*Organometallics* **2003,** *22,* 3748−3752

# Computational Studies of the Origin of Regiospecificity in the [4+2] Diels−Alder Reaction between $R_2B{=}NR_2'$ Compounds and Substituted *cis*-Butadienes

Thomas M. Gilbert[1]

*Department of Chemistry and Biochemistry, Northern Illinois University,*
*DeKalb, Illinois 60115*

*Received May 12, 2003*

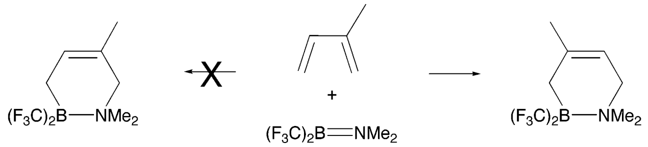
Computational studies comparing the energetics of [4+2] Diels−Alder-like cyclizations of aminoboranes $R_2B{=}NR_2'$ ($R = H$, $CF_3$; $R' = H$, $CH_3$) with substituted *cis*-2-R″-1,3-butadienes ($R'' = CH_3$, $NH_2$, $CF_3$) show that the regiospecificity observed experimentally derives from the transition state barrier heights rather than the reaction exothermicities. When R″ is an electron-donating group such as $CH_3$ or $NH_2$, the model predicts a preference for the 5-R″-1-bora-2-azacyclohex-4-ene product; that is, the R″ group favors proximity to the boron atom. When R″ is an electron-withdrawing group such as $CF_3$, the model predicts a preference for the 4-R″-1-bora-2-azacyclohex-4-ene product; that is, the R″ group favors proximity to the nitrogen atom. The predictions are in accord with experimental results and organic frontier molecular orbital theory, although the aminoboranes exhibit a surprising degree of discrimination between similarly charged carbon atoms.

## Introduction

In 1990, Bürger, Brauer, and co-workers reported the observation of [4+2] Diels−Alder-like reactions between a series of methyl-substituted *cis*-1,3-butadienes and the aminoboranes $(F_3C)_2B{=}NR'_2$ ($R' = CH_3$, $CH_2CH_3$), forming the expected 1-aza-2-boracyclohex-4-enes (Scheme 1).[2] Intriguing features of the reactions included their lack of 1,3-diaza-2,4-diboracyclobutadiene side products (from dimerization of the aminoboranes) and that they occur below room temperature. However, most notable was the fact that the reactions apparently gave 100% regiospecificity for the 4-R″-1-aza-2-boracyclohex-4-ene product (Scheme 1). No 5-R″-1-aza-2-boracyclohex-4-ene isomer was detected. The mechanistic reasons for this outcome were not explored.

Regioselectivity in organic Diels−Alder cycloadditions is generally understood. Semiquantitative frontier molecular orbital concepts[3] or more sophisticated approaches[4] provide broadly accurate predictions of the favored isomer for a variety of substituted dienes and dienophiles. However, how one might apply these concepts to the aminoborane Diels−Alder reaction is not obvious. For example, the polar nature of the "double" bond might mean that small differences in charge/electron density on the terminal carbons of the diene will be more important in determining regiospecificity than would be true in the less polar organic system; aminoboranes might discriminate more completely than olefins. Furthermore, the polar, heteroatom nature of the double bond makes description of the aminoborane as an electron-rich or electron-poor dienophile difficult. Also, the substantial difference in bonding radii between boron and nitrogen might create a preference for a transition state or product where the smaller nitrogen encounters less steric crowding despite counterproductive electronic concerns.

**Scheme 1**



Over the past few years, my research group has computationally examined a variety of structures and reactions of amino- and iminoboranes, with an eye toward using chemical reactivity to evaluate the extent to which the B−N multiple bond behaves like a carbon−carbon multiple bond.[5] In keeping with this theme, studies of the basis for the regiospecificity in the Brauer/Bürger Diels−Alder reaction follow. As one might expect, the regiospecificity originates in the relative stabilities of the transition states, but the energetics involved and the discrimination shown by the aminoboranes proved quite remarkable.

## Computational Methods

All calculations were performed with the Gaussian 98 suite of programs.[6] Each molecule and transition state was fully

---

[1] Correspondence to this author at Northern Illinois University. E-mail: tgilbert@marilyn.chem.niu.edu.

[2] Ansorge, A.; Brauer, D. J.; Bürger, H.; Dörrenbach, F.; Hagen, T.; Pawelke, G.; Weuter, W. *J. Organomet. Chem.* **1990**, *396*, 253−267.

[3] Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*, 3rd ed.; Harper & Row: New York, 1987; Chapter 11.

[4] Kahn, S. D.; Pau, C. F.; Overman, L. E.; Hehre, W. J. *J. Am. Chem. Soc.* **1986**, *108*, 7381−7396.

[5] (a) Gilbert, T. M. *Organometallics* **1998**, *17*, 5513−5520. (b) Gilbert, T. M. *Organometallics* **2000**, *19*, 1160−1165. (c) Gilbert, T. M.; Gailbreath, B. D. *Organometallics* **2001**, *20*, 4727−4733. (d) Gilbert, T. M. *Organometallics* **2003**, *22*, 2298−2304.

10.1021/om030356u CCC: $25.00

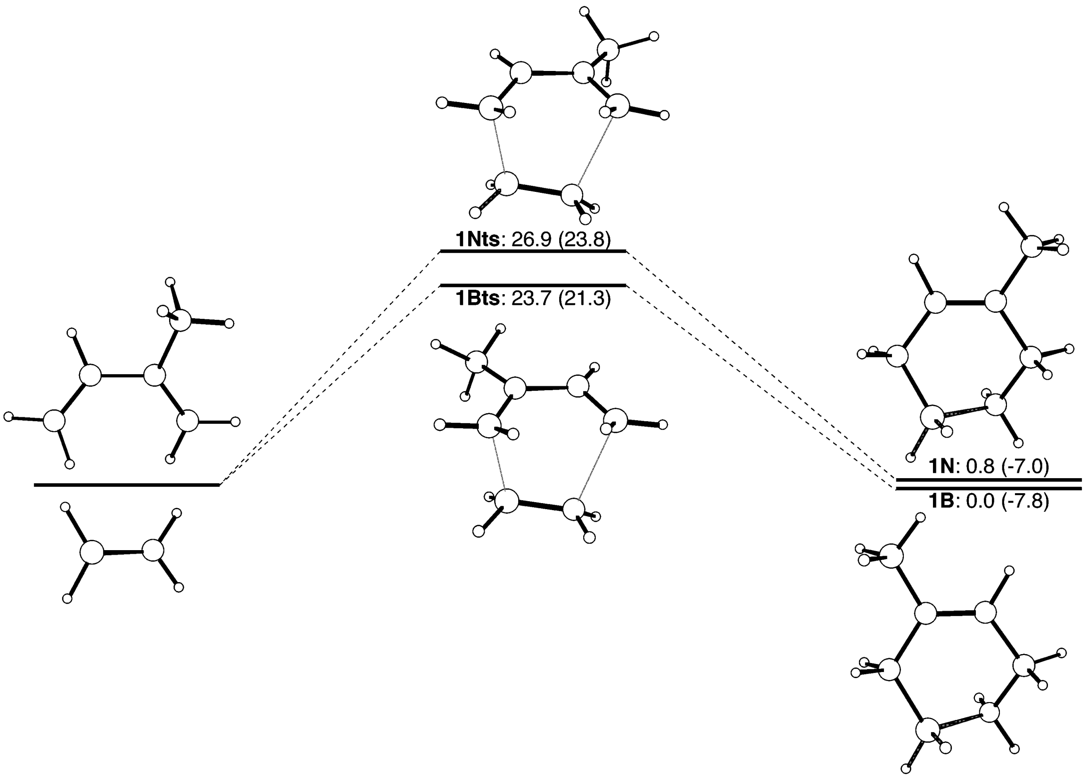


**Figure 1.** Structures and energies for the transition states and products on the reaction path for $H_2B{=}NH_2$ + *cis*-2-methyl-1,3-butadiene. Values in parentheses from the MP2/6-31+G(d) model; values without parentheses from the B3LYP/6-31+G(d) model.

optimized without constraints using the Hartree−Fock/6-31+G(d) approach. The natures of all stationary point structures were determined by analytical frequency analysis, which also provided zero-point energies (ZPEs). ZPEs were scaled by 0.9153 when used to correct the raw energy values.[7] The structures were then reoptimized at the B3LYP/6-31+G(d) and MP2/6-31+G(d) levels, except for the molecules derived from $(F_3C)_2B{=}NMe_2$, for which only the former model was employed.

Except as noted in the Results and Discussion section, the structural data for the species studied are unexceptional. Therefore structural data in the form of optimized Cartesian coordinates and of selected bond distances and angles, as well as absolute energies, for all the species reported at each correlated model employed are stored as Supporting Information. In general, the MP2 and B3LYP models predicted similar structures for the reaction components, so only the B3LYP/6-31+G(d) structural data are discussed hereafter. The only exceptions will be the transition state structures, for which the models tend to predict somewhat different distances for the forming B−C and N−C bonds.

Relative energies for the molecules studied appear in Figures 1 and 2 and Table 1. The correlated models predict somewhat different energies for those cases where comparisons were possible. One sees in the figures that the MP2 model consistently predicts lower activation barriers by ca. 3 kcal mol$^{-1}$ and more exothermic reactions by ca. 8 kcal mol$^{-1}$ than does the B3LYP model. Such observations are commonplace when the MP2 and B3LYP models are compared.[8] Since only the B3LYP/6-31+G(d) approach was used for the larger molecules, only these energetic data will be discussed hereafter.

Natural bond order (NBO) calculations were performed using the NBO subroutine in the Gaussian98 program.[9] B3LYP/6-31+G(d)-optimized structures were used as the starting points for these.

## Results and Discussion

**Overview of the $R_2B{=}NR_2'$ and *cis*-Butadiene Molecules.** The predicted structures of $H_2B{=}NH_2$ and $(F_3C)_2B{=}NMe_2$ have appeared previously,[5b] calculated using the 6-31G(d) basis set. Inclusion of diffuse functions here with the 6-31+G(d) basis set causes the B=N bond distances to change only by 0.004 Å for the parent aminoborane (to 1.397 Å) and 0.001 Å for the substituted one (to 1.382 Å). This further suggests that the experimentally determined B=N distance is artifactually long [1.43(2) Å], owing to correlation between the B−N and N−C distances.[10] More support for this view comes from comparison of the bonds peripheral to the BN core. The B−C bonds in $(F_3C)_2B{=}NMe_2$ lengthen substantially, from 1.617 to 1.626 Å. This brings the predicted structure more into line with the experimen-

---

(6) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, A D.; Rabuck, K. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople. J. A. *Gaussian 98*, Revision A.7; Gaussian, Inc.: Pittsburgh, PA, 1998.

(7) Scott, A. P.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 16502−16513.

(8) See, for example: Foresman, J. B.; Frisch, A. *Exploring Chemistry with Electronic Structure Methods*; Gaussian, Inc.: Pittsburgh, PA, 1993; Chapters 6 and 8.

(9) Gaussian NBO 3.1. Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899−926.

(10) Hausser-Wallis, R.; Oberhammer, H.; Bürger, H.; Pawelke, G. *J. Chem. Soc., Dalton Trans.* **1987**, 1839−1845.

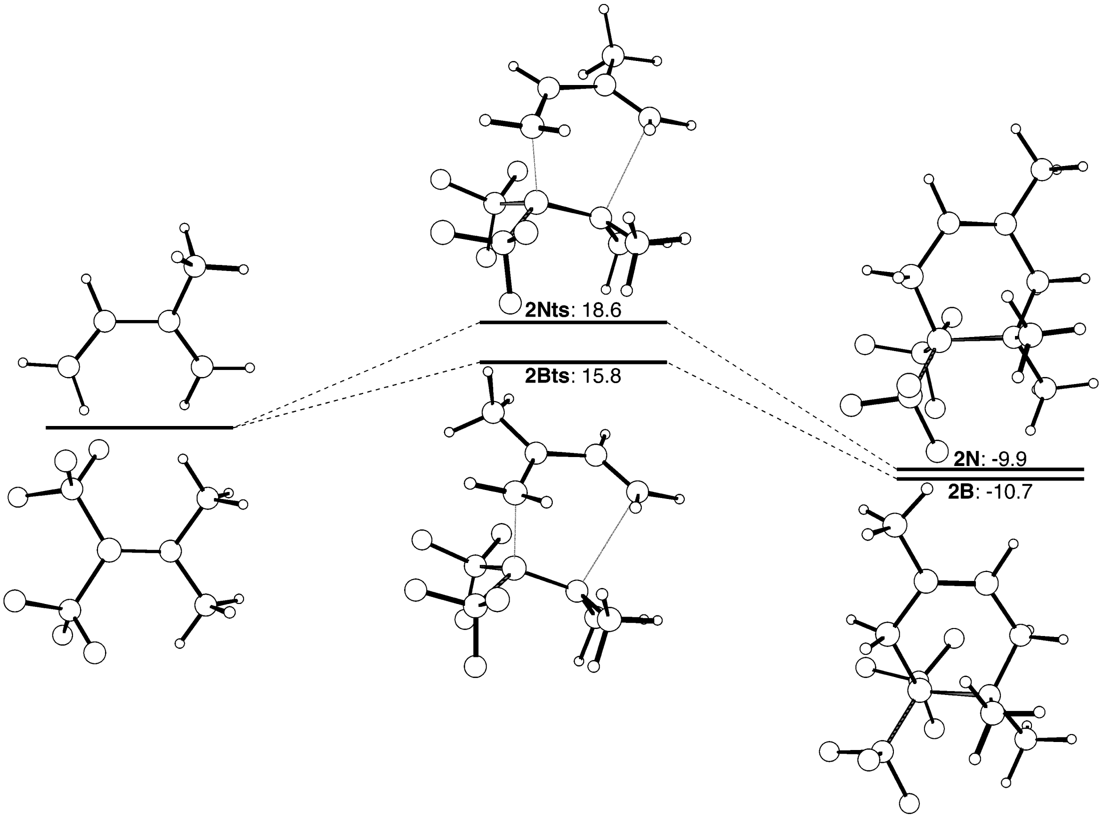


**Figure 2.** Structures and energies (B3LYP/6-31+G(d) model) for the transition states and products on the reaction path for $(F_3C)_2B{=}NMe_2$ + *cis*-2-methyl-1,3-butadiene.

**Table 1. Predicted Energies [6-31+G(d) basis set, kcal mol$^{-1}$] for [4+2] Diels−Alder Cyclization Reactions $R_2B{=}NR'_2 + H_2C{=}C(R'')CH{=}CH_2$**

| reaction | B3LYP barrier | B3LYP energy | MP2 barrier | MP2 energy |
|---|---|---|---|---|
| $H_2B{=}NH_2 + H_2C{=}C(Me)CH{=}CH_2 \rightarrow$ **1Bts** $\rightarrow H_2BNH_2CH_2CHC(Me)CH_2$, **1B** | 23.7 | 0.0 | 21.3 | −7.8 |
| $H_2B{=}NH_2 + H_2C{=}C(Me)CH{=}CH_2 \rightarrow$ **1Nts** $\rightarrow H_2BNH_2CH_2C(Me)CHCH_2$, **1N** | 26.9 | 0.8 | 23.8 | −7.0 |
| $(F_3C)_2B{=}NMe_2 + H_2C{=}C(Me)CH{=}CH_2 \rightarrow$ **2Bts** $\rightarrow (F_3C)_2BNMe_2CH_2CHC(Me)CH_2$, **2B** | 15.8 | −10.7 | | |
| $(F_3C)_2B{=}NMe_2 + H_2C{=}C(Me)CH{=}CH_2 \rightarrow$ **2Nts** $\rightarrow (F_3C)_2BNMe_2CH_2C(Me)CHCH_2$, **2N** | 18.6 | −9.9 | | |
| $H_2B{=}NH_2 + H_2C{=}C(NH_2)CH{=}CH_2 \rightarrow$ **3Bts** $\rightarrow H_2BNH_2CH_2CHC(NH_2)CH_2$, **3B** | 16.7 | −1.2 | 15.8 | −8.7 |
| $H_2B{=}NH_2 + H_2C{=}C(NH_2)CH{=}CH_2 \rightarrow$ **3Nts** $\rightarrow H_2BNH_2CH_2C(NH_2)CHCH_2$, **3N** | 30.4 | 3.4 | 27.0 | −4.7 |
| $(F_3C)_2B{=}NMe_2 + H_2C{=}C(NH_2)CH{=}CH_2 \rightarrow$ **4Bts** $\rightarrow (F_3C)_2BNMe_2CH_2CHC(NH_2)CH_2$, **4B** | 3.4 | −11.5 | | |
| $(F_3C)_2B{=}NMe_2 + H_2C{=}C(NH_2)CH{=}CH_2 \rightarrow$ **4Nts** $\rightarrow (F_3C)_2BNMe_2CH_2C(NH_2)CHCH_2$, **4N** | 20.2 | −7.4 | | |
| $H_2B{=}NH_2 + H_2C{=}C(CF_3)CH{=}CH_2 \rightarrow$ **5Bts** $\rightarrow H_2BNH_2CH_2CHC(CF_3)CH_2$, **5B** | 26.9 | −1.7 | 23.0 | −9.8 |
| $H_2B{=}NH_2 + H_2C{=}C(CF_3)CH{=}CH_2 \rightarrow$ **5Nts** $\rightarrow H_2BNH_2CH_2C(CF_3)CHCH_2$, **5N** | 24.0 | −1.5 | 20.9 | −9.0 |
| $(F_3C)_2B{=}NMe_2 + H_2C{=}C(CF_3)CH{=}CH_2 \rightarrow$ **6Bts** $\rightarrow (F_3C)_2BNMe_2CH_2CHC(CF_3)CH_2$, **6B** | 23.1 | −10.6 | | |
| $(F_3C)_2B{=}NMe_2 + H_2C{=}C(CF_3)CH{=}CH_2 \rightarrow$ **6Nts** $\rightarrow (F_3C)_2BNMe_2CH_2C(CF_3)CHCH_2$, **6N** | 20.8 | −10.5 | | |

tally determined one (B−C = 1.623(4) Å). However, the N−C bonds change little, lengthening slightly from 1.469 to 1.472 Å, putting them farther from the experimental values of 1.453(7) Å. This indicates that the experimental N−C distances are probably too short, in keeping with the B=N distance being too long.

The *cis*-butadienes exhibit the expected nonplanar structures, with C−C−C−C torsion angles ranging from 32.7° to 39.5°. The C=C bond lengths and C−C−C−C torsions appear to show a trend to decreasing lengths and smaller angles, respectively, as the electronegativity of the peripheral group increases. This is in accord with qualitative expectations.

**Reactions between *cis*-2-Methyl-1,3-butadiene and $R_2B{=}NR'_2$.** A comparison of the two pathways involving the parent aminoborane $H_2B{=}NH_2$ reacting with *cis*-2-methyl-1,3-butadiene leading to the isomeric products **1N** and **1B**[11] appears in Figure 1. One sees that the 1-aza-2-bora-4,5-cyclohexadienes are nearly isoenergetic, with **1B** slightly more stable. The struc-

---

[11] Transition states and products are labeled systematically as follows. An odd number implies a structure derived from $H_2B{=}NH_2$; an even number implies a structure derived from $(F_3C)_2B{=}NMe_2$. The letter N means a structure in which the peripheral group on the added butadiene lies near the nitrogen atom of the aminoborane, while B means a structure in which the peripheral group lies near the boron atom. Transition states are labeled ts.

tural parameters for both are nearly identical, except for the relative position of the methyl group. It thus appears that the regiospecificity of the reaction does not arise from a difference in stability of the isomeric rings. It should be noted that the models predict at best only slight exothermicity for the reaction, so its likelihood of occurring experimentally is low.

The transition states **1Nts** and **1Bts** leading to the products differ more in energy, with **1Bts** more stable by ca. 3 kcal $mol^{-1}$. This evidently accounts for the exclusive formation of **1B** experimentally. However, since the barriers are similar, it is plausible that if the reaction were conducted at high temperature rather than at 0 °C, both products might form.

The computational data do not provide an obvious structural reason for the greater stability of **1Bts**. The asymmetry of the transition states was discussed previously and is characteristic of an array of aminoborane cyclization reactions.[5,12] The bond distances and angles involving most atoms in the transition states are quite similar. Surprisingly, this includes the forming $B-C_B$ bond,[13] which is only slightly longer in **1Bts** than in **1Nts** (1.865 vs 1.863 Å). This argues against steric effects dictating the position of the methyl group in the transition state. The only significant structural difference between the two appears in the forming $N-C_N$ bonds, with that in **1Bts** some 0.05 Å longer than that in **1Nts** (2.310 vs 2.253 Å). This runs counter to the concept that a shorter distance implies a stronger interaction and therefore greater stability. Since in most of the systems discussed here the forming $N-C_N$ bond in the **nBts** transition state is longer than its analogue in the **nNts** transition state, it seems unlikely that this determines the relative stabilities of the transition states.

A comparison of the two pathways involving the substituted aminoborane $(F_3C)_2B{=}NMe_2$ reacting with *cis*-2-methyl-1,3-butadiene leading to **2N** and **2B** appears in Figure 2. Again the products are nearly isoenergetic, with the experimentally exclusive **1B** 0.8 kcal $mol^{-1}$ more stable. The two are structurally similar. Both predicted structures agree reasonable well with the experimental structure of the analogue derived from *cis*-2,3-dimethyl-1,3-butadiene determined by single-crystal X-ray diffraction; only the experimental B═N distance (1.621 Å) disagrees substantively with the computational prediction (1.674 Å). However, it is well-known that squeezing or stretching the dative single bond in $R_3B-NR_3$ molecules requires little energy,[14] so it is possible that the short experimental distance arises from solid state crystal-packing forces. Both pathways are reasonably exothermic, in keeping with the experimental formation of **2B** through this process. As above, the regiospecificity is traced to the 2.8 kcal $mol^{-1}$ greater stability of transition state **2Bts** as compared to **2Nts**. The barrier for the reaction is 15.8 kcal $mol^{-1}$, a value in keeping with the reaction occurring at 0 °C.

**Reactions between *cis*-2-Amino-1,3-butadiene and $R_2B{=}NR'_2$.** The predicted structural data for *cis*-2-amino-1,3-butadiene[15] show the nitrogen to prefer a somewhat pyramidal geometry, indicating that only a fraction of the lone pair electron density is donated to the carbon skeleton. However, this affects the reaction pathways substantially. Structurally, the transition states and products resemble those predicted above; thus the reader should mentally substitute amino groups for the butadiene methyl substituents in Figures 1 and 2 to envision the processes. The only notable differences appear in the distances for the forming $B-C_B$ bonds in the transition states. They are shorter in each case (1.863 vs 1.827 Å, **1Nts** vs **3Nts**; 1.865 vs 1.777 Å, **1Bts** vs **3Bts**; 1.816 vs 1.793 Å; **2Nts** vs **4Nts**; 1.824 vs 1.717 Å, **2Bts** vs **4Bts**), stemming from the greater Lewis basicity of the electron-rich butadiene.

Energetically, in both cases, the B-oriented products **3B** and **4B** are more stable than their counterparts **3N** and **4N** by ca. 4 kcal $mol^{-1}$ (Table 1). However, the major difference in the pathways arises in the transition states, where **3Bts** and **4Bts** are 11–17 kcal $mol^{-1}$ lower in energy than **3Nts** and **4Nts**. This obviously translates to a huge preference for the formation of **3B** and **4B**. Note that the increased stabilities of **3Bts** and **4Bts** correlate with their shorter B–CB bond forming distances as compared to those for **3Nts** and **4Nts**, in contrast to the situation above. The barriers here are lower than those for the methylbutadiene case above, so it is likely that $H_2B{=}NH_2$ would react with *cis*-2-aminobutadiene at a sufficiently low temperature for this to compete with [2+2] dimerization of the aminoborane. The barrier for the reaction involving $(F_3C)_2B{=}NMe_2$ is so low (3.4 kcal $mol^{-1}$) that it is difficult to conceive of competitive side reactions.[16] This might prove an excellent way to make precursors to boron-containing amino acids for boron neutron capture therapy.[17]

**Reactions between *cis*-2-Trifluoromethyl-1,3-butadiene and $R_2B{=}NR'_2$.** Again, the structural data for these systems resemble those for the methylated systems above, so Figures 1 and 2 represent the molecules well in general terms. As one would expect qualitatively, the electron poverty of the (trifluoromethyl)butadiene translates to long $B-C_B$ distances in the transition states (1.863 vs 1.962 Å, **1Nts** vs **5Nts**; 1.865 vs 1.923 Å, **1Bts** vs **5Bts**; 1.816 vs 1.897 Å; **2Nts** vs **6Nts**; 1.824 vs 1.912 Å, **2Bts** vs **6Bts)**.

The isomeric products **5N/5B** and **6N/6B** of the reactions between 2-(trifluoromethyl)butadiene and the aminoboranes are predicted to be essentially isoenergetic within a pair (Table 1), although again the B-oriented isomers appear very slightly more stable. However, in contrast to the results for the neutral donor methyl and donor amino butadienes, the N-oriented transition states **5Nts** and **6Nts** are predicted to lie 2–3 kcal $mol^{-1}$ below the B-oriented analogues **5Bts** and

---

(12) Hirao, H.; Fujimoto, H. *J. Phys. Chem. A* **2000**, *104*, 6649–6655.

(13) Hereafter, the carbon bonding to boron will have the symbol $C_B$ and that bonding to nitrogen $C_N$.

(14) Haaland, A. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 992–1007.

(15) The reader is reminded (courtesy of a reviewer) that parent eneamines rearrange readily to imines; thus 2-amino-1,3-butadiene does not exist as such at room temperature. We use this molecule simply as an example of an extremely electron-rich butadiene, such as the stable $CH_2{=}C(NMe_2)CH{=}CH_2$.

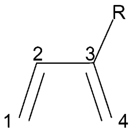
(16) A reviewer pointed out that a high-temperature process in which decyclization of **4B** became possible (because the barrier for this is only 14.9 kcal $mol^{-1}$) might allow the formation of side product **4N**, for which the decyclization barrier is 27.6 kcal $mol^{-1}$. Since these reactions are generally run at low temperatures, I had not considered this possibility, and thank the reviewer for suggesting it.

(17) Soloway, A. H.; Tjarks, W.; Barnum, B. A.; Rong, F.-G.; Barth, R. F.; Codogni, I. M.; Wilson, J. G. *Chem. Rev.* **1998**, *98*, 1515–1562.

**Table 2. NBO Charges, Using the B3LYP/6-31+G(d) Model**

| | B | | N | |
|---|---|---|---|---|
| $H_2B{=}NH_2$ | 0.409 | | −1.086 | |
| $(F_3C)_2B{=}NMe_2$ | 0.670 | | −0.661 | |
| | $(F_3C)_2$*C* | | *C*$(Me)_2$ | |
| $(F_3C)_2C{=}CMe_2$ | −0.284 | | 0.110 | |
| | 1[a] | 2 | 3 | 4 |
| *cis*-1,3-butadiene | −0.418 | −0.260 | −0.260 | −0.418 |
| *cis*-2-methyl-1,3-butadiene | −0.418<br>(0.000)[b] | −0.245<br>(0.015) | −0.063<br>(0.197) | −0.426<br>(−0.008) |
| *cis*-2-amino-1,3-butadiene | −0.411<br>(0.007) | −0.261<br>(−0.001) | 0.125<br>(0.385) | −0.526<br>(−0.108) |
| *cis*-2-trifluoromethyl-1,3-butadiene | −0.395<br>(0.023) | −0.259<br>(0.001) | −0.171<br>(0.089) | −0.363<br>(0.055) |

[a]



[b] Values in parentheses are with respect to *cis*-1,3-butadiene, i.e., charge on $C_n$ (*cis*-substituted-1,3-butadiene) − charge on $C_n$ (*cis*-1,3-butadiene).

**6Bts**. It thus appears that the experimentally plausible reaction between $(F_3C)_2B{=}NMe_2$ and 2-(trifluoromethyl)butadiene would provide nearly exclusively the isomer **6N**. The term "experimentally plausible" applies because the barriers associated with this reaction are relatively high, so that only the substituted aminoborane, which does not dimerize readily, will remain monomeric long enough to undergo the Diels−Alder reaction.

**NBO Calculations.** Regioselectivity in organic Diels−Alder reactions is framed in terms of orbital matching. Substituents that affect the charge or orbital coefficient on the terminal carbons of the diene direct the incoming dienophile to orient itself to accommodate this. The discussion below is couched in terms of charge, but one should realize that the charge derives from the orbital coefficient, so that the two correlate.

Table 2 gives the NBO charges on the boron and nitrogen atoms of the two aminoboranes.[18] One sees that the polar nature of the B═N double bond is reflected in the charges: the boron is substantially positive, and the nitrogen negative. The charges for the carbon atoms in $(F_3C)_2C{=}CMe_2$ are given for comparison. The polarity in the C═C bond is far smaller than that in the B═N bond. Thus one anticipates that the aminoboranes might discriminate more between the charges on the terminal carbons of the butadienes.

Charges for all carbons on the butadienes studied here as well as for *cis*-1,3-butadiene also appear in Table 2. One sees that substitution at the 3 position has little effect on the charges at carbons 1 and 2, implying that little of the donor/acceptor capacity of the substituent is exported to these. The strongly electron-withdrawing trifluoromethyl substituent increases the positive charge on the two, particularly on carbon 1, in line with expectation.

The charge on carbon 4 changes more dramatically than does that on carbon 1. Replacing the hydrogen with the weakly donating methyl group increases the negative charge slightly, substituting with the strongly donating amino group increases it by over 0.1 $e^-$, while substituting with the electron-withdrawing trifluoromethyl group decreases the negative charge by 0.05 $e^-$. All of these are in line with expectation, and they point directly to the origin of the regiospecificity in the Diels−Alder reaction. *cis*-2-Amino-1,3-butadiene carries an increased negative charge on carbon 4. This attracts the positively charged boron and repels the negatively charged nitrogen on the aminoborane, lowering the energy of **3Bts**/**4Bts** with respect to **3Nts**/**4Nts**. The energy difference tracks the size of the change in negative charge. Similarly, the increased positive charge on carbon 4 in *cis*-2-trifluoromethyl-1,3-butadiene repels the boron and attracts the nitrogen, so that attaining transition states **5Nts/6Nts** is easier than attaining **5Bts/6Bts**.

The reaction between *cis*-2-methyl-1,3-butadiene and the aminoboranes points out the high degree of discrimination the experimental reaction apparently obtains. The negative charge on carbon 4 increases only slightly when the methyl group replaces the hydrogen. Yet this translates to a difference of 3 kcal $mol^{-1}$ in the relative stabilities of transition states **1Bts**/**2Bts** vs **1Nts**/**2Nts**, and to exclusive formation of products **1B**/**2B**. This suggests that a number of pericyclic reactions that provide multiple products in organic systems might prove far more isomer-specific when aminoborane analogues are used.

## Conclusions

The computational data trace the regiospecificity of the Diels−Alder reaction between aminoboranes and 2-substituted butadienes to a high degree of discrimination between relative charges at the terminal carbons of the diene by the polar aminoborane B═N bond. The discrimination manifests itself in the relative energies of the isomeric transition states, which governs the product distributions. Since even the relatively small 3 kcal $mol^{-1}$ difference in transition state stabilities in the 2-methylbutadiene system translates to exclusive formation of one isomer experimentally, it is difficult to conceive of substituents that would provide a mixture of isomeric products. This should prove useful to synthesists searching for highly regiospecific processes involving boron or nitrogen compounds.

**Supporting Information Available:** Cartesian coordinates, absolute energies, and selected bond distances and angles of all molecules examined at the applicable model levels. This material is available free of charge via the Internet at http://pubs.acs.org.

OM030356U

---

(18) NBO charges are discussed here because they generally give more interpretable trends than do Mulliken charges. A useful discussion on this topic appears in: Bachrach, S. M. In *Reviews in Computational Chemistry*; Lipkowitz, K., Boyd, D. B., Eds.; VCH: New York, 1994; Vol. 5, Chapter 3. The trends in Mulliken charges from the G98 output mirror those for the NBO charges.