

## Density Functional Study on [3+2]-Dipolar Cycloaddition Reaction of the *N*-heterocyclic Carbene Boryl Azide with Olefins

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The cycloaddition reactions of the *N*-heterocyclic carbene boryl azide with methyl acrylate, butenone, and hexafluoropropene have been investigated theoretically. Solvent effects on these reactions have been explored by calculation that included a polarizable continuum model (PCM) for the solvent (C<sub>6</sub>H<sub>6</sub>). The title reaction could produce 4- and 5-substituted 1,2,3-triazolines, respectively. The reaction systems have the higher chemical reactivity with the low barriers and could be favored. Yet the smaller differences have been found to occur in energetics, and the cycloaddition reactions occur for *s-trans* conformations over *s-cis* conformations. The calculations indicated that the cycloaddition reaction of the alkenes have certain regioselectivity.

**Key Words :** Cycloaddition reaction, Boryl azide, Olefin, Density functional study

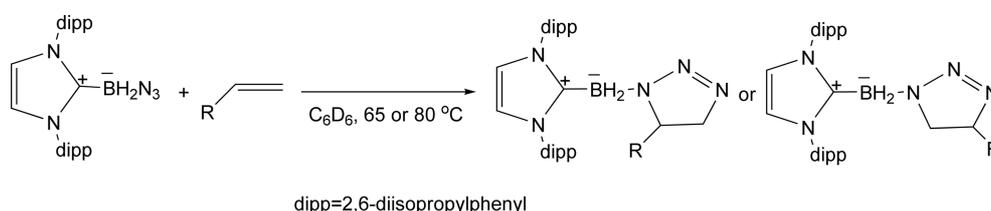
### Introduction

*N*-Heterocyclic carbenes (NHCs) are widely used Lewis bases and boranes are popular Lewis acids.<sup>1,2</sup> However, the combination of an *N*-heterocyclic carbene (NHC) with a borane typically results in a complex called an *N*-heterocyclic carbene borane. NHC-boranes are formally analogous to many other Lewis acid/Lewis base complexes and many are so stable.<sup>3</sup> Instead, they are unearthing a surprisingly rich chemistry for organic compounds that can provide unusual new boron compounds and reactive intermediates. Carbene-boranes have significant potential as reagents in organic synthesis and as initiators in polymer chemistry.<sup>4-12</sup> And the study of carbene-boranes as reactants has led to the synthesis of diverse stable compounds with unusual boron substituents and bonding patterns.<sup>13-23</sup> Curran group make heteroatom-substituted NHC-boranes starting from the parent complex 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene borane and produce unusual functionalized NHC-borane compounds including boryl azides [R = 1,3-bis-(2,6-diisopropylphenyl)-imidazol-2-ylidene borane azide]. Because such functionalized boranes R are rare, little is known about their chemistry, such as cycloaddition reactions. Recently, Curran and co-worker reported<sup>24</sup> that a prototypical NHC-boryl azide behaves as an electron-rich [1,3]-dipole in cycloaddition reactions with electron-poor alkenes to provide remarkably stable NHC-boryl triazolines (Scheme 1).

So far as we know, the only experimental report on this reaction was given by Curran *et al.*, who investigated that R react with the asymmetric olefins having high selectivity in yields ranging from 40% to 89%. To gain systematic insight into the mechanism of the [3+2]-dipolar cycloaddition reaction, in this paper, we have carried out a theoretical study at the DFT level on the reaction of R with H<sub>2</sub>C=CHCOOCH<sub>3</sub>, H<sub>2</sub>C=CHCOCH<sub>3</sub> and F<sub>2</sub>C=CFCH<sub>3</sub>, and which are alkenes with electron withdrawing groups (methyl acrylate, for example). The main objectives are to provide further analysis of the structures and energetics of the two [3+2]-dipolar cycloaddition reactions in the gas phase and also further investigate the effects of solvents on the thermodynamic and kinetic properties of these reactions, which are expected to provide some helpful information to experimentalists who are interested in this area.

### Computational Methods

Full optimization of geometries for all stationary points involved in [3+2] cycloaddition reaction has been calculated using the density functional theory (DFT) method based on the hybrid of Becke's three-parameter exchange functional and the Lee, Yang, and Parr correlation functional (B3LYP).<sup>25</sup> This hybrid DFT method (B3LYP) has been shown to be quite reliable for finding both the geometries and energies for studying cycloaddition reaction. The 6-31G basis set



**Scheme 1.** dipolar cycloaddition reactions of 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene dihydridoboron azide with alkenes.

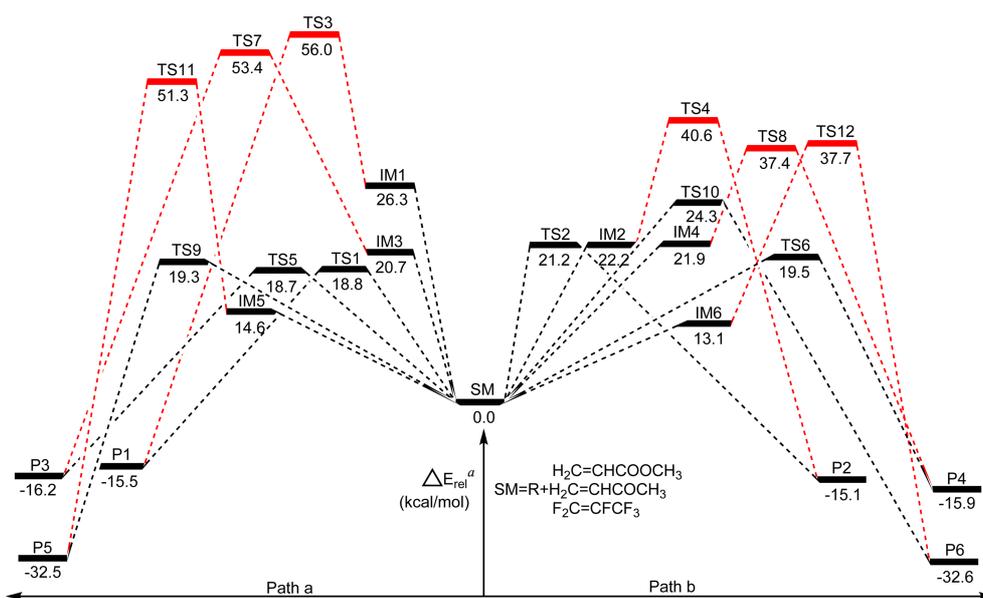
with polarization (d) and (p)<sup>26</sup> were selected for all the atoms. Vibrational frequency calculations done at the same level of theory were used to characterize all of the stationary points as either minima (with all real frequencies) or transition states (with only one imaginary frequency) and to obtain zero-point energies (ZPE) corrections. Furthermore, the intrinsic reaction coordinate (IRC) calculations<sup>27</sup> are performed to confirm that the optimized transition states correctly connect two relevant minima. The charges population analyses for some key atoms were discussed in terms of natural bond orbital (NBO) calculation.<sup>28,29</sup> To consider the effect of the solvent on the reactions of interest, the polarized continuum model (PCM)<sup>30,31</sup> was applied, and single-point energy calculations were done at the B3LYP/PCM/6-311++G(d,p)//B3LYP/6-31G(d,p) level of theory using the geometries along the minimum energy pathway. In the PCM calculations, C<sub>6</sub>H<sub>6</sub> ( $\epsilon = 2.27$ ) was used as the solvent, corresponding to the experimental conditions. All computations reported here are carried out using the Gaussian 03 program suit.<sup>32</sup>

## Results and Discussion

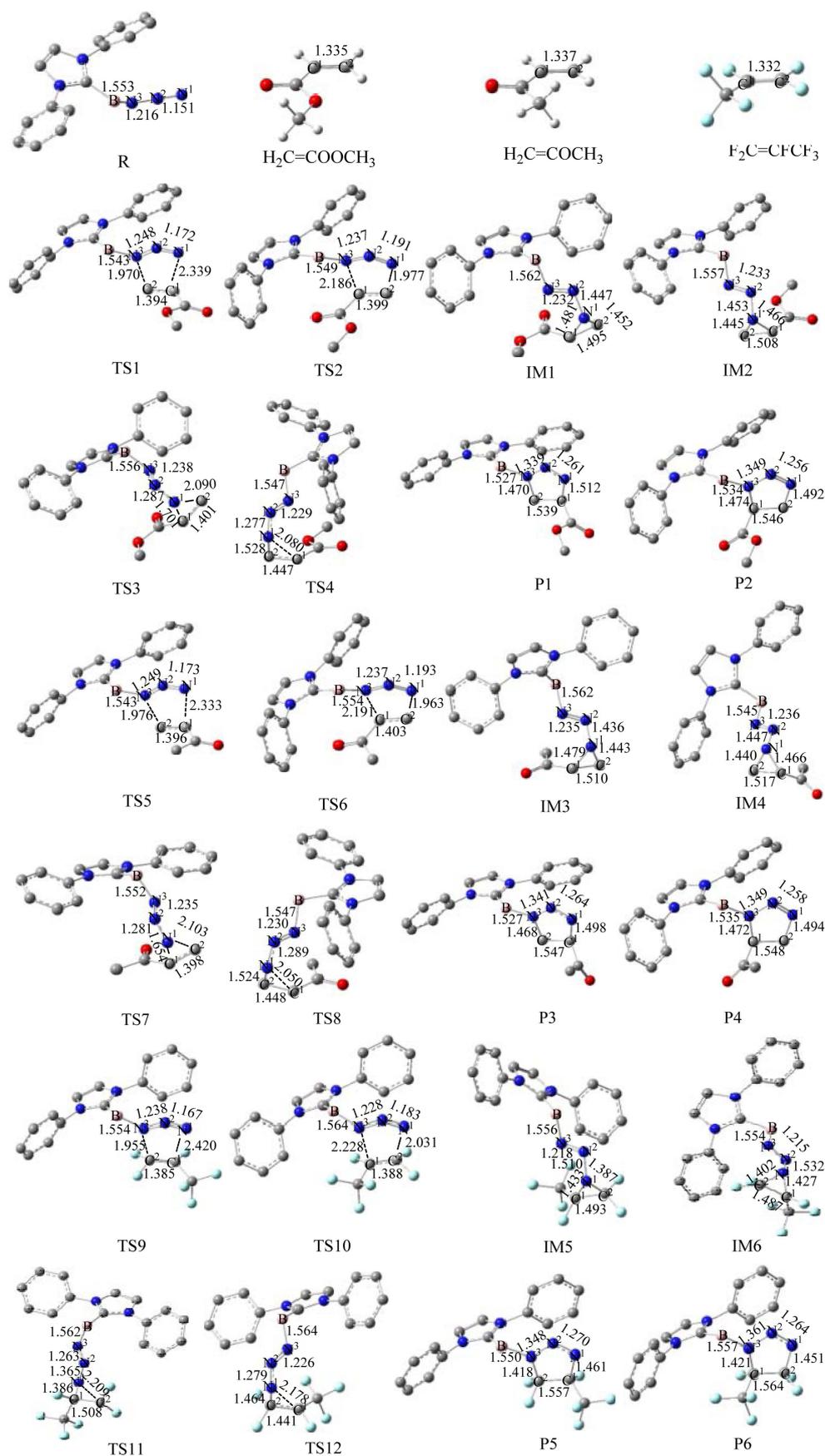
By means of the interrelationship of reactants, products, and transition states as well as their relative energies, the potential energy surface profiles of the pathways corresponding to the title reactions are depicted in Figure 1. The optimized geometries for the reactants, intermediates, transition states, and products of the reaction systems are presented schematically in Figure 2 along with selected key geometry parameters (*e.g.*, bond lengths). The energetic data at the B3LYP/PCM/6-311++G(d,p)//B3LYP/6-31G(d,p) level including ZPE corrections are listed in Table 1. Unless otherwise noted, the relative energies discussed in subsequent sections refer to the value in C<sub>6</sub>H<sub>6</sub> solvent. The HOMO–

LUMO orbital energy gaps for the reactants studied are gathered in Table 2. In order to keep the computational cost low, the original R was selected with the *N*-phenyl conjugation in the system as a model.

**The [3+2] Cycloaddition Reaction of NHC- boryl Azide with H<sub>2</sub>C=CHCOOCH<sub>3</sub>.** The energy profile for the pathways a and b of the reaction of NHC- boryl azide with H<sub>2</sub>C=CHCOOCH<sub>3</sub> is represented in Figure 1. The structures of the various critical points located on the potential surface along with the values of the most relevant geometry parameters are shown in Figure 2. The pathways involve a one-step mechanism leading to two possible five-membered ring products where the group of the reagents adds to the  $\pi$  bond to form the new C–N single bonds. The reaction of R with H<sub>2</sub>C=CHCOOCH<sub>3</sub> could produce P1 through the transition states TS1 and TS3 in path a. In the transition structure TS1, the new forming C<sup>1</sup>–N<sup>1</sup> and C<sup>2</sup>–N<sup>3</sup> bond distances are 2.339 and 1.970 Å, respectively. The C<sup>1</sup>–C<sup>2</sup>, N<sup>1</sup>–N<sup>2</sup> and N<sup>2</sup>–N<sup>3</sup> distances are elongated by 0.059, 0.021 and 0.032 Å respectively upon going from the reactants to the transition state. However, the B–N<sup>3</sup> bond length in TS1 shortens 0.010 Å than that of the reactant structure. The two carbon centers still retain their initial *sp*<sup>2</sup> hybridization. These changes in the bond lengths are attributed to partial formation of five-membered ring product P1. The NBO charges for the N<sup>1</sup>, N<sup>2</sup>, and N<sup>3</sup> atoms in R are –0.3595, 0.3984, and –0.4654 au, respectively. On the basis of the frontier orbital theory, with the maximum overlapping principle in 1,3 dipolar cycloaddition reaction of N<sup>1</sup> and N<sup>3</sup> atoms in HOMO and two carbon of olefin in LUMO, the negative charge found for N<sup>1</sup> and N<sup>3</sup> atoms make the electrophilic attack  $\pi$  bond of C<sup>1</sup>=C<sup>2</sup> on the N<sup>1</sup> and N<sup>3</sup> more feasible than that of the N<sup>2</sup> atom. In P1, not only do the carbon atoms display *sp*<sup>3</sup> hybridization, but also the C–C–N–N–N fragment exhibits the typical shape



**Figure 1.** Energy profiles for pathway a and b, the relative energies are given in kcal/mol. <sup>a</sup>These values, in kcal/mol, were calculated at the B3LYP/PCM/6-311++G(d,p)//B3LYP/6-31G(d,p) level of theory using single-point PCM calculations to model the effect of the solvent (C<sub>6</sub>H<sub>6</sub>).



**Figure 2.** Optimized structures for path **a** and **b** shown in Figure 1 with selected structural parameters (hydrogen atoms are omitted for clarity and bond lengths are presented in Å).

**Table 1.** Thermodynamic properties (total energy with zero-point energy, relative energy in gas phase and in solution) of the structures in Figure 1<sup>a</sup>

Species	$E_{t, \text{gas}}$ (a. u.)	$E_{r, \text{gas}}$ (kcal/mol)	$E_{t, \text{sol}}$ (a. u.)	$E_{r, \text{sol}}$ (kcal/mol)	$\Delta E^{\ddagger}_{\text{sol}}$ (kcal/mol)
R+H <sub>2</sub> C=CHCOOCH <sub>3</sub>	-1184.72215	0.0	-1185.39717	0.0	
TS1	-1184.69498	17.0	-1185.36716	18.8	18.8
TS2	-1184.69671	16.0	-1185.36337	21.2	21.2
IM1	-1184.68130	25.6	-1185.35526	26.3	
IM2	-1184.68491	23.4	-1185.36180	22.2	
TS3	-1184.63714	53.3	-1185.30798	56.0	29.7
TS4	-1184.66063	38.6	-1185.33251	40.6	18.4
P1	-1184.74269	-12.9	-1185.42191	-15.5	
P2	-1184.74493	-14.3	-1185.42129	-15.1	
R+H <sub>2</sub> C=CHCOCH <sub>3</sub>	-1109.49640	0.0	-1110.14219	0.0	
TS5	-1109.46943	16.9	-1110.11246	18.7	18.7
TS6	-1109.47330	14.5	-1110.11104	19.5	19.5
IM3	-1109.46602	19.1	-1110.10924	20.7	
IM4	-1109.45917	23.4	-1110.10724	21.9	
TS7	-1109.42388	45.5	-1110.05714	53.4	32.7
TS8	-1109.43861	36.3	-1110.08253	37.4	15.5
P3	-1109.51913	-14.3	-1110.16808	-16.2	
P4	-1109.52055	-15.2	-1110.16752	-15.9	
R+F <sub>2</sub> C=CFCF <sub>3</sub>	-1591.61203	0.0	-1592.37733	0.0	
TS9	-1591.58934	14.2	-1592.34655	19.3	19.3
TS10	-1591.58509	16.9	-1592.33858	24.3	24.3
IM5	-1591.59663	9.7	-1592.35410	14.6	
IM6	-1591.59937	7.9	-1592.35651	13.1	
TS11	-1591.54283	43.4	-1592.29561	51.3	36.7
TS12	-1591.56377	30.3	-1592.31731	37.7	24.6
P5	-1591.67284	-38.2	-1592.42916	-32.5	
P6	-1591.67333	-38.5	-1592.42930	-32.6	

<sup>a</sup>These values, in kcal/mol, were calculated at the B3LYP/PCM/6-311++G(d,p)/B3LYP/6-31G(d,p) level of theory using single-point PCM calculations to model the effect of the solvent (C<sub>6</sub>H<sub>6</sub>)

**Table 2.** B3LYP/6-31G\*\* HOMO-LUMO orbital energy gaps  $\Delta E$  between reacting systems

Interacting orbitals	$\Delta E$	
	ev	Kcal/mol
HOMO (R)- LUMO (H <sub>2</sub> C=CHCOOCH <sub>3</sub> )	-0.15	-94.13
HOMO (H <sub>2</sub> C=CHCOOCH <sub>3</sub> )- LUMO (R)	-0.23	-144.33
HOMO (R)- LUMO (H <sub>2</sub> C=CHCOCH <sub>3</sub> )	-0.13	-81.58
HOMO (H <sub>2</sub> C=CHCOCH <sub>3</sub> )- LUMO (R)	-0.21	-131.78
HOMO (R)- LUMO (F <sub>2</sub> C=CFCF <sub>3</sub> )	-0.18	-112.95
HOMO (F <sub>2</sub> C=CFCF <sub>3</sub> )- LUMO (R)	-0.24	-150.60

with the C=C bond rotated single bond from 1.394 Å in TS1 to 1.539 Å. The cycloaddition reaction produce P1 through TS1 with a barrier of 18.8 kcal/mol and exothermic by 15.5 kcal/mol.

Moreover, the interaction of the C=C double bond of H<sub>2</sub>C=CHCOOCH<sub>3</sub> with the N<sup>1</sup> atom would give the preliminary intermediate IM1 in path a. In IM1, this is a polarized complex with distances between N<sup>1</sup> and two *sp*<sup>3</sup>-hybridized carbon atoms of 1.481 and 1.452 Å, respectively. Furthermore, the C<sup>1</sup>-C<sup>2</sup> bond has lost a little of its single

bond character and is now 1.495 Å. Meanwhile, the N<sup>1</sup>-N<sup>2</sup>, N<sup>2</sup>-N<sup>3</sup> and B-N<sup>3</sup> bond lengths are 1.447, 1.232 and 1.562 Å, respectively. Following the product P1 is also formed through a three-membered ring transition structure TS3 with the bond of N<sup>1</sup>-C<sup>2</sup> broken. The breaking bond N<sup>1</sup>-C<sup>2</sup> is 2.090 Å and the N<sup>1</sup>-C<sup>1</sup>, C<sup>1</sup>-C<sup>2</sup> bonds in TS3 are now 1.701 and 1.401 Å, respectively. Table 1 and Figure 1 showed that the energy of activation for this route is calculated to be 56.0 kcal/mol for TS3. Comparison of the structure of TS1, the activation energy for TS3 is higher than that for TS1 by 37.2 kcal/mol. The reaction proceed along TS3 is prohibitive in typical reaction conditions.

A new product P2 would be obtained when the N<sup>1</sup> or N<sup>3</sup> atoms of R attack  $\pi$  bond of H<sub>2</sub>C=CHCOOCH<sub>3</sub> along the opposite direction through the transition states TS2 and TS4. TS2 and TS4 have only one imaginary frequency of 400.7 and 423.9i cm<sup>-1</sup> respectively, and IRC calculations confirmed that the TS connect the corresponding intermediate and product. Figure 2 show that the two new N<sup>1</sup>-C<sup>2</sup> and C<sup>1</sup>-N<sup>3</sup> bond distances in TS2 are 1.977 and 2.186 Å, respectively. In TS4, the N<sup>1</sup>-C<sup>1</sup> and N<sup>1</sup>-C<sup>2</sup> bonds are 2.080 and 1.528 Å, respectively. The transition state structures would contribute to form the stable product P2. Examination of Figure 1 and

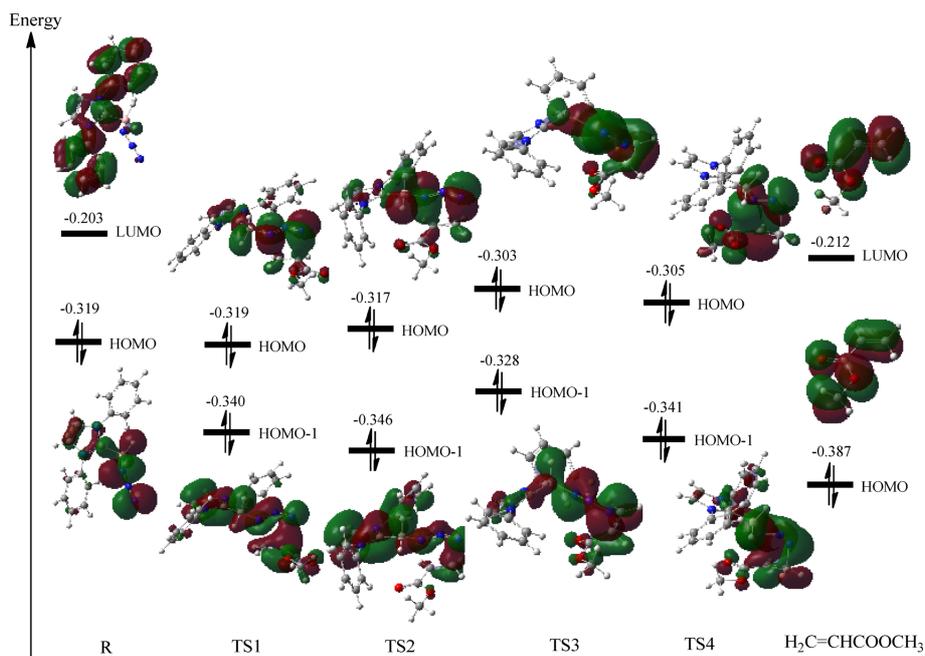
Table 1 show that the reaction pathway *via* TS2 needs to overcome a barrier of 21.2 kcal/mol, and the reaction *via* TS4 needs to overcome the higher barrier of 40.6 kcal/mol. This step to P2 is exothermic by  $-15.1$  kcal/mol. Our calculated results show that the pathway a (TS1) and pathway b (TS2) are complete reaction with the close reaction barriers to produce triazolines (P1 and P2), which are also consistent with the experimental observations of Curran *et al.*

**The [3+2] Cycloaddition Reaction of NHC- boryl Azide with  $\text{H}_2\text{C}=\text{CHCOCH}_3$ .** To better understand the chemical reactivity and stereoselectivity of NHC- boryl azide toward different olefins, we have theoretically investigated the [3+2] cycloaddition reaction of R with  $\text{H}_2\text{C}=\text{CHCOCH}_3$ . Following the originally proposed mechanism and the model studies, the similar reaction pathways are displayed in Figure 1 and the structural parameters are presented in Figure 2. The transition state structures TS5-8 and product P3-4 are very similar to that of TS1-4 and P1-2, respectively. The bond distance  $\text{C}^1\text{-C}^2$  and  $\text{N-N}$  of five-membered ring have lost their double-bond character and now have bond lengths in the range of 1.396-1.548 and 1.173-1.447 Å, respectively. The trend of the NHC-boryl azide reaction barrier with  $\text{H}_2\text{C}=\text{CHCOCH}_3$  is TS5 (18.7 kcal/mol) < TS6 (19.5 kcal/mol) < TS8 (37.4 kcal/mol) < TS7 (53.4 kcal/mol), as shown in Figure 1 and Table 1. The reaction barrier to produce P3 becomes slightly lower by 0.8 kcal/mol than that to P4 and the exothermicity of the reaction becomes by 16.2 kcal/mol at the same level of theory.

**The [3+2] Cycloaddition Reaction of NHC- boryl Azide with  $\text{F}_2\text{C}=\text{CFCF}_3$ .** We have done additional calculations to begin to study the reaction changing the olefin to  $\text{F}_2\text{C}=\text{CFCF}_3$ . Examination of Figure 2 shows that two complex IM5 and IM6 are formed when the two molecules move toward one

another. The transition state (TS9) ( $468.9 \text{ i cm}^{-1}$ ) and (TS11) ( $248.7 \text{ i cm}^{-1}$ ) were found for the reaction of R with  $\text{F}_2\text{C}=\text{CFCF}_3$  on the pathway a to P5 product. The geometry of TS9 and TS11 are similar to that of TS1, TS5 and TS3, TS7, respectively. The reactions *via* TS9 and TS11 (in Fig. 1) have barriers of 19.3 and 51.3 kcal/mol respectively, and the pathway is exothermic by about 32.5 kcal/mol. In the pathway b, the geometry of TS10 ( $506.2 \text{ i cm}^{-1}$ ) and TS12 ( $310.5 \text{ i cm}^{-1}$ ) are very similar to that of TS2, TS6 and TS4, TS8. The reaction has barriers of 24.3 and 37.7 kcal/mol and is exothermic by about 32.6 kcal/mol at the same level of theory. We found that the cycloaddition reaction proceeds along pathway a much less easily than pathway b of R with  $\text{F}_2\text{C}=\text{CFCF}_3$ .

**Comparison of [3+2] Cycloaddition Reactions of NHC-boryl Azide with Olefins.** In comparison of the NHC- boryl azide with  $\text{H}_2\text{C}=\text{CHCOOCH}_3$ ,  $\text{H}_2\text{C}=\text{CHCOCH}_3$  and  $\text{F}_2\text{C}=\text{CFCF}_3$  cycloadditions run through lower activation barriers. The two possible reaction pathways have competition or selectivity. The activation barriers of the reaction for the pathway a is quite low, 18.7-19.3 kcal/mol, whereas in the course of the reaction systems for the pathway b is equal to 19.5-24.3 kcal/mol, and the reaction occurs more easily along pathway a. For  $\text{F}_2\text{C}=\text{CFCF}_3$ , the exothermicity of the reaction becomes higher by 32.5-32.6 kcal/mol. We observed that the barrier heights for the reactions increase in the following order, with computed barrier heights given in parentheses:  $\text{H}_2\text{C}=\text{CHCOCH}_3$  (18.7-19.5 kcal/mol) <  $\text{H}_2\text{C}=\text{CHCOOCH}_3$  (18.8-21.2 kcal/mol) <  $\text{F}_2\text{C}=\text{CFCF}_3$  (19.3-24.3 kcal/mol). Because the fluorine atoms of five-membered product P3 have the stronger electronegativity than the oxygen atoms of products P1 and P2, the effect of the solvent in benzene formed the stronger hydrogen bonds by fluorine



**Figure 3.** Spatial plots of the frontier molecular orbitals for R,  $\text{H}_2\text{C}=\text{CHCOOCH}_3$ , and HOMO and HOMO-1 calculated for the transition states TS1-4. The orbital energies are given in eV.

and nitrogen atoms of P1, which reduced the bond energies and stability for five-membered ring intermediate. Table 1 shows that solvent medium products for  $R+H_2C=COOCH_3$  and  $R+H_2C=COCH_3$ , are more stable than gas medium, but in the case of  $R+F_2C=CF_2CF_3$ , it was reverse.

It is interesting to see why the activation barriers are lower in the  $H_2C=CHCOCH_3$  than those in the  $F_2C=CF_2CF_3$ . The answer can be derived simply from an argument based on the frontier orbitals approximation (FOA). According to the approximation, the stabilization effect is due to the (highest occupied molecular orbital-lowest unoccupied molecular orbital) HOMO-LUMO reactant orbitals interaction which is proportional to the overlap integral  $S$  and to  $1/\Delta\epsilon$ ,  $\Delta\epsilon = \epsilon_D^{HOMO} - \epsilon_A^{LUMO}$  where is the energy separation between the two orbitals of the donor  $D$  and acceptor  $A$  molecules.<sup>33</sup> In the  $R-H_2C=CHCOCH_3$  cycloaddition, the HOMO-LUMO energy separation is smaller than that in the  $R-H_2C=CHCOOCH_3$  and  $R-F_2C=CF_2CF_3$  one (Table 2). Thus, the activation barriers in the former reaction are expected to be lower than those in the latter one. We plotted the frontier molecular orbitals for  $R$  and  $H_2C=CHCOOCH_3$ , and the highest and the second highest occupied molecular orbitals (HOMO and HOMO-1) calculated for the transition states TS1-4 (Fig. 3). These two occupied orbitals are relevant to bond formation and cleavage during the reaction process. The above comparison is qualitatively consistent helps to provide a reasonable explanation for understanding these types [3+2] cycloaddition reactions.

### Conclusion

In this theoretical study, [3+2]-dipolar cycloaddition reaction of the  $N$ -heterocyclic carbene boryl azide with the asymmetric alkenes have been investigated at the B3LYP/PCM/6-311++G(d,p)/B3LYP/6-31G(d,p) level of theory. There are two possible five-membered products of the reactions through four transition states. In two reaction products, the energy barriers for  $H_2C=CHCOCH_3$ ,  $H_2C=CHCOOCH_3$  and  $F_2C=CF_2CF_3$  are the smaller because of the lower reaction barriers (18.7-24.3 kcal/mol). While the reactions produce the *s-trans* conformations (pathway a) is favored over *s-cis* conformations (pathway b). These steps are exothermic by 15.1-32.6 kcal/mol. We calculations indicated that the cycloaddition reaction of the different alkenes have some regioselectivity. The computed results predict that the reactions could take place easily and be in good agreement with the experimental observations.

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