predicted on the PES. Further theoretical studies confirmed these results, but the isomer \textit{jj} was found as yet another low-lying energy minimum [147]. Natural Resonance Theory analysis of the H-bridged isomers reveals leading Lewis structures with Si-Si single bonding in the $C_{2v}$ isomer and double bonding in the $C_s$ isomer, while triple bonding in the $C_{2h}$ isomer [148]. Subsequent calculations on Ge$_2$H$_2$, Sn$_2$H$_2$ and Pb$_2$H$_2$ showed that the energy minimum structures and their relative energies are similar to that of the Si$_2$H$_2$ PES [149].

The theoretical predictions about the unusual structures \textit{ii} and \textit{kk} were confirmed in the case of Si$_2$H$_2$ by spectroscopic studies in low-temperature matrixes by Bogey \textit{et al.} [150]. Further hydrogen-bridged structures were identified in low-temperature matrixes also for Ge$_2$H$_2$, Sn$_2$H$_2$, and Pb$_2$H$_2$ besides Si$_2$H$_2$ by Andrews and co-workers [151]. In 2005 high level calculations were performed by Frenking \textit{et al.} on the PES of X$_2$H$_2$ (X = Si, Ge, Sn, Pb) [152]. They found that doubly bridged structures are global minima while after analyzing the bonding orbitals of the systems they assumed the stability of these structures is due to the interactions between the SiH moieties in the electronic ground state (Scheme 23).

The shape of the minimum energy structure of the Si$_2$H$_4$ molecule has been studied for more than twenty years. The first disilene (Si$_2$R$_4$), isolated and characterized in 1981, was thought to be planar, like ethylene [101]. The early ab initio studies have focused primarily on the two
isomers of Si$_2$H$_4$, disilene (II) (H$_2$Si-SiH$_2$) and silylsilylene (H$_3$Si-SiH). Although, all of the theoretical studies found that disilene (H$_2$Si-SiH$_2$) is the lowest energy isomer, the predictions differed on whether it (H$_2$Si-SiH$_2$) has a planar or bent structure. In 1990, Trinquier suggested planar form [82a], in 1991, Pople and co-workers predicted the trans-bent structure [153], and in 2000, the DFT calculations of Pak et al. yielded a near-planar trans-bent structure [154]. Infrared spectra supported the trans-bent structure for disilene (Scheme 24). Trinquier [82b] also discussed the bonding character of the mono- (mm) and dibridged (trans-, nn and cis-, oo) forms in details (Scheme 24), however, in the case of Si$_2$H$_4$ and Ge$_2$H$_4$ he did not find the monobridged isomers. Finally, Schaefer et al. found that unexpectedly a monobridged isomer is the global minimum on the Si$_2$H$_3$ PES and the monobridge structure has also comparable stability with the global minimum disilene on the Si$_2$H$_4$ PES [100]. Their results were proved experimentally with Fourier transform microwave spectroscopy measurements.

\[ \text{E=Si, Ge, Sn, Pb} \]

Scheme 24.
In spite of the numerous publications about the mono-H-bridged and di-H-bridged structures, fairly slight number of publications discusses bridged isomers of three-membered rings. One of them found low lying bridged isomers in the system of Si$_3$H$_2$ and Si$_3$H$_2^+$, and showed that the global minimum of the Si$_3$H$_2^-$ system is a mono-H-bridged structure [155].
3 OVERVIEW OF QUANTUM CHEMISTRY

Erwin with his psi can do
calculations quite a few.
But one thing has not been seen
just what does psi really mean.
Walter Hückel, trans. by Felix Bloch

In the first part of this chapter the basis of quantum chemistry [156] (the quantum mechanical origin, the different approximations, the HF and post-HF methods) will be briefly reviewed. The second section introduces three theories (Atoms in Molecules Theory, Natural Resonance Theory and Isodesmic and Homodesmic reactions) which belongs to more specialized areas of quantum chemistry and are not covered by every textbook in the field.

3.1 Wave function based methods

In quantum theory the time dependent Dirac equation, which includes the relativistic effects, describes time evolution of the state of a microsystem properly. However, except for the numerical solution of very small systems, we can not solve the Dirac equation in its original form. In most cases, the time-independent Schrödinger equation (1) that neglects the relativistic effects is considered:

\[ \hat{H} \psi = E \psi, \quad (1) \]

where \( E \) is the energy of the system, \( \psi \) is the wave function \( \hat{H} \) is the Hamiltonian operator or shortly the Hamiltonian. The Hamiltonian is built up from a potential (V) and a kinetic (T) term:

\[ \hat{H} = \hat{V} + \hat{T} \]

\( \hat{V} \) is the potential operator and \( \hat{T} \) is the kinetic energy operator.

\( \hat{H} \psi = E \psi \)

is still too cumbersome to evaluate in most cases.

\( \hat{H} \psi = E \psi \)

is too cumbersome to evaluate in most cases.

\( \hat{V} \psi \)

is too cumbersome to evaluate in most cases.
\[ \hat{H} = \hat{V} + \hat{T} \quad (2) \]

The potential energy operator contains the nuclear-nuclear (\( \hat{V}_{NN} \)) and electron-electron repulsions (\( \hat{V}_{ee} \)), and the nuclear-electron attraction (\( \hat{V}_{Ne} \)) while the kinetic energy of the nuclei \( \hat{T}_N \) and the electrons \( \hat{T}_e \) are involved in \( \hat{T} \). For a many electron system:

\[
\hat{H} = e^2 \left[ \sum_a \sum_{\beta \neq a} \frac{Z_a Z_{\beta}}{R_{a\beta}} + \sum_i \sum_{j < i} \frac{1}{r_{ij}} - \sum_i \sum_{a < i} \frac{Z_a}{r_{ia}} \right] - \frac{\hbar^2}{2m} \sum_{i=1}^N \nabla_i^2 - \frac{\hbar^2}{2M_a} \nabla_a^2 \quad (3)
\]

where \( m \) and \( e \) are the mass and charge of the electron, \( M_\alpha \) and \( Z_\alpha \) are the mass and charge of \( \alpha \) nucleus, \( R_{\alpha\beta} \) is the distance between the \( \alpha \) and \( \beta \) nuclei, \( r_{i\alpha} \) between the i electron and the \( \alpha \) nuclei, and \( r_{ij} \) between the i and j electrons, respectively. \( \nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \) is a second order differential operator called Laplacian and generally abbreviated by \( \Delta \). The summation goes over \( N \) electrons and \( n \) nuclei.

Wavefunctions in general are complex quantities with \( 4n+4N \) variables; each nucleus and electron has one spin- and three space coordinates.

\[ \Psi = \Psi(x_1, y_1, z_1, s_1, x_2, y_2, z_2, s_2, \ldots, x_n, y_n, z_n, X_1, Y_1, Z_1, S_1, X_2, Y_2, Z_2, S_2, \ldots, X_N, Y_N, Z_N) \quad (4) \]

Except for the simplest systems, the exact analytical solution of the Schrödinger equation can not be achieved\(^\dagger\dagger\) and most often further approximations are introduced. Considering the fact that the light electrons can promptly follow the motion of the much heavier nuclei Born and Oppenheimer showed that, to a very good approximation, the motions of the nuclei and the electrons could be considered separately. Thus, the nuclei are fixed in space for the purpose of calculating the electronic wavefunction\(^\ddagger\ddagger\), and the nuclei then move in the potential generated by the electrons. According to the B-O approximation, the wavefunction is written in product form.

\[ \Psi_s = \Psi_s \Psi_n \quad (5) \]

where \( \Psi_s \) is the total wavefunction of the system. Writing the Hamiltonian as

\(^\dagger\dagger\) The numerical solution is also limited by computational cost.

\(^\ddagger\ddagger\) The wavefunction of electrons.
Overview of Quantum Chemistry: Wave Function Based Methods

\[ \hat{H} = \hat{H}_e + \hat{H}_n \]  

one can arrive to

\[ \hat{H}_e \Psi_e = E_e \Psi_e \]  

where \( E_e \) (the electronic energy) is a function of the nuclear coordinates and it is often referred to as the potential energy (hyper)surface (PES). In the critical points of the potential energy surface the gradient is zero and the eigenvalues of second derivates matrix (Hessian) can be used to characterize the critical points. Of these, from the chemists’ point of view, the most important ones are the minima corresponding to stable structures and the first-order saddle points corresponding to transition states. Following the routes with the steepest descent from a first-order saddle point one can reach two minima. This path is called the intrinsic reaction coordinate (IRC), and it gives some indication on the changes during the reaction.

Further simplifications are introduced by using the independent particle model, in which the interaction between the electrons is approximated by an average one-electron potential \( V_i^{\text{eff}}(i) \). The Hamiltonian is written as:

\[ \hat{H} = \sum_{i=1}^{N} [\hat{h}_i + V_i^{\text{eff}}(i)] = \sum_{i=1}^{N} \hat{F}(i) \]  

where \( \hat{h}_i \) is a one electron operator, containing the kinetic energy operator of electron \( i \) and the electron-nuclear attraction potential energy term, and \( \hat{F}(i) \) is called the Fock-operator. The electronic wave function now can be written in terms of one-electron functions, which depend only on the coordinates of one electron.

To satisfy the antisymmetry criterion an appropriate linear combination of the products of the above mentioned one-electron functions has to be used. This linear combination is a determinant (\( \Phi \), the Slater-determinant). For \( N \) electrons, including the normalization constant:

\[ \Phi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_1(1) \cdots \varphi_1(N) \\ \vdots \\ \varphi_N(1) \cdots \varphi_N(N) \end{vmatrix} \]  

(9)
where \( \varphi_i \) are the one-electron wave functions, which are the product of the one-electron orbital \( (\psi_i, \text{depending on } x_i, y_i, z_i) \) and one-electron spin functions \( (\eta_i, \text{depending on the spin variable of electron } i) \).

In the Hartree-Fock method, the variational principle is used to find the minimum of the energy and the corresponding one-electron wave functions, leading to the Hartree-Fock (HF) equations:

\[
\hat{F}(i)\varphi_i = \varepsilon_i \varphi_i \quad i = 1, \ldots, N
\]

As the Fock operators contain the hitherto unknown one-electron wave functions an iterative procedure is used, in which a starting \( \{ \psi_0 \} \) function series is used to construct the Fock operators, than the HF equations are solved, resulting in a new \( \{ \psi \} \) series of functions and the energy. With these new functions the process is repeated until the change of the energy between two cycles becomes smaller than a given threshold. In this case it is said that the self consistent field (SCF) is reached.

To avoid numerical solution of the HF equations the Hartree-Fock-Roothan (HFR) method is used, in which the one-electron wave functions are constructed as the linear combinations of pre-defined basis functions \( \{ \chi_\mu \} \), and when deriving the HF equations only the coefficients are to be determined.

\[
\psi_i = \sum_{\mu=1}^{m} c_{\mu i} \chi_\mu \quad i = 1, \ldots, N
\]

Using an infinite basis set an infinite number of one-electron wave functions would be obtained from the solution of the HFR equation together with infinite number of eigenvalues. The use of finite basis sets instead of infinite is a further necessary approximation, therefore its size and quality is a very important factor.

On one hand the number of basis functions is limited by the number of electrons and the spherical symmetry of the atom. On the other hand it is limited by the computational resources. Because of their computational efficiency Gaussian-type basis functions are used widely. In the double zeta (DZ) and triple zeta (TZ) basis sets the number of basis functions is twice or three times larger than in the minimum basis set. Basis sets in which there are multiple basis functions corresponding to each valence atomic orbital, are called the valence double, triple, or quadruple-
zeta basis sets. The basis sets often contain polarization and diffuse functions. Polarization functions make the basis set more flexible enabling to get information on the surroundings around the atom. In the case of hydrogen atom, they are of p or d type, while for heavier elements d or f type functions are used. Diffuse functions are especially important in the description of weak interactions and anions. Recently, the correlation consistent basis sets which include the polarization functions, proposed by Dunning have become very popular (cc-pVDZ, cc-pVTZ [157], etc.). The advantage of Dunning basis sets is the ability to generate a sequence of energies, which can be used to extrapolate the basis set limit (the best result that can be achieved within the approximations of a certain methodology).

The HFR method can be used to calculate the energy of the system, but with increasing basis set, the energy converges to the so-called HF limit, which is always higher than the exact solution of the non-relativistic Schrödinger equation. The correlation energy (the energy difference between the HF-limit on a given basis and the exact, non-relativistic solution) is a consequence of the one-electron model in the HF-method. The absolute value of the correlation energy is very small compared to the total energy of the system, but it may have a very important influence on quantities, which arise as energy differences e.g. activation energies and relative energies.

Modern quantum chemical methods try to take into account the correlation between the electrons by improving the wave function. The main strategy is to use the one-electron wave functions obtained in the HF-method to develop the exact wave function of the system. Exciting electrons from the occupied orbitals to the virtual ones it is possible to create excited determinant wave functions. In the CI method the wave function is the linear combination of the different determinants:

\[ \Psi = \sum_{i=1}^{\infty} C_i \Phi_i \] (12)

The finite size of the basis set limits the number of determinants. The wave function obtained from a finite basis set is called FCI (full CI). This calculation includes every singly, doubly etc. excited determinants. The variational principle is used to determine the coefficients of the determinants. Due to the large number of determinants FCI calculations can only be performed for molecules with a few atoms. Therefore, it is necessary to select from those determinants, which are important for the improvement of the wave function.
In the cases when the systems cannot be described with one single determinant (*static electron correlation*) and/or several determinants with a large coefficient is necessary for the good description (*non-dynamic electron correlation*) multiconfigurational self-consistent field method (MCSCF) may be applied to calculate the properties of the system. In this calculation a selected set of determinants are used as reference instead of the single determinant and the orbital coefficients are usually optimized simultaneously with the CI coefficients in a variational procedure.

Various approaches, such as CI, CC and MP calculations, have been developed for systems, for which the cumulated effect of many excited determinants with small coefficient is very important (*dynamic electron correlation*). As the number of determinants is very large a systematic series of calculations were developed based in the CI-method. For example, in the CISD every singly and doubly excited determinants are taken into account. The serious drawback of these methods is that they are not size-consistent. The problem of size-consistency is solved by the coupled-cluster methods, which use an exponential operator to produce the excited determinants (\( \Psi = e^{\hat{T}} \Phi_0 \)). The \( \hat{T} \) operator can be written in the “\( \hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + ... \)” form, where the subscript denotes the excitation levels. Depending on the order of the \( \hat{T} \) operator, CCS, CCSD, CCSDT etc. methods have been developed. One of the most popular methods which include the dynamic electron correlation in the calculation uses perturbation methodology; this is the Many Body Perturbation Theory or Møller-Plesset methods. The HF wave function as non-perturbed system is used to develop the improved wave function. Including higher order of perturbation, the correlation energy can be estimated better and better. The disadvantage of the MP-methods is that they are not variational methods and the obtained energy may be lower or higher than the exact solution. However, it is possible, that using higher order, one gets nearer to the exact solution. The two, most often used methods are MP2 and MP4, in which the energy is calculated up to the second and the fourth term of the expansion series. An important advantage of the MP2 method is that it accounts for about 90% of the correlation energy and it is size-consistent.

---

\[ \text{Footnote: It is also valid for the coupled-cluster (CC) methods.} \]
Modern density functional theory was created by Hohenberg, Kohn, and Sham in 1964-65, following early successes by Slater. The original hopes for this theory were modest: to provide a more realistic framework for electronic-structure calculations in solids than the Hartree approximations. Thanks to the new developments, however, DFT offer opportunities for atomic and molecular calculations at a relatively high level of precision with a reasonable computational cost.

The electron density instead of the wave function of the system is used in DFT.

\[
\rho(r) = N \int_{-\infty}^{\infty} \ldots \int_{-\infty}^{\infty} \Psi^*(1,2,\ldots,N)\Psi(1,2,\ldots,N) \, dx_1 \ldots dx_N \, d\sigma_i \tag{13}
\]

where \( x_i \)'s are spatial and spin variables and \( \sigma_i \)'s are spin variables.

From wavefunction normalization,

\[
\int \rho(r) \, dr = N . \tag{14}
\]

The Hohenberg-Kohn theorem states that in principle, the ground-state density \( \rho(r) \) of an electronic system determines all the states of the system. E.g. its ground state energy can be written:

\[
E_s[\rho] = T[\rho] + V_{\text{ex}}[\rho] + V_{\text{ext}}[\rho] = F_{\text{HK}}[\rho] + \int \rho(r) v(r) \, dr \tag{15}
\]

where \( T[\rho] \) is the kinetic energy functional, \( V[\rho] \) are the potential energy functional (the constant nuclear-nuclear repulsion term is not included in the equation). \( F_{\text{HK}}[\rho] \) is the Hohenberg-Kohn functional which contains the electron-electron repulsion term and the kinetic energy functional.

The second Hohenberg-Kohn theorem provides the possibility to determine the electron density via variational method:

\[
E_v[\rho] \geq E_0 \tag{16}
\]

The difficulty of the solution of equation (16) is that the components of the Hohenberg-Kohn functional, \( F_{\text{HK}} \), are not known. In Kohn-Sham theory the ground state of \( N \) electrons is considered in an external potential \( v(r) \) and the \( \rho(r) \) is formed from the self-consistent solution of the one-electron equations.
Hence, \( F_{HK}[\rho] \) can be written as:

\[
F_{HK}[\rho] = T_s[\rho] + J[\rho] + E_{xc}[\rho]
\]

(17)

where \( T_s[\rho] \) is the kinetic energy functional of the non-interacting system, \( J[\rho] \) is the classical electron-electron repulsion term from \( V_{ee}[\rho] \) and \( E_{xc} \) is the exchange correlation functional. The latter includes the correlation energy \( E_c = T_s[\rho] - T[\rho] \) and exchange energy \( E_x = V_{ee} - J[\rho] \) parts.

With a given functional \( (F_{HK}[\rho]) \) the solution of the variational problem can be found by solving the following Kohn-Sham equation:

\[
\left[ -\frac{\hbar^2}{2m} \nabla^2 + v_{\text{eff}}(\mathbf{r}) \right] \phi_i = \varepsilon_i \phi_i
\]

(18)

where \( v_{\text{eff}}(\mathbf{r}) \) is an effective potential, \( \phi_i \) a one-electron function (Kohn-Sham orbitals). A similarity transformation can be used to obtain the canonical Kohn-Sham equation, which can be solved in an iterative manner similarly to the one used in the case of the HF equations.

Since the exact \( E_{xc}[\rho] \) is not known, there is no practical way to construct the \( F_{HK}[\rho] \) functional. Therefore, approximate functionals must be applied for \( E_{xc} \) and the accuracy of DFT calculation strongly depends on the used functional. Dividing \( E_{xc} \) into \( E_x \) and \( E_c \) the three most popular approximations introduced are the local density approximation (LDA), the generalized gradient approximation (GGA) and the exact-exchange hybrid. For example, the very popular B3LYP functional contains Becke’s three-parameter exchange functional [158] in conjunction with the Lee-Yang-Parr correlation functional [159]. The \( E_x \) part (B3) contains parameters optimized to atomization energies, ionization energies etc, therefore it can be regarded as a semi empirical method.
3.3 Atoms in Molecules theory

The atoms in molecules (AIM) model of molecules was proposed by Bader in 1990 [160]. This theory is based on the topological analysis of the electron density. Since the electron density is the function of three-dimensional space, it is possible to partition it according to atomic or bonding characteristics in order to distinguish the reactive centers and other specific parts of the molecule.

In this theory, an atom can be alternatively defined as a region (called basin) of real space bounded by surfaces through which there is a zero flux in the gradient vector field of the electron density \( \rho(\mathbf{r}) \). These zero-flux surfaces which separate basins of neighboring atoms are called interatomic surfaces. Notice that such atoms in a molecule are not spherical and they extend over all the space with sharp boundaries between two atoms. Thus, the topology of the electron density can be used to define where one atom ends and the next begins. One of the useful aspects of this space partitioning is, that within certain physical properties of the atoms, for instance the atomic charges, deduced by integration over the whole basin can be uniquely defined and calculated.

To characterize the structure of molecules Bader introduced so called critical points of \( \rho(\mathbf{r}) \). Critical points are those where the gradient of the electron density is zero: these can be maxima, minima, and saddle points, which can be distinguished using the second derivatives of the electron density, i.e. the Hessian matrix:

\[
\begin{pmatrix}
\frac{\partial^2 \rho}{\partial x^2} & \frac{\partial^2 \rho}{\partial x \partial y} & \frac{\partial^2 \rho}{\partial x \partial z} \\
\frac{\partial^2 \rho}{\partial y \partial x} & \frac{\partial^2 \rho}{\partial y^2} & \frac{\partial^2 \rho}{\partial y \partial z} \\
\frac{\partial^2 \rho}{\partial z \partial x} & \frac{\partial^2 \rho}{\partial z \partial y} & \frac{\partial^2 \rho}{\partial z^2}
\end{pmatrix}
\]

Depending on the rank of Hessian and the sign of the eigenvalues four types of critical points can be defined. The positions of the nuclei are in the local maximum of the electron density \( \rho(\mathbf{r}) \), i.e. where Hessian has three negative eigenvalues. Bond critical points (BCP) are where \( \rho(\mathbf{r}) \) has maximum in two directions and a minimum in one direction of space (one
positive and two negative eigenvalues). Points where the \( \rho(r) \) has maximum value in one direction and minimum value in two directions of space are called *ring critical points* (RCP). In points, where Hessian has three positive eigenvalues, viz. in the local minimum of \( \rho(r) \) are the positions of *cage critical points* (CCP).

Obviously, the electron density has local maximum at the nucleus. If two neighboring nuclei are connected via a single line of locally maximum density, termed the *bond path* (BP) or maximum electron density (MED) path, it is said that, chemical bonding exists between the two atoms. The bond path is a universal indicator of chemical bonding of all kinds; weak, strong, closed-shell, and open-shell interactions. The point on the bond path with the lowest value of the electron density (minimum along the path) is the bond critical point and it is at that point where the bond path intersects the interatomic surface separating the two bonded atoms. The critical points and network of chemical bonds together represent the *molecular graph* of the molecule. A molecular graph and the characteristics of the density at the bond critical points provide a concise summary of the bonding within a molecule or crystal. In my research I used the AIM theory to discover and clarify the molecular structure of nontrivial molecules with the help of their molecular graphs.

### 3.4 Natural Resonance Theory

The theory of resonance has been described in essentially every textbook of chemistry and is used by essentially every chemist. However, despite its widespread usage, resonance theory now serves primarily as a descriptive tool rather than as a quantitative theory of chemical structure. The basic concept of representing a molecule as an “average” of two or more idealized structural forms traces back at least to Kekule’s famous 1865 benzene dream. The concepts and nomenclature of resonance theory as presently understood by most chemists were established by Pauling and Wheland based on a valence bond superposition assumption for the wave function \( \psi \). Unlike the Pauling-Wheland treatment the Natural Resonance Theory [161] approach is based on the one-particle reduced density matrix \( \hat{\Gamma} \):

\[
\hat{\Gamma} = N \int \psi(1, 2, \ldots N) \psi^*(1, 2, \ldots N) \, d2\ldots dN
\]

Its approximation in resonance-averaged form
Overview of Quantum Chemistry: Natural Resonance Theory

\[ \hat{\Gamma} \approx \sum_{\alpha} w_{\alpha} \hat{\Gamma}_{\alpha} \]  \hspace{1cm} (20)

\[ w_{\alpha} \geq 0, \sum_{\alpha} w_{\alpha} = 1 \]  \hspace{1cm} (21)

where \( \hat{\Gamma}_{\alpha} \) is an idealized density matrix for resonance structure \( \alpha \).

Given the true density operator \( \hat{\Gamma} \) and a set of candidate density operators for idealized localized resonance structures \( \{ \hat{\Gamma}_{\alpha} \} \), one can formulate a least squares variational functional for the unknown weighting factors \( \{ w_{\alpha} \} \).

\[ \delta_{\alpha} = \min_{\{ w_{\alpha} \}} \left\| \hat{\Gamma} - \sum_{\alpha} w_{\alpha} \hat{\Gamma}_{\alpha} \right\|, \]  \hspace{1cm} (22)

where \( \| \| \) denotes the matrix norm in a matrix representation of an operator. The variational ‘error’ \( \delta_{\alpha} \) evidently vanishes if, and only if, \( \sum_{\alpha} w_{\alpha} \hat{\Gamma}_{\alpha} \) is an exact representation of the true \( \hat{\Gamma} \).

Also, \( \delta_{\alpha} \) is a measure of the error in describing \( \hat{\Gamma} \) with the chosen resonance structures \( \hat{\Gamma}_{\alpha} \) providing an internal criterion of accuracy of the resonance expansion.

In the Natural Resonance Theory each \( \hat{\Gamma}_{\alpha} \) is constructed from quantities that can be obtained from natural bond orbital (NBO) analysis using an arbitrary wave function. First, the optimal natural bond orbitals are extracted for a localized Lewis resonance structure. Having these NBOs doubly occupied, one readily constructs the idealized Lewis-type wavefunction: 

\[ \psi_{L} = \det \{ \mathcal{U}_{\alpha} \}^{2} (\mathcal{U}_{\alpha}^{2} \ldots), \]  

where the \( \mathcal{U}_{\alpha} \) are doubly occupied NBOs representing localized electron-pair bonds or lone pairs of the formal Lewis structure. Analogous to (19) it gives the idealized density matrix \( \hat{\Gamma}_{\alpha} \) for the resonance structure \( \alpha \).

In the framework of \textit{ab initio} molecular orbital theory, the NRT expansion was shown to reproduce the true delocalization pattern with high accuracy (typically 80-90\% or more of the delocalization density, itself a small fraction of the total electron density) for a variety of
molecules and basis set levels. However, similarly to other theories, the NRT framework does not provide a definition for aromaticity.

3.5 Isodesmic and homodesmic reactions

Isodesmic reactions were introduced and defined by Pople and co workers in 1970 [162]. A chemical reaction is said to be isodesmic if the number and type of bonds are equal on both sides of the equation and only the neighborhood of the bonds are altered. These reactions can, in principle, be purely hypothetical.

Isodesmic reactions can be used to quantify different effects, such as aromaticity, resonance, hyperconjugation, ring strain and substitution, on the stability. Calculation of isodesmic reaction energies is a convenient way to examine and quantify the stability of reactive intermediates and short-lived reactants in a thermochemical sense.

The usage of isodesmic reaction seems to be a simple and cheap (from the point of view of CPU time) way to calculate a number of important properties mentioned above, but when used several facts and criteria must be taken into account. For instance, the original motivation behind the use of isodesmic reactions is the cancelation of systematic computational errors, arised from basis sets deficiencies (such as BSSE) and inadequacies in the treatment of electronic energy between the two sides of a reaction. The minimization of these errors by means of a choice of a theoretical method where the complete basis set limit is reached and where a high level of electron correlation is included is critical to get accurate reaction energies. On the other hand, the minimization can be achieved via usage of the same types of species on both sides of the reaction. In the latter case, the inherent errors associated with computation would disappear due to cancellation and allow high accuracy even in simple calculations. It should also be remembered that different isodesmic reactions may/must be set up in order to estimate the properties of distinct species. Different isodesmic reactions will give different results without one being systematically better than the other.

Homodesmic reactions are an improved form of isodesmic reactions in which not only the number of different bonds, but also the number of tertiary, quaternary, etc. atoms, must be equal on the left and right sides of the equation. The concept was proposed in 1975 to assess stabilization energies in cyclic conjugated hydrocarbons, then expanded to the studies of
destabilization from the ring strain. The results from calculations are on improvement in accuracy over bond separation reactions, although with an expense of longer computational time because of more complicate structures needed for balances. In addition, when large fragments are considered in the equation the number of conformations can be another weak point of these reactions. It depends on the problem (and also on the investigator) whether the most stable conformation or the more resemble conformation is used on the right side of the equation.

3.6 Laplacian of the electron density, ELF and Wiberg-index

While the topology of the electron density provides a faithful mapping of the concepts of atoms, bonds and structure, it provides no indication of maxima in corresponding to the electron pairs. The Laplacian of the density is the scalar derivative of the gradient vector field of the electron density. Thus, it determines where the electronic charge will locally augment its value, and where it will depletes its value. A maximum of this function denotes a position at which the electron density is maximally concentrated. It has been found that the local maxima of the function correspond very well to the regions of bonding according to the VSEPR theory. Hence, the regions of charge concentration defined by the Laplacian of the electron density correspond to the regions of space dominated by the presence of a single pair of electrons.

The Electron Localization Function (ELF) was introduced by Becke and Edgecombe [163] and first applied to a great range of systems, from atoms to molecules and solids. They associated the localization of an electron with the probability density to find a second like-spin electron near the reference point. The smaller this probability density the higher localized an electron is. It is important to have in mind that the image of localized electrons in a bond or as a lone pair are only good models in order to understand the chemistry but they do not have any physical realization.

The Wiberg Bond Index (WBI) was introduced by Wiberg in 1968 [164]. WBI arises from the manipulation of the density matrix, namely it expresses the sums of squares of density matrix elements. The Wiberg index is a widely used to describe the bond order of a chemical bond.
4 RESULTS

Let us place at the end of every chapter … the two letters used by the Roman judges when they did not understand a pleading.

N. L. – Non Liquet – It is not clear.

Voltaire

As we mentioned in the Chapter 2 the first stable carbene which had been synthesized was a five-membered ring. During the last two decades, the majority of the prepared stable carbenes were imidazol derivatives. These compounds have all five-membered ring skeletal and are classified into four families (Figure 1); NHCs (A), thiazolylidenes [B], PHCs [C] and CAACs [D]. It was believed for a long time that these electron-deficient species could only be stable when at least one heteroatom connects to the divalent center. In 2006, however, a three-membered highly strained ring compound, a cyclopropenylidene derivative was synthesized which can not be classified among any family (E). Also, cyclopropenylidene is the only stable carbene, which has no heteroatom substituent directly linked to the carbene centre [165] and so, it violates the experiences of 15 years.

![Figure 1. Five-membered ring carbene skeleton and cyclopropenylidene framework](image)

It is easy to recognize that diaminocyclopropenylidene, 1-NH$_2$ (Scheme 25), is a structural isomer of the Arduengo carbene with hydrogen substituents (4). Thus, comparing their energies one may get a simple explanation for the stability of the new compound. However, our first calculations showed that diamino-cyclopropenylidene is less stable than imidazole-2-ylidene by ca. 40 kcal/mol. Therefore, a deeper investigation of the conspicuous stability is required.
On the other hand, since \( q \) and \( y \) were bottled just after the first stable carbene of Arduengo, the question of the relative stability of the related species \( 9 \) and \( 24 \) also arises. Are the silicon \( 9 \) and germanium \( 24 \) analogues stable enough to be synthesized?

In the following two subchapters we explain the prominent stability of cyclopropenylidene and answer the latter question. We focus on the stability of divalent heavy rings (\( \text{Si}_3 \), \( \text{Si}_2\text{Ge} \), \( \text{Si}_2\text{C} \)) in the third section of this chapter.
4.1 Stability of amino disubstituted cyclopropenylidene

The calculations in this work were performed by the Gaussian 98 [166] and 03 [167] program packages. The figures were prepared by the Molden [168], AIM2000 [169] and Corel Draw programs, and the schemes by ChemDraw Ultra.

In chapters 4.1, 4.2 and 4.3 geometry optimization and frequency analysis were performed at the B3LYP/cc-pVTZ [170] and MP2/cc-pVTZ [171] levels. Each geometry was fully optimized, as verified by the frequency analysis. In order to obtain accurate energetic and geometric data the investigated molecules were re-optimized at the CCSD/6-311++G(d,p) [172] level of theory. To characterize the extent of aromaticity in the ring structures the NBO framework was used; Natural Resonance Theory [173] (NRT) analysis was performed at the B3LYP/cc-pVTZ level. The isomerisations were calculated at MP2/cc-pVTZ level. For the hydride ion addition and complexations the 6-311++G(d,p) basis set was used with MP2 level of theory. Because of the size problem, dimerization calculations were performed at B3LYP/cc-pVTZ level. Thermochemical values were computed at 298 K using the equations on statistical quantum mechanics implemented in Gaussian.

4.1.1 Thermodynamic stability

The computed relative energies and Gibbs free energies for the observed isomers (Scheme 26) of the C₃H₂ and C₃(NH₂)₂ potential energy surfaces are summarized in Table 4. Our calculations provide the same stability order on the C₃H₂ PES that was previously reported [174]; the global minimum appears to be at cyclopropylidene (1-H), while vinylidenecarbene (2-H) and propargylene (3-H) seem to be less stable by 14.40 kcal/mol and 30.01 kcal/mol, respectively.

![Chemical structures](image1)

Scheme 26.
Table 4: Relative energies and Gibbs free energies (in kcal/mol) of the investigated isomers on the C$_3$H$_2$ and C$_3$(NH$_2$)$_2$ potential energy surfaces.

|          | B3LYP/cc-pVTZ |          | B3LYP/cc-pVTZ |          |          | MP2/cc-pVTZ |          | MP2/cc-pVTZ |          |          | CCSD/ |          |
|----------|----------------|----------|----------------|----------|----------|-------------|----------|-------------|----------|----------| 6-311++G(d,p) |          |
|          | H  | NH$_2$ |          | H  | NH$_2$ |          | H  | NH$_2$ |          |          |          |       |          |
| cis-1    | 0.00 | 0.00 | 0.08 | 0.00 | 0.00 | 0.00 | 0.13 | 0.00 | 0.08 | 0.00 | 0.23 |
| trans-1  | 11.15 | 10.15 | 1.23 | 0.69 | 19.56 | 18.44 | 3.48 | 1.89 | 14.40 | 3.99 |          |
| 2        | 20.14 | 17.42 | 1.34 | 0.11 | 32.80 | 30.02 | 9.49 | 8.68 | 30.01 | 8.23 |          |
| 3        |          |          |          |          |          |          |          |          |          |          |          |

Although different halogen (R=F, Cl, Br) [175] and alkyl (R=CH$_3$, (CH$_3$)$_2$CH, (CH$_3$)$_3$C) [176] substituents have already been tested on the stability of the C$_3$R$_2$ system, the effect of the amino groups remains undiscovered. Four isomers, 2-NH$_2$ and 3-NH$_2$ and the two conformers of cyclopropylidene derivative, were found by replacing the hydrogen substituents with NH$_2$ groups. The sum of the bond angles around N is 349.0º and 347.8º in the case of cis-1-NH$_2$ and trans-1-NH$_2$ conformations (Scheme 27). Their energy difference is negligible (0.23 kcal/mol). The stability order is the same as in the case of the C$_3$H$_2$ system, however, the energy differences between the first few isomers are definitely smaller.

$$\delta = \delta_1 + \delta_2 + \delta_3 = 347.8^\circ$$

Since diaminocyclopropenylidene is a structural isomer of Arduengo carbene, the comparison of their potential energies may provide a simple rationalization of the stability of the newly synthesized three membered ring carbene. The relative stability of the C$_3$N$_2$H$_4$ carbene derivatives are depicted in Figure 2. As expected, the Arduengo carbene, 4 is the most stable isomer due to the known strong stabilizing effect of the nitrogens neighboring the carbene center [53]. It is followed in energy by two hitherto unknown five-membered rings (5 and 6). Diamino-
cyclopropenylidene (1-NH$_2$) is only the fourth in the line lying a considerable 42.75 kcal/mol higher than 4.

Thus, it is somewhat surprising that bis(diisopropylamino)cyclopropenylidene was possible to synthesize. To answer this obvious contradiction we studied the different factors of the stability in details.

Three main factors determine the stability of carbenes: the substituent effect, the delocalization and possible aromaticity of the ring and the ring strain. Using appropriate isodesmic reactions (Scheme 28) one can quantify the extent of these effects. The energy of reaction (1) ($\Delta E_1$) measures the net stabilization [177], including the contribution of $\pi$ electron donation of nitrogens, the electron delocalization (including aromaticity) and ring strain, relative to the triplet ground state carbene (X=C) and the singlet ground state silylene (Si) and germylene (Ge). In reaction (2) the strain and the delocalization are considered assuming that the substituent effect in both sides of the equation is the same. In both reactions (1) and (2) all the reactants and products were fully optimized. To estimate the ring strain ($\Delta E_{strain}$), reaction (3) was designed.
where the molecules at the left-hand side were optimized with bond angles fixed at the values found in the respective ring while at the right-hand side they were fully optimized in cis- form. To compare the extent of the individual factors, the overall substituent effect on the carbene center can be defined as the difference between the reaction energies of equations (1) and (2) ($\Delta E_{\text{subs}} = \Delta E_1 - \Delta E_2$) while the ring effect is estimated by subtracting the reaction energy of (3) from that of (2) ($\Delta E_{\text{ring}} = \Delta E_2 - \Delta E_{\text{strain}}$).

\[
\begin{align*}
\text{XH}_2 + \text{NH}_2\text{-CH}=\text{CH-NH}_2 & \rightarrow \text{XH}_2 + \text{NH}_2\text{-CH}=\text{CH-NH}_2 \\
\text{H}_3\text{C}-\text{NH}_2 & \rightarrow \text{X}-\text{NH}-\text{CH}_3 + \text{CH}_2\text{CH}_2
\end{align*}
\]

Scheme 28

The calculated data are summarized in Table 5. The total stabilization energies meet the expectation; Arduengo carbene ($\Delta E_{\text{Arduengo}} = 105.7$ kcal/mol) is more stable than the newly synthesized three-membered carbene ($\Delta E_{\text{NH}_2} = 64.4$ kcal/mol).
Table 5. Calculated isodesmic reaction energies (in kcal/mol) at B3LYP/cc-pVTZ level.

<table>
<thead>
<tr>
<th></th>
<th>(\Delta E_1)</th>
<th>(\Delta E_2)</th>
<th>(\Delta E_{\text{strain}})</th>
<th>(\Delta E_{\text{subs}})</th>
<th>(\Delta E_{\text{ring}})</th>
<th>(\Delta E_4^{***})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-H</td>
<td>18.34</td>
<td>1.29</td>
<td>-58.6</td>
<td>17.05</td>
<td>59.89</td>
<td>1.74</td>
</tr>
<tr>
<td>1-NH(_2)</td>
<td>64.4</td>
<td>36.65</td>
<td>-60.51</td>
<td>27.75</td>
<td>97.17</td>
<td>4.14</td>
</tr>
<tr>
<td>4</td>
<td>105.73</td>
<td>23.97</td>
<td>-25.44</td>
<td>81.76</td>
<td>49.41</td>
<td>42.24</td>
</tr>
<tr>
<td>9-H</td>
<td>-2.48</td>
<td>-4.54</td>
<td>-40.14</td>
<td>2.06</td>
<td>35.6</td>
<td>-9.53</td>
</tr>
<tr>
<td>9-NH(_2)</td>
<td>34.28</td>
<td>33.6</td>
<td>-38.73</td>
<td>0.68</td>
<td>72.34</td>
<td>-5.24</td>
</tr>
<tr>
<td>19</td>
<td>88.53</td>
<td>27.72</td>
<td>-7.47</td>
<td>60.81</td>
<td>35.19</td>
<td>21.24</td>
</tr>
<tr>
<td>24-H</td>
<td>-3.91</td>
<td>-6.99</td>
<td>-39.5</td>
<td>3.08</td>
<td>32.5</td>
<td>-10.81</td>
</tr>
<tr>
<td>24-NH(_2)</td>
<td>31.48</td>
<td>29.47</td>
<td>-38.04</td>
<td>2.01</td>
<td>67.51</td>
<td>-6.69</td>
</tr>
<tr>
<td>34</td>
<td>61.13</td>
<td>32.58</td>
<td>-5.67</td>
<td>28.54</td>
<td>38.25</td>
<td>27.83</td>
</tr>
</tbody>
</table>

It can be recognized that the stabilization effect of \(\pi\) electron donation from the nitrogen atoms is about three times larger in the Arduengo carbene (\(\Delta E_{\text{subs}}^{1-NH_2} = 81.8\) kcal/mol) than in the 1-NH\(_2\) (\(\Delta E_{\text{subs}}^{1-NH_2} = 27.8\) kcal/mol). This is not surprising as in the former molecule the nitrogen lone pair acts directly while in the latter it has only an indirect interaction. In contrast, the effect of the

*** When we submitted the above results to the *Organometallics*, one of the reviewer suggested reaction (4) to estimate the ring effect and ring strain together. He wrote: “A better way to calculate the effect of cyclization + strain is by the following equation: \(1-NH_2 + CH_4 + XH_4 \rightarrow HXC(NH_2)=CH(NH_2) + H_3X-CH_3\). This equation breaks the ring but leaves the conjugation between the empty p-orbital on X, the nitrogen lone pairs and the C=C double bond.”

Indeed, in equation (4) the ring is broken but the delocalization remains in the X-(N)C=C-N system. However, the substituent effect is not the same on the two sides of the equation, which was primarily aimed with reaction (2). Nevertheless, we calculated the reaction energies (4); it is tabulated in the last column (\(\Delta E_4\)) of Table 5. Unfortunately, we could not draw new conclusion from the data. Therefore we did not use them in our study.
ring is almost the double in the three-membered ring (97.2 kcal/mol) than in Arduengo carbene (49.4 kcal/mol). In the parent molecule 1-H it is considerably smaller but also overcomes that of 4. The stabilization effect of the ring involves two feasible processes; the π electron shift toward the divalent centre and the cyclic delocalization. As expected, the ring strain destabilizes both molecules, however, it is significantly larger in the three-membered ring (~60.5 kcal/mol) than in 4 (~25.4 kcal/mol).

Since the ring stabilization is surprisingly large in 1-NH₂, we tried to gain more insight in the possible aromaticity using the Natural Resonance Theory. Five Lewis structures (A, B, C, D and E) shown in Scheme 29 are relevant for describing the resonance hybrid of 1-NH₂. In the parent molecule 1-H obviously only A, B and C resonance structures can be assumed. Structure A corresponds to a non-aromatic carbene which contains a localized C=C double bond while B and C indicate the possible resonance Lewis structures for the aromatic ring. D and E represent charge separated electronic structures in which negative charge shift stabilizes the carbene center like in B and C, but they are ylidic and non-aromatic structures. Similarly, five-membered rings can be described with the analogous non-aromatic (A) and two aromatic (B and C) Lewis structures (Scheme 30). Obviously, the ylidic structures are missing in this case. The total weights of the aromatic hybrid structure (F) and the ylide hybrid structure (G) have been calculated simply as a sum of the weights of the suitable Lewis structures. For instance, the weight of G equals to the sum weight of D and E.

Scheme 29.
In this theory, the criterion of aromaticity is that the ratio of the weight of aromatic and non-aromatic resonance structures should be larger than 1. The higher this fraction, the larger the aromatic character of the given molecule.

Table 6. Weights of main resonance structures in percentages calculated at B3LYP/cc-pVTZ level.

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
<th>G</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-H</td>
<td>56</td>
<td>19</td>
<td>19</td>
<td>-</td>
<td>-</td>
<td>38</td>
<td>-</td>
</tr>
<tr>
<td>1-NH₂</td>
<td>7</td>
<td>17</td>
<td>17</td>
<td>22</td>
<td>22</td>
<td>34</td>
<td>44</td>
</tr>
<tr>
<td>4</td>
<td>-</td>
<td>36</td>
<td>36</td>
<td>-</td>
<td>-</td>
<td>72</td>
<td>-</td>
</tr>
<tr>
<td>9-H</td>
<td>83</td>
<td>5</td>
<td>5</td>
<td>-</td>
<td>-</td>
<td>10</td>
<td>-</td>
</tr>
<tr>
<td>9-NH₂</td>
<td>52</td>
<td>8</td>
<td>8</td>
<td>7</td>
<td>7</td>
<td>16</td>
<td>14</td>
</tr>
<tr>
<td>24-H</td>
<td>84</td>
<td>5</td>
<td>5</td>
<td>-</td>
<td>-</td>
<td>10</td>
<td>-</td>
</tr>
<tr>
<td>24-NH₂</td>
<td>52</td>
<td>8</td>
<td>8</td>
<td>7</td>
<td>7</td>
<td>16</td>
<td>14</td>
</tr>
</tbody>
</table>

It can be seen from the data (Table 6) that, in agreement with the previous investigations [57], 4 has strong aromatic character (the weight of F is \( w_F = 72\% \) whereby the carbene center is also stabilized. In the case of 1-H the localized form (A) is dominant (\( w_A = 56\% \)) and the molecule is only moderately aromatic (\( w_F = 38\% \)). This was also stated earlier considering the bond lengths and heats of bond separation reactions [71]. However, in the amino-substituted three-membered ring (1-NH₂) the weight of the localized A form is almost zero and the ylidic structures become more preferable. The contribution of the charge separated form G is 44% while the aromatic form F is represented only by 34%. Since the electrons of the amino groups are donated to the \( \pi \) system, a significant electron surplus is evolved in the ring and the Hückel-rule is violated. The
Results: Stability of Amino Disubstituted Cyclopropenylidene

aromaticity is diminished, although an enhanced stabilization due to the ylidal charge separation takes place.

4.1.2 Kinetic stability

Reactions of singlet carbenes can be sorted into three classes: structural isomerisation, nucleophilic attack on the unfilled p-orbital of the carbene and dimerization. The ability of cyclopropenylidene derivatives for these reactions was investigated by the rearrangement of \(1-NH_2\) to \(1-NH_2'\) (Scheme 31), addition of a hydride ion (Scheme 33) and calculating the dimerization energy \(\Delta E_{\text{dim}}\), respectively.

![Scheme 31](image)

We found that the isomerisation (5) of \(1-NH_2\) to \(1-NH_2'\) is a slightly favorable process (\(\Delta E_{\text{iso}}\) in Table 7) and occurs in one step with a huge barrier (\(\Delta E^*_{\text{iso}}\)). The activation barrier of the hydride ion addition of \(1-NH_2\), which is more relevant for the kinetic stability of carbenes, is comparable with that of imidazol-2-ylidene (4) and much higher than that of imidazolin-2-ylidene (8, Scheme 32).
Table 7. Reaction energies and activation energies for isomerisation ($\Delta E_{\text{Iso}}$ and $\Delta E^*_{\text{Iso}}$), hydride ion addition/ammonia complexation ($\Delta E_{\text{Nuc}}$ and $\Delta E^*_{\text{Nuc}}$) and dimerization (in kcal/mol).

<table>
<thead>
<tr>
<th></th>
<th>$\Delta E_{\text{Iso}}$</th>
<th>$\Delta G_{\text{Iso}}$</th>
<th>$\Delta E^*_{\text{Iso}}$</th>
<th>$\Delta G^*_{\text{Iso}}$</th>
<th>$\Delta E_{\text{Nuc}}$</th>
<th>$\Delta G_{\text{Nuc}}$</th>
<th>$\Delta E^*_{\text{Nuc}}$</th>
<th>$\Delta G^*_{\text{Nuc}}$</th>
<th>$\Delta E_{\text{dim}}$</th>
<th>$\Delta G_{\text{dim}}$</th>
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<tbody>
<tr>
<td>1-NH$_2$</td>
<td>-14.45</td>
<td>-15.01</td>
<td>65.34</td>
<td>60.51</td>
<td>-33.40</td>
<td>9.42</td>
<td>8.93</td>
<td>-12.98</td>
<td>0.69</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>-29.47</td>
<td>-29.73</td>
<td>43.26</td>
<td>39.31</td>
<td>-11.42</td>
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<td>11.42</td>
<td>-10.68</td>
<td>1.20</td>
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<td>8</td>
<td>-24.52</td>
<td>-24.35</td>
<td>43.53</td>
<td>39.90</td>
<td>-11.13</td>
<td>4.70</td>
<td>1.54</td>
<td>2.00</td>
<td>-35.46</td>
<td>-19.84</td>
</tr>
<tr>
<td>9-NH$_2$</td>
<td>a</td>
<td>a</td>
<td>68.24</td>
<td>63.85</td>
<td>b</td>
<td>b</td>
<td>-</td>
<td>c</td>
<td>c</td>
<td></td>
</tr>
<tr>
<td>19</td>
<td>29.45</td>
<td>26.65</td>
<td>56.15</td>
<td>52.33</td>
<td>b</td>
<td>b</td>
<td>-</td>
<td>-</td>
<td>18.70</td>
<td>31.53</td>
</tr>
<tr>
<td>23</td>
<td>34.94</td>
<td>32.20</td>
<td>73.83</td>
<td>69.90</td>
<td>2.99</td>
<td>6.26</td>
<td>-</td>
<td>-</td>
<td>-8.65</td>
<td>6.10</td>
</tr>
<tr>
<td>24-NH$_2$</td>
<td>a</td>
<td>a</td>
<td>65.63</td>
<td>61.14</td>
<td>-2.65</td>
<td>5.33</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

a No stable cyclic product was found.
b No stable complex was found.
c No stable dimer was found.

Scheme 32.

We also studied the complex formation of carbenes with ammonia using MP2/aug-cc-pVTZ level of theory, but the calculations suggest that these carbenes do not form nucleophilic complexes.

Scheme 33.

The estimated dimerization Gibbs free energy for diaminocyclopropenylidene (1-NH$_2$), considering the general route of dimerization in which a double bond is formed between the two
monomers, is 0.7 kcal/mol, similar to that of the Arduengo carbene (1.20 kcal/mol) [178]. In contrast, 1-H dimerizes in a very exothermic reaction (-39.3 kcal/mol).

4.1.3 Conclusion
In order to explain the kinetic and thermodynamic stability of the recently synthesized bis(diisopropylamino)cyclopropenylidene we investigated diaminocyclopropenylidene and found that the three-membered cyclopropenylidene (1-NH$_2$) is less stable by 42.75 kcal/mol than the Arduengo carbene. The main stabilizing factor in 1-NH$_2$ is the significant $\pi$-electron shift from the amino substituents, via a non-aromatic ylidic structure. It turns out that 1-NH$_2$ is stable against the nucleophilic complexation, hydride ion addition, structural isomerism and dimerization reaction. According to the data, its high kinetic stability is comparable with that of the known stable five-membered ring carbenes. The rational explanation for the synthesizability of bis(diisopropylamino)cyclopropenylidene is its substantial kinetic stability. In 2007, Lavallo wrote that “At the moment it is not clear if amino groups are necessary to confer stability to this family of carbenes” [179]. Now, the results presented above have revealed that amino substituents or strong $\pi$ electron donating groups are necessary to stabilize cyclopropenylidene derivatives.
4.2 Synthesizability of the heavy analogues of cyclopropenylidene

4.2.1 Thermodynamic stability

Silacyclopentadiene (f), and its 14 C$_2$SiH$_2$ isomers were theoretically investigated by Frenking et al. [75] while the infrared spectra of several of these isomers were experimentally observed by Maier et al. using a matrix-spectroscopic technique [76]. The effect of different halogen substituents [77], the ionization potentials, the electron affinities [78] and the triplet isomers [79] were also studied for this system. The study of the related germanium compounds involving germacyclopropenylidene (g) belongs to a less explored field of chemistry.

Scheme 34.

Scheme 34 shows the observed isomers on the SiC$_2$R$_2$ and GeSi$_2$R$_2$ (R=H, NH$_2$) potential energy surfaces. Their relative energy and Gibbs free energy is collected in Table 8. The SiC$_2$H$_2$ PES was determined using HF method and DZ basis set by Frenking et al. in 1986 [75]. In their study, the 11-H and 12-H were obtained as high lying minima, however, using more accurate
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methods we could not localize these structures. The geometry, electronic structure and relative stability of the hydrogen and halogen substituted silacyclopropenyldene (9-H), vinylidensilylene (12-H) and ethynylysilylene (13-H) and that of the germanium analogues (24-H, 27-H and 28-H) have already been investigated by Kassae et al. [77, 80]. Switching of global minima was predicted for both heavy systems: instead of 9 and 24, 14 and 29 become the global minimum of the corresponding PES using electronegative halogen substituents. From the data of Table 8 a similar tendency can be recognized with π electron donating amino groups. The acyclic 14-NH₂ and 29-NH₂ represent the global minimum while the three-membered rings (9-NH₂ and 24-NH₂) containing heavy divalent element become the second most stable isomers.

Figure 3. Stability order of the XC₂N₂H₄ silylene and germylene (X=Si, Ge) derivatives at the CCSD/6-311++G** level. (Upper numbers refer to the silylene series, while lower numbers symbolize the germylene species).
Table 8. Relative energies and Gibbs free energies (in kcal/mol) of the investigated isomers on the \( \text{XC}_2\text{H}_2 \) and \( \text{XC}_2(\text{NH}_2)_2 \) (X=Si, Ge) potential energy surfaces.

<table>
<thead>
<tr>
<th></th>
<th>B3LYP/cc-pVTZ</th>
<th></th>
<th></th>
<th></th>
<th>MP2/cc-pVTZ</th>
<th></th>
<th></th>
<th></th>
<th>CCSD/6-311++G**</th>
<th></th>
</tr>
</thead>
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Results: Synthesizability of the Heavy Analogues of Cyclopropenylidene

The stability order of the \( \text{XC}_2\text{N}_2\text{H}_4 \) silylene and germylene (X=Si, Ge) derivatives are plotted in Figure 3. The relative stability and aromaticity of the diazasilole isomers were previously published by Veszprémi and co-workers [180]. Extending this order with \( 9\text{-NH}_2 / 24\text{-NH}_2 \) and \( 14\text{-NH}_2 / 29\text{-NH}_2 \), the three-membered ring silylene/germylene are the fourth most stable structure and lie 53.5 and 48.7 kcal/mol higher than the most stable five-membered derivatives.

As it can be seen from Table 5 the total stabilization energy (\( \Delta E \)) is found to be ca. 30 kcal/mol in both diamino-substituted three-membered rings (9-NH2, 24-NH2), which is about half of that calculated for 1-NH2. This stabilization is significantly smaller than in the corresponding stable five-membered ring compounds. Similarly to carbenes, the ring effect is high, about the double than in 19 or 34. The most conspicuous observation shown in Table 5 is that the substituents have negligible effect in the three-membered rings, while they remarkably stabilize 19 and 34. The stabilization caused by the delocalization plays important role but its effect is extremely diminished by the strain (ca. 38 kcal/mol).

The moderate stability of \( 9\text{-NH}_2 \) and \( 24\text{-NH}_2 \), compared to the parent carbene 1-NH2, can be explained with both the reduced aromaticity and ylidic character (Table 6). As a matter of fact, the electron shift is considerably diminished compared to the respective carbene and the highest contribution (52%) corresponds to the localized structure A.

4.2.2 Kinetic stability

To estimate the kinetic stability of \( 9\text{-NH}_2 \) and \( 24\text{-NH}_2 \), their isomerization, dimerization, and nucleophilic complexation were considered. The latter is inspired to predict the reactivity of heavy carbenes toward a nucleophilic attack [181] (An example for the ammonia-heavy divalent molecule adduct is shown in Figure 4). From the calculations (Table 7) it can be recognized that the isomerization of \( 9\text{-NH}_2 \) and \( 24\text{-NH}_2 \) is not a likely process (Scheme 31); it occurs in a multistep process via open chain intermediates. The products are not stable and during the optimization they transformed into acyclic species. We found, however, that the activation barriers are prohibitively high for the first, ring opening step: for \( 9\text{-NH}_2 \Delta G^\ddagger_{\text{iso}} \) is 63.9 kcal/mol and \( \Delta G^\ddagger_{\text{iso}} \) is 61.1 kcal/mol for 24-NH2.
The immunity of silylenes and germynes against nucleophilic attack is investigated via their complexation ability with ammonia. We found stable complexes for 15 and 24-NH2 (Figure 4) and their formation is a slightly endothermic process ($\Delta E_{\text{Nuc}}$ are -2.99 and -2.65 kcal/mol) with positive $\Delta G_{\text{Nuc}}$ values. Therefore, their formation is not probable.

In accordance with the previous predictions no stable adduct exists between Denk silylene (11) and ammonia [181]. Similarly, during the MP2/6-311++G(d,p) calculations no stable Si$^+$NH$_3$ bonded complex of the three-membered silylene (9-NH$_2$) has been found.

Generally, two major mechanisms are relevant for the dimerization reaction of silylenes and germynes; the „classical” disilene formation (Scheme 35, left) [82] and a donor-acceptor adduct which is produced via the overlap of a substituent’s lone pair and the p orbital of the divalent center („bridge” way, Scheme 35, right). The relationship between stability and dimerization ability of silylenes was investigated by Oláh et al. [65].

To investigate the dimerization ability of silylenes and germynes we calculated their dimerization Gibbs free energies. In every case the kinetically favorable route was considered. Accordingly, compounds 19 and 23, which proved to be stable experimentally, have $\Delta G_{\text{dim}}$...
values 31.5 and 6.1 kcal/mol, respectively. No dimer was found in either case of amino disubstituted three-membered rings (9-NH$_2$ and 24-NH$_2$) which supports the stability of these compounds against dimerization.

4.2.3 Conclusion

The silicon (9-NH$_2$) and germanium (24-NH$_2$) analogues of diaminocyclopropenylidene show smaller stabilization energy than the carbene derivative 1-NH$_2$. The three-membered silicon and germanium species are less stable by 49-53 kcal/mol than the corresponding five-membered rings. In these molecules the localized divalent structure is dominant and both the $\pi$-conjugation and aromaticity are weaker than in 1-NH$_2$. Investigating their reactions we found that, however, both amino disubstituted three-membered silylene and germylene have high kinetic stability. According to our results, in contrast to the general tendency of stability order, in cyclopropenylidene analogues stability is decreasing in the sequence of carbene/silylene/germylene. Nevertheless, our results suggest that due to the appropriate kinetic stability, the silicon and germanium derivatives can be promising targets for synthetic chemists.
4.3 Synthesizability of „heavy-weight” cyclopropenylidene derivatives

4.3.1 Therodynamic stability

The kinetic and thermodynamic stability of three-membered rings containing Si=Si double bond and a divalent carbon/silicon/germanium atom (38, 48, 58 in Scheme 36, respectively) are considered in this chapter. The complete potential energy surfaces for CSi₂H₂, CSi₂(NH₂)_2, Si₃H₂, Si₃(NH₂)_2, GeSi₂H₂, GeSi₂(NH₂)_2 were successfully calculated. The relevant structures are schematically depicted in Scheme 36, while their relative energies and Gibbs free energies are listed in Table 9 (p.68).

![Figure 5. Stability order of the most stable CSi₂(NH₂)_2 isomers (R=NH₂) at the CCSD/6-311++G** level.](image)
Undulant energy surfaces were observed for CSi$_2$R$_2$ (R=H, NH$_2$) where the nine isomers cover a wide energy range. The energy order among the isomers is: 41-H < 39-H < 42-H < 40-H < 44-H < 45-H < 38-H < 43-H with hydrogen substituents and 42-NH$_2$ < 41-NH$_2$ < 39-NH$_2$ < 46-NH$_2$ < 45-NH$_2$ < 40-NH$_2$ < 38-NH$_2$ < 44-NH$_2$ < 43-NH$_2$ with amino substituents (Figure 5 and Table 9). As one can see from the enumeration, the global minimum of the CSi$_2$H$_2$ surface is an exotic ring structure 41-H with planar geometry and C$_2$V symmetry in good accordance with the
previous findings [182]. The cyclopropenylidene analogue (38-H) is a high-lying species and predicted to be less stable than the global minimum by 80.77 kcal/mol.

On the other hand, 42-NH₂, a chain-like isomer with cumulated double bonds and a lone pair on the γ silicon, is predicted to be the most stable isomer using NH₂ substituents. It is even more stable than the five-membered ring carbene 47 by ca. 30 kcal/mol. Similarly to the hydrogen substituted species 41-NH₂ has monobridge structure and shows unexpected stability, while the three-membered ring isomer containing carbene center (38-NH₂) is a very unstable structure.

For Si₃H₂ the planar singlet cyclotrisilapropenylidene 48-H was found to be the lowest-energy structure among the nine isomers (Table 9). In accordance with previous investigations structure 49-H and 50-H are low-lying species (~1.5 kcal/mol) while 51-H and 52-H are situated higher than the global minimum by 5.57 kcal/mol and 5.64 kcal/mol, respectively. The four most stable species can be transformed to each other via an isomerization process demonstrated by Ikuta and Wakamatsu in their theoretical work [155]. Open-chain isomers 54-H and 55-H differ only in the geometric arrangements of substituent connected to silicon in terminal α position and represent quite unstable species being about 20 kcal/mol above than 48-H. Both the trisilapropargylene (56-H) and the silicon analogue of vinylidencarbene (53-H) were found to be first and second order saddle points of the energy surface, respectively.
Replacing the hydrogen substituents to NH₂ groups it can be seen that structures 48-NH₂, 50-NH₂, and 51-NH₂ have similar relative energies (Table 9) while structure 52-NH₂ becomes the global minimum on the Si₂R₂ PES (R=NH₂) lying more than 5 kcal/mol lower in energy than the other structures. The only exception, which can compete with the stability of 52-NH₂ is 49-NH₂. However, if we consider the heavy five-membered silylene (57, Figure 6) it turns out that it is even more stable than the strongly bent 52-NH₂.
Let us focus on the geometry and electronic structure of the unique structure \(52\) which is found to be the most stable isomer with \(\pi\)-electron donating substituents. Its molecular model, Bader’s molecular graph, leading natural resonance structure, Laplacian distribution in the Si–Si–Si plane and electron localization functions (ELF) are depicted in Figure 7. As it can be seen \(52\)-\(\text{NH}_2\) has a strongly bent geometry around the central Si\(\beta\) atom and the N-Si\(\alpha\) bonds show above and below the Si–Si–Si plane. The bond Si\(\beta\)-Si\(\gamma\) is slightly shorter than the Si\(\alpha\)-Si\(\beta\) bond while the distance between Si\(\alpha\) and Si\(\gamma\) is longer than the usual Si-Si single bond length. The lack of the bond critical point between Si\(\alpha\) and Si\(\gamma\) atoms (and obviously the absence of a ring critical point) clearly suggests an open-chain structure which is also supported by the Laplacian of the electron density. On the image of the latter a lone-pair localized on the terminal Si\(\gamma\) is straight recognizable and also a lone-pair is foreshadowed on Si\(\beta\). A charge separated hybrid structure is evolved from the leading resonance structures in which both \(\beta\) and \(\gamma\) silicones, connected by a double bond, bear an electron pair. The electron localization functions provide further evidence for lone pair at \(\beta\) and \(\gamma\) positions while Wiberg bond indices predict Si\(\alpha\)-Si\(\beta\) single \((n_{\text{wiberg}}=1.23)\) bonding and Si\(\beta\)=Si\(\gamma\) double \((n_{\text{wiberg}}=1.92)\) bonding\(^{\dagger\dagger\dagger}\). As a result, the best representation of \(52\)-

\(^{\dagger\dagger\dagger}\) Wiberg indices for reference structures: Si\(_2\)H\(_4\): 1.9120, Si\(_2\)H\(_6\): 0.9810; Si\(_2\)(NH\(_2\))\(_4\): 1.3467; Si\(_2\)(NH\(_2\))\(_6\): 0.9284
Results: Synthesizability of „Heavy-Weight” Cyclopropenylidene derivatives

NH$_2$ is an open chain charge separated structure with double bond between Si$_{\beta}$ and Si$_{\gamma}$ and single bond between Si$_{\alpha}$ and Si$_{\beta}$ and containing lone pair electrons at $\beta$ and $\gamma$ positions.

Changing one silicon in the three-membered silicon ring to germanium we obtain the same framework of structures as described in the case of Si$_3$R$_2$. 22 isomers are resulted by the possible permutations of the germanium position in these structures. For instance isomer 58 and 59 with double bond between the atoms in the $\alpha$ and $\gamma$ positions and a lone pair at the $\beta$ position correspond to structure 48 on the Si$_3$R$_2$. Three isomers are predicted to compete with the global minimum 58-H on the Si$_2$GeH$_2$ PES. The lone pair electron of these low-lying structures is always located on the germanium atom. In addition, it can be concluded that germylenes are always more stable than silylenes from the same class of structure: 58 is more stable than 59, 60 is more stable than 61 and so on. It is not a surprise, as it is known that germanium forms stable divalent compounds, such as GeI$_2$ and GeCl$_2$. Conversion between these isomers can be assumed via the same mechanism as suggested for the Si$_3$H$_2$ surface by Ikuta et al.

With the exception of 68-H (17 kcal/mol), the open chain 69-H-79-H are high-energy molecules lying more than 20 kcal/mol higher than the global minimum 58-H. Using strong $\pi$ electron donating substituents 68-NH$_2$ became the most stable isomer (Table 9). (On the Si$_2$GeN$_3$H$_4$ PES, the five-membered ring germylene (80) is the global minimum (Figure 6). 68-NH$_2$ is the most stable diamino- isomer.) The extreme stability of structure 68-NH$_2$ was shown up when we tried to optimize the isomer 62-NH$_2$ and 67-NH$_2$ at CCSD/6-311++G** level: in both cases the geometry of 68-NH$_2$ was received. Structure 69-NH$_2$ with divalent silicon atom in terminal position is located 35.96 kcal/mol higher than 68-NH$_2$. The cyclopropenylidene analogue 58-NH$_2$ is only the third most stable isomer (8.75 kcal/mol). Chain-like species containing two-electron-three-center bond (61-66) are moderately unstable species lying in the range of 20-30 kcal/mol above the global minimum.
Table 9. Relative energies and Gibbs free energies (in kcal/mol) of the investigated isomers on the XSi$_2$H$_2$ and XSi$_2$(NH)$_2$$_2$ (X=C, Si, Ge) potential energy surfaces.

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Results: Synthesizability of „Heavy-Weight” Cyclopropenylidene derivatives

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<td>27.14</td>
<td>24.02</td>
<td>30.84</td>
<td>21.48</td>
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It is known that one of the unique features of the energy surfaces when going from carbon down in the periodic table is the appearance of the two-electron three center bonds. Accordingly, the existence of these non-classical bonds were evinced in 49-H, 50-H, 51-H using natural atomic and bond orbital analysis and geometry consideration [155]. The double bond character of Siα-Siγ in 48-H was proven in the same study.

It can be seen from Table 10 that the hydrogen substituted carbene species (38-H) is significantly destabilized by ring strain (ΔEstrain= -41.2 kcal/mol) and, as one can expect, represents an unstable structure. On the other hand, two phenomena were perceived for the amino substituted analogue (38-NH2); a very high substituent effect (ΔEsubs= 77.3 kcal/mol, which is similar to that of Arduengo carbene) and a negative value for the ring effect (ΔErings= - 31.3 kcal/mol). Since, these effects compensate each other the calculated net stabilization energy is only 16.7 kcal/mol. It is known that the properties of the silicon and germanium compounds are more similar to each other than to that of the same carbon compound. Our calculations
confirm this trend: both stabilization and destabilization factors have the same extent in 48 and 58. For instance considering the amino substituted structures, the ring effects ($\Delta E_{\text{ring}}$) are 48.4 and 46.0 kcal/mol for the silylene and germylene, respectively. The destabilization due the ring strain is around 30 kcal/mol in both structures. As a result, the isodesmic reaction (1) possesses a similar stability for GeSi$_2$(NH$_2$)$_2$ and Si$_3$(NH$_2$)$_2$. Two important facts can be concluded when the data are compared to those of the species containing C=C double bond: the ring strain is always smaller in the heavier rings (~ 10 kcal/mol) and the net stabilization is ca. 10 kcal/mol smaller in the heavier rings.

Table 10. Calculated isodesmic reaction energies (in kcal/mol) at B3LYP/cc-pVTZ level.

<table>
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<tr>
<th></th>
<th>$\Delta E_1$</th>
<th>$\Delta E_2$</th>
<th>$\Delta E_{\text{strain}}$</th>
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<th>$\Delta E_{\text{ring}}$</th>
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<td>-31.25</td>
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<td>6.84</td>
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<td>4.36</td>
<td>38.56</td>
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<td>8.75</td>
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<td>2.65</td>
<td>36.32</td>
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<tr>
<td>58-NH$_2$</td>
<td>19.38</td>
<td>18.47</td>
<td>-27.53</td>
<td>0.91</td>
<td>46.00</td>
</tr>
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</table>

NRT calculations suggest a unique dominant resonance structure for the amino disubstituted heavy ring (Table 11) with carbene center (38-NH$_2$). In the framework H the carbon is connected to both silicon atoms through double bonds (see Scheme 37). The characteristic in-plane lone pair of the divalent carbon is missing and the two electrons on the out-of-plane orbital participate in a delocalized four electron three center bond. This structure may explain the high substituent effect (Table 10) and the four electrons exclude the aromaticity. In the near future we will perform further investigations to find out which effects cause the dramatic change in the electronic structure (1-NH$_2$ is ylidic, 48-NH$_2$ is silylene, while in 38-NH$_2$ structure H is dominant) when carbon atoms are replaced by silicons.

\[ \text{Scheme 37.} \]
Results: Synthesizability of „Heavy-Weight“ Cyclopropenylidene derivatives

Similarly to 1-H, 48-H and 58-H show only moderate aromatic character (36% and 48%) and the localized structure A is the leading resonance structure. On the other hand, the aromatic structure F is dominant in the case of the amino disubstituted silylene (66%) and germylene (56%) rings, while the low contribution (<10%) of G reflects the weak interaction of the divalent center and the amino groups.

Table 11. Weights of main resonance structures in percentages calculated at B3LYP/cc-pVTZ level.

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
<th>G</th>
<th>H</th>
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</thead>
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<td>36</td>
<td>-</td>
<td>-</td>
<td>72</td>
<td>-</td>
<td>-</td>
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<tr>
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<td>9</td>
<td>-</td>
<td>-</td>
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<td>18</td>
<td>-</td>
<td>-</td>
<td>36</td>
<td>-</td>
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<td>33</td>
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<td>66</td>
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<td>2</td>
<td>2</td>
<td>56</td>
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4.3.2 Kinetic stability

Similarly to the method applied for the carbon ring silylene and germylene species we estimated the kinetic stability of the amino substituted heavier species investigating isomerization, dimerization, and nucleophilic complexation reactions. We found that none of the investigated molecules form stable complex with ammonia or form stable dimer adduct. Instead of dimerization, a special donor-acceptor complex was found in which hydrogen bonds between silylene lone pair and the amino substituent’s hydrogen (vice versa between the monomers) cover the attractive intermolecular forces among the monomers (Figure 8). Similarly to 9-NH₂ and 24-NH₂ the isomerization (Scheme 31) occurs through a ring opening step for 48-NH₂ and 58-NH₂ with the activation barriers of 36.2 and 48.5 kcal/mol, respectively. For the carbene, 38-NH₂, the isomerization is a one-step process through a 51.5 kcal/mol energy barrier.
From the results it can be assumed that, these molecules have no electrophilic reactivity, i.e. the cyclic delocalization causes sufficient electron density above the divalent center. However, taking into account the facile conversion among the low-lying isomers with hydrogen substituents (Figure 9, [155]), it can be assumed that similar rearrangements can also occur with amino substituents. Accordingly, $38\text{-NH}_2$ easily converts into the more stable $41\text{-NH}_2$ through $T-2$ (Figure 9), while the respective silylene $48\text{-NH}_2$ and germylene $58\text{-NH}_2$ may form (along the path having $T-3$) $49\text{-NH}_2$ or $52\text{-NH}_2$ and $60\text{-NH}_2$ or $68\text{-NH}_2$, respectively. These self reactions can hinder the successful synthesis of $38\text{-NH}_2$, $48\text{-NH}_2$ and $58\text{-NH}_2$.

Figure 8. Van der Waals complex between two $58\text{-NH}_2$ monomers.

Figure 9. Schematic diagram of the energy relationships between the isomers and transition states on the $Si_3H_2$ PES.
4.3.3 Conclusion

In this chapter the thermodynamic and kinetic stability of cyclic XSi$_2$R$_2$ (R=H, NH$_2$) carbenes (X=C), silylenes (X=Si) and germylenes (X=Ge) have been investigated. The potential energy surfaces of these heavy ring analogues are more complicated than those of the corresponding carbon ring species, for instance 22 isomers were found on the GeSi$_2$R$_2$ PES, while GeC$_2$R$_2$ contains only 11 isomers. We found that none of the cyclic heavy divalent rings are global minimum on the corresponding PES; carbene 38-NH$_2$ is the seventh most stable structure lying 58.15 kcal/mol higher than the global minimum, while silylene 48-NH$_2$ and germylene 58-NH$_2$ are located 6.96 (fourth) and 8.75 kcal/mol (third) higher, respectively, than the most stable open-chain bent structure. However, we believe that none of these structures are synthesizable because of the facile isomerization revealed for the Si$_3$H$_5$ system.

4.4 The mechanism of isomerization of cyclotrimetallenes

In the summary of cyclotrometallenes beside the synthesis, appearance and structure of cyclotrimetallenes (see 2.3) we also briefly mentioned several of their extraordinary reactions. One of these reactions was the isomerization of 3$H$-disilagermirene (II) to 1$H$-disilagermirene (III) reported in 2000 (Scheme 38) [127]. It was remarkable in several ways; the analogous carbon reaction was never observed, the product was the first (and is the only) synthesized 3$H$-disilagermirene and the product was the first stable compound with Si=Ge double bond.

Moreover, shortly afterwards other substituent migration reactions were discovered for cyclotrigermenes (see 2.3.2). Despite this, the number of the theoretical works concerning the reactivity of cyclotrimetallenes is very limited. Therefore, in the last two subchapters we study the substituent migration reactions of various cyclotrimetallenes (Scheme 39).
In good agreement with the experimental observation we found that the rearrangement of 3H-disilagermirene to 1H-disilagermirene is exothermic. This can be explained by the $\pi$-$\sigma^*$ conjugation concept (Scheme 40) [183]; the interaction of the high-lying $\pi$-orbitals of the endocyclic $X_\beta$=$X_\gamma$ double bonds and the low-lying $\sigma^*$-orbitals of the exocyclic $X_\alpha$-$Y$ bonds causes higher electronic stabilization in III than in II.

Investigating the mechanism of isomerisation of cyclotrimetallenes some low-energy bridge isomer with three-membered ring skeleton was found. The calculations suggested that the stability of these strange isomers is always comparable to that of the corresponding cyclotrimetallene.

In the fourth subchapter we interpret the mechanism of the substituent migration of cyclotrimetallenes in details while in the last one we deal with the structure and stability of the mono- and dibridge isomers and their role in the isomerization reactions.

Geometry optimizations and frequency analysis were performed with the hybrid B3LYP functional and the correlation-consistent, polarized cc-pVTZ basis set. The reliability of the
B3LYP/cc-pVTZ level of theory was validated for Si$_3$H$_4$ and Si$_2$GeH$_4$. MP2 and CCSD methods were used with the 6-311++G** basis set for the migration reaction of Si$_2$GeH$_4$ to check the reliability of the selected level of theory. It was found that although the calculated B3LYP energies were not quantitatively precise; the trends of the energies and geometries at the stationary points are close to the results of higher level calculations. Therefore in this work all geometries were fully optimized at the B3LYP/cc-pVTZ level of theory. Second derivatives and harmonic vibrational frequencies were calculated for all stable molecules and transition states were investigated. The existence of only one imaginary frequency was checked for transition states. IRC calculations were performed for all the reaction paths at the B3LYP/cc-pVDZ level to confirm the reaction coordinates from transition states to stable products. In these cases geometries were fully optimized at the same level of theory (B3LYP/cc-pVDZ). All calculated energy data were corrected with the zero-point energy (ZPE [184]). Atomic populations were obtained using the Natural Population Analysis (NPA) in order to compute atomic charges.

![Scheme 41](image)

The mechanism of substituent migration were studied on the B, C, D and E rings (Scheme 41) with silyl (R=SiH$_3$) substituents and A, B and C rings with hydrogen substituents (R=H). The calculated thermodynamical data and selected geometrical parameters are given in Tables 12 and 13, respectively. As all the reactions follow the same mechanism (with the exception of cyclopropene) only one reaction is discussed in details (Scheme 42 (blue) and Figure 10). In the case of cyclopropene as it is expected, the H migration proceeds in one step through an energetic transition state (Scheme 42, red). The transition state has C$_s$ symmetry in which the moving hydrogen is situated above the C-C bond. All the other reactions proceed in a two-step mechanism via a stable intermediate.
4.4.1 Energetic aspect of the reaction

The rate determining step of the reaction is the first step. It can be concluded from Table 12 that the energy of the intermediate is close to the reactant. During the second step of the reaction the silyl group (R₂) rotates and moves back to its original position. This motion is very flexible and has a small barrier. The energy barrier for cyclotrigermene is two-three times lower than for the other rings which is in accordance with the observation of a circumambulatory motion has been reported only over cyclotrigermene. Rearrangement of 3H-disilagermirene to 1H-disilagermirene is the only exothermic reaction which also agrees with the observation. The highest activation barrier (34.06 kcal/mol) belongs to the isomerization of disilagermirene, which is conceivable at 393 K. However, introducing bulkier groups is believed to further lower the barrier. An overall trend can be concluded that the more Ge the ring contains, the lower the barrier on the rate determining step gets. Similar trend can be observed for the intermediate (I): with the increasing number of germanium atoms in the ring, the intermediate structure is getting more stable: rings D and E are more stable than the final product. The barrier of the second step is small. In the cyclotrisilene migration T2 is lower in energy than the intermediate, in the case of D and E rings it is lower than the product. This may suggest a third step of the reaction. Since the structures of T2 and the final product are almost identical, the possible second intermediate is probably also very similar. Any calculational attempts made to find this step, however, resulted in either the product or the T2 transition state.
The variation of charge distribution clearly demonstrates the nucleophilic character of silyl migration and the electrophilic character of hydrogen migration. For example, in the case of siladigermirene (D) the charge of $Y_a$ changes from -0.175 to -0.027 while $X_2$ is getting more negative (from -0.027 to -0.154) and it bears the maximum negative charge (-0.300) in the intermediate. With H-substituents $X_g$ becomes more positive (from 0.116 to 0.351) and $Y_a$ becomes more negative (from 0.242 to 0.035).

Table 12. Thermodynamic data of stationary points in substituent migration reactions (in kcal/mol) and NBO charges. All values were obtained at the B3LYP/cc-pVTZ level.

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<th>$\Delta G$</th>
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<th>$Y_a$</th>
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<td>-0.066</td>
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### Alien Molecules on Earth

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<td></td>
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<td></td>
<td>I</td>
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<td>-4.23</td>
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<td>0.00</td>
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<td></td>
<td>product</td>
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<td>0.00</td>
<td>-0.173</td>
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</table>

### 4.4.2 Geometry change during the reaction

The rearrangement reactions start with the shift of the silyl group (R₁, see Scheme 41 for the numbering) from the saturated ring atom (Y₁) toward an unsaturated one. In the transition state T₁ the moving SiH₃ group is situated above the ring, almost halfway between its original and final position. On the other hand the silyl group on the opposite side of the ring (R₂) bends strongly.
Results: The Mechanism of Isomerisation of Cyclotrimetallenes

behind the ring plane forming a pronounced pyramidal structure at $X_b$. In this manner T1 is an asymmetric monobridge structure (Figure 10). As the reaction proceeds, the moving silyl group ($R_1$) acquires a position near to that of the product. On the contrary, $R_2$ bends further toward to $Y_a$ and forms a new three-membered ring with $X_b$ and $Y_a$. The resulting stable intermediate is a new monobridge structure. Thus, both the transition state (T1) and the intermediate (I) has monobridge structures being of the different type. In the second step of the reaction, the bridging group turns back to the original position via a combined motion with rotation. The transition from the monobridge structure to the trans-bent product is very similar to the scheme described in the case of $M_2H_2$ ($M = \text{Si, Ge, Sn, and Pb}$) [185].

Table 13. Selected geometric data of substituent migration reactions. All values were obtained at the B3LYP/cc-pVTZ level and are given in Å and degree.

<table>
<thead>
<tr>
<th>Ring</th>
<th>$R_1, R_2, R$</th>
<th>stat.point</th>
<th>$r(X_bX_g)$</th>
<th>$r(X_gY_a)$</th>
<th>$r(Y_aX_b)$</th>
<th>$r(R_1Y_a)$</th>
<th>$r(R_1X_g)$</th>
<th>$r(R_2X_b)$</th>
<th>$\omega$</th>
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<td>2.338</td>
<td>2.338</td>
<td>4.068</td>
<td>2.348</td>
<td>54.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>T1</td>
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<td>2.545</td>
<td>2.731</td>
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<td>2.338</td>
<td>2.134</td>
<td>4.068</td>
<td>2.362</td>
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<td>3.905</td>
<td>2.354</td>
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<td>3.889</td>
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<td>2.453</td>
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<td>2.509</td>
<td>2.509</td>
<td>4.088</td>
<td>2.423</td>
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<td>4.129</td>
<td>2.405</td>
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<tr>
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<td>2.435</td>
<td>3.939</td>
<td>2.393</td>
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</tr>
<tr>
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<td>2.509</td>
<td>2.309</td>
<td>4.088</td>
<td>2.411</td>
<td>2.423</td>
<td>62.6</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>H</td>
<td>reactant</td>
<td>2.116</td>
<td>2.305</td>
<td>2.305</td>
<td>1.490</td>
<td>3.342</td>
<td>1.486</td>
<td>54.6</td>
</tr>
<tr>
<td></td>
<td></td>
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<td>1.600</td>
<td>1.954</td>
<td>1.521</td>
<td>61.6</td>
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<tr>
<td></td>
<td></td>
<td>I</td>
<td>2.473</td>
<td>2.243</td>
<td>2.291</td>
<td>3.359</td>
<td>1.486</td>
<td>1.735</td>
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</tr>
<tr>
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<td>T2</td>
<td>2.525</td>
<td>2.248</td>
<td>2.244</td>
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<td>1.486</td>
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<td>2.305</td>
<td>2.116</td>
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<td>1.490</td>
<td>1.486</td>
<td>62.6</td>
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<tr>
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<td>2.376</td>
<td>1.546</td>
<td>3.449</td>
<td>1.488</td>
<td>52.9</td>
</tr>
</tbody>
</table>
At the beginning of the reaction the double bond $r(X_bX_g)$ is slightly elongated (Table 13), the bond length maximum is evolved in the first transition state or in the intermediate. In these structures the $X_b-X_g$ bond is longer than the usual $X-X$ ($X = \text{Si, Ge}$) single bond. Nevertheless, the existence of the ring critical points in all cases indicates that the rings are not opened during the reaction. However, if the ring contains at least one germanium atom the $X_g-Y_\alpha$ bond has broken in the first transition structure, and the rings are opening. The motion of the migrating group is characterized by the $r(Y_\alpha R_1)$ and $r(X_g R_1)$ distances while $r(X_b R_2)$ describes the formation of the bridge structure. As one can see, the wandering group already got its final position product in the intermediate and in the second step of the reorganization just the opening of the wedged group by combined moving with rotation.

### 4.4.3 Detected stable monobridge?

Since the calculations suggest that the stability of the bridged intermediate is always comparable to the final product (in two cases it is more stable), the question arises why this structure has never been observed. The next chapter deals with the stability of bridged structures. Hereinafter we discuss an interesting reaction where a bridged-structure may be observed.

![Scheme 43](image)

When Kira and co-workers synthesized the first stable cyclic disilene, hexakis(trialkylsilyl)tetrasilacyclobutene (VI), they observed its facile photochemical conversion to tetrasilabicyclo[1.1.0]butane V and its thermal reversion back to VI (Scheme 43) [117]. Using
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deuterium labeled V and VI, this isomerization was revealed to proceed via 1,2-silyl migration as proposed for the isomerization of 3H-disilagermene. No X-ray analysis is available for V and also the direct measurements of the $^{29}$Si and $^{13}$C NMR spectra of V failed because it was obtained only in a low concentration in solution and was converted to VI during sample concentration. The arrangement of the bulky substituents was determined by $^1$H NMR and UV spectroscopy.

Later, in 2003, the same group reported the photochemical isomerization of cyclotrisilene (IV) to the corresponding bicyclotetrasilane (V) (Scheme 44). The three possible 1,2-silyl migrations a, b, c (black) suggested by Kira [141], are illustrated in Scheme 45.

From these concerted reaction paths a leads to bicyclotetrasilane (V). Path b leads to the reactant while path c is a decomposition which occurs via an unstable structure. Paths b and c consist of
an „above-the-ring” step and are considered as subsidiary. The alternative $b'$, $b''$ and $ab$ paths are evolved from the rearrangement mechanism discussed above. Following the same discussion the formation of a closed shell intermediate $V'$ ($b'$) can be assumed, which can react further in two different ways: as the structure of $V'$ is close to the product $V$, the formation of $V$ via a $SiBuMe_2$ group migration is a facile step ($ab$), or the monobridge intermediate $V'$ opens resulting cyclotrisilene being identical to the reactant (IV).

![Diagram](image1)

**Scheme 46.**

Because of the similarity of the structures $V'$ and $V$ (Scheme 46), the compound detected by UV spectroscopy and determined as the product ($V$) in path $a$ could be the bridged intermediate ($V'$) in the reaction if it occurs via the $b'$, $b''$ steps.
The comparison of the stationary points energies of (Figure 11) predicts a mechanism through a monobridge intermediate $V'$ for the rearrangement from $IV$ to $V$, i.e. through the $b'$, $ab$ paths. However, it also supports the previous suggestion that the $V$ is detected, which can form tetrasilacyclobutene $VI$. According to previous studies [149b] the four-membered ring ($VI$) is more stable than the bicyclobutane ($V$), which supports the observed isomerisation from $V$ to $VI$ [186].

4.4.4 Conclusion

The mechanism of substituent migration was studied on different unsaturated three-membered carbon, silicon and germanium rings with silyl and hydrogen substituents. All the reactions (with the exception of cyclopropene) proceed in a two-step mechanism via a stable intermediate. The rate determining step of the reaction is the first step. The barrier of the second step is small and the energy of the intermediate is close to the reactant. Both the first transition state ($T1$) and the intermediate ($I$) has monobridge structures of different type. The rearrangement of cyclotrisilene can be interpreted with the same, two steps mechanism.

4.5 Bridged and Distorted Structures

According to the calculated results, the stability of bridged intermediates is comparable to that of product. Although, up to now nobody could synthesize these bridged species with bulky groups. Though the bulkier groups kinetically stabilize the reactive center and seem to be essential during the actual synthesis, it may destabilize the bridge structure. Therefore, we investigated the relevant isomers on various $X_2YR4$ PESs (Scheme 47) and the effect of substituent size on the stability of bridged species.
4.5.1 Geometry considerations

Considering the possible stable isomers of trimetallenes listed in Scheme 47, one may encounter ring (81-88) and open-chain structures (89-92). There are some other possible isomers on the YX₂R₄ potential surfaces that are not discussed in this study (for Si₃H₄ PES see ref [187]). Selected geometrical parameters compared with experimental data of different structures on the investigated PESs are tabulated in Table 14. The first two structures (81 and 82) are “classical” unsaturated rings (Scheme 47). The geometry around the X₃=X₄ double bond in 81 and 82 was found to be planar (A, B, C) or trans-bent (D, E) (Figure 12).
Results: Bridged and Distorted Structures

Figure 12. Example of a planar (Si$_2$GeH$_4$) and a \textit{trans}-bent (SiGe$_2$(SiH$_3$)$_4$) structure.

This observation meets the expectations since disilene, digermene, and distannene generally exhibit a \textit{trans}-bent structure. The length of Si=Si, Si=Ge, and Ge=Ge double bonds with silyl substituents are 2.132 Å (exptl data: 2.138(2) Å), 2.191 Å, and 2.309 Å (exptl data: 2.239(4) Å), respectively. As expected, the double bonds are shorter than in the corresponding acyclic derivatives ($r$(Si,Si) = 2.202(1) Å and $r$(Ge,Ge) = 2.3568(6) Å). Rings containing a divalent atom fall into class 83 and 84. The symmetry of 84 is typically C$_2$, rarely C$_{2v}$. Representatives of classes 85 and 86 have remarkable dibridge structures. The dibridge is formed between the unsaturated atoms by their two ligands. One can imagine the three-membered dibridge ring as adduct of a dibridge X$_2$H$_2$ and an XH$_2$ moiety. Topological analysis showed no formal bond between the pillar atoms (Figure 12).

Figure 13. Topological analysis of the dibridge (left, Si$_3$H$_4$) and monobridge (right, Si$_2$Ge(SiH$_3$)$_4$) structures.
The distance between the two pillar atoms bridged by a hydrogen is 2.576 Å, which is much longer than the usual Si-Si single bond ($r$(Si,Si) = 2.352 Å in Si$_2$H$_6$). In the dibridge isomers the topology of the original three-membered ring has been modified to a cage of the ring atoms and the two bridged substituents (Figure 13). This exotic structure, however, becomes a first order saddle point on the PES with silyl substituents. The only difference between the two monobridge structures 87 and 88 is the position of the formally unsaturated bond: homonuclear in 87 and heteronuclear in 88. In these structures the bond between the pillar atoms is longer than the usual X-Y (X,Y= Si, Ge) single bond. The detailed topological analysis of the monobridge structure is discussed below.

Generally, the central angle $\omega$($X_\alpha$-$X_\beta$-$X_\gamma$)) increases with the substitution of silicon atoms with germanium (C, D, E) and converges to 60°. We found that the heteronuclear double bonds are always surprisingly short: 2.191 and 2.230 Å in C and D with silyl substituents, respectively. Replacing the hydrogen substituents with silyl groups, the $X_\alpha$-$X_\beta$ and $X_\beta$-$X_\gamma$ bonds elongate, while the central $\omega$($X_\alpha$-$X_\beta$-$X_\gamma$)) angle does not differ too much from $\omega$($X_\alpha$-$X_\beta$-$X_\gamma$)) in the H-substituted derivatives.

<table>
<thead>
<tr>
<th>ring</th>
<th>isomer</th>
<th>Substituents</th>
<th>$r$(Y$_a$X$_b$) (Å)</th>
<th>$r$(X$<em>a$Y$</em>\omega$) (Å)</th>
<th>$r$(X$<em>b$X$</em>\gamma$) (Å)</th>
<th>$\omega$ (°)</th>
<th>ref.</th>
</tr>
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<td>2.334</td>
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<tr>
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<td></td>
<td>Si$^{t}$Bu$_2$Me</td>
<td>2.364(3)</td>
<td>2.352(3)</td>
<td>2.138(2)</td>
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<td>2.522(4)</td>
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Results: Bridged and Distorted Structures

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<td>2.330(2)</td>
<td>4.080(2)</td>
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</table>

With the exception of carbon derivatives, all the isomers with an open geometry (89-92) are significantly bent around the central atom. True divalent isomers are the representatives of class 89 and 90, while class 91 and 92 form allenic structures. The Laplacian distributions show a clear lone pair around the central atom and a delocalized π-system of 89 and 90. No lone pairs can be found in class 91 and 92. The central angle is also larger in structures 91 and 92 than in 89 and 90.

4.5.2 Energetic Considerations

The relative energies of isomers 81-92 were investigated (Table 15), and the relationship between these structures was determined. We found the well-known fact that the cyclopropyl derivatives (A) behave differently from the other rings containing heavy atoms. The energies of its isomers cover a wide range; both three-membered-ring isomers, cyclopropene and carbene structures, lie more than 25 kcal/mol higher than the most stable linear allene structure, while the mono and dibridge isomers are assigned to first- and second-order saddle points, respectively.
Table 15. Relative energies (kcal/mol) and symmetries of the investigated isomers.

<table>
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<td>13.13</td>
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<td>1.53</td>
</tr>
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<td>R=H</td>
<td>70.77</td>
<td>5.43</td>
<td>1.44</td>
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<td>0.00</td>
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<tr>
<td>R=H</td>
<td>70.77</td>
<td>5.43</td>
<td>-</td>
<td>0.00</td>
<td>11.77</td>
</tr>
<tr>
<td>R=SiH</td>
<td>123.13&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.65</td>
<td>15.04</td>
<td>2.49</td>
<td>14.33</td>
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<tr>
<td>R=SiH</td>
<td>123.13&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.65</td>
<td>-</td>
<td>2.49</td>
<td>-</td>
</tr>
<tr>
<td>R=SiH</td>
<td>84.57&lt;sup&gt;a&lt;/sup&gt;</td>
<td>3.64</td>
<td>19.01</td>
<td>3.83</td>
<td>13.54</td>
</tr>
<tr>
<td>R=SiH</td>
<td>84.57&lt;sup&gt;a&lt;/sup&gt;</td>
<td>3.64</td>
<td>15.59</td>
<td>3.83</td>
<td>16.05</td>
</tr>
<tr>
<td>R=SiH</td>
<td>-</td>
<td>0.00</td>
<td>0.00</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>R=SiH</td>
<td>-</td>
<td>0.00</td>
<td>11.93</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>R=SiH</td>
<td>0.00</td>
<td>-</td>
<td>10.83</td>
<td>15.62</td>
<td>17.56</td>
</tr>
<tr>
<td>R=SiH</td>
<td>0.00</td>
<td>-</td>
<td>10.83</td>
<td>19.25</td>
<td>13.23</td>
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</tbody>
</table>

<sup>a</sup> First order saddle point. <sup>b</sup> Second order saddle point.

The PES of the cyclotrisilene derivatives (B) is considerably flat. With hydrogen substituents the global minimum is the open-chain silylene, while the dibridged structure is the second most stable isomer. On the other hand, with silyl substituents the cyclic structures become more preferable. As we substitute silicon atoms with germaniums (C, D, E), germynenes become more preferable, and the bridge structures are always assigned to global minima. In series C the most stable isomer is the open structure 89 (R = H) or the cyclic structure 83 (R = SiH<sub>3</sub>). Open-chain isomers with <i>C</i><sub>r</sub> symmetry, 89 and 90, are divalent compounds and mainly favorable with hydrogen substituents. Allenic open-chain species with <i>C</i><sub>2</sub> symmetry, i.e., 91 and 92, are stabilized by silyl groups. As one can see from Table 15, depending on the substituents, one of the isomers (89 or 90) or (91 or 92) can be found on the PES but never both of them.

4.5.3 Ring versus open-chain structures

Structures 83 (and the asymmetric analogue 84) and 89 (and the asymmetric analogue 90) seem quite similar to each other at first glance. 83 and 84 are three-membered rings with a divalent atom in <i>α</i>-position, with fairly small <i>ω</i> bond angles and <i>C</i><sub>2</sub> (or <i>C</i><sub>2v</sub>) symmetry, stabilized by silyl substituents. 89 and 90 are also divalent compounds, but they are open-chain with <i>C</i><sub>r</sub> symmetry,
mainly favorable with hydrogen substituents. Both the cyclic and acyclic types prefer
germanium as a divalent atom. However, remarkable electronic differences can be found with
further investigations. Topological and electronic properties clearly show a bond that closes the
ring in 83 and 84, while no such bond exists in 89 and 90 (Figure 14).

One can easily distinguish between these isomers on the basis of bond angles and symmetry
considerations, and the results can be proved with bond order, charge distribution, or molecular
orbital analysis. The investigation of the critical points obtained from the topological analysis of
the electron density shows a ring critical point in 83 and 84, which is missing in 89 and 90. The
Wiberg bond indices suggest three single bonds between the ring atoms in 83 and 84 (for ring B:
\( n_{Wiberg}(\text{Si}_\beta-\text{Si}_\gamma) = 0.96, n_{Wiberg}(\text{Si}_{\alpha\gamma}-\text{Si}_{\beta\gamma}) = 1.05 \)). In 89 and 90 an enhanced interaction between \( Y_\alpha \) and \( X_\beta \) (in B: \( n_{Wiberg}(\text{Si}_{\alpha\gamma}-\text{Si}_\beta) = 1.34, n_{Wiberg}(\text{Si}_\beta-\text{Si}_\gamma) = 0.65 \)) is observed. The Laplacian
distributions of electron densities demonstrate (Figure 15) the appearance of an in-plane electron
pair on \( Y_\alpha \) in both 83/84 and 89/90, proving that they are silylenes. Indeed, in 89 and 90 there is
a delocalized \( \pi \)-system perpendicular to the plane containing the three heavy atoms skeleton.
4.5.4 Effect of Bulky Substituents

In the previous chapter we introduced the mechanism of silyl group migration for different ring compounds. For the heavy species the reaction follows a two-step mechanism via a stable intermediate. As the number of Ge atoms increases, the intermediate gets more and more stable. Moreover, in some cases the intermediate is more stable than the reactant or the product.

Comparable stability of the monobridge intermediate and the final product during the substituent migration reaction poses the question of why a bridged intermediate has never been observed. Although the bulkier groups kinetically stabilize the reactive center and seem to be essentially helpful during the actual synthesis, it seems that their presence hinders the formation of bridge structures. To answer this question, we compared the geometry and relative stability of the intermediate and the product with different bulky substituents (Scheme 48, Table 16).

![Scheme 48.](image)

Table 16. Relative energies of the reactants, intermediates, and products (in kcal/mol).

<table>
<thead>
<tr>
<th></th>
<th>93</th>
<th>94</th>
<th>95</th>
<th>96</th>
<th>97</th>
<th>98</th>
<th>99</th>
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<th>101</th>
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<tbody>
<tr>
<td>reactant</td>
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<td>0</td>
<td>0</td>
<td>0</td>
<td>0.0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>intermediate</td>
<td>5.9</td>
<td>5.6</td>
<td>6.5</td>
<td>-</td>
<td>-3.2</td>
<td>3.5</td>
<td>7.2</td>
<td>5</td>
<td>11</td>
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<tr>
<td>product</td>
<td>3.6</td>
<td>4.6</td>
<td>6.5</td>
<td>8.9</td>
<td>-3.1</td>
<td>3.7</td>
<td>4.6</td>
<td>3.7</td>
<td>2.2</td>
</tr>
<tr>
<td>$\Delta E[^{b}]$</td>
<td>2.3</td>
<td>1</td>
<td>-0.1</td>
<td>-</td>
<td>-0.2</td>
<td>2.6</td>
<td>1.3</td>
<td>8.7</td>
<td></td>
</tr>
</tbody>
</table>

\[^{a}\]All values were obtained at the B3LYP/6-31G* level. \[^{b}\]$\Delta E$ is the energy difference between the intermediate (I) and the product. \[^{c}\]B3LYP/cc-pVTZ level.
Results: Bridged and Distorted Structures

One can easily track the steric effect of growing substituents to the geometry of the bridge structures (Figure 16, Scheme 48). The bulkier bridging substituent (R₂) induces a larger deviation from the ideal bridge structure. On the other hand, substituents that are not forming the bridge orientation directly (R) strengthen the trend, although with a smaller efficiency.

![Figure 16. The change of the geometry of intermediates with increasing size of substituents. For simplicity, only the position of the ring atoms and the connected silicones are shown.](image)

Using SiH₃ and Si(SiH₃)₃ substituents (Figure 17), the trend seems to fail, as the bigger groups cause smaller distortions in geometry (comparing 93 with 100 or 94 with 101). A possible explanation is the electronic effect of the substituents. If the bridging group (R₂) is SiH₃ or Si(SiH₃)₃, there are energetically also well distinguishable intermediates having a monobridge orientation. Thus with these substituents, one can predict a two-step mechanism with an intermediate during the isomerization process. Increasing the size of the other substituents (R) has a negligible effect on the geometry.

![Figure 17. Intermediate geometry of compounds containing SiH₃ and Si(SiH₃)₃ groups with increasing size of substituents. For simplicity, only the position of the ring atoms and the connected silicones are shown.](image)

The distortion caused by the bulky substituents can be so large that one cannot even distinguish between intermediate and product. That can be proved comparing the relative energies of intermediates (I) and products (P) (ΔE), which are approaching each other progressively from 93
to 96. In the case of 95 $\Delta E$ is less than 0.1 kcal/mol, and for 96, which has been synthesized, calculations predict just one structure and a one-step mechanism of the isomerization reaction.

In the photochemical isomerization of cyclotrisilene, which was reported by Kira, one of the substituents is Si(Si'Bu₂Me)_3; that is, assuming the above-discussed mechanism, the group migration can occur via a monobridged intermediate. According to these results and considering the electronic effect of the Si(SiC₉H₇)₃-type substituents, there is hope to synthesize bridged silicon compounds despite the substituent bulkiness.

4.5.5 Bridged or distorted structure?

Our calculations suggest the existence of the intermediate in many cases. However, studying these compounds, one may ask whether a structure has a bridged or only a distorted geometry. The easiest way to define the bridge structure is based on the topological analysis of the electron density; the existence of a ring critical point between the two pillar and the bridge atoms proves the proper structure. In the absence of a ring critical point it is only a distorted geometry. Topological analysis of the bridged isomers of B, C, D, and E demonstrates the bond between the two pillar atoms. The bridging ligand can be bonded to both pillar atoms (Figure 13) or to only one of them (Figure 18). It depends on the actual ring atoms. Nevertheless, the existence of the ring critical point in all cases indicates that the $X_\alpha X_\beta X_\gamma$ rings are not opened in these isomers. Yet, we found that only the disilagermirene ring with silyl substituents has real bridge geometry (Figure 13 (right)).

![Figure 18. Topological analysis of a strongly distorted but not bridge structure.](image-url)
4.5.6 Conclusions

Novel ring (81-88) and open-chain structures (89-92) (see Scheme 47) have been found on the $X_2YR_4$ ($X, Y = \text{Si, Ge}$) PESs.

On the one hand, open-chain silylenes with hydrogen substituents belong to global minima; the dibridge structures are also favorable. On the other hand, the cyclic structures become more preferable with silyl substituents. As we substitute silicon atoms with germanium, germilenes become more preferable. The structures where the bridge is between two germanium atoms are always assigned to global minima.

The stability and geometry of the monobridged structure (87), which is intermediate in the isomerization of cyclotrimetallenes, depend on steric and electronic effects. The bulkier the bridging substituents applied ($R_2$), the larger the deviation from ideal bridge structure. This trend fails using SiH$_3$ and Si(SiH$_3$)$_3$ substituents (Figure 18) due to different electronic effects of the SiH$_3$ group. A remarkable observation can be made for monobridge (87) structures: ring critical points always appear in real monobridge structures. In the absence of the ring critical point, intermediates have only distorted geometry without a monobridge. It has also been found that only the disilagermirene ring with silyl substituents has real bridge geometry.
5 SUMMARY

This thesis dealt with divalent, unsaturated and bridged three-membered ring compounds of Group 14 elements. In the first part the thermodynamic and kinetic stability of several three-membered divalent compounds were investigated. The synthesizability of hitherto unknown molecules was considered based on the results. The second part gave an account of the mechanism of the unique 1,2-silyl migration reaction in cyclotrimetallenes. Finally, the structure, stability and synthesizability of three-membered bridged molecules were presented. Our results can be summarized as follows:

1. The main stabilizing factor in three-membered diaminocyclopropenylidene (1-NH$_2$) is the significant $\pi$-electron shift from the amino substituents to the ring, via a non-aromatic ylidylic structure. However 1-NH$_2$ is less stable than the isostructural Arduengo carbene by 42.75 kcal/mol, its high kinetic stability is comparable with that of the known stable five-membered ring carbenes. The rational explanation for the synthesizability of bis(diisopropylamino)-cyclopropenylidene is its substantial kinetic stability.

2. Unlike 1-NH$_2$, in three-membered silylene (9-NH$_2$) germylene (24-NH$_2$) derivatives the localized divalent structure is dominant and both the $\pi$-conjugation and aromaticity are weaker than in 1-NH$_2$. Our results suggest, however, both amino disubstituted three-membered silylene and germylene have appropriate kinetic stability to be promising targets for synthetic chemists.

3. In contrast to the general tendency of stability order, in cyclopropenylidene analogues stability is decreasing in the sequence of carbene/silylene/germylene.

4. We found that none of the cyclic heavy divalent rings is global minimum on the corresponding PES; carbene 38-NH$_2$ is the seventh most stable structure lying 58.15 kcal/mol higher than the global minimum, while silylene 48-NH$_2$ and germylene 58-NH$_2$ are located 6.96 and 8.75 kcal/mol higher, respectively, than the most stable open-chain
bent structure. Moreover, a self reaction, i.e. inter-conversion among isomers, may hinder their successful synthesis.

5. Investigating the substituent migration on different unsaturated three-membered carbon, silicon and germanium rings we discovered a two-step mechanism via a stable intermediate. The rate determining step of the reaction is the first step while the activation barrier of the second step is small. In many cases the monobridge intermediate (I) shows comparable stability with the reactant and product.

6. The geometry and stability of the bridge structure (87) strongly depends on the steric and electronic effects of the bridge substituents. The bulkier the bridging substituents applied ($R_2$), the larger the deviation from ideal bridge structure. This trend fails using SiH$_3$ and Si(SiH$_3$)$_3$ substituents due to different electronic effects of the SiH$_3$ group.

7. Based on AIM theory we gave a simple definition for bridged structures; the existence of a ring critical point between the two pillar and the bridge atoms proves a real bridged structure. In the absence of the ring critical point, intermediates have only distorted geometry without a monobridge. It has also been found that only the disilagermirene ring with silyl substituents has real bridge geometry.
List of Publications


*B. Pintér and T. Veszprémi*: Synthesizability of the heavy analogues of disubstituted cyclopropenylidene: a theoretical study. (accepted in *Organometallics*).

**Publications not included in the thesis:**


6 REFERENCES


[177] In this reaction methene was calculated in its ground triplet state.
[178] An earlier study predicted 0.9 kcal/mol for dimerization Gibbs free energy.