

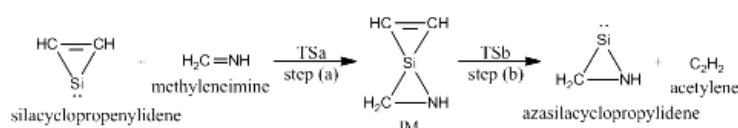
THEORETICAL STUDY ON THE REACTION MECHANISM BETWEEN SILACYCLOPROPENYLIDENE AND METHYLENEIMINE

Wenxing HE and Xiaojun TAN*

College of Medical and Life Science, University of Jinan, Jinan, Shandong, 250022, People's Republic of China

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The reaction mechanism between silacyclopropenylidene and methyleneimine has been systematically investigated employing the second-order Møller-Plesset perturbation theory (MP2) method in order to better understand the reactivity of unsaturated silylene with the double bond carbonitride methyleneimine. Geometry optimizations



and vibrational analyses have been performed for the stationary points on the potential energy surface of the system. Calculations show that the spiro-Si-heterocyclic intermediate and three-membered heterocyclic silylene compound could be produced through cycloaddition reaction and subsequent dissociation reaction between silacyclopropenylidene and methyleneimine. Introducing electron donating group in the silacyclopropenylidene makes the cycloaddition reaction easier. Introducing electron attracting group produces the opposite effect. The present study is helpful to understand the reactivity of silacyclopropenylidene and evolution of silicon-bearing molecules in space, and offers an alternative approach to the formation of heterocyclic silylene compound.

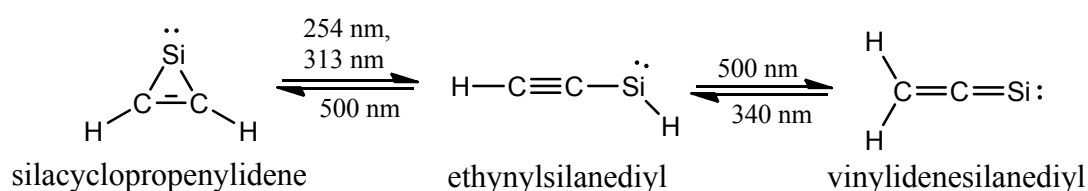
INTRODUCTION

Silicon is one of the ten most abundant elements in the cosmos and hence silicon-bearing molecules are important in astrochemistry.¹⁻⁴ There are eleven silicon-bearing molecules that have been detected in space corresponding to almost 10% of the total number of known astronomical molecules.⁵ Since the silicon-bearing molecules played a vital role in the chemical evolution of the interstellar medium and the formation of silicon-carbide dust grains in the circumstellar envelopes of carbon-rich stars like IRC+10216,⁶ the molecular processes involved in the formation of organosilicon molecules such as silicon carbide (SiC) and silicon dicarbide (SiC₂) together with their hydrogenated counterparts (C₂H₂Si) have received considerable attention from the astronomical and physical chemistry communities in recent years.⁷⁻

¹⁰ Owing to the similarity of C₂H₂Si to known astronomical molecules (SiC, SiC₂), those of the composition of C₂H₂Si might be abundant in space as well.¹¹

C₂H₂Si is a class of highly unsaturated silylene. Initial experimental evidence for C₂H₂Si isomers in the laboratory was reported by the Maier's group^{12,13}. By the pulsed flash pyrolysis of the gaseous mixture of 2-ethynyl-1, 1, 1-trimethyldisilane and argon, silacyclopropenylidene (*c*-C₂H₂Si) was isolated in an argon matrix at 10 K. As displayed in Scheme 1, irradiation of matrix-isolated silacyclopropenylidene resulted in a series of photochemical rearrangements leading to ethynylsilanediyl (HCCSiH), vinylidenesilanediyl (H₂CCSi). According to theoretical calculations, silacyclopropenylidene is the most stable C₂H₂Si species.¹⁴⁻¹⁵

* Corresponding author: chm_tanxj@ujn.edu.cn

Scheme 1 – The transformation of three $\text{C}_2\text{H}_2\text{Si}$ isomers.

There are many theoretical and experimental investigations on the $\text{C}_2\text{H}_2\text{Si}$ isomers.¹⁶⁻¹⁸ In addition, the relative stabilities, structures, and dipole moments of the $\text{C}_2\text{H}_2\text{Si}$ isomers have been investigated extensively.¹⁹ Schaefer *et al.* performed anharmonic vibrational analyses of the electronic ground states of the four $\text{C}_2\text{H}_2\text{Si}$ isomers employing second-order vibrational perturbation (VPT2) theory.²⁰ Relative stabilities and structural characters of silyenic C_2HXSi ²¹ and dialkyl substituted $\text{C}_2\text{X}_2\text{Si}$ ²² species are calculated at different levels of theory. The microwave rotational spectrum of vinylidenesilanediyl and its isotopic species were observed in a pulsed supersonic molecular beam by Fourier transform microwave spectroscopy.²³

The bimolecular collision of the simplest silicon-bearing radical silylidyne (SiH) with acetylene (C_2H_2) and ethylene (C_2H_4) can be considered as a prototype mechanism leading to the formation of organosilicon molecules in circumstellar envelopes.²⁴⁻²⁵ These reactions could supply the molecular feedstock of organosilicon molecules necessary to account for the ubiquitous presence of interstellar silicon-carbide grains via a “bottom up” synthesis starting with small silicon-bearing precursor molecules as proposed here. However, the reactions of the most stable $\text{C}_2\text{H}_2\text{Si}$ species (including substituted C_2HXSi , X=OH, NH_2 , and CH_3), silacyclopropenylidene, have not been reported up to now. As the carbenic analogue of silacyclopropenylidene, the reactivity of cyclopropenylidene has been studied.^{26,27} In the present study, we have performed comprehensive theoretical investigation of the reaction mechanism between silacyclopropenylidene and double bond carbonitride methyleneimine by employing the second-order Møller-Plesset perturbation theory (MP2) method in order to better understand the silacyclopropenylidene reactivity and evolution of silicon-bearing molecules in space. The present research offered an alternative approach to the formation of heterocyclic silylene compound.

CALCULATION METHOD

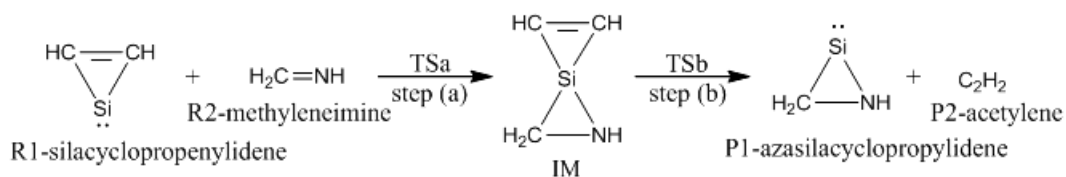
The second-order Møller-Plesset perturbation (MP2) theory method²⁸ in combination with the 6-311+G* basis set has been employed to locate all the stationary points along the reaction pathway without imposing any symmetry constraints. Frequency analyses have been carried out to confirm the nature of the minima and transition states. Moreover, intrinsic reaction coordinate (IRC) calculations have also been performed to further validate the calculated transition states connecting reactants and products. Additionally, the relevant energy quantities, such as the reaction energies and barrier heights, have been corrected with the zero-point vibrational energy (ZPVE) corrections.

To further refine the calculated energy parameters, single point energy calculations for the reaction have been performed at the CCSD(T)/6-311+G* level of theory based on the optimized geometries at the MP2/6-311+G* level of theory. As summarized in Table 1, two levels can give consistent results for the calculated reaction profile. For the sake of simplicity, the energetic results at the MP2/6-311+G* level of theory have been mainly discussed below if not noted otherwise.

All the calculations have been performed using Gaussian 98 program.²⁹

RESULTS AND DISCUSSION

As displayed in Scheme 2, the possible pathway for the title reaction has been proposed. The geometric parameters for the reactants (R1-silacyclopropenylidene, R2-methyleneimine), transition states (TS), intermediate (IM), and products (P1- azasilacyclopropylidene, P2-acetylene) involved in the pathway are displayed in Fig. 1. The calculated relative energies for the available stationary points and the corresponding reaction profile are illustrated in Fig. 2.



Scheme 2 – The proposed pathway for the addition reaction between silacyclopropenylidene and methyleneimine.

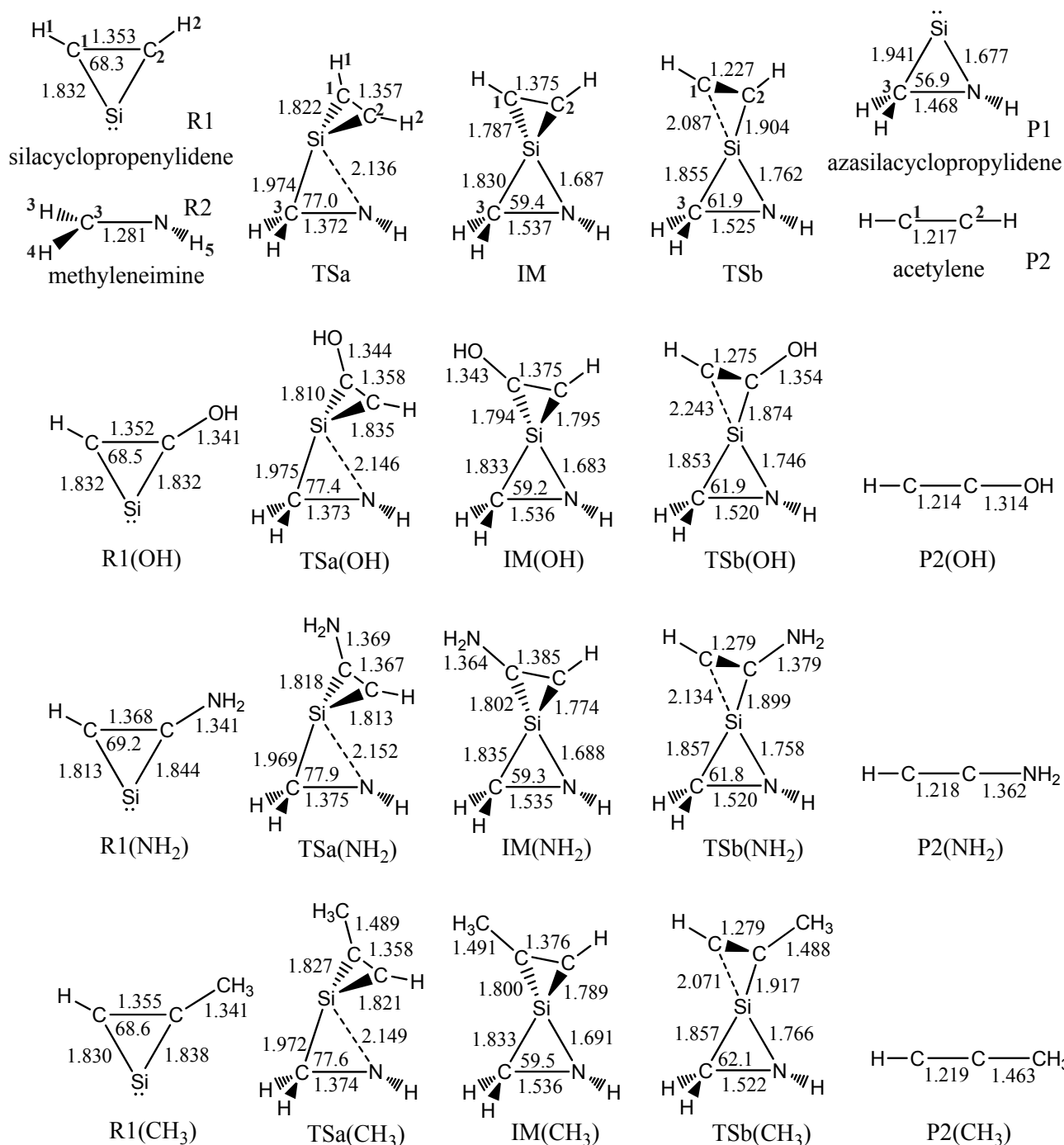


Fig. 1 – Optimized structures of the reactants (silacyclopropenylidene and methyleneimine), transition states (TS), intermediates (IM), and products (azasilacyclopropylidene and acetylene) in the reaction at the MP2/6-311+G* level of theory, where the bond length and bond angle are in angstrom and degree, respectively.

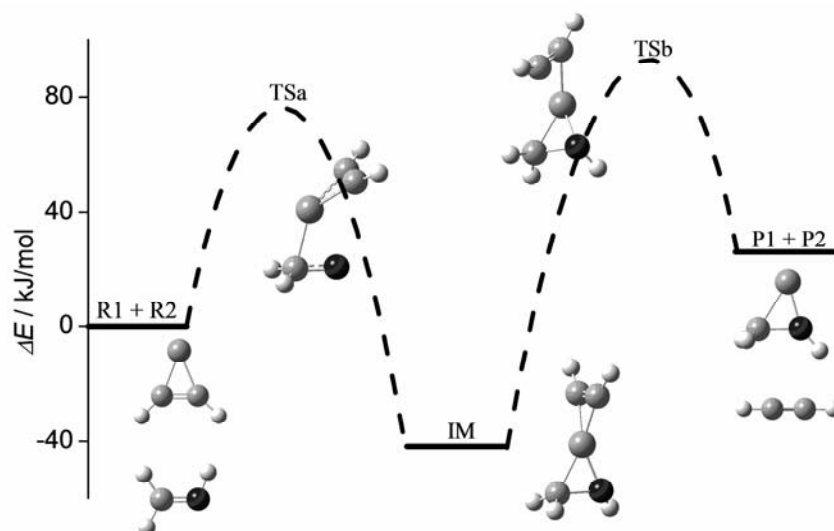


Fig. 2 – The profile for the reaction between silacycpropenylidene and methyleneimine at the MP2/6-311+G* level of theory.

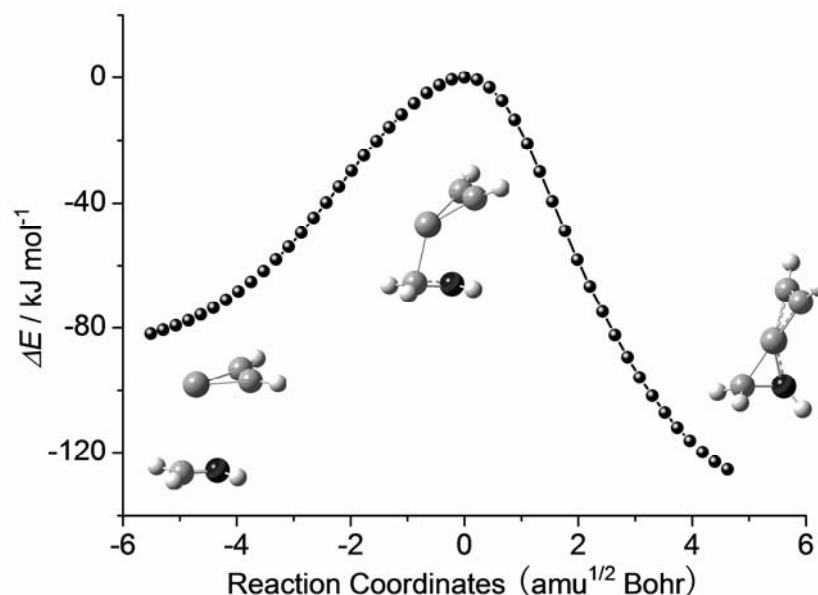


Fig. 3 – The selected configuration and energy changes along the reaction coordinate of step (a) between silacycpropenylidene and methyleneimine.

1. Step (a): cycloaddition reaction process to form a spiro-Si-heterocyclic intermediate (IM)

Along the reaction, the intermediate (IM) is formed via a cycloaddition reaction process with an energy barrier of 85.4 kJ/mol. The unique imaginary frequency calculated for the corresponding transition state, TSa, in the step (a) is $362i \text{ cm}^{-1}$ at the MP2/6-311+G* level of theory.

As shown in Fig. 1, in TSa, R1 and R2 fragments are approaching each other; the distances of Si-C³ and Si-N are 1.974 and 2.136 Å, respectively. Thus, two new bonds, namely Si-C³ and Si-N, are being formed in the transition state

TSa. At the same time, the distance of C³-N in R2 fragment of TSa reached 1.372 Å, which is 0.091 Å longer than that in methyleneimine. Based on the bond length data, the double bond C³-N in methyleneimine is being transformed into a single bond in TSa. The formation of new σ bonds of Si-C³ and Si-N and the cleavage of π bond of C³-N occur simultaneously. As shown in Fig. 3, those changes of configuration and energy can be further validated by an IRC calculation on the basis of TSa.

IM is spiro-Si-heterocyclic compound. Unlike with the singlet silylene R1 (silacycpropenylidene),

all of the outer electrons of Si atom in IM are bonded, therefore IM is more stable than the reactants. However, there are two three-membered rings in IM. The tension of a small ring is large; therefore IM can open its ring through cleavage of the Si-C bond.

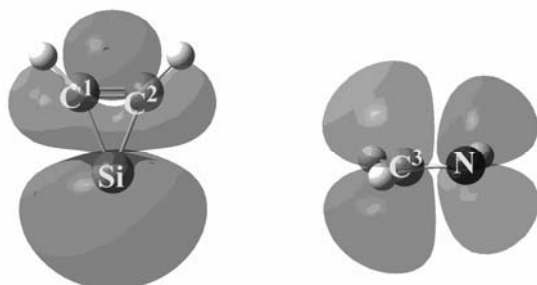


Fig. 4 – The calculated HOMO orbital for silacyclopropenylidene (left) and LUMO orbital for methyleneimine (right).

The frontier orbitals (HOMO and LUMO) of a chemical species are quite important to define their reactivity and determine the way in which the molecule interacts with other species.³⁰ The reaction process can be understood from the frontier molecular orbital theory qualitatively. As displayed in Fig. 4, the C³-N bond is characterized by the π antibonding orbital, which can be reflected from the LUMO of methyleneimine. As for silacyclopropenylidene, the activity of the Si site can be reflected from the largest contribution on the Si atom to the components of the whole HOMO. Therefore, the Si atom in silacyclopropenylidene can react with the C-N bond of methyleneimine. Based on the above analysis, the more the electron density on the Si atom is, the easier the cycloaddition reaction process will be. Introduction of electron donating group in silacyclopropenylidene will increase the electron density on the Si atom, which will better facilitate the cycloaddition reaction between silacyclopropenylidene and methyleneimine.

Introduction of electron attracting group will lead to the opposite effect. As summarized in Table 1, introduction of the electron donating group, CH₃, decreased the barrier energy of step (a). On the contrary, electron attracting groups, OH and NH₂, increased those barrier energies.

2. Step (b): dissociation process to form heterocyclic silylene compound and acetylene

As mentioned above, IM is a spiro-Si-heterocyclic compound; it can open its three-membered ring to form the heterocyclic silylene compound and acetylene through a dissociation process. Si-C¹ and Si-C² bonds in IM will be opened to form two products via TSb in step (b), where the barrier is 138.1 kJ/mol.

The unique imaginary frequency of TSb is $381i\text{ cm}^{-1}$. In TSb, the bond lengths of Si-C¹ and Si-C² are 2.087 and 1.904 Å, which are longer 0.300 and 0.117 Å than that in the IM, respectively, showing the bond of Si-C¹ and Si-C² will be ruptured. Simultaneously, the bond length of C¹-C² shortens to 1.277 Å, indicating the bond of C¹-C² will be transferred from a double bond in IM to a triple bond in P2. As shown in Fig. 5, those changes of bond lengths and energies can be further validated by an IRC calculation on the basis of TSb.

The two products of the title reaction are azasilacyclopropylidene and acetylene. The former is a three-membered heterocyclic silylene compound. Like as the reactant silacyclopropenylidene, azasilacyclopropylidene has the characteristics of silylene. Azasilacyclopropylidene has not only lone pair electrons, but also has a small heterocyclic ring. Therefore, azasilacyclopropylidene should be very active and act as a potential reaction reagent in organic chemistry. The present study offered an alternative approach to form the active heterocyclic silylene compound.

Table 1

The calculated relative energies (in kJ/mol) with respect to the isolated reactants at the MP2/6-311+G* level of theory considering the ZPVE corrections^a

| Species | X=H | X=OH | X=NH ₂ | X=CH ₃ |
|---------|---------------|-------|-------------------|-------------------|
| TSa | 85.4 (95.9) | 94.2 | 100.4 | 82.4 |
| IM | -39.6 (-18.1) | -35.2 | -29.8 | -41.1 |
| TSb | 88.5 (115.0) | 120.3 | 122.7 | 88.5 |
| P1+P2 | 22.3 (31.8) | 83.8 | 81.4 | 24.8 |

^a The data in parentheses refer to the results at the CCSD(T)//MP2/6-311+G* level of theory considering the ZPVE corrections.

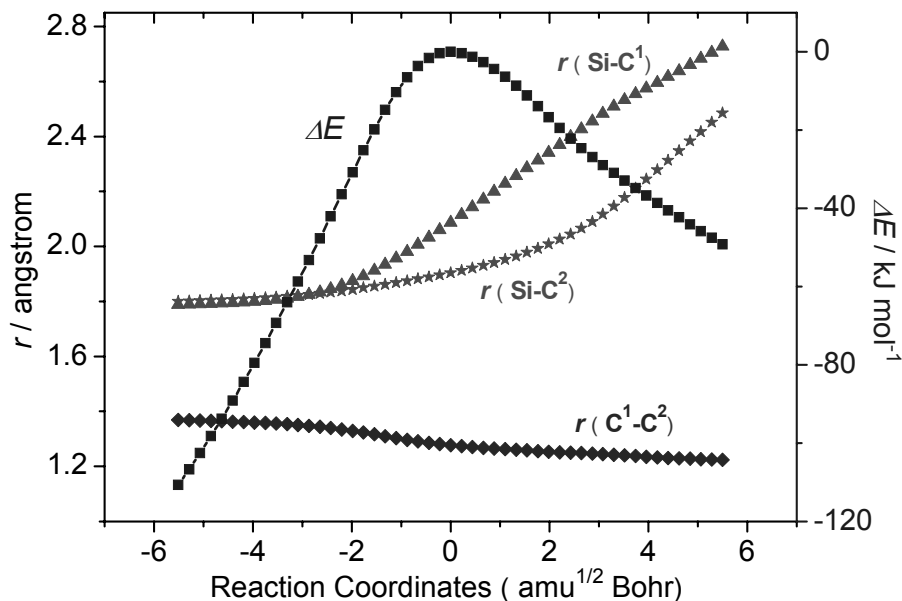


Fig. 5 – The selected bond lengths and energy changes along the reaction coordinates of step (b) between silacyclopropenylidene and methyleneimine.

CONCLUSIONS

In this study, the addition reaction mechanism between silacyclopropenylidene and methyleneimine has been systematically investigated employing the MP2/6-311+G* level of theory. There are steps (a) and (b) along the reaction pathway. The spiro-Si-heterocyclic intermediate was produced through step (a). Introducing electron donating group in the silacyclopropenylidene made the cycloaddition step easier, and the electron attracting group produced the opposite effect. The three-membered heterocyclic silylene compound azasilacyclopropylidene and small molecule acetylene were produced through step (b). The present study is helpful to understand the reactivity of silacyclopropenylidene and evolution of silicon-bearing molecules in space, and offered an alternative approach to the formation of the heterocyclic silylene compound.

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REFERENCES

1. D. L. Kokkin, N. J. Reilly, R. C. Fortenberry, T. D. Crawford and M. C. McCarthy, *J. Chem. Phys.*, **2014**, *141*, 044310.
2. M. Guélin, S. Muller, J. Cernicharo, M. C. McCarthy and P. Thaddeus, *Astron. Astrophys.*, **2004**, *426*, L49-L52.
3. M. C. McCarthy, C. A. Gottlieb and P. Thaddeus, *Mol. Phys.*, **2003**, *101*, 697-704.
4. M. Guélin, S. Muller, J. Cernicharo, A. J. Apponi, M. C. McCarthy, C. A. Gottlieb and P. Thaddeus, *Astron. Astrophys.*, **2000**, *363*, L9-L12.
5. H. P. Müller, S. Thorwirth, D. A. Roth and G. Winnewisser, *Astron. Astrophys.*, **2001**, *370*, L49-L52.
6. L. M. Ziurys, *PNAS*, **2006**, *103*, 12274-12279.
7. G. Maier, H. P. Reisenauer and H. Egenolf, *Eur. J. Org. Chem.*, **1998**, *7*, 1313-1317.
8. A. V. Orden, R. A. Provencal, T. F. Giesen and R. J. Saykally, *Chem. Phys. Lett.*, **1995**, *237*, 77-80.
9. C. A. Rice and J. P. Maier, *J. Phys. Chem., A* **2013**, *117*, 5559-5566.
10. D. L. Kokkin, S. Brünken, K. H. Young, N. A. Patel, C. A. Gottlieb, P. Thaddeus and M. C. McCarthy, *Astrophys. J., Suppl. Ser.*, **2011**, *196*, 17-21.
11. S. Thorwirth and M. E. Harding, *J. Chem. Phys.*, **2009**, *130*, 214303.
12. G. Maier, H. P. Reisenauer and H. Pacl, *Angew. Chem., Int. Ed. Engl.*, **1994**, *33*, 1248-1250.
13. G. Maier, H. Pacl, H. P. Reisenauer, A. Meudt and R. Janoschek, *J. Am. Chem. Soc.*, **1995**, *117*, 12712-12720.
14. F. Gernot, B. R. Richard and F. S. Henry, *J. Am. Chem. Soc.*, **1986**, *108*, 2169-2173.
15. D. L. Cooper, *Astrophys. J.*, **1990**, *354*, 229-231.
16. M. Z. Kassae, S. M. Musavi, F. Buazar and M. Ghambarian, *J. Mole. Struc.: THEOCHEM*, **2005**, *722*, 151-160.
17. I. Shigeru, S. Toshiaki and W. Souichi, *J. Chem. Phys.*, **2004**, *121*, 3478-3485.
18. E. Chamorro, J. C. Santos, C. A. Escobar and P. Perez, *Chem. Phys. Lett.*, **2006**, *431*, 210-215.
19. M. Holger and E. W. David, *J. Phys. Chem. A*, **2013**, *117*, 13868-13877.
20. Q. Y. Wu, Q. Hao, J. J. Wilke, A. C. Simmonett, Y. Yamaguchi, Q. S. Li, D. C. Fang and H. F. Schaefer, *Mole. Phys.*, **2012**, *110*, 783-800.

21. M. Z. Kassae, S. M. Musavi and M. Ghambarian, *Heteroatom Chem.*, **2007**, *18*, 283-293.
22. M. Z. Kassae, S. M. Musavi, S. Soleimani-Amiri and M. Ghambarian, *Heteroatom Chem.*, **2006**, *17*, 619-633.
23. M. C. McCarthy and P. Thaddeus, *J. Mol. Spectrosc.*, **2002**, *211*, 228-234.
24. D. Talbi, *Chem. Phys.*, **2005**, *313*, 17-23.
25. S. N. Parker, A. V. Wilson, R. I. Kaiser, N. J. Mayhall and M. Head-Gordon, *Astrophys. J.*, **2013**, *770*, 33-47.
26. X. J. Tan, W. H. Wang, Y. Jing, F. Wang and P. Li, *Monatsh. Chem.*, **2014**, *145*, 1109-1115.
27. X. J. Tan, Z. Li, Q. Sun, P. Li and W. H. Wang, *Bull. Korean Chem. Soc.*, **2012**, *33*, 1934-1939.
28. M. Head-Gordon, J. A. Pople and M. J. Frisch, *Chem. Phys. Lett.*, **1988**, *153*, 503-507.
29. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. AlLaham, M. A. Peng, A. Nanayakkara, C. Gonzalez, C. Challacombe, P. M.W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. HeadGordon, E. S. Replogle and J. A. Pople, Gaussian 98, Revision A.9 (Gaussian Inc., Pittsburgh, PA, 1998).
30. I. Fleming, "Frontier orbitals and organic chemical reactions, Wiley, London, 1976.

