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A Theoretical Study of the Reaction of Alkynylboranes with Butadiene: Competition between Cycloaddition and Alkynylboration

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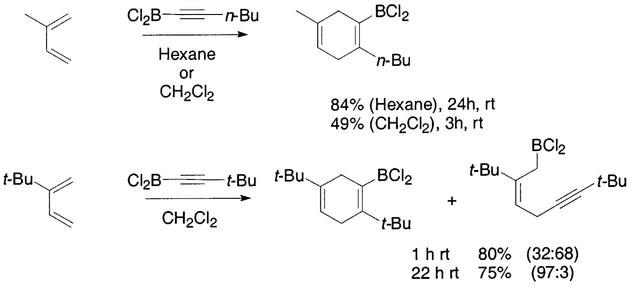
The reactions of alkynyldihaloboranes and alkynyldialkylboranes with butadiene have been explored by using DFT methods at the B3LYP level with the 6-31G* basis set. Transition structures for the concerted [4+2] cycloaddition have been found for the alkynylborane derivatives. Along with these, another reactive pathway has been found for the cycloaddition process with transition structures of high [4+3] character. The transition structures for the 1,4-alkynylboration processes have also been found. The geometries computed for the cycloaddition transition structure with high [4+3] character and the 1,4-alkynylboration transition structures are surprisingly similar though leading to different products. IRC calculations suggest that the [4+3] cycloaddition and alkynylboration pathways are associated by a zwitterionic structure.

Introduction

The Diels−Alder (DA) reaction is one of the most important carbon−carbon bond-forming reactions in organic synthesis.[1] The use of vinylboranes as DA dienophiles has been extensively studied both experimentally[2] and theoretically.[3] However, the use of alkynylboranes has been given little attention. As far as we know, the use of alkynylboranes in DA reactions has been studied only by Singleton et al. Initially, they described the use of [(trimethylsilyl)ethynyl]-9-BBN as a good dienophile that showed an unusual electronic preference for the "meta" Diels−Alder product.[4] More recently, they have reported the reaction of alkynyldihaloboranes with 1,3-dienes.[5] The reactions with isoprene in hexanes afforded the 1,4-cyclohexadiene products in high yields and high regioselectivity. However, the reactions of 2-*tert*-butylbutadiene and 2-phenylbutadiene in dichloromethane led to formation of the cycloaddition product, along with the enynes, which result from the 1,4-alkynylboration of the dienes (Scheme 1).

SCHEME 1



Experimental data given for the reaction after protodeboronation.
Following Singleton's paper, we assumed the same yields and ratios for the borane products.

To have an insight into the outcome of these processes and study the competition between the DA cycloaddition and the 1,4-alkynylboration, we have studied the reactions between different alkynylboranes and 1,3-butadienes computationally. Previous ab initio RHF calculations predicted [4 atom + 3 atom] transition structures, as have also been described more extensively for vinylboranes. The computed RHF geometries showed strong [4+3] character, with the B−C1 forming bonds more advanced than the C1−C2. This result has been used to suggest other pericyclic processes, such as the 1,4-alkynylboration of alkynyldihaloboranes. These reactions would have to proceed through a zwitterionic intermediate that then would simultaneously lead to the alkynylboration product and the cycloaddition product.

The aim of this theoretical study is to gain a better understanding on the factors controlling the choice between these reaction pathways. Herein we present the result of the theoretical study for the reactions between 1,3-butadiene and different alkynylboranes in order to have an insight into the outcome of these processes and

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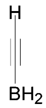
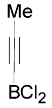
study the competition between Diels−Alder cycloaddition and 1,4-alkynylboration.



$HC\equiv CBH_2$

1



$MeC\equiv CBCl_2$

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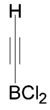


$HC\equiv CBCl_2$

3

$MeC\equiv CBMe_2$

4

$HC\equiv CBMe_2$

5

Computational Methods

Geometries for all the stationary structures along the reaction paths have been fully optimized at the B3LYP[6] level using the standard 6-31G* basis set.[7] Some of the transition structures were first optimized with the semiempirical AM1 method, using MOPAC 93,[8] and/or ab initio methods at the restricted Hartree−Fock (RHF) level of theory with the 6-31G* basis sets, using CADPAC[9] 6.0 and 6.5, before B3LYP/6-31G* optimization. Frequency calculations were performed to characterize the nature of the stationary points, and to determine zero-point energies, enthalpies, and free energies. All the transition structures were found to have only one negative imaginary frequency, corresponding to the movement in the direction of the reaction coordinate. Natural bond orbital (NBO) analysis was performed for the evaluation of the forming bonds as well as the interaction between the boron of the dienophile and the terminal carbon in the butadiene. Intrinsic Reaction Coordinate (IRC) calculations starting at the saddle points were carried out at the B3LYP/6-31G* level to check the connections between the transition structures and the reactants and products. All the DFT calculations were carried out with the Gaussian 98 program.[10]

Results and Dicussion

We have studied the reactions of butadiene with ethynylborane (**1**), dichloropropynylborane (**2**), ethynyldichloroborane (**3**), dimethylpropynylborane (**4**), and ethynyldimethylborane (**5**). We paid special attention to the results found for dichloropropynylborane (**2**), as this is a good model for the alkynylboranes used in the literature. The calculations carried out for the reaction of butadiene and dichloropropynylborane (**2**) gave a surprising result, as three transition structures were found. Two of them, **TS-A2** and **TS-B2**, correspond to the cycloaddition process, while **TS-C2** corresponds to the alkynylboration process (Figure 1). **TS-A2** has mainly [4+2] character, while **TS-B2** has mainly [4+3] character. **TS-C2** is suggestive of the alkynylboration process from the starting material, but IRC analysis leads to the corresponding 1,4-cyclohexadienylborane and the alkynylboration product, not the reactants. Scheme 2 summarizes the three reaction pathways found and the zwitterionic structure (**7**) that we have observed in the IRC calculations for both **TS-B** and **TS-C** pathways. This structure **7** appears as a nearly horizontal area in the reaction coordinate, but the gradient is not quite zero and so it cannot be characterized as a minimum, nor as a transition structure. Similar flat areas of potential energy surfaces (PES) have been previously described.[11] The results of the IRC studies suggest a possible bifurcation of the reaction path toward the two different products.[12]

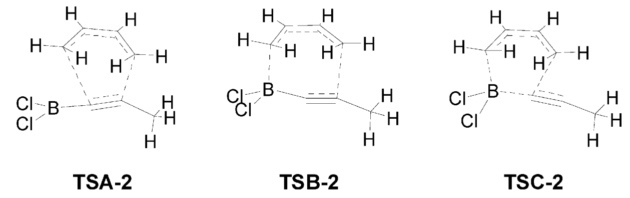
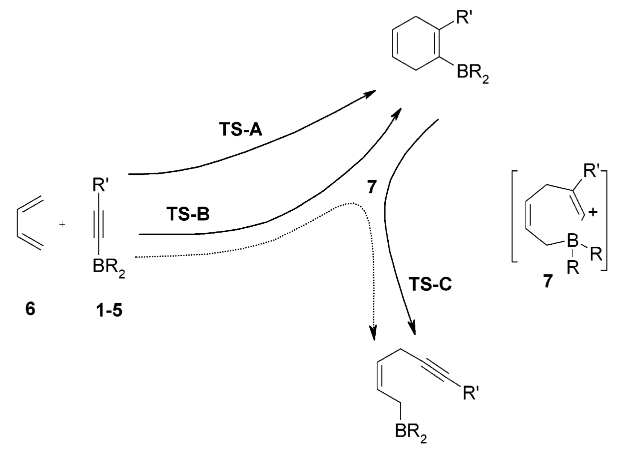


FIGURE 1. Transition structures found for the reaction between 1,3-butadiene and dichloropropynylborane (**2**).

SCHEME 2



Geometries. The cycloadditions of butadiene with dichloropropynylborane (**2**), ethynyldichloroborane (**3**), dimethylpropynylborane (**4**), and ethynyldimethylborane (**5**) led to concerted transition structures. The geometries of the TSs are presented in Figure 2. Recently, we have reported similar geometries in the case of vinylborane.[3b] We found all transition structures to be asynchronous with C2−C3 bond lengths being shorter than C1−C6 distances. In addition, the degree of asynchronicity is higher for those TSs with chlorine substituents on the boron atom than for their methyl analogues. Furthermore, the transition structures for the reaction with ethynyldichloroborane (**3**) and ethynyldimethylborane (**5**),

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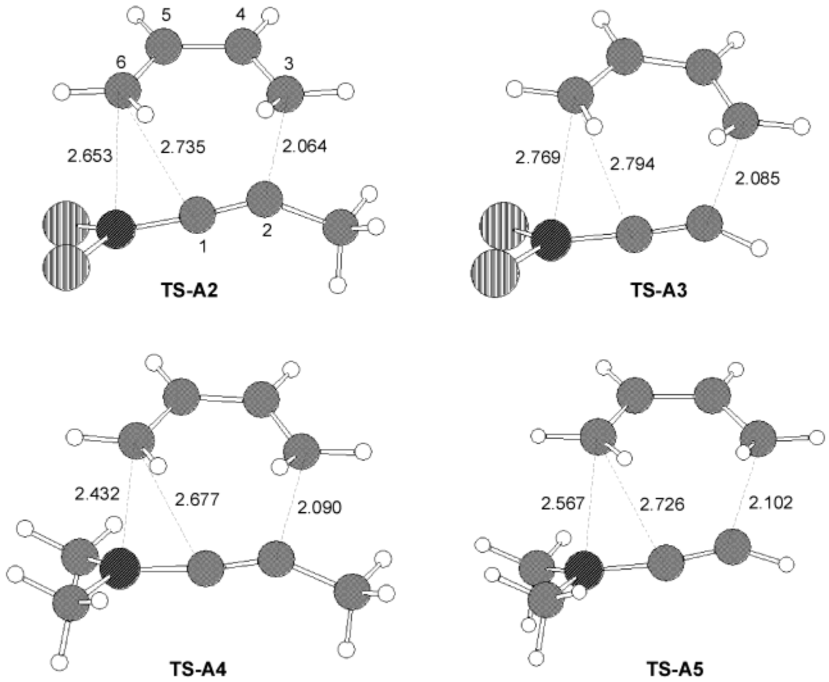

FIGURE 2. B3LYP/6-31G* optimized geometries of **TS-A2** to **TS-A5**. All distances are in Å.

TS-A3 and **TS-A5**, respectively, are slightly more asynchronous than their counterparts with the methyl group in the terminal carbon of the alkynylborane, **TS-A2** and **TS-A4**.

These transition structures exhibit nonclassical [4+3] secondary orbital interactions, as previously observed by Singleton[5a] and corroborated by our studies on the Diels–Alder reaction of vinylborane. While forming bond lengths are similar for all the systems, C6–B distances slightly vary from alkynyldialkylboranes to alkynyldihaloboranes. Transition structures for the reaction of alkynyldialkylboranes showed shorter C6–B distances, and hence more [4+3] character, with distances of 2.432 Å for **TS-A4** and 2.567 Å for **TS-A5**, while for alkynyldihaloboranes the degree of [4+3] character is less noticeable, with lengths of 2.653 (**TS-A2**) and 2.769 Å (**TS-A3**).

Analysis of the imaginary frequencies for these transition structures indicates in all cases the atom pairs C2–C3 and C1–C6 have a bonding movement in the TSs. However, the size of the C2–C3 movement is greater than that corresponding to the C1–C6 movement. Intrinsic reaction paths (IRC) were determined at the B3LYP level to establish the connectivity between the transition structures and the reactants. All the IRC profiles of the transition structures **TSA2** to **TSA5** led to the final Diels–Alder products and the reactants, demonstrating that the reactions follow a concerted cycloaddition mechanism to form the corresponding cycloadducts.

Previous ab initio RHF calculations by Singleton on ethynylborane and ethynyldichloroborane with butadiene showed transition structures with C6–B forming bonds considerably more advanced than the bonding between C2 and C3. We found similar transition structures (**TS-B**) in the case of ethynylborane (**1**) and dichloropropynylborane (**2**) at the B3LYP/6-31G* level of calculation, although the corresponding transition structure for ethylnyldichloroborane (**3**) could not be found. Figure 3 displays the geometries calculated for these systems. The most remarkable feature of these transition structures is the fact that the asynchronicity is now reversed relative to the **TS-A** cycloaddition transition structures. In this case, C6–B distances are shorter than C2–C3 distances, thereby giving rise to a significantly stronger [4+3] character.

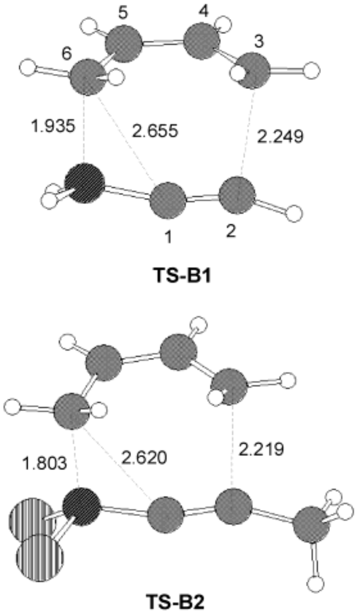

FIGURE 3. B3LYP/6-31G* optimized geometries of **TS-B1** and **TS-B2**. All distances are in Å.

In transition structure **TS-B1**, the bond distance C6–B is 1.935 Å, longer than in **TS-B2** (1.803 Å). In both transition structures, the boron is significantly pyramidalized, with the H–B–H bond angle ca. 116° for **TS-B1** and the Cl–B–Cl bond angle ca. 113° for **TS-B2**. This

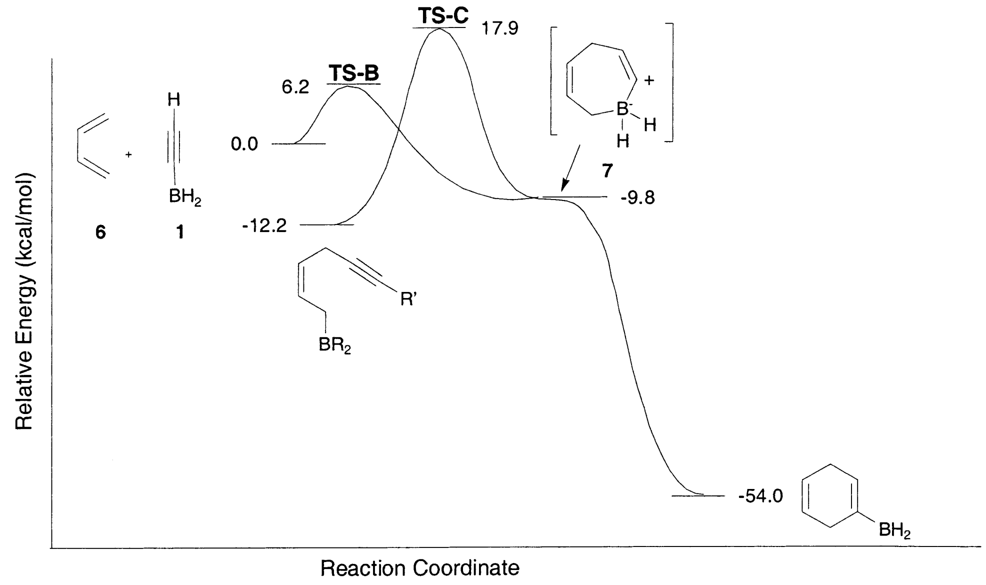

FIGURE 4. Energy profile for the reaction between 1,3-butadiene and ethynylborane (**1**).

observation agrees with the advanced formation of the C−B bond in these systems. The distances C1−C6 and C2−C3 are similar for both transition structures, 2.655 and 2.249 Å respectively for **TS-B1** and 2.620 and 2.219 Å for **TS-B2**.

The analysis of the unique imaginary frequency of **TS-B1** and **TS-B2** indicates that these transition structures are associated with the formation of the C6−B bond and the C2−C3 bond. Despite this, when we performed an IRC calculation in order to investigate the formation of a possible dipolar intermediate, such as **7** in Scheme 2, we observed an inflection on the IRC path where the gradient is close to zero. Minimization of this structure (**7**) led to the corresponding 1,4-cyclohexadienylborane (Figure 4).

Singleton et al. previously suggested the possibility of a stepwise mechanism operating along with the direct Diels−Alder pathway in order to explain the alkynylboration products obtained together with the cycloadducts in the reactions between alkynyldihaloboranes and 1,3-dienes, in dichloromethane. Similarly, in a recent study by Rastelli[13] et al. on the 1,3-dipolar cycloaddition of nitrones with vinylboranes, a similar dipolar intermediate was found, which, like ours, could not be characterized as a stationary point.

Special attention is required for the alkynylboration process. In their work on the Diels−Alder reaction of alkynyldichloroboranes, Singleton et al. suggested that the alkynylboration of the diene could happen by a concerted mechanism where the transition structure would have similar geometry to the RHF transition structure described for the cycloaddition reaction. Computationally, transition structures for the boration reaction using nitrones and vinylboranes have been reported.[13] Nevertheless in this case, the reactants formed a complex where the boron atom and the nitrone oxygen is already formed. The dotted line in Scheme 2 represents a possible pathway for the alkynylboration process direct from the reactants, and through **7**. Although we performed a thorough investigation of the potential energy surface, we could not find any transition structures for such a pathway. Instead, we have found transition structures **TS-C1** to **TS-C5**, leading to the corresponding enynes for all the dienophiles studied (Figure 5). We have observed that these transition structures result from the equilibrium between the cyclohexadienylboranes and the alkynylboration products. IRC calculations were performed on the transition structures for the reaction with ethynylborane, **TS-C1**, and dichloropropynylborane, **TS-C2**. They confirmed that these transition structures for the alkynylboration reaction are directly connected to the enyne product. Nevertheless, when the transition structures were launched toward the reactants, the IRC calculation produces a flat region that corresponds to the zwitterionic seven-membered ring structure that was observed in the case of **TS-B1** and **TS-B2** and led to the cyclohexadienylborane product when minimized.

In **TS-C1**, **TS-C2**, and **TS-C3**, the C6−B bond lengths, 1.672, 1.655, and 1.647 Å, respectively, indicate that this bond is nearly formed. Slightly longer C6−B bond lengths were observed in the case of **TS-C4** and **TS-C5**, 1.711 and 1.697 Å, respectively. On the other hand, the distance between C1 and B, ca. 1.60 Å, is significantly longer compared to that of the cycloaddition processes.

If we compare the bond length C1−C3, which is also being formed in the TSs, we observed that **TS-C1**, **TS-C3**, and **TS-C5**, with no substitution in the terminal carbon of the alkynylborane, give shorter distances, 1.778, 1.872, and 1.844 Å, respectively, than **TS-C2** and **TS-C4**, with a methyl group substitution at the alkynylborane, 2.088 and 1.958 Å, respectively. Conversely, in the case of these latter TSs, it is observed that the presence of the methyl groups slightly shortens the distance between the C2 and C3 atoms.

The study of the vibration associated with the imaginary frequency for the alkynylboration transition structures corresponded in all cases with the motion of the C1 and C3 carbon atoms along the C−C bond formation.

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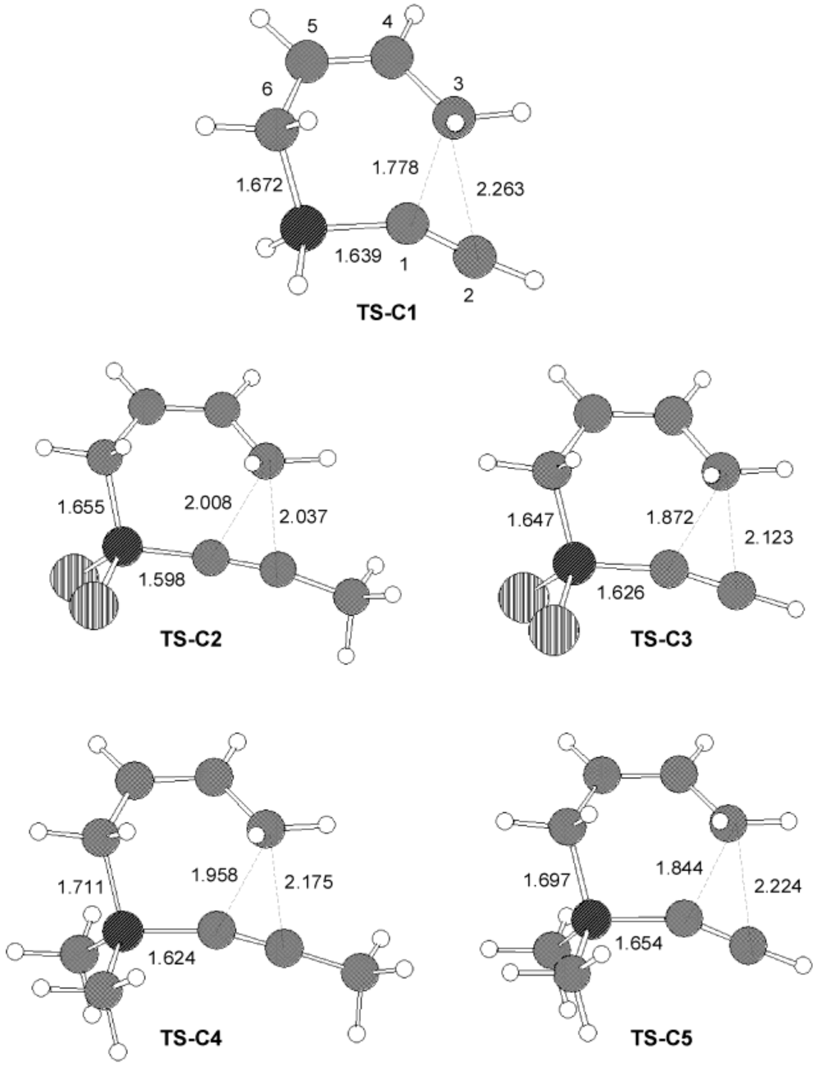

FIGURE 5. B3LYP/6-31G* optimized geometries of **TS-C1** to **TS-C5**. All distances are in Å.

However, it is remarkable that the contribution of C2−C3 was noticeable for the reaction with dichloropropynylborane (**2**) and ethynyldichloroborane (**3**). This is in agreement with the fact that the reaction coordinate shows a flat region with a seven-membered ring structure as a result of C2 and C3 coming closer.

TABLE 1. Activation Energies, Enthalpies, and Gibbs Energies (kcal mol^{-1}) for the Reaction between Butadiene and Alkynylboranes, with Respect to Reactants[a]

TS	$\Delta E^{\ddagger}_{0}$	$\Delta E^{\ddagger}_{298}$	$\Delta H^{\ddagger}_{298}$	$\Delta G^{\ddagger}_{298}$
TS-A2	21.24	19.41	20.90	33.92
TS-A3	15.16	13.59	14.48	27.73
TS-A4	22.23	19.73	22.53	34.21
TS-A5	17.22	15.20	16.25	30.45
TS-B1	8.40	6.19	6.96	20.85
TS-B2	21.73	19.76	21.18	34.95
TS-C1	19.86	17.93	18.27	32.45
TS-C2	23.37	21.39	22.79	36.52
TS-C3	24.10	22.31	23.04	37.61
TS-C4	31.37	28.93	31.40	43.58
TS-C5	33.31	31.24	31.86	47.48

[a] Calculated at the B3LYP/6-31G* theory level.

Energetics. The computed activation energies, zero-point energies, enthalpies, and Gibbs energies are collected in Table 1.

If we compare **TS-A2** and **TS-A4** with the respective analogues without substitution at the terminal carbon of the alkynylborane, **TS-A3** and **TS-A5**, we observed that the energy barriers decrease by 6.08 and 5.01 kcal/mol, respectively. This fact agrees with **TS-A3** and **TS-A5** being earlier transition structures as indicated by longer forming bonds. On passing from dichloro to dimethyl substitution on the boron, an increase on the energy differences is observed in the range of 1.00−2.01 kcal/mol. Thus, the calculation correctly predicts that dichloroalkynylboranes should be more reactive that the dimethyl counterparts as expected for a higher electophilicity of the boron.

When analyzing the energies for the two transition structures with strong [4+3] character, we observed a very low energy barrier for the **TS-B1**, 8.40 kcal/mol, compared to **TS-B2**, 21.73 kcal/mol. Again, this indicates that the steric hindrance caused by introducing substituents in the alkynylborane results in a later transition structure and therefore higher activation energy. All the attempts to find a similar **TS-B** transition structure in the case of ethynyldichloroborane (**3**) were unsuccessful.

On the other hand, the fact that no similar structures were found for the **TS-B** pathway in the case of dimethylpropynylborane (**4**) and ethynyldimethylborane (**5**), with methyl substitution at the boron atom, can be explained in terms of the decrease in the nucleophilic character of the boron due to the methyl substitution.

Although the transition structures found for the alkynylboration process correspond to the interconversion between the DA products and the alkynylboration products, we have calculated the activation energies related to the reactants. We assumed that the zwitterionic structure found in the IRC of **TS-B** and **TS-C** pathways plays an important role in the formation of the alkynylboration products. Once the reactants reach this seven-membered-ring structure, they could then lead to the DA product or follow the alkynylboration pathway. The computed activation energies for the alkynylboration reactions were in all cases computed higher that the ones corresponding to the concerted cycloaddition pathway transition structures (**TS-A**). However, while for the reaction with ethynylborane the increase in energy when passing from **TS-B1** to **TS-C1** is 11.74 kcal/mol, for the reaction with dichloropropynylborane the difference in energy between **TS-B2** and **TS-C2** is only 1.63 kcal/mol (and 1.98 kcal/mol between **TS-A2** and **TS-C2**). Furthermore, for the reaction with ethynyldichloroborane, the energy difference between **TS-A3** and **TS-C3** is considerably higher, 8.72 kcal/mol. This interesting result predicts that the methyl substitution on the terminal carbon atom of the alkynylborane stabilizes the alkynylboration transition structure by donating charge to the partial positive charge generated on C1 and C2 along the electrophilic attack by the boron to the butadiene. The transition structures for the reaction of ethynyldimethylborane (**4**) and dimethylpropynylborane (**5**), **TS-C4** and **TS-C5**, energy barriers are considerably higher, by ~8 kcal/mol, compared to the corresponding dichloro analogues.

The energies of both cycloaddition and alkynylboration products were calculated. For all the systems, the energies of the cyclohexadienylboranes were between 34 and 46 kcal/mol more stable than the corresponding enynes, and so are the thermodynamic products of the reaction. We believe that, for the systems we have studied, there is no direct route from the starting materials to the enyne product, as extensive searches of the potential energy surface have not localized a transition structure for this process. However, we cannot definitively rule out this possibility. The experimental results on more substituted systems show that the enyne predominates at short reaction times while the cycloadduct is the major product when the reaction is left for longer, which suggests that the enyne is the kinetic product, in these cases. This is consistent with our calculations, if we assume that the additional substituents perturb the potential energy surface sufficiently to make **7** a stationary point, or create a direct path from the starting materials to the enyne, and we predict the enyne product would not be formed if **2** and **6** were used as reactants.

Bond Order Analysis. Natural bond order analysis was performed at the optimized geometries to give us an idea of the extent of bond formation or bond breaking along the reaction pathways. The results are gathered in Table 2. First, we analyzed the bond order (BO hereafter) values calculated for the direct cycloaddition pathways. We confirmed that these cycloadditions take place through concerted and asynchronous transition structures with higher C2−C3 bond orders than C1−C6 bond orders. The bond order values for the C2−C3 forming bonds are ca. 0.40, whereas BO values for the C1−C6 bond are ca. 0.13 for alkynyldichloroboranes and 0.15 for alkynyldimethylboranes. It is noteworthy that, as previously found in the case of vinylboranes, the bond order values found between C6 and B are noticeable. This finding evidences the [4+3] character in these concerted transition structures. We have observed that the C6−B bond order values decrease as the asynchronicity of the transition structures increases. For the reaction with dichloropropynylborane (**2**) and ethynyldichloroborane (**3**), we have found that C6−B bond order values are only slightly smaller than the respective C1−C6, in about 0.02. More interestingly, for the alkynyldialkylboranes, **TS-A5** showed similar values for the BO of C1−C6 and C6−B (0.14 and 0.15, respectively), but for **TS-A4** the BO calculated for the C1−C6 forming bond is smaller by about 0.03 than the value of C6−B (0.16 and 0.19, respectively). From these results, we observed that the C6−B bond order value decreased as the asynchronicity of the transition structures increased.

TABLE 2. Natural Bond Orders at the B3LYP/6-31G* Level of Theory for the Transition Structures of the Reactions between Butadiene and Alkynylboranes

TS	C1−C6	C2−C3	C6−B	C1−C3	C1−B
TS-A2	0.15	0.41	0.13		1.08
TS-A3	0.12	0.39	0.10		1.07
TS-A4	0.16	0.40	0.19		1.03
TS-A5	0.14	0.38	0.15		1.03
TS-B1	0.09	0.30	0.48		1.04
TS-B2	0.07	0.31	0.62		0.93
TS-C1	0.01	0.21	0.81	0.62	0.80
TS-C2	0.02	0.37	0.81	0.38	0.81
TS-C3	0.01	0.30	0.82	0.51	0.77
TS-C4	0.02	0.28	0.75	0.44	0.81
TS-C5	0.01	0.24	0.77	0.55	0.76

Both **TS-B1** and **TS-B2** presented strong [4+3] character, with C6−B bond order values of 0.48 and 0.62, respectively. The high value shown for **TS-B2** with dichloropropynylborane (**2**) corroborates the idea that this transition structure is relatively late in the reaction coordinate. In addition to this, nonclassical [4+3] secondary orbital interactions are stronger in **TS-B2**, as expected from chlorine-substituted boron, and, therefore, more electrophilic.

Finally, in relation to the transition structures for the alkynylboration process, high values for the C6−B bond orders were observed, varying in the range of 0.75 to 0.82. These values indicate that the formation of this bond is very advanced in the transition structure. It is worth noting that the higher C6−B bond order values correspond to the transition structures with dichloro substitution, **TS-C2** (0.81) and **TS-C3** (0.82), as expected for a more electrophilic boron in the dienophile. The bond order values for the C1−C3 forming bonds for TS−C are also high, varying in the range 0.38−0.62. The high values found for the C2−C3 bond orders (0.21−0.37) are interesting, as this bond takes part in the reaction coordinate with the proposed seven-membered-ring structure. On the other hand, it can be observed that the BO values for the C1−B bond are considerably smaller when passing from **TS-A** and **TS-B** to **TS−C**, indicating that this bond is breaking in the latter transition structures.

Conclusion

The molecular mechanism of the reaction of 1,3-butadiene and different alkynylboranes has been investigated using DFT methods. For the cycloaddition reaction, we have found two different pathways leading to the same cyclohexadienylborane products: the classical concerted [4+2] cycloaddition, with some degree of [4+3] secondary orbital interactions involving the B atom, and in some cases transition structures with strong [4+3] character. Transition structures connecting the cycloaddition with the alkynylboration products have also been found. Geometry optimizations of the products have been carried out, and the cyclohexadienes are the thermodynamic products. IRC calculation for the **TS-B** and **TS-C** pathways showed that there is a nearly flat region in the reaction coordinate that corresponds to a seven-membered-ring structure. Although this structure was not quite a stationary point, solvent effects or substituents effects may perturb the potential energy surface sufficiently to make it a stationary point and so could influence the preferred pathway toward the cycloaddition or the alkynylboration product.

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Supporting Information Available: Cartesian coordinates and absolute energies of all reactants, transition structures, and products reported in the paper; table of total energies and relative energies for the stationary points corresponding to the reaction between butadiene and alkynylboranes. This material is available free of charge via the Internet at http://pubs.acs.org.

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