

## Theoretical Study on the Mechanism of the Addition Reaction between Cyclopropenylidene and Formaldehyde

Xiaojun Tan,\* Zhen Li,<sup>†</sup> Qiao Sun,<sup>†</sup> Ping Li,<sup>‡,\*</sup> and Weihua Wang<sup>‡</sup>

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

\*E-mail: chm\_tanxj@ujn.edu.cn

<sup>†</sup>Australian Institute for Bioengineering and Nanotechnology, The University of Queensland, QLD 4072, Australia

<sup>‡</sup>School of Chemistry and Chemical Engineering, Qufu Normal University, Qufu, Shandong, 273165, People's Republic of China

\*E-mail: lpsdu@sdu.edu.cn

Received December 22, 2011, Accepted March 14, 2012

The reaction mechanism between cyclopropenylidene and formaldehyde has been systematically investigated employing the MP2/6-311+G\* level of theory to better understand the cyclopropenylidene reactivity with carbonyl compound. Geometry optimization, vibrational analysis, and energy property for the involved stationary points on the potential energy surface have been calculated. Energies of all the species are further corrected by the CCSD(T)/6-311+G\* single-point calculations. It was found that one important reaction intermediate (INTa) has been located firstly *via* a transition state (TSa). After that, the common intermediate (INTb) for the two pathways (1) and (2) has been formed *via* TSb. At last, two different products possessing three- and four-membered ring characters have been obtained through two possible reaction pathways. In the reaction pathway (1), a three-membered ring alkyne compound has been obtained. As for the reaction pathway (2), it is the formation of the four-membered ring conjugated diene compound. The energy barrier of the rate-determining step of pathway (1) is lower than that of the pathway (2), and the ultima product of pathway (2) is more stable than that of the pathway (1).

**Key Words :** Cyclopropenylidene, Formaldehyde, Addition reaction, Theoretical study

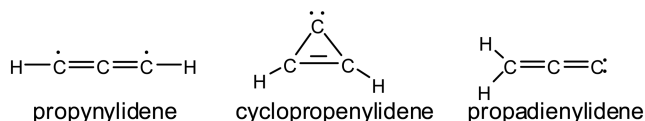
### Introduction

Carbene can be defined as divalent carbon intermediates, where the carbene carbon is linked to two adjacent groups by covalent bonds and possesses two nonbonding electrons. It is well known that carbene plays an important role in organic chemistry, especially for the addition reaction with C=C and C=O double bond.<sup>1-4</sup> Therefore, the studies of carbene have attracted more attentions theoretically and experimentally. For example, carbene can be used to provide simple and direct synthesis for small-ring, highly strained compounds, as well as those that are hardly synthesized through conventional ways.<sup>5</sup> The reactions between carbene or substituted carbene and some small molecules have been studied theoretically by Lu *et al.*<sup>6-8</sup> Apeloig *et al.* extensively studied the mechanisms and stereoselectivity of carbene addition to olefin experimentally and theoretically.<sup>9,10</sup> Recently, the reactions between carbene and small-ring strained molecules, such as epoxyethane and azacyclopropane, have been investigated theoretically.<sup>11,12</sup>

As the simplest vinylidene carbene, C<sub>3</sub>H<sub>2</sub> is a class of highly unsaturated carbenes, which is of great interest for the chemistry of carbon-rich gas-phase environments. As displayed in Scheme 1, three isomers have been located on its potential energy surface. Here, propynylidene is the only C<sub>3</sub>H<sub>2</sub> isomer with a triplet electronic ground state and the cyclopropenylidene and propadienylidene are in singlet state.<sup>13-16</sup> Moreover, all of them can be interconverted by

photolysis.<sup>17-19</sup> The structural characters, thermochemistry, and isomerization of C<sub>3</sub>H<sub>2</sub> carbenes have been investigated extensively.<sup>13,18,20-22</sup> It was found that the singlet cyclopropenylidene is the most stable isomer among the three species,<sup>23-26</sup> which is lower in energy by about 42-59 and 59-92 kJ/mol than that of propadienylidene and propynylidene, respectively.<sup>27-31</sup> These highly reactive carbene molecules are fundamentally important not only within the context of organic chemistry,<sup>32,33</sup> but also within the context of the chemistry of the interstellar medium.<sup>34-38</sup> Recently, the formation mechanism of the C<sub>3</sub>H<sub>2</sub> carbene has been proposed by Goulay *et al.* using tunable vacuum ultraviolet photoionization and time-resolved mass spectrometry.<sup>39</sup> The photophysics of cyclopropenylidene has been studied by femtosecond time-resolved photoionisation and photoelectron spectroscopy.<sup>40</sup>

Chotima *et al.* have reported that cyclopropenylidene could act as ligand in palladium catalysed coupling reactions.<sup>41,42</sup> By appending  $\pi$ -electron-donating amino groups to the triangular skeleton, a stable cyclopropenylidene derivative have been prepared by Bertrand's group.<sup>43</sup> More recently, the gas-phase high-resolution absorption spectrum



**Scheme 1.** The three isomers of C<sub>3</sub>H<sub>2</sub>.

of cyclopropenylidene has been observed using a Fourier transform infrared spectrometer.<sup>44</sup>

On the other hand, less is known about the reaction mechanism between cyclopropenylidene and unsaturated carbonyl compound to the best of our knowledge due to the high reactivity of the cyclopropenylidene. In the absence of experimental information, a theoretical investigation on the title reaction appears to be highly desirable. Therefore, in the present study, the reaction mechanism between cyclopropenylidene and formaldehyde have been systematically investigated employing the second-order Møller-Plesset perturbation theory (MP2) method so as to better understand the cyclopropenylidene reactivity with the carbonyl compounds. Hopefully, the present results, such as the intermediates and reaction mechanisms, not only can promote the progress of the relevant experiments, but also can provide insights into the reactivity of C<sub>3</sub>H<sub>2</sub> carbene with carbonyl compounds as well as to enrich the available data for the relevant cyclopropenylidene chemistry.

### Calculation Method

The MP2 method and the 6-311+G\* basis set have been employed to locate all the stationary points along the reaction pathways. Frequency analyses have been carried out to confirm the nature of the minima and transition states at the MP2/6-311+G\* level of theory, *i.e.*, all the reactants, intermediates, and products have been characterized by no imaginary frequency. The calculated transition states have unique imaginary frequency. 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 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 have been performed at the CCSD(T)/6-311+G\* level of theory based on the stationary points optimized at the MP2/6-311+G\* level of theory. As summarized in Table 1, both levels can give consistent results for the calculated reaction profile of the addition reaction. For the sake of simplicity, the energetic results at the CCSD(T) /6-311+G\*/MP2/6-311+G\* level have been mainly discussed below if not noted otherwise.

All the calculations have been performed using Gaussian 98 program.<sup>45</sup>

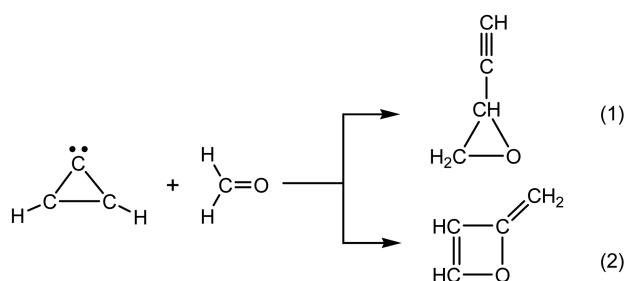
### Results and Discussion

As displayed in Figure 1, two possible reaction pathways for the addition reaction between cyclopropenylidene and formaldehyde have been proposed. Correspondingly, the calculated relative energies for the available stationary points have been summarized in Table 1. Here, as for the geometry of the cyclopropenylidene, the calculated results are well consistent with the high-level theoretical results at

**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<sup>a</sup>

Pathways	Relative Energies			
<b>Pathway (1)</b>	<b>TSa</b>	<b>INTa</b>	<b>TSb</b>	<b>INTb</b>
	33.8(38.0)	-95.4(-77.7)	101.8(98.2)	76.4(68.9)
	<b>TS1</b>	<b>P1</b>		
	175.3(167.3)	-186.7(-168.0)		
<b>Pathway (2)</b>	<b>TS2a</b>	<b>INT2a</b>	<b>TS2b</b>	<b>INT2b</b>
	194.3(182.7)	-137.1(-132.8)	125.1(127.5)	31.4(11.7)
	<b>TS2c</b>	<b>P2</b>		
	64.0(53.3)	-227.6(-218.9)		

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



**Figure 1.** The proposed two reaction pathways for the addition reaction between cyclopropenylidene and formaldehyde.

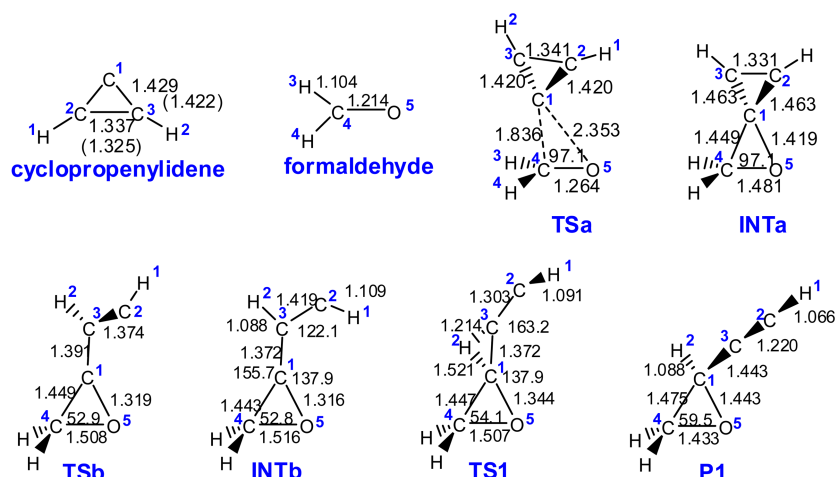
the CCSD(T)/cc-pVTZ level of theory<sup>18</sup> as displayed in Figure 2, reflecting the reliability of the level of theory adopted here.

**Reaction Pathway (1): Three-membered Ring Product Channel.** The geometric parameters for the reactants (cyclopropenylidene and formaldehyde), transition states (TSa, TSb and TS1), intermediates (INTa, INTb), and product (P1) involved in the reaction pathway (1) are displayed in Figure 2. Here, a three-membered ring product P1 has been obtained. The corresponding reaction profile is illustrated in Figure 3.

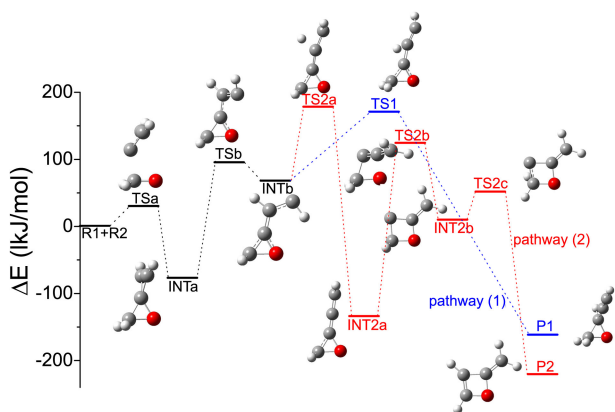
Firstly, the intermediate INTa is formed *via* a barrier of 38.0 kJ/mol. The calculated unique imaginary frequency of the transition state TSa is 362.7i cm<sup>-1</sup> at the MP2/6-311+G\* level of theory. As shown in Figure 2, the distances from C<sup>1</sup> to C<sup>4</sup> and O<sup>5</sup> atoms in TSa are 1.836 and 2.353 Å, and the bond lengths of C<sup>2</sup>-C<sup>3</sup>, C<sup>1</sup>-C<sup>2</sup>, and C<sup>4</sup>-O<sup>5</sup> are only slightly changed (1.341 vs 1.337, 1.420 vs 1.429, 1.264 vs 1.214 Å) compared with the reactants, respectively. The smoothness of the full IRC shown in Figure 4 further indicates that TSa connects reactants and the three-membered ring intermediate INTa.

Due to the existence of tension in the three-membered ring, the second step of the pathway (1) is that C<sup>1</sup>-C<sup>2</sup> bond in INTa opens to form an intermediate INTb *via* TSb, where the barrier is 175.9 kJ/mol. The unique imaginary frequency of transition state TSb is 476.8i cm<sup>-1</sup>, so the transition state can be affirmed as the real one.

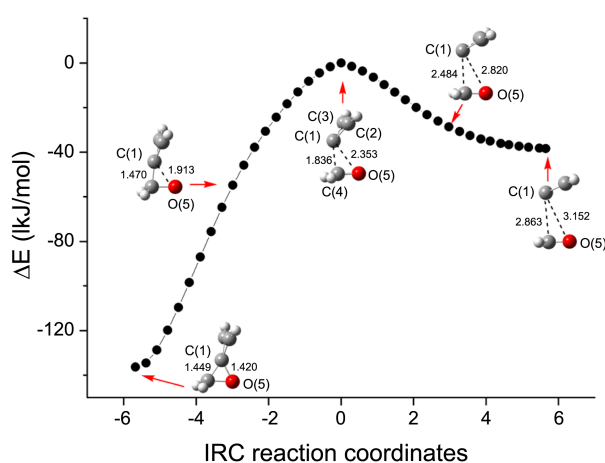
In INTb, the C<sup>3</sup> atom adopts *sp*<sup>2</sup> hybridization and the C<sup>2</sup>-



**Figure 2.** Optimized structures of the reactants (cyclopropenylidene and formaldehyde), transition states (TSa, TSb, and TS1), intermediates (INTa and INTb), and product (P1) in the reaction pathway (1) at the MP2/6-311+G\* level of theory, where the bond length and bond angle are in angstrom and degree, respectively. The data in parentheses refer to the results at the CCSD(T)/cc-pVTZ level of theory.



**Figure 3.** Reaction profile for the reaction pathways (1) and (2) between cyclopropenylidene and formaldehyde at the CCSD(T)/6-311+G\*/MP2/6-311+G\* level of theory.



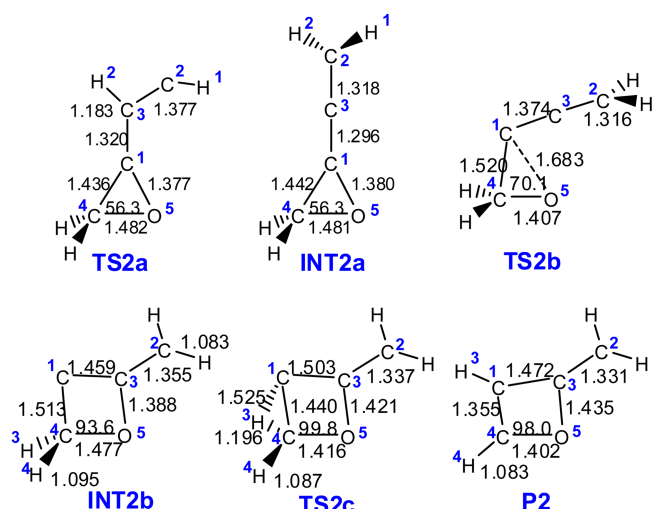
**Figure 4.** IRCs of TSa, where the selected structures have been given along the IRCs.

C<sup>3</sup> and C<sup>1</sup>-C<sup>3</sup> bonds have been changed to the single and double bond, respectively. As for the C<sup>2</sup> atom, it has a pair of lone electrons, making the INTb exhibit the carbene

characters. In other words, INTb is unstable and can rearrange to a more stable structure.

By shifting the H<sup>2</sup> atom on the C<sup>3</sup> atom to the adjacent C<sup>1</sup> atom, INTb can be converted to P1 *via* TS1, and the unique imaginary frequency of TS1 is 1008.9i cm<sup>-1</sup>. Here, P1 is the most stable structure along the pathway (1). Obviously, in P1, the C<sup>1</sup> atom is *sp*<sup>3</sup> hybridization and both the C<sup>3</sup> and C<sup>2</sup> atoms are *sp* hybridization. Therefore, the C<sup>3</sup>-C<sup>2</sup> bond is a triple bond (1.220 Å), which is rather shorter than that of the C<sup>1</sup>-C<sup>3</sup> bond (1.443 Å).

For the pathway (1), three steps need to surmount transition state. The corresponding barriers of the three steps are 38.0, 175.9, and 98.4 kJ/mol, respectively. Therefore, the second step is the rate-determining step along the pathway (1).



**Figure 5.** Optimized structures of the transition states (TS2a, TS2b, and TS2c), intermediates (INT2a and INT2b), and product (P2) in the reaction pathway (2) at the MP2/6-311+G\* level of theory, where the bond length and bond angle are in angstrom and degree, respectively.

**Reaction Pathway (2): Four-membered Ring Product Channel.** The geometric parameters for the stationary points in the reaction pathway (2) are given in Figure 5. The corresponding reaction profile is illustrated in Figure 3. As illustrated in Figure 5, a four-membered ring product (P2) has been generated in the pathway (2).

Similar to the reaction pathway (1), the intermediates INTa and INTb have been formed successively in the pathway (2). As described above, in the pathway (1), INTb can be converted to P1 *via* TS1 by shifting the H<sup>2</sup> atom on the C<sup>3</sup> atom to the adjacent C<sup>1</sup> atom. However, in pathway (2), INTb can be converted to INT2a *via* TS2a by shifting the H<sup>2</sup> atom on the C<sup>3</sup> atom to the adjacent C<sup>2</sup> atom. Here, the unique imaginary frequencies of the transition states TS2a, TS2b, and TS2c are 559.4i, 616.7i, and 832.1i cm<sup>-1</sup>, respectively.

As displayed in Figure 5, in INT2a, the C<sup>3</sup> atom adopts *sp* hybridization and the C-C bond lengths are 1.318 (C<sup>2</sup>-C<sup>3</sup>) and 1.296 Å (C<sup>1</sup>-C<sup>3</sup>), which are intermediate between the general C=C double bond (about 1.33 Å) and CC triple bond (about 1.20 Å), respectively. Due to the existence of tension in the three-membered ring, the fourth step of the pathway (2) is that C<sup>1</sup>-O<sup>5</sup> bond in INT2a opens to form an intermediate INT2b *via* TS2b, where the barrier is 260.3 kJ/mol. In addition, in TS2b, the C<sup>1</sup>-O<sup>5</sup> bond has been elongated to 1.683 Å, denoting the rupture of the C<sup>1</sup>-O<sup>5</sup> bond. On the other hand, the distance between C<sup>3</sup> and O<sup>5</sup> atoms is 1.868 Å, indicating the formation of the C<sup>3</sup>-O<sup>5</sup> bond.

INT2b is a four-membered structure, and there is a pair of lone electrons on the C<sup>1</sup> atom. For this reason, INT2b is characteristic of carbene. The fifth step of the pathway (2) is that one H atom on the C<sup>4</sup> of INT2b is transferred to the C<sup>1</sup> atom to form a more stable structure P2 *via* TS2c, where the barrier is 41.6 kJ/mol. Based on the analysis of the imaginary frequency and the calculation of the IRC, it can be proved that TS2c connects the INT2b and P2 indeed.

In P2, the bond lengths of C<sup>2</sup>-C<sup>3</sup> and C<sup>1</sup>-C<sup>4</sup> are 1.331 and 1.355 Å, respectively, which is slightly longer than that of the normal C=C double bond. At the same time, the bond length of C<sup>1</sup>-C<sup>3</sup> is 1.472 Å, which is slightly shorter than that of the normal C-C single bond. Moreover, further energy analyses suggest that the P2 is lower in energy by about 218.9 kJ/mol than those of reactants. From the calculated bond length and the stability, P2 is a stable conjugated diene and it is the ultima product of the pathway (2).

In summary, the barrier heights of the five steps in the pathway (2) are 38.0, 175.9, 113.8, 260.3, and 41.6 kJ/mol, respectively. Therefore, the fourth step is the rate-determining step along the pathway (2).

**Comparisons of the Two Reaction Pathways.** As mentioned above, three- and four-membered ring products can be produced between cyclopropenylidene and formaldehyde through two different reaction pathways. The barrier heights of the rate-determining step in the pathways (1) and (2) are 175.9 and 260.3 kJ/mol, respectively. Therefore, the reaction pathway (1) is the most favorable channel from the kinetic viewpoint. On the other hand, the corresponding products P1

and P2 have been stabilized by about 168.0 and 218.9 kJ/mol relative to the reactants, respectively. Therefore, the most favorable product P2 should be confirmed, implying that the reaction pathway (2) is a favorable channel from the thermodynamical viewpoint.

## Conclusions

In this study, the reaction mechanism between cyclopropenylidene and formaldehyde has been systematically investigated employing the MP2/6-311+G\* level of theory. It was found that two ultimate products P1 and P2 can be formed through two pathways (1) and (2). The barriers of the rate-determining step of the pathways (1) and (2) are 175.9 and 260.3 kJ/mol, respectively. On the other hand, the corresponding products P1 and P2 have been stabilized by 168.0 and 218.9 kJ/mol relative to the reactants, respectively. Therefore, the reaction pathway (1) is the most favorable reaction to occur kinetically. However, the high stability of P2 among the available products suggests that the pathway (2) is a favorable process thermodynamically.

**Acknowledgments.** This work is supported by NSFC (21003082), the Project of Shandong Province Higher Educational Science and Technology Program (J09LB01, J09LB17), and the Foundation for Outstanding Young Scientist in Shandong Province (BS2009HZ014, BS2010NJ009).

## References

1. Mitani, M.; Kobanashi, Y.; Koyama, K. *J. Chem. Soc., Perkin Trans I* **1995**, 653.
2. Garcia, M.; Campo, C. D.; Llama, E. F. *Tetrahedron Lett.* **1993**, 49, 8433.
3. Garcia, M.; Campo, C. D.; Llama, E. F. *J. Chem. Soc., Perkin Trans I* **1995**, 1771.
4. Kostikov, R. R.; Khlebnikov, A. F.; Bespalov, V. Y. *J. Phys. Org. Chem.* **1993**, 6, 83.
5. Wang, Y.; Li, H. *Acta Phys-Chim. Sin.* **2004**, 20, 1339.
6. Stang, P. J. *J. Am. Chem. Res.* **1982**, 15, 348.
7. Lu, X. H.; Wang, Y. X. *J. Phys. Chem. A* **2003**, 107, 7885.
8. Lu, X. H.; Wang, Y. X. *J. Mole. Struct. (THEOCHEM)* **2004**, 686, 207.
9. Apeloig, Y.; Kami, M.; Stang, P. J. *J. Am. Chem. Soc.* **1983**, 105, 4781.
10. Fox, D. P.; Stang, P. J.; Apeloig, Y.; Karni, M. *J. Am. Chem. Soc.* **1986**, 108, 750.
11. Tan, X. J.; Li, P.; Wang, W. H.; Zheng, G. X.; Yang, X. L. *Struct. Chem.* **2009**, 20, 671.
12. Tan, X. J.; Li, P.; Wang, W. H.; Zheng, G. X.; Wang, Q. F. *J. Serb. Chem. Soc.* **2010**, 75, 649.
13. Herges, R.; Mebel, A. *J. Am. Chem. Soc.* **1994**, 116, 8229.
14. Maier, G.; Reisenauer, H. P.; Schwab, W.; Carsky, P.; Hess, B. A.; Schaad, L. J. *J. Am. Chem. Soc.* **1987**, 109, 5183.
15. Seburg, R. A.; DePinto, J. T.; Patterson, E. V.; McMahan, R. J. *J. Am. Chem. Soc.* **1995**, 117, 835.
16. MacAllister, T.; Nicholson, A. *J. Chem. Soc., Faraday Trans.* **1981**, 77, 821.
17. Seburg, R. A.; MacMahon, R. *Angew. Chem., Int. Ed. Engl.* **1995**, 34, 2009.
18. Seburg, R. A.; Patterson, E. V.; Stanton, J. F.; McMahan, R. J. *J. Am. Chem. Soc.* **1997**, 119, 5847.

19. Maier, G.; Reisenauer, H. P.; Schwab, W.; Carsky, P.; Spirko, V.; Hess, B. A.; Schaad, L. J. *J. Chem. Phys.* **1989**, *91*, 4763.
  20. Juana, V.; Michael, E. H.; Jurgen, G.; John, F. S. *J. Phys. Chem. A* **2009**, *113*, 12447.
  21. Taatjes, C. A.; Klippenstein, S. J.; Hansen, N.; Miller, J. A.; Cool, T. A.; Wang, J.; Law, M. E.; Westmoreland, P. R. *Phys. Chem. Chem. Phys.* **2005**, *7*, 806.
  22. Lau, K. C.; Ng, C. Y. *Chin. J. Chem. Phys.* **2006**, *19*, 29.
  23. Gleiter, R.; Hoffmann, R. *J. Am. Chem. Soc.* **1968**, *90*, 5457.
  24. Shepard, R.; Banerjee, A.; Simons, J. *J. Am. Chem. Soc.* **1979**, *101*, 6174.
  25. Lee, T. J.; Bunge, A.; Schaefer, H. F. *J. Am. Chem. Soc.* **1985**, *107*, 137.
  26. Montgomery, J. A.; Ochterski, J. W.; Petersson, G. A. *J. Chem. Phys.* **1994**, *101*, 5900.
  27. Hehre, W. J.; Pople, J. A.; Lathan, W. A.; Radom, L.; Wasserman, E.; Wasserman, Z. R. *J. Am. Chem. Soc.* **1976**, *98*, 4378.
  28. Jonas, V.; Bohme, M.; Frenking, G. *J. Phys. Chem.* **1992**, *96*, 1640.
  29. Takahashi, J.; Yamashita, K. *J. Chem. Phys.* **1996**, *104*, 6613.
  30. Fan, Q.; Pfeiffer, G. V. *Chem. Phys. Lett.* **1989**, *162*, 472.
  31. Walch, S. P. *J. Chem. Phys.* **1995**, *103*, 7064.
  32. Kirmse, W. *Carbene Chemistry*, 2nd ed.; Academic Press: New York, 1971.
  33. Jones, M.; Moss, R. A. *Carbenes* Wiley: New York, 1973.
  34. Herbst, E. *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 595.
  35. Herbst, E.; Leung, L. M. *Astrophys. J. Suppl. Ser.* **1989**, *69*, 271.
  36. Winnewisser, G. *Top. Curr. Chem.* **1981**, *99*, 39.
  37. Hayatsu, R.; Anders, E. *Top. Curr. Chem.* **1981**, *99*, 1.
  38. Thaddeus, P.; Gottlieb, C. A.; Mollaaghababa, R.; Vrtilek, J. M. *J. Chem. Soc. Faraday Trans.* **1993**, *89*, 2125.
  39. Goulay, F.; Adam, J. T.; Meloni, G.; Talitha, M. S.; David, L. O.; Craig, A. T.; Luc, V.; Stephen, R. L. *J. Am. Chem. Soc.* **2009**, *131*, 993.
  40. Patrick, H.; Juliane, K.; Ingo, F.; Giovanni, P.; Lionel, P.; Jean-Michel, M. *Phys. Chem. Chem. Phys.* **2011**, PMID 22173743.
  41. Chotima, R.; Dale, T.; Green, M.; Hey, T. W.; McMullin, C. L.; Nunns, A.; Orpen, A. G.; Shishkov, I. V.; Wass, D. F.; Wingad, R. L. *Dalton Trans.* **2011**, *40*, 5316.
  42. Duncan, F. W.; Mairi, F. H.; Thomas, W. H.; Guy, O.; Christopher, R.; Richard, L. W.; Michael, G. *Chem. Commun.* **2007**, *26*, 2704.
  43. Vincent, L.; Yves, C.; Bruno, D.; Wolfgang, W. S.; Guy, B. *Science* **2006**, *312*, 722.
  44. Pradeep, R.; Varadwaj, R. F.; Kentarou, K. *J. Phys. Chem. A* **2011**, *115*, 8458.
  45. Frisch, M. J. et al., *Gaussian 98*, Gaussian Inc.: Pittsburgh, PA, 1998.
-