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Pericyclic Reactions between Iminoboranes $RB\equiv NR'$ and Alkynes: [4 + 2] vs [2 + 2] Transition States[†]

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Computational comparisons of the [2 + 2] cyclization and [4 + 2] ene-type reactions between iminoboranes $RB\equiv NR'$ and alkynes $HC\equiv C(R'')$ show that the latter are strongly preferred. The preference arises from the [4 + 2] reactions exhibiting lower barriers and greater exothermicities than do the [2 + 2] reactions. This behavior mimics that of reactions between alkynes and supports viewing iminoboranes, particularly $(F_3C)B\equiv NMe$ and higher fluorinated analogues, as acting like polar alkynes. The hypothetical 1-aza-2-boracyclohexyne $\overline{BC(CF_3)_2CF_2CH_2C(Me)_2N}$ shows remarkable potential reactivity, in that its [4 + 2] ene-type reaction with propyne exhibits no activation barrier. This arises from the loss of ring strain energy in the azaboracyclohexyne as the propyne approaches and the B−C bond forms.

Introduction

Computational modeling of the reaction coordinates of the supra-suprafacial [2 + 2] cyclization reactions of alkenes and alkynes shows that all three combinations are symmetry forbidden. This translates to the cyclizations exhibiting high activation barriers, as confirmed by experiment and theory.[2,3] Theory further shows that alkene−alkene and alkene−alkyne cyclizations exhibit transition states that, while of high energy, are readily located stable stationary points on the potential surface. In contrast, the analogous transition state for [2 + 2] dimerization of an alkyne is a 4*n* antiaromatic system and, thus, is rarely a stable stationary point. In general, the model predicts the alkynes to rotate with respect to each other as they approach to avoid the antiaromatic cyclic transition state (Scheme 1).

These observations provide means by which one can characterize alkenes and alkynes computationally by their reactivities rather than by their physical properties. They also allow one to distinguish between alkenes and alkynes through their reactivities. This contrasts with symmetry-allowed reactions such as [4 + 2] cyclizations and ene-type reactions, where alkenes and alkynes show similar (generally six-membered) transition states. We believe this concept also provides a methodology for examining the extent of multiple bonding in heteroatom systems, where using alkene-/alkyne-like physical characteristics (or theoretical bond characterization procedures) has often given ambiguous results.[4]

We previously modeled [2 + 2] and [4 + 2] reactions between aminoboranes $R_2B{=}NR_2$ and alkenes/dienes, showing that aminoboranes exhibit transition states and energetics consistent with viewing them as polar alkenes.[5] It seemed appropriate to extend this work to iminoboranes $RB\equiv NR'$,[6] with a particular focus on whether a supra-suprafacial [2 + 2] reaction between an iminoborane and an alkyne would exhibit a transition state as a stable stationary point or not. The analogous [2 + 2] dimerizations of iminoboranes exhibited stable stationary point transition states in a previous study.[7]

We report here modeling studies of the [2 + 2] reactions between iminoboranes $RB\equiv NR'$ ($R = H, CF_3$; $R' = H, Me$) and ethyne and [2 + 2] and [4 + 2] ene-type reactions between the iminoboranes and propyne. The [2 + 2] processes do not appear to have stable stationary point transition states but involve a reaction coordinate where the triply bonded species rotate with respect to each other. The [4 + 2] reactions exhibit lower transition state barrier energies and generally greater exothermicities than do the [2 + 2] processes. Thus, despite their polar nature, iminoboranes behave chemically as if they contain $B\equiv N$ triple bonds. Finally, we discuss the remarkable pericyclic reactions of a cyclic iminoborane (a 1-aza-2-boracyclohexyne),[8] which involve very low barriers and sizable exothermicities.

[†] This paper is dedicated to Professor John C. Gilbert, Department of Chemistry and Biochemistry, University of Texas at Austin, on the occasion of his 65th birthday, and in appreciation of his pioneering studies of the chemistry of cycloalkynes.

(1) E-mail: tgilbert@marilyn.chem.niu.edu.

(2) Woodward, R. B.; Hoffmann, R. *The Conservation of Orbital Symmetry*; Academic Press: New York, 1970.

(3) However, polar alkenes of certain types undergo [2 + 2] cyclizations, and several reactions of polar alkynes imply [2 + 2] cyclizations as intermediate processes. See: Smith, M. B.; March, J. *March's Advanced Organic Chemistry*, 5th ed; Wiley: New York, 2001; Chapter 15.

(4) For interesting examples, see: (a) Power, P. P. *Chem. Rev.* **1999**, *99*, 3463−3503. (b) Robinson, G. H. *Acc. Chem. Res.* **1999**, *32*, 773−782.

(5) (a) Bissett, K. M.; Gilbert, T. M. *Organometallics*, **2004**, *23*, 850−854. (b) Gilbert, T. M. *Organometallics* **1998**, *17*, 5513−5520.

(6) Paetzold, P. *Adv. Inorg. Chem.* **1987**, *31*, 123−170.

(7) Gilbert, T. M. *Organometallics* **2003**, *22*, 2298−2304.

(8) Gilbert, T. M., *Organometallics* **2000**, *19*, 1160−1165.

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Scheme 1

"Transition State" Region

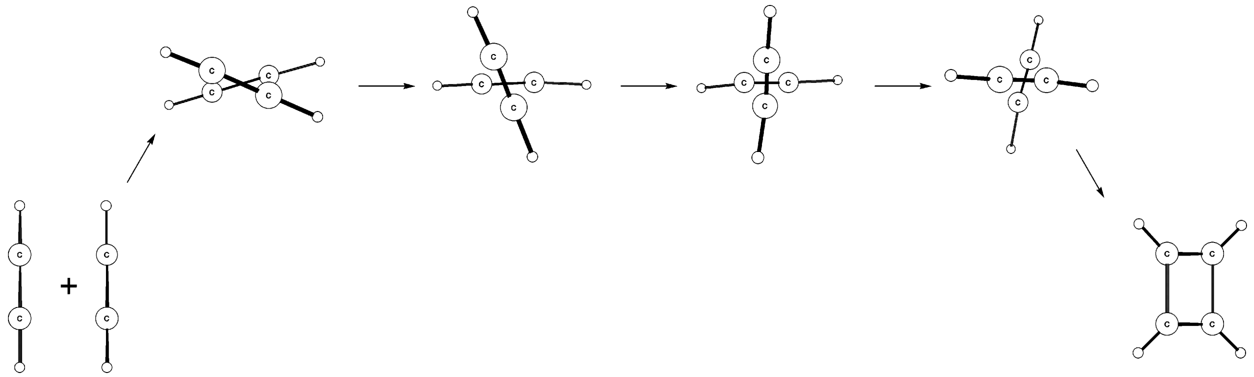

Table 1. Predicted Energies (6-311++G(d,p) Basis Set, kcal/mol) for [2 + 2] Cyclization and [4 + 2] Ene-Type Reactions of RB≡NR′ and HC≡C(R″) (R = H, F$_3$C, *t*-F$_9$C$_4$; R′ = H, Me, *t*-Bu; R″ = H, Me) and between BC(CF$_3$)$_2$CF$_2$CH$_2$CMe$_2$N and HC≡C(R″) (R″ = H, Me) Using Various Models[a]

reacn	MP2		B3LYP		MPW1K	
	ΔE_{ts}	ΔE	ΔE_{ts}	ΔE	ΔE_{ts}	ΔE
HB≡NH (**1**) + HC≡CH → HBCHCHNH (**1c**)	*52*	−9.9	*53*	−8.7	*51*	−23.8
HB≡NH (**1**) + HC≡C(CH$_3$) → HBCHC(CH$_3$)NH (**1cN**)	*57*	−13.8	*48*	−10.5	*59*	−25.6
HB≡NH (**1**) + HC≡C(CH$_3$) → HBC(CH$_3$)CHNH (**1cB**)	*51*	−8.9	*55*	−5.8	*53*	−20.8
HB≡NH (**1**) + HC≡C(CH$_3$) → H$_2$NBHCHCCH$_2$ (**1aN**)	16.9	−30.0	16.2	−34.7	12.9	−41.5
HB≡NH (**1**) + HC≡C(CH$_3$) → H$_2$BNHCHCCH$_2$ (**1aB**)	44.8	−8.0	42.3	−13.4	42.7	−19.2
(F$_3$C)B≡NMe (**2**) + HC≡CH → (F$_3$C)BCHCHNMe (**2c**)	*53*	−17.1	*53*	−12.9	*49*	−28.7
(F$_3$C)B≡NMe (**2**) + HC≡C(CH$_3$) → (F$_3$C)BCHC(CH$_3$)NMe (**2cN**)	*45*	−21.9	*45*	−14.9	*43*	−30.8
(F$_3$C)B≡NMe (**2**) + HC≡C(CH$_3$) → (F$_3$C)BC(CH$_3$)CHNMe (**2cB**)	*50*	−17.1	*52*	−10.4	*43*	−26.2
(F$_3$C)B≡NMe (**2**) + HC≡C(CH$_3$) → H(Me)NB(CF$_3$)CHCCH$_2$ (**2aN**)	11.5	−37.1	13.5	−38.9	10.0	−46.7
(F$_3$C)B≡NMe (**2**) + HC≡C(CH$_3$) → H(F$_3$C)BN(Me)CHCCH$_2$ (**2aB**)	37.2	−16.3	39.5	−17.4	40.5	−24.2
(F$_3$C)$_3$CB≡NCMe$_3$ (**3**) + HC≡CH → (F$_3$C)$_3$CBCHCHNCMe$_3$ (**3c**)			*62*	−2.0	*62*	−18.6
(F$_3$C)$_3$CB≡NCMe$_3$ (**3**) + HC≡C(CH$_3$) → (F$_3$C)$_3$CBCHC(CH$_3$)NCMe$_3$ (**3cN**)			*58*	−1.9	*55*	−19.0
(F$_3$C)$_3$CB≡NCMe$_3$ (**3**) + HC≡C(CH$_3$) → H(Me$_3$C)NB[C(CF$_3$)$_3$]CHCCH$_2$ (**3aN**)			29.8	−16.7	25.8	−25.3
BC(CF$_3$)$_2$CF$_2$CH$_2$CMe$_2$N (**4**) + HC≡CH → BC(CF$_3$)$_2$F$_2$CH$_2$CMe$_2$NCHCH (**4c**)			*29*	−37.8	*27*	−54.6
BC(CF$_3$)$_2$CF$_2$CH$_2$CMe$_2$N (**4**) + HC≡C(CH$_3$) → BC(CF$_3$)$_2$CF$_2$CH$_2$CMe$_2$NC(Me)CH (**4cN**)			*25*	−39.3	*15*	−55.8
BC(CF$_3$)$_2$CF$_2$CH$_2$CMe$_2$N (**4**) + HC≡C(CH$_3$) → HN(CMe$_2$)CH$_2$CF$_2$C(CF$_3$)$_2$BCHCCH$_2$ (**4aN**)				−65.9		−74.9

[a] Approximate barrier energies from potential energy surface scans are given in italics. ΔE_{ts} is the energy required to reach the transition state from the reactants (the barrier); ΔE is the overall reaction energy.

Computational Methods

All calculations, including NBO analyses,[9] were performed with the Gaussian 98 suite of programs.[10] Each molecule and stationary point 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.[11] The structures were then reoptimized using the models given in Table 1 and the 6-311++G(d,p) basis set. The large basis set was selected because the [4 + 2] ene-type reactions involve the transfer of a hydrogen atom, making it advisable to model hydrogens as completely as the heavier atoms. The 6-311++G(d,p) basis set augments the triple-ζ functions on the hydrogens with diffuse and polarization functions.

For reactions where a stable stationary point transition state could not be located ([2 + 2] cyclizations and the [4 + 2] ene-type reaction of 1-aza-2-boracyclohexyne **4**), the energies and structures of the transition state regions were estimated using potential energy scans. The reaction coordinate for the [2 + 2] cycloaddition reactions involved stepwise increases of

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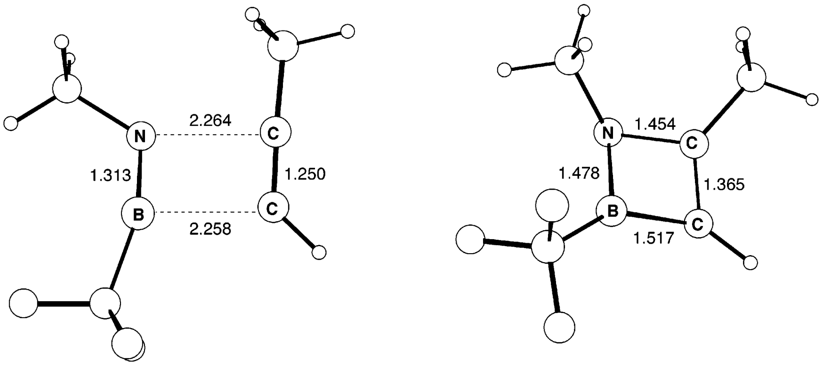
(9) Glendening, E. D.; Badenhoop, J. K.; Reed, A. E.; Carpenter, J. E.; Bohmann, J. A.; Morales, C. M.; Weinhold, F. *NBO 5.0*; Theoretical Chemistry Institute, University of Wisconsin: Madison, WI, 2001.

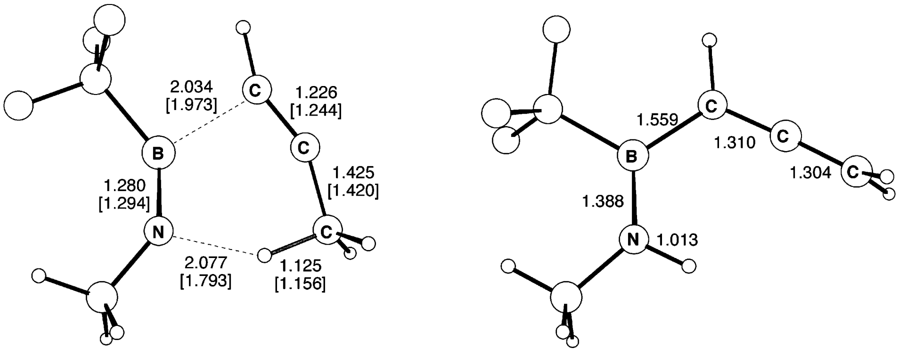
(10) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Rega, N.; Salvador, P.; Dannenberg, J. J.; Malick, D. K.; Rabuck, A. 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.11.4; Gaussian, Inc.: Pittsburgh, PA, 2002.

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



"2cNts" 2cN

Figure 1. B3LYP/6-311++G(d,p) optimized structures of the "transition state" **2cNts** and 1-aza-2-boracyclobutadiene product **2cN** of the [2 + 2] cyclization between $(F_3C)B{\equiv}NMe$ and propyne. Distances are in Å.



2aNts 2aN

Figure 2. B3LYP/6-311++G(d,p) optimized structures of the transition state **2aNts** and product **2aN** of the [4 + 2] ene-type reaction between $(F_3C)B{\equiv}NMe$ and propyne. Selected MP2/6-311++G(d,p) optimized distances in the transition state **2aNts** are given in brackets. Distances are in Å.

the distance between a point midway between the boron–nitrogen bond and one midway between the carbon–carbon bond of the cyclic product, allowing all other distances and angles to optimize at each step (known as a "relaxed" scan). Since the "barriers" obtained by this approach are approximate, they appear in Table 1 as values with no decimal place and in italics. We view them as being correct (within the errors of the model) to at worst ±10 kcal/mol, since the maximum energy change between the "transition state" step and the step right before it was rarely in excess of this and was generally smaller. Since the barriers for the [2 + 2] reactions are uniformly greater than those for the [4 + 2] reactions, their exact values are less important anyway. Several reaction coordinates for the [4 + 2] ene-type reaction of the 1-aza-2-boracyclohexyne **4** were examined, including incrementally changing the carbon–boron distance while allowing optimization of all other parameters, and incrementally changing the carbon–hydrogen distance while allowing optimization of all other parameters. All these scans indicated that, once the carbon and boron are sufficiently close, transfer of hydrogen from carbon to nitrogen occurs without a barrier. Thus, no barrier value appears in Table 1.

Relative energies for the reactions studied appear in Table 1. We examined the results of three different models, because we have observed substantive differences in the predictions of the B3LYP and MP2 models for boron–nitrogen compounds.[7,12] As one can see in the table, the models predict fairly similar barriers for all systems but often differ in predicting reaction energies. In general, the MPW1K approach predicts more exothermic reactions than do the other two. The MPW1K reaction energies are probably incorrect, given this result and the fact that Truhlar et al. noted that the MPW1K model predicts atomization energies poorly.[13] However, it predicts barriers well, and since it turns out that the outcomes of the reactions examined depend largely on the barriers, we include the MPW1K data in Table 1. The reaction energies given should be viewed as bounds on the actual values.

Except as noted in the Results and Discussion, the structural data for the species studied are unexceptional. In general, all models predicted similar structures for the reaction components. The only exceptions involved the transition-state structures, for which the DFT-based and MP2-based models tend to predict somewhat different distances for the forming B–C and N–C/N–H bonds. Since the B3LYP and MP2 models give similar energies, but only the former allows optimization of the larger complexes, structural data appearing in the figures are B3LYP/6-311++G(d,p) values except as noted. Optimized Cartesian coordinates and absolute energies at this level for all the stationary point species reported are given as Supporting Information.

Results and Discussion

[2 + 2] and [4 + 2] Reactions of HB≡NH (1) and $(F_3C)B{\equiv}NMe$ (2) with Ethyne/Propyne. The reactions between the smaller iminoboranes and ethyne/propyne are grouped because they exhibit similar energies and structures. As representative of the classes, the "transition state" **2cNts** and 1-aza-2-boracyclobutadiene product **2cN**[14] structures for the [2 + 2] cycloaddition reaction between $(F_3C)B{\equiv}NMe$ and propyne

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(12) Gilbert, T. M. *J. Phys. Chem. A* **2004**, *108*, 2550–2554.

(13) (a) Lynch, B. J.; Truhlar, D. G. *J. Phys. Chem. A* **2001**, *105*, 2936–2941. (b) Zhao, Y.; Pu, J.; Lynch, B. J.; Truhlar, D. G. *Phys. Chem. Chem. Phys.* **2004**, *6*, 673–676.

appear in Figure 1, while the analogous components **2aNts** and **2aN** for the [4 + 2] ene-type reaction between $(F_3C)B{\equiv}NMe$ and propyne appear in Figure 2. Reaction barriers and energies appear in Table 1.

One sees that the barrier energies for the [2 + 2] cyclizations, though approximate, are extremely high and are mostly unaffected by substitution of CF_3/CH_3 for H on the iminoborane core. This contrasts markedly with the behavior of aminoboranes, where substitution leads to substantially lower barriers (and more exothermic reactions). The transition state "structure" shows the rotation of the molecules with respect to each other as they avoid forming an antiaromatic four-membered ring. We note that the structure shown in Figure 1 shows a point where only a slight rotation (as characterized by the B−N−C−C torsion angle of ca. 5°) is present. This is an artifact of the scan procedure; continuing the relaxed scan optimization process makes the rotation more pronounced with little energy change, such that the triple-bond axes ultimately adopt nearly orthogonal orientations. The high barriers and twisted structures hold whether the substituted carbon on propyne approaches the boron or the nitrogen of the iminoborane. Overall, the barriers indicate that [2 + 2] cyclizations between iminoboranes and alkynes are unlikely and would require high temperatures to occur.

The data show that, if the reactants traverse the barrier, all the products form exothermically. Here the electronic effect of substitution on the iminoborane core appears: the trifluoromethyl-/methyl-substituted systems **2c/2cN/2cB** undergo reactions 4−8 kcal/mol more exothermic than do the parent systems. The 1-aza-2-boracyclobutadienes adopt nonplanar structures to avoid 4*n* antiaromaticity within the ring; the B−N−C−C ring torsion angles in the various rings are ca. 20°. One sees in Figure 1 that the ring bond distances are consistent with the presence of BN and CC double bonds and somewhat short BC and NC single bonds. Thus, the π-bonding appears localized, as it would be in cyclobutadiene.

Comparing the energies for the isomeric **1cN**/**1cB** and **2cN**/**2cB** shows that the isomer with N bound to the substituted carbon is consistently more stable than that with B bound to the substituted carbon. Similarly, the [4 + 2] ene-type reactions that form **1aB**/**2aB** show substantial barriers nearly as large as those for the [2 + 2] cyclizations and, thus, are only slightly more probable experimentally. Consequently, we chose not to model the reactions that would form **3cB**, **3aB**, **4cB**, and **4aB**.

The [4 + 2] ene-type reactions forming **1aN**/**2aN** exhibit the lowest barriers and greatest exothermicities by far of the reactions in this class and, thus, are the most likely to occur experimentally. The low barriers arise because, as in organic pericyclic reactions, the reactants form a six-membered, 4*n* + 2 transition state (Figure 2). The transition-state geometry of **2aNts** shown may be misleading. The two hybrid DFT models suggest that the transition state contains a slightly lengthened C−H bond and a very long (if present at all) N−H interaction. However, frequency calculations indicate that the imaginary frequency associated with this structure maps a path for hydrogen transfer; therefore, the structure found represents the correct transition state for the desired reaction within the model chemistry. The MP2 model finds a structure more in keeping with the idealized six-membered transition state, with longer C−H and much shorter N−H interactions (Figure 2; values in brackets). Since the three models predict similar energies, the actual atomic positions in the transition state are clearly not crucial in determining the relative energy here, but the observation provides a cautionary point in drawing conclusions relating geometries and energies from a single computational model.[12] Whenever possible, perturbational and DFT models should be compared when attempting such correlations.

The acyclic products **1aN**/**2aN** present no unusual structural features, save that the five-atom chain is planar, whereas in the analogous compounds derived from aminoboranes, the atoms were skewed. This may reflect some delocalization of electron density from the allenyl moiety into the B−C bond. However, the bond distance data are inconsistent with this notion, as the BC distance is appropriate for an sp^2−sp^2 BC single bond, rather than one of somewhat greater order.

[2 + 2] and [4 + 2] Reactions of $(F_3C)_3CB{\equiv}NCMe_3$ (3) with Ethyne/Propyne. When we studied the dimerizations and Diels−Alder reactions of iminoboranes,[7] we noted that placing a trifluoro-*tert*-butyl group and *tert*-butyl group on the boron and nitrogen, respectively, gave an iminoborane **3** kinetically resistant to both reactions. It seemed worthy to compare the reactivity of **3** toward ethyne and propyne with the previous work. One sees in Table 1 that all reactions involving **3** show increased barriers with respect to **1** and **2** to the extent of 10−15 kcal/mol. This probably reflects the increased steric repulsion associated with bending the iminoborane substituents away from the incoming alkyne and toward each other as the transition state is approached. This reorientation is probably similar, regardless of whether the reaction is a [2 + 2] cyclization or a [4 + 2] ene-type process; therefore, the energy changes are similar. However, the exothermicities behave differently. The [2 + 2] cyclizations are affected only slightly by the increased steric bulk around the iminoborane core, with exothermicities about 5−8 kcal/mol smaller than for the smaller iminoboranes. In contrast, the exothermicity of the [4 + 2] ene-type reaction decreases by ca. 17 kcal/mol: over twice as much. The explanation for this appears to lie in the ability of the products to minimize steric contacts. Because of its nonplanar ring, the 1-aza-2-boracyclobutadiene **3cN** is able to orient its trifluoro-*tert*-butyl and *tert*-butyl substituents in a sort of trans fashion, so that they do not interact much (Figure 3). In **3aN**, the substituents are constrained to coplanarity in the vinyl-group-like aminoborane core; therefore, they repel in a destabilizing way (Figure 3). Further evidence for this idea comes from the bond length data. The

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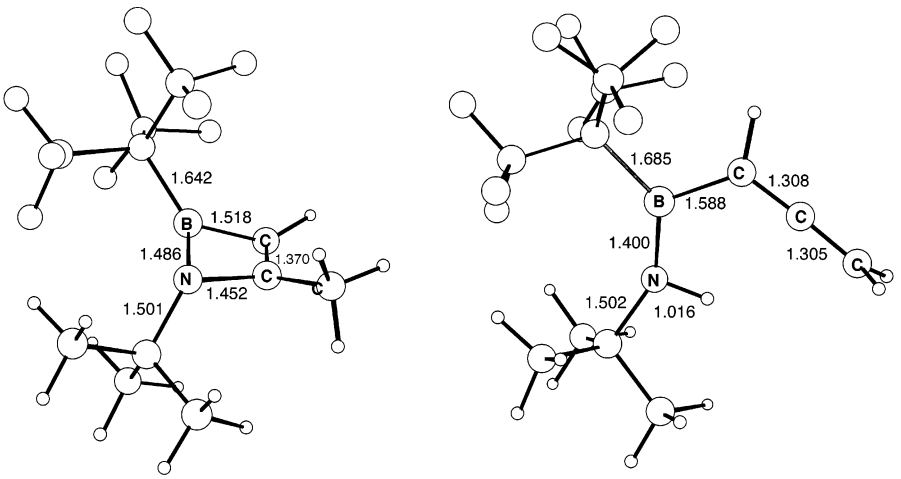
(14) Transition states and products are labeled systematically as follows. Compound **1** is $HB{\equiv}NH$, and **1** followed by characters implies a structure derived from it. The same holds for $(F_3C)B{\equiv}NMe$ (**2**), $(F_3C)_3CB{\equiv}NC(CH_3)_3$ (**3**), and the 1-aza-2-boracyclohexyne **4**. The letter c means that the product contains a 1-aza-2-boracyclobutadiene ring, while the letter a means the product is acyclic. The letter N means a structure in which the methyl group of the added propyne lies near the nitrogen atom of the aminoborane, while B means a structure in which the methyl group lies near the boron atom. Transition states are labeled ts.



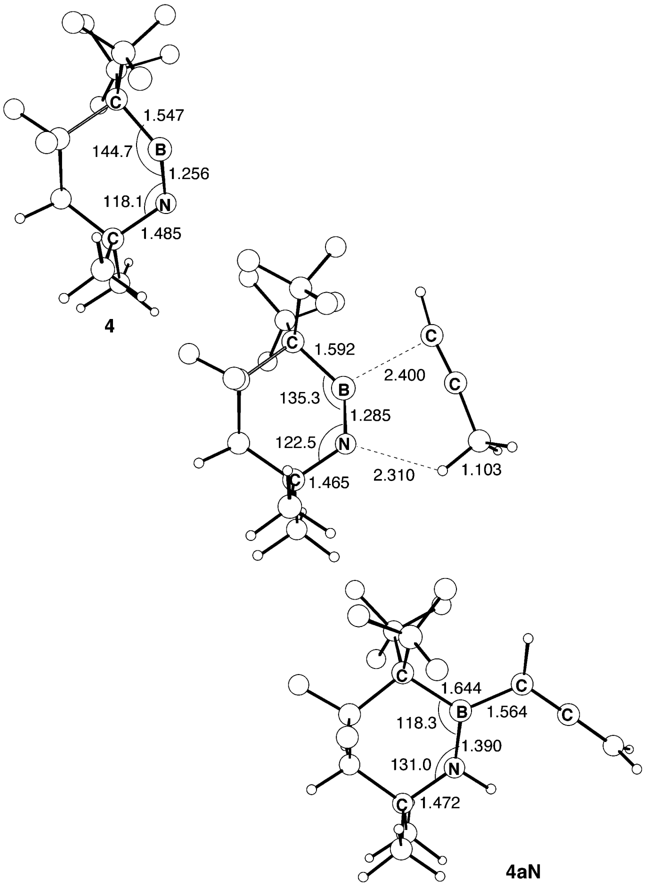
3cN **3aN**

Figure 3. B3LYP/6-311++G(d,p) optimized structures of cyclic **3cN** and acyclic **3aN**, showing the skewed geometry of the substituents in the former and the coplanarity of the substituents in the latter. Distances are in Å.

B−C(CF_3)$_3$ and N−CMe$_3$ distances in sterically congested **3aN** are 1.685 and 1.502 Å, while in less congested **3cN** they are 1.642 and 1.501 Å. Similarly, the ring atom distances of less substituted **2cN** are essentially identical with those of **3cN** (Figures 1 and 3), while the BC and BN distances are detectably longer in **3aN** than in **2aN** (Figures 2 and 3). Apparently most of the responsibility for steric relief lies on the boron atom.

[2 + 2] and [4 + 2] Reactions of $\overline{BC(CF_3)_2CF_2CH_2C(CH_3)_2N}$ (4) with Ethyne/Propyne. Gilbert and coworkers have explored the chemistry of cycloalkynes, noting several rapid and unique reactions that they undergo.[15] We previously reported the likely structural and bonding aspects and isomerization reactions of analogous azaboracycloalkynes, noting that 1-aza-2-boracyclohexyne appeared to be the smallest ring capable of containing a BN triple bond.[8] In view of the competition between the enhanced reactivities of cyclic triply bonded species and the decreased reactivity of **3** vs **1** and **2**, we thought it appropriate to examine the potential pericyclic reactivity of the 1-aza-2-boracyclohexyne **4**, which combines the two characteristics. The structure of **4** appears in Figure 4. The ring core of the molecule is similar to that of the parent and is notable mostly for the asymmetry around the BN triple bond. While structurally one might predict that the N atom possesses a lone pair (since the angles around N approximate a trigonal-planar geometry), making the BN interaction at most a double bond, NBO analysis suggests the presence of a BN triple bond.

The reaction energetics (Table 1) bear out the prediction of enhanced reactivity for **4**. The [2 + 2] cyclization reactions forming **4c** and **4cN** show the lowest barriers and highest exothermicities of any reported here. Indeed, the energies associated with the formation of **4c** are such that this reaction might occur experimentally. It would be interesting to see if this holds true.



4 **4aN**

Figure 4. B3LYP/6-311++G(d,p) optimized structures of **4**, a point along the potential surface between isolated **4** and propyne, and **4aN**. Distances are in Å and angles in degrees.

The reaction of **4** with propyne shows the usual preference for the [4 + 2] ene-type reaction vs [2 + 2] cyclization, with a notable twist. There appears to be no barrier for the ene-type process. The components of the reaction appear in Figure 4, which includes a structure from a scan of the potential surface along the reaction coordinate for B−C bond formation. One sees that the most notable change in the structure of **4** as the propyne molecule approaches is that the ring more

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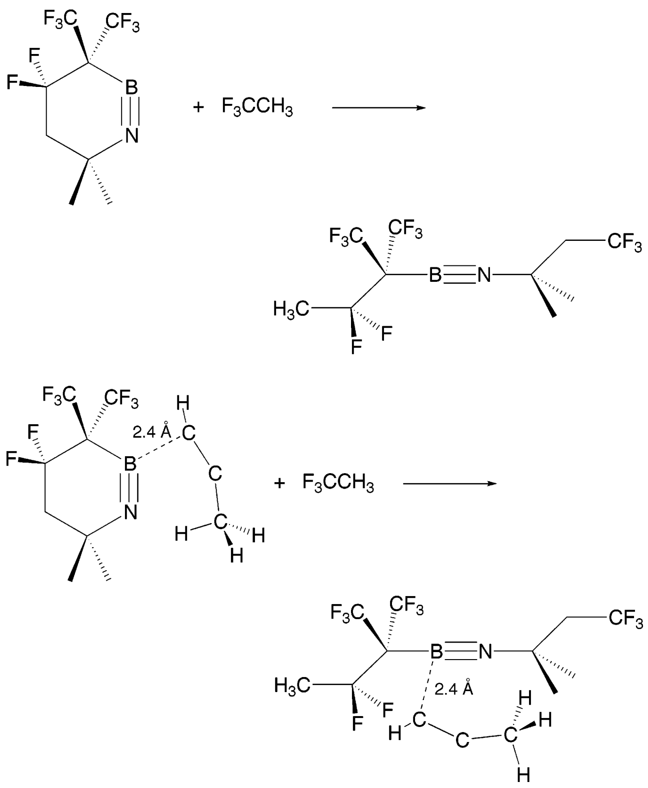
[15] (a) Gilbert, J. C.; Hou, D.-R. *Tetrahedron* **2004**, *60*, 469−474. (b) Gilbert, J. C.; Hou, D.-R. *J. Org. Chem.* **2003**, *68*, 10067−10072. (c) Bachrach, S. M.; Gilbert, J. C.; Laird, D. W. *J. Am. Chem. Soc.* **2001**, *123*, 6706−6707. (d) Laird, D. W.; Gilbert, J. C. *J. Am. Chem. Soc.* **2001**, *123*, 6704−6705. (e) Gilbert, J. C.; Kirschner, S. *Adv. Theor. Interesting Mol.* **1998**, *4*, 203−244.

Scheme 2



closely approximates a hexagon. This should lead to a decrease in ring strain energy along the path and thus account for the lack of a barrier. It probably also accounts for the lowered barriers in the formation of **4c** and **4cN** and the increased exothermicities of all three reactions.

To test this idea, we determined the ring strain energy (RSE) of **4** and of the intermediate point on the potential energy surface shown in Figure 4.[16] The group equivalent reactions[17] used appear in Scheme 2. The RSE of **4** is predicted to be ca. 28 kcal/mol, very similar to that of the parent 1-aza-2-boracyclohexyne (ca. 32 kcal/mol). The RSE for the intermediate point is ca. 2 kcal/mol, which is dramatically smaller. It thus appears that interaction between the boron and the approaching carbon lowers the BN bond order, so that the ring angles can adopt values that decrease the RSE. Alternatively, one can view the approach of the carbon allowing formation of pseudo-trigonal-planar boron, which is unstrained in the context of a six-membered ring, and then reorganization of the BN triple bond to a bond of smaller order and a lone pair on the nitrogen. In any event, the outcome is that the loss of RSE and the energy of forming the BC bond counter any barrier associated with repulsion of **4** and propyne as they interact.

Conclusions

The work described above constitutes the strongest evidence we have modeled that iminoboranes, especially those with electron-withdrawing CF_3 groups on or near the boron atom, contain polar but alkyne-like B≡N triple bonds. Support comes from the facts that (1) crossover [2 + 2] cyclization of iminoboranes requires traversing very high barriers, (2) such cyclizations do not exhibit stationary point transition states but, rather, positions where the triple-bond axes are substantially twisted with respect to each other, and (3) [4 + 2] ene-type reactions show dramatically lower barriers than do the [2 + 2] reactions. That all known iminoboranes oligomerize to some degree could be cited as evidence that iminoboranes should be viewed as containing a nitrogen atom with a free lone pair and an electron-deficient boron atom. However, the data here are inconsistent with such a view.

To our knowledge, no [4 + 2] ene-type reactions of iminoboranes have been reported. The data presented here suggest they are viable targets and could give rise to fascinating products. In particular, reactions involving **4** show lowered barriers and, thus, could cover a broad range. We hope this work will spur syntheses of **3** and **4** or similar species and the exploration of their reactivities.

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Supporting Information Available: Listings of Cartesian coordinates and absolute energies of all molecules examined at the B3LYP/6-311++G(d,p) level. This material is available free of charge via the Internet at http://pubs.acs.org.

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[16] For speed, the RSE calculations used the 6-31+G(d) rather than the 6-311++G(d,p) basis set.

[17] Bachrach, S. M. *J. Chem. Educ.* **1990**, *67*, 907−908.