



Műegyetem 1782

# ALIEN MOLECULES ON EARTH

Balázs Pintér

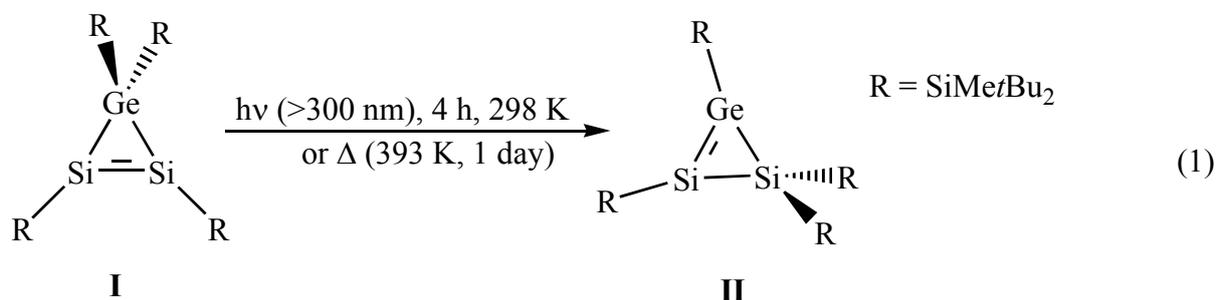
PhD thesis

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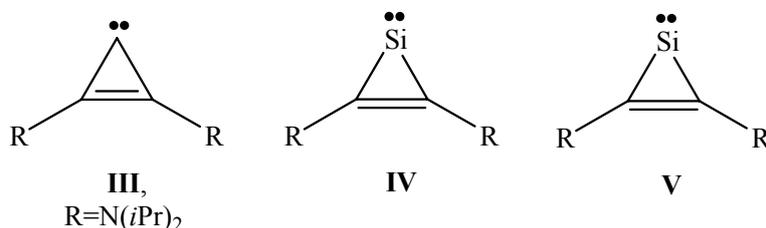
# 1 INTRODUCTION

The researches on which this thesis is based were inspired by two experimental observations; in 2000 the isomerization of 3*H*-disilagermirene (**I**) to 1*H*-disilagermirene (**II**) was reported by Sekiguchi's group<sup>1</sup> (Scheme 1) and in 2006 the synthesis of a new carbene, cyclopropenylidene (**III**, Scheme 2), was managed by Bertrand's group<sup>2</sup>.



**Scheme 1.**

Isomerization reaction (1) was remarkable in several ways; the analogous carbon reaction was never observed, the product (**II**) was the first (and is the only) synthesized 1*H*-disilagermirene and the product was the first stable compound with Si=Ge double bond. Shortly afterwards other substituent migration reactions were discovered for cyclotrimetallenes. Since, my primary goal was to reveal the mechanism of the substituent migration reactions of cyclotrimetallenes. Investigating the mechanism low-energy intermediates having bridge structures with three-membered ring skeletal were found. Moreover, the stability of these strange isomers is always comparable to that of the corresponding cyclotrimetallene. So, I also dealt with the structure and stability of mono- and dibridge isomers and their role in the isomerization reactions of cyclotrimetallenes.



**Scheme 2.**

On Earth cyclopropenylidene is highly reactive, and acts as an intermediate in numerous organic chemical reactions. All previous efforts to isolate it under laboratory conditions have failed until 2006, when Bertrand and co-workers could stabilize cyclopropenylidene by attaching amino groups. During the last two decades, the majority of the prepared stable carbenes were imidazol derivatives. 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. Cyclopropenylidene, however, is a three-membered highly strained ring compound which can not be classified among any family of carbenes. Also, cyclopropenylidene is the only stable carbene, which has no heteroatom substituent directly linked to the carbene centre and so, it violates the experiences of 15 years. Therefore, the main aim of my project was the investigation of the conspicuous stability of cyclopropenylidene. I was also looking for the answer to the question whether the silicon (**IV**) and germanium analogues (**V**) are stable enough to be synthesized?

<sup>1</sup> Lee, V. Y.; Ichinohe, M.; Sekiguchi, A.; Takagi, N.; Nagase, S. *J. Am. Chem. Soc.* **2000**, *122*, 9034.

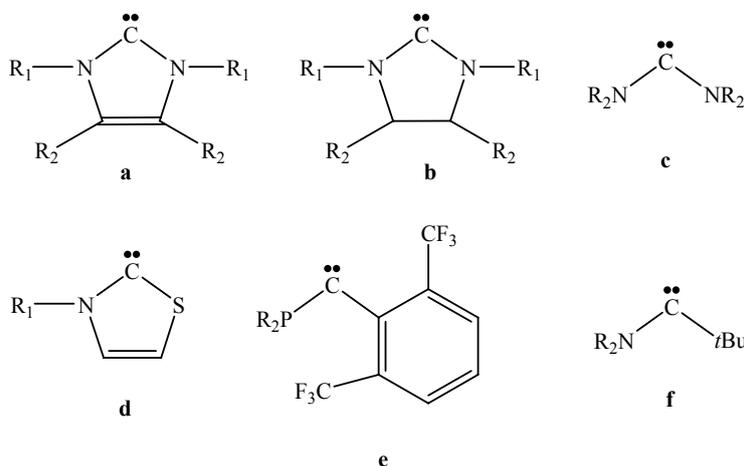
<sup>2</sup> Lavallo, V.; Canac, Y.; Donnadiou, B.; Schoeller, W. W.; Bertrand, B. *Science* **2006**, *312*, 722.

## 2 LITERATURE SURVEY

The main keywords of this thesis are *divalent*, *unsaturated* and *bridged three-membered ring compounds of group 14*. Accordingly, this chapter contains three main sections dealing with the literature of divalent, unsaturated and bridged structures separately.

### 2.1 Divalent group 14 compounds

Most of the divalent carbon and silicon compounds are very reactive intermediates with short lifetime. It was only in 1991, when the first stable carbene was synthesized by Arduengo's group (**a**)<sup>3</sup>. Related carbenes with various substituents also reported<sup>4</sup>. 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 (**b**)<sup>5</sup>, the first stable open-chain carbene, bis-diisopropylcarbene was synthesized in 1996 (**c**)<sup>6</sup>, thiazol-2-ylidene (**d**) which did not contain two stabilizing amino groups was bottled in 1997<sup>7</sup> and the preparation of **e** and **f** which feature only one heteroatom substituent were also reported<sup>8</sup>. The first carbene, which has no heteroatom substituent directly linked to the carbene center (**III**) was even isolated in 2006.



**Scheme 3**

The chemistry of silylenes is evolving parallel to that of carbenes and girt by increasing interest to this day. The first stable silylene, the silicon analogue of Arduengo carbene (**g**), was synthesized by Denk *et al.* in 1994<sup>9</sup> (Scheme 4). The preparation of **g** was followed by the synthesis of its saturated analogue, **h**<sup>10</sup> and the preparation of the benzo and (**i**) pyrido-fused (**j**) silylenes<sup>11</sup>. All of these

<sup>3</sup> Arduengo, A. J., III; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1991**, *113*, 361.

<sup>4</sup> Arduengo III, A. J.; Rasika Dias, H. V.; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1992**, *114*, 5530.

<sup>5</sup> Arduengo III, A. J.; Goerlich, J.; Marshall, W. *J. Am. Chem. Soc.* **1995**, *117*, 11027.

<sup>6</sup> Alder, R. W.; Allen, P. R.; Murray, M.; Orpen, A. G. *Angew. Chem.* **1996**, *108*, 1211.

<sup>7</sup> Arduengo, A. J., III; Goerlich, J. R.; Marshall, W. *J. Liebigs Ann.* **1997**, 365.

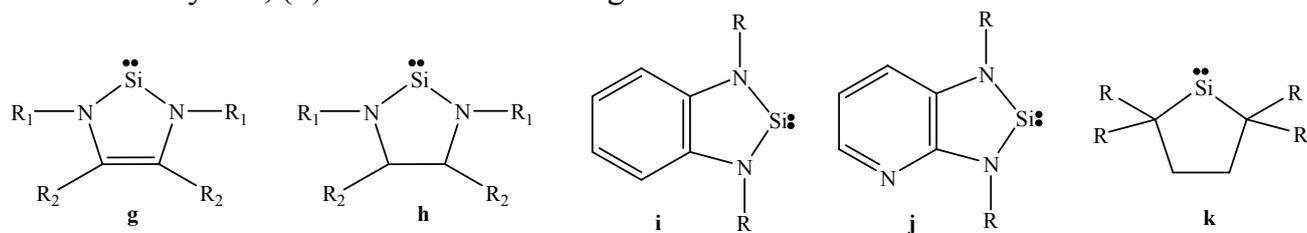
<sup>8</sup> Lavallo, V.; Canac, Y.; Prasang, C.; Donnadieu, B.; Bertrand, G. *Angew. Chem. Int. Ed.* **2005**, *44*, 5705.

<sup>9</sup> Denk, M.; Lennon, R.; Hayashi, R.; West, R.; Belyakov, A. V.; Verne, H. P.; Haaland, A.; Wagner, M.; Metzler, N. *J. Am. Chem. Soc.* **1994**, *116*, 2691.

<sup>10</sup> Denk, M.; Green, J. C.; Metzler, N.; Wagner, M. *J. Chem. Soc., Dalton Trans.* **1994**, 2405.

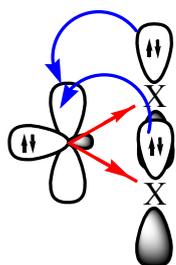
<sup>11</sup> (a) Gehrhus, B.; Lappert, M. F.; Heinicke, J.; Boese, R.; Blaser, D. *J. Chem. Soc., Chem. Commun.* **1995**, 1931.; (b) Heinicke, J.; Oprea, A.; Kindermann, M. K.; Kárpáti, T.; Nyulászi, L.; Veszprémi, T. *Chem. Eur. J.* **1998**, *4*, 541.

molecules are stabilized by two nitrogen atoms bonded to the divalent center. More recently, Kira *et al.* have isolated a silylene, (**k**)<sup>12</sup> with no such nitrogen stabilization.



**Scheme 4.**

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, first using bulky groups around the reactive center (kinetic stabilization), second stabilizing the electron configuration via appropriate substituents (thermodynamic stabilization).

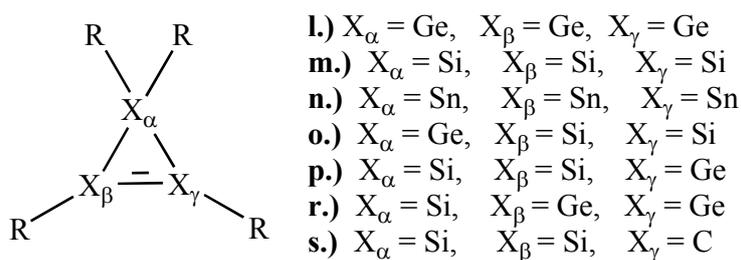


Scheme 5 shows the main stabilization effect of these hypovalent structures. Singlet carbenes and silylenes have a lone pair in the plane of the molecule and an empty p orbital perpendicular to the plane. Functional groups which have occupied p orbital parallel to that of divalent center and liable to donate this electron pair to the empty p of C or Si stabilize the singlet electron configuration. To protect the carbenes against self-reactions their electrophilic reactivity must be masked.

**Scheme 5.**

The new carbene is a stable (**III**), 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, 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<sup>13</sup>.

## 2.2 Cyclotrimetallenes



**Scheme 6.**

The synthesis of the first cyclotrimallene, cyclotrigermene (**I**), reported by Sekiguchi *et al.* in 1995<sup>14</sup> constituted an important milestone for the chemistry of unsaturated three-membered ring compounds. Hereby, cyclotrimetallenes became of interest and a number of experimental and theoretical results were achieved in the field aiming to answer the question how these compounds can be stable with the reactive endocyclic metal-metal double bond and ring strain of Baeyer and Pitzer types. The three-

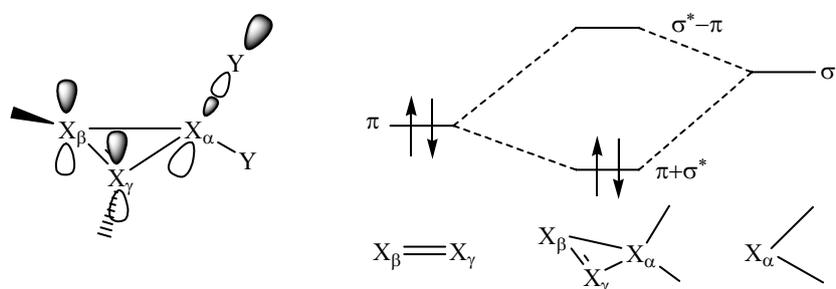
<sup>12</sup> Kira, M.; Ishida, S.; Iwamoto, T.; Kabuto, C. *J. Am. Chem. Soc.* **121**, **1999**, 9722.

<sup>13</sup> Holschumacher, D.; Hrib, C. G.; Jones, P. G.; Tamm, M. *Chem. Commun.* **2007**, 3661.

<sup>14</sup> A. Sekiguchi, H. Yamazaki, C. Kabuto, H. Sakurai, S. Nagase; *J. Am. Chem. Soc.* **1995**, **117**, 8025

membered unsaturated rings containing metalloids of group 14 investigated in the thesis were synthesized in the last twelve years. The syntheses of two cyclotrisilenes (**m**) with different substituents were reported in 1999<sup>15</sup>. Wiberg *et al.* bottled the cyclotristannene (**n**) in the same year<sup>16</sup>. As the next step after the isolation of cyclotrisilene, cyclotrigermene, and cyclotristannene the synthesis of the heteronuclear disilagermirene (**o**) was reported in 2000. Moreover, due to an extraordinary 1,2-migration (see Scheme 1) it immediately provided the appearance of two types of disilagermirenes, 3*H*-disilagermirene (**o**) and 1*H*-disilagermirene (**p**). Two other representatives of unsaturated ring compounds containing two different group 14 elements, 1*H*-siladigermirene (**r**)<sup>17</sup> and disilacyclopropene (**s**)<sup>18</sup> 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.

Similarly to the divalent species, there are two ways to stabilize these reactive species. Electronic stabilization can be achieved increasing 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 (Scheme 7). The ring strain can be decreased by using electropositive silyl substituents. However, the synthesis of cyclotrimetallenes could be achieved using bulky substituents which protect the reactive site of the molecule.



**Scheme 7.**

The reactivity of cyclotrimetallenes, which combines the chemical properties of both cyclotrimetallanes and dimetallenes, was found to be very diverse and unique. One of the most interesting features of these compounds is the migration of the halogen atoms over the three-membered ring skeleton. A similar phenomenon was observed for disilagermirene by Sekiguchi *et al.* (Scheme 1). Under irradiation a bulky group from the saturated atom (Ge) migrates to one of the unsaturated silicones. The isomerization of 3*H*-disilagermirene (**I**) to 1*H*-disilagermirene (**II**) 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.

### 2.3 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. 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.

<sup>15</sup> (a) T. Iwamoto, C. Kabuto, M. Kira; *J. Am. Chem. Soc.* **1999**, 121, 886.; (b) T. Iwamoto, C. Kabuto, M. Kira; *J. Am. Chem. Soc.* **1999**, 121, 886.

<sup>16</sup> N. Wiberg; H.-W. Lerner, S.-K. Vasisht, S. Wagner, K. Karaghiosoff, H. Nöth, W. Ponikwar; *Eur J. Inorg. Chem.* **1999**, 1211

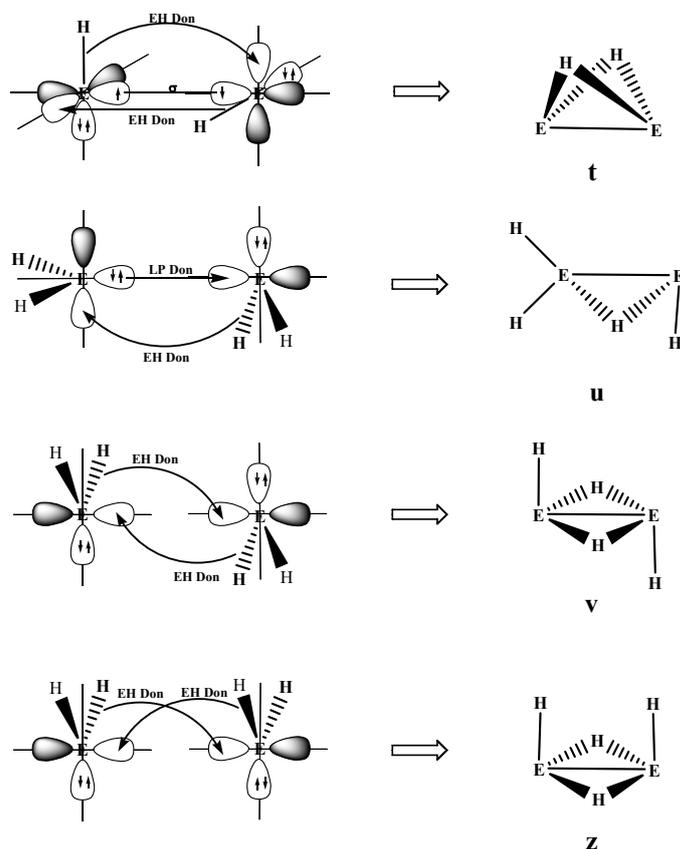
<sup>17</sup> Lee, V. Y.; Yasuda, H.; Ichinohe, M.; Sekiguchi, A. *J. Organomet. Chem.* **2007**, 692, 10.

<sup>18</sup> Igarashi, M.; Ichinohe, M.; Sekiguchi A. *J. Am. Chem. Soc.* **2007**, 129, 12660

The energetically lowest lying form of  $\text{Si}_2\text{H}_2$  was found to be the doubly hydrogen-bridged butterfly structure **t** (Scheme 8). The theoretical predictions about the unusual structures **t** was confirmed in the case of  $\text{Si}_2\text{H}_2$  by spectroscopic studies in low-temperature matrixes by Bogey *et al.*<sup>19</sup>.

Trinquier discussed the bonding character of the mono- (**u**) and dibridged (*trans*-, **v** and *cis*-, **z**) forms in details, however, in the case of  $\text{Si}_2\text{H}_4$  and  $\text{Ge}_2\text{H}_4$  he did not find the monobridged isomers. Finally, Schaefer *et al.* found that unexpectedly a monobridged isomer is the global minimum on the  $\text{Si}_2\text{H}_3$  PES and the monobridge structure has also comparable stability with the global minimum disilene on the  $\text{Si}_2\text{H}_4$  PES<sup>20</sup>. Their results were proved experimentally with Fourier transform microwave spectroscopy measurements.

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-member rings.



E=Si, Ge, Sn, Pb

**Scheme 8.**

### 3 COMPUTATIONAL METHODS

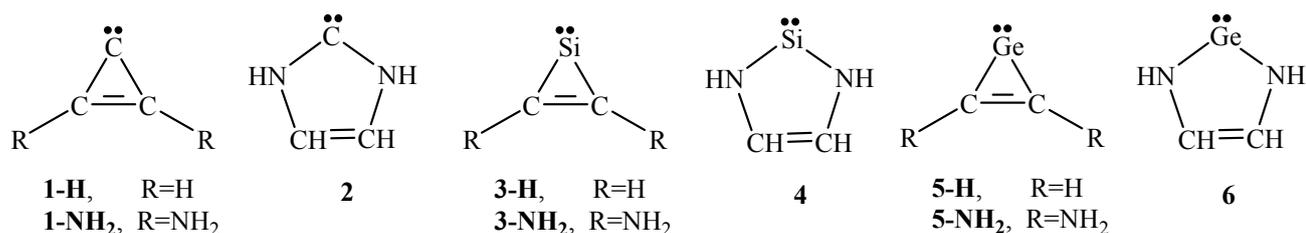
The calculations were performed by the Gaussian 98 and 03 program packages. In chapters 4.1, 4.2 and 4.3 geometry optimization and frequency analysis were performed at the B3LYP/cc-pVTZ and MP2/cc-pVTZ levels. The investigated molecules were re-optimized at the CCSD/6-311++G(d,p) level of theory. Natural Resonance Theory (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. In chapters 4.4 and 4.5 all geometries were fully optimized at the B3LYP/cc-pVTZ level of theory. 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. Atomic populations were obtained using the Natural Population Analysis (NPA), in order to compute atomic charges.

<sup>19</sup> Bogey, M.; Bolvin, H.; Demuyneck, C.; Destombes, J.-L. *Phys. Rev. Lett.* **1991**, *66*, 413.

<sup>20</sup> Sari, L.; McCarthy, M. C.; Schaefer III, H. F.; Thaddeus, P. *J. Am. Chem. Soc.* **2003**, *125*, 11410.

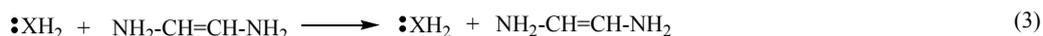
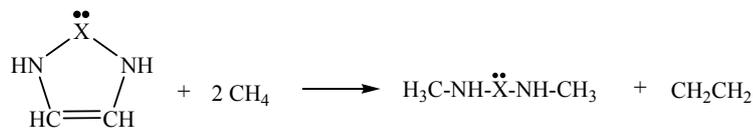
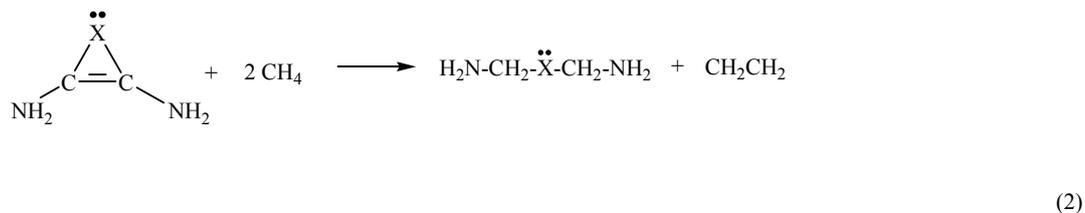
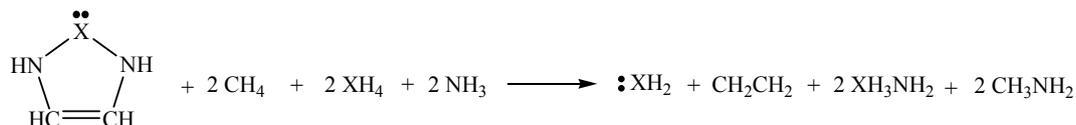
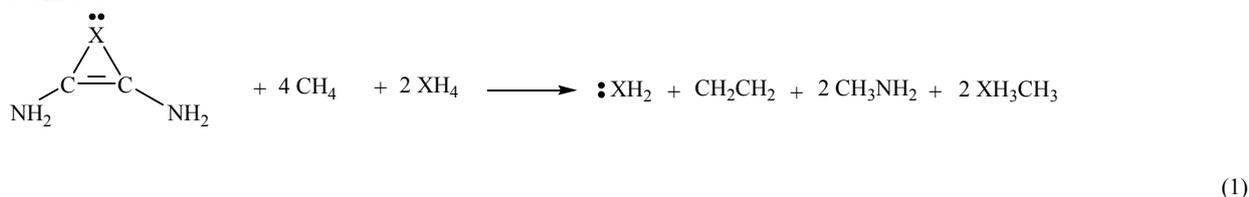
## 4 RESULTS

### 4.1 Stability of amino disubstituted cyclopropenylidene



**Scheme 9.**

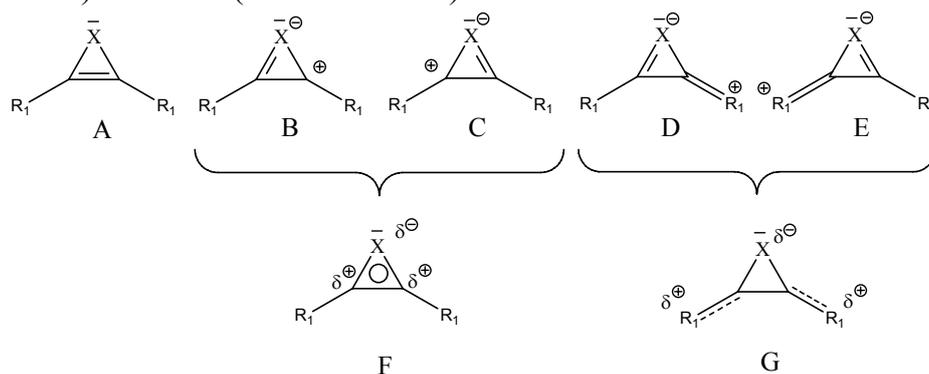
Studying thermodynamic stability of the recently synthesized bis(diisopropylamino)-cyclopropenylidene we found that the diamino substituted three-membered cyclopropenylidene (**1-NH<sub>2</sub>**) is less stable by 42.75 kcal/mol than the Arduengo carbene (**2**, Scheme 9). Three main factors determine the stability of carbenes: the substituent effect, the delocalization and possible aromaticity of the ring and the ring strain. Using appropriate isodesmic reactions (Scheme 10) I quantified the extent of these effects.



**Scheme 10.**

The total stabilization (based on reaction 1) energies meet the expectation; **2** (105.7 kcal/mol) is more stable than the newly synthesized three-membered carbene **1-NH<sub>2</sub>** (64.4 kcal/mol). 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 (81.8 kcal/mol) than in the **1-NH<sub>2</sub>** (27.8 kcal/mol). In contrast, the effect of the ring is almost the double in the three-membered ring (97.2 kcal/mol) than in **2** (49.4

kcal/mol). As expected, the ring strain destabilizes both molecules, however, it is significantly larger in **1-NH<sub>2</sub>** (-60.5 kcal/mol) than in **2** (-25.4 kcal/mol).

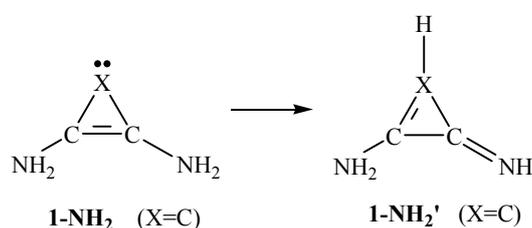


**Scheme 11**

Using Natural Resonance Theory (NRT) calculations I found that, in agreement with the previous investigations, **2** has strong aromatic character (72%, from the analogous resonance structures of the five-membered ring, Table 1) whereby the carbene center is also stabilized. However, in the amino-substituted three-membered ring (**1-NH<sub>2</sub>**) the ylidic structures (**G**, Scheme 11) 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 aromaticity is diminished, although an enhanced stabilization due to the ylidic charge separation takes place.

**Table 1.** Weights of main resonance structures in percentages calculated at B3LYP/cc-pVTZ level.

	<b>A</b>	<b>B</b>	<b>C</b>	<b>D</b>	<b>E</b>	<b>F</b>	<b>G</b>
<b>1-H</b>	56	19	19	-	-	38	-
<b>1-NH<sub>2</sub></b>	7	17	17	22	22	34	44
<b>2</b>	-	36	36	-	-	72	-
<b>3-H</b>	83	5	5	-	-	10	-
<b>3-NH<sub>2</sub></b>	52	8	8	7	7	16	14
<b>5-H</b>	84	5	5	-	-	10	-
<b>5-NH<sub>2</sub></b>	52	8	8	7	7	16	14



**Scheme 12.**

The kinetic stability of cyclopropenylidene derivatives was investigated by the rearrangement of **1-NH<sub>2</sub>** to **1-NH<sub>2</sub>'** (Scheme 12), addition of a hydride ion and calculating the dimerization energy. It turns out that **1-NH<sub>2</sub>** is stable against the nucleophilic complexation, hydride ion addition, structural isomerism and dimerization reaction. According to the data, the high kinetic stability of it is comparable with that of the known stable five-membered ring carbenes.

Since, the rational explanation for the synthesizability of bis(diisopropylamino)-cyclopropenyliene is its substantial kinetic stability. The results presented above have revealed that amino substituents or strong  $\pi$  electron donating groups are necessary to stabilize cyclopropenyliene derivatives.

## 4.2 Synthesizability of the heavy analogues of cyclopropenyliene

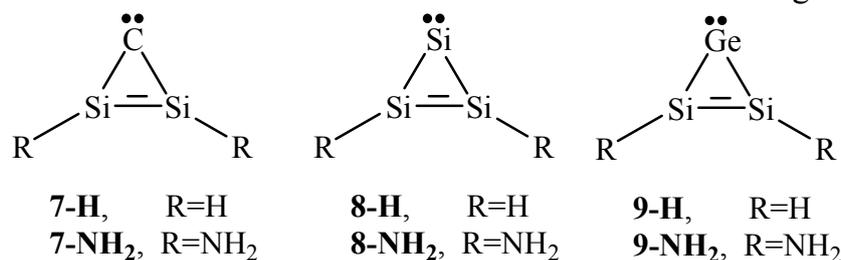
The three-membered silicon and germanium species are less stable by 49-53 kcal/mol than the corresponding five-membered rings. The total stabilization energy is found to be ca. 30 kcal/mol in both diamino-substituted three-membered rings (**3-NH<sub>2</sub>**, **5-NH<sub>2</sub>**), which is about half of that calculated for **1-NH<sub>2</sub>**. This stabilization is significantly smaller than in the corresponding stable five-membered ring compounds (**4** and **6**). The stabilization caused by the delocalization plays important role but its effect is extremely diminished by the strain (ca. 38 kcal/mol). In these molecules the localized divalent structure is dominant and both the  $\pi$ -conjugation and aromaticity are weaker than in **1-NH<sub>2</sub>**.

Investigating their reactions we found that, however, both amino disubstituted three-membered silylene and germylene have high kinetic stability. For instance, the activation barriers are prohibitively high for the first, ring opening step of the isomerization: for **3-NH<sub>2</sub>**  $\Delta G^{\ddagger}_{\text{iso}}$  is 63.9 kcal/mol and  $\Delta G^{\ddagger}_{\text{iso}}$  is 61.1 kcal/mol for **5-NH<sub>2</sub>**. No dimer was found in either case of amino disubstituted three-membered rings (**3-NH<sub>2</sub>** and **5-NH<sub>2</sub>**) which supports the stability of these compounds against dimerization.

According to our results, in contrast to the general tendency of stability order, in cyclopropenyliene 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” cyclopropenyliene derivatives

The thermodynamic and kinetic stability of **7**, **8** and **9** has also been investigated (Scheme 13). I found that none of the cyclic heavy divalent rings are global minimum on the corresponding PES. Two important facts can be concluded from isodesmotic reactions 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.

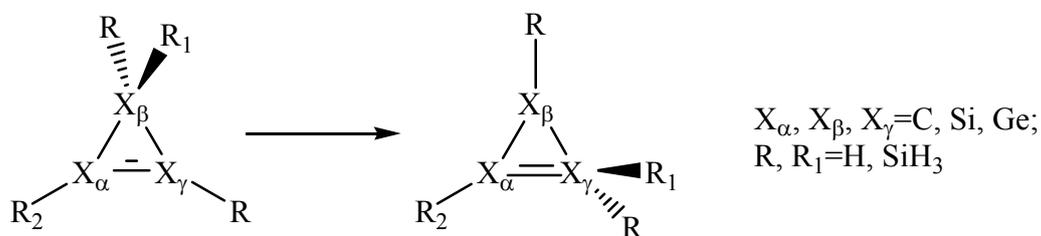


**Scheme 13.**

Investigating their kinetic stability I found that none of these structures are synthesizable because of the facile isomerization revealed for the Si<sub>3</sub>H<sub>2</sub> system. According to these findings the heavy rings would isomerize into a more stable open-chain isomer.

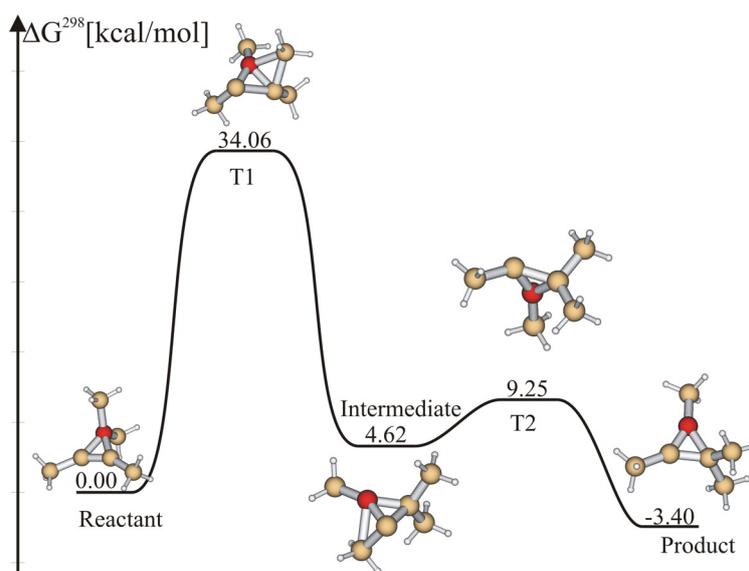
## 4.4 The mechanism of isomerization of cyclotrimetallenes

The mechanism of substituent migration was studied on different unsaturated three-membered carbon, silicon and germanium rings with silyl and hydrogen substituents (Scheme 14).



**Scheme 14.**

All the reactions (with the exception of cyclopropene) proceed in a two-step mechanism (Figure 1) 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 observed for cyclotrisilene can be interpreted with the same two steps mechanism.

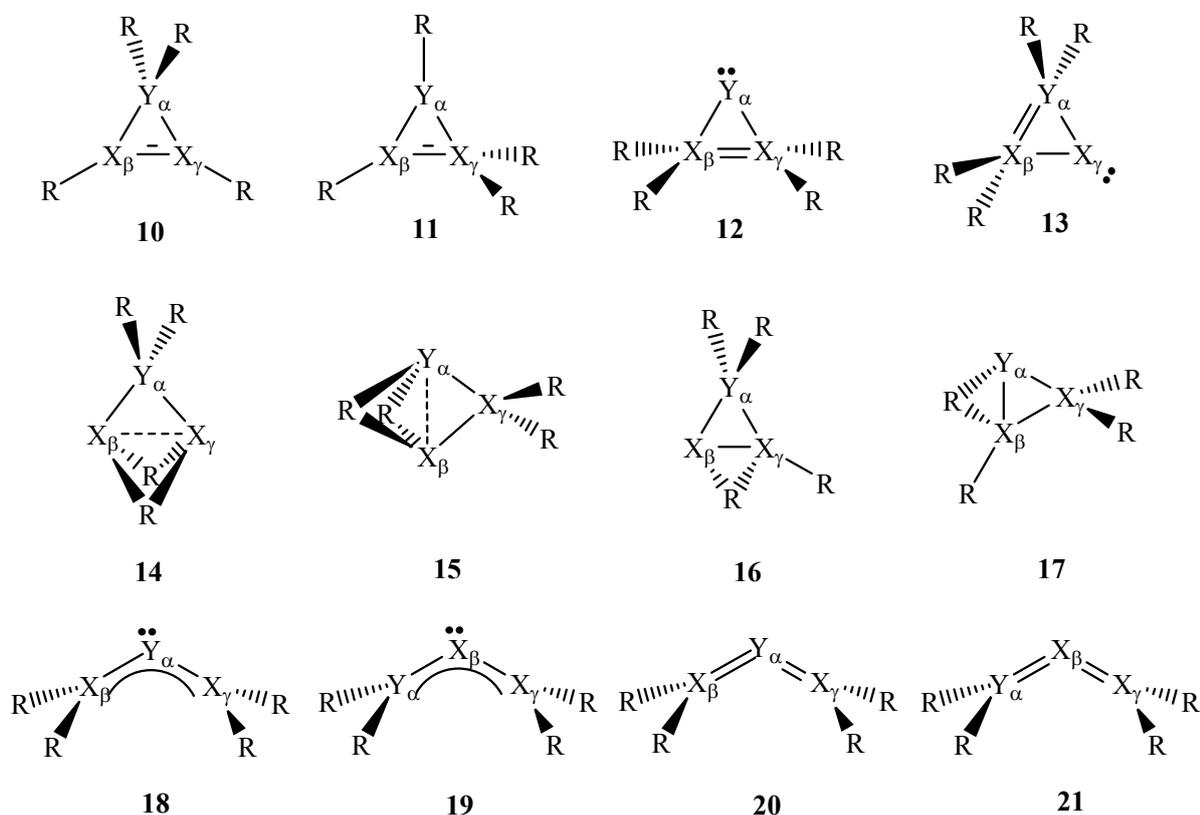


**Figure 1. Free-energy diagram at the B3LYP/cc-pVTZ level of theory for the substituent migration reaction.**

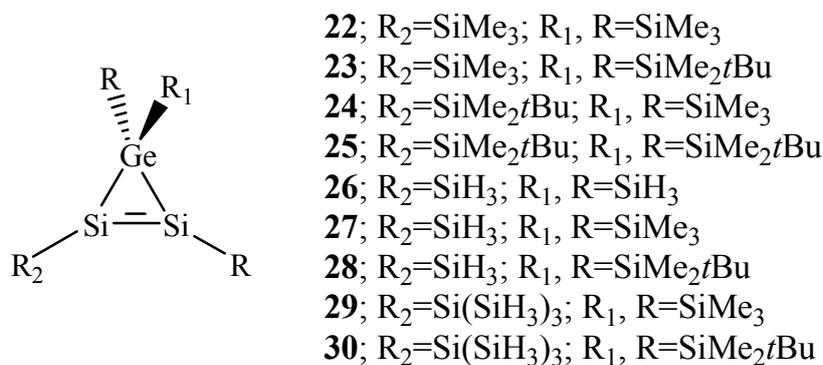
The rearrangement reactions start with the shift of the silyl group ( $R_1$ ) from the saturated ring atom ( $X_\beta$ ) toward an unsaturated one. In the transition state T1 the moving  $\text{SiH}_3$  group is situated above the ring, almost halfway between its original and final position. On the other hand the silyl group on the opposite side of the ring ( $R_2$ ) bends strongly behind the ring plane forming a pronounced pyramidal structure at  $X_\alpha$ . 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  $X_\beta$  and forms a new three-membered ring with  $X_\alpha$  and  $X_\beta$ . The resulting stable intermediate is a new monobridge structure. In the second step of the reaction, the bridging group turns back to the original position via a combined motion with rotation.

### Bridged and Distorted Structures

Novel ring (**10-17**) and open-chain structures (**18-21**) (Scheme 15) have been found on the  $X_3R_4$  ( $X = \text{Si, Ge, R} = \text{H, SiH}_3$ ) PESs.

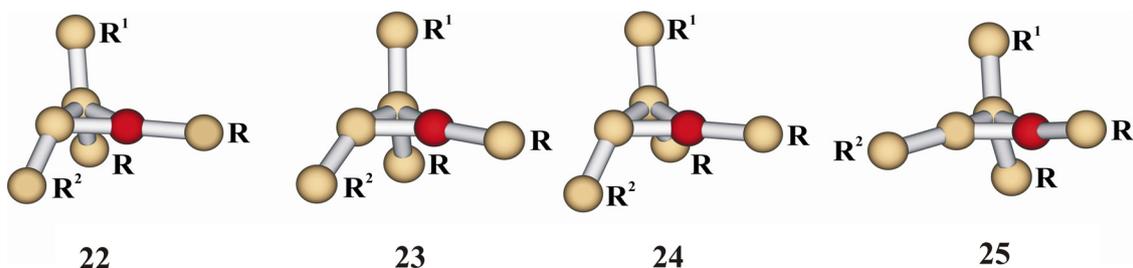


On the one hand, open-chain silylenes (**18**) with hydrogen substituents belong to global minima, while the dibridge structures (**14**) are also favorable. On the other hand, the cyclic structures become more preferable with silyl substituents. As we substitute silicon atoms with germanium, germilenes become more preferable. The structures where the bridge is between two germanium (**14**) atoms are always assigned to global minima.



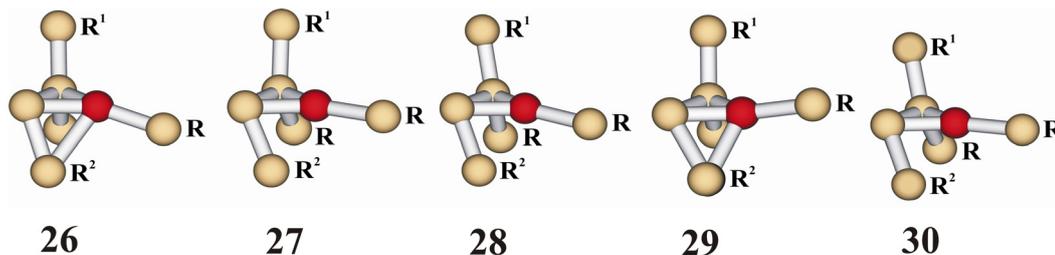
**Scheme 16**

The stability and geometry of the monobridged structure (**16**), 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 (Figure 2, for numbering see Scheme 16).



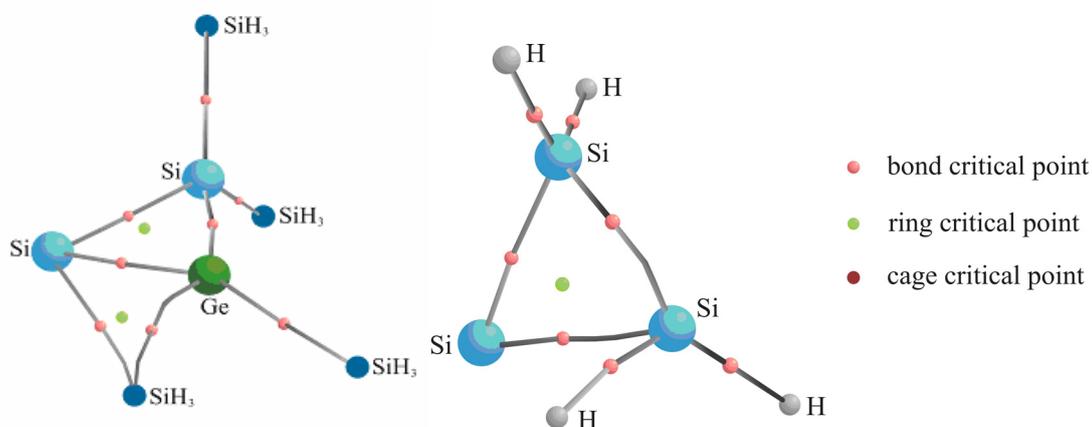
**Figure 2.** The change of the geometry of intermediates with increasing size of substituents. For simplicity, only the position of the ring atoms and the connected silicones are shown.

This trend fails using  $\text{SiH}_3$  and  $\text{Si}(\text{SiH}_3)_3$  substituents (Figure 3) due to different electronic effects of the  $\text{SiH}_3$ .



**Figure 3.** Intermediate geometry of compounds containing  $\text{SiH}_3$  and  $\text{Si}(\text{SiH}_3)_3$  groups with increasing size of substituents. For simplicity, only the position of the ring atoms and the connected silicones are shown.

A remarkable observation can be made for monobridge (**16**) structures: ring critical points always appear in monobridge structures (Figure 4, left). In the absence of the ring critical point, intermediates have only distorted geometry (Figure 4, right) without a monobridge. It has also been found that only the disilgermirene ring with silyl substituents has real bridge geometry.



**Figure 4.** Topological analysis of the bridge (left) and distorted (right) structures

## 5. THESIS

1. I have shown that the main stabilizing factor in three-membered diaminocyclopropenyldiene (**1-NH<sub>2</sub>**) is the significant  $\pi$ -electron shift from the amino substituents to the ring, via a non-aromatic ylidic structure. [3]
2. I have shown that the rational explanation for the synthesizability of bis(diisopropylamino)-cyclopropenyldiene is its substantial kinetic stability.[3]
3. I have shown that unlike **1-NH<sub>2</sub>**, in three-membered silylene (**3-NH<sub>2</sub>**) germylene (**5-NH<sub>2</sub>**) derivatives the localized divalent structure is dominant and both the  $\pi$ -conjugation and aromaticity are weaker than in **1-NH<sub>2</sub>**. However, both diamino substituted three-membered silylene and germylene have appropriate kinetic stability to be promising targets for synthetic chemists. [3]
4. I have found that in contrast to the general tendency of stability order of divalent carbon, silicon and germanium compounds in cyclopropenyldiene analogues stability is decreasing in the sequence of carbene/silylene/germylene. [3]
5. I have shown that the divalent  $\text{CSi}_2\text{R}_2$ ,  $\text{Si}_3\text{R}_2$  and  $\text{GeSi}_2\text{R}_2$  compounds can not be synthesized because of an isomerization reaction. [Thesis, Chapter 4.3, unpublished]
6. I have determined that the isomerization of cyclotrimetallenes occurs via a two-step mechanism through a stable intermediate having monobridge structure. The rate determining step of the reaction is the first step while the activation barrier of the second step is small. [1]
7. I have shown that the geometry and stability of the bridged structure strongly depend on the steric and electronic effects of the bridging substituents. I 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. [2]

## List of Publications

[1] *T. Veszprémi, A. Olasz and B. Pintér*: Structure and Isomerization of Cyclotrimetallenes; *Silicon Chemistry*, **2007**, 3, 187. (impact factor -)

[2] *B. Pintér, A. Olasz, K. Petrov and T. Veszprémi*: Cyclotrimetallenes: Bridged and distorted structures, *Organometallics*, **2007**, 26, 3677. (impact factor 3.632)

[3] *B. Pintér and T. Veszprémi*: Synthesizability of the heavy analogues of disubstituted cyclopropenylidene: a theoretical study. (accepted in *Organometallics*) (impact factor 3.632)

### Publications not included in the thesis:

[4] *B. Pintér, F. De Proft, T. Veszprémi and P. Geerlings*: Regioselectivity in the [2+2] cycloaddition reaction of triplet carbonyl compounds to substituted alkenes (Paterno-Büchi reaction) : A Spin-polarized Conceptual DFT approach. *J. Chem. Sci.* **2005**, 117, 561. (impact factor 1.032)

[5] *B. Pintér, F. De Proft, V. Van Speybroeck, K. Hemelsoet, M. Waroquier, E. Chamorro, T. Veszprémi and P. Geerlings*: Spin-polarized conceptual DFT study of the regioselectivity in ring closures of radicals. *J. Org. Chem.* **2007**, 72, 348. (impact factor 3.790)

[6] *B. Pintér, F. De Proft, T. Veszprémi and P. Geerlings*: Theoretical study of the orientation rules in photonucleophilic aromatic substitutions. *J. Org. Chem.* **2008**, 73, 1243. (impact factor 3.790)