Theoretical Evaluation of the Origin of the Regio- and Stereoselectivity in the Diels−Alder Reactions of Dialkylvinylboranes: Studies on the Reactions of Vinylborane, Dimethylvinylborane, and Vinyl-9-BBN with *trans*-Piperylene and Isoprene

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Abstract: Ab initio and DFT calculations have been performed to study the origin of the regio- and stereoselectivity of the Diels−Alder reactions of dialkylvinylboranes with substituted dienes. B3LYP/6-31G* energies of the transition structures for the reactions of dimethylvinylborane and vinyl-9-BBN with *trans*-piperylene and isoprene yielded calculated ratios which are in very good agreement with experimental values. Nonclassical carbon−boron [4+3] secondary orbital interactions seem to account for the high *endo* stereoselectivity of these reactions. However, C−B interactions become less important when the bulkiness of the alkyl groups attached to boron increases. Both *endo* and *exo* transition structures for the reactions of dimethylvinylborane and vinyl-9-BBN adopt classical [4+2] character. This study also extends Singleton's investigation on butadiene to regioselectivity. FMO theory has been used to rationalize the lack of regioselectivity in the reactions of dimethylvinylborane. The anomalous meta regioselectivity of the Diels−Alder reaction of vinyl-9-BBN with *trans*-piperylene is mainly caused by steric effects.

Introduction

The Diels−Alder reaction is one of the most widely used and efficient approaches to carbon−carbon bond formation. Although there is a vast amount of work in this area, new methodologies continue to emerge in the chemical literature.[1] The synthetic utility of dialkylvinylboranes as Diels−Alder dienophiles has been investigated by Singleton et al.[2] The [4+2] cycloadditions of these boron activated alkenes exhibited a number of striking features such as high reactivity, regioselectivity, and *endo* stereoselectivity. Table 1 shows the experimental results obtained in the Diels−Alder reactions of dimethylvinylborane (**2**) and vinyl-9-BBN (**3**) with some simple substituted dienes such as *trans*-piperylene (**4**), isoprene (**5a**), and myrcene (**5b**) (Scheme 1).

The experimental results obtained with these and other vinylboranes[3] show that the properties of this class of dienophiles can be optimized by choice of the alkyl groups attached to the boron atom.

Previous ab initio RHF calculations showed that nonclassical [4+3] secondary orbital interactions played an important role

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(1) For a recent review see: Dell, C. P. *J. Chem. Soc., Perkin Trans. 1* **1998**, 3873.

(2) (a) Singleton, D. A.; Martinez, J. P. *J. Am. Chem. Soc.* **1990**, *112*, 7423. (b) Singleton, D. A.; Martinez, J. P. *Tetrahedron Lett.* **1991**, *32*, 7365. (c) Singleton, D. A.; Martinez, J. P.; Watson, J. V. *Tetrahedron Lett.* **1992**, *33*, 1017. (d) Singleton, D. A.; Martinez, J. P.; Ndip, G. M. *J. Org. Chem.* **1992**, *57*, 5768. (e) Singleton, D. A.; Martinez, J. P.; Watson, J. V.; Ndip, G. M. *Tetrahedron.* **1992**, *48*, 5831.

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Table 1. Regioselectivity and *Endo* Stereoselectivity of Diels−Alder Reactions of Dialkylvinylboranes

diene	dienophile	regioselectivity[a]	*endo* stereoselectivity
4	**2**	50:50	>90% for each regioisomer
	3	>98:2	92:8
5a	**2**		
	3	93:7	
5b	**2**	61:39	
	3	96:4	

[a] The ratios given are for meta:ortho products for *trans*-piperylene (**4**) and for para:meta products for isoprene (**5a**) and myrcene (**5b**).

Scheme 1
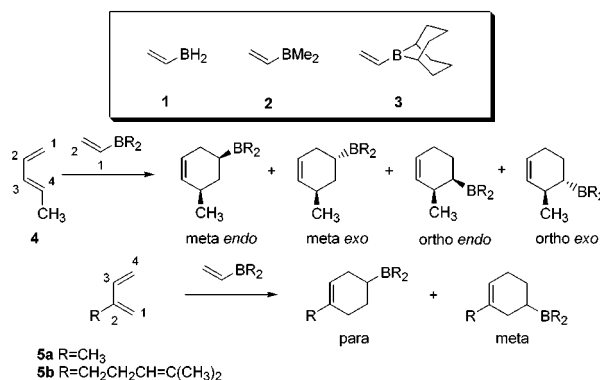
in the *endo* transition states for the reactions of butadiene with vinylborane (**1**) and dimethylvinylborane (**2**).[4] However, some important aspects of these intriguing Diels−Alder reactions remained unanswered.

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Studies on the Diels−Alder Reactions of Vinylboranes

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To fully assess the importance of electronic and steric effects in the outcome of the Diels−Alder reactions of dialkylvinylboranes, we carried out an ab initio and DFT investigation. First, we aimed to clarify why *endo* transition structures adopt [4+3] character whereas *exo* transition structures have [4+2] character. In addition, we wanted to rationalize one of the most remarkable features of these reactions, namely, the high anomalous meta regioselectivity observed in the reactions of 1-substituted butadienes with highly substituted boranes such as vinyl-9-BBN (**3**).

Computational Methods

For the reactions of vinylborane (**1**) and dimethylvinylborane (**2**), geometry optimizations of the transition structures and the reactants were carried out by using ab initio methods at the restricted Hartree−Fock (RHF) level of theory with the 3-21G and 6-31G* basis sets[5] and with DFT methods, using the B3LYP[6] functional with the 6-31G* basis set. For the reactions of vinyl-9-BBN (**3**), the transition structures and the reactants were first optimized with the semiempirical AM1 method[7] and then optimized at the B3LYP/6-31G* level of theory. Frequency calculations were used to confirm the nature of the stationary points. All transition state structures had only one imaginary harmonic vibrational frequency corresponding to the formation of the C−C bonds. Ab initio and DFT calculations for the reactions of vinylborane (**1**) and dimethylvinylborane (**2**) were carried out with CADPAC[8] 6.0 and 6.5. For the reactions of vinyl-9-BBN (**3**), semiempirical calculations and DFT calculations were performed with MOPAC 93[9] and GAUSS-IAN 98,[10] respectively. Natural bond orders were calculated at the B3LYP/6-31G* level with GAUSSIAN 98.

Results and Discussion

To investigate the origin of the regio- and stereoselectivity of the Diels−Alder reactions of dialkylvinylboranes, we extended Singleton's studies on the reactions of butadiene by examining the reactions of *trans*-piperylene (**4**) and isoprene (**5a**) with vinylborane (**1**) and dimethylvinylborane (**2**). The transition structures obtained for isoprene can also be used as models for the reactions of myrcene (**5b**).

Geometries. Figures 1−4 show the transition structures obtained for the four possible modes of addition for each
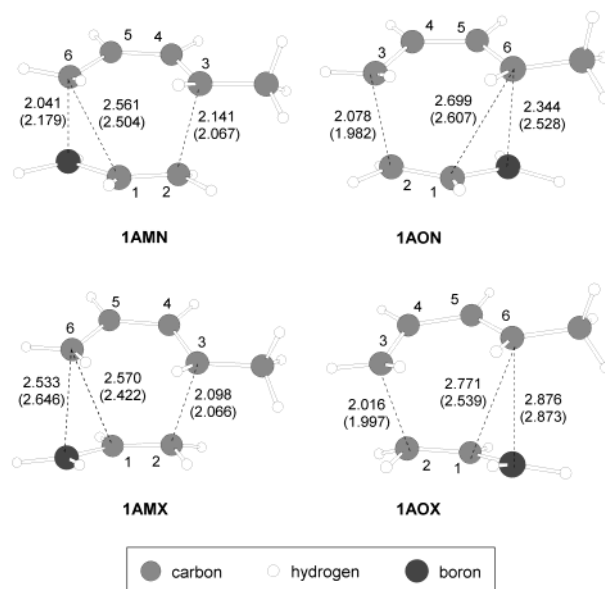

Figure 1. Transition structures for the reaction of vinylborane (**1**) and *trans*-piperylene (**4**) with B3LYP/6-31G* and RHF/6-31G* (in parentheses). All distances are Å.
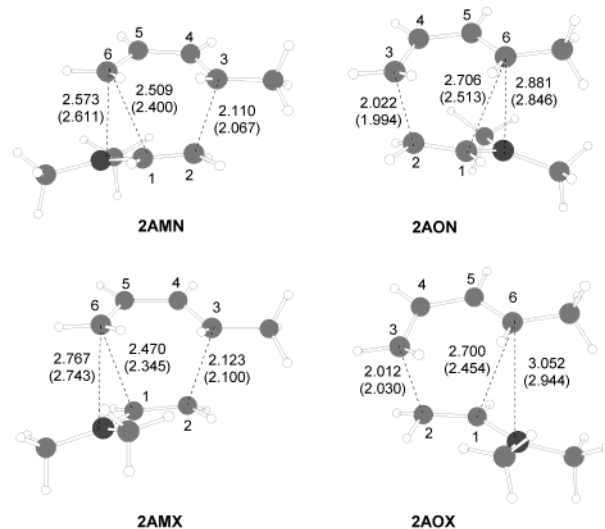

Figure 2. Transition structures for the reaction of dimethylvinylborane (**2**) and *trans*-piperylene (**4**). See Figure 1 for key.

reaction.[11] All transition structures are asynchronous, with forming C2−C3 bonds lengths being shorter than C1−C6 distances.

Ortho transition structures are more asynchronous than the corresponding meta counterparts for the reactions of *trans*-piperylene (**4**) (Figures 1 and 2), whereas there is not much difference in asynchronicity between meta and para transition structures for the reactions of isoprene (**5a**) (Figures 3 and 4). Furthermore, *exo* transition structures are slightly more asynchronous than the corresponding *endo* transition structures for the reactions of vinylborane (**1**) (Figures 1 and 3) while *endo*

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(11) We named the transition states as follows: the number indicates the dienophile, i.e., 1 for vinylborane (**1**), 2 for dimethylvinylborane (**2**), and 3 for vinyl-9-BBN (**3**). Then we added A for (*E*)-1,3-pentadiene (*trans*-piperylene, **4**) and B for 2-methylbutadiene (isoprene, **5a**). Finally, we used O, M and P for *ortho*, *meta* and *para* regiochemistry and N and X for *endo* and *exo* stereochemistry. For example, **2AOX** is the transition state corresponding to the reaction between dimethylvinylborane and trans-piperylene leading to the *ortho* regioisomer with an *exo* stereochemistry.
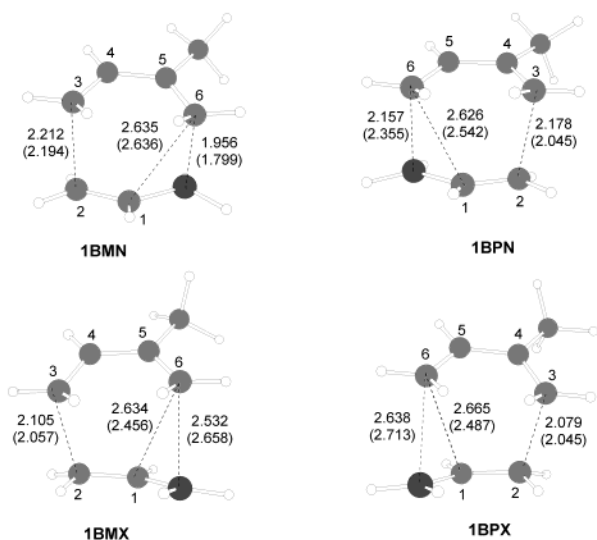
Figure 3. Transition structures for the reaction of vinylborane (**1**) and isoprene (**5a**). See Figure 1 for key.
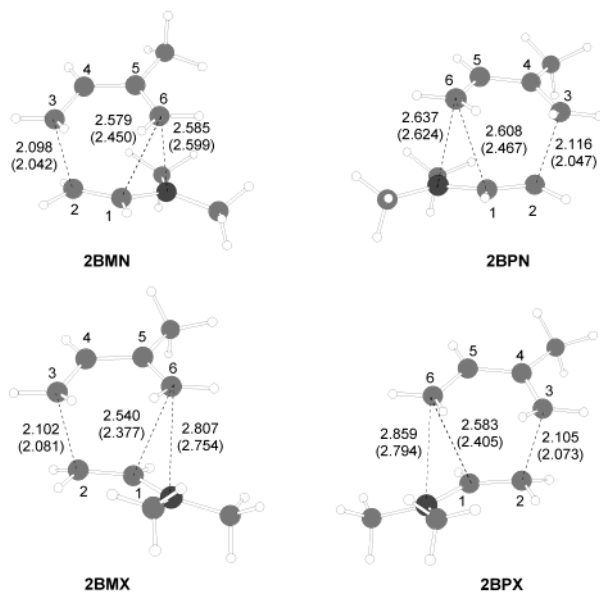

Figure 4. Transition structures for the reaction of dimethylvinylborane (**2**) and isoprene (**5a**). See Figure 1 for key.

transition structures are as asynchronous as *exo* transition structures for the reactions of dimethylvinylborane (**2**) (Figures 2 and 4).

In each *endo* transition structure for all the reactions of vinylborane (**1**) (Figures 1 and 3), we observed that C-6 is always closer to the boron than to C-1. These results are in agreement with the [4 atom + 3 atom] character of the *endo* transition structures previously found by Singleton for the reactions of vinylborane (**1**) and dimethylvinylborane (**2**) with 1,3-butadiene.[4]

In contrast, *exo* transition structures corresponding to the reactions of vinylborane (**1**) both have some degree of [4+2] and [4+3] character since forming C1−C6 bonds lengths are similar to C6−B distances.

The transition structures for the reactions of *trans*-piperylene (**4**) with dimethylvinylborane (**2**) (Figure 2) are generally slightly less asynchronous than the ones corresponding to the reactions of vinylborane (**1**) (Figure 1). For isoprene (**5a**) (Figures 3 and 4), this is only true for *exo* transition structures.

In addition, C1−C6 forming bonds distances are shorter than C6−B distances in all *endo* and *exo* transition structures for

the reactions of dimethylvinylborane (**2**) (Figures 2 and 4). Consequently, both *endo* and *exo* transition structures for the reactions of *trans*-piperylene (**4**) and isoprene (**5a**) with dimethylvinylborane (**2**) adopt classical [4+2] character. This demonstrates that the addition of two methyl groups to the boron atom weakens the C−B interaction and makes transition structures become more synchronous and have [4+2] character. These results are in contrast to Singleton's observation based on the transition structures for the reactions of butadiene which suggested that *endo* transition states adopt [4+3] character whereas *exo* transition structures have [4+2] character.[12] The effect of substitution could be rationalized based on steric premises since it appears that, when the bulkiness of the substituents increases, steric factors operate governing the interactions in the transition structures. However, it is plausible that other factors contribute to this substituent effect. For instance, the methyl groups may well donate electron density to the electron-deficient boron, weakening the [4+3] C−B orbital overlap and consequently increasing the [4+2] character of the transition states.

Energetics. As for many other Diels−Alder reactions, RHF methods compute higher activation energies than DFT methods. It is well documented that RHF theory gives activation energies substantially above experimental values while methods that include electron correlation reproduce activation energies nicely.[13] On the other hand, it is also known that the inclusion of electron correlation in geometry optimizations slightly modifies RHF geometries. In this case, RHF geometries were modified to some extent (up to 0.31 Å for 3-21G and 0.25 Å for 6-31G*). Consequently, we will only discuss the results obtained with B3LYP/6-31G* energies of the fully optimized B3LYP/6-31G* geometries (Table 2).

The calculated activation energies for the reactions of vinylborane (**1**) with *trans*-piperylene (**4**) predict the formation of a 93:7 mixture of the *endo* meta and *endo* ortho products.[14] Similarly, the calculated activation energies for the reactions of vinylborane (**1**) and isoprene (**5a**) favor *endo* transition structures over the *exo* ones, predicting the formation of a 88: 12 mixture of the meta and para regioisomers. The addition of two methyl groups to the boron increases the energy barriers compared to the reactions of vinylborane (**1**) and decreases the energy differences between *endo* and *exo* transition structures. The calculated ratio for the reaction of dimethylvinylborane (**2**) with *trans*-piperylene (**4**) agrees very well with the experimentally observed ratio since it predicts the formation of a 46:54 mixture of the meta and ortho products with 96:4 and 91:9 *endo*/ *exo* ratios for the meta and the ortho regioisomers, respectively. For the reaction of dimethylvinylborane (**2**) with isoprene (**5a**), the computed ratio predicts a 60:40 mixture of the para and

(12) Had we only analyzed the results of the RHF/6-31G* calculations for the reactions of vinylborane (**1**), we would have agreed with Singleton's conclusion that *endo* transition structures have [4+3] character and *exo* transition structures have [4+2] character. We repeated Singleton's RHF/ 6-31G* calculations for the reactions of vinylborane (**1**) with 1,3-butadiene and also reinvestigated the transition structures with the B3LYP/6-31G* level of theory. Although we corroborated the [4+3] character of the *endo* transition structures with both methods, we found that while the RHF/6-31G* *exo* transition structure exhibits classical [4+2] character, the B3LYP/ 6-31G* result suggests that the *exo* mode of addition has some degree of both [4+2] and [4+3] character.

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(14) All product ratios were computed from the equation $k_1/k_2 = e^{-\Delta E^\ddagger/RT}$, where $\Delta E^\ddagger$ is the difference between the calculated activation energies for the two processes $T = 298.15$ K and $R = 1.9872$ cal K^{-1} mol^{-1}.

Table 2. Energetics of the Diels−Alder Reactions of Vinylborane (**1**) and Dimethylvinylborane (**2**) with *trans*-Piperylene (**4**) and Isoprene (**5a**)

TS	$\Delta E^{\ddagger}$(RHF/6-31G*) (kcal mol^{-1})	E_{rel} (kcal mol^{-1})	$\Delta E^{\ddagger}$(B3LYP/6-31G*) (kcal mol^{-1})	E_{rel} (kcal mol^{-1})	calcd ratios
1AMN	36.84	0.00	11.46	0.00	
1AON	38.20	1.36	12.97	1.51	93:7 meta/ortho
1AMX	41.39	4.55	17.03	5.57	100:0 *endo/exo*
1AOX	41.68	4.84	16.83	5.37	
2AMN	41.39	0.00	18.48	0.10	
2AON	42.19	0.80	18.38	0.00	46:54 meta/ortho
2AMX	43.33	1.94	20.43	2.05	96:4 and 91:9 *endo/exo*
2AOX	44.05	2.65	20.04	1.66	
1BMN	32.84	0.00	8.99	0.00	
1BPN	35.51	2.67	10.17	1.18	12:88 para/meta
1BMX	40.69	7.85	15.92	6.92	
1BPX	39.90	7.06	15.41	6.42	
2BMN	40.41	0.52	17.00	0.23	
2BPN	39.89	0.00	16.77	0.00	60:40 para/meta
2BMX	42.68	2.79	19.40	2.63	
2BPX	42.11	2.22	18.90	2.13	

Table 3. Reaction Energies of the Diels−Alder Reactions of Vinylborane (**1**) and Dimethylvinylborane (**2**) with *trans*-Piperylene (**4**)

product	ΔE(B3LYP/6-31G*) (kcal mol^{-1})	E_{rel} (kcal mol^{-1})
1AMN	−29.68	0.00
1AON	−28.65	1.03
1AMX	−29.18	0.50
1AOX	−29.23	0.45
2AMN	−30.38	0.00
2AON	−28.63	1.75
2AMX	−29.74	0.64
2AOX	−29.91	0.47

Table 4. Natural Bond Orders at the B3LYP/6-31G* Level for the Transition Structures of the Diels−Alder Reactions of Vinylborane (**1**) and Dimethylvinylborane (**2**) with *trans*-Piperylene (**4**) and Isoprene (**5a**)

TS	C1−C6	C2−C3	C6−B
1AMN	0.16	0.41	0.40
1AON	0.16	0.45	0.25
1AMX	0.23	0.44	0.15
1AOX	0.19	0.49	0.09
2AMN	0.23	0.44	0.14
2AON	0.20	0.49	0.10
2AMX	0.27	0.43	0.08
2AOX	0.22	0.49	0.06
1BMN	0.11	0.36	0.47
1BPN	0.14	0.38	0.33
1BMX	0.21	0.43	0.16
1BPX	0.20	0.45	0.13
2BMN	0.21	0.44	0.15
2BPN	0.19	0.42	0.13
2BMX	0.24	0.44	0.08
2BPX	0.23	0.43	0.07

meta products would be formed, which is in excellent agreement with the experimental result obtained with myrcene (**5b**).

To gain further insight into the origin of the energy barriers we determined whether the calculated energy barriers correlated with the overall reaction enthalpies. Consequently, we calculated the energies of the products of the reactions of vinylborane (**1**) and dimethylvinylborane (**2**) with *trans*-piperylene (**4**) (Table 3). We observed that products did not follow the same energy trend as transition structures. This result supports the fact that the interactions in the transition structures determine the energy barriers and hence control the outcome of the reaction.

Stereoselectivity. That *endo* transition structures are more stabilized than *exo* ones due to [4+3] secondary orbital interactions is evident from the Natural Bond Order analysis (Table 4). A number of trends emerge from this analysis. To begin with, examination of the forming C−C bond orders confirms that these Diels−Alder reactions occur through concerted and asynchronous transition structures with higher C2−C3 bond orders than C1−C6 bond orders. *Endo* transition structures exhibit higher C6−B bond order values (0.47−0.25 for **1** and 0.15−0.10 for **2**) than *exo* transition structures (0.16−0.09 for **1** and 0.08−0.06 for **2**).

This suggests that [4+3] secondary orbital interactions account for the relative stability of *endo* transition structures. The high values obtained for the C6−B bond orders in *endo* transition structures (even higher than C1−C6 bond orders in *endo* transition structures for the reactions of **1**) highlight the magnitude of C−B secondary orbital interactions. This analysis substantiates the existence of nonclassical [4+3] secondary orbital interactions as a special type of controversial secondary

orbital interaction.[15] Bond order analysis also evidences the effect of substitution on boron since C6−B bond orders are considerably smaller for the reactions of dimethylvinylborane (**2**) compared to vinylborane (**1**). For example, in *endo* transition structures, bond orders vary in the ranges 0.15−0.10 and 0.47−0.25, respectively. However, [4+3] secondary interactions in *endo* transition structures for the reactions of dimethylvinylborane (**2**) seem to be strong enough to control the stereoselectivity of the reaction.

Singleton previously raised the question about the origin of the intriguing paradoxical behavior of *endo* and *exo* transition structures in adopting [4+3] versus [4+2] character.[4] The results obtained in this DFT investigation indicate that both *endo* and *exo* transition structures exhibit considerable [4+3] character for the reactions of *trans*-piperylene (**4**) and isoprene (**5a**) with vinylborane (**1**) while the corresponding transition structures for the reactions of dimethylvinylborane (**2**) adopt classical [4+2] character. Nonetheless, the higher [4+3] character in *endo* transition structures compared to *exo* transition structures can be explained in terms of overall orbital overlap. Figure 5 shows a schematic representation of three possible geometric disposi-

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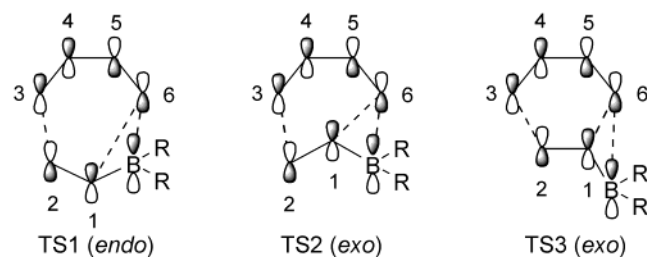
Figure 5.

Table 5. Frontier Molecular Orbital Energy Gaps for the Reactions of **4** and **5a** with **1** and **2** (in eV)

|	**1**	**2**
$HOMO_4-LUMO_{dienophile}$	3.98	4.68
$LUMO_4-HOMO_{dienophile}$	7.45	7.00
$HOMO_{5a}-LUMO_{dienophile}$	4.21	4.91
$LUMO_{5a}-HOMO_{dienophile}$	7.34	6.89

tions of the HOMO of the diene and the LUMO of the dienophile in the transition structures. The bond order analysis indicates that in *endo* transition structures the dienophile can adopt a geometric disposition that leads to a good overlap between B and C6 and C2 and C3 and also allows a considerable degree of interaction between C1 and C6 (TS1). On the other hand, if C2 and B in *exo* transition structures are located adequately so as to obtain good overlap with the C3 and C6, respectively, C1 becomes very close to the atoms in the diene experiencing repulsive secondary orbital interactions with C3 and C4 (TS2). Consequently, calculated *exo* transition structures adopt geometries similar to TS3, where C1 and C2 overlap with C6 and C3 but the boron moves quite far away from C6 and therefore the [4+3] secondary orbital interaction becomes weaker.

Regioselectivity. The calculated 46:54 meta/ortho ratio for the reaction of dimethylvinylborane (**2**) with *trans*-piperylene (**4**) agrees very well with the experimentally observed 50:50 ratio. Similarly, for the reaction of isoprene (**5a**) with dimethylvinylborane (**2**) the computed 60:40 para/meta ratio is in excellent agreement with the experimental result obtained with myrcene (**5b**) (61:39).

Table 5 shows that these reactions are dominated by diene HOMO–dienophile LUMO interactions. The LUMO coefficients of the dienophiles demonstrate that frontier orbitals of vinylboranes are highly polarized. Indeed, the LUMO coefficients on boron (~0.4) are much higher than the coefficients on C1 (~0.2). However, the HOMO coefficients on C1 and C4 of both *trans*-piperylene (**4**) and isoprene (**5a**) are very similar (~0.3 for both carbons). These FMO arguments could then be used to interpret the lack of regioselectivity for the reactions of dimethylvinylborane (**2**) with both *trans*-piperylene (**4**) and myrcene (**5b**).

Calculations with vinyl-9-BBN (3). For the reaction of *trans*-piperylene (**4**) with the bulkier vinyl-9-BBN (**3**), the anomalous meta regioselectivity increases significantly (meta/ortho ratio >98:2). In the same way, when vinyl-9-BBN (**3**) is used as the dienophile, the para isomer is experimentally obtained as the major product with both isoprene (**5a**) and myrcene (**5b**). These observations motivated us to perform calculations for the reactions with vinyl-9-BBN (**3**). We first obtained the transition structures for the reactions of vinyl-9-BBN using RHF/AM1 and then optimized these initial geometries with B3LYP/6-31G* (Figures 6 and 7).

We found asynchronous transition structures with [4+2] character for each mode of addition. Once more, this proves
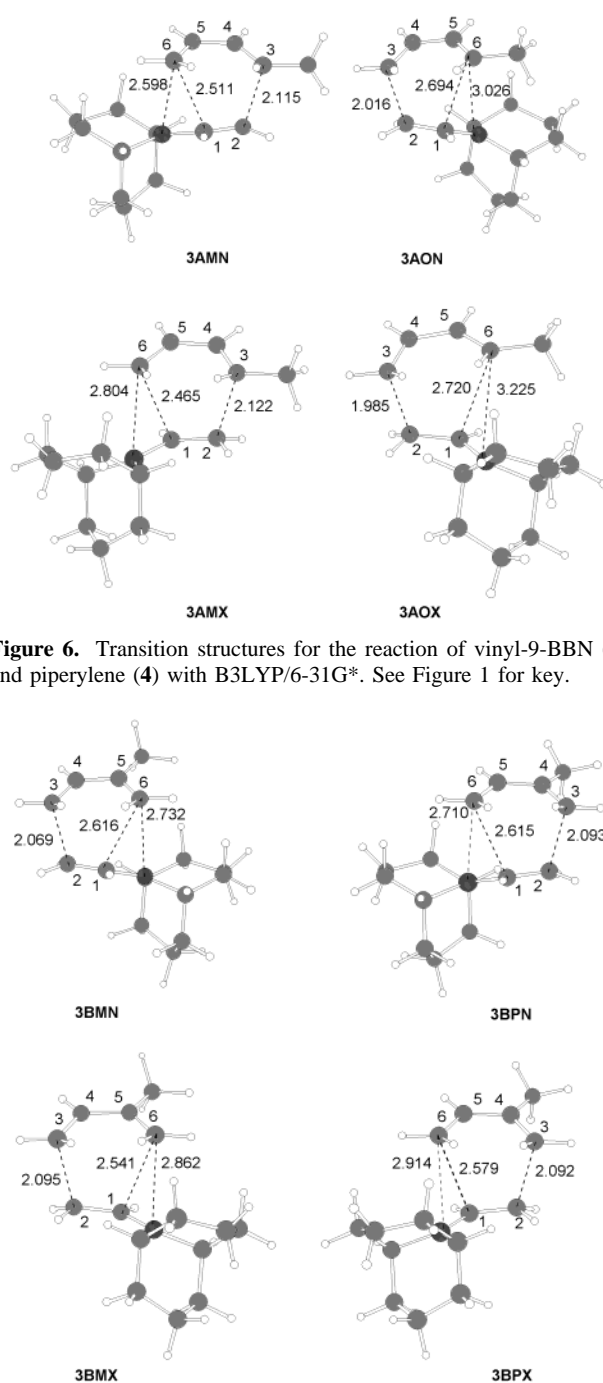
Figure 6. Transition structures for the reaction of vinyl-9-BBN (**3**) and piperylene (**4**) with B3LYP/6-31G*. See Figure 1 for key.
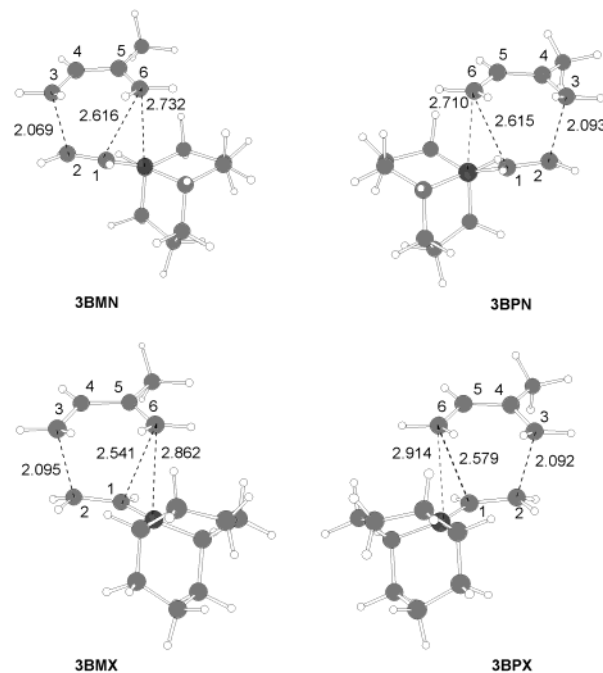
Figure 7. Transition structures for the reaction of vinyl-9-BBN (**3**) and isoprene (**5a**) with B3LYP/6-31G*. See Figure 1 for key.

that the addition of alkyl groups to the boron atom weakens C–B [4+3] secondary orbital interactions. Regarding the energetics, calculations predict a 80:20 meta/ortho ratio for the reaction with *trans*-piperylene (**4**) with 95:5 and 85:15 *endo/exo* ratios for the meta and ortho regioisomers, respectively, and a 88:12 para/meta ratio for the reaction with isoprene (**5a**) (Table 6). While the computed results underestimate the experimental regioselectivity for the reaction with *trans*-piperylene (**4**), the increase of regioselectivity compared to the reactions with dimethylvinylborane (**2**) is correctly reproduced. Furthermore, the calculated stereoselectivity for the reaction with *trans*-piperylene (**4**) agrees very well with the experimental value.[16]

The HOMO coefficients on the terminal carbons of the dienes are again very similar. Consequently, these high regioselectivi-

Table 6. Energetics of the Diels−Alder Reactions of Vinyl-9-BBN (**3**) with *trans*-Piperylene (**4**) and Isoprene (**5a**) with B3LYP/6-31G*

TS	$\Delta E^{\ddagger}$ (kcal mol^{-1})	E_{rel} (kcal mol^{-1})	calcd ratios
3AMN	18.85	0.00	
3AON	19.74	0.89	80:20 meta/ortho
3AMX	20.60	1.75	95:5 and 85:15 *endo/exo*
3AOX	20.75	1.89	
3BMN	18.41	1.28	
3BPN	17.14	0.00	88:12 para/meta
3BMX	19.55	2.41	
3BPX	19.10	1.97	

ties cannot be explained wholly in terms of FMO theory. However, the geometries of the transition structures suggest that steric effects play an important role in determining the regiochemical outcome of these reactions.

For instance, in the ortho transition structure **3AON** the carbon of the methyl group of *trans*-piperylene (**4**) is only 2.89 Å away from one of the hydrogen atoms of the 9-BBN portion of the dienophile (Figure 6). This distance is lower than the sum of the van der Waals radii of carbon (1.7 Å) and hydrogen (1.2 Å), which evidences the important clash experienced between the substituents in the reactants. Furthermore, the distance between the carbon of the methyl group and the boron atom is 3.53 Å. A similar picture is observed for **3AOX**, where the corresponding distances are 3.09 and 3.79 Å, respectively. These interactions also account for the higher asynchronicity of ortho transition structures compared to the meta counterparts.

Since the methyl of *trans*-piperylene (**4**) and the 9-BBN portion of the dienophile lie on different ends in meta transition structures (**3AMN** and **3AMX**), these distances are much longer and therefore these structures are less sterically congested. The dihedral angle C1−C2−C3−C6 is another structural feature to be analized. This angle adopts values of −15.0° and 9.3° in **3AMN** and **3AON**, respectively. This indicates that when the substituents of the dienophile and the diene are close to each other (as in **3AON**), the carbons involved in bond formation are twisted to minimize the repulsive steric interactions. In addition to these key structural features, a number of close contacts between hydrogens are observed in both meta and ortho transition structures for the reaction with *trans*-piperylene (**4**).

The transition structures for the reactions with isoprene (**5a**) show similar patterns of interactions between the atoms of the methyl group of the diene and the 9-BBN substituent of the

dienophile (Figure 7). This is evidenced by a similar degree of asynchronicity in meta and para transition structures. However, the distance between the carbon of the methyl group of isoprene and one of the hydrogens of the 9-BBN portion (2.81 Å) can be used again to explain the lower stability of **3BMN** compared to **3BPN**.

Conclusions

We have used ab initio and DFT methods to investigate the origin of the regio- and stereoselectivity of the Diels−Alder reactions of dialkylvinylboranes with substituted dienes. DFT calculations successfully reproduced experimental regio- and stereoselectivities for the reactions of dimethylvinylborane (**2**) and vinyl-9-BBN (**3**). Although we have confirmed that nonclassical carbon−boron [4+3] secondary orbital interactions exist in these species, we have shown that they become less important when the bulkiness of the alkyl groups attached to the boron increases. Both *endo* and *exo* transition structures for the reactions of dimethylvinylborane (**2**) and vinyl-9-BBN (**3**) adopt classical [4+2] character. However, C−B secondary orbital interactions seem to account for the high *endo* stereoselectivity of the Diels−Alder reactions under study. We have also extended Singleton's study by investigating the origin of the regioselectivity. While the lack of regioselectivity in the reactions of dimethylvinylborane (**2**) with both *trans*-piperylene (**4**) and myrcene (**5b**) has been rationalized based on FMO theory, steric effects dominate the regioselectivity preferences of bulky dialkylvinylboranes such as vinyl-9-BBN (**3**).

Supporting Information Available: Cartesian coordinates and absolute energies of all reactants, transition structures, and products reported in the paper; energies and atomic coefficients of the frontier molecular orbitals of the reactants; Mulliken overlap populations for the transition structures of the Diels−Alder reactions of vinylborane and dimethylvinylborane with *trans*-piperylene and isoprene; calculated entropies for the transition structures of the Diels−Alder reactions of vinyl-9-BBN with *trans*-piperylene and isoprene; and side and top views of the transition structures for the reactions of vinyl-9-BBN with *trans*-piperylene and isoprene (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(16) We also analyzed the entropy contribution for the reactions of vinyl-9-BBN (**3**). The calculated entropies favor *endo* transition states over the *exo* counterparts. In addition, only small energy differences are obtained for regioisomeric transition structures if the contributions from the entropies are considered. Consequently, the calculated ratios were slightly modified and still favored the experimentally observed products.