Computational Prediction of Regiospecificity in the [4+2] Diels–Alder Cyclizations between the Iminoborane $(F_3C)_3C-B\equiv N-(t\text{-}Bu)$ and Substituted *cis*-Butadienes

Thomas M. Gilbert[1]

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

Received September 1, 2005

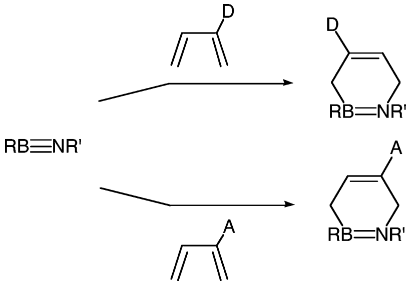
Density functional theory studies comparing the energetics of [4+2] Diels–Alder-like cyclizations of the iminoborane $(F_3C)_3C-B\equiv N-(t\text{-}Bu)$ with substituted *cis*-2-R-1,3-butadienes (R = CH_3, NH_2, CF_3) predict that some reactions will display regiospecificity derived from the transition state barrier heights. When R is an electronically near-neutral group (CH_3), the models predict no preference, and so no regiospecificity. When R is an electron-donating group (NH_2), the models predict a strong preference for the 5-R-1-bora-2-azacyclohexa-1,4-diene product; that is, the R group favors proximity to the boron atom. When R is an electron-withdrawing group (CF_3), the models predict a preference for the 4-R-1-bora-2-azacyclohexa-1,4-diene product, with the R group in proximity to the nitrogen atom. NBO charges provide an explanation for the specificity, in that the atomic charges within the transition state structures match properly for the orientations indicated. Frontier molecular orbital (FMO) coefficients of the reaction participants also support the suggested regiospecificities.

Introduction

While the “organic” reactions of aminoboranes [$(F_3C)_2B{=}NMe_2$, in particular] have been studied extensively,[2] considerably less is known of the analogous reaction chemistry of iminoboranes $RB\equiv NR$. This lack unquestionably reflects the preference for such molecules to oligomerize. Paetzold,[3] Nöth,[4] and co-workers initially developed the field of iminoborane reaction chemistry, and recently Meller[5] and co-workers have made important contributions. Germane to the work detailed herein, the former showed that iminoboranes containing bulky substituents react with cyclopentadiene at low temperatures to form bicyclic systems in Diels–Alder fashion. However, reactivity appeared limited to this diene, and oligomerization of the iminoborane represented a viable competing pathway.

Computational studies have suggested energetic parameters for the pericyclic reaction pathways for iminoboranes.[6] A key finding was that models predicted similar barriers and exothermicities for dimerization and for Diels–Alder cyclizations with dienes for the experimentally known $(F_5C_6)-B\equiv N-(t\text{-}Bu)$, but a strong preference for the latter pathway for the bulkier $(F_3C)_3C-B\equiv N-(t\text{-}Bu)$.[6b] Other computational work[7] provided an explanation for the regiospecificity observed when the aminoborane $(F_3C)_2B{=}NMe_2$ cyclizes with *cis*-2-methyl-1,3-butadiene[8] to form exclusively 4-Me-1-aza-2-boracyclohex-4-ene. This showed further that placing other electron-donating substituents such as NH_2 on the diene should provide this regioisomer, while dienes containing electron-withdrawing groups such as CF_3 should give the other regioisomer, 5-R-1-aza-2-boracyclohex-4-ene.

Scheme 1



The work described below combines these issues through computational study of the possibility of regiospecificity in the Diels–Alder-like cyclizations of the iminoborane $(F_3C)_3C-B\equiv N-(t\text{-}Bu)$. One might expect that the enhanced reactivity of triple bonds versus double bonds would result in decreased selectivity, but in fact the density functional theory (DFT) models employed indicate that iminoboranes should undergo cycloadditions that are regiospecific in accord with those of aminoboranes (Scheme 1). Regiospecificity derives from the relative stabilities of the transition states, in

---

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

[2] Pawelke, G.; Bürger, H. *Appl. Organomet. Chem.* **1996**, *10*, 147–174.

[3] (a) Paetzold, P. *Adv. Inorg. Chem.* **1987**, *31*, 123–170. (b) Paetzold, P. *Pure Appl. Chem.* **1991**, *63*, 345–350.

[4] Nöth, H.; Geisberger, G.; Linti, G.; Loderer, D.; Rattay, W.; Salzbrenner, E. *Pure Appl. Chem.* **1991**, *63*, 351–355.

[5] (a) v. Steuber, E.; Elter, G.; Noltemeyer, M.; Schmidt, H.-G.; Meller, A. *Organometallics* **2000**, *19*, 5083–5091. (b) Albrecht, T.; Elter, G.; Meller, A. *Chem. Commun.* **1998**, 2583.

[6] (a) Bissett, K. M.; Gilbert, T. M. *Organometallics* **2004**, *23*, 5048–5053. (b) Gilbert, T. M. *Organometallics* **2003**, *22*, 2298–2304. (c) Gilbert, T. M.; Gailbreath, B. D. *Organometallics* **2001**, *20*, 4727–4733.

[7] Gilbert, T. M. *Organometallics* **2003**, *22*, 3748–3752.

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

10.1021/om050754s CCC: $30.25

Table 1. Barriers and Energies (kcal/mol) of [4+2] Cyclizations between Substituted Butadienes and $(F_3C)_3C{-}B{\equiv}N{-}(t\text{-}Bu)$ (6-31+G* basis set)

product		MPW1K	MPW1	PBE1	MPW	PBE	Av[a]
2MeN	barrier	22.5	21.0	18.2	17.7	13.7	18.6
	energy	−24.5	−18.6	−22.1	−10.8	−15.7	−18.3
2MeB	barrier	22.2	20.9	18.1	17.7	13.5	18.5
	energy	−25.1	−19.2	−22.7	−11.6	−16.4	−19.0
2(NH$_2$)N	barrier	24.4	22.3	20.8	18.5	15.6	20.3
	energy	−24.7	−18.7	−21.0	−10.8	−14.6	−18.0
2(NH$_2$)B	barrier	8.7	8.7	6.9	7.3	4.1	7.1
	energy	−26.1	−20.2	−22.6	−12.6	−16.4	−19.6
2(CF$_3$)N	barrier	23.5	22.0	19.2	18.7	14.6	19.6
	energy	−25.4	−19.4	−23.0	−11.7	−16.7	−19.2
2(CF$_3$)B	barrier	28.6	26.3	23.4	20.9	17.3	23.3
	energy	−26.3	−20.4	−23.8	−12.6	−17.4	−20.1

[a] Av is the average of the five model energies. The reader is directed to the Computational Methods section for comments regarding the appropriateness of calculating an average of model energies.

some cases quite dramatically. NBO charge calculations provide a semiquantitative rationale for the observed energetics, in that the preferred reactions match the charges of the combining species optimally. Frontier molecular orbital (FMO) coefficients of the reacting species are also consistent with the suggested regiospecificities.

Computational Methods

All calculations were performed with the Gaussian98 suite of programs.[9] Each molecule and transition state was fully 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.[10] The structures were then reoptimized using the DFT models given in Table 1, which lists barriers (relative energies of the transition state structures) and energies (relative energies of the products). The mPWPW91 and mPW1PW91[11] (shortened to MPW and MPW1 in Table 1) and PBEPBE[12] and PBE1PBE[13] (shortened to PBE and PBE1 in Table 1) models were used as coded in the program; the MPW1k model was employed using the IOp procedure reported.[14] These were selected to provide a range of pure (mPWPW91, PBEPBE) and hybrid (mPW1PW91, MPW1K, PBE1PBE) approaches.

Multiple models were used to provide a computational "error bar" for the results.[15] Average values of the energies are given in Table 1. It should be noted, as was pointed out by a reviewer, that energetic calculations are not independent measurements that can be related statistically, but represent models with individual strengths and flaws. By way of defending the concept, here only second-generation[16] DFT models were used to calculate the averages; it would be more inappropriate to average energies from DFT and perturbation theory models, or from DFT models of substantially different generations (first and third, for example). However, it is true that calculating the averages of energies from different models is misleading. Moreover, the average values are not weighted and probably should be. It is known, for instance, that the MPW1K model generally predicts barriers accurately, but predicts too-exothermic reaction energies.[14] Similarly, pure DFT models such as MPW and PBE generally underestimate barriers (as they appear to in these calculations). The reader should understand that the averages here are meant to define the central points of the "error bars" and not to imply accurate statistical examination of the values. As a consequence, no standard deviations or the like were calculated. The averages should be viewed as guidelines rather than statistically correct mean values. This does not alter the discussion below.

To investigate whether the reaction energies were converged using the 6-31+G(d) basis set, test calculations were carried out employing the parent iminoborane $HB{\equiv}NH$. Its reaction energies with the three butadienes listed to form the parent analogues of **2MeN/2MeB**, **2(NH$_2$)N/2(NH$_2$)B**, and **2(CF$_3$)N/2(CF$_3$)B**[17] were determined using all models in Table 1 and the 6-31+G(d), 6-311+G(d), and 6-311++G(d,p) basis sets. The data indicated that expanding the basis set had little effect on the energies. For example, the MPW1K model predicted values of −55.8, −56.0, and −52.9 kcal/mol for the formation of the parent of **2(NH$_2$)N** as the basis set size increased, and similarly values of −57.9, −58.1, and −55.0 kcal/mol for the formation of the parent of **2(NH$_2$)B**. The relative energy trends were maintained through these tests as well. Thus the 6-31+G(d) basis set appears adequate to describe the reactions studied here using DFT approaches.

In general, the DFT models predict similar molecular structures. As a result, only optimized Cartesian coordinates using the MPW1K/6-31+G(d) model are stored as Supporting Information. Except as noted, the discussion below involves distances and angles predicted by this approach.

Natural bond order (NBO) calculations were performed using the NBO subroutine in the Gaussian98 program,[18] using the MPW1K/6-31+G(d)-optimized structures and wave functions.

Results and Discussion

Overview of $(F_3C)_3C{-}B{\equiv}N{-}(t\text{-}Bu)$, 1. The predicted structure of **1** at the B3LYP/6-31+G(d) level has appeared previously.[6b] Despite the extreme steric bulk of the substituents, the BN distance is quite short, with a predicted average of 1.237 ± 0.009 Å over the five models. The C−B−N−C core is predicted to be rigorously linear, with the substituents adopting a nearly eclipsed conformation. The latter is in keeping with a number of experimental and computational observa-

---

(9) 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.11; Gaussian, Inc.: Pittsburgh, PA, 1998.

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

(11) Adamo, C.; Barone, V. *J. Chem. Phys.* **1998**, *108*, 664−675. It should be noted that this functional was coded incorrectly into Gaussian 98, leading to a slight error. Commentary on this may be found on the World Wide Web at http://comp.chem.umn.edu/info/mpw1k.pdf.

(12) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *77*, 3865−3868.

(13) Perdew, J. P.; Burke, K.; Ernzerhof, M. *J. Chem. Phys.* **1996**, *105*, 9982−9985.

(14) Lynch, B. J.; Truhlar, D. G. *J. Phys. Chem. A* **2001**, *105*, 2936−2941.

(15) Check, C. E.; Gilbert, T. M. *J. Org. Chem.*, in press.

(16) Zhao, Y.; Pu, J.; Lynch, B. J.; Truhlar, D. G. *Phys. Chem. Chem. Phys.* **2004**, *6*, 673−676.

(17) Transition states and products are labeled systematically in the text and Table 2 as follows. The first digit 2 indicates a transition state or product derived from 1. The substituent on the butadiene is given next. The following letter N means a structure in which the peripheral group on the added butadiene lies near the nitrogen atom of the iminoborane, while B means a structure in which the peripheral group lies near the boron atom. Transition states are labeled ts.

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

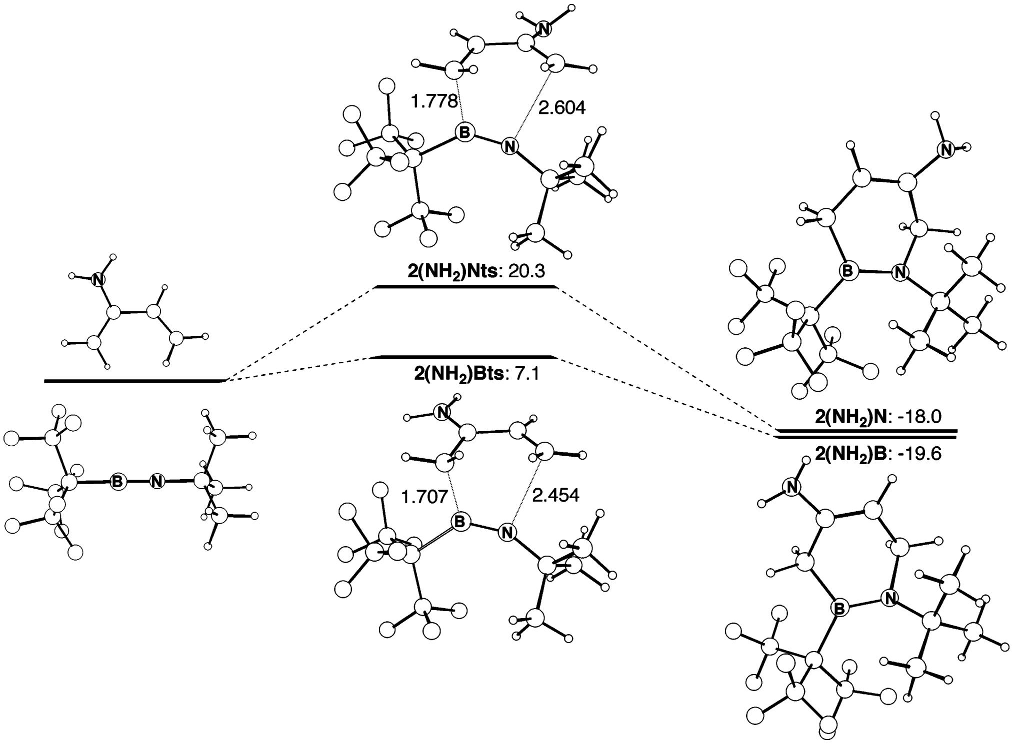


Figure 1. Predicted structures [MPW1K/6-31+G(d)] and energies (averages from Table 1) for the transition states and products on the reaction paths for **1** + *cis*-2-amino-1,3-butadiene.

tions, a recent example being the predicted structure of 2-butyne.[19]

Reactions between *cis*-2-Methyl-1,3-butadiene and 1. Predicted barriers and reaction energies for the two pathways for reaction between 1 and *cis*-2-methyl-1,3-butadiene leading to the isomeric products **2MeN** and **2MeB** appear in Table 1.[17] One sees that the barriers and energies are essentially identical, indicating little likelihood that this cyclization will exhibit regioselectivity.[20] This contrasts markedly with the analogous cyclization involving the aminoborane $(F_3C)_2B{=}NMe_2$, where the barrier leading to the boron-proximal product (i.e., the analogue to **2MeB**) was some 3 kcal/mol lower than that leading to the N-proximal isomer.[7] This suggests that the rule of thumb "greater reactivity means less selectivity" holds here for the more reactive iminoboranes as compared to the less reactive aminoboranes.

The predicted structural data are consistent with the observation of similar barriers and energies, in that they vary little between isomers. For example, the forming $B{-}C_B$[21] bond lengths in the transition states **2MeNts** and **2MeBts** are 1.776 and 1.801 Å, respectively, while the forming $N{-}C_N$ bond lengths are 2.568 and 2.684 Å. While these appear to differ quite a bit, when compared to the analogous values for the amino- and trifluoromethyl-substituted butadiene cyclizations (see below), they do not. By way of foreshadowing, the reader should note that both bond lengths in **2MeBts** are the longer of the pairs.

Reactions between *cis*-2-Amino-1,3-butadiene[22] and 1. The reaction energetics appear in Table 1 and in Figure 1. While the models predict similar exothermicities for the reactions (although **2(NH$_2$)B** appears slightly more stable), the barriers differ substantially. Transition state **2(NH$_2$)Bts** is predicted to lie some 13 kcal/mol lower in energy than **2(NH$_2$)Nts**, translating to a considerable preference for the formation of **2(NH$_2$)B** over **2(NH$_2$)N**. This process appears likely to exhibit complete regiospecificity for the former isomer.

The difference in barrier height correlates with the transition state structures. **2(NH$_2$)Bts** exhibits much shorter $B{-}C_B$ and $N{-}C_N$ distances than does **2(NH$_2$)Nts**. The former is 0.071 Å shorter; the latter 0.150 Å shorter. These differences contrast with those for **2MeBts** and **2MeNts** above, where the corresponding values are 0.025 and 0.118 Å, and where the former exhibit the *longer* distances. This suggests an exceptional difference between the ability of the electron-donating capacity of the amino and methyl groups to affect the reactivity in these systems. Put another way, the models indicate that the iminoboranes are so reactive that extreme donating groups must be present on the butadiene to create regioselectivity.

The preference for the amino group to occupy the site closest to the iminoborane boron mimics that observed in aminoboranes. This will be explored quantitatively

---

(19) Frolov, Y. L.; Knizhnik, A. V. *J. Struct. Chem.* **2002**, *43*, 856–857.

(20) A reviewer queried the inconsistency between these cyclizations displaying sizable barriers when the reaction between $(F_5C_6)B{\equiv}N(t\text{-}Bu)$ and cyclopentadiene occurs at low temperature. While the answer is not entirely certain as the requisite calculations and experiments have not yet been performed, the data in ref 6b indicate that cyclizations involving cyclopentadiene display lower barriers than those involving *cis*-butadiene, possibly due to decreased ring strain in the transition state for cyclizations involving the former.

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

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

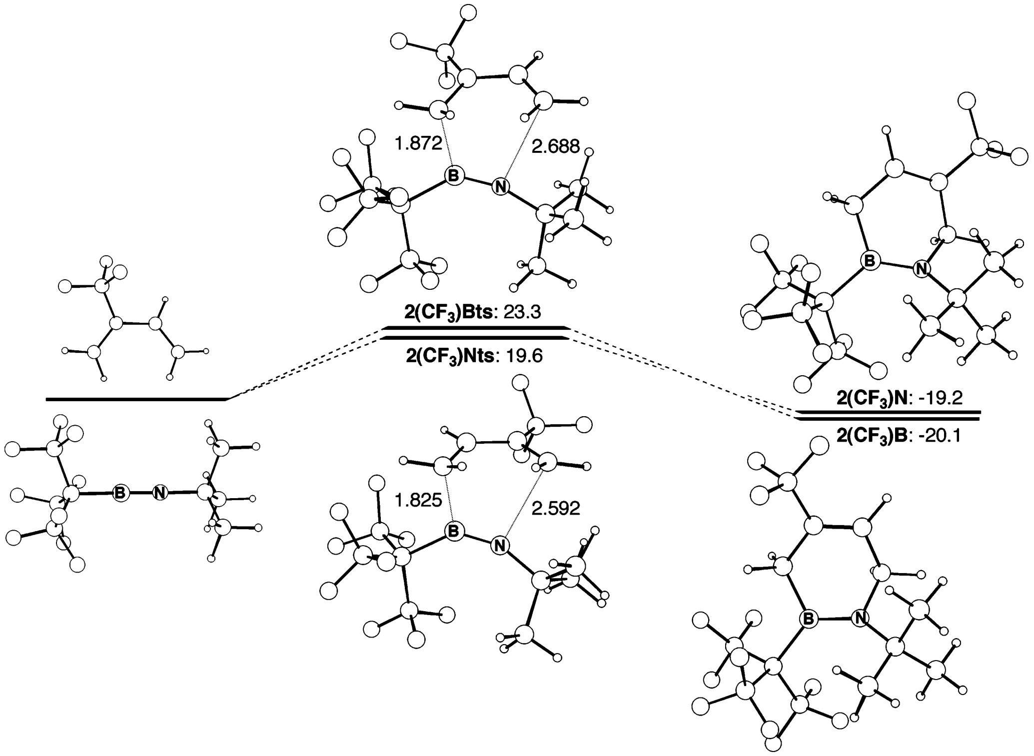


Figure 2. Predicted structures [MPW1K/6-31+G(d)] and energies (averages from Table 1) for the transition states and products on the reaction paths for **1** + *cis*-2-trifluoromethyl-1,3-butadiene.

below, but one can note for now that this orientation puts the electron-donor amino group (and its associated carbons) near the electron-acceptor boron, which makes intuitive sense.

Reactions between *cis*-2-Trifluoromethyl-1,3-butadiene and 1. Energetic data appear in Table 1 and Figure 2. The products **2(CF$_3$)B** and **2(CF$_3$)N** appear identically stable, but the barriers to them differ. In this case, transition state **2(CF$_3$)Nts** is more stable by ca. 4 kcal/mol, so it seems this cyclization will preferentially form the N-proximal isomer. The stability gap between transition states is smaller than that for the amino systems above, so one speculates that this cyclization is likely to be regioselective rather than regiospecific. However, it was previously observed that the completely regiospecific cyclization between $(F_3C)_2B{=}NMe_2$ and 2-methylbutadiene apparently results from a difference in barrier energy of only ca. 3 kcal/mol.[7] It is exciting to see that, even with very reactive iminoboranes, electron-rich butadienes will apparently give one cyclic isomer, while electron-poor butadienes will give the other.

Again the structural data correlate with barrier energy. As one would expect qualitatively, the electron poverty of the (trifluoromethyl)butadiene translates to **2(CF$_3$)Nts** and **2(CF$_3$)Bts** exhibiting the longest B$-$C$_B$ distances in any transition state studied (Figure 2). As one would expect from the discussion above, the preferred transition state **2(CF$_3$)Nts** exhibits the shorter B$-$C$_B$ and N$-$C$_N$ distances. The difference between B$-$C$_B$ distances of 0.047 Å is longer than that seen for the methylbutadiene case above (0.025 Å), again characterizing the lack of electronic distinction and in turn lack of regioselectivity in the latter.

Interestingly, the N$-$C$_N$ distances in the transition states are quite similar to those of **2MeNts** and **2MeBts**, suggesting that they represent very weak, dispersion-like interactions rather than partially formed bonds. However, this suggestion remains unproven because our previous studies showed that N$-$C$_N$ distances in forming bonds are quite model dependent, in particular being much shorter in MP2 calculations than in B3LYP calculations.[6,7]

NBO and FMO 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 iminoborane **1**.[23] The charges reflect the polar nature of the B≡N triple bond: the boron is substantially positive, and the nitrogen negative. Charges for carbons of the butadienes studied here also appear in Table 2. One sees that the charges at carbon CH (adjacent to the substituted carbon C$_{sub}$) and the β carbon CH$_2\beta$ change little regardless of the donor/acceptor capacity of the substituent. In contrast, the charge on CH$_2\alpha$ changes substantially and predictably, becoming more negative when the donor NH$_2$ is the substituent and more positive when the acceptor CF$_3$ is. Comparing charges on CH$_2\alpha$, and CH$_2\beta$, one sees that the two are nearly identical for 2-methylbutadiene, that CH$_2\alpha$ is substantially more negative for 2-aminobuta-

---

[23] 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.

Table 2. NBO Charges on Various Atoms in the Transition States and Products (MPW1K/6-31+G* level)

	B	N	$CH_2\alpha$	C_{sub}	CH	$CH_2\beta$
1	0.917	−0.785				
$CH_2C(Me)CHCH_2$			−0.441	−0.064	−0.253	−0.431
$CH_2C(NH_2)CHCH_2$			−0.554	0.139	−0.266	−0.418
$CH_2C(CF_3)CHCH_2$			−0.374	−0.179	−0.269	−0.407

	B	N	C_B	C_{sub}	CH	C_N
2MeNts	0.821	−0.797	−0.737	−0.150	−0.038	−0.272
2MeN	1.053	−0.800	−0.911	−0.056	−0.204	−0.279
2MeBts	0.817	−0.819	−0.740	0.179	−0.336	−0.277
2MeB	1.053	−0.797	−0.903	0.009	−0.267	−0.292
2(NH$_2$)Nts	0.815	−0.781	−0.728	0.054	−0.085	−0.335
2(NH$_2$)N	1.041	−0.787	−0.905	0.145	−0.300	−0.288
2(NH$_2$)Bts	0.813	−0.853	−0.814	0.362	−0.398	−0.257
2(NH$_2$)B	1.017	−0.772	−0.904	0.216	−0.381	−0.288
2(CF$_3$)Nts	0.829	−0.794	−0.701	−0.260	−0.044	−0.259
2(CF$_3$)N	1.032	−0.780	−0.918	−0.188	−0.123	−0.284
2(CF$_3$)Bts	0.833	−0.784	−0.693	0.010	−0.311	−0.291
2(CF$_3$)B	1.039	−0.781	−0.909	−0.117	−0.197	−0.303

Table 3. Orbital Coefficients[a] on Various Atoms in 1 and *cis*-Butadienes (MPW1K/3-21G level)

	B	N	$CH_2\alpha$	C_{sub}	CH	$CH_2\beta$
1[b]	0.496	0.425				
$CH_2C(Me)CHCH_2$[c]			0.339	0.251	0.216	0.292
$CH_2C(NH_2)CHCH_2$[c]			0.424	0.194	0.085	0.152
$CH_2C(CF_3)CHCH_2$[c]			0.292	0.218	0.271	0.320

[a] The coefficients are the absolute values for the "outer" components of the valence atomic orbitals (designated $3p_z$ in program output). [b] Coefficients for the lowest-lying B−N π* orbitals (LUMO pair of *E* symmetry) for **1** constrained to C_{3v} symmetry. Coefficients for π* MOs built from atomic p_x and p_y orbitals are identical by symmetry. [c] Coefficients for the HOMOs of the butadienes where the C4 core was fixed in a coplanar conformation.

diene, and that $CH_2\beta$ is somewhat more negative for 2-trifluoromethylbutadiene. It is largely these relative charges on the CH_2 moieties, and how they match that on the boron atom, that determine the regiospecificity in the Diels−Alder reaction.

The **2Me** systems show marked charge consistency for both the transition state and product isomers. Except for atoms C_{sub} and CH, which are not directly bonding to the iminoborane, the charges on related atoms differ by less than 0.03 e$^-$. This again points to a likely lack of regioselectivity for this cyclization. However, the charge on C_B in amino-substituted **2(NH$_2$)Bts** is nearly 0.1 e$^-$ more negative than that in **2(NH$_2$)Nts**. One can view this as the boron inducing C_B to increase its negative charge, so as to accommodate boron's positive charge. Atom C_B corresponds to $CH_2\alpha$ in the free diene for the former and to $CH_2\beta$ in the latter. The former C_B has a more negative charge and can more efficiently use the donor properties of the amino group to increase its negative charge in the transition state; thus the boron prefers to bind to it. Thus **2(NH$_2$)Bts** is preferred over **2(NH$_2$)Nts**, so formation of **2(NH$_2$)B** dominates. An analogous analysis applies to the trifluoromethyl-substituted systems. The more negatively charged $CH_2\beta$ of the free diene binds to the positively charged boron, giving rise to a preference for transition state **2(CF$_3$)Nts** and for isomer **2(CF$_3$)N**. The electron-acceptor characteristics of the CF_3 group augment this preference in that C_N, which corresponds to $CH_2\alpha$ in **2(CF$_3$)Nts**, exhibits a more positive charge because the nearby CF_3 group can withdraw electrons efficiently. This makes the CH_2 group more attractive to the negatively charged nitrogen atom.

Frontier molecular orbital (FMO) theory provides further support for the suggested regioselectivities. As noted above, the charge and coefficient are related, so this support is not entirely independent. However, FMO theory complements the discussion of charges in transition states by focusing on orbital coefficients in the reactants as its gauge in predicting regioselectivity.[24] Coefficients for **1** and the three *cis*-butadienes appear in Table 3. (For ease in interpretation, these were determined at the MPW1K/3-21G level.) One sees that the larger coefficients of the π* orbitals of dienophile **1** lie on the boron. In the methyl- and amino-substituted butadienes, the terminal carbon bearing the largest coefficient in the HOMO is $CH_2\alpha$ (that adjacent to the substituted carbon). Alignment of the largest coefficients of diene and dienophile thus predicts a preference for formation of **2MeB/2(NH$_2$)B**, in concert with the transition state energies and charges. The substantial difference between the values of the coefficients for 2-aminobutadiene (0.272) indicates a strong preference for the favored isomer; the smaller difference for 2-methylbutadiene (0.047) suggests a smaller preference, if any. 2-Trifluoromethylbutadiene exhibits a larger coefficient on $CH_2\beta$, marking a preference for isomer **2(CF$_3$)N**. The small difference between coefficient values (0.028) is in keeping with the small difference in stabilities between **2(CF$_3$)Nts** and **2(CF$_3$)Nts**. Overall, the FMO results mirror the NBO charge results and support the observed differences in transition state energies.

Conclusions

The computational data suggest that 2-substituted butadienes containing good electron donors will exhibit considerable regioselectivity, and likely regiospecificity, when allowed to react with appropriate iminoboranes in a Diels−Alder fashion. Butadienes containing acceptors will probably show regioselectivity, but may not be regiospecific. Those with neutral substituents such as methyl will probably show minimal or no selectivity. All these predictions stem from the ability of the polar iminoborane B≡N bond to discriminate between relative charges/coefficients at the terminal carbons of the diene. Discrimination manifests itself in the relative energies of the isomeric transition states, which governs the product distributions. Iminoboranes do not discriminate as effectively as aminoboranes appear to, a result likely stemming from the greater reactivity of the triple bond versus the double bond.

Supporting Information Available: Cartesian coordinates and absolute energies of all molecules examined at the MPW1K/6-31+G(d) level. This material is available free of charge on the Internet at http://pubs.acs.org.

OM050754S

---

[24] The literature regarding FMO theory is vast. Two papers of use in preparing this one were: (a) Hirao, H.; Ohwada, T. *J. Phys. Chem. A* **2005**, *109*, 816−824. (b) Kahn, S. D.; Pau, C. F.; Overman, L. E.; Hehre, W. J. *J. Am. Chem. Soc.* **1986**, *108*, 7381−7396.