Organometallics **2003,** *22,* 2298−2304

Computational Studies of Pericyclic Reactions of Iminoboranes. [4+2] Diels−Alder vs [2+2] Dimerization of RB≡NR′ Compounds

Thomas M. Gilbert[1]

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

Received February 7, 2003

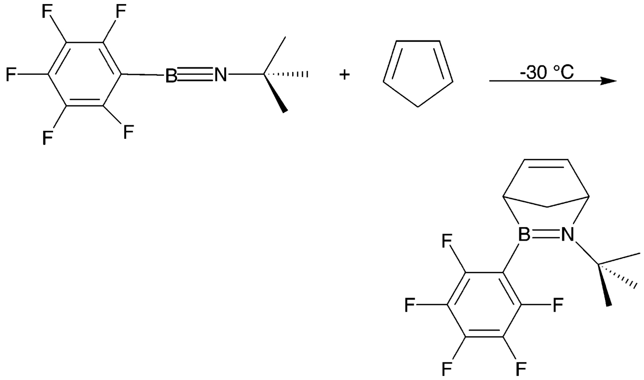
Computational studies comparing the energetics of [2+2] dimerization of iminoboranes RB≡NR′ (R = H, Me, CF_3, C_6F_5, t-C_4F_9; R′ = H, Me, t-C_4H_9) with their [4+2] Diels−Alder-like cyclizations with *cis*-butadiene and cyclopentadiene show that generally the product distributions depend on the transition state barrier heights rather than the reaction exothermicities. Dimerization is favored when the iminoborane carries small substituents; a slight preference exists for the [4+2] reaction for (F_5C_6)B≡N(t-C_4H_9), while the very bulky (t-F_9C_4)B≡N(t-C_4H_9) strongly prefers the [4+2] cyclization reaction. These results concur with the limited experimental data available. The data suggest general characteristics for iminoboranes likely to prefer [4+2] cyclization to dimerization. Also, the use of cyclopentadiene as the eneophile is contraindicated because of the strain incorporated into the azaborabicycloheptadiene product. Iminoborane [4+2] reactions employing acyclic dienes such as *cis*-butadiene or larger cyclic dienes such as 1,3-cyclohexadiene appear more likely to succeed.

Introduction

In 1979, Paetzold and co-workers reported the observation of a [4+2] Diels−Alder reaction between cyclopentadiene and the iminoborane (F_5C_6)B≡N(t-C_4H_9), forming the expected heterobicycloheptadiene (Scheme 1).[2] This reaction was notable for two major reasons: it showed that properly designed iminoboranes (the boron−nitrogen analogues of alkynes) will preferentially react with dienes rather than oligomerize to diazadiboracyclobutadienes or borazines,[3] and it occurred below room temperature, whereas most organic Diels−Alder reactions of dienes and alkynes require elevated temperatures. Unfortunately, further exploration of the scope of this reaction has not appeared in the literature; Paetzold stated in a later review[4] that only the above reaction and an analogous one using (Me_3Si)(t-C_4H_9)N−B≡N(t-C_4H_9)[5] provided [4+2] cycloaddition products.

Over the past few years, my research group has computationally examined a variety of structures and reactions of “doubly” and “triply” bonded group 13−group 15 systems, with an eye toward using chemical reactivity to evaluate the extent to which the group 13−15 atom “multiple bond” behaves like a carbon−carbon multiple bond.[6] It appeared worthy to examine Paetzold’s iminoborane reactions, both to investigate further how closely these alkyne analogues mimic alkynes in their reactivity and to determine how peripheral group substitution of the iminoboranes affects the energetics of the reactions and “tips the balance” from [2+2] dimerization to [4+2] Diels−Alder chemistry. Detailed studies of reactions involving the parent HB≡NH, the methyl-substituted MeB≡NMe, the fluorinated (F_3C)B≡NCH_3, the extremely bulky (t-F_9C_4)B≡N(t-C_4H_9), and the experimentally employed molecule (F_5C_6)B≡N(t-C_4H_9) appear below.

Scheme 1



Computational Methods

All calculations were performed with the GAUSSIAN 98 suite of programs.[7] Each molecule was fully optimized without constraints using the Hartree−Fock model and either the 6-31+G* basis set (for compounds involving smaller iminoboranes) or the 3-21G basis set (for compounds involving (t-F_9C_4)B≡N(t-C_4H_9) and (F_5C_6)B≡N(t-C_4H_9)). The natures of all stationary point structures were determined by analytical

---

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

[2] Paetzold, P.; Richter, A.; Thijssen, T.; Würtenberg, S. *Chem. Ber.* **1979**, *112*, 3811−3827.

[3] For recent examples, see: v. Steuber, E.; Elter, G.; Noltemeyer, M.; Schmidt, H.-G.; Meller, A. *Organometallics* **2000**, *19*, 5083−5091, and references therein.

[4] Paetzold, P. *Adv. Inorg. Chem.* **1987**, *31*, 123−170.

[5] Paetzold, P.; Schröder, E.; Schmid, G.; Boese, R. *Chem. Ber.* **1985**, *118*, 3205−3216.

[6] (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.

10.1021/om0300880 CCC: $25.00
Publication on Web 04/24/2003

Table 1. Predicted Structural Data for RB≡NR′ Molecules

	MP2/6-31+G*			B3LYP/6-31+G*		
	B≡N	B−H	N−H	B≡N	B−H	N−H
HB≡NH	1.250	1.172	0.999	1.241	1.172	0.996
	B≡N	B−C	N−C	B≡N	B−C	N−C
MeB≡NMe	1.254	1.550	1.420	1.244	1.547	1.412
$(F_3C)B{\equiv}NMe$	1.246	1.577	1.422	1.235	1.577	1.415
$(F_5C_6)B{\equiv}N(t\text{-}C_4H_9)$				1.241	1.529	1.428
$(t\text{-}F_9C_4)B{\equiv}N(t\text{-}C_4H_9)$				1.235	1.575	1.432

frequency analysis, which also provided zero-point energies (ZPEs). ZPEs were scaled by the appropriate factor when used to correct the raw energy values.[8] The structures were then reoptimized at the B3LYP/6-31+G* and MP2/6-31+G* levels, save for the largest molecules, for which only the former model was employed.

The structural and energetic data for the molecules studied appear in the figures and tables. In general, the MP2 and B3LYP models predicted similar structures for the reactant iminoboranes and the cyclic products, so only the B3LYP/6-31+G* structural data are discussed hereafter. The models generally predicted somewhat different structures for the transition states, so typically both results are discussed below. Optimized Cartesian coordinates for all the molecules reported at each correlated model employed are available as Supporting Information.

The correlated models predict somewhat different energies for those cases where comparisons were possible. One sees in Table 2 that the MP2 model consistently predicts lower activation barriers and more exothermic reactions than does the B3LYP model. However, the extent of the difference between models appears random, varying from 1 to 14 kcal mol^{-1}. Such observations are commonplace when the MP2 and B3LYP models are compared.[9] Truhlar and co-workers have shown that both models generally perform only fairly at predicting barrier heights and transition state geometries.[10] However, they are minimally resource-intensive and accepted and appreciated by the chemical community at large, so they were used here. Since only the B3LYP/6-31+G* approach was used for the larger molecules (the MP2/6-31+G* approach for molecules containing more than about 20 non-hydrogen atoms requires more computer resources than currently available in our environment), only these energetic data will be discussed hereafter, but the reader may wish to refer to the tables for MP2 data where available.

Results and Discussion

Overview of the RB≡NR′ Molecules. The predicted structures of HB≡NH and MeB≡NMe have appeared previously;[6b] those for $(F_3C)B{\equiv}NMe$, $(F_5C_6)B{\equiv}N(t\text{-}C_4H_9)$, and $(t\text{-}F_9C_4)B{\equiv}N(t\text{-}C_4H_9)$ are reported here for the first time. As expected, all five are calculated to have collinear R−B≡N−R atoms with short B−N distances. No structural parameters seem exceptional, so for brevity characteristic data are collected in Table 1 rather than in the figures. One sees the expected shortening of the B≡N bond when comparing that for MeB≡NMe with that for $(F_3C)B{\equiv}NMe$, where the electron-withdrawing fluoroalkyl groups increase the boron's Lewis acidity. Concomitantly, the B−C distance lengthens. This contrasts with the behavior of $(F_3C)C{\equiv}CMe$ vs MeC≡CMe, where the C−C single bond lengths are similar.[11] Similar B−C bond lengthening was observed in $(F_3C)_2B{=}NMe_2$ and was ascribed to repulsion between the boron and carbon atoms owing to their both carrying a positive charge.[12] The steric demands of the *tert*-butyl group on the nitrogen as compared to a methyl group result in a ca. 0.016 Å lengthening of the N−C bond.

Reactions of HB≡NH. The dimerization of the parent aminoborane appears in Figure 1a. The dimer, 1,3-diaza-2,4-diboracyclobutadiene, appears to the right in the figure with some structural data. The parameters predicted here agree with those published previously.[6b] The structure of the transition state, which has not been previously described, appears to the left in the figure. It lies early in the reaction coordinate, as judged by the length of the forming B−N bonds (ca. 2.2 Å) vs the B−N bond lengths in the dimer (ca. 1.45 Å). The transition state is rather asymmetric, with one forming B−N bond shorter than the other, and the B≡N triple bonds exhibiting different lengths. It is also “puckered”, in that the two borons and two nitrogens are not coplanar. This observation mimics that observed when one models the dimerization of ethyne. For the organic system, the [2+2] dimerization is orbital symmetry-forbidden; thus its “transition state” shows the alkynes nearly at right angles to each other. The B3LYP and MP2 models predict the associated B−N−B−N torsion angle τ in the iminoborane transition state to be 16.9° and 36.4°, respectively. The difference between models appears substantial; however, since the models predict similar barriers, the energy required to twist the iminoboranes with respect to each other is probably small. This view finds support in potential energy scans around the transition state using the B3LYP model; the data suggest that changes of more than 40° in the B−N−B−N torsion require little energy. Table 2 gives the reaction energetics; one can see that the dimerization is quite exothermic (ca. 50 kcal mol^{-1}), but has an appreciable activation energy (ca. 17 kcal mol^{-1}).

The computationally predicted transition state and product of the [4+2] Diels−Alder reaction between HB≡NH and *cis*-butadiene appear in Figure 1b. The product 1-aza-2-bora-1,4-cyclohexadiene shows no unusual structural features. Like its all-carbon analogue, it is planar. The B−N bond distance of 1.398 Å suggests the presence of a B−N double bond rather than a single or dative bond.

The transition state shows a marked asymmetry. The boron atom lies 2.005 Å from its bonding carbon, while

---

(7) 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.

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

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

(10) (a) Lynch, B. J.; Truhlar, D. G. *J. Phys. Chem. A* **2002**, *106*, 842−846. (b) Lynch, B. J.; Truhlar, D. G. *J. Phys. Chem. A* **2001**, *105*, 2936−2941. (c) Lynch, B. J.; Fast, P. L.; Harris, M.; Truhlar, D. G. *J. Phys. Chem. A* **2000**, *104*, 4811−4815.

(11) Laurie, V. W. *J. Chem. Phys.* **1959**, *30*, 1101−02.

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

Table 2. Predicted Reaction Energies for RB≡NR Systems, Using the 6-31+G* Basis Set

	MP2		B3LYP	
reaction	barrier	energy	barrier	energy
$HB{\equiv}NH + HB{\equiv}NH \rightarrow$ $HBNHBHNH$	16.0	−51.8	17.7	−48.6
$HB{\equiv}NH + cis\text{-}CH_2CHCHCH_2 \rightarrow$ $HBNHCH_2CHCHCH_2$	17.2	−42.2	19.0	−38.7
$HB{\equiv}NH + cC_5H_6 \rightarrow$ $HBNHCHCHCHCH(\mu\text{-}CH_2)$	15.4	−18.9	19.8	−9.8
$MeB{\equiv}NMe + MeB{\equiv}NMe \rightarrow$ $MeBN(Me)B(Me)NMe$	14.3	−50.4	18.5	−43.0
$MeB{\equiv}NMe + cis\text{-}CH_2CHCHCH_2 \rightarrow$ $MeBN(Me)CH_2CHCHCH_2$	17.7	−41.3	22.8	−33.6
$MeB{\equiv}NMe + cC_5H_6 \rightarrow$ $MeBN(Me)CHCHCHCH(\mu\text{-}CH_2)$	14.2	−21.1	23.3	−7.8
$(F_3C)B{\equiv}NMe + (F_3C)B{\equiv}NMe \rightarrow$ $(F_3C)BN(Me)B(CF_3)N(Me)$	5.3	−62.4	12.2	−55.5
$(F_3C)B{\equiv}NMe + cis\text{-}CH_2CHCHCH_2 \rightarrow$ $(F_3C)BN(Me)CH_2CHCHCH_2$	7.5	−53.2	11.6	−45.0
$(F_3C)B{\equiv}NMe + cC_5H_6 \rightarrow$ $(F_3C)BN(Me)CHCHCHCH(\mu\text{-}CH_2)$	4.4	−31.3	10.9	−18.0

	B3LYP	
reaction	barrier	energy
$(F_5C_6)B{\equiv}N(t\text{-}C_4H_9) + (F_5C_6)B{\equiv}N(t\text{-}C_4H_9) \rightarrow$ $(F_5C_6)BN(t\text{-}C_4H_9)B(C_6F_5)N(t\text{-}C_4H_9)$	23.4	−40.0
$(F_5C_6)B{\equiv}N(t\text{-}C_4H_9) + cis\text{-}CH_2CHCHCH_2 \rightarrow$ $(F_5C_6)BN(t\text{-}C_4H_9)CH_2CHCHCH_2$	22.0	−23.9
$(F_5C_6)B{\equiv}N(t\text{-}C_4H_9) + cC_5H_6 \rightarrow$ $(F_5C_6)BN(t\text{-}C_4H_9)CHCHCHCH(\mu\text{-}CH_2)$	20.8	−4.0
$(t\text{-}F_9C_4)B{\equiv}N(t\text{-}C_4H_9) + (t\text{-}F_9C_4)B{\equiv}N(t\text{-}C_4H_9) \rightarrow$ $(t\text{-}F_9C_4)BN(t\text{-}C_4H_9)B(t-F_9C_4)N(t\text{-}C_4H_9)$	38.4	−1.6
$(t\text{-}F_9C_4)B{\equiv}N(t\text{-}C_4H_9) + cis\text{-}CH_2CHCHCH_2 \rightarrow$ $(t\text{-}F_9C_4)BN(t\text{-}C_4H_9)CH_2CHCHCH_2$	27.8	−2.7
$(t\text{-}F_9C_4)B{\equiv}N(t\text{-}C_4H_9) + cC_5H_6 \rightarrow$ $(t\text{-}F_9C_4)BN(t\text{-}C_4H_9)CHCHCHCH(\mu\text{-}CH_2)$	25.2	7.8

the nitrogen atom lies 2.698 Å from its bonding carbon (hereafter, the carbon bonding to boron will have the symbol C_B and that bonding to nitrogen C_N). The B−N bond distance of 1.293 Å is only 0.05 Å longer than that predicted for free HB≡NH, while 0.1 Å shorter than that in the azaboracyclohexadiene product. Thus one should view the transition state as “early” on the reaction coordinate. Furthermore, the data suggest that the cyclization should be viewed as initially a Lewis acid−base reaction between the electron-poor boron and the donor ene π bond. Once this occurs, and the transition state is attained, the boron and C_B need move only ca. 0.42 Å to bond fully, while the nitrogen and C_N must move ca. 1.2 Å to complete their bonding.

The transition state asymmetry recalls that predicted computationally for [4+2] Diels−Alder reactions between aminoboranes $R_2B{=}NR_2$ and *cis*-butadiene.[6a] There the asymmetry was characterized as repulsion between the nitrogen and C_N, which was overcome through bonding of the boron to C_B followed by withdrawal of electron density from C_N through resonance, making C_N sufficiently Lewis acidic to attract the basic nitrogen. Subsequently, Hirao and Fujimoto refocused this argument,[13] suggesting that the Lewis acidity of the boron dominates the structure of the transition state. Their view held that the boron bonding to C_B determines the position of the transition state on the reaction coordinate, and nitrogen bonding to C_N comes into play after the B−C_B interaction is established. While the explanations differ in formalism rather than fundamentals, the extreme shortness of the B−C_B distances and the differing N−C_N distances in the transition states described below suggest that the Hirao/Fujimoto view is more appropriate. I will return to this point later.

As an aside, one should note that the MP2 model predicts a somewhat more symmetric transition state (2.036 and 2.455 Å for the B−C_B and N−C_N distances, respectively), but the asymmetry is still substantial. Both the observation of transition state asymmetry and the MP2 model giving a more symmetric structure recur throughout the systems studied here. It may be that the latter phenomenon causes (wholly or in part) the above-noted result that the MP2 model predicts lower activation barriers. Too few data exist to test this rigorously. Regardless, both models predict that the transition state is asymmetric and differ only in the extent of the asymmetry.

---

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

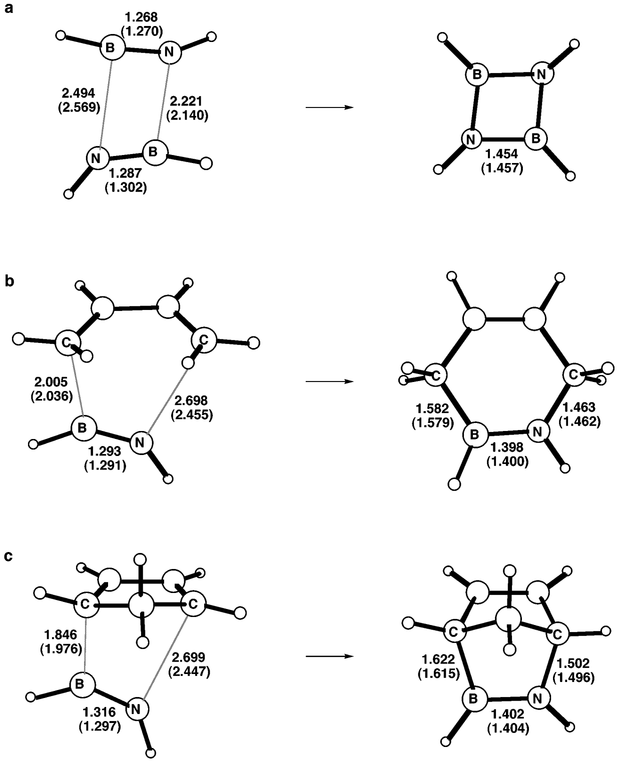


Figure 1. Predicted structures of the transition state and product for the reaction between (a) HB≡NH and itself; (b) HB≡NH and *cis*-butadiene; and (c) HB≡NH and cyclopentadiene. Numbers free of parentheses were obtained at the B3LYP/6-31+G* level; those in parentheses were obtained at the MP2/6-31+G* level.

The activation barrier for the [4+2] reaction is only slightly higher than that for the [2+2] dimerization (Table 2). While the exothermicity of the Diels−Alder reaction is some 10 kcal mol^{-1} less than that of the dimerization, both are sufficiently exothermic that the reactions might be experimentally competitive.

In Figure 1c are the transition state and product of the related reaction between iminoborane and cyclopentadiene. The transition state differs from that for the *cis*-butadiene case only in that the boron atom is somewhat closer to C4 here (B−C = 1.846 Å). However, since the two models used differ dramatically in predicting the interatomic distance, it is unclear what significance one should assign to this. One notes that the N−C$_N$ distances predicted are identical for both dienes and that the activation barriers are similar as well (Table 2).

By contrast, the bicyclic 1-aza-2-borabicycloheptadiene is substantially less stable than the monocycle (Table 2). The difference probably arises from the greater strain energy present in the bicycle. The B−C$_B$ and N−C$_N$ distances support this view; they are some 0.4 Å longer in the bicyclic compound than in the monocycle, suggesting that strain is being relieved through bond lengthening. However, the azaborabicycloheptadiene lies sufficiently below the transition state (ca. 32 kcal mol^{-1}) that once formed, it would not readily undergo retro Diels−Alder processes. Since the barrier to the [4+2] reaction appears similar to that for dimerization of the iminoborane, theory predicts that treatment of cyclopentadiene with HB≡NH would probably provide at least some bicyclic material along with the diazadiboracyclobutadiene.

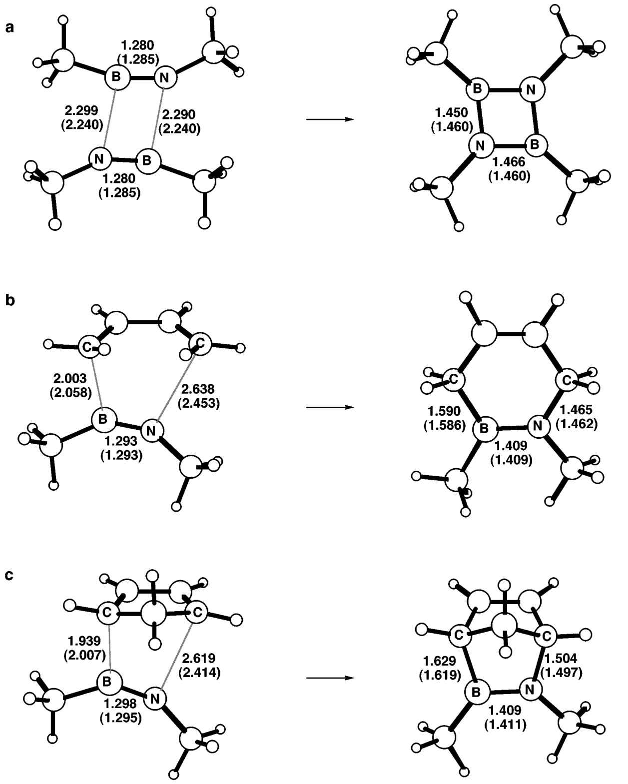


Figure 2. Predicted structures of the transition state and product for the reaction between (a) MeB≡NMe and itself; (b) MeB≡NMe and *cis*-butadiene; and (c) MeB≡NMe and cyclopentadiene. Numbers free of parentheses were obtained at the B3LYP/6-31+G* level; those in parentheses were obtained at the MP2/6-31+G* level.

Reactions of MeB≡NMe. The dimerization of dimethyliminoborane to permethyl-1,3-diaza-2,4-diboracyclobutadiene appears in Figure 2a; it shows features similar to the parent system. Again the transition state is puckered and lies early on the reaction coordinate. As above, the degree of puckering depends on the model, with the B3LYP approach predicting a more planar transition state (B−N−B−N torsion angle $\tau = 9.7°$) than the MP2 model ($\tau = 29.5°$). However, the transition state is symmetric, in contrast to the parent. Energetically the dimerization is exothermic, but requires crossing a moderate barrier, similar in magnitude to that for the parent iminoborane (Table 2).

The transition states and products for the two Diels−Alder reactions of MeB≡NMe, one involving *cis*-butadiene and the other cyclopentadiene, appear in Figure 2b,c. The general features of both systems differ little from those described above. Substitution of methyl for hydrogen decreases the N−C$_N$ distances in the transition states. This argues against the view noted above that repulsion between the nitrogen and C$_N$ dictates the structure of the transition state; if true, the more basic methylated nitrogen atom would lie farther from C$_N$. Decreasing the Lewis acidity of the boron appears to have little structural effect, although the transition state B−C$_B$ distance in the reaction using cyclopentadiene seems to lengthen somewhat. Owing to the unusual spread of distances in the parent, however, this view is tentative.

Somewhat surprisingly, the reaction energetics for the methylated system are quite similar to those of the

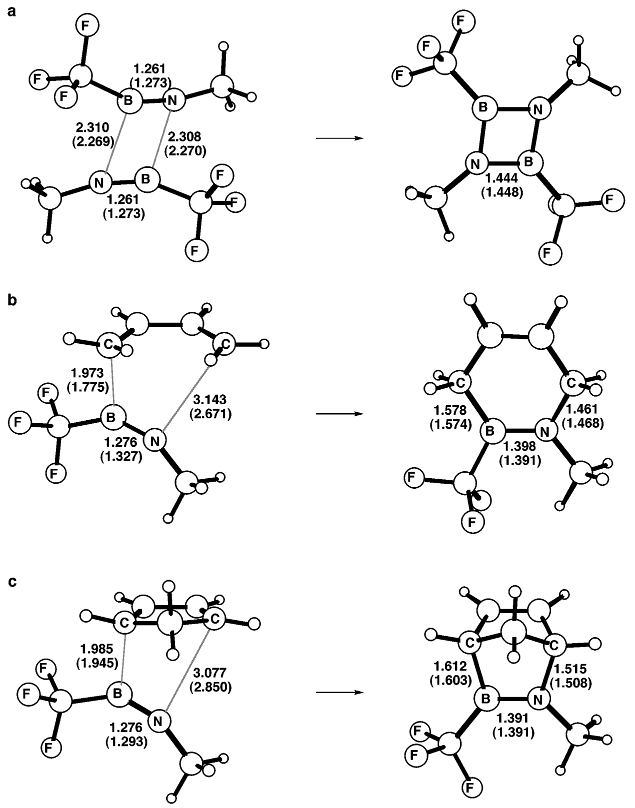


Figure 3. Predicted structures of the transition state and product for the reaction between (a) $(F_3C)B\equiv NMe$ and itself; (b) $(F_3C)B\equiv NMe$ and *cis*-butadiene; and (c) $(F_3C)B\equiv NMe$ and cyclopentadiene. Numbers free of parentheses were obtained at the B3LYP/6-31+G* level; those in parentheses were obtained at the MP2/6-31+G* level.

parent (Table 1). This contrasts with the $Me_2B{=}NMe_2$/$H_2B{=}NH_2$ comparison, where methyl substitution increased the activation barrier and lowered the stability of the cyclic product.[6a] Apparently methylation of the iminoborane does not create sufficient steric congestion to affect the energetics much.

Reactions of $(F_3C)B\equiv NMe$. The dimerization appears in Figure 3a and differs from the permethyl system above only in that both models predict a highly puckered transition state, with $\tau = 34.9°$ (B3LYP) and 37.7° (MP2). This angular relationship decreases substantially as the product forms, as τ in the diazadiboracyclobutadiene is only 11.6° (B3LYP)/18.3° (MP2). This path from reactants to products exhibits a much lower barrier and greater exothermicity than do the systems above (Table 2), consistent with the increased Lewis acidity of the boron engendered by the substitution of the trifluoromethyl group for a methyl group. The B−N distance in the bis(trifluoromethyl)diazadiboracyclobutadiene is shorter than that in the analogous permethyl system, showing the effect of the increased Lewis acidity of the boron atom.

The computationally predicted Diels−Alder reaction between $(F_3C)B\equiv NMe$ and *cis*-butadiene appears in Figure 3b. Despite the increased steric congestion caused by the fluorine atoms, the product 1-aza-2-bora-1,4-cyclohexadiene is planar and exhibits a shorter B−N bond than its permethyl analogue. The asymmetry of the transition state is the greatest here of any [4+2] cycloaddition system studied, with an approximately 1 Å difference between the $B-C_B$ and $N-C_N$ distances. One sees that the transition state looks like a BR_3 molecule, with unusual B−X distances, but without a substantial $N-C_N$ interaction. Despite this, the reaction barrier energy is small, similar to that for dimerization of the iminoborane, and the overall reaction energy quite exothermic. One predicts that treatment of $(F_3C)B\equiv NMe$ with *cis*-butadiene should afford some azaboracyclohexadiene along with the diazadibora dimer.

The [4+2] reaction between $(F_3C)B\equiv NMe$ and cyclopentadiene (Figure 3c) shows a similarly distorted transition state. However, the barrier associated with this appears lower than that for dimerization, according to both models. Although the overall reaction is not as exothermic as dimerization (Table 2), the data suggest that this process would yield more Diels−Alder product than dimer. The low barrier required should allow the reaction to be conducted at low temperature, so the lower barrier to the retro-Diels−Alder process should not pose a problem. The 1-aza-2-borabicycloheptadiene product shows structural features combining the issues noted above: long $B-C_B$ and $N-C_N$ distances to relieve strain, but a short B−N distance resulting from the increased boron Lewis acidity.

Reactions of $(F_5C_6)B\equiv N(t\text{-}C_4H_9)$. As noted in the Introduction, this iminoborane represents an example of one that experimentally undergoes a [4+2] cycloaddition with cyclopentadiene. The computational results for $(F_5C_6)B\equiv N(t\text{-}C_4H_9)$ thus provide benchmarks against which the reaction barriers and energies for other iminoboranes can be measured.

The transition state and product diazadiboracyclobutadiene for the dimerization of this bulky iminoborane appear in Figure 4a. One sees that the transition state is far more asymmetric than those located above for [2+2] dimerizations. In fact, the transition state appears to involve incipient formation of only one B−N bond, for which the distance is 2.126 Å. The other B−N bond-forming distance (2.632 Å) is substantially longer than any analogous B−N distance seen above. The B−N−B−N torsion angle τ is 61.3°. So in essence the molecules bind in stepwise fashion, with one new B−N bond nearly formed in the transition state, but the other not formed until well after this point. The steric bulk of the iminoborane raises the transition state barrier by some 10 kcal mol^{-1} compared to that for $(F_3C)B\equiv NMe$ (Table 2), despite the increased Lewis basicity of the nitrogen atom imparted by the *tert*-butyl group. However, the overall reaction is still quite exothermic, so any molecules combining and crossing the barrier are unlikely to dissociate later. As one expects from consideration of both steric repulsion and increased Lewis acidity at boron and basicity at nitrogen, the B−N distance in the bis(pentafluorophenyl)diazadiboracyclobutadiene is shorter than that in the permethyl analogue but longer than that in the bis(trifluoromethyl) compound. Despite the steric congestion, the ring puckers only slightly, with $\tau = 9.4°$. Possibly this arises because the planar phenyl rings twist to avoid collisions with the *tert*-butyl groups; the rings are essentially coplanar.

Figure 4b shows the Diels−Alder reaction between the iminoborane and *cis*-butadiene. As usual, the transition state is asymmetric, but less so than that of the $(F_3C)B\equiv NMe$ case above. Despite the increased steric

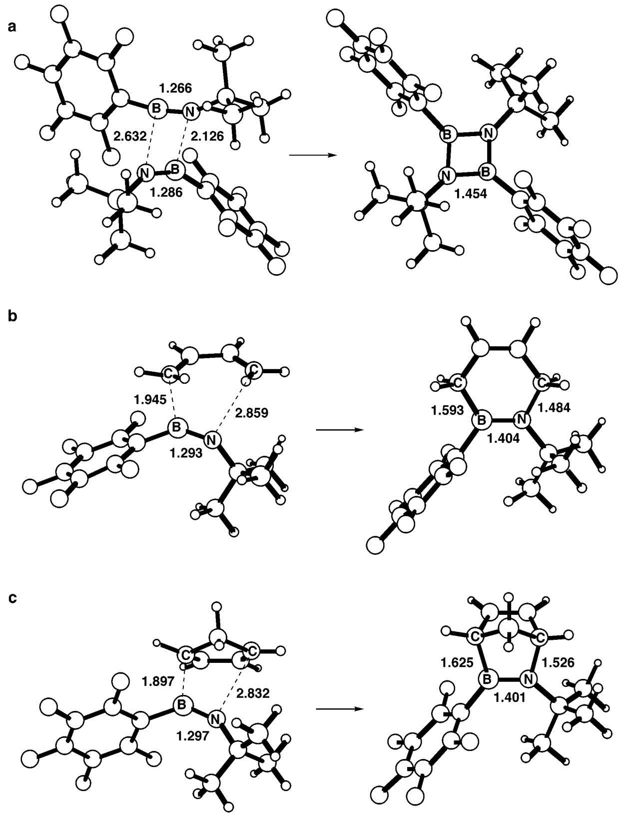


Figure 4. Predicted structures of the transition state and product for the reaction between (a) $(F_5C_6)B{\equiv}N(t\text{-}C_4H_9)$ and itself; (b) $(F_5C_6)B{\equiv}N(t\text{-}C_4H_9)$ and *cis*-butadiene; and (c) $(F_5C_6)B{\equiv}N(t\text{-}C_4H_9)$ and cyclopentadiene, at the B3LYP/6-31+G* level.

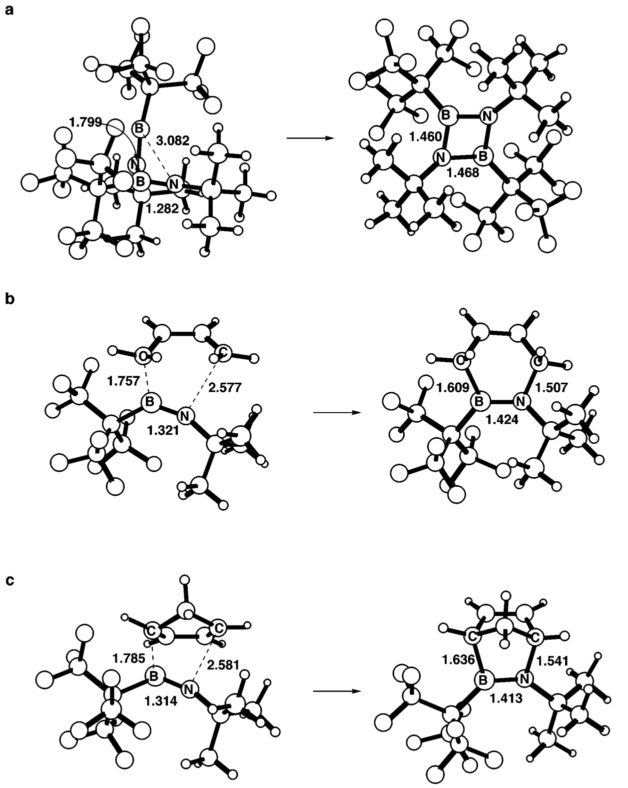


Figure 5. Predicted structures of the transition state and product for the reaction between (a) $(t\text{-}F_9C_4)B{\equiv}N(t\text{-}C_4H_9)$ and itself; (b) $(t\text{-}F_9C_4)B{\equiv}N(t\text{-}C_4H_9)$ and *cis*-butadiene; and (c) $(t\text{-}F_9C_4)B{\equiv}N(t\text{-}C_4H_9)$ and cyclopentadiene, at the B3LYP/6-31+G* level.

bulk of the *tert*-butyl group and its better electron donor capacity as compared to a methyl group, the N−C_N distance in the transition state is far shorter than that for the (trifluoromethyl)methyliminoborane. This argues strongly against the view that nitrogen−carbon repulsions determine the structure of the transition state. The transition state lies 22.0 kcal mol^{-1} above the reactant energies, again about 10 kcal mol^{-1} higher than in the $(F_3C)B{\equiv}NMe$ case. The 1-aza-2-bora-1,4-cyclohexadiene product is essentially planar, again probably because the pentafluorophenyl ring twists to minimize steric interaction with the nearby *tert*-butyl group.

The model of the experimental reaction appears in Figure 4c. Structurally the transition state and product present no features not mentioned in similar contexts above. The energetic data, however, provide a clear picture of the principle underlying formation of the azaborabicycloheptadiene vs the diazadiboracyclobutadiene. The Diels−Alder reaction is 36 kcal mol^{-1} less exothermic than dimerization, so that if thermodynamics controlled the process, none of the former would be observed. However, the barrier difference favors the [4+2] cyclization by 2.6 kcal mol^{-1}. Thus the fact that azaborabicycloheptadiene is observed in the reaction is kinetically determined.

Reactions of $(t\text{-}F_9C_4)B{\equiv}N(t\text{-}C_4H_9)$. To investigate the interplay between steric and electronic effects in determining the preference for [4+2] processes vs [2+2] iminoborane dimerization, the reactions of the extremely bulky (perfluoro-*tert*-butyl)(*tert*-butyl)iminoborane compound were examined. While this compound is unknown experimentally, the methods employed to prepare other perfluoroalkyl borane systems[14] should prove applicable to its synthesis.

The dimerization of the iminoborane appears in Figure 5a. The diazadiboracyclobutadiene product exhibits extremely long B−N bonds, in keeping with the congestion around the ring. The ring puckers such that the B−N−B−N torsion $\tau = 17.5°$, twice as large as that for $(F_5C_6)B{\equiv}N(t\text{-}C_4H_9)$. This demonstrates the added steric demand of the three-dimensional $t\text{-}F_9C_4$ moiety as compared to the two-dimensional F_5C_6 ring.

The iminoboranes approach each other nearly orthogonally to reach the transition state, with the B−N−B−N torsion $\tau = 82.4°$. This probably reflects both electronic issues and the energetic difficulties associated with pushing the bulky peripheral ligands toward each other. One sees that the first-forming B−N bond is quite short (1.799 Å), while the other B−N distance (3.082 Å) can scarcely be considered an interaction. Thus as above, the dimerization process should be viewed as stepwise, with the second B−N bond forming well after the first.

The energetic data (Table 2) reinforce the structural data. The transition state barrier to dimerization is 38.4 kcal mol^{-1}, larger than that of any smaller iminoborane by 15−26 kcal mol^{-1}. The overall reaction is only slightly exothermic, so it appears likely that $(t\text{-}F_9C_4)B{\equiv}N(t\text{-}C_4H_9)$ would not dimerize under reaction conditions required for the [4+2] reaction (see below).

---

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

The Diels–Alder reaction between the iminoborane and *cis*-butadiene appears in Figure 5b. The azaboracyclohexadiene product is notable in that it adopts a boat conformation rather than a planar one. This allows the adjacent perfluoro-*tert*-butyl and *tert*-butyl substituents to avoid each other somewhat. Further relief of steric congestion arises from the longest B–N, $B-C_B$, and $N-C_N$ distances of any molecule of this type reported here.

The transition state for the [4+2] reaction shows unexpectedly short $B-C_B$ and $N-C_N$ distances when compared to the transition state for the perfluorophenyl system above. One can rationalize the short $B-C_B$ distance as resulting from the increased Lewis acidity of the boron attached to a perfluoro-*tert*-butyl group rather than a perfluorophenyl group, but the difference of almost 0.3 Å between $N-C_N$ distances is hard to explain. NBO calculations[15] on the two systems did not provide an obvious answer. It may simply be that the boron, because it is closer to C_B, "carries" the nitrogen closer to C_N.

The energy data (Table 2) show that, like the dimerization reaction, the Diels–Alder reaction is only slightly exothermic. However, the barrier to reaction is 10 kcal mol^{-1} less for the [4+2] process, a larger gap by far than any analogous one above. Thus here the [4+2] cyclization is not merely competitive with dimerization of iminoborane, but likely outweighs it substantially. While it is not straightforward to predict an experimental product ratio from (gas phase) barrier heights, the large gap suggests that a mixture of iminoborane and *cis*-butadiene would provide far more azaboracyclohexadiene than diazadiboracyclobutadiene.

Figure 5c shows the [4+2] reaction between the iminoborane and cyclopentadiene. In keeping with the data presented above, the transition state is more compact than that for the perfluorophenyl system, while the product ring is more expanded. The energy data (Table 2) follow the normal trends: the barrier to the reaction is slightly lower than that for the reaction using *cis*-butadiene, while the product is less stable. Here, however, the loss of stability arising from increased strain causes the reaction to be endothermic. However, the endothermicity is not great, so that possibly substitution of 1,3-cyclohexadiene for cyclopentadiene in the experiment would allow the reaction to occur.

Conclusions

The computational data show that the preference for [2+2] dimerization of iminoboranes over [4+2] Diels–Alder cyclizations arises largely from the lower transition state barriers associated with the former reaction. While the formation of dimers is generally also more exothermic than is the Diels–Alder reaction, when *cis*-butadiene is the eneophile, the difference is sufficiently small to be generally irrelevant.

So the question becomes how to force the [4+2] reaction barrier below the [2+2] barrier. Comparison of the energetic data for $(F_3C)B{\equiv}NMe$ vs $MeB{\equiv}NMe$ shows that electron-withdrawing fluorinated groups on boron lower the barrier and increase the reaction exothermicity for both reactions, but they affect the [4+2] reaction barrier so much that it becomes nearly identical with that for the [2+2] reaction. This suggests that biasing the process toward the [4+2] reaction requires enhancing the boron Lewis acidity. This agrees with the experimental observations that $(F_5C_6)B{\equiv}N(t\text{-}C_4H_9)$ and $(Me_3Si)(t\text{-}C_4H_9)N{-}B{\equiv}N(t\text{-}C_4H_9)$[16] prefer the [4+2] cyclization. The data further indicate that attaching bulky substituents to the boron and nitrogen atoms raises both reaction barriers, but affects that for the dimerization more. Presumably this occurs because the dimer transition state puts four large substituents in proximity to each other, while the Diels–Alder transition states must organize the spatial requirements of only two large groups.

The experimentally successful $(F_5C_6)B{\equiv}N(t\text{-}C_4H_9)$ meets these criteria reasonably well. The perfluorophenyl group combines electron withdrawal and steric bulk, while the *tert*-butyl substituent on nitrogen adds more bulk to lessen the opportunity for [2+2] dimerization. However, even with this combination, the [2+2] and [4+2] barriers are so close in energy that one expects competitive formation of the associated products. It is unclear whether this holds experimentally, as the product and byproduct yields were not given in the original report.[2] The problem with using perfluorophenyl as the boron-bound substituent is its planarity, which lessens the three-dimensional space it requires. Using the very bulky perfluoro-*tert*-butyl group on boron overcomes this, raising the barrier to dimerization well above that for [4+2] chemistry. However, this approach lowers the reaction exothermicity such that the iminoborane might not react with the diene at all. Clearly the most efficient [4+2] reaction requires a fluorinated substituent intermediate in size; I leave it to the synthetic chemist to determine the optimal choice.

Another approach to enforcing a preference for [4+2] over [2+2] reactivity requires using a less strained diene than cyclopentadiene. Its use as the eneophile is contraindicated in these [4+2] cyclizations owing to the strain inherent in the resulting azaborabicycloheptadienes. That the only experimental examples of [4+2] reactivity employ this diene reflects the fact that it is forced to contain cis double bonds, while butadiene (for example) consists of mostly the trans isomer at room temperature. However, if one photochemically generated a mixture of butadienes enriched in the cis isomer, the *cis*-butadiene would undoubtedly react more efficiently with an iminoborane than does cyclopentadiene. Alternatively, one could use a less strained cyclic diene, such as 1,3-cyclohexadiene; this would probably also react more readily with an iminoborane than does cyclopentadiene.

Supporting Information Available: Cartesian coordinates and total energies in hartrees of all molecules examined at the applicable model levels. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0300880

---

[15] NBO is part of the Gaussian suite. Gledening, E. D.; Badenhoop, J. K.; Reed, A. E.; Carpenter, J. E.; Weinhold, F. Theoretical Chemistry Institute, University of Wisconsin, Madison, 1996.

[16] The Lewis acidity of the boron in this compound appears to be enhanced by delocalization of electron density between the boron and the two nitrogen atoms. See ref 5.