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Reactivity of Borylenes toward Ethyne, Ethene, and Methane

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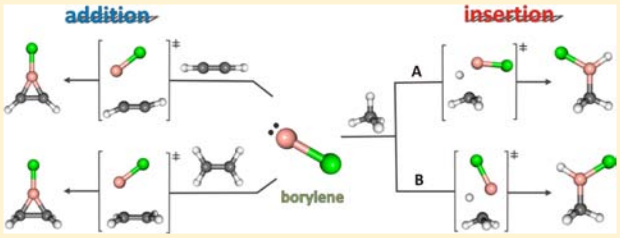
S *Supporting Information*

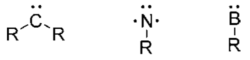
ABSTRACT: The electronic and geometric structure of various substituted borylenes BR (where R = H, F, Cl, Br, CH_3, Ph, NH_2, NHMe, and NMe_2) in their lowest singlet and triplet electronic states was investigated by computational means using hybrid density functional (B3LYP) and second-order Møller−Plesset perturbation theories combined with 6-311+G** and cc-pVTZ basis sets. The reactivity of singlet borylenes towards prototypical saturated and unsaturated hydrocarbons was examined by the MP2 method in conjugation with the cc-pVTZ basis set and also by coupled cluster [CCSD(T)] computations in combination with the aug-cc-pVTZ basis set. To study the energetics and the mechanism of the addition reaction of borylenes to unsaturated CC bonds, ethyne and ethene are chosen as model compounds. The insertion reaction of borylene into a C−H bond of methane was also investigated. The addition reactions of borylenes to multiple C−C bonds are strongly exothermic. In case of the BH molecule the reactions proceed without barrier and are the most exothermic. For the insertion reaction of borylenes into methane, two approaches could be identified. Again, the smallest reaction barriers and highest reaction energies were computed for the BH insertion, while the highest barriers and the smallest exothermicities were obtained for the BF molecule. On the basis of frontier molecular orbital energies, barrier heights, reaction energies, and transition state geometries BH is the most electrophilic borylene, followed by BPh, while aminoborylenes and BF are the most nucleophilic ones among the investigated derivatives. Accordingly, reactions of BH have the smallest barriers (if there is one at all) and the largest reaction energies, while the reactions of BF have the highest barriers and the smallest reaction energies.



1. INTRODUCTION

Neutral subvalent compounds of carbon and nitrogen, carbenes **1** and nitrenes **2**, are seminal reactive intermediates in organic chemistry. Their chemistry is well developed and summarized in numerous reviews and monographs.[1,2]

Chart 1



1 2 3

The boron analogues of **1** and **2** are sometimes called borenes or boranediyls, but more commonly borylenes **3**. Similarly to **1** and **2**, free borylenes **3** are rather rare reactive intermediates. Seminal work by Timms in the 1960s has shown that BF formed by passing BF_3 over hot boron is readily reacting with alkynes.[3,4] The high-temperature reaction between BX_3 and boron was used to prepare a number of borylenes (X = H, F, Cl, Br, I) in the gas phase and to study their structure by microwave spectroscopy. Since then, occasional trapping reactions of borylenes have been reported. These involve the 1984 photogeneration of triphenylsilylborylene Ph_3SiB from $(Ph_3Si)_3B$ in organic glasses. Although it was not possible to observe the borylene directly by spectroscopy in this experiment, the reaction products isolated after warming the glass matrix to room temperature are in support of a transient borylene. In the absence of a trapping agent, the borylene inserts into the tertiary CH bond of glass forming 3-methylpentane or into the C−O bond of tetrahydrofuran. Photolysis in the presence of bis(trimethylsilyl)ethyne results in isolation of the corresponding borirene at room temperature.[5] Grigsby and Power concluded in their 1996 study of the metal reduction of arylboron dihalides with bulky substitution at the ortho positions of the phenyl ring that an intermediate borylene underwent intramolecular insertion into C−C σ bonds.[6] Similarly, reduction of chloroborane derivatives stabilized by N-heterocyclic carbenes (NHC) resulted in trapping products that were ascribed to result from NHC-stabilized borylenes that undergo C−H insertion reactions or [2 + 1] cycloaddition.[7−9] The barrier for the cycloaddition of BH•NHC to naphthalene was computed to be 2.6 kcal mol^{-1} using the B3LYP functional.[7] However, an alternative mechanism has recently been suggested to account for the trapping with naphthalene.[10] Ito et al. invoked the borylene TbtB (Tbt: 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl) as a transient intermediate in the photoreaction of $TbtB(SeMe)_2$ with benzil and phenanthrenequinone that produced the boronic ester of 9,10-dihydroxyphenanthrene in both cases.[11] Very recently, a NHC-stabilized borylene was suggested as an intermediate in the photochemical isomerization of C,C-chelate $BMes_2$.[12]

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Stabilizing borylenes is possible either by transition metal centers or by nucleophilic carbenes. The transition metal chemistry of borylenes is well developed and a number of reviews are available.[13−18] Some of these complexes can be used for photochemical transfer of the borylene ligand onto organic substrates providing a convenient access to borirenes,[19−21] or 1,4-diboracyclohexadiene and 1,4-dibora-1,3-butadiene complexes.[22] Nucleophilic carbenes have also been used successfully to stabilize borylenes. While one NHC does not result in an isolable NHC-stabilized BH molecule,[7−9] use of two cyclic (alkyl)(amino)carbenes (CAAC) allowed isolation of $(CAAC)_2BH$.[23,24]

Direct spectroscopic observations of free organoborylenes BR are scarce: Andrews et al. observed by IR spectroscopy ethynylborylene formed by codeposition of boron atoms and ethyne in an argon matrix at 15 K.[25] More recently, one of us reported that the photoinduced decomposition of diazidophenylborane $PhB(N_3)_2$ yields inter alia phenylborylene that could be identified by comparison of its IR spectrum (and that of its $[D]_5$ isotopomer) with the computed vibrational spectra.[26] Phenylborylene was found to undergo photochemically induced insertion into an ortho-CH bond of the phenyl ring to give benzoborirene.[26]

The reactivity summarized above for borylenes BR is in line with expectations based on carbene chemistry. However, details of the reaction mechanisms, exothermicities of borylene reactions and barrier heights are not known. This prompted us to investigate by computational means (i) the influence of substitents [R = H, F, Cl, Br; R = CH_3; R = Ph; R = NH_2, $NHCH_3$, $NH(CH_3)_2$] on the electronic structure of borylenes BR, and (ii) the mechanisms for the reactions of these borylenes toward ethyne, ethene, and methane as prototypical representatives of alkynes, alkenes, and alkanes. The variation of frontier orbital energies, singlet/triplet energy splitting, exothermicities, barrier heights, and transition state geometries is discussed in terms of the change of philicity of the borylene.

2. COMPUTATIONAL DETAILS

The computations of HOMO/LUMO energies of borylene employed the B3LYP[27,28] hybrid density functional as implemented[29] in Gaussian 09[30] in combination with 6-311+G**[31] basis set. In addition, second-order Møller−Plesset perturbation theory (MP2)[32] was employed to optimize minima and transition structures using 6-311+G** and cc-pVTZ[33] basis sets. Harmonic vibrational frequencies were computed analytically and confirmed the nature of the stationary points as minima, or first or higher order saddle points. Energies were refined using coupled cluster theory employing singles, doubles and a perturbative estimate of triples excitations [CCSD(T)][34] in conjunction with cc-pVTZ and aug-cc-pVTZ[33] basis sets. The frozen core approximation was applied in MP2 and CCSD(T) calculations. Unscaled zero-point vibrational energy (ZPE) corrections from MP2/cc-pVTZ frequency calculations were included. Additionally, intrinsic reaction coordinate (IRC)[35,36] paths were calculated at the MP2/6-311+G** level of theory for each reaction. All energies were calculated relative to separated reactants.

3. RESULTS AND DISCUSSION

3.1. Geometry and Electronic Structure of Borylenes.

The electron lone pair of borylenes is best described by an sp orbital (see Figure 1). This comprises the highest occupied molecular orbital (HOMO) of borylenes. In addition, two empty *p* orbitals are available at boron, and these form a doubly degenerate set of lowest unoccupied molecular orbitals (LUMO and LUMO+1) in borylenes of $C_{\infty v}$ and C_{3v} symmetry. Therefore, the triplet state is $^3\Pi$ for these borylenes. For BCH_3 this state will be unstable with respect to a Jahn−Teller distortion into a $^3A'$ and a $^3A''$ state. While the latter is a minimum, the former is a first order saddle point that is 0.3 kcal mol^{-1} higher in energy at the B3LYP/6-311+G** level of theory. At lower symmetry (C_{2v} or C_s for R = Ph, NRR′), the degeneracy is lifted due to interaction with the substituent R. Two distinct triplet states are therefore available ($^3B_1$ and $^3B_2$ in C_{2v}, $^3A''$ and $^3A'$ in C_s, respectively), and their energetic order depends on the nature of the substituent (vide infra).[37]

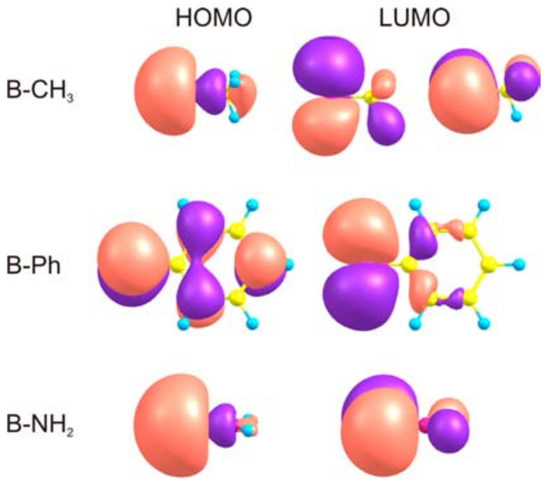


Figure 1. Molecular orbitals of borylenes in their singlet ground state as computed at the B3LYP/6-311+G** level of theory.

For several diatomic borylenes experimental bond lengths are available for their singlet states. The experimental r_e values compare reasonably well with the computed bond lengths (Table 1). The differences between experiment and theory are 0.015 Å or smaller. It should be noted that better agreement with experiment has been achieved previously using higher level CCSD(T) computations. Such computations are computationally very demanding for the larger borylenes and not deemed necessary as the present investigation aims at elucidating trends among substituted borylenes investigated here.[38]

Comparing the B−R bond distances of the lowest energy triplet states with the corresponding singlet states, it is observed that the bonds are shorter in the high spin states for all but two cases (Tables 1 and 2). These are BF and BCH_3.

In carbene chemistry, the concept of carbenic philicity is well established.[42−44] Depending on the substituents, the philicity can change from electrophilic over ambiphilic to nucleophilic. Inductively withdrawing substituents with free electron pairs (−I, +M), such as OR, NR_2, stabilize the singlet relative to the triplet state and enhance the nucleophilic character of the carbene.

Typical nucleophilic carbenes are dimethoxycarbene $C(OMe)_2$ and the diaminocarbenes $C(NR_2)_2$, including N-heterocyclic carbenes. As in borylenes only one position is available for substitution, a similarly strong stabilizing effect of +M substitutents as in carbenes is not expected. Yet, the behavior of borylenes BR is expected to parallel that of carbenes CR_2. One theoretical measure for carbene philicity is the energy of the frontier molecular orbitals (FMO). These were successfully used for rationalizing experimentally derived carbene selectivity indices m_{CXY}. Following common practice the FMO energies of the borylenes BR (Table 3) were

Table 1. Comparison of Computed and Experimental B−R (R = H, F, Cl, Br) Bond Distances (in Å) in Borylene Molecules in Their Lowest Energy Singlet (S) and Triplet (T) States

method	BH		BF		BCl		BBr	
	S	T ($^3\Pi$)	S	T($^3\Pi$)	S	T($^3\Pi$)	S	T($^3\Pi$)
B3LYP/6-311+G**	1.235	1.193	1.271	1.321	1.730	1.718	1.908	1.874
MP2/6-311+G**	1.230	1.187	1.273	1.324	1.710	1.710	1.890	1.866
MP2/cc-pVTZ	1.227	1.184	1.268	1.317	1.717	1.709	1.883	1.854
exp.[a]	1.232[b]		1.263[c]		1.715_9		1.888_2	

[a] r_e values taken from NIST Chemistry WebBook[39] unless noted otherwise. [b] r_e value taken from Fernando et al.[40] [c] r_e value taken from Cazzoli et al.[41]

Table 2. Comparison of Computed and Experimental B−R (*R* = C, N) Bond Distances (in Å) in Borylene Molecules in Their Lowest Energy Singlet (S) and Triplet (T) States at the B3LYP and MP2 Levels of Theory

method	BCH_3		BPh		BNH_2		BNHMe		$BNMe_2$	
	S	T ($^3A''$)	S	T ($^3B_1$)	S	T ($^3B_2$)	S	T ($^3A'$)	S	T ($^3B_2$)
B3LYP[a]	1.534	1.549	1.534	1.481	1.377	1.372	1.375	1.368	1.375	1.370
MP2[a]	1.545	1.559	1.547	1.513	1.384	1.383	1.383	1.379	1.383	1.380
MP2[b]	1.541	1.553	1.542	1.507	1.380	1.378	1.379	1.375	1.381	1.376

[a] 6-311+G**. [b] cc-pVTZ basis set.

computed at the B3LYP level of theory in conjunction with the 6-311+G** basis set.

Table 3. Molecular Orbital Energies (in eV), HOMO-LUMO Gap (in eV), and Singlet−triplet Energy Splitting (ΔE_{ST}, in kcal mol^{-1}) Computed at the B3LYP/6-311+G Level of Theory for Borylene Molecules B−R**

R	HOMO	LUMO	LUMO+1	$\text{Gap}_{\text{H-L}}$	ΔE_{ST}	state
H	−6.52	−2.62	−2.62	3.90	26.0	$^3\Pi$
F	−7.91	−1.47	−1.47	6.44	77.7	$^3\Pi$
Cl	−7.38	−2.17	−2.17	5.21	54.5	$^3\Pi$
Br	−7.31	−2.38	−2.38	4.93	50.1	$^3\Pi$
CH_3	−6.02	−1.66	−1.66	4.36	37.3	$^3A''$
Ph	−5.85	−2.48	−1.67	3.37	31.5	$^3B_1$
NH_2	−6.24	−1.50	−0.44	4.74	44.8	$^3B_2$
NHMe	−6.04	−1.45	−0.20	4.59	44.0	$^3A'$
NMe_2	−5.93	−1.23	−0.18	4.70	45.3	$^3B_2$

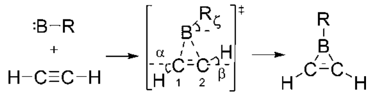
Compared to BH, the electronegativity of the fluorine atom results in a decrease of the HOMO energy: the B−F bond has an increased B(p) character and consequently the B(s) character of the lone pair at boron is increased. The energy of the LUMO is increased due to interaction with the lone pairs of fluorine. From fluorine to bromine, the HOMO energies increase while the LUMO energy drops, as expected. In the aminoborylenes the HOMO and LUMO energies are increased due to antibonding interaction with the fragment orbitals of the π donating NR_2 groups. The methyl group results in a significant upshift of the LUMO that is antibonding between B(p) and CH_3 fragment orbitals due to the electron-donating ability of CH_3 by hyperconjugation. However, the phenyl group only has a small influence on the LUMO energy. It shows a bonding interaction between the B(p) orbital and a π^* orbital of the phenyl ring. Thus, BPh has the second lowest LUMO energy among the borylenes investigated. On the basis of the FMO data, the BH followed by BPh are expected to be the most electrophilic borylenes, while BF is the one with the highest nucleophilic character.

The singlet−triplet energy splitting (ΔE_{ST}) of BH has previously been determined experimentally to 29.8 kcal mol^{-1} in favor of the singlet state.[45] The value (26 kcal/mol) computed at the B3LYP/6-311+G** underestimates this gap somewhat, but the accuracy is sufficient for analysis of the substituent effect on ΔE_{ST} (see Table 3). The singlet−triplet energy gap changes as expected. It increases to 78 kcal mol^{-1} for BF. In the halide series, ΔE_{ST} decreases from F to Br, similar to the behavior that is well established for the related carbenes. The aminoborylenes have ΔE_{ST} values that are larger than in BH but smaller by ca. 5 kcal mol^{-1} than in BBr.

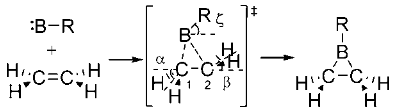
Still smaller ΔE_{ST} values are computed for the organyl substituted borylenes. A ΔE_{ST} of 37 kcal mol^{-1} results for BCH_3 and this indicates that the hyperconjugative interaction favors the singlet more than the triplet state by roughly 11 kcal mol^{-1}. In the BPh molecule the degeneracy of the two p orbitals at boron is lifted due to overlap with the π system. The B(p_z) orbital of b_1 symmetry is lower in energy, and the $^3B_1$ state is preferred over the $^3B_2$ state (note that the HOMO is of a_1 symmetry). The singlet−triplet gap is only 32 kcal mol^{-1}, indicating that the phenyl ring results in the least stabilization of the singlet state among the substituents studied. Again, this finding is in agreement with the established trends in carbene chemistry.[46]

3.2. Reactivity of Borylenes. As mentioned in the preceding sections, we attempted to examine by computational means the reactivity of various substituted borylenes toward saturated and unsaturated hydrocarbons. Intramolecular reactions of BCH_3 and BNH_2 were studied previously.[47] In this part we give insight into the mechanisms of the reactions and describe the dependence of the energetics on the substitution pattern. Here we focus on the philicity of borylenes, also in terms of the geometry of transition states for addition reactions following earlier analyses for carbenes by Houk et al.[48] As in the case of carbene cycloaddition, the tilt angle ζ (see Schemes 1 and 2) is an important geometrical parameter reflecting the philicity of borylene. For the ideal

Scheme 1. Mechanism of Borylene Addition to Ethyne



Scheme 2. Schematic Representation of Addition of Borylene to Ethene



nucleophile this angle would equal 90° and in case of ideal electrophile this angle would be 0°. The distortion of hydrogen atoms of ethyne (ethene) from linearity (planarity) in the transition state (given as α and β angles in Schemes 1 and 2) of the addition reaction is also discussed in terms of borylene philicity.[43,48] Another useful parameter for estimation of philicity employed by Houk et al.[48] and considered in this paper is the ratio of B−C1/B-C2 distances in the transition state. For electrophilic borylene, this ratio would increase and tend toward 1 while with increasing nucleophilic character this ratio would decrease.

During our study, we were able to locate different conformers (see the SI for more details) of the particular transition states and products but only those with the lowest energies were taken into account for determining the reaction energies and barrier heights. For all types of reactions, van der Waals complexes between borylene and organic substrate were found on the potential energy surfaces. As they do not play a significant role in the description of the reaction energetics, we only briefly report them. All of these complexes will be discussed extensively in a separate paper.

3.2.1. Addition to the C≡C Triple Bond of Ethyne. The addition of borylenes to a C≡C triple bond results in formation of a borirene (Scheme 1). The reaction is very strongly exothermic (Table 4, Figure 2). The exothermicity and the reaction barrier heights by and large follow the LUMO energies. BH and BPh show the highest exothermicity and the lowest barriers (there is no barrier for BH). Among the halides, the exothermicity decreases and the barrier increases from Br to F, as expected based on the LUMO energies. Aminoborylenes have LUMO energies similar to BF, but their reactivity in terms of barrier height and exothermicity is similar to that of BCl. The barrier is highest for the $BNMe_2$ molecule.

Table 4. Reaction Barriers (in kcal mol^{-1}) and Reaction Energies (in kcal mol^{-1}) Computed for the Addition of Borylenes BR to Ethyne at the CCSD(T)/aug-cc-pVTZ//MP2/cc-pVTZ + ZPE Level of Theory

R	barrier	reaction energy
H	not existing	−96.1
Ph [a]	+1.0	−90.8
CH_3	+1.6	−87.1
Br	+4.0	−75.1
NH_2	+5.5	−71.2
NHMe	+4.7	−71.3
NMe_2	+6.5	−71.0
Cl	+5.9	−70.9
F	+11.0	−53.2

[a] Using the cc-pVTZ basis set.

Most of the transition states are of C_s symmetry with atoms R−B−C1−C2 lying in the symmetry plane. Only the transition states of BPh and $BNMe_2$ are distorted to C_1 symmetry. Important dihedral angles for BPh and $BNMe_2$ TS are given in Figure 3. The shortest C1−B distance was calculated for the BF transition state (2.002 Å) and the longest one for the BPh transition state (2.461 Å). Among aminoborylenes, the C−B distances are similar to that for the BBr TS, and the shortest distance was found for $BNMe_2$.

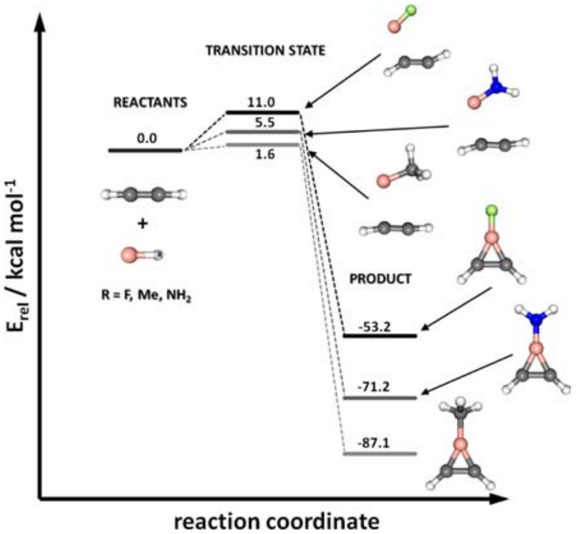


Figure 2. Selected reaction paths for borylene addition to ethyne calculated at the CCSD(T)/aug-cc-pVTZ//MP2/cc-pVTZ+ZPE level of theory.

The largest value of the tilt angle was obtained for the BF transition state, 44.2°. Values of this angle diminish from F to Br. The smallest values were found for the BPh and BCH_3 transition states. Also, a large tilt angle was found for the $BNMe_2$ transition state and it is comparable to that computed for the BF molecule. The increase of the tilt angle from 36° in BNHMe to 44° in $BNMe_2$ may, however, be primarily a consequence of steric repulsion within the transition structure as barrier height and exotherimicity of the reaction hardly change.

The distortions of H−C−C angles of ethyne from linearity in the TS are smallest for the BPh molecule and largest for fluorine substituted borylene. In case of aminoborylenes, this distortion is similar to that of BBr for BNH_2 and BNHMe; for $BNMe_2$ it is larger, but this again is primarily attributed to steric interactions.

The smallest ratio of the BC1/BC2 distance was computed for BF (0.76) and the largest one (0.88) for the BPh transition state. For BCl, BBr, and BCH_3 transition states, the ratios equal to 0.80, 0.82, and 0.87, respectively. Among aminoborylenes, the ratio values amount to 0.81 for BNH_2, 0.81 for BNHMe and 0.79 for $BNMe_2$.

Interesting may be the finding of an intermediate in the reaction of fluoroborylene with ethyne at the MP2/6-311+G** level of theory. This intermediate corresponds to a shallow minimum: it is 0.02 kcal/mol lower in energy than the TS for its disappearance. Upon ZPE correction the energy of the intermediate becomes 0.5 kcal/mol higher than the TS. This species could not be obtained at the MP2/cc-pVTZ level of theory. For remaining borylenes intermediates in the addition reaction could not be found.

3.2.2. Addition to the C=C Double Bond of Ethene. The addition of borylenes to alkenes yields boriranes (Scheme 2). The reaction is significantly less exothermic than borirene formation.

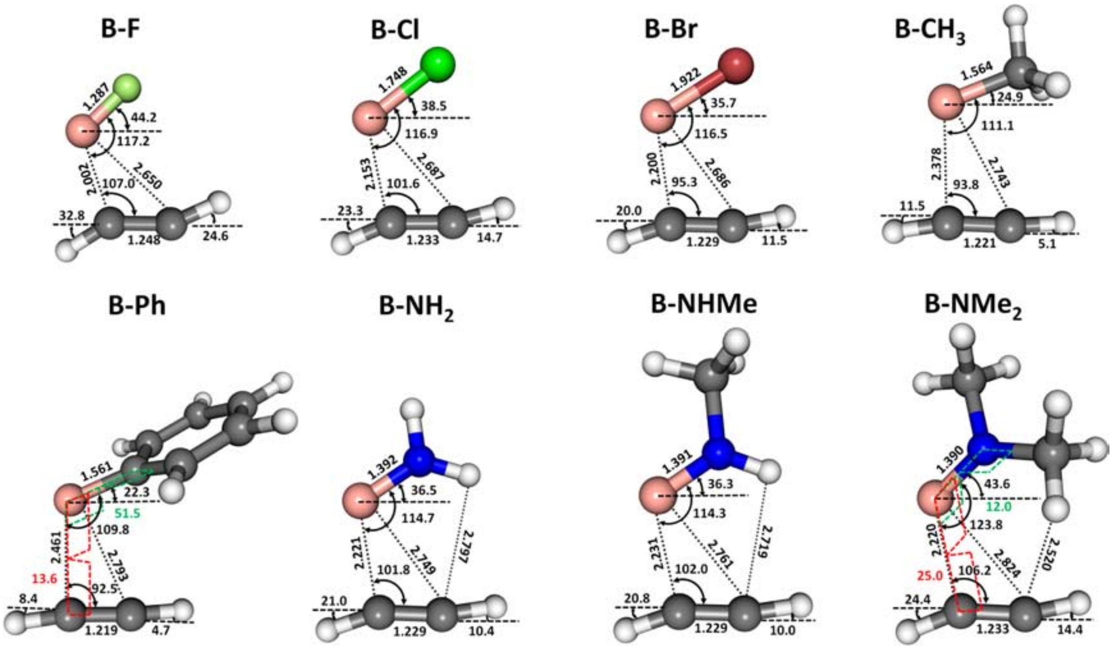


Figure 3. Geometries of the transition structures computed for the addition of borylenes BR to ethyne at the MP2/cc-pVTZ level of theory. Important bond lengths are given in Å, bond angles and dihedral angles are given in degrees.

The latter is an aromatic heterocycle isoelectronic to the cyclopropenylium cation and its formation thus may be more favorable than formation of the borirane molecule. The addition can proceed without barrier on the potential energy surface for the parent BH molecule. As found for addition to ethyne, the barrier increases and the exothermicity decreases among the halides from Br to F (Table 5, Figure 4). Similarly to ethyne addition, the carbon substituted borylenes have the lowest barriers and the largest exothermicities. The aminoborylenes, however, have reactivity parameters similar to those for BBr.

Table 5. Reaction Barriers (in kcal mol^{-1}) and Reaction Energies (in kcal mol^{-1}) Computed for the Addition of Borylenes BR to Ethene at the CCSD(T)/aug-cc-pVTZ//MP2/cc-pVTZ+ZPVE Level of Theory

R	barrier	reaction energy
H	not existing	−69.8
Ph [a]	+1.5 [b]	−67.7
CH_3	+1.8	−62.7
Br	+4.0	−52.8
NH_2	+4.8	−55.4
NHMe	+3.7	−56.7
NMe_2	+6.1	−57.0
Cl	+6.5	−48.8
F	+13.6	−32.2

[a] Using the cc-pVTZ basis set. [b] With respect to TS1.

Two transition states were obtained at the MP2/cc-pVTZ level of theory for the reaction of phenylborylene with ethene. These differ by the relative orientation of the phenyl group (Figure 5). The energy difference between the two transition states is 0.2 kcal/mol without ZPE correction with TS1 being higher in energy. With ZPE correction these transition states become isoenergetic. TS1 is considered in the following discussion.

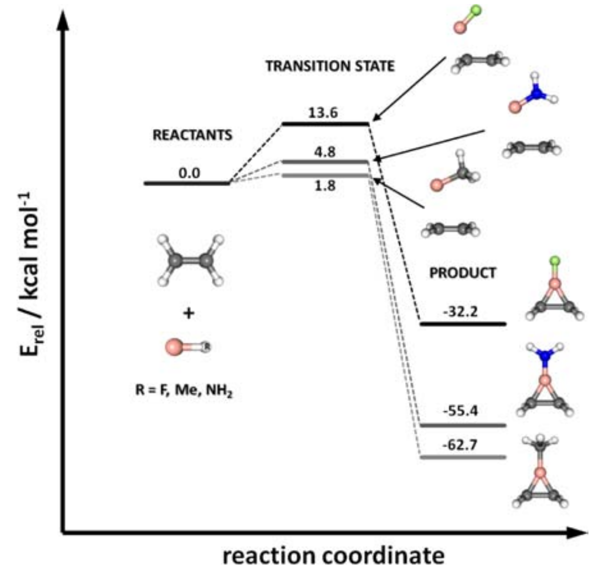


Figure 4. Selected reaction paths of borylene addition to CC double bond of ethene calculated at the CCSD(T)/aug-cc-pVTZ//MP2/cc-pVTZ+ZPE level of theory.

By analogy to reactions with ethyne most of the transition states have a plane of symmetry (C_s point group) except for the BPh transition state. In contrast to the addition to ethyne, the TS of $BNMe_2$ has a plane of symmetry. The shortest C1−B distance was also computed for BF and the longest one for the BPh transition state.

The largest tilt angle was found for the BF transition state just as for reactions with ethyne, and the smallest one for the BPh transition state. Aminoborylenes have tilt angles similar to BBr. Also, a large tilt angle was obtained for the $BNMe_2$ transition state, but as in the case of addition to CC triple bond, the increased value is likely a consequence of steric interaction between one methyl group and an ethene CH_2 fragment.

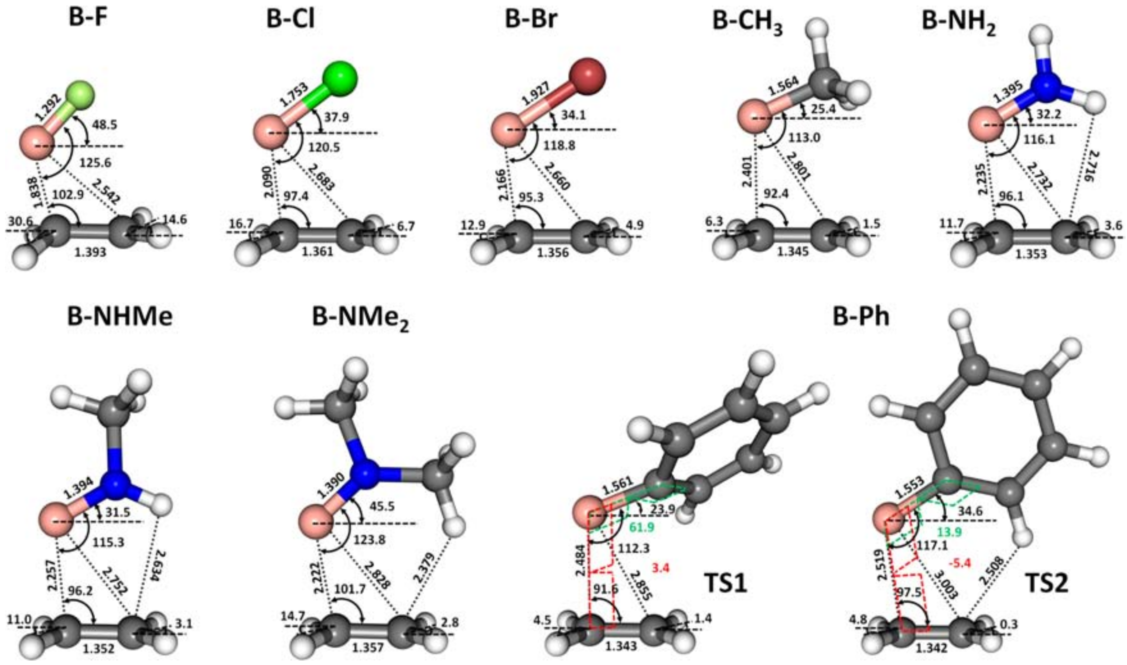


Figure 5. Geometries of the transition structures computed for the addition of borylenes BR to ethene at the MP2/cc-pVTZ level of theory. Important bond lengths are given in Å, bond angles, and dihedral angles are given in degrees.

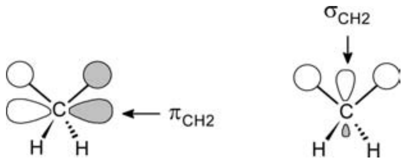
The greatest distortion from planarity of CH_2 groups of ethene in transition structures was obtained for the fluoroborylene TS and the smallest one for the phenylborylene TS. The CH_2 group distortions of the aminoborylene TSs are similar to the ones obtained for bromoborylene TS.

Also, for addition of borylenes to CC double bonds, the smallest ratio of the BC1/BC2 distance was found for the fluoroborylene transition state (0.72), while the largest ratio was obtained for the phenylborylene transition state with a value of 0.87. For the other haloborylenes, the ratios equal to 0.81 and 0.79 for BBr and BCl, respectively. The ratio equals 0.86 for BCH_3. In case of aminoborylenes, the ratios amount to 0.82 for BNH_2, 0.82 for BNHMe, and 0.79 for $BNMe_2$.

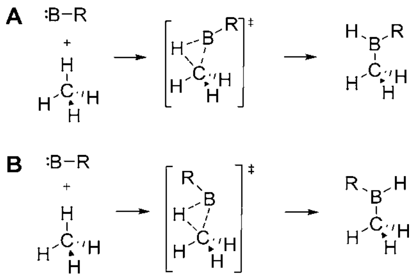
Similarly to the reaction of ethyne with fluoroborylene, an intermediate connecting two TSs on the PES of the BF reaction with ethene could be obtained, but now both at the MP2/6-311+G** and MP2/cc-pVTZ levels of theory. The intermediate lies just 0.6 kcal/mol (0.2 kcal/mol with ZPE) below the first transition state and 0.6 kcal/mol (0.4 kcal/mol with ZPE) below the transition state for ring closure.

3.2.3. Insertion into the C–H Bond of Methane. In their analysis of the insertion of singlet methylene (CH_2) into the C–H bonds of saturated hydrocarbons, Bach et al.[49] identified two approaches on the basis of frontier molecular orbital theory (FMO). Depending on the site of the attack of carbene on the hydrocarbon, σ_{CH2} and π_{CH2} approaches can be distinguished (Scheme 3). By analogy to carbenes, the insertion reaction of borylenes into the carbon–hydrogen bond of methane can also occur according to two approaches (Scheme 4, Figure 6). In the terminology introduced by Bach et al.[49] approach A of borylene insertion follows a π_{CH2} fashion, whereas approach B is inverted π_{CH2}. Contrary to methylene, borylene insertion reaction according to the σ_{CH2} approach leads to a second order saddle point rather than to a transition state (see Supporting Information). The transition states obtained via the A approach are of C_s symmetry except for BPh and BCH_3 but the ones obtained for approach B are of C_1 symmetry. Higher barriers were computed for the reaction approach B shown in Scheme 4. For both approaches, the barrier decreases with increasing exothermicity (based on the most stable rotamer B for both approaches). In contrast to the addition reactions to multiple CC bonds, the CH insertion of BH has a barrier, but it is the smallest one among the studied borylenes. Again, the highest barrier occurs for the BF molecule due to the high electronegativity of fluorine. The barriers among aminoborylenes are of comparable heights with the largest value found for $BNMe_2$. The higher barrier for $BNMe_2$ than for other aminoborylenes is the consequence of steric repulsion.

Scheme 3. Two Possible Approaches for Carbene Insertion into Methane According to Bach et al.[49]



Scheme 4. Two Approaches of Addition of Borylene to a Carbon–Hydrogen Bond of Methane



For approach B, the reaction has a significantly larger barrier than for approach A. Differences in geometries of both

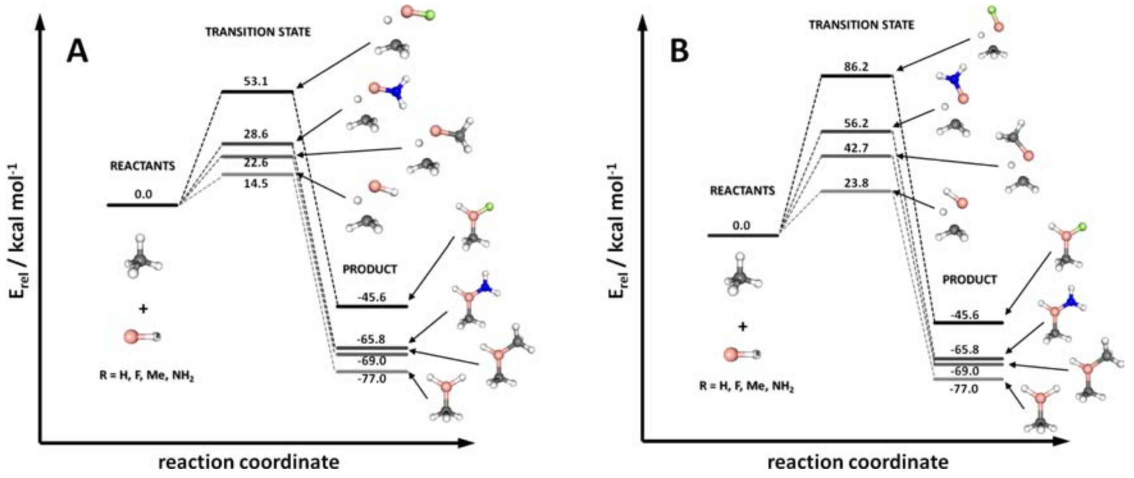


Figure 6. Selected reaction paths for borylene insertion into a C−H bond of methane calculated at the CCSD(T)/aug-cc-pVTZ//MP2/cc-pVTZ +ZPE level of theory.

Table 6. Reaction Barriers (in kcal mol^{-1}) and Reaction Energies (in kcal mol^{-1}) Computed for the Insertion of Borylenes BR to C−H Bond of Methane at the CCSD(T)/aug-cc-pVTZ//MP2/cc-pVTZ +ZPE Level of Theory

R	barrier A	barrier B	reaction energy [b]
H	+14.5	+23.8	−77.0
Ph [a]	+21.3	+36.5	−74.2
CH_3	+22.6	+42.7	−69.0
NH_2	+28.6	+56.2	−65.8
NHMe	+27.1	+53.5	−66.9
NMe_2	+30.7	+54.9	−65.7
Br	+33.8	+53.8	−62.9
Cl	+37.4	+61.4	−59.9
F	+53.1	+86.2	−46.6

[a] Using the cc-pVTZ basis set. [b] Energy with reference to rotamer B.

transition states are notable (Figures 7 and 8). In the case of transition states A, the distances between boron and hydrogen atoms are smaller than in transition states found for approach B. According to IRC calculations (MP2/6-311+G**), the hydrogen atom from methane shifts toward the boron atom to form an almost linear BHR species soon after the TS. Then the HBR fragment bends and the boron−carbon distance diminishes until the boron−carbon bond is formed (Figure 9A). The carbon−boron distance, however, is shorter in the case of transition states B, while the B−R bond is longer than in transition states A. In reaction B, the formation of the hydrogen−boron and carbon−boron bond proceeds in a more synchronous fashion. At the same time, the CH_3 fragment rotates until rotamer B is formed (Figure 9B).

An interesting observation is that the reaction of phenylborylene with methane via approach B does not lead to methylphenylborane according to IRC computations at the MP2/6-311+G** and MP2/cc-pVTZ levels of theory (Scheme 5). The product obtained is 7-methyl-7-boranorcaradiene. At these levels of theory, the hydrogen atom shifts to one of the carbon atoms of the phenyl ring and the boron atom forms a bond with the carbon atom of methane. In the next stage of the reaction, two B−C bonds are formed. In contrast to MP2 calculations, the IRC path calculated at the B3LYP/6-311+G** level of theory leads to the expected methylphenylborane. The

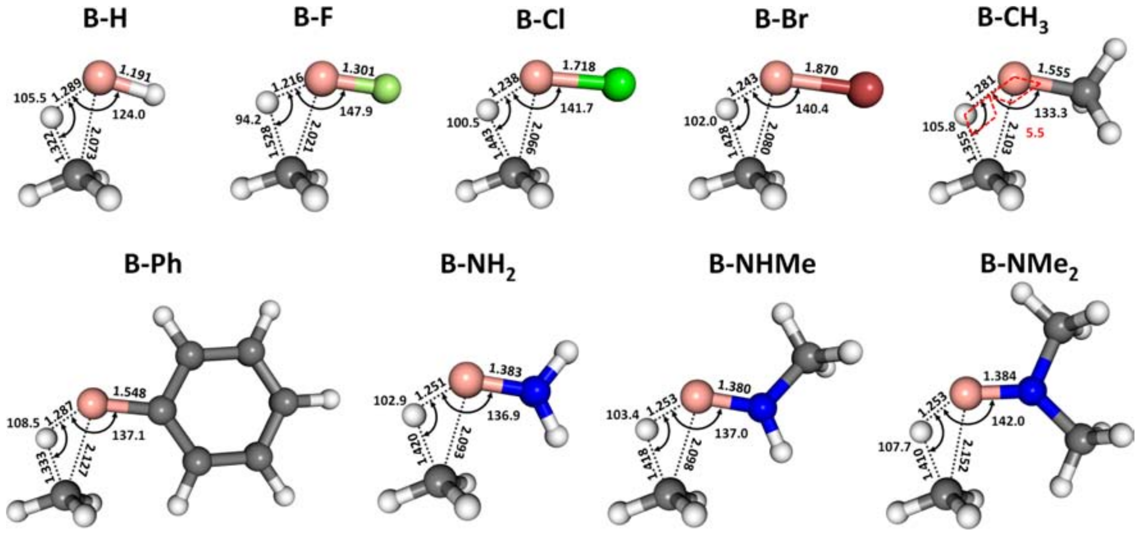


Figure 7. Geometries of the transition structures computed for the insertion of borylenes BR into a C−H bond of methane according to approach A at the MP2/cc-pVTZ level of theory. Important bond lengths are given in Å, bond angles, and dihedral angles are given in degrees.

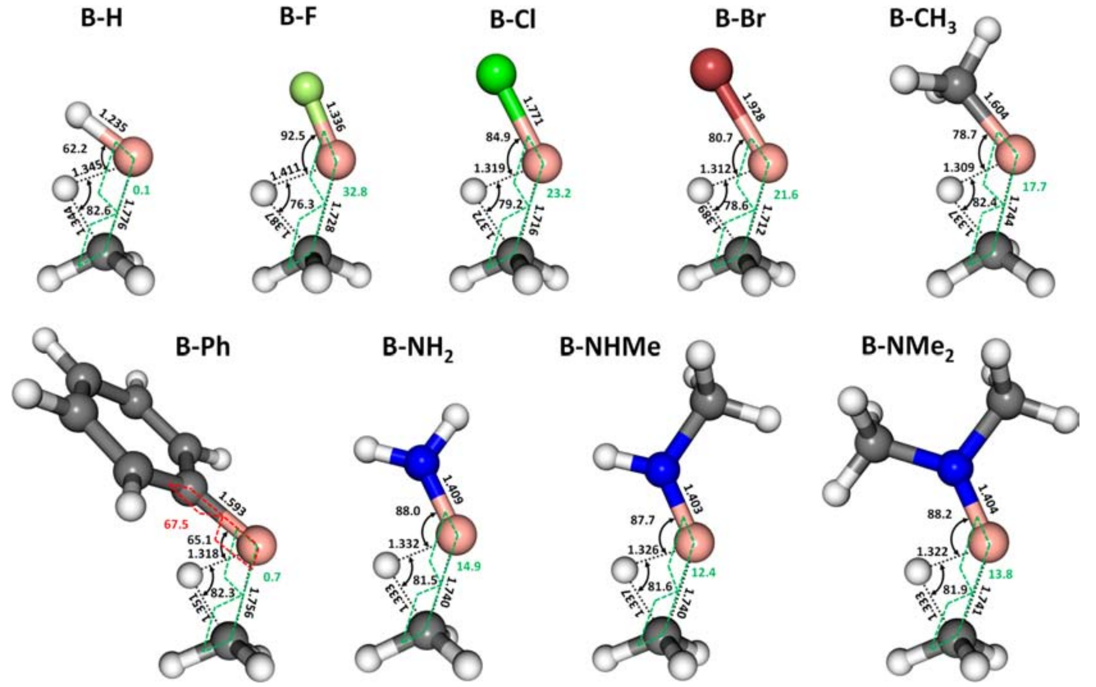


Figure 8. Geometries of the transition structures computed for the insertion of borylenes BR into a C−H bond of methane according to approach B at the MP2/cc-pVTZ level of theory. Important bond lengths are given in Å, bond angles, and dihedral angles are given in degrees.

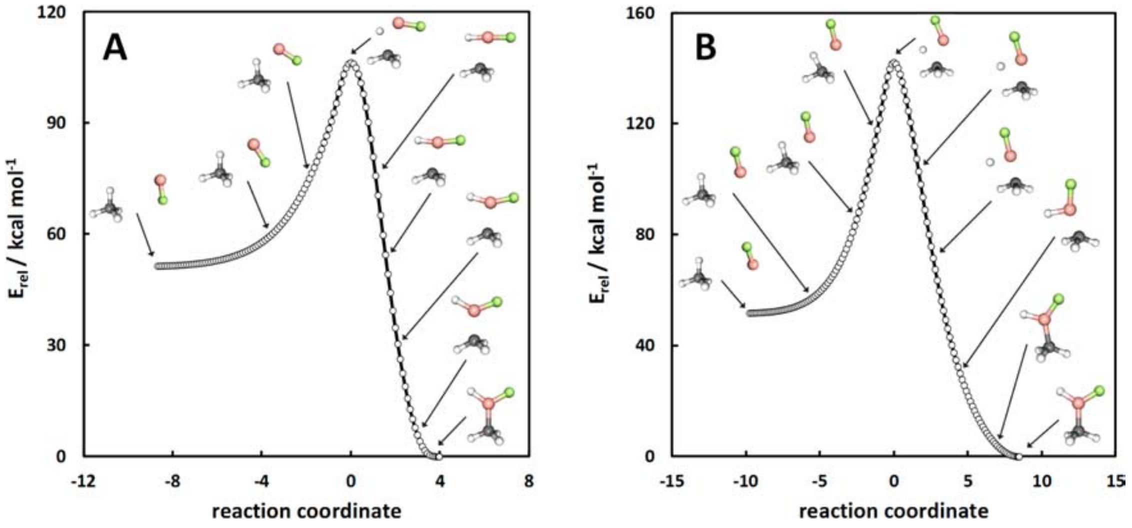
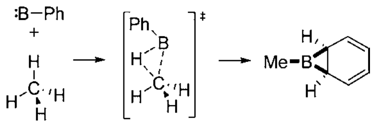


Figure 9. Calculated IRC reaction paths (MP2/6-311+G**) for the insertion of fluoroborylene into C−H bond for (A) approach A and (B) for approach B.

Scheme 5. Formation of 7-Methyl-7-boranorcaradiene



computed (MP2/6-311+G**) IRC path shows that reaction of methane with phenylborylene via approach A leads to methylphenylborane.

Finally, as expected the products of C−H insertion, $RBHCH_3$, are thermodynamically unstable with respect to dimerization. The formation of the dimers with two bridging hydrogen atoms becomes less favorable along the series H < Ph < CH_3 < Cl < Br < F < NH_2 < NHMe < NMe_2. The aminoborane derivatives prefer the formation of the B_2N_2 four membered ring motif, in agreement with NMR investigations of Me_2NBHMe (see Supporting Information for energy data).[50]

3.2.4. Comparison of the Borylenes. The reactivity in terms of computed barrier heights and exothermicities decreases for borylenes in the following order for addition reactions:

$$\mathrm{H} > \mathrm{Ph} > \mathrm{CH_3} > \mathrm{Br} \approx \mathrm{NHMe} > \mathrm{NH_2} > \mathrm{Cl} > \mathrm{NMe_2} > \mathrm{F}$$

The geometric parameters of the TS (tilt angle, ratio of carbon−boron distances, and distortion of the unsaturated organic substrate) are in line with increasing nucleophilicity along the above series of substituents. Considering the LUMO energies, aminoborylenes are comparable to BF, but the barriers are larger and the exothermicities are smaller for BF. With respect to CH bond insertion, the above order changes inasmuch as the aminoborylenes are more reactive than the haloborylenes.

4. CONCLUSIONS

The computational study of the reactivity of various substituted borylenes BR (where R = H, Ph, CH_3, Br, Cl, F, NH_2, NHMe, NMe_2) performed at the CCSD(T)/aug-cc-pVTZ//MP2/cc-pVTZ + ZPE level of theory showed that the reactions of borylenes with prototypical saturated (methane) and unsaturated (ethene and ethyne) hydrocarbons are strongly exothermic. The addition to the triple C≡C bond is the most exothermic process of all examined here. The addition of BH to multiple CC bonds proceeds without barrier, but on the other hand, the insertion of BH into the C−H bond of methane has the smallest reaction barrier. The largest reaction energies were obtained for the BH molecule, followed by BPh and BCH_3 for all type of reactions. The highest barriers and smallest exothermicities were computed for fluoroborylene. Among the halides, the barrier decreases and exothermicity increases from F to Br for both types of reactions. Aminoborylenes have the reaction energies and barrier heights comparable with those obtained for BBr.

The philicity of borylenes was analyzed on the basis of their FMO energies and the transition states geometries of addition reactions. The largest value of tilt angle ζ was found for the transition states of the BF addition to ethyne and ethene, while the smallest one for transition states of the BPh additions. The largest distortions from linearity/planarity of hydrogen atoms of ethyne/ethene were found for the BF and the smallest for BPh transition states. Also, the B−C1/B−C2 distance ratios are smallest for the BF and largest for the BPh transition states. This makes fluoroborylene the most nucleophilic and phenylborylene most electrophilic next to the BH among all studied borylenes. This conclusion is in agreement with the results of the analysis of frontier molecular orbital energies of substituted borylenes.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Complete ref 30, geometries computed at the B3LYP/6-311+G** level, reaction energies and barrier heights at the B3LYP and MP2 levels, intrinsic reaction coordinates, energies of borane dimerizations, Cartesian coordinates of all stationary points. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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